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MOLECULAR-BEAM SCATTERING

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ABSTRACT

The molecular-beam technique has been used in three different experimental arrangements to study a wide range of inter-atomic and molecular forces.

Chapter 1 reports results of a low energy (0.2 kcal/mole) elastic scattering study of the He-Ar pair potential. The purpose of the study was to accurately characterize the shape of the potential in the well region, by scattering slow He atoms produced by expanding a mixture of He in N₂ from a cooled nozzle. No new information was obtained, due to an inaccuracy of the measurement of the Ar beam velocity, and the large spread in He velocities produced by the mixed-gas expansion.

Chapter 2 contains measurements of the vibrational predissociation spectra and product translational energy for clusters of water, benzene, and ammonia. The experiments show that most of the product energy remains in the internal molecular motions. The major hindrance to extracting potential information from the spectra is the inability to properly account, in model calculations, for large amplitude motion present in the clusters.

Chapter 3 presents measurements of the reaction $\text{Na}(3^2P_{3/2}) + \text{HCl}(^1\Sigma^+_{v=0}) \rightarrow \text{NaCl}(^1\Sigma^+) + \text{H}(^2S)$ at collision energies of 5.38 and 19.4 kcal/mole. This is the first study to resolve both scattering angle and velocity for the reaction of a short lived (16 nsec) electronic excited state. The large reaction enhancement observed in the excited state, as well as the absence of a measureable alignment or orientation polarization dependence, are consistent with the expected electron jump mechanism for this reaction. The product translational energy and recoil angle distributions are consistent with an early repulsive energy release.

Appendices I and II describe computer programs written to analyze molecular beam expansions to extract information characterizing their velocity distributions, and to calculate accurate laboratory elastic scattering differential cross sections accounting for the finite apparatus resolution. Appendix III contains experimental results which attempted to determine the efficiency of optically pumping the $\text{Li}(2^2P_{3/2})$ and $\text{Na}(3^2P_{3/2})$ excited states. A simple three-level model for predicting the steady-state fraction of atoms in the excited state is included.

Dedication

This thesis is dedicated to my parents, Marion and Atlee, for sacrificing much of their time and energy to enable me to pursue my academic interests, and to Julie Patrusky, for supporting me with her love.

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The diverse experiments of this thesis are a tribute to the foresight of Professor Yuan Lee. Working in his molecular beam laboratory has always been exciting. The hard work required usually paid off with astonishing success, and I will always be amazed by Yuan's "second sense" for thinking up qualitatively new experiments, or in ascertaining the origin of experimental trouble. In regards to the last point, I always thought that Yuan's ability to find my mistakes (the closed gate valve incident) were a testament to his long exposure to the daily comings and going of laboratory work, where sometime in the past, a graduate student, or himself, had committed a similar error.

The main advantage of working with Yuan were the graduate students and post docs he attracted. Everyone was helpful. In particular, Chris Becker, Piero Casavecchia, Carl Hayden, Hoi-Sing Kwok, Jim Lisy, Andre Tramer, Hartmut Schmidt and Paul Weiss all worked hard on the projects of this thesis. These experiments would never have been possible without them.

During my stay at Berkeley, I became especially close to Scott Anderson, Doug Krajnovich, and Dan Neumark. I could always talk to them about all matters of science, and they usually had good advice to offer. Doug, in particular, was helpful in steering my way through the interpretation of the reactive scattering work.

Professor Klemperer (Harvard) and Professor John Hemminger (Irvine) were the first to interest me in experimental chemistry,

especially molecular beam experiments. I owe much to them for guiding me at this impressionable stage.

Finally, special thanks go to the individuals at LBL - Fred and Ed, Ed Voronin, Charlie Taylor, Dick Escobales and especially Ann Weightman. These people were always helpful, and a pleasant reminder that there were some advantages to working at LBL.

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I. ELASTIC SCATTERING OF Ar-He AT LOW ENERGIES

A. INTRODUCTION

In the last decade, remarkable progress in understanding the theoretical basis of intermolecular forces has been made.¹ The development of the molecular beam technique has figured prominently in the experimental testing of the predictions of theories of intermolecular bonding. In particular, for the noble gas pair interactions, it has been possible to derive accurate experimental intermolecular potentials from measurements of the energy dependence of the angle-resolved differential cross-sections, and to relate these derived potentials to ab initio and semi-empirical theories of intermolecular forces.²

Despite general agreement between theory and experiment, the pair potentials involving He are still thought to be poorly characterized experimentally in the well region of the intermolecular potential.³ Most theories assume that the long range potential follows the well-known dispersion series ($-C_6/r^6 - C_8/r^8 - \dots$), while the short range repulsive core shape is modeled by the Born-Mayer $A \exp(-ar)$ function. The major difference between theories is the manner in which the potential is interpolated between these two limiting ranges, in the well region.

Experimental determinations of the He-rare gas potentials show differences outside of the stated errors of the respective experiments.^{4,5,6,7} For example, the binding energy of the He-Ar potential is reported to be known to an accuracy of 3 percent,¹ yet, the best experiments were performed at collision energies 10-30 times

that of the derived well depths. This suggests that the well region may not be sensitively probed at these elevated collision energies, because the centrifugal potential screens it from contributing significantly to the scattering. In Fig. 1, the classical turning points are shown for a few partial waves at three collision energies using the best experimentally derived He-Ar potential. The effect of reducing the collision energy on the range of the potential probed is clearly seen.

An additional problem associated with the experimental determination of the potential involves the form of the model potential function chosen to be fit to the data. Many parameterizations use the well depth as a scaling factor, i.e., $V(r) = \epsilon f(r/r_m)$, where ϵ is the well depth, r_m the internuclear separation at the potential minimum, $f(x)$ the reduced, dimensionless potential, and $V(r)$ the intermolecular potential. Changing ϵ , consequently, affects the whole of the potential. If care is not exercised and several distinct parameterizations not tested, optimizing ϵ may result in an improved fit to the potential in the range of the experimental collision energy, but degrading the fit in the well region.⁴ As the exact form of the potential is unknown, to construe this derived ϵ obtained at a high collision energy relative to the well depth, as the true well depth, is actually an extrapolation to low collision energy. Depending on the ratio of the collision energy to the true well depth, E/ϵ , this extrapolation may or may not be accurate.

Four differential cross-section measurements have been published on the He-Ar potential.⁴⁻⁷ Table 1 summarizes the collision energy (E), energy resolution ($\Delta E/E$), the derived well depths (ϵ) and bond lengths (r_m) of these studies. The large variation in the potential parameters, especially ϵ , is evident. In the most recent and accurate study by Aziz, et al.,⁷ it was suggested that the discrepancy between the published potential values is related to the method of analysis of the small angle ($\theta < 5^\circ$) scattering data. The authors say that the error in the data in this range is dominated by systematic experimental errors and not the statistical counting errors as assumed in several other studies.^{4,6}

With this historical background, a new set of scattering experiments was planned for the He-Ar system. The goal of the experiments was to measure the differential cross-sections for a wide range of collision energies ($E/\epsilon = 30, 5, 2$) and to simultaneously fit all the data to a single potential. By covering a large range of collision energies, and utilizing flexible potential forms, the above-mentioned problems with the ϵ scaling parameter can be avoided. To insure that the collision energy was chosen sufficiently low to accurately probe the potential minimum, a series of computer simulations were performed to show the sensitivity of the data at a particular energy to the potential parameters. Experimentally, the technique of aerodynamic deceleration of He by N_2 was used to achieve the low He velocities necessary for a reduced collision energy of $E/\epsilon = 2$. The characteristics of the velocity distributions produced in this manner and the

problems associated with this method of beam production were investigated.

The structure of this chapter is as follows: In the second section, the experimental method and data error analysis are described. The third section details the beam velocity measurements needed for an accurate knowledge of the absolute distribution of collision energies. The fourth section sketches the feasibility of a direct deconvolution of the experimental data to obtain a potential independent of a presupposed analytical form. The final section is devoted to suggested improvements in the experiment. Two appendices describe general computer programs written to analyze the data and to plan experiments.

D. EXPERIMENTAL ARRANGEMENT

The differential cross-sections were measured in a new rotating detector, crossed beams apparatus the details of which are given elsewhere.⁸ Briefly, two supersonic molecular beams, each doubly differentially pumped, are crossed in a collision chamber. The Ar beam is 100 percent amplitude modulated at 150 Hz by a tuning fork chopper located in the second differential pumping region. The scattered He atoms are detected by a rotating mass spectrometer consisting of an electron bombardment ionizer, r-f quadrupole mass filter, and a Daly ion counter. The detector rotates in the plane defined by the atomic beams. The pulses from the Daly counter are discriminated, then counted by standard pulse counting electronics. From the phase of the tuning fork modulation, the ion pulses are

routed to either of two counters, depending on whether the Ar beam is blocked or unblocked. The difference between the counters gives the signal at a particular detector angle.

To obtain sufficient signal to noise ratios for the complete angular range measured, separate scans were made of smaller intervals. The variation of the signal count rate with angle of three orders of magnitude meant that different detector settings (emission current or quadrupole transmission) were necessary to reduce pulse pile-up effects in the counting electronics at small angles, without sacrificing sensitivity at large angles.

Each of the smaller angular intervals was scanned an even number of times, alternating the scan direction to minimize the systematic errors introduced by the large He background which is correlated with the detector position (see Fig. 2). The high intensity of the He beam coupled with the low pumping speed for He by ion pumps, results in a background count rate roughly $10^3 - 10^4$ times larger than the signal count rate. When the detector angle is changed, the finite time constant for the detector pressure to equilibrate to the different He gas load results in a monotonic increase or decrease in the He count rate at the new angle, depending on the direction of rotation of the detector. For example, if all scans were made in the same direction from small to large angles, the signals obtained would be systematically high. As the background channel is always accumulated after the signal and background channel, the background channel would be smaller by an amount proportional to the rate of the He background decrease with

time. By reversing the scan direction, the data is biased an equal amount in favor of the background channel. The sum of the bidirectional scans would subsequently average out all linear correlations of the He background with detector angle.

The above effect is most prominent at small angles where the background is largest, and the counting times usually shortest. To properly quantify the magnitude of this error, a careful study of the time dependence of the signal after rotating the detector to a small angle from either direction should be done. Likewise, if the detector is rotated directly from a small angle to a large angle at which the background is substantially lower, the time dependence of the signal at the new large angle position will show if, within the statistical errors, the decrease of the He background with time has measurable effects.

Within the data statistical uncertainty, there was no need to correct for long term fluctuations in detector response, beam intensities, etc. as done in a previous study.⁴ It was found that for scans made on separate days with all machine indicators unchanged, the signal levels agreed within 1.5 percent. This was taken as the inherent stability of the experiment. No long term signal could be obtained more accurately than this error.

The smaller angular intervals were joined together to produce the complete angular scan. Care was taken to insure that adjacent scans overlapped for many points to reduce systematic scaling errors between large and small angles. To ascertain the error introduced by the

scaling, a confidence limit for the scale factor, α , was calculated. This was done by expanding the χ^2 error about the optimal scale value, α_0 ,

$$\chi^2(\alpha) = \chi^2(\alpha_0) + \frac{1}{2} \frac{d^2\chi^2}{d\alpha^2} (\alpha - \alpha_0)^2 \quad (1)$$

and using the curvature of the fit, $d^2\chi^2/d\alpha^2$, to measure the change in scale factor which produces a given change in the fit. The change in α_0 necessary to increase χ^2 by 1/3 of the data error for the points used in the scaling was taken as a measure of the scaling error. This estimate of the scaling error was always less than $\alpha_0 \cdot 10^{-6}$, and no correction for it was made.

The first order dead time correction was computed from the equation

$$TCR = \frac{MCR}{1 - MCR \cdot PW} \quad , \quad (2)$$

where TCR is the true count rate, MCR is the measured count rate and PW is the discriminator pulse width (50 nanoseconds). The correction was applied to both data channels to obtain the true signal, the difference of the corrected channels. The error at each angle was incremented by the change in the signal introduced by the dead time correction.

Several additional systematic errors were investigated for their effects on the data, and found to be either negligible or uncorrectable with the measured experimental parameters. For example, there is

a variation in phase of the detected product with laboratory angle. The phase and gate width of the chopper gating circuit was set by first maximizing the modulated Ar signal looking directly at the modulated Ar beam, then adjusting for the difference in arrival time of the He atoms from the collision center using the measured He and Ar velocities (see Sec. C below). If the elastically scattered He atoms had the same laboratory velocity at all angles, and this velocity was the same as the He beam (reference) velocity, no correction would be necessary. In general, the He is moving faster in the laboratory at larger scattering angles. If the laboratory velocity at a given angle, θ , is $V_0(1 + \alpha)$, V_0 being the He beam velocity for which the phase/gate width is set, the time difference for arrival of the He at this angle from its reference value will be

$$\Delta t = \frac{L}{V_0} \frac{\alpha}{1 + \alpha} \quad (3)$$

In this equation, L is the flight distance to the detector from the collision volume ($L = 30$ cm). At the maximum angle detected, $\Delta t = .06$ msec for the Newton diagram in Fig. 3(a) and $\Delta t = .16$ msec for the diagram in Fig. 3(b). From the measured Ar beam modulation function, the rise time (10-90 percent of full scale) for the gated Ar beam is .5 msec. These phase delays are thus neglected, being within the rise time of the chopper function.

Secondly, the angular calibration of the apparatus was checked by locating the first minimum/maximum in the laboratory cross sections on

both sides of the He beam. These minima/maxima correspond to a common center-of-mass scattering angle. For the liquid nitrogen cooled He data, with a 1 percent velocity spread, a single Newton diagram determination of the location of the primary beam gives no angular offset within the expected accuracy. The absolute angular accuracy of the measurements is taken as better than $\pm 1/4^\circ$. A more precise determination of the offset could be obtained from a detailed fit to the first two oscillations on both sides of the He beam.

As noted above, the signal is derived from the difference between two large numbers. It is possible for the background to be incorrectly accounted for by this difference if the attenuation of the He beam by the presence of the Ar is of the order of the signal error. Figure 2 shows the background count rate as a function of angle. The asymptotic value for angles larger than 27° is the sum of the inherent detector background, and an effusive component from the main scattering chamber when the He beam is operating. The step in the He count rate over the angular range $22-27^\circ$ is from back scattered He beam gas which begins to hit the front of the detector at these angles, and increases the scattering of He beam gas into the detector. At angles less than 10° , the count rate begins to increase exponentially. At this position, the detector begins to view direct effusive He gas from the differential pumping region. Small angle scattering of the He beam from background gas and other He beam atoms moving at different velocities also begins to contribute at these small angles.

When the Ar beam is unblocked by the chopper, the He beam is attenuated by the amount $e^{-n\sigma L}$, where n is the Ar beam gas density

at the scattering zone, σ is the total cross section for scattering He out of the beam, and L is a characteristic length of the collision volume. The He background then changes when the Ar beam is blocked or unblocked. The difference between the two counters will give

$$(S + B_{\text{on}}) - B_{\text{off}} = S + (e^{-n\sigma L} - 1)(B_{\text{corr}}) \quad (4)$$

Here, B_{on} and B_{off} are the background counts with the Ar beam on and off respectively, S is the true signal, $e^{-n\sigma L}$ the attenuation factor for the He beam, and B_{corr} the background He counts correlated with the Ar modulation.

To quantify this effect, an estimate of the Ar beam gas density at the collision zone, as well as the total scattering cross section, is needed. The number density at the scattering center, n , is given by

$$n = \frac{K}{4\pi} n_0(T_0, P_0) \left(\frac{r}{d}\right)^2, \quad (5)$$

where the peaking factor, K , is 2 for a monatomic gas, $n_0(T_0, P_0)$ is the gas density at the nozzle, r is the nozzle radius, and d is the distance between the nozzle and the collision volume. Equation (5) is derived from the total gas flow through the nozzle from a model developed by Habets.⁹ The model assumes that the intensity is linear with gas flow. For the experimental conditions used in the present study, the beams are operated near the high pressure limit where non-ideal background gas interactions begin to affect the expansion. The beam

intensities are maximized, so small changes in nozzle backing pressure produce no increase in beam intensity. In this regime, there is no linear relation between beam intensity and backing pressure. Hence, Eq. (5) is an upper bound for the beam density in the scattering volume. For the Ar beam source the parameters are $r = .0038$ cm, $d = 5.75$ cm, and $n_0 = 2 \times 10^{19}/\text{cm}^3$, giving a density of $1.5 \times 10^{12}/\text{cm}^3$ at the collision volume. The total cross section for scattering out of the He beam is conservatively assumed to be $\sim 5\text{\AA}^2$. The fractional attenuation of the primary (He) beam is then 2.5×10^{-4} . Using Eq. (4), the error bars at each angle should be increased by the factor $2.5 \times 10^{-4} * B_{\text{corr}}$. B_{corr} is assumed bounded by the quantity $B(\theta) - B(\theta_{\text{max}})$ where $B(\theta)$ is the background count rate measured at the detector angle θ , and $B(\theta_{\text{max}})$ is the large angle background count rate which is taken to be uncorrelated with the tuning fork. The angle dependence of the background shown in Fig. 2 then gives the shape of this correction.

The attenuation correction, when applied to the signals measured here, gave a differently shaped cross section, suggesting that for angles larger than $\sim 10^\circ$, the data is much less affected than this model predicts. The potentials derived from the data corrected for the modeled attenuation effect were substantially at odds with what one would reasonably expect on physical grounds, as well as having large χ^2 errors. As a large component of the He count rate is a result of pressure buildup in the detector (and this should be uncorrelated with the chopper modulation), the upper bound chosen for

B_{corr} is probably too high. For this reason, no correction for the attenuation was made to the data as it affected the cross sections to an unreasonable extent, and the proper experimental measurements to account for it were not available.

To experimentally measure the attenuation effect, the background He level with and without the Ar beam must be measured. The background He levels can be measured by the time-of-flight (TOF) technique. To measure a fractional difference of 2×10^{-4} in the background would take ~ 1000 seconds if the average He count rate was $\sim 10^6/\text{sec}$, ~ 1 millisecond of time of the TOF spectrum was averaged to determine the background, and the TOF wheel speed was ~ 400 Hz. As the Ar beam is on or off for large time intervals, this method would not measure the background correlated on the chopper time scale. It would indicate if the attenuation of the He beam had an observable effect which would need to be accounted for in the data analysis.

The final systematic effect investigated concerns the fraction of He atoms which undergo multiple collisions before leaving the collision volume. The intense He beam used at the .4 kcal/mole collision energy (660 psi backing pressure, 30 μ nozzle diameter, nozzle-collision volume distance of 6.75 cm) produces a He atom density of $1.4 \times 10^{14}/\text{cm}^3$ at the scattering volume. The density of scattered He atoms in the collision volume, N_{He}^* , is given by

$$N_{\text{He}}^* = N_{\text{He}} \left(\frac{N_{\text{He}} N_{\text{Ar}} \sigma_{\text{Ar-He}} v_{\text{Ar-He}}^{\text{rel}} V}{N_{\text{He}} A v_{\text{He}}} \right) = 2.1 \times 10^{10}/\text{cm}^3 \quad (6)$$

In Eq. (6), N_{He} and N_{Ar} are the number densities of the He and Ar beams at the collision volume, $\sigma_{\text{Ar-He}}$ is the total cross section for He-Ar scattering, $v_{\text{Ar-He}}^{\text{rel}}$ is the relative velocity between the He and Ar beams, V the collision volume, v_{He} the He beam velocity, and A the cross sectional area of the He beam. The numerator of the parenthetical expression in Eq. (6) is the number of He atoms scattered per second from the collision volume, and the denominator is the number of He atoms entering the collision volume per second. Hence, the parenthetical expression is the percentage of He atoms scattered. The number of singly scattered atoms, $N_{\text{He**}}$, which collide with the undeflected He beam atoms (the most probable multiple collision event) is given by

$$N_{\text{He**}} = \frac{N_{\text{He}}^* N_{\text{He}} \sigma_{\text{He*He}} v_{\text{He*He}}^{\text{rel}} V}{2 \sin \theta} \quad , \quad (7)$$

where $\sigma_{\text{He*He}}$ is the collision cross section for He-He collisions and $v_{\text{He*He}}^{\text{rel}}$ the relative velocity between the colliding He atoms. The factor $2 \sin \theta$ accounts for the overlap of the incident He beam with the He scattered at an angle θ . Normalizing Eq. (7) to the singly scattered He signal will give the fraction of He atoms multiply scattered, $f_{\text{He**}}$,

$$f_{\text{He**}} = \frac{N_{\text{He}}^* N_{\text{He}} \sigma_{\text{He*He}} v_{\text{He*He}}^{\text{rel}} V}{2 \sin \theta N_{\text{Ar}} N_{\text{He}} \sigma_{\text{ArHe}} v_{\text{ArHe}}^{\text{rel}} V} \quad . \quad (8)$$

Combining Eqs. (6) and (8) one obtains for $f_{\text{He}^{**}}$

$$f_{\text{He}^{**}} = \frac{N_{\text{He}} \sigma_{\text{He}^{*}-\text{He}}(\theta) v_{\text{He}^{*}-\text{He}}^{\text{rel}}(\theta) L}{2 \sin \theta v_{\text{He}}} \quad (9)$$

In Eq. (9), L is a characteristic length of the collision volume. The angular dependence of Eq. (9) is approximated by modeling the $\text{He}^{*}-\text{He}$ collision cross section by the classical cross section for orbiting collisions. For He atoms deflected by colliding with Ar through an angle θ with respect to the incident He beam, the orbiting cross section with the remaining undeflected He beam will be

$$\sigma_{\text{orb}}^{\text{He}^{*}-\text{He}}(\theta) = \pi \left(\frac{6 C_6}{\mu v_{\text{rel}}^2(\theta)} \right)^{1/3} \quad (10)$$

where C_6 is the C_6 coefficient for the He-He potential.¹¹ The laboratory solid angle into which these orbiting collisions are redistributed is $\sim \sin^2 \theta$. The fraction of the signal lost at each angle, $f(\theta)$, after substituting numerical values in (9) and (10) is

$$f(\theta) = 3 \times 10^{-6} (\sin \theta)^{4/3} \quad (11)$$

Therefore, even at small angles, the effect is negligible under the strong assumption that all of the orbiting collisions are lost.

C. BEAM VELOCITY CHARACTERIZATION

A knowledge of the absolute velocity distribution of the atomic beams is necessary for the quantitative determination of the potentials. The method used to obtain the velocity distributions is described in Appendix 1. The extracted velocity distribution parameters are listed in Table II. The ion flight time delay (in microseconds) was not measured, but computed from the canonical $3(M(\text{amu}))^{1/2}$ relation established by previous tests for 75 volt ions with negligible initial velocity.

For the neat, high pressure He beam expanded from the liquid nitrogen cooled nozzle, the error in the velocity is determined by the ratio of the ionizer length to the neutral flight path, or $1/92$.

The velocity distribution of this beam is extremely narrow. At the time the velocity was measured, no means of delaying the start of the multi-channel scaler (MCS) was available to allow a high resolution window to be centered about the peak He beam velocity. Consequently, a larger dwell time (decreased resolution) was necessary to bring the velocity distribution within the 255 channels available in the MCS.

A direct deconvolution of the He velocity data (see Appendix 1) shows the observed width to be dominated by the time response of the apparatus. The velocity distribution width parameter, β , is poorly determined for this beam, but must be greater than the value listed. The distribution in velocities is already so small, that the error in determining β does not affect the data analysis below.

The measured He flow velocity for the liquid nitrogen cooled nozzle determined an effective nozzle temperature of 88°K. At this temperature, the predicted flow velocity of a mixture of 30 percent N_2 in He would be 5.71×10^4 cm/sec from the average mass of the gas mixture. The measured value of 5.85×10^4 cm/sec is 2.5 percent faster, consistent with either (or both) a small 5 percent additional contribution to the heat capacity from the cooling of the N_2 rotations, or an error of 2 percent in the gas mixture ratio.

The aerodynamically decelerated He beam (30 percent N_2 in He) has a broad velocity distribution. When higher nozzle backing pressures were applied, the N_2 /He beam would form various $(N_2)_m(He)_n$ clusters. With only moderate pressures, the ratio of clustered to unclustered He could be easily changed, obtaining totally condensed beams of large clusters if desired. The hydrodynamic deceleration, as noted above, does lower the velocity as predicted, but the onset of cluster formation ultimately restricts the speed ratios to small values.

The Ar beam was cooled by a 93°K copper block and measured on a third apparatus with a 62 cm flight path. This apparatus was used to reduce the gas load of Ar into the detector of the crossed beams scattering machine so subsequent experiments would have a small mass 20 background. The thermocouple temperature of the copper cooling block predicted an Ar velocity of 3.1×10^4 cm/sec if the Ar gas at the nozzle was in equilibrium with this temperature. The measured value of 4.08×10^4 cm/sec is much faster. The implications of this difference on the derived potentials will be discussed in more detail below.

D. DETERMINATION OF THE INTERACTION POTENTIALS FROM EXPERIMENTAL DIFFERENTIAL CROSS SECTIONS

The determination of interaction potentials from differential cross section data has followed two methods. The most desirable of these is to invert the scattering data to obtain a numerical potential using semiclassical^{10,11,12} or quantum mechanical¹³ algorithms. The inversion involves two steps. First, the laboratory differential cross section must be fit by a set of phase shifts. Three approaches to this problem have been published. The first, by Buck,¹¹ involves parameterizing the phase shifts by analytical functions, then varying the function parameters to fit the observed data. The second method, by Kleingbeil,¹⁰ uses a non-linear least squares fit of the phase shifts to the observed data, assuming the Born approximation to be valid beyond a critical impact parameter. The third method, by Gerber and Shapiro,¹³ is based on the unitary properties of the scattering wave equation to obtain the phase shifts. Shapiro¹⁴ has devised a method for transforming experimental data to the center-of-mass frame which is necessary before the phase shifts can be obtained by the unitary scheme.¹³ The only application of these techniques to derive a true quantum mechanical potential from experimental data is by Gerber, et al.¹⁵ for the He-Ne potential.

All of the methods suffer from the necessity of assuming that either a single set of phase shifts is responsible for the observed scattering, or that an energy-angle scaling relationship, which can be correct for the velocity averaging effects, is known. Any geometrical

averaging by the experiment from the finite detector or collision volume sizes can be accounted for by comparing the laboratory differential cross sections with transformed and geometrically averaged center-of-mass differential cross sections. For neat He beams where speed ratios in excess of 100 are possible,¹⁶ a single set of phase shifts should dominate the observed scattering.

To test this assumption, the laboratory data taken at the .4 kcal/mole collision energy were fit under three different assumptions. First, a single Newton diagram was averaged only over the detector and collision volume dimensions. Second, allowance was made for the variation of the phase shifts at different positions in the collision volume. In general, this is necessary when the beam velocity spread, $\Delta v/v_0$, along a streamline is less than the beam's angular divergence, $\sin \theta \geq \Delta v/v_0$. If this inequality holds, the velocity transverse to the beam centerline will contribute more to the distribution of collision energies than the inherent velocity spread along the centerline. Third, a full averaging procedure including velocity averaging over each beam as well as positional averaging over the detector and collision volumes was done. The variation in the potentials determined under the three different sets of averaging conditions tests the ability of a single set of phase shifts to mimic the true laboratory measurements. For the .4 kcal/mole collision energy, all potential parameters were within 1 percent of each other for each of the three averaging conditions. It is, therefore, reasonable to assume the laboratory cross sections obtained with $\Delta v/v_0 \sim .01$ at the collision

energy .4 kcal/mole are well-approximated by a single set of phase shifts.

This brief discussion underscores the importance of using the highest speed ratios obtainable. Correcting for the finite velocity dispersion can only be done rigorously by the forward convolution method described below. If the experimental velocity averaging is small and well represented by a single set of phase shifts, the next step is to fit a sufficient number of laboratory angular measurements over an extensive angular range to obtain a converged set of phase shifts. For reasons cited below, we assume that this step can be done using available non-linear fitting routines.

The extraction of a potential from a set of phase shifts involves a semiclassical^{10,11} or a quantum mechanical inversion.¹³ The semiclassical procedure was tested first due to its relative computational simplicity. Two sets of quantum mechanical phase shifts for He-Ar were calculated at the energies of two experimental measurements from an assumed He-Ar potential. Parameterizing the potential, $V(r)$, and internuclear separation, r , by u

$$\begin{aligned} V(r(u)) &= E*(1 - \exp(-2*T(u))) \\ r(u) &= u*\exp(-T(u)), \quad 0 \leq u \leq \quad, \end{aligned} \tag{12}$$

it can be shown¹⁰ that

$$T(u) = \frac{2}{\pi K} \int_u^{\infty} (b^2 - u^2)^{1/2} \frac{d\eta(b)}{db} db, \tag{13}$$

where $k = 2\pi(2\mu E)^{1/2}/h$, E is the collision energy, b the impact parameter, and $\eta(b)$, the phase shift curve. Given the phase shift curve and a value for u , Eq. (13) is solved for $T(u)$ by an adaptive Chebeshev quadrature scheme discussed by Kleingbeil.¹⁰ Once u , and $T(u)$ are known, Eqs. (12) are used to obtain $r(u)$ and $V(r(u))$. The potential $V(r)$ is easily obtained by solving these equations for many values of u . The chief numerical obstacle (for the diffractive scattering of He-Ar at these energies) to the solution of Eq. (13) is computing the derivative of the phase shift curve, $\frac{d\eta}{db}$, at an arbitrary impact parameter, b . Spline, as well as 2, 3, 4, and 5 point Lagrangian interpolations were tested. The results are displayed in Fig. 4.

Since quantum mechanical phase shifts were computed and used as input to the inversion program, one does not expect to recover the exact potential by the semiclassical inversion scheme. By necessity, any phase shifts derived from experimental data would be quantum mechanical. The extracted potentials show two pathologies. First, the repulsive wall has oscillations which make the potential multi-valued. In solving the equations for V and r in this range, V is always increasing with decreasing u while r oscillates as it approaches the classical turning point ($u = 0$). This oscillation results from the difficulty in interpolating a derivative which decreases monotonically with increasing impact parameters in this range due to the sparseness of negative phase shifts. Second, at the higher collision energy, the phase shifts produce a potential which

has a spurious hump, whose details are sensitive to the type of interpolation scheme. The hump is associated with the maximum of the phase shift curve. The density of phase shifts near the maximum is low, so the numerical interpolation of a first derivative is poor. The sign of the interpolated first derivative changes several times in this region, producing a second minimum. To avoid these shortcomings, the repulsive wall and well region of the phase shift curve need to be represented by functions whose first derivatives behave properly.

Shapiro¹⁵ has outlined a quantum mechanical procedure for obtaining the potential from phase shifts using a distorted wave Born approximation. A set of reference potentials is used to continue the asymptotic dispersion series to smaller internuclear distances. The method improves if good reference potentials are available, and is not limited by a small number of significant phase shifts. For the He-Ar system, this method was not tested for its ability to recover a known potential from its phase shifts, because the computational complexity was too great to implement the algorithm from the published information.

The direct inversion procedures are seen to involve assumptions which are dependent on the system measured, as well as the experimental conditions. The errors introduced by these assumptions are difficult to assess. The only experimentally tested method¹⁵ for removing the velocity dependence of the averaging assumes that a velocity-laboratory angle scaling relation holds for all angles over the spread of collision energies of the experiment (2 percent). For the He-Ne system,¹⁵ the deconvoluted-inverted potential seemed as accurate as any derived

by assuming a potential form. For diffractive scattering, the method, although complex, appears promising. For these reasons, the forward convolution method was used to obtain potentials from the current measurements.

The forward convolution method uses a computer program to simulate an elastic scattering experiment, and through a least squares optimization of potential parameters, determine a best fit potential. The advantage of the forward convolution method is its stability. The method can achieve an accuracy dependent only on the knowledge of the experimental conditions. Moreover, because a single potential curve can be used to generate differential cross sections at different energies, multiple energy scattering experiments can be used simultaneously in the potential optimization. In the extreme case, a purely numerical potential consisting of a set of points $V(r_i)$, $\{i = 1-N\}$, can be optimized to derive a potential independent of any assumption of the potential shape, by using multiple experimental cross sections covering a wide range of collision energies. The convergence of this method to the correct potential should be easy, since a good guess of the initial potential can be made using flexible analytic potential forms.

The strong angular dependence of the diffractive oscillations necessitated writing a computer program which accurately accounts for the geometrical and velocity averaging of the experimental apparatus. Appendix 2 describes the program and numerical methods used to solve the scattering equations.

As an example of how the program can be used, a best fit SPHD¹⁷ Ar-He potential was calculated assuming a range of approximations and

averaging effects. The solid line shown in Fig. 5(a) is a perfect experiment, consisting of one Newton diagram with an infinitesimally small detector. Curve A(●) allows for angular averaging of the detector (acceptance angle $.56^\circ$) and beam divergences (1.40° He beam, 1.5° Ar beam), while restricting the scattering to a plane. The differential cross section of curve A(—) allows the phase shifts to vary with the position in the collision volume, to show the importance of beam angular divergence when the velocity dispersion along the centerline is small. Curves B(—) and B(—) are the three dimensional analogs of curves A(●), A(—). Here, the detector is treated as a two dimensional aperture and the collision volume has three dimensions. Curve C(—) includes velocity averaging over the atomic beam velocity distribution as determined by time-of-flight analysis. Finally, curve C(—) represents the fully averaged cross section for the actual experimental conditions. The detector size and collision volume are twice those of curve C(—). From this series of approximations, the role of finite apertures in determining the amplitude of the oscillations is seen to be especially important in the region of the minima.

The Ar-He data was analyzed by simultaneously fitting the potential parameters to the three different collision energy cross sections. Each data set was simulated by a different set of averaging parameters, chosen to give accuracy without sacrificing computational speed. The potential fit to the highest energy data ⁷ was the initial starting point for the optimization. Exhaustive variation of the potential parameters resulted in no major change from the starting potential

values, even though the two low energy data sets were poorly fit. Figure 6 shows the individually best fit cross sections and potential parameters for the three collision energies. Figure 7 compares the differential cross sections predicted by the individually best fit potentials for the other data sets.

Since the simultaneous fitting was unable to find a compromise "best" fit, it seemed best to investigate origins of other systematic errors in the experiments. As noted above, the Ar velocity for the low collision energies was higher than expected from the temperature of the cooling block. If the measured Ar velocity was in error, by changing its value we should be able to improve both of the low energy fits to the optimized high energy potential. Indeed, for $v_{Ar} = 3.7 \times 10^4$ cm/sec, both low energy cross sections are predicted well within data errors by the Aziz⁷ potential (see Fig. 8), and better than any potential optimized to them separately. The origin of the possible error in the Ar velocity is not clear. Most likely, the conditions of the Ar source during the scattering experiment were not the same as those measured in the time-of-flight apparatus. For this reason, no improvement in the potential was obtained from the present work.

E. SUGGESTED IMPROVEMENTS

The present study has shown that for an accurate determination of the He-Ar pair potential several experimental improvements are needed. First, an optimal size for the detector aperture and collision volume will yield more precise values for the amplitude of the diffractive

oscillations. These features are sensitive to the well shape. Second, initial experiments should measure the shape of the minimum of an oscillation for various beam conditions and aperture sizes. This would be fruitful in deciding the resolution of the experiment as well as verifying the computer simulations of the averaging effects.

The systematic errors noted above can also be reduced. The counting electronics can be maximized for minimum pile-up by using a 10 nanosecond discriminator pulse width. A smaller dwell time to measure the He beam velocity will provide a precise determination of the velocity distribution. Additional collimation of the He beam will reduce the small angle background. (A triple slit collimation arrangement as used in the cluster photofragmentation studies of Chapter 2 would be ideal.) A nonuniform angular grid near the minima and maxima of the oscillations to accurately determine positions on both sides of the primary beam, will be useful for determining angular offsets. Of course, modifications which reduce the background help minimize modulated background also. For He which is inefficiently pumped by ion pumps, turbomolecular pumps should offer substantial improvements.

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Table 1. Experimental parameters and conditions from previous scattering studies of He-Ar.

Author	Year	References	Collision Energy (kcal/mole)	Energy Resolution	Well Depth (kcal/mole)	r (Å)
Chen	1973	4	.48	.14	.048	3.54
Smith	1977	5	1.37	.18	.060	3.46
			.42	.18		
Keil	1978	6	1.45	.20	.0406	3.57
Aziz	1979	7	1.572	.028	.058	3.44

Table 2. Velocity distribution parameters.

Gas	Nozzle Temperature	$V_0 (10^4 \text{ cm/sec})$	$\beta (10^{-8} \text{ sec}^2/\text{cm}^2)$	χ^2
He	88°K	9.57	75.5	2.8
He/N ₂	88°K	5.85	1.47	29.
Ar	93°K	4.08	4.55	2.9

FIGURE CAPTIONS

- Fig. 1. Collision energy and angular momentum dependence of the classical turning points for the He-Ar potential.
- Fig. 2. Angular dependence of the He detector background.
- Fig. 3. Newton diagrams for elastic He-Ar scattering at collision energies of .479 kcal/mole and .244 kcal/mole.
- Fig. 4. Semiclassical inversion of phase shifts to determine the intermolecular potential.

(A) Potentials extracted from phase shifts computed for a collision energy of .479 kcal/mole using (—) -5 point Lagrange, (—) -4 point Lagrange, (...) 3 point Lagrange, and (-.-) spline interpolations.

(B) Same as (A) except the phase shifts were computed at the collision energy .244 kcal/mole. Points are only indicated at positions where they differ from previously plotted points of the other interpolation types.

- Fig. 5. Effect of experimental averaging on the observed cross sections.

(A) (—) Perfect experiment. (•) Spatial averaging over the detector aperture and collision volume for in-plane scattering only. (—) Same as (•) except the collision energy and phase shifts depend on the position in the collision volume.

(B) (—) Spatial averaging as for curve A(•), except now full three dimensional scattering allowed. (—) Same as curve B(—), but the phase shifts vary with position in the collision volume.

(C) (—) Same as curve A(•), with velocity averaging over the experimental velocity distributions. (—) Same as C(—), but in-plane collision volume dimensions and detector slits are twice as large. This corresponds to the conditions of the experiments performed here.

Fig. 6. Comparison of experimental and best fit cross sections obtained at each collision energy (—) calculated points, (—) experimental points with 1 standard deviation error bars.

(a) $E = 1.57$ kcal/mole, (b) $.479$ kcal/mole, (c) $.244$ kcal/mole.

Fig. 7. Comparison of best fits of Fig. 6 at the other two data sets. (—) - calculated points, (—) experimental points with 1 standard deviation error bar.

(A) Best fit $.479$ kcal/mole potential compared to 1.57 kcal/mole data.

(B) Best fit $.244$ kcal/mole potential compared to 1.57 kcal/mole data.

(C) Best fit 1.57 kcal/mole potential compared to $.244$ kcal/mole data.

(D) Best fit 1.57 kcal/mole potential compared to $.479$ kcal/mole data.

(E) Best fit $.244$ kcal/mole potential compared to $.479$ kcal/mole data.

(F) Best fit $.479$ kcal/mole potential compared to $.244$ kcal/mole data.

Fig. 8. Comparison of observed elastic scattering laboratory cross section with the Buck⁷ Ar-He potential when the Ar velocity is 3.4×10^4 cm/sec. (a) $E_{\text{col}} = .45$ kcal. (b) $E_{\text{col}} = .20$ kcal/mole. (—) - Calculated cross section, (—) observed cross section with 1σ error bars. The poor fit for angles smaller than 5° in part A is sensitive to details of the averaging procedure and to the outer well of the potential.

XBL 834-9239

Fig. 1

Fig. 2

XBL 834-9240

Fig. 3

XBL 834-9238

Fig. 4

XBL 834-9478

Fig. 5

Fig. 6

KBL 834 9479

Fig. 7

XBL 834-9476

Fig. 8

APPENDIX I. TIME-OF-FLIGHT MEASUREMENT PROCEDURE

A. THEORY AND METHODS FOR TOF CALIBRATION

The purpose of this appendix is to explain in detail the procedure for performing time-of-flight (TOF) calibration measurements. The result of the calibration measurements is to assign a correct length (L) to the path the molecules travel in a particular experimental configuration. In conjunction with time information, (t), a velocity distribution, (L/t), can then be determined.

To measure the flight path from the interaction zone or TOF wheel to the ionizer, a known velocity distribution is used as calibrant. The standard practice is to use the rare gas nozzle distributions which are defined by assuming a Maxwellian velocity distribution superimposed on the bulk flow velocity. Because the electron bombardment ionizer is sensitive to number density, the velocity dependence of the assumed number density distribution is important. From standard texts¹ a Maxwellian velocity distribution is

$$e^{-\frac{M}{2kT_s}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \quad (1)$$

where T_s is the source temperature. For our model, this is the distribution an observer would see moving at the flow velocity, where T_s is the terminal beam temperature (usually $\leq 10^\circ\text{K}$ for rare gases). However, the observations made in the laboratory frame distort the distribution because of the constraints imposed on the molecular

trajectories by the defining apertures. This distortion is now derived.

Let the $+z$ direction be along the beam centerline. For practical measurements the nozzle can be treated as a point source^{2a,2b} and the detector as a circular disk of radius r at a distance L from the nozzle. The beam flow velocity in the laboratory reference frame is $(0, 0, v_F)$. The laboratory frame molecular velocity including the random Maxwellian velocity is $(v_x, v_y, v_z + v_F)$, where (v_x, v_y, v_z) is the Maxwellian velocity in the mass flow frame of reference. The detector aperture limits the transverse velocity perpendicular to the beam axis by $(v_{\text{transverse}}) \leq \frac{r}{L} (v_z + v_F)$. The measured laboratory number density distribution of velocities (v_L) is then

$$e^{-\beta v_z^2} dv_z \int_0^{\frac{r}{L}(v_z+v_F)} e^{-\beta \rho^2} \rho d\rho = e^{-\beta (v_L - v_F)^2} (e^{-\beta v_L^2 r^2 / L^2} - 1) dv_L \quad (2)$$

where $\rho = (v_x^2 + v_y^2)^{1/2}$, $\beta = \frac{M}{2kT}$ and $v_L = v_z + v_F$. For a standard detector arrangement, $\frac{r}{L} < \frac{0.005}{5}$ and the expression (2) can be expanded in a power series of the variable $x = (\alpha v_L r) / (v_F L)$, where $\alpha = v_F(\beta)^{1/2}$ is the speed ratio, i.e.

$$\exp\left(\frac{-\alpha^2 (v_L - v_F)^2}{v_F^2}\right) \left(x^2 - \frac{x^4}{2} + \dots\right) \quad (3)$$

When the exponential term is maximized ($v_L = v_F$), the second term in the power series expansion will contribute less than 1 percent when $\alpha \leq 100$. For all beams except high pressure He beams or He seeded beams, the speed ratios are usually much less than this value. For speed ratios near 100, the distributions are then sufficiently narrow with respect to the dwell time and ionizer resolution that the width cannot be directly measured with the present flight lengths, so the approximation can be used for all α .

In conclusion, the observed velocity distribution, $P(v_L)$ is proportional to

$$P(v_L)dv_L \sim v_L^2 \exp(-\beta(v_L - v_F)^2) dv_L \quad (4)$$

This expression agrees with that derived by Habets^{2b} using somewhat different arguments. To compare with the result from the multichannel scaler (MCS), the Jacobian from velocity to time is

$$dv_L = \frac{v_L^2}{L} dt. \quad (5)$$

The number density distribution experimentally measured is then

$$\frac{v_L^4}{L} e^{-\beta(v_L - v_F)^2} dt \quad (6)$$

with $v_L = \frac{L}{t}$, and t regarded as the independent variable.

The procedure is to use Eq. (4) with known rare gas expansion conditions so that v_F and β can be determined. By using the time location of the observed peak (t_p) in the velocity distribution, the effective length L to the ionizer can be determined by $L = v_F \cdot t_p$.

The direct output from the MCS can be used to obtain a good first approximation to L . First, the total time offset must be measured. The time offset is given by

$$t_{\text{offset}} = t_E - t_{\text{ion}} - t_{\text{trigger}} + t_D + t_{\text{wheel}}. \quad (7)$$

t_E is the electronic offset given by the time between the leading edge of the trigger pulse at the MCS trigger input and the maximum of the photodiode signal. t_{ion} is the ion flight time to be described below. t_{trigger} is the width of the trigger pulse sent to the MCS. t_D is a deliberate offset to displace the TOF for long flight paths. t_{wheel} is the time delay resulting from the offset between the peak of the photodiode signal and the time when the wheel slit is centered on the detector slit. t_{wheel} is measured by rotating the wheel clockwise and counterclockwise and averaging the two results. The t_{trigger} delay results from the design of the MCS. The 1 MHz internal clock is disabled for the duration of the trigger pulse, so the clock begins to decrement the dwell time counter within 50 nsecs after the end of the trigger pulse. The ion flight time is determined by measuring the time difference between the peak velocities for different ion masses originating from a common molecule. The use of

multiply charged rare gas ions has been observed to result in incorrect (overestimation) of ion flight times. Krajnovich³ has successfully used a 1 percent CF_3I mixture in He to obtain narrow velocity distributions with ion mass fragments over a large mass range. The possible source of error in this method is the translational energy released in the ion fragmentation which could distort the measurement. A comparison of the fragment distribution widths will indicate if this is important. The various mass fragment peaks can be used to fit the constant C in the expression $C(M)^{1/2}$ for the ion flight times. As all the ions originate from the same neutral velocity distribution, the difference in time between the ion fragment peaks is a result of the different fragment ion velocities in the mass spectrometer. Neglecting the initial neutral velocity, the ion velocity for a fixed ion energy will depend on the inverse square root of the mass. For 75 volt ions and 250 volt extraction voltage the canonical value for C is $3 \text{ } \mu\text{secs}/(\text{amu})^{1/2}$.

The predicted maximum velocity from Eq. (6) is

$$v_p = \frac{v_F}{2} + \frac{v_F}{2} \left(1 + \frac{8}{Bv_F^2}\right)^{1/2} \quad \text{or} \quad v_F = \frac{v_p^2 - 2.0/B}{v_p} \quad (8)$$

where

$$v_F \text{ (cm/sec)} = 2.039 \times 10^4 \left(\frac{T_{\text{nozzle}}(^{\circ}\text{K}) - T_{\text{terminal}}(^{\circ}\text{K})}{M(\text{amu})} \right)^{1/2} \quad (9)$$

The nozzle temperature is measured with a thermocouple using an ice bath reference. The terminal temperature is obtained from the half width of the velocity distribution by

$$T_{\text{terminal}}(\text{K}^{\circ}) = 8.679 \times 10^{-9} m(\text{amu}) (\Delta v(\text{cm/sec}))^2 \quad (10)$$

where

$$\Delta v = \frac{L \cdot \Delta t}{t_{1/2} \cdot t_0 \cdot t_D} \quad (11)$$

In Eq. (11), L is the flight length to be determined and can be guessed by previous knowledge for an initial correction. Δt is the number of channels between the maximum and half height of the distribution, $t_{1/2}$ is the half height channel number corrected for the offset time, t_0 is the peak channel number corrected for the offset time, and t_D is the dwell time. Using these values, $L(\text{cm}) = v_p(\text{cm/sec}) \cdot t_0(\text{sec})$. The agreement between L values determined from Ar, Kr, and Xe expansions should be ± 0.3 percent.

To compare the accuracy of this direct method, the more accurate peak fitting by the KELVIN program was used to iterate on T_{terminal} and L until agreement was found. The results are reported in Table I.

The sources of errors which can bias the above procedure, which are within experimental control, are the purity of rare gas used for calibration and the count rate limitations of the MCS. The first effect can be quite noticeable because several minutes after flowing a

new rare gas it is still possible to detect a clean TOF at the preceeding mass. The experimentalist should wait until all traces of the old gas disappear. Gas cylinders can contain impurities when they are low in pressure. A cursory mass scan at atmospheric and rare gas peaks during the purge time can check for this source of contamination.

The count rate limit cannot be determined by using the observed count rate on the count rate meter, since most of the signal is arriving in a small time interval, roughly 1/200 of the rate meter duty cycle. The MCS scalers are rated at ~30 MHz with a minimum data pulse width of 20 nanoseconds. For 1 percent accuracy in the largest channel, the instantaneous count rate should not exceed 1 MHz.

An additional source of bias was thought to be the manner in which the dual scalers toggle back and forth as the channels advance. If a data pulse is present at the transition from one channel to the next, then, depending on its width, four alternatives are possible. First, if the data pulse is short, then the partial pulse transmitted to either scaler will be too short to trigger the counters. Conversely, if each portion is sufficiently long then the pulse will be counted twice. The intermediate range occurs when one half of the pulse is sufficient, and the other insufficient to trigger the corresponding counter. These effects were empirically investigated using a digital delay generator/pulse generator arrangement to measure the delay between a single data pulse relative to the trigger pulse with an accuracy of 10 nanoseconds. The results are shown in Fig. 1. From these measurements, it is seen that for pulse widths greater than 30

nanoseconds, the multiple counting dominates. However, the effect of the problem is not significant except for very large total counts.

The reason for this is as follows.

Assume the data in channels i , $i+1$ is fit by a linear equation to be determined below. If C_i , C_{i+1} are the total counts in these channels, then the linear fit will be

$$y = \frac{(C_{i+1} + C_i)}{2t_i t_D} x + \frac{C_{i+1} + C_i}{2t_D} + \frac{(C_i - C_{i+1})t_i}{t_D^2} \quad (12)$$

where t_i is the i^{th} channel time, t_D the dwell time, and

$$C_{i+1} = \int_{t_i}^{t_{i+1}} y dx; \quad C_i = \int_{t_{i-1}}^{t_i} y dx. \quad (13)$$

The number of counts centered about the channel transition in a time interval 2Δ is

$$\int_{t_{i-\Delta}}^{t_{i+\Delta}} y dx = \frac{\Delta(C_{i+1} + C_i)}{t_D} = \frac{\Delta}{t_D} N. \quad (14)$$

Consequently, for $\Delta = 30$ nanoseconds, and $t_D = 2$ microseconds, the correction is $4.5 \times 10^{-3} N$, where 30 percent overcounting has been assumed. This compares with the statistical error $(N)^{1/2}$ when $N = 5 \times 10^5$ counts. With longer dwell times the effect is even less

important. The behavior on the 1 microsecond dwell time scale is not nearly as good as the 2 microsecond results, and should be avoided. The data presented here refers to a particular MCS unit and may not be transferable to other units.

The imperfect gas correction to the enthalpy for Ar at 1000 torr, 288°K amounts to $\sim -0.2^{2b}$, and can be neglected here in determining V_0 (Eq. (8)) from the nozzle temperature. Condensation effects will perturb the terminal temperature and velocity by the heat of condensation added to the flow and by ionizer fragmentation to the monomer mass. This can be checked by observing higher polymer masses, and lowering the pressure if necessary.

Several studies² have shown that a two component velocity distribution gives a much improved fit to the data. This was not investigated but the systematic differences observed in the calculated and experimental data here are similar to those reported by the above studies using a one component distribution. For most chemical experiments, the one component fit is adequate.

The assumption of the one component distribution was tested indirectly by attempting a direct deconvolution of the measured distribution. For every channel, a narrow velocity distribution ($\beta = 10^6$) centered on that channel was convoluted over the ionizer and shutter functions. The spread of this "delta function" input into adjacent channels defines a matrix C which takes the true channel distribution into the observed one. The inverse of this matrix $C^{-1} = D$ will then relate the observed channel distribution to the

true distribution free of ionizer and shutter effects. This deconvoluted distribution can then be transferred simply to a velocity distribution. In Fig. 2 the results for two rather different expansions, a high pressure He beam and a He/N₂ anti-seeded beam are shown. The high pressure beam indicates that the distribution is completely contained within the convolution effects. The large oscillations are a result of the narrow distribution and the change in sign of adjacent entries of the inverse matrix, D. A simple two channel average noticeably removes this effect. The anti-seeded distribution shows no significant difference between the measured and deconvoluted results. This is a consequence of the broadness of the distribution. The direct deconvolution result is not as useful as the trial and fit method, because the information is not as compact as the simple two parameter fit. However, it is useful as a guide to the magnitude of the broadening induced by the measurements.

For laser photofragmentation experiments the distance from the collision zone to the TOF wheel must be added to the TOF distance. The collision zone-wheel distance is measured with the transit while the wheel is spinning to reduce the warp error caused by the 5 mil stainless steel wheel material.

Finally, the emission current and extractor voltage affect the modeling of the detection process by a nonuniform electron distribution which can shield the ions from the extraction field or ionize the neutral species nonuniformly. These can be experimentally measured by using a narrow He beam whose experimental width is dominated by the

ionizer. Until this behavior is known, a more accurate deconvolution of the TOF spectra is not warranted.

B. TIME-OF-FLIGHT PROGRAM KELVIN AND DIRECTIONS FOR USE

This section describes the salient features of the FORTRAN program KELVIN used to fit time-of-flight data to deduce velocity distributions. The current version draws heavily on its predecessor written by J. Valentini. The basic difference is the improved efficiency in the calculation, by using a digital filter devised by R. Sparks. It also has an improved search procedure to find the best fit parameters.

The nominal structure is to simulate the effects of the finite ionizer length and slit widths on a measured velocity distribution by calculating a shutter function for the slit overlap which is used as a digital filter. This is applied to the trial velocity distribution which has been convoluted for the ionizer length. The ionizer is treated as a simple sum of 10 identical point ionizers with slightly different lengths from the collision zone. Using a Marquardt algorithm, the parameters are varied until one of three criteria is satisfied.

- 1) The change in parameters is less than 0.005 of their respective magnitudes.
- 2) The value of χ^2 has reached a value such that the data has been fit to the 90 percent confidence limit.
- 3) Twenty complete iterations have occurred without either 1) or 2) occurring.

KELVIN can analyze any number of time-of-flight distributions. Each velocity distribution needs the same number of input parameter

records. The number of data records in each distribution will vary. The final data set is followed by a blank record. Input records needed for each velocity distribution (all numbers F10.1 format, except where noted) are:

Record

1. Title
2. Mass (amu), channel width (μ sec), nominal neutral flight length (cm), ionizer length (cm), channel offset (channels).
3. Beginning channel number (15), ending channel number (15).
4. Wheel frequency (Hz), wheel diameter (cm), wheel slit width (mm), collimating slit width (mm).
5. etc. Data (8F10.1)

Output consists of the title with a list of the parameters used, followed by the input data, and the shutter function calculated for the dwell time used. "Offset" should include all the corrections from Eq. (7) divided by the dwell time to obtain the number of channels (fractional values allowed) by which the observed TOF distribution is uniformly offset.

The intermediate reduced standard deviations and parameter changes are listed with each iteration.

The final parameters are listed along with the number of iterations, calculated data, and the change in the fitted parameters that would produce a fit which would differ by an additional standard deviation at each point.

A graph of the two distribution is also produced.

The parametrized velocity distribution has the form

$$p(v) = v^2 e^{-\beta(v-v_0)^2}$$

where v_0 is the mass flow velocity, and $\beta = 1/(\alpha)^2$, where α is the average relative velocity in the mass flow frame of reference. The speed ratio is the dimensionless number $v_0(\beta)^{1/2}$. The flow velocity is in units of 10,000 cm/sec.

REFERENCES

1. F. Reif, Fundamentals of Statistical and Thermal Physics, p. 264, McGraw-Hill (1965).
2. (a) U. Bossel, R. David, M. Faubel, K. Winkelmann, Rarified Gas Dynamics, p. 235.
(b) A. Habets, "Supersonic Expansion of Argon into Vacuum," Ch. 2,5 Thesis, University of Eindhoven, Holland, 1977.
3. D. Krajnovich, private communication.

Table 1. Comparison of computer fitted parameters with those obtained by iteratively solving Eqs. (6) and (7) in the text.

	Computer Fit			First Iteration			Second Iteration		
	L(cm)	β	v_0	L	β	v_0	L	β	v_0
Ar	16.46	2.751	5.517	16.75	2.662	5.616	16.544	2.740	5.536
Kr	16.46	5.136	3.807	16.75	4.970	3.875	16.512	5.115	3.820
Xe	16.46	8.111	3.058	16.75	7.838	3.113	16.477	8.067	3.068

FIGURE CAPTIONS

Fig. 1. Transition effects in the dual scalars (a) 25 nanosecond data pulse width, 2 microsecond dwell time. (b) 40 nanosecond data pulse width, 2 microsecond dwell time. (c) 50 nanosecond data pulse width, 2 microsecond dwell time. (d) 40 nanosecond data pulse width, 3 microsecond dwell time. ▲ total counts in channels 10 and 11. ■ total counts in channel 10. ● total counts in channel 11.

Fig. 2. (a) Deconvoluted He beam. — Initial data. ● Deconvoluted data. ▲ Deconvoluted with 2 channel average.
(b) Deconvoluted He/N₂ beam. ● Initial data. ▲ Deconvoluted data (displaced by one channel).

XBL 813-8538

Fig. 1

XBL 813-8537

Fig. 2

PROGRAM KELVIN

FUNCTION- DETERMINES PARAMETERS VZRO AND BETA
CHARACTERIZING A SONIC NOZZLE VELOCITY DISTRIBUTION
FROM AN EXPERIMENTALLY MEASURED TIME-OF-FLIGHT
DISTRIBUTION, USING A LEAST SQUARES FITTING PROCEDURE.

INPUT- DESCRIBED IN SUBROUTINE 'INPUT'

OUTPUT- OUTPUT CONSISTS OF A TITLE WITH THE LIST OF
PARAMETERS USED, FOLLOWED BY THE INPUT DATA, AND THE
SHUTTER FUNCTION. THE INTERMEDIATE REDUCED STANDARD
DEVIATIONS AND THE PARAMETER CHANGES ARE LISTED WITH
EACH ITERATION. THE FINAL PARAMETERS ARE LISTED ALONG
WITH THE NUMBER OF ITERATIONS AND THE FINAL CALCULATED
BEST FIT DISTRIBUTION. AN ESTIMATE OF THE ERROR IN THE
DERIVED PARAMETERS IS GIVEN. THIS ERROR IS THE CALCULATED
CHANGE THAT IS PREDICTED NEEDED TO UNIFORMLY INCREASE THE
FITTING ERROR AT EACH POINT BY ONE STANDARD DEVIATION.
A GRAPH OF THE INPUT AND CALCULATED DISTRIBUTIONS IS
PRODUCED. ALL OUTPUT IS FOR A LINE PRINTER.

ROUTINES CALLED- INDATA, VELO, FIT, LPFLT

AUTHOR- M. F. VERNON

LAST REVISION DATE- FEBRUARY 15, 1983.

COMMON/ PAR/ CHAN, LMID, DL, BCHAN, ECHAN, NCHAN, MASS, MAXE, OFFSET
COMMON/ TRIP/ WIDTH, HZ, DIA, SA, SB, TRP(19), ITRSI2, ITRSHF, IFLAG
DIMENSION EXPT(255), SIGCAL(255), SIGCA1(255), SIGCA2(255)
DIMENSION YPL1(256), YPL2(256), XPL(256)
REAL MASS, LMID
INTEGER BCHAN, ECHAN, NCHAN

INPUT DATA

1003 CONTINUE
CALL INDATA(EXPT, BETA, VZRO)

FITTING ROUTINE TAKEN FROM 'DATA REDUCTION AND ERROR ANALYSIS
FOR THE PHYSICAL SCIENCES' BY PHILIP R. BEVINGTON.
PROGRAM 11-5 CURFIT WHICH IS A MARQUARDT ALGORITHM FOR A NON-
LINEAR LEAST SQUARES FIT WITH IMPROVED STABILITY NEAR A MINIMUM
WAS THE MODEL FOR THIS PROCEDURE.
ALL CALCULATIONS ARE PERFORMED WITH VZRO IN KILOMETERS/SECOND.
OUTPUT IS IN UNITS OF 10**4 CM/SEC

```

C      CALCULATE FIRST ATTEMPT AT A FIT WITH TRIAL VALUES.
C
      SF=0.
      CALL VELO(BETA,VZRO,SIGCAL,SIGCA1,SIGCA2)
      CALL FIT(SIGCAL,EXFT,SF,DC)
      ILOW=BCHAN+ITRSHF
      IHIGH=ECHAN-ITRSHF
      IFIT=20
      FLAMIA=.001
      CH=FLOAT(NCHAN-4-2*ITRSHF)
      WRITE(6,300)

C
C      THIS IS THE LEAST SQUARES FITTING LOOP
C
      DO 1000 JCYC=1,IFIT

C      DFDV IS THE FIRST DERIVATIVE WITH RESPECT TO PEAK VELOCITY.
C      DFDW IS THE FIRST DERIVATIVE WITH RESPECT TO PEAK WIDTH.
C
C      W IS THE WEIGHTING FACTOR.
C      B1 AND B2 IS THE BETA MATRIX.
C      A11,A12,A22 IS THE ALPHA MATRIX
C      THESE PARAMETERS ARE DEFINED IN BEVINGTON.
C
      B1=0.
      B2=0.
      A11=0.
      A12=0.
      A22=0.
      SUM=0.

C
C      DO LOOP ONLY EXTENDS OVER CHANNELS WHICH AREN'T TRUNCATED BY THE
C      SHUTTER FUNCTION.
C
      DO 1001 I=ILOW,IHIGH
      DFDH=SIGCA2(I)*SF
      DFDV=SIGCA1(I)*SF
      W=1./EXFT(I)
      D=EXFT(I)-SIGCAL(I)
      DW=D*W
      R1=B1+ DW*DFDV
      R2=B2+ DW*DFDH
      A11=A11+DFDV*DFDV*W
      A22=A22+DFDH*DFDH*W
      A12=A12+DFDV*DFDH*W
      SUM=SUM+D*DW
1001 CONTINUE

C
C      CALCULATE THE CHI SQUARED ERROR.
C      NOTE THAT THERE ARE FOUR PARAMETERS IN THE FIT TO THE DATA.

```

```

C      THESE ARE THE DC LEVEL, THE SCALE FACTOR, THE PEAK WIDTH AND
C      VELOCITY.
C
C      CHI1=SUM/CH
C
C      ADJUST PARAMETERS AS NECESSARY
C      A1 AND A2 IS THE CURVATURE MATRIX. A1NV AND A2NV IS INVERSE.
C      FLAMDA IS THE FACTOR WHICH DETERMINES THE EXTENT OF THE GRADIENT
C      INFLUENCE ON THE SEARCH.
C
71  CONTINUE
    A1=1.+FLAMDA
    DEN2=SQRT(A11*A22)
    A2=A12/DEN2
    DEN1=A1*A1-A2*A2
    A1NV=A1/DEN1
    A2NV=-A2/DEN1
    DVZRO=B1*A1NV/ABS(A11)+B2*A2NV/DEN2
    DBETA=B1*A2NV/DEN2 +B2*A1NV/ABS(A22)
C
C      IF BETA IS FORCED TO GO NEGATIVE, THEN THE DISTRIBUTION IS
C      NARROW RELATIVE TO THE SHUTTER FUNCTION. DBETA IS HALVED UNTIL
C      THE VALUE OF BETA IS POSITIVE. IFLAG IS SET TO 1 SINCE THE MORE
C      ACCURATE INTEGRATION OVER THE CHANNEL WIDTH IS NECESSARY FOR THIS
C      CASE.
C
221  IF(BETA+DBETA)225,225,220
225  IFLAG=1
    DBETA=DBETA/2.
    GOTO 221
C
C      CALCULATE THE DISTRIBUTION AT THE NEW VALUE OF BETA AND VZRO.
C
220  SF=0.
    CALL VELO(BETA+DBETA,VZRO+DVZRO,SIGCAL,SIGCA1,SIGCA2)
    CALL FIT(SIGCAL,EXPT,SF,DC)
    SUM=0.
    DO 1010 I=ILOW,IHIGH
1010  SUM=SUM+(EXPT(I)-SIGCAL(I))*2/EXPT(I)
    CHI2=SUM/CH
    WRITE(6,216) CHI2,DBETA/100.,DVZRO*10.
C
C      IF THE NEW VALUE OF CHISQR. IS LARGER THAN THE OLD VALUE, MAKE
C      THE GRADIENT CONTRIBUTION 10 TIMES LARGER AND TRY AGAIN.
C
    IF(CHI1-CHI2) 95,101,101
95   FLAMDA=10.*FLAMDA
    GOTO 71
C
C      STOP FITTING IF PARAMETERS OPTIMIZED

```

```

C
C      A IS THE NUMBER OF STANDARD DEVIATIONS EACH CALCULATED POINT
C      DIFFERS FROM THE DATA ON THE AVERAGE
C
101  A=SQRT(SUM/FLOAT(NCHAN-2*ITRSHF))
      VZRO=VZRO+DVZRO
      BETA=BETA+DBETA
      FLAMDA=FLAMDA/10.

C
C      THE SEARCH ENDS IF IFIT ITERATIONS HAVE HAPPENED WITHOUT THE
C      FOLLOWING CONDITIONS HAVING BEEN SATISFIED.
C      IF THE VALUES OF BETA AND VZRO ARE CHANGING LESS THAN .005
C      OF THEIR PREVIOUS VALUE, OR THE DATA HAS BEEN FIT WITHIN THE 90
C      PER CENT CONFIDENCE LIMIT, I.E. A22.
C
      IF(A.LE.2.) GOTO 1002
      IF((ABS(DBETA).LE.(.005*BETA)).AND.(ABS(DVZRO).LE.(.005*VZRO)))
1    GOTO 1002
1000  CONTINUE
      JCYC=JCYC-1
1002  WRITE(6,301)
      WRITE(6,1210)BETA/100.,VZRO*10.,VZRO*SQRT(BETA),10./SQRT(BETA),
1    JCYC,A
      IF(JCYC.EQ.IFIT) WRITE(6,219)
      EBETA=SQRT(A2NV/A22)
      EVZRO=SQRT(A1NV/A11)
      WRITE(6,217) EBETA/100.,EVZRO*10.
      T=DSQRT((1.+2.*A)*SUM)
      ER2=T*EBETA/100.
      EV2=T*EVZRO*10.
      WRITE(6,218) ER2,EV2

C
C      PLOT DATA
C
      WRITE(6,205)

C
C      DATA IS SCALED HERE FOR THE LINE PRINTER PLOTS
C
      NPTS=ECHAN-BCHAN-2*ITRSHF
      XSTEP=5./FLOAT(NPTS)
      J=1
      DC=EXPT(BCHAN+3)
      XPL(1)=0.
      TT=9.9/(EXPT(MAXE)-DC)
      WRITE(6,206)(I,SIGCAL(I),I=ILOW,IHIGH)
      DO 1005 I=ILOW,IHIGH
      YPL1(J)=(EXPT(I)-DC)*TT
      YPL2(J)=(SIGCAL(I)-DC)*TT
      J=J+1
      XPL(J)=XPL(J-1)+XSTEP
1005  CONTINUE

```

[illegible]


```

      IHIGH=ECHAN-ITRSHF
      RCHAN=0.
      XINV=0.
      X=0.
      Y=0.
      YX=0.
      YYX=0.

C
C      LEAST SQUARES DETERMINATION OF SCALE FACTOR AND DC BACKGROUND
C
      DO 30 I=ILOW,IHIGH
      Y=Y+SIGCAL(I)
      XINV=XINV+1./EXPT(I)
      YX=YX+SIGCAL(I)/EXPT(I)
      YYX=YYX+SIGCAL(I)*SIGCAL(I)/EXPT(I)
      RCHAN=RCHAN+1.
      X=X+EXPT(I)
30    CONTINUE
      DELTA=XINV*YYX-YX*YX
      DC=(RCHAN*YYX-YX*Y )/DELTA
      SCALE=(XINV*Y-RCHAN*YX)/DELTA

C
C      FINALLY SCALE THE DATA
C
      DO 40 I=RCHAN,ECHAN
      SIGCAL(I)=SIGCAL(I)*SCALE+DC
40    CONTINUE
      RETURN
      END

SUBROUTINE BIG(SIGCAL,MAX)

C
C      FUNCTION- Finds the maximum in a tof spectrum
C
C      INPUT- SIGCAL, ARRAY TO BE SEARCHED FOR MAXIMUM
C
C      OUTPUT- MAX, THE INDEX OF THE ARRAY SIGCAL OF THE LARGEST ELEMENT
C
C      ROUTINES CALLED-NONE
C
C      AUTHOR-M.F. VERNON
C
C      LAST REVISION DATE-FEBRUARY 15,1983
C
C
C
COMMON/PAR/CHAN,LMID,DL,BCHAN,ECHAN,NCHAN,MASS,MAXE,OFFSET
INTEGER BCHAN,ECHAN

```

```

DIMENSION SIGCAL(255)
MAX=0
SIGMAX=0.0
DO 1 I=BCHAN,ECHAN
IF (SIGCAL(I) .LT. SIGMAX) GO TO 1
SIGMAX=SIGCAL(I)
MAX=I
1 CONTINUE
IF(MAX .EQ. 0) WRITE (6,255)
255 FORMAT('0 NO MAXIMUM FOUND')
RETURN
END

```

SUBROUTINE TRAP1

```

C
C
C FUNCTION- CALCULATE THE SHUTTER FUNCTION TRAPEZOID.
C
C INPUT- ALL INPUT PASSED THROUGH THE COMMON ARRAY TRIP
C
C OUTPUT-THE ELEMENTS OF THE COMMON BLOCK TRIP, TRP,
C ITRSZ,AND ITRSHF ARE COMPUTED IN THIS ROUTINE.
C
C ROUTINES CALLED-NONE
C
C AUTHOR-M.F. VERNON
C
C LAST REVISION DATE-FEBRUARY 15,1983
C
C
C COMMON/TRIP/WIDTH,HZ,DIA,SA,SB,TRP(19),ITRSIZ,ITRSHF,IFLAG
C DATA PI,CON/3.14159265,100000./
C
C DEFINITION OF INPUT PARAMETERS in common block trip
C SA=WHEEL SLIT WIDTH IN MILLIMETERS
C SB=DETECTOR SLIT WIDTH IN MILLIMETERS
C WIDTH= CHANNEL TIME IN MICROSECONDS
C DIA=DIAMETER FROM CENTER OF WHEEL TO DETECTOR SLIT IN CM.
C T=ONE HALF THE NUMBER OF CHANNELS PER MILLIMETER TRAVEL OF WHEEL
C TT=HALF THE NUMBER OF SLITS FOR BASE OF TRAPEZOID
C TA=HALF THE NUMBER OF SLITS FOR THE TOP OF TRAPEZOID
C ITT=INTEGRAL VERSION OF TT
C ITA=INTEGRAL VERSION OF TA
C ITRSZ=NUMBER OF CHANNELS AFFECTED BY DIGITAL FILTER
C ITRSHF DEFINED BY ITRSZ=2*ITRSHF+1
C
C
C T=CON/(PI*DIA*HZ*2.*WIDTH)
C TT=T*(SA+SB)
C SA=AMIN1(SA,SB)
C TA=TT-SA*T*2.

```

```

      ITT=INT(TT-.5)
      ITA=INT(TA-.5)
C
C   CHECK IF BASE OF TRAPEZOID LESS THAN ONE CHANNEL WIDE
C
      IF(TT.LE..5) GOTO 90
      ITRSIZ=1+2*(ITT+1)
      ITRSHF=ITT+1
C
C   CHECK IF TOP OF TRAPEZOID MORE THAN ONE CHANNEL WIDE
C
      IF(TA.GE..5) GOTO 40
C
C   TRAPEZOID CORNER OCCURS WITHIN THE FIRST CHANNEL
C
      TRP(10)=(TT-TA*TA-.25)/(TT-TA)
C
C   CHECK IF TRAPEZOID BASE OCCURS WITHIN FIRST CHANNEL
C
      IF(ITT.EQ.0) GOTO 30
C
C   TRAPEZOID EDGE SPREAD OVER ITT CHANNELS
C
      DO 20 I=1,ITT
      TRP(10+I)=(TT-FLOAT(I))/(TT-TA)
20    TRP(10-I)=TRP(10+I)
C
C   CHANNEL WHERE EDGE HITS BASE
C
30    TRP(11+ITT)=(TT-.5-FLOAT(ITT))*2/(2.*(TT-TA))
      TRP(9-ITT)=TRP(11+ITT)
      GOTO 75
C
C   CASE WHERE TOP OF TRAPEZOID AT LEAST ONE CHANNEL WIDE.
C
40    TRP(10)=1.
C
C   DOES TOP OF TRAPEZOID EXTEND OVER MORE THAN ONE CHANNEL?
C
      IF(ITA.EQ.0.) GOTO 50
C
C   IF SO THEN ALL THESE CHANNELS HAVE UNIT AREA
C
      DO 45 I=1,ITA
      TRP(10+I)=1.
45    TRP(10-I)=1.
C
C   IS EDGE OF TRAPEZOID CONTAINED WITHIN ONE CHANNEL.
C
50    IF(ITT.EQ.ITA) GOTO 70
C

```

```

C      AREA FOR CORNER OF TRAPEZOID.
C
TERM=FLOAT(ITA)+1.5-TA
TRP(11+ITA)=1.-TERM*TERM/(2*(TT-TA))
TRP(9-ITA)=TRP(11+ITA)

C
C      CHANNELS WITH EDGE OF TRAPEZOID, BUT NO CORNERS
C
C      CHECK IF THERE ARE PURE EDGE CHANNELS
C
IF(2+ITA-ITT.GT.0) GOTO 60
ILOW=2+ITA
DO 55 I=ILOW,ITT
TRP(I+10)=(TT-FLOAT(I))/(TT-TA)
55 TRP(10-I)=TRP(10+I)

C
C      CHANNEL WHERE EDGE HITS BASE
C
60 TRP(11+ITT)=(TT-.5-FLOAT(ITT))*2/(2.*(TT-TA))
TRP(9-ITT)=TRP(11+ITT)
GOTO 75

C
C      CASE WHERE EDGE CONTAINED IN ONE CHANNEL
C
70 TRP(11+ITT)=(TA+TT-1)*.5-FLOAT(ITA)
TRP(9-ITT)=TRP(11+ITT)
GOTO 75

C
C      CASE WHERE ALL OF TRAPEZOID IN ONE CHANNEL
C
90 TRP(10)=1.
ITRSIZ=1
ITRSHF=0

C
C      NORMALIZE SO TRAPEZOID HAS UNIT AREA
C
75 SUM=0.
AREA=TA+TT
ILOW=10-ITRSHF
IHIGH=10+ITRSHF
DO 77 I=ILOW,IHIGH
TRP(I)=TRP(I)/AREA
77 SUM=SUM+TRP(I)
WRITE(6,103)
103 FORMAT(//)
WRITE(6,1000)(TRP(I),I=ILOW,IHIGH)
1000 FORMAT(1H,'SHUTTER FUNCTION TRAPEZOID', 2X,19F4.3)
WRITE(6,103)
RETURN
END

```

```

SUBROUTINE HALF(EXPT,H)

C
C
C   FUNCTION- FIND THE VALUE OF THE HALF MAX POINT FOR
C   GUESSING AN INITIAL VALUE OF BETA
C
C   INPUT-EXPT, THE ARRAY OF EXPERIMENTAL POINTS FOR THE
C   TOF DISTRIBUTION
C
C   OUTPUT- H, THE VALUE OF THE LOCATION OF THE HALF MAXIMUM
C   POINT, IN REAL FORMAT. FRACTIONAL CHANNELS ARE NEEDED
C   FOR THE HIGH SPEED RATIO DISTRIBUTIONS
C
C   ROUTINES CALLED-NONE
C
C   AUTHOR-M.F. VERNON
C
C   LAST REVISION DATE- FEBRUARY 15,1983
C
COMMON/FAR/CHAN,LMID,DL,BCHAN,ECHAN,NCHAN,MASS,MAXE,OFFSET
DIMENSION EXPT(255)
REAL MASS,LMID
INTEGER BCHAN,ECHAN,NCHAN

C
C   CALCULATE CHANNEL NUMBER OF APPROXIMATE HALF HEIGHT
C
C
C   ASSUME DC LEVEL GIVEN BY THE COUNTS IN THE THIRD CHANNEL
C
DC=EXPT(BCHAN+3)

C
C   MAXE IS THE CHANNEL NUMBER OF THE PEAK OF THE DISTRIBUTION
C
H=(EXPT(MAXE)+DC)/2.
DO 10 I=BCHAN,MAXE

C
C   ASSUME FIRST CHANNEL WHOSE SIGNAL IS LARGER THAN THE CALCULATED
C   HALF HEIGHT IS THE CORRECT CHANNEL
C
IF(EXPT(I).LT,H) GOTO 10

C
C   LINEARLY INTERPOLATE TO FIND THE FRACTIONAL CHANNEL
C   LOCATION OF THE HALF HEIGHT POINT
C
T1=(EXPT(I)-EXPT(I-1))
B=EXPT(I)+EXPT(I-1)-T1*FLOAT(2*I-1)

```

```

      B=B/2.
      H=(H-B)/T1
      GOTO 20
10    CONTINUE
20    RETURN
      END

```

SUBROUTINE INDATA(EXPT,BETA,VZRO)

```

C
C
C      FUNCTION- READ IN DATA AND PARAMETERS
C
C      INPUT ALL NUMBERS F10.1 FORMAT EXCEPT WHERE NOTED
C
C      CARD                CONTENTS
C      1                    TITLE
C      2      MASS(AMU),CHANNEL WIDTH(MICROSECONDS),NOMIAL
C              NEUTRAL FLIGHT LENGTH(CM),IONIZER LENGTH(CM),
C              CHANNEL OFFSET(CHANNELS)
C      3      BEGINNING CHANNEL NUMBER, ENDING CHANNEL NUMBER(215)
C      4      WHEEL FREQUENCY(HZ),WHEEL DIAMETER(CM),WHEEL SLIT
C              WIDTH(MM),COLLIMATING SLIT WIDTH(MM)
C      5      DATA(BF10.1)
C      ETC.
C
C      A BLANK CARD TERMINATES PROGRAM. MULTIPLE DATA SETS
C      CAN BE RUN BY REPEATING THE CARDS 1-4 FOR EACH DATA
C      SET
C
C      OUTPUT- EXPT IS THE EXPERIMENTAL DATA, BETA AND VZRO
C      THE FIRST TRIAL VALUES FOR THE VELOCITY DISTRIBUTION
C      PARAMETERS
C
C      ROUTINE CALLED-NONE
C
C      AUTHOR-M.F. VERNON
C
C      LAST REVISION DATE- FEBRUARY 15, 1983
C
C
C      DIMENSION EXPT(255),TITLE(20)
C      COMMON/PAR/CHAN,LMIID,DL,BCHAN,ECHAN,NCHAN,MASS,MAXE,OFFSET
C      COMMON/TRIP/WIDTH,HZ,DIA,SA,SB,TRP(19),ITRSIZ,ITRSHF,IFLAG
C      INTEGER BCHAN,ECHAN,BC,EC
C      REAL MASS,LMIID
C      READ(5,102) TITLE

```

```

      READ(5,101) MASS,CHAN,LMID,DL,OFFSET
      IF(MASS .EQ. 0.0) STOP
      READ(5,100) BCHAN,ECHAN
      BC=BCHAN
      EC=ECHAN
      NCHAN=ECHAN-BCHAN+1
      READ(5,101) HZ,DIA,SA,SB
      READ(5,101) (EXPT(I), I=BCHAN,ECHAN)
      WRITE(6,204) TITLE

C
C      WRITE INPUT DATA TO OUTPUT FILE
C
      WRITE(6,200) MASS
      WRITE(6,201) CHAN,BC,EC,LMID,DL
      WRITE(6,104) OFFSET
      WRITE(6,211) HZ,DIA,SA,SB
      WRITE(6,103)
      WRITE(6,205)
      WRITE(6,215) (I,EXPT(I), I=BCHAN,ECHAN)
      WRITE(6,103)
      WIDTH =CHAN
      IFLAG=0
      CALL TRAP1

C
C      GENERATE ESTIMATE OF BETA AND VZRO
C
      CALL BIG(EXPT,MAXE)
      VZRO=LMID/(FLOAT(MAXE)+OFFSET)/.1/CHAN
      CALL HALF(EXPT,H)
      VTEM=LMID/(H+OFFSET)/.1/CHAN
      BETA=.693/((VTEM-VZRO)**2)
      VZRO=VZRO**2/(VZRO+1./BETA)

C
C
C      FORMAT STATEMENTS
C
102 FORMAT(20A4)
100 FORMAT(3I5)
101 FORMAT(8F10.1)
204 FDRMAT(1H1,20A4)
200 FDRMAT('0  MASS =',F7.3)
201 FDRMAT('  CHANNEL WIDTH =',F4.1,' MICROSECONDS; BEGINNING CHANNEL
1  =',I3,', ENDING CHANNEL =',I3,', FLIGHT LENGTH =',F5.2,' CM; IONI
1ZER LENGTH =',F5.2,' CM.')
```

```

104 FDRMAT(3X,'OFFSET= ',F4.1,' CHANNELS')
211 FDRMAT('  WHEEL FREQ. =',F4.0,' HZ; WHEEL DIAMETER =',F4.1,' CM;
1SLOT WIDTH = ',F4.2,' MM; DETECTOR APERTURE =',F4.2,' MM')
```

```

103 FDRMAT(////)
20  FDRMAT(10X,'I N P U T  D I S T R I B U T I O N',/)
25  FDRMAT(8(3X,I3,1X,F9.1))

```

RETURN
END

SUBROUTINE LPPLT (X1,Y1,NPT1,X2,Y2,NPT2,N0)

```

C
C   LINE PRINTER PLOT ROUTINE
C
C   AUTHOR- F. HUISKEN
C
C   LAST REVISION DATE- UNKNOWN
C
  DIMENSION IPA(120),IX1(300),IY1(300),IX2(300),IY2(300)
  DIMENSION X1(300),X2(300),Y1(300),Y2(300)
  DATA L1,L2,L3,L4,LS,LD,LA / 1H1,1H2,1H3,1H4,1H5,1H0,1H* /
  DATA LB,LI,LM,LP / 1H ,1H1,1H-,1H+ /
  DATA DX,DY / 0.025,0.125 /
  WRITE(6,2001)
  IF (N0 .EQ. 9) GOTO 20
  IF (N0 .EQ. 1) LNO=L1
  IF (N0 .EQ. 2) LNO=L2
  IF (N0 .EQ. 3) LNO=L3
  IF (N0 .EQ. 4) LNO=L4
  GOTO 21
20  CONTINUE
  LNO=LS
  WRITE (6,2003)
21  CONTINUE
  DO 1 I=1,NPT1
    IF (X1(I) .LT. DX) X1(I)=DX
    IF (Y1(I) .LT. -3.+DY) Y1(I)=-3.+DY
    IX1(I)=INT((X1(I)+DX)/(2.*DX))
    IY1(I)=INT((Y1(I)+3.+DY)/(2.*DY))+4
1   CONTINUE
  DO 10 I=1,NPT2
    IF (X2(I) .LT. DX) X2(I)=DX
    IF (Y2(I) .LT. -3.+DY) Y2(I)=-3.+DY
    IX2(I)=INT((X2(I)+DX)/(2.*DX))
    IY2(I)=INT((Y2(I)+3.+DY)/(2.*DY))+4
10  CONTINUE
  DO 2 I=1,18
    IPA(I)=LB
2   CONTINUE
  DO 7 N=1,57
    N2=60-N+1
    DO 3 I=19,120
      IPA(I)=LB
3   CONTINUE
  IPA(20)=LI

```



```

      IF ((FLODAT(NZ)/B.-NZ/B) .GT. 1.E-6) GOTO 5
      IPA(19)=LM
      IPA(20)=LM
      IF (NZ .NE. 16) GOTO 5
      DO 4 I=21,120
      IPA(I)=LM
      IF ((FLODAT(I)/10.-I/10) .LE. 1.E-6) IPA(I)=LP
4     CONTINUE
5     CONTINUE
      DO 6 I=1,NPT1
      IF (IY1(I) .NE. NZ) GOTO 6
      IPA(20+IX1(I))=LO
6     CONTINUE
      DO 12 I=1,NPT2
      IF (IY2(I) .NE. NZ) GOTO 12
      IND=20+IX2(I)
      IF (IPA(IND) .EQ. LB) IPA(IND)=LND
      IF (IPA(IND) .EQ. LO) IPA(IND)=LA
      IF (IPA(IND) .EQ. LM) IPA(IND)=LNO
12    CONTINUE
7     CONTINUE
C
C
C     FORMAT STATEMENTS
C
C
2001 FORMAT ('H1)
2003 FORMAT (1H /)
      WRITE (6,2000) (IPA(I),I=1,120)
2000 FORMAT (120A1)
      RETURN
      END

```

SUBROUTINE VELO(BETA,VZRO,SIGCAL,SIG1,SIG2)

```

C
C     FUNCTION-CALCULATES THE TDF SPECTRA AVERAGED OVER THE IONIZER
C     LENGTH AND SHUTTER FUNCTION
C
C
C     INPUT- BETA AND VZRO ARE THE PARAMETERS FOR THE TRIAL
C     VELOCITY DISTRIBUTION FUNCTION.
C
C     OUTPUT-SIGCAL,SIGCA1,SIGCA2 THE CALCULATED TDF DISTRIBUTION
C     AND ITS DERIVATIVE WITH RESPECT TO VZRO AND BETA RESPECTIVELY
C
C     ROUTINES CALLED-NONE
C
C     AUTHOR-M.F. VERNON
C

```

```

C
COMMON/FAR/CHAN,LMID,DL,BCHAN,ECHAN,NCHAN,MASS,MAXE,OFFSET
COMMON/TRIP/WIDTH,HZ,DIA,SA,SB,TRP(19),ITRSIZ,ITRSHF,IFLAG
DIMENSION SIGTEM(255),SIGCAL(255)
DIMENSION SIGCA1(255),SIGCA2(255),SIG1(255),SIG2(255)
REAL MASS,LMID,L
INTEGER BCHAN,ECHAN
N=3

C
C      ZERO ARRAYS
C      SIGCA1, SIGCA2 CONTAIN THE ANALYTICAL DERIVATIVES OF THE
C      DISTRIBUTION WITH RESPECT TO VZRO AND BETA RESPECTIVELY.
C      THE SHUTTER FUNCTION CONVOLUTED RESULTS ARE RETURNED IN
C      SIG1, SIG2.
C
      DO 5 I=BCHAN,ECHAN
        SIGCAL(I)=0.
        SIGTEM(I)=0.
        SIGCA1(I)=0.
        SIGCA2(I)=0.
        SIG1(I)=0.
        SIG2(I)=0.
5      CONTINUE
      ILOW=ECHAN+ITRSHF
      IHIGH=ECHAN-ITRSHF

C
C      NINT IS THE GRID SIZE FOR THE SIMPSON'S RULE INTEGRATION
C      OVER THE CHANNEL WIDTH. IF THE BEAM WIDTH IS VERY NARROW, THEN
C      SET IFLAG=1 AND THIS INTEGRATION IS PERFORMED, ELSE USE IFLAG=0
C      AND THE ROUTINE IS ROUGHLY 6 TIMES FASTER.
C      NINT SHOULD PROBABLY BE ODD.
C      SEE 'INTRODUCTION TO NUMERICAL ANALYSIS BY HILDEBRAND,SECOND
C      ED., PG. 93.
C      THE CURRENT VALUE OF NINT IS CHOSEN SUCH THAT IF A FINER GRID
C      IS NEEDED, THEN THE SIMULATION OF THE EXPERIMENT BY THIS PROGRAM
C      IS PROBABLY MORE IN ERROR.
C
      NINT=11

C
C      DIVIDE IONIZER INTO NION INTERVALS
C      NOTE THAT NION SHOULD BE ODD
C
      NION=11

C
C      THESE CONSTANTS ARE USED IN THE INTERVALS FOR THE IONIZER
C      INTEGRATION AND THE CHANNEL WIDTH INTEGRATION.
C
      S2=FLOAT(NINT-1)
      N12=NINT-2
      NMID=(NION+1)/2
      S=FLOAT(NION-1)

```

```

C1=CHAN#.1
C2=CHAN#.1*(-.5)

C
C   THE 40 DO LOOP TREATS EACH POINT IN THE IONIZER EQUALLY, AND
C   MODELS THE EXPERIMENT BY NION INDEPENDENT AND SLIGHTLY DISPLACED
C   IONIZERS.
C
DO 40 I=1,NION
L=LMIID+FLOAT(I-NMIID)*DL/S
DO 35 J=BCHAN,ECHAN
IF(IFLAG.EQ.0) GOTO 30

C
C   THE DO LOOP PERFORMS THE SIMPSON'S RULE INTEGRATION
C
C   T1 IS THE LEFT EDGE OF THE CHANNEL.
T1=C1*(FLOAT(J-1)+OFFSET)
V1=L/T1
X1=V1**N*EXP(-BETA*((V1-VZRO)**2))/T1
W1=0.
W2=0.
W=0.

C
C   DT IS THE STEP LENGTH IN TIME SPACE FOR THE INTEGRATION
C   OVER THE CHANNEL WIDTH
C
DT=C1/S2
DO 25 K=1,N12,2
T2=T1+DT
T3=T2+DT
V2=L/T2
V3=L/T3
X2=V2**N*EXP(-BETA*((V2-VZRO)**2))/T2
X3=V3**N*EXP(-BETA*((V3-VZRO)**2))/T3
W=W+X1+4.*X2+X3
W1=W1+X1*2.*BETA*(V1-VZRO)+X2*8.*BETA*(V2-VZRO)+X3*2.*BETA*(V3-VZRO)
W2=W2-X1*(V1-VZRO)**2-X3*(V3-VZRO)**2-4.*X2*(V2-VZRO)**2
X1=X3
T1=T3
25 CONTINUE
SIGTEM(J)=SIGTEM(J)+W*DT/3.

C
C   DERIVATIVE OF INTENSITY WITH RESPECT TO VZRO.
C
SIGCA1(J)=SIGCA1(J)+W1*DT/3.

C
C   DERIVATIVE OF INTENSITY WITH RESPECT TO BETA.
C
SIGCA2(J)=SIGCA2(J)+W2*DT/3.
GOTO 35
C

```

```

C      APPROXIMATE THE AREA OF THE VELOCITY DISTRIBUTION IN THIS
C      CHANNEL BY ITS VALUE AT THE MIDPOINT.
C
30    T=C1*(FLOAT(J)+OFFSET)+C2
C
C      CALCULATE THE VELOCITY OF THE PARTICLE DETECTED IN CHANNEL J
C      IF IT WAS IONIZED AT THIS DISTANCE L FROM THE COLLISION ZONE
C
      V=L/T
C
C      USING THE GIVEN VELOCITY DISTRIBUTION, CALCULATE THE RELATIVE
C      AMOUNT EXPECTED TO HAVE THIS VELOCITY
C
      C=V**N*EXP(-BETA*(V-VZRO)**2) /T
C
C      DERIVATIVE OF INTENSITY WITH RESPECT TO VZRO.
C
      SIGCA1(J)=SIGCA1(J)+2.*BETA*(V-VZRO)*C
C
C      DERIVATIVE OF INTENSITY WITH RESPECT TO BETA.
C
      SIGCA2(J)=SIGCA2(J)+C*(-(V-VZRO)**2)
      SIGTEM(J)=SIGTEM(J)+C
35    CONTINUE
40    CONTINUE
      DO 60 I=ILOW,IHIGH
C
C      CONVOLUTE NOW OVER THE SHUTTER FUNCTION USING THE TRAP
C      ARRAY AS A DIGITAL FILTER
C
      ITEMP=10-I
      JLOW=I-ITRSHF
      JHIGH=I+ITRSHF
      DO 55 J=JLOW,JHIGH
      K=J+ITEMP
      SIG1(I)=SIG1(I)+TRP(K)*SIGCA1(J)
      SIG2(I)=SIG2(I)+TRP(K)*SIGCA2(J)
55    SIGCAL(I)=SIGCAL(I)+TRP(K)*SIGTEM(J)
60    CONTINUE
      RETURN
      END

```

APPENDIX II. ELASTIC SCATTERING PROGRAM FOR THE
COMPARISON OF LABORATORY ANGULAR DISTRIBUTIONS
CALCULATED FROM THE CENTER OF MASS
FRAME DIFFERENTIAL CROSS SECTION

A. INTRODUCTION

The program described below was based on previous versions which already existed in our laboratory to allow the analysis of elastic scattering data to be handled at a level of accuracy comparable with the present experimental capabilities. This program begins with an assumed potential form and computes laboratory angular distributions, corresponding to the experimental conditions, from the differential center-of-mass cross section. Basically, the program accounts for the finite detector size, the finite velocity spread of the initial beams and the finite collision volume.

The program is designed to allow, in practice, the computation of the laboratory distribution to any numerical accuracy depending only on the limitation of the computing budget. It is based on a direct simulation of the experiment so that the program can be used to investigate the effects of misalignment, velocity distributions, and other experimental parameters on the observed scattering. This is helpful in designing a good experiment with the experimental conditions chosen to resolve the required features.

In the sections below, the input record structure, several basic program uses, and a program listing provides the user with the necessary information to quickly begin to make calculations.

A description of the scattering equation and the program's numerical methods to solving it is given in Section B. This section should be read before reading the program listing to gain a crude knowledge of the program layout.

Two different phase shift routines are included to fit a particular system's need. Both routines have the capability of interpolating phase shifts - that is, the phase shifts are calculated for a uniformly distributed subset of partial waves (the subset is under user control) and the remaining phase shifts interpolated between their values at these points as needed. In this way, when the number of partial waves becomes large, computing efficiency can still be realized. One routine calculates exact phase shifts using a slightly modified program written by R. J. Leroy at the University of Waterloo, while the other calculates JWKB phase shifts.¹ An alternative published method for the exact phase shift calculation uses the log-derivative integration scheme.² Also, a second order JWKB method³ has been used to improve the accuracy of the semiclassical phase shifts. The latter two routines were not implemented here due to time limitations.

In developing this computer code, commercial software was used whenever possible. In particular, the least squares routine, based on the Levenberg-Marquardt algorithm, was taken from the Minpack library. The only machine dependent routines (CDC 7600) are "SECOND" and "VECPRO." "SECOND" returns the time since the program began execution and is used for locating the sections of the program which determine

the execution efficiency. "VECPRO" is a CDC assembly code routine for performing dot products quickly. Dummy routines to substitute for these are included.

Modifications to the program to perform other than elastic scattering with number density sensitive detectors can easily be implemented. To change the detector aperture shape, modify subroutines "FINT" and "MULSMP." To change the atomic beam cross sectional shapes, modify subroutine "WEIGHTS." To change the energy dependence of the cross section, the velocity dependence of the detection efficiency, or the Jacobian, modify subroutine "CMANG." To change the beam velocity distribution shape, modify subroutine "NOZZLE."

Proper execution of the computer program was checked by verifying internal selfconsistency or comparing with published data. Recovery of a known data set was used to check the least squares routine. The phase shifts were compared with published values for a reference Lennard-Jones potential.⁵ A test of the averaging was done by comparing parameters derived from least square fits to the He-Ar data obtained by Aziz, et al.⁴

B. DESCRIPTION OF PROGRAM METHODS

The DFCS is calculated by directly simulating the scattering process. The basic equation to be solved is

$S(\theta)$ = number of scattered particles/sec into the detector
positioned at laboratory angle θ

$$= \int_0^\infty n_1(|\vec{v}_1|) dv_1 \int_0^\infty n_2(|\vec{v}_2|) dv_2 |\vec{v}_2 - \vec{v}_1|^* \quad (1)$$

$$\int_{-L_x}^{L_x} dx \int_{-L_y}^{L_y} dy \int_{-L_z}^{L_z} dz \int_A \frac{d\sigma}{d\Omega}(\theta) dA \quad ,$$

where $n_1(|\vec{v}_1|)$ and $n_2(|\vec{v}_2|)$ are the number densities of the primary and secondary beams at the speeds $|\vec{v}_1|$, $|\vec{v}_2|$, respectively. $|\vec{v}_2 - \vec{v}_1|$ is the relative collision velocity. $\frac{d\sigma}{d\Omega}(\theta)$ is the center-of-mass cross section for scattering at the center-of-mass angle which correlates to the detector positioned at the nominal laboratory angle θ . The integration over the beam velocities (dv_1, dv_2) and the collision volume (dx, dy, dz) is handled by choosing discrete samples of each variable with a suitable weighting factor, and summing the results, i.e.,

$$S(\theta) = \sum_{\substack{i,j \\ k,l,m}} w_{ijklm} n_1(|\vec{v}_i|) n_2(|\vec{v}_j|) |\vec{v}_i - \vec{v}_j|^* \int_A \frac{d\sigma}{d\Omega}(\theta_{ijklm}) dA \quad (2)$$

Gauss-Hermite quadrature is used for the velocity integrals. The collision volume integration is performed by Gauss-Legendre quadrature.

For fixed values of the primary and secondary beam speeds and for each point in the collision volume, the scattering to a fixed point on

the detector is a simple matter of geometry, using the center-of-mass $\rightarrow$ laboratory transformation characterizing the intersection. The finite dimensions of the detector are accounted for by an adaptive Simpson's rule integration which chooses points on the detector and calculates the lines between these points and the collision volume grid points. Such lines intersect the Newton sphere in 0, 1, or 2 points. The partial waves are then summed at the center-of-mass scattering angles determined by the intersections, and the center-of-mass cross section is computed by summing the partial waves. The cross sections at the intersection points are weighted by both their inverse lab velocities (since the electron bombardment detector is sensitive to density, not flux), and the Jacobian factor which transforms areas in the center-of-mass to areas in the laboratory frame. The adaptive Simpson's rule continues to calculate by adding points at the detector until the scattering has converged to 1/10 the error in the data, or 1 percent if no data errors are supplied.

This procedure has the advantage that by increasing the volume grid and the number of Newton diagrams, an effectively exact treatment of the scattering can be realized. The two dimensional detector integration proceeds as in the one dimensional case until the desired convergence has been obtained.

Singular behavior in the Jacobian will result in numerical problems when the detector is tangent to the Newton sphere. Numerically, the only way to properly account for this is to transform the domain of integration from the detector to the center-of-mass. By

conservation of flux, the center-of-mass flux scattered through the boundary viewed by the detector is the same flux that would be experimentally observed in the laboratory frame. This removes the singularity but replaces it with an integration which has a complicated boundary. Although this boundary can be defined parametrically through the intersection equation, several cases can occur, each of which deserves separate treatment. Also, it is unclear whether any new physical information would be contained in treating this case properly. For this reason, the program will not handle this case.

The summation of the partial waves involves the product of trigonometric functions of the phase shifts along with the Legendre functions of the scattering angle. These vector products are performed using a fast vector product routine written in CDC assembly code. The "vectors" are defined from the scattering amplitude, $f(\theta)$, as follows:

$$\begin{aligned}
 f(\theta) &= \frac{1}{2ik} \sum_{\ell} (2\ell + 1) P_{\ell}(\cos\theta) (e^{2i\eta_{\ell}} - 1) \\
 &= \sum_{\ell} \frac{1}{k} \left(\frac{2\ell + 1}{2} \right) P_{\ell}(\cos\theta) \sin 2\eta_{\ell} \\
 &\quad + i \sum_{\ell} \frac{1}{k} \left(\frac{2\ell + 1}{2} \right) P_{\ell}(\cos\theta) (1 - \cos 2\eta_{\ell}) \\
 &= \frac{1}{k} \left(\sum_{\ell} \vec{P}_{\ell} * \vec{S}_{\ell} + i \sum_{\ell} \vec{P}_{\ell} * \vec{C}_{\ell} \right) ,
 \end{aligned} \tag{3}$$

where

$$\begin{aligned}
 \vec{P} &= \left(\frac{1}{2}P_0(\cos\theta), \frac{3P_1(\cos\theta)}{2}, \dots, \frac{(2\ell+1)}{2}P_\ell(\cos\theta), \dots \right), \\
 \vec{S} &= (\sin 2\eta_0, \sin 2\eta_1, \dots, \sin 2\eta_\ell, \dots), \\
 \vec{C} &= (\cos 2\eta_0 - 1, \cos 2\eta_1 - 1, \dots, \cos 2\eta_\ell - 1, \dots), \\
 \frac{d\sigma}{d\Omega}(\theta) &= |f(\theta)|^2 = \frac{1}{k^2} \left(\sum \vec{P}_\ell \cdot \vec{C}_\ell \right)^2 + \left(\sum \vec{P}_\ell \cdot \vec{S}_\ell \right)^2, \text{ and}
 \end{aligned} \tag{4}$$

$$\cos\theta = \cos\Theta.$$

The center-of-mass angles at which these summations are performed are determined in the subroutine CMANG. Therefore, at every detector angle, CMANG calculates the angles, and INTENS sums the partial waves at those angles.

The approximation which sets all phase shifts for the collision volume points equal to the most probable one can be used whenever the beam velocity spread ($\Delta v/v_0$) is larger than the beam spatial angular divergence ($\frac{XL}{PRINOZ}$).

If both input masses are equal, the program only sums over even (odd) phase shifts depending on the parameter IBOSE. This is to allow for nuclear symmetry oscillations. If one wants to avoid this option when scattering particles of the same mass, merely change one of the input masses by a small amount so that the particles are not mathematically equal, yet for all practical purposes they will be physically equal.

The program produces a timing summary which allows one to locate those parts of the program to optimize. For JWKB phase shifts, approximately 70-80 percent of the total computing time is used to sum the partial waves at the center-of-mass angles and compute Legendre functions. The fast dot product code uses $IINT * NVOL * (285 + 8 * NETA)$ μ secs where $NVOL = NCOLX * NCOLY * NCOLZ$ and IINT is the number of calls to the INTENSE subroutine. This is typically about 30 percent of the total computing time. Therefore, there is little optimization possible without additional assumptions which limit the number of center-of-mass scattering angles where the intensity is evaluated.

C. GEOMETRY OF SCATTERING

Let: (x, y, z) label a point in the region where the particles collide.

$(-x_1, 0, 0)$ locate the primary nozzle considered as a point source.

$(0, -y_2, 0)$ locate the secondary nozzle considered as a point source.

v_1 be the speed of the primary beam.

v_2 be the speed of the secondary beam.

$\frac{v_1 * (x_1 + x, y, z)}{(x_1 + x)^2 + y^2 + z^2)^{1/2}}$ is the velocity of the primary beam which passes through the point (x, y, z) with speed v_1 .

$$= (v_1^x, v_1^y, v_1^z)$$

$\frac{v_2(x, y + y_2, z)}{(x^2 + (y + y_2)^2 + z^2)^{1/2}}$ is the velocity of the secondary beam which passes through the point (x, y, z) with speed v_2 .

$$= (v_2^x, v_2^y, v_2^z)$$

$$(v_{cm}^x, v_{cm}^y, v_{cm}^z) = (M_1 v_1^x + M_2 v_2^x, M_1 v_1^y + M_2 v_2^y,$$

$$M_1 v_1^z + M_2 v_2^z) / (M_1 + M_2) + (x, y, z)$$

are the lab coordinates for the location of the tip of the center-of-mass velocity vector.

$$\frac{M_2}{(M_1 + M_2)} * ((v_1^x - v_2^x)^2 + (v_1^y - v_2^y)^2 + (v_1^z - v_2^z)^2)^{1/2} = v_{1S}$$

is the speed of the primary product or the radius of the Newton sphere.

(x_D, y_D, z_D) is a point in the laboratory on the detector surface.

$(r_D \cos \theta_D, r_D \sin \theta_D, z_D)$ is this same point on the detector, now labeled by r_D , the distance from the collision zone center to the detector entrance, and θ_D is the angle the detector makes with respect to the primary beam.

Now we wish to derive an expression which relates the line connecting this point on the detector to the point (x, y, z) in the collision volume, and find the points where this line will intersect the Newton sphere.

Let (x^1, y^1, z^1) be a point of intersection. It must satisfy the following equations:

$$(x^1 - v_{cm}^x)^2 + (y^1 - v_{cm}^y)^2 + (z^1 - v_{cm}^z)^2 = v_{1S}^2 \quad (5)$$

$$(x^1, \frac{y - y_D}{x - x_D} x^1 + \frac{xy_D - x_D y}{x - x_D}, \frac{z - z_D}{x - x_D} x^1 + \frac{xz_D - x_D z}{x - x_D}) = (x^1, y^1, z^1) \quad (6)$$

Equation (5) is the Newton sphere equation and Eq. (6) is the linear line sight equation between the detector point and the collision volume point.

When Eq. (6) is substituted into Eq. (5), two solutions are obtained for x^1 which are the front/back sides of the Newton sphere. Of course, the solutions can be degenerate or nonexistent.

To simplify the solution, redefine Eq. (6) as

$$y^1 = M_y x^1 + b_y \quad (7)$$

$$z^1 = M_z x^1 + b_z$$

Equation (5) then gives for x^1

$$A(x^1)^2 + Bx^1 + C = 0, \text{ where} \quad (8)$$

$$A = (1 + M_y^2 + M_z^2)$$

$$B = -2(v_{cm}^x + M_y(v_{cm}^y - b_y) + M_z(v_{cm}^z - b_z))$$

$$C = (v_{cm}^x)^2 + (b_y - v_{cm}^y)^2 + (b_z - v_{cm}^z)^2 - (v_{1S})^2.$$

Depending on the discriminate of the quadratic equation, a number of distinct solutions are possible. Even if two distinct solutions are found, they still must be checked to see that the laboratory velocity is in the detector's direction. For light particles, the backward scattered product may be traveling away from the detector. If $x^1 > 0$, then this condition will be satisfied.

To find the cosine of the angle in the center-of-mass frame between the scattered product and the relative velocity vector, the equations are

$$\cos(\theta_{cm}) = \frac{\vec{N} \cdot \vec{\theta}}{|\vec{N}| |\vec{\theta}|}, \quad (9)$$

$$\vec{N} = (x^1 - v_{cm}^x, y^1 - v_{cm}^y, z^1 - v_{cm}^z),$$

$$\vec{\theta} = (v_1^x - v_2^x, v_1^y - v_2^y, v_1^z - v_2^z).$$

Zare⁶ has shown in a straightforward way that the transformation of the center-of-mass flux through a surface to the same flux in a different surface in the laboratory frame involves the elastic Jacobian factor, J ,

$$J = \frac{v_{lab}^2}{u_{cm}^2 \cos(\vec{v}_{lab}, \vec{u}_{cm})}, \quad (10)$$

where $\vec{v}_{lab}$ is the particle's laboratory velocity, $\vec{u}_{cm}$ is the particle's velocity in the center-of-mass frame, and $\cos(\vec{v}_{lab}, \vec{u}_{cm})$ is the cosine of the angle between the velocity of the particle in the two frames. To compare with number density detection, we must scale by an additional factor of $1/|\vec{v}_{lab}|$. Therefore,

$$I(\theta) = \frac{d\sigma}{d\Omega}(\theta) * \frac{|\vec{v}_{lab}|}{(u_{cm})^2 \cos(\vec{u}_{cm}, \vec{v}_{lab})} \quad (11)$$

relates the flux in the center-of-mass frame for the area viewed by the detector at the laboratory scattering angle θ , to the number density detected in the laboratory frame, $I(\theta)$.

The above equations for the intersection point are not valid if the detector is looking into the secondary beam. To treat this case or general placement of the detector, the subroutine CMANG must be modified so that a new set of non-singular quadratic equations are defined.

D. INPUT RECORD STRUCTURE

All real numbers are in F10.3 format, all integers are in I10 format. Record numbers in parentheses are optional depending on the choice of input parameters. Examples are provided in Section F.

Record	Type	Parameters
1	20A4	Title
2	Real	MPRI, BETA1, VZRO1, PRINOZ
3	Real	MSEC, BETA2, VZRO2, SECNOZ
4	Real	XL, YL, ZL, ALIM(1), BLIM(1), ALIM(2), BLIM(2), DETRAD
5	Real	RANGE(2), RANGE(3), RANGE(4), RANGE(5)
6	Int	NCOLX, NCOLY, NCOLZ, NPRI, NSEC, NANG, IINT, IAPPRX
7	Int	NETA, NSKP, NPRI1, NSETS, NOPT, NLST, NPAR, NITER
8	Int	NPRI2, MAXIT, IBOSE
9	Real	XSTART, XSTEP, RNPHAS, ERROR Note: For JWK8 phase shifts, all parameters on Card 9 must be zero.
10,11	Real	A(1) → A(15)
(Optional)	Int	INDEX(1) → INDEX(NLST)
(Optional)	Real	FTOL, XTOL, FACTOR, EPSFCN
12	Real	(ANGLE(1), DATA (1)) → (ANGLE(NANG), DATA(NANG))
(Optional)	Real	(EDAT(1) → EDAT(NANG))
13	Int	IRPT
etc.		

E. DEFINITION OF PARAMETERS

MPRI/MSEC	Mass (amu) of primary/secondary beams.
BETA1/BETA2 VZR01/VZR02	Primary/secondary nozzle beam number density velocity distribution parameters, defined by $P(v) = v^2 \exp(-B(v-v_0)^2)$.
PRINOZ/SECNOZ	Distance of primary and secondary nozzles from collision center.
XL, YL, ZL	Dimensions of collision volume in X,Y,Z directions as determined by the molecular beam defining slits.
ALIM(2), BLIM(2)	Bottom and top positions of detector aperture, i.e., $BLIM(2) - ALIM(2) = \text{Detector height}$.
ALIM(1), BLIM(1)	<p>Detector width = $BLIM(1) - ALIM(1)$. Note: The ALIM, BLIM arrays can be used to see the effects of detector aperture misalignment. The center of the detector coordinates are determined by the laboratory angle. The symmetric, aligned limits are</p> <p style="margin-left: 40px;"> $ALIM(1) = -\text{Detector width}/2$ $BLIM(1) = -ALIM(1)$ $ALIM(2) = -\text{Detector height}/2$ $BLIM(2) = -ALIM(2)$. </p> <p>To give a net in plane offset, add (or subtract) the offset from both ALIM(1) and BLIM(1). Similarly, for vertical offsets, add (or subtract) the offset to ALIM(2) and BLIM(2). To improve speed when using the full two dimensional detector integration, set $ALIM(2) = 0$. This assumes that the scattering is symmetric with respect to the scattering plane, and therefore, only the top half of the detector needs to be integrated.</p>
DETRAD	Distance from collision center to defining aperture on detector.
RANGE(2), RANGE(3)	RMIN, RMAX for plotting the potential.
RANGE(4), RANGE(5)	<p>VMIN, VMAX for plotting the potential.</p> <p>Note: RANGE defines a rectangle for plotting the potential. Any points outside the rectangle are not plotted. RANGE can be used to focus on a particular region of the potential.</p>

NCOLX, NCOLY, NCOLZ	Number of integration points in X,Y,Z directions for collision volume integration. Maximum of 5 in any single direction.
NPRI, NSEC	Number of integration quadrature points for the primary/secondary beams. Limited to a maximum of 10 each.
NANG	Number of laboratory angles where calculations are to be performed. Limited to 100 maximum.
IINT	<p>=0, treats the detector as a point located at the center of the detector coordinates.</p> <p>=1, treats the detector as a horizontal slit in the plane of the molecular beams.</p> <p>=2, treats the detector as a full two-dimensional aperture.</p>
IAPPRX	<p>=0, each point in the collision volume has its own phase shifts, computed from the intersection angles defined by the nozzle positions and intersection point.</p> <p>=1, all points have the same phase shifts corresponding to the dominate collision point as determined by the integration weighting scheme.</p> <p>=2, all collision volume points for all Newton diagrams have the same phase shifts.</p>
NETA	Number of phase shifts or maximum phase shift.
NSKP	Interval used in interpolating phase shifts.
NPRI1	<p>=0, no phase shift printing.</p> <p>=1, lists the collision energies and phase shifts for each Newton diagram. Caution - this generates much output if more than 1 Newton diagram and 1 collision volume point are used.</p>
NSETS	The number of data sets to be used simultaneously in a least squares fit. NSETS must be less than 4.

NOPT	<p>=1, calculates differential cross sections (DFCS) with no data.</p> <p>=2, calculates DFCS with data, but no data errors.</p> <p>=3, calculates DFCS with data and data errors.</p>
NLST	<p>=0, no least squares fitting.</p> <p>=1, a least squares fit to the data will be performed for NLST variables.</p>
NPAR	Number of parameters in potential function.
NITER	The maximum number of cross sections allowed in the least squares fitting. If N parameters are varied, then N+1 cross sections per iteration are needed if the first try at improving the fit is successful. If three parameters are simultaneously changed, and three iterations are desired, then approximately 13 cross sections will be calculated.
NPRI2	<p>=0, no printing.</p> <p>=1, intermediate values for the detector integration are printed. This is useful in estimating the change of the scattering intensity over the detector height.</p>
MAXIT	Maximum number of iterations in the adoptive Simpson's integration over the detector (usually 4 is sufficient).
IBOSE	<p>=1, then only even Legendre terms are summed over when the nuclei are identical.</p> <p>=2, then only odd Legendre terms are summed over when the nuclei are identical.</p>
XSTART	In reduced distance units, the starting point for the Numerov integration for the exact phase shifts.
XSTEP	In reduced distance units, the step size for the Numerov integration.
RNPHAS	The number of steps in the Numerov phase shift integration.

ERROR	Maximum error, in radians, for the phase shifts calculated by the exact Numerov method.
A(1)-A(15)	Potential parameters needed as defined in the subroutines, "POT" and "PREPOT."
INDEX(1)	Array containing the list of variables to be varied in least squares fit. If a potential has 10 parameters (NPAR=10), but only the third, fifth and seventh are to be varied, then INDEX(1)=3, INDEX(2)=5, INDEX(3)=7, with NLST=3.
XTOL	Fractional change in parameters used as a convergence test in least square fits. Fitting terminates when all parameters are changing by less than XTOL of their value.
FTOL	Same as XTOL, but refers to the fractional change in the chi square value.
FACTOR	Controls length of initial step size in least squares fitting of parameters. Values between 0.1 - 1000.0 are normal, with larger values representing larger parameter changes on first iteration.
EPSFCN	An estimate of the reliability of the numerical derivatives. This parameter should be several orders of magnitude smaller than XTOL or FTOL.
(ANGLE(I), DATA(I))	Pairs giving the experimental intensity at a given detector angle. The angles are measured relative to the primary beam, positive direction measured toward the secondary beam.
EDAT(I)	Errors associated with the measured data.
IRPT	<p>=0, the program stops.</p> <p>=1, read in a new set of potential parameters, all data and other input remaining unchanged from previous values, and calculate a DFCS for this potential. This parameter assumes NLST=0.</p> <p>=2, begin again at card 1, with completely new input.</p>

F. EXAMPLES OF SEVERAL STANDARD PROGRAM USES.

The control variables are designed to allow easy interchange among several basic uses. These uses are:

- a) Calculate a hypothetical DFCS to test various resolution effects including collision volume size, velocity beam spreads, phase shift accuracy, and detector integration mode. In this case, read in records 1-12 inclusive. Record 12 contains the two numbers, $ANGLE(1)$ = Starting Lab Angle, and $DATA(1)$ = Angle Step Size, which differs from the standard definition for these parameters. If a single job testing several sets of resolution effects is desired, follow this record with either $IRPT=1$, if only the potential is to be changed, or $IRPT=2$ if, in addition, any other parameters are to be changed. For this last case records 1-12 need to be input again. A blank record terminates the program's execution. Make $NLST=0$, $NOPT=1$, and $NITER=1$, on record 7.
- b) Calculate a DFCS with data and possibly data errors. Read in records 1-12 inclusive with $NOPT = 2$ or 3 , $NLST = 0$, and $NITER = 1$. Again, $IRPT$ will allow several runs of this type in a single job. Previously calculated data points can be input producing a graph comparing the angular distributions corresponding to different machine parameters, to locate where the data are most affected. The program will scale the calculation to the input cross section.

Obviously, if no least squares fitting is desired, this mode allows one to test potentials in a trial and error mode which is helpful in determining the general range for the potential parameters.

- c) Least Squares. The optional records between 11 and 12 are needed, with the parameters described above. Because the calculation can be expensive, it is a good practice to begin with NITER=1 to see how long a single iteration takes.

G. CHANGING THE POTENTIAL FORM

To change the potential form, the user must supply two subroutines for each potential.

1. JWKB phase shifts

```
SUBROUTINE POT (X, A, V, VP, L, RM)
  DIMENSION X(10), A(15), V(10), VP(10)
```

The array X, on input, contains the reduced, dimensionless, distances needed for the semi-classical phase shifts. $X \cdot A(2)$ is the distance in angstroms. The two potential parameters $A(1)$ and $A(2)$ must be the well depth and r_m . L is the number of entries in the X array ($L \leq 10$). The subroutine POT must evaluate the reduced potential at the points, x, and return the potential values and first derivatives in the corresponding entries of the arrays V and VP, respectively.

```
SUBROUTINE PREPOT (A, RM)
  DIMENSION A(15)
```

PREPOT checks the potential parameters to insure that they are self-consistent. It is called once each time the potential is changed. For example, the HFD potential includes r_m explicitly in its form, so PREPOT insures that r_m is consistent with all the other parameters. The ESMSV and similar forms use PREPOT to determine spline coefficients. If your particular potential does not need to use PREPOT, then supply the following dummy routine.


```

SUBROUTINE PREPOT (A, RM)
DIMENSION A(15)
Return
End

```

Since all phase shift routines work in reduced units, they assume that $A(1) = \epsilon$, and $A(2) = r_m$. The potential subroutines must be consistent with this convention.

2. Numerov Phase Shifts

```

SUBROUTINE POT (X, A, V, VP, L, RM)
DIMENSION A(15), X(10), V(10), VP(10)

```

On input, X contains the reduced positions where the potential needs to be calculated for JWKB corrections to the exact phase shift. On output, V(I) is the reduced potential at X(I), and X(I) equals $1/X^2(I)$, i.e. the reduced centrifugal potential.

```

SUBROUTINE PREPOT (A, RM)
DIMENSION A(15)
Common/PTNL/V(6001), XM2(6001), XSTART, XSTEP, RNPHAS, ERROR

```

On input, RNPHAS is the number of points used in the Numerov integration, XSTART is the starting point for the integration and XSTEP is the step size. The routine calculates the reduced potential for the RNPHAS points starting at XSTART, and stepping by XSTEP, and stores the results in the V array. The XM2 array contains the corresponding values of the fraction $1/X(I)^2$ for the centrifugal potential. The routine must insure the self-consistency of the potential parameters as described above for the JWKB shifts.

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3. M. Keil, J. T. Slankas, A. Kuppermann, J. Chem. Phys. 70, 482 (1979).
4. R. A. Aziz, et al., J. Chem. Phys., 71, 2637 (1979).
5. R. Bernstein, J. Chem. Phys. 33, 795 (1960).
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	PROGRAM ELASTIC(INPUT,OUTPUT,TAPE6,TAPE8,TAPE10,TAPES=INPUT)	TEST.2
C		TEST.3
C		TEST.4
C	ELASTIC SCATTERING PROGRAM FOR SPHERICALLY SYMMETRIC INTERACTIONS	TEST.5
C	INPUT VARIABLES ARE DEFINED IN THE ROUTINE INPUT.	TEST.6
C		TEST.7
C		TEST.8
C	AUTHOR- M.F.F VERNON	
C		
C	LAST REVISION DATA- APRIL 17, 1983	
C		
	COMMON/SAVE/IDIN(5),PNOZ(5),SNOZ(5),NTA(5),DTA(5),ID(5),NCX(5),	SAVE.2
	\$NCY(5),NCZ(5),IIRR(5),ISIMAX(5),IP1MAX(5),NBP(5),NBS(5),HT(5),	SAVE.3
	\$WD(5),NAGL(5),DRD(5),ALM1(5),ALM2(5),BLM1(5),BLM2(5),NPRIN1(5),	SAVE.4
	\$VELO1(5,10),VLWT1(5,10),VELO2(5,10),VLWT2(5,10),CC1(7,5),XCV(5,5)	SAVE.5
	\$YCV(5,5),ZCV(5,5),WCV(5,5),WYCV(5,5),WZCV(5,5),ANGUH(3,100),	SAVE.6
	\$ERRPT(3,100),DATUM(3,100),DTSN1(3,100),DTCN1(3,100),NSETS	SAVE.7
	COMMON/LST/EINV(300),INDEX(15),VPAR(15),RH,FTOL,XTOL,MAXFEV,FACTORLST.2	LST.2
	\$EPSFCN	LST.3
	DIMENSION A(15),DMHY(100),SCAL(100),DMHY3(100)	TEST.11
	COMMON/GEONTY/PRINOZ,SECNOZ,PRISPD,SECSPD,XCOL,YCOL,ZCOL,MPRI,	GEONTY.2
	IMSEC,SNDT,CSDT,NOPT,NPRI1	GEONTY.3
	\$,NPRI2,MAXIT	GEONTY.4
	REAL MPRI,MSEC,MTOT	GEONTY.5
	COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF	DAT.2
	COMMON/TH/TIME(10),ICH,INTS,SPMAX,SPMIN	TH.2
	DIMENSION TITLE(20)	TEST.15
	DIMENSION RANGE(5)	TEST.16
9	CONTINUE	TEST.17
	CALL SECOND(TIME(10))	TEST.18
C		TEST.19
C	READ IN DATA AND EXPERIMENTAL CONDITIONS	TEST.20
C		TEST.21
	CALL INPUT(A,RM1,INTERMS,NPAR,TITLE)	TEST.22
	NN=1	TEST.23
	IF(INTERMS.NE.0) GOTO 200	TEST.24
C		TEST.25
C	NO LEAST SQUARES FIT	TEST.26
C		TEST.27
3	WRITE(6,117)	TEST.28
	WRITE(6,2)(A(I),I=1,NPAR)	TEST.30
	CALL SECOND(T1)	TEST.32
	CALL POTPLOT(A,RM1)	TEST.33
	CALL SECOND(T2)	TEST.34
	TIME(9)=T2-T1+TIME(9)	TEST.35
C		TEST.36
C	CALCULATE DFCS FOR INITIAL PARAMETERS	TEST.37
C		TEST.38
	CALL DFCS(A,SCAL,CHI,RM1)	TEST.39
	IF(NOPT-1) 250,250,275	TEST.40
C		TEST.41
C	PLOT ANGULAR DISTRIBUTION, NO DATA	TEST.42

C		TEST.43
250	CALL SECOND(T1)	TEST.44
	CALL XPLOT(-110101,1,-1,0,1,-1,0,0.,1,ANGLE,SCAL,NANG,1HX)	TEST.45
	CALL SECOND(T2)	TEST.46
	TIME(9)=T2-T1+TIME(9)	TEST.47
	GOTO 10	TEST.48
275	CALL SECOND(T1)	TEST.49
C		TEST.50
C	PLOT ANGULAR DISTRIBUTION WITH DATA	TEST.51
C		TEST.52
	WRITE(6,14)	TEST.53
	WRITE(6,8)CHI	TEST.54
	RANGE(1)=1.	TEST.55
	RANGE(2)=ANGLE(1)	TEST.56
	RANGE(3)=ANGLE(NANG)	TEST.57
	RANGE(5)=SPHAX	TEST.58
	RANGE(4)=SPHIN	TEST.59
	CALL XPLOT(-110101,1,-1,0,1,-1,0,RANGE,2,ANGLE,SDAT,NANG,1HE,ANGL	TEST.60
	-E,SCAL,NANG,1HC)	TEST.61
C		TEST.62
C	PLOT ANGULAR DISTRIBUTION DIFFERENCES	TEST.63
C		TEST.64
	RANGE(1)=0.	TEST.65
	DO 274 I=1,NANG	TEST.66
	DMY(I)=SCAL(I)-SDAT(I)	TEST.67
	DMY3(I)=-EDAT(I)	TEST.68
274	CONTINUE	TEST.69
	CALL XPLOT(-59101,1,-1,0,1,-1,0,RANGE,3,ANGLE,DMY,NANG,1HX,ANGL	TEST.70
	-E,EDAT,NANG,1HO,ANGLE,DMY3,NANG,1H+)	TEST.71
	CALL SECOND(T2)	TEST.72
	TIME(9)=TIME(9)+T2-T1	TEST.73
	GOTO 10	TEST.74
C		TEST.75
C	LEAST SQUARES SECTION	TEST.76
C	*****	TEST.77
200	CONTINUE	TEST.78
	CALL SECOND(T1)	TEST.79
C		TEST.80
C	PLOT POTENTIAL	TEST.81
C		TEST.82
	CALL POTPLOT(A,RH1)	TEST.83
	CALL SECOND(T2)	TEST.84
	TIME(9)=T2-T1+TIME(9)	TEST.85
	CALL SECOND(TS)	TEST.86
	WRITE(6,14)	TEST.87
	WRITE(6,4)	TEST.88
	DO 4445 I=1,15	TEST.90
	VPAR(I)=A(I)	TEST.91
4445	CONTINUE	TEST.92
	CALL LSTSOR(INTERNS,SCAL)	TEST.93
C		TEST.94
C	PLOT FITTED DISTRIBUTIONS FOR EACH DATA SET AFTER LEAST SQUARES	TEST.95
C	TERMINATES	TEST.96

C		TEST.97
4459	CONTINUE	TEST.98
	CALL SWITCH (NN)	TEST.99
	CALL BFC5(A,SCAL,CHI,RM1)	TEST.100
	WRITE(6,72) SF	TEST.101
	WRITE(6,73)CHI	TEST.102
C		TEST.103
C	PLOT ANGULAR DISTRIBUTION DIFFERENCES	TEST.104
C		TEST.107
	CALL SECOND(T1)	TEST.108
	DO 190 I=1,NANG	TEST.109
	DMY(I)=SCAL(I)-SDAT(I)	TEST.110
	DMY3(I)=-EDAT(I)	TEST.111
190	CONTINUE	TEST.112
	CALL XPLOT(-118101,1,-1,0,1,-1,0,0,,3,ANGLE,DMY,NANG,1HX,ANGLE, -EDAT,NANG,1HO,ANGLE,DMY3,NANG,1H+)	TEST.113
		TEST.114
C		TEST.115
C	PLOT ANGULAR DISTRIBUTION	TEST.116
C		TEST.117
	CALL XPLOT(-118101,1,-1,0,1,-1,0,0,,2,ANGLE,SDAT,NANG,1HE,ANGLE, -SCAL,NANG,1HO)	TEST.118
	CALL SECOND(T2)	TEST.119
	TIME(9)=TIME(9)+T2-T1	TEST.120
	WRITE(6,12)	TEST.121
10		TEST.122
C		TEST.124
C	WRITE OUT CALCULATED TABLES	TEST.125
C		TEST.126
	WRITE(6,221)	TEST.127
	WRITE(6,13)	TEST.130
	WRITE(6,5)(ANGLE(I),SCAL(I),I=1,NANG)	TEST.131
	WRITE(10,18)(TITLE(I),I=1,20)	TEST.133
	DO 17 I=1,NANG	TEST.135
	SCAL(I)=EXP(SCAL(I))	TEST.136
17	CONTINUE	TEST.137
	WRITE(10,7)(ANGLE(I),SCAL(I),I=1,NANG)	TEST.138
	WRITE(6,13)	TEST.140
	WRITE(6,11)	TEST.141
	WRITE(6,13)	TEST.143
	WRITE(6,5)(ANGLE(I),SCAL(I),I=1,NANG)	TEST.144
	NN=NN+1	TEST.145
	IF(NN.LE.NSETS) GOTO 4459	TEST.146
C		TEST.147
C	READ IN PARAMETER TO SEE IF AN ADDITIONAL DATA SET TO BE ANALYZED	TEST.148
C		TEST.149
	READ(5,1)IRPT	TEST.150
	IF(IRPT.NE.1) GOTO 15	TEST.152
	READ(5,2)(A(I),I=1,15)	TEST.153
	CALL PREPOT(A,RH)	TEST.154
	GOTO 3	TEST.155
15	CONTINUE	TEST.156
C		TEST.157
C	TIMING INFORMATION	TEST.158
C		TEST.159

SWITCH.8

OUTPUT- ALL COMMON BLOCKS CONTAIN THE DATA FOR SET J

ROUTINES CALLED-NONE

AUTHOR-H.F. VERNON

LAST REVISION DATE-FEBRUARY 16,1983

C
C
C
C
C
C
C
C
C

COMMON/TRIG/DETSIN(100),DETCOS(100)	SWITCH.9
COMMON/ETA/STHE(8000),CTHE(8000),META,DETA,IDENT	ETA.2
\$,IDOSE	ETA.3
COMMON/AA/DETWD,DETHT,DETRAD,E	AA.2
COMMON/GEOMTY/PRINOZ,SECOZ,PRISPD,SECSPD,XCOL,YCOL,ZCOL,NPRI,	GEOMTRY.2
INSEC,SNBT,CSBT,MOFT,NPRI1	GEOMTRY.3
\$,NPRI2,MAXIT	GEOMTRY.4
REAL NPRI,MSEC,MTOT	GEOMTRY.5
COMMON/SAVE/IDIN(5),PHOZ(5),SMOZ(5),NTA(5),DTA(5),ID(5),NCX(5),	SAVE.2
\$NCY(5),NCZ(5),IIRR(5),ISIMAX(5),IPIMAX(5),NBP(5),NBS(5),HT(5),	SAVE.3
\$WD(5),NAGL(5),DRD(5),ALM1(5),ALM2(5),BLM1(5),BLM2(5),NPRIN1(5),	SAVE.4
\$VELO1(5,10),VLWT1(5,10),VELO2(5,10),VLWT2(5,10),CC1(7,5),XCV(5,5)	SAVE.5
\$,YCV(5,5),ZCV(5,5),WXCVC(5,5),MYCV(5,5),WZCV(5,5),ANGUM(3,100),	SAVE.6
\$ERRPT(3,100),DATUM(3,100),DTSN1(3,100),DTCN1(3,100),NSETS	SAVE.7
COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF	DAT.2
COMMON/INTEG/IINT	INTEG.2
COMMON/EN/ENERGY(125),CMTH1(125),CMTH2(125),WGHT1(125),WGHT2(125),EN.2	EN.3
INCOLX,NCOLY,NCOLZ,IAPPRX	LIMITS.2
COMMON/LIMITS/ALIM(2),BLIM(2)	VOL.2
COMMON/VOL/X(5),Y(5),Z(5),WX(5),WY(5),WZ(5)	BEAM.2
COMMON/BEAM/VPRI(10),VSEC(10),WPRI(10),WSEC(10),NPRI,NSEC,IPRIM,	BEAM.3
+ISECON	WH.2
COMMON/WH/C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,MTOT	SWITCH.21
IINT=IDIN(J)	SWITCH.22
PRINOZ=PHOZ(J)\$SECOZ=SMOZ(J)\$META=NTA(J)\$DETA=DTA(J)	SWITCH.23
IDENT=ID(J)\$NCOLX=NCX(J)\$NCOLY=NCY(J)\$NCOLZ=NCZ(J)	SWITCH.24
IAPPRX=IIRR(J)\$ISECON=ISIMAX(J)\$IPRIM=IPIMAX(J)\$NPRI=NBP(J)	SWITCH.25
NSEC=NBS(J)\$DETHT=HT(J)\$DETWD=WD(J)\$NANG=NAGL(J)	SWITCH.26
DETRD=DRD(J)\$ALIM(1)=ALM1(J)\$ALIM(2)=ALM2(J)\$BLIM(1)=BLM1(J)	SWITCH.27
BLIM(2)=BLM2(J)\$NPRI1=NPRIN1(J)	SWITCH.28
DO 4020 I=1,NPRI	SWITCH.29
VPRI(I)=VELO1(J,I)	SWITCH.30
WPRI(I)=VLWT1(J,I)	SWITCH.31
4020 CONTINUE	SWITCH.32
DO 4025 I=1,NSEC	SWITCH.33
VSEC(I)=VELO2(J,I)	SWITCH.34
WSEC(I)=VLWT2(J,I)	SWITCH.35
4025 CONTINUE	SWITCH.36
DO 4030 I=1,NCOLX	SWITCH.37
X(I)=XCV(J,I)	SWITCH.38
WX(I)=WXCVC(J,I)	SWITCH.39
4030 CONTINUE	SWITCH.40
DO 4035 I=1,NCOLY	

	Y(I)=YCV(J,I)	SWITCH.41
	MY(I)=MYCV(J,I)	SWITCH.42
4035	CONTINUE	SWITCH.43
	DO 4040 I=1,NCOLZ	SWITCH.44
	Z(I)=ZCV(J,I)	SWITCH.45
	MZ(I)=MZCV(J,I)	SWITCH.46
4040	CONTINUE	SWITCH.47
	IMAX=MAGL(J)	SWITCH.48
	DO 4050 I=1,IMAX	SWITCH.49
	ANGLE(I)=ANGUN(J,I)	SWITCH.50
	EDAT(I)=ERRPT(J,I)	SWITCH.51
	SDAT(I)=DATUM(J,I)	SWITCH.52
	BETSIN(I)=BTSN1(J,I)	SWITCH.53
	BETCOS(I)=BTCN1(J,I)	SWITCH.54
4050	CONTINUE	SWITCH.55
	C1=CC1(1,J)	SWITCH.56
	C2=CC1(2,J)	SWITCH.57
	C3=CC1(3,J)	SWITCH.58
	C4=CC1(4,J)	SWITCH.59
	C5=CC1(5,J)	SWITCH.60
	C6=CC1(6,J)	SWITCH.61
	C7=CC1(7,J)	SWITCH.62
	RETURN	SWITCH.63
	END	SWITCH.64

SUBROUTINE LSTSQR(NTERMS,FVEC)
 DIMENSION FVEC(1)

LSTSQR.2
 LSTSQR.3
 LSTSQR.4
 LSTSQR.5
 LSTSQR.6
 LSTSQR.7
 LSTSQR.8
 LSTSQR.9
 LSTSQR.10
 LSTSQR.11
 LSTSQR.12
 LSTSQR.13
 LSTSQR.14
 LSTSQR.15
 LSTSQR.16
 LSTSQR.17
 LSTSQR.18

FUNCTION- LSTSQR CONTROLS THE NONLINEAR LEAST SQUARES FITTING OF
 THE OBSERVED DATA TO THE CALCULATED SIMULATION.

ARGUMENTS- NTERMS, AN INTEGER VARIABLE EQUAL TO THE NUMBER OF
 PARAMETERS VARIED IN THE LEAST SQUARES FIT
 FVEC- THE ARRAY OF FUNCTIONS TO BE MINIMIZED.

FVEC(I)=(DATA(I)-CALC(I))/SQRT(ERROR(I))

WHERE DATA(I) IS THE OBSERVED INTENSITY AT THE ITH ANGLE
 CALC(I) IS THE CALCULATED INTENSITY AT THIS ANGLE, AND
 ERROR(I) IS THE ERROR IN THE OBSERVED DATA AT THIS ANGLE

SUBPROGRAMS- SORT
 - FCN,LNDIF

AUTHOR-H.F. VERMIL

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DIMENSION FJAC(300,10),DIAG(10),IPVT(10),QTF(10),WA1(10),WA2(10) LSTSQR.21
 DIMENSION WA3(10),WA4(300),VTMP(10) LSTSQR.22


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COMMON/SAVE/IDIN(5),PNOZ(5),SNOZ(5),NTA(5),DTA(5),ID(5),NCX(5), SAVE.2
$NCY(5),NCZ(5),IIRR(5),ISIMAX(5),IP1MAX(5),NDP(5),NDS(5),HT(5), SAVE.3
$ WD(5),NAGL(5),DRB(5),ALM1(5),ALM2(5),BLM1(5),BLM2(5),NPRIN1(5), SAVE.4
$VELD1(5,10),ULMT1(5,10),VELD2(5,10),ULMT2(5,10),CC1(7,5),XCV(5,5) SAVE.5
$YCV(5,5),ZCV(5,5),WXCVC(5,5),WYCV(5,5),WZCV(5,5),ANGUM(3,100), SAVE.6
$ERRPT(3,100),DATUM(3,100),DTSN1(3,100),DTCM1(3,100),NSETS SAVE.7
COMMON/LST/EINV(300),INDEX(15),UPAR(15),RM,FTOL,XTOL,MAXFEV,FACTORLST.2
$EPSFCN LST.3
COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF DAT.2
EXTERNAL FCN LSTSQR.26
C LSTSQR.27
C INITIAL PARAMETERS TO LEAST SQUARE ROUTINE LSTSQR.28
C FOR A MORE COMPLETE DESCRIPTION OF THESE PARAMETERS SEE THE LSTSQR.29
C LISTING FOR THE PROGRAM LNDIF. LSTSQR.30
C LSTSQR.31
LDFJAC=300 LSTSQR.32
NPRINT=1 LSTSQR.33
GTOL=0. LSTSQR.34
MODE=1 LSTSQR.35
M=0 LSTSQR.36
DO 100 I=1,NSETS LSTSQR.37
M=M+NAGL(I) LSTSQR.38
100 CONTINUE LSTSQR.39
N=NTERMS LSTSQR.40
WRITE(6,12)(UPAR(I),I=1,15) LSTSQR.41
WRITE(6,559) XTOL,FTOL LSTSQR.44
C LSTSQR.47
C LOAD THE ARRAY OF THE PARAMETERS TO BE VARIED LSTSQR.48
C LSTSQR.49
DO 10 I=1,NTERMS LSTSQR.50
VTHP(I)=UPAR(INDEX(I)) LSTSQR.51
10 CONTINUE LSTSQR.52
C LSTSQR.53
C SINCE THE NONLINEAR FUNCTIONS ARE JUST THE DIFFERENCES BETWEEN LSTSQR.54
C THE CALCULATED AND OBSERVED SIGNAL,WEIGHTED BY THE ERROR, LSTSQR.55
C THE SORT OF THE DATA ERROR IS NEEDED SO THAT THE SUM OF THE LSTSQR.56
C SQUARES OF THE FUNCTIONS IS THE CHI SQUARE ERROR. LSTSQR.57
C LSTSQR.58
IJ=0 LSTSQR.59
DO 16 J=1,NSETS LSTSQR.60
IMAX=NAGL(J) LSTSQR.61
DO 15 I=1,IMAX LSTSQR.62
EINV(I+IJ)=1./SQRT(ERRPT(J,I)) LSTSQR.63
15 CONTINUE LSTSQR.64
IJ=IJ+NAGL(J) LSTSQR.65
16 CONTINUE LSTSQR.66
WRITE(6,1) LSTSQR.67
WRITE(6,889) LSTSQR.68
C LSTSQR.71
C LNDIF IS THE MINPACK DRIVER FOR THE NONLINEAR LEAST SQUARES FIT LSTSQR.72
C LSTSQR.73
CALL LNDIF(FCN,M,N,VTHP,FVEC,FTOL,XTOL,GTOL, MAXFEV,EPSFCN,DIAG, LSTSQR.74
$MODE,FACTOR,NPRINT,INFO,NFEV,FJAC,LDFJAC,IPVT,QTF,WA1,WA2,WA3,WA4) LSTSQR.75

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C                                     LSTSQR.76
C   WRITE OUT RESULTS OF LEAST SQUARES FIT WITH INFORMATION ON THE LSTSQR.77
C   EXIT CONDITION FROM THE MINPACK ROUTINE LSTSQR.78
C                                     LSTSQR.79
C   WRITE(6,2) LSTSQR.80
C   WRITE(6,1000) NFEV LSTSQR.83
C   WRITE(6,13)(UPAR(I),I=1,15) LSTSQR.85
C   WRITE(6,2) LSTSQR.88
C   WRITE(6,1001) INFO LSTSQR.89
C   IF(INFO.EQ.0) WRITE(6,550) LSTSQR.91
C   IF(INFO.EQ.1) WRITE(6,551) LSTSQR.92
C   IF(INFO.EQ.2) WRITE(6,552) LSTSQR.93
C   IF(INFO.EQ.3) WRITE(6,553) LSTSQR.94
C   IF(INFO.EQ.4) WRITE(6,554) LSTSQR.95
C   IF(INFO.EQ.5) WRITE(6,555) LSTSQR.96
C   IF(INFO.EQ.6) WRITE(6,556) LSTSQR.97
C   IF(INFO.EQ.7) WRITE(6,557) LSTSQR.98
C   IF(INFO.EQ.8) WRITE(6,558) LSTSQR.99
C                                     LSTSQR.119
C   ON RETURN TO THE MAIN PROGRAM, REPLACE THE OLD PARAMETERS BY THE LSTSQR.120
C   NEW ONES. LSTSQR.121
C                                     LSTSQR.122
C   DO 20 I=1,NTERMS LSTSQR.123
C   UPAR(INDEX(I))=VTMP(I) LSTSQR.124
20  CONTINUE LSTSQR.125
C   RETURN LSTSQR.126
C
C
C   FORMAT STATEMENTS
C
C
12  FORMAT(10X,* ON INPUT TO THE LEAST SQUARES PROGRAM, PARAMETERS ARE LSTSQR.42
* ,/,10(2X,E10.3),/,10(2X,E10.3)) LSTSQR.43
559  FORMAT(10X,* VARIABLE CONVERGENCE (XTOL)=*,E14.7,/,10X, LSTSQR.45
* CONVERGENCE FOR NORM OF RESIDUALS (FTOL)=*,E14.7) LSTSQR.46
889  FORMAT(1X,* L2 NORM OF RESIDUALS*,30X,* INTERMEDIATE PARAMETER VALUE LSTSQR.69
* ,/,) LSTSQR.70
2   FORMAT(/) LSTSQR.81
1   FORMAT(/) LSTSQR.82
1000 FORMAT(5X,* NUMBER OF FUNCTION EVALUATIONS *,I5,/) LSTSQR.84
13  FORMAT(10X,* ON EXIT FROM THE LEAST SQUARES PROGRAM, PARAMETERS LSTSQR.86
* ARE*,/,5(2X,E14.7),/,5(2X,E14.7),/,5(2X,E14.7)) LSTSQR.87
1001 FORMAT(10X,* EXIT CONDITION PARAMETER *,I5) LSTSQR.90
550  FORMAT(2X,* IMPROPER INPUT PARAMETERS TO LMDIF ROUTINE*,/) LSTSQR.100
551  FORMAT(2X,* BOTH ACTUAL AND PREDICTED RELATIVE REDUCTIONS IN THE LSTSQR.101
* SUM OF SQUARES ARE AT MOST FTOL*,/) LSTSQR.102
552  FORMAT(2X,* RELATIVE ERROR BETWEEN TWO CONSECUTIVE ITERATES OF THE LSTSQR.103
* PARAMETERS IS AT MOST XTOL*,/) LSTSQR.104
553  FORMAT(2X,* RELATIVE ERROR BETWEEN TWO CONSECUTIVE ITERATES OF THE LSTSQR.105
* PARAMETERS ON TWO CONSECUTIVE ITERATIONS IS LESS*,/,2X,* THAN FTOL LSTSQR.106
* AND XTOL RESPECTIVELY*,/) LSTSQR.107
554  FORMAT(2X,* SOLUTION VECTOR IS ORTHOGONAL TO JACOBIAN. TRY A NEW *, LSTSQR.108
* STARTING POINT TO INSURE THIS IS NOT*,/,2X,* A MAXIMUM OR SADDLE LSTSQR.109

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      @POINTS,/)                                LSTSQR.110
555  FORMAT(2X, #MAXIMUM ALLOWED NUMBER OF FUNCTION EVALUATIONS HAS BE LSTSQR.111
      $EN REACHED$,/)                          LSTSQR.112
556  FORMAT(2X, #FTOL IS TOO SMALL. NO FURTHER REDUCTION IN SUM OF SQUARE LSTSQR.113
      $S IS POSSIBLE$,/)                      LSTSQR.114
557  FORMAT(2X, #XTOL IS TOO SMALL. NO FURTHER IMPROVEMENT IN THE$ LSTSQR.115
      $ APPROXIMATE SOLUTION X IS POSSIBLE$,/) LSTSQR.116
558  FORMAT(2X, #GTOL IS TOO SMALL. THE FUNCTION IS ORTHOGONAL TO THE LSTSQR.117
      $JACOBIAN WITHIN THE MACHINE PRECISION$,/) LSTSQR.118
      END                                       LSTSQR.127

SUBROUTINE FCN(M,N,X,FVEC,IFLAG)                LSTSQR.128
                                          FCN.2
                                          FCN.3
C      FUNCTION-FCN IS THE INTERFACE ROUTINE WHICH CALCULATES THE
C      FUNCTIONS                                FCN.4
C      USED IN THE NONLINEAR LEAST SQUARES ROUTINE. FCN.5
C
C      PARAMETERS-M, ON INPUT, IS THE NUMBER OF DATA POINTS FCN.6
C      N- ON INPUT IS THE NUMBER OF PARAMETERS IN THE LEAST SQUARES FIT FCN.7
C      X, ON INPUT, IS THE ARRAY OF POTENTIAL PARAMETER VALUES FCN.8
C      FVEC- ON OUTPUT IS AN ARRAY WHICH IS THE DIFFERENCE IN THE FCN.9
C      OBSERVED AND CALCULATED DATA WEIGHTED BY THE SQUARE ROOT OF THE FCN.10
C      ERROR FOR EACH ANGLE. FCN.11
C      IFLAG- ON INPUT CONTROLS THE PRINTING OF INTERMEDIATE FCN.12
C      ITERATION VALUES FCN.13
C
C      SUBPROGRAMS- DFCS,PREPOT,ENORM FCN.14
C      -SWITCH FCN.15
C      FCN.16
C      FCN.17
C      AUTHOR M.F. VERNON
C
C
C      FCN.19
C      FCN.20
C      LAST REVISION DATE- FEBRUARY 16,1983
C
C      COMMON/SAVE/IDIN(5),PHOZ(5),SMOZ(5),NTA(5),DTA(5),ID(5),NCX(5), SAVE.2
C      $NCY(5),NCZ(5),IIRR(5),ISIMAX(5),IPIMAX(5),NBP(5),NBS(5),HT(5), SAVE.3
C      $WD(5),NAGL(5),DRD(5),ALM1(5),ALM2(5),BLM1(5),BLM2(5),NPRIN1(5), SAVE.4
C      $VELO1(5,10),VLWT1(5,10),VELO2(5,10),VLWT2(5,10),CC1(7,5),XCV(5,5) SAVE.5
C      $,YCV(5,5),ZCV(5,5),WXCVC(5,5),MYCVC(5,5),WZCVC(5,5),ANGUM(3,100), SAVE.6
C      $ERRPT(3,100),DATUM(3,100),DTSM1(3,100),DTEN1(3,100),NSETS SAVE.7
C      COMMON/LST/EINV(300),INDEX(15),UPAR(15),RH,FTOL,XTOL,MAXFEV,FACTOR,LST.2
C      $,EPSFCN LST.3
C      COMMON/TH/TIME(10),ICH,INTS,SPHAX,SPHIN TH.2
C      COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF DAT.2
C      INTEGER M,N,IFLAG FCN.25
C      REAL X(N),FVEC(M),SCAL1(100) FCN.26
C
C      FCN.27
C      PLACE THE PARAMETERS TO BE VARIED IN THEIR PROPER POSITION FCN.28
C      FCN.29
C      FCN.30
      DO 10 I=1,N

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	VPAR(INDEX(I))=X(I)	FCN.31
10	CONTINUE	FCN.32
C		FCN.33
C	CALCULATE THE DFCS	FCN.34
C		FCN.35
	RH1=RH	FCN.36
	CALL PREPOT(VPAR,RH1)	FCN.37
	IJ=0	FCN.38
	DO 30 J=1,NSETS	FCN.39
	CALL SWITCH(J)	FCN.40
	CALL DFCS(VPAR,SCAL1,DHY,RH1)	FCN.41
C		FCN.42
C	SET UP NON-LINEAR FUNCTIONS	FCN.43
C		FCN.44
	DO 20 I=1,NANG	FCN.45
	FVEC(IJ+I)=(SDAT(I)-SCAL1(I))*EINV(IJ+I)	FCN.46
20	CONTINUE	FCN.47
	IJ=IJ+NANG	FCN.48
30	CONTINUE	FCN.49
C		FCN.50
C	IF INTERMEDIATE PRINTING INFORMATION IS NEEDED, DO SO HERE.	FCN.51
C		FCN.52
	IF(IFLAG.NE.0) GOTO 50	FCN.53
	FNORM=ENORM(N,FVEC)	FCN.54
	WRITE(6,111) FNORM,(INDEX(I),X(I),I=1,N)	FCN.55
50	RETURN	FCN.57
C		
C		
C	FORMAT STATEMENTS	
C		
111	FORMAT(1X,F10.4,20X,5(2X,I2,1X,F10.4),/,31X,5(2X,I2,1X,F10.4))	FCN.56
	END	FCN.58
		FCN.59
	SUBROUTINE POTPLOT(A,RH)	POTPLOT.2
C		POTPLOT.3
C	FUNCTION- PLOTS THE POTENTIAL ON A LINE PRINTER. THE AREA PLOTTED	POTPLOT.4
C	IS DEFINED BY	POTPLOT.5
C	XMIN=RANGE(2),XMAX=RANGE(3),YMIN=RANGE(4),YMAX=RANGE(5)	POTPLOT.6
C	IF ANY POINTS ARE OUTSIDE THIS BOUNDARY THEY ARE NOT PLOTTED.	POTPLOT.7
C	THIS ENABLES ONE TO COMPARE DIFFERENT POTENTIALS ON AN	POTPLOT.8
C	INDEPENDENT SCALE. IF EXACT OR JWKB PHASE SHIFTS ARE USED, THEN	POTPLOT.9
C	THE POTENTIAL IS EXPRESSED IN DIFFERENT UNITS. ISKP DETERMINES	POTPLOT.10
C	WHICH TYPE OF PHASE SHIFTS ARE USED	POTPLOT.11
C		POTPLOT.12
C	PARAMETERS- A, ON INPUT CONTAINS THE POTENTIAL PARAMETERS	POTPLOT.13
C	RH IS THE REDUCED MASS	POTPLOT.14
C		POTPLOT.15
C	SUBPROGRAMS- POT,XPLOT,SQRT	POTPLOT.16
C		POTPLOT.17

C	AUTHOR H.F. VERNON	
C		POTPLOT.19
C	LAST REVISION DATE- FEBRUARY 16,1983	
C		
C	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR	PTNL.2
	COMMON/RNG/RANGE(5)	RNG.2
	DIMENSION XX(100),VV(100),VT(10),X(10),VP(10),A(15)	POTPLOT.22
	DIMENSION RN(5)	POTPLOT.23
C		POTPLOT.24
C	MAKE A COPY OF THE COMMON BLOCK TO PASS AS A SUBROUTINE ARGUMENT	POTPLOT.25
C		POTPLOT.26
	DO 10 I=1,5	POTPLOT.27
	RN(I)=RANGE(I)	POTPLOT.28
10	CONTINUE	POTPLOT.29
	XMIN=RANGE(2)	POTPLOT.30
C		POTPLOT.31
C	DETERMINE THE UNITS OF THE POTENTIAL ENERGY BY DECIDING WHAT	POTPLOT.32
C	TYPE OF PHASE SHIFTS ARE USED	POTPLOT.33
C		POTPLOT.34
	ISKP=0	POTPLOT.35
	IF(XSTART*XSTEP#RNPHAS.NE.0.) ISKP=1	POTPLOT.36
	BZ=RN#A(1)#A(2)#A(2)*349.757/16.8573	POTPLOT.37
	STEP=(RANGE(3)-RANGE(2))/100.	POTPLOT.38
	TEST=ABS(RANGE(4))	POTPLOT.39
	DO 100 I=1,10	POTPLOT.40
	ISTART=10*(I-1)	POTPLOT.41
C		POTPLOT.42
C	CALCULATE POTENTIAL IN BLOCKS OF 10 POINTS	POTPLOT.43
C		POTPLOT.44
	DO 90 J=1,10	POTPLOT.45
	X(J)=XMIN/A(2)	POTPLOT.46
90	XMIN=XMIN+STEP	POTPLOT.47
	CALL POT(X,A,VT,VP,10,RN)	POTPLOT.48
	DO 80 J=1,10	POTPLOT.49
	II=ISTART+J	POTPLOT.50
C		POTPLOT.51
C	IF EXACT PHASE SHIFTS ARE USED, THEN THE POSITION AND ENERGY HAVE	POTPLOT.52
C	TO BE CONVERTED TO BE CONSISTENT WITH THE JMKR UNITS	POTPLOT.53
C		POTPLOT.54
	IF(ISKP.EQ.1) VT(J)=VT(J)/BZ	POTPLOT.55
	IF(ISKP.EQ.1) X(J)=SORT(1./X(J))	POTPLOT.56
C		POTPLOT.57
C	CONVERT FROM REDUCED TO REAL UNITS	POTPLOT.58
C		POTPLOT.59
	VV(II)=VT(J)#A(1)	POTPLOT.60
	XX(II)=X(J) #A(2)	POTPLOT.61
80	CONTINUE	POTPLOT.62
100	CONTINUE	POTPLOT.63
C		POTPLOT.64
C	XPLOT IS THE SANDIA LINE PRINTER PLOT ROUTINE	POTPLOT.65
C		POTPLOT.66
	CALL XPLOT(-180100,1,-1,0,1,-1,0,RN,1,XX,VV,100,1H#)	POTPLOT.67

RETURN
END

POTPLOT.68
POTPLOT.69

SUBROUTINE SCALE(X,V)

POTPLOT.70

FUNCTION-SCALES CALCULATED TO OBSERVED CROSS SECTIONS.
CHOOSE BEST ADDITIVE CONSTANT WHICH MINIMIZES CHISQR
ON INPUT, X CONTAINS THE SCATTERING DISTRIBUTION. ON OUTPUT, X
CONTAINS THE LOG OF THE CALCULATED SCATTERING DISTRIBUTION,
SCALED TO MINIMIZE CHI SQUARE ERROR.
V, ON OUTPUT, IS THE CHI SQUARE ERROR.

SCALE.2
SCALE.3
SCALE.4
SCALE.5
SCALE.6
SCALE.7
SCALE.8
SCALE.9
SCALE.10
SCALE.11
SCALE.12

SUBPROGRAMS-ALOG

AUTHOR-H.F. VERNON

SCALE.14

LAST REVISION DATE-FEBRUARY 16,1983

COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF
DIMENSION X(1)

DAT.2
SCALE.16
SCALE.17
SCALE.18
SCALE.19

CONVERT TO LOG SCALE

DO 9 I=1,NANG
X(I)=ALOG(X(I))
CONTINUE

SCALE.20
SCALE.21
SCALE.22
SCALE.23

FIND ADDITIVE CONSTANT TO MINIMIZE LEAST SQUARE ERROR

SCALE.24
SCALE.25

S=0.
V=0.
R=0.
DO 10 I=1,NANG
R=R+(X(I)-SDAT(I))/EDAT(I)
S=S+1./EDAT(I)

SCALE.26
SCALE.27
SCALE.28
SCALE.29
SCALE.30
SCALE.31

CONTINUE

SCALE.32
SCALE.33

SF IS THE SCALE FACTOR, OR ADDITIVE CONSTANT ON A LOG SCALE

SCALE.34
SCALE.35

SF=R/S

SCALE.36
SCALE.37

RETURN SCALED DATA AND CHI SQUARE ERROR

SCALE.38
SCALE.39

DO 11 I=1,NANG
X(I)=X(I)-SF
V=V+(X(I)-SDAT(I))*2/EDAT(I)
CONTINUE
RETURN
END

SCALE.40
SCALE.41
SCALE.42
SCALE.43
SCALE.44
SCALE.45

C	NPRI/NSEC; MASS(AMU) OF PRIMARY/SECONDARY BEAMS	INPUT.48
C		INPUT.49
C	BETA1,BETA2,VZRO1,VZRO2; PRIMARY/SECONDARY NOZZLE BEAM VELOCITY	INPUT.50
C	DISTRIBUTION PARAMETERS. SEE SUBROUTINE NOZZLE FOR FUNCTIONAL	INPUT.51
C	DEPENDENCE. IDEALLY, THESE PARAMETERS SHOULD BE FIT USING THE	INPUT.52
C	KELVIN PROGRAM	INPUT.53
C		INPUT.54
C	PRINOZ/SECNOZ; DISTANCE OF PRIMARY/SECONDARY NOZZLE FROM CENTER OF	INPUT.55
C	COLLISION ZONE	INPUT.56
C		INPUT.57
C		INPUT.58
C	XL,YL,ZL; DIMENSIONS OF COLLISION VOLUME IN X,Y,Z DIRECTIONS AS	INPUT.59
C	DETERMINED BY THE MOLECULAR BEAM DEFINING SLITS.	INPUT.60
C	ALIM(1),BLIM(1)-- ARE THE DETECTOR WIDTH ENDPOINTS RELATIVE TO THE	INPUT.61
C	DETECTOR CENTER.	INPUT.62
C	ALIM(2),BLIM(2)-- ARE THE DETECTOR HEIGHT ENDPOINTS RELATIVE TO	INPUT.63
C	THE DETECTOR CENTER. ALIM IS THE LOWER INTEGRATION LIMIT AND	INPUT.64
C	MUST BE LESS THAN BLIM.	INPUT.65
C		INPUT.66
C	DETRAD; LOCATION OF DETECTOR DEFINIG APERTURE FROM THE CENTER OF	INPUT.67
C	THE COLLISION ZONE.	INPUT.68
C		INPUT.69
C	RANGE(2)=XMIN,RANGE(3)=XMAX,RANGE(4)=YMIN,RANGE(5)=YMAX FOR THE	INPUT.70
C	POTENTIAL PLOT.	INPUT.71
C		INPUT.72
C	NCOLX,NCOLY,NCOLZ; NUMBER OF INTEGRATION POINTS IN X,Y,Z	INPUT.73
C	DIRECTIONS FOR COLLISION VOLUME INTEGRATION. MAXIMUM OF 5 IN EACH	INPUT.74
C	DIRECTION.	INPUT.75
C		INPUT.76
C	NPRI,NSEC; NUMBER OF NEWTON DIAGRAMS FOR PRIMARY/SECONDARY BEAMS.	INPUT.77
C	LIMITED TO A MAXIMUM OF 10 EACH.	INPUT.78
C		INPUT.79
C	NANG; NUMBER OF LABORATORY ANGLES WHERE CALCULATION IS TO BE PER-	INPUT.80
C	FORMED.	INPUT.81
C		INPUT.82
C	IINT=0, THEN POINT DETECTOR LOCATED AT CENTER OF DETECTOR .	INPUT.83
C	IINT= 1 IF ONLY INTEGRATE OVER DETECTOR WIDTH(IN PLANE)	INPUT.84
C	IINT= 2 IF FULL TWO DIMENSIONAL DETECTOR INTEGRATION TO BE DONE.	INPUT.85
C		INPUT.86
C	IAPPRX=1 THEN ALL THE POINTS IN THE COLLISION VOLUME HAVE THE	INPUT.87
C	SAME PHASE SHIFTS.	INPUT.88
C	IAPPRX=0, THEN ALL POINTS IN THE COLLISION ZONE HAVE THEIR OWN	INPUT.89
C	PHASE SHIFTS COMPUTED FROM THE ANGLES DEFINED BY THE NOZZLE	INPUT.90
C	POSITIONS AND THE INTERSECTION POINT.	INPUT.91
C	IAPPRX=2, THEN ALL POINTS IN THE COLLISION VOLUME FOR ALL NEWTON	INPUT.92
C	DIAGRAMS HAVE THE SAME PHASE SHIFTS- NAMELY THOSE FOR THE MOST	INPUT.93
C	PROBABLE NEWTON DIAGRAM.	INPUT.94
C		INPUT.95
C	NPRI1 =1 PRINTS OUT COLLISION ENERGIES OF EACH NEWTON DIAGRAM	INPUT.96
C	AND THE PHASE SHIFTS. CAUTION-MUCH PRINT.	INPUT.97
C	NPRI1=0 ; NO PHASE SHIFT PRINTING.	INPUT.98
C		INPUT.99
C	NSETS- THE NUMBER OF DATA SETS USED IN A SINGLE LEAST SQUARE FIT,	INPUT.100

C	ALL DATA SETS MUST HAVE A COMPLETE DATA DECK AS THOUGH IRPT=2	INPUT.101
C	(SEE BELOW). ADDITIONALLY, NSETS MUST BE THE SAME FOR EACH DATA	INPUT.102
C	SET. A DUMMY VALUE FOR IRPT MUST BE GIVEN FOR EACH DATA SET,	INPUT.103
C	EXCEPT FOR THE LAST ONE READ WHICH WILL BE EXECUTED AS NORMAL.	INPUT.104
C		INPUT.105
C		INPUT.106
C	NITER IS THE ALLOWED NUMBER OF FUNCTION CALLS BY THE LEAST	INPUT.107
C	SQUARES ROUTINE BEFORE TERMINATION.	INPUT.108
C		INPUT.109
C	META; MAXIMUM VALUE OF THE ORBITAL ANGULAR MOMENTUM	INPUT.110
C		INPUT.111
C	MSKP; STEP SIZE IN THE ORBITAL ANGULAR MOMENTUM QUANTUM NUMBER	INPUT.112
C	FOR CONSTRUCTING PHASE SHIFT GRID FOR INTERPOLATION.	INPUT.113
C		INPUT.114
C	MOPT =1, DFCS CALCULATED BUT NO DATA SUPPLIED.	INPUT.115
C	MOPT =2, DFCS CALCULATED WITH DATA, BUT NO ERRORS.	INPUT.116
C	MOPT =3, DFCS CALCULATED WITH DATA AND ERRORS.	INPUT.117
C		INPUT.118
C	MLST#0, THEN LEAST SQUARES FIT TO DATA WILL BE PERFORMED FOR	INPUT.119
C	MLST VARIABLES. IF MLST=0, NO LEAST SQUARES FIT.	INPUT.120
C		INPUT.121
C	MPAR ; THE NUMBER OF PARAMETERS IN THE POTENTIAL.	INPUT.122
C		INPUT.123
C	MPRI2=1, THEN EACH APPROXIMATION TO THE DETECTOR INTEGRAL IS	INPUT.124
C	PRINTED.	INPUT.125
C	=0, THEN PRINTING SUPPRESSED	INPUT.126
C		INPUT.127
C	MAXIT- MAXIMUM NUMBER OF ITERATIONS IN THE ADAPTIVE SIMPSON'S	INPUT.128
C	INTEGRATION OVER THE DETECTOR.	INPUT.129
C		INPUT.130
C	XSTART- BEGINNING POINT FOR THE NUMEROV INTEGRATION OF PHASE	INPUT.131
C	SHIFTS (IN REDUCED UNITS)	INPUT.132
C		INPUT.133
C	XSTEP- STEP LENGTH FOR NUMEROV INTEGRATION, IN REDUCED UNITS.	INPUT.134
C	RNPHAS- NUMBER OF STEPS IN NUMEROV INTEGRATION	INPUT.135
C		INPUT.136
C	ERROR- WHEN THE JUKB CORRECTED PHASE SHIFTS AGREE TO WITHIN	INPUT.137
C	ERROR RADIANs ON TWO CONSECUTIVE MODES, THE PHASE SHIFT IS CON-	INPUT.138
C	SIDERED CONVERGED	INPUT.139
C		INPUT.140
C	IBOSE- WHEN NUCLEI ARE IDENTICAL, IBOSE=1 SUMS OVER EVEN PARTIAL	INPUT.141
C	WAVES ONLY.	INPUT.142
C	IBOSE=2, SAME BUT OVER ODD PARTIAL WAVES.	INPUT.143
C	IF NUCLEI ARE NOT IDENTICAL, IBOSE SET TO 1 INTERNALLY AND NEED	INPUT.144
C	NOT BE SUPPLIED	INPUT.145
C		INPUT.146
C		INPUT.147
C	NOTE-----	INPUT.148
C	XSTART,XSTEP,RNPHAS,ERROR ALL MUST BE ZERO WHEN JUKB PHASE SHIFTS	INPUT.149
C	ARE USED.	INPUT.150
C		INPUT.151
C	A; VECTOR CONTAINING THE POTENTIAL PARAMETERS	INPUT.152
C	ALL 15 ENTRIES OF A ARE READ ON INPUT, SO DUMMY VALUES MUST BE	INPUT.153

C	GIVEN FOR THE UNUSED ENTRIES.	INPUT.154
C		INPUT.155
C	INDEX: CONTAINS THE LIST OF WHICH PARAMETERS ARE TO BE VARIED IN	INPUT.156
C	LEAST SQUARES FIT. IF POTENTIAL HAS, SAY, 10 PARAMETERS, BUT	INPUT.157
C	ONLY THE THIRD, FIFTH, AND SEVENTH ARE TO BE VARIED, THEN	INPUT.158
C	INDEX(1)=3,INDEX(2)=5,INDEX(3)=7 WITH NLST=3.	INPUT.159
C		INPUT.160
C	FTOL IS THE UPPER BOUND FOR THE RELATIVE VARIATION IN THE CHI-	INPUT.161
C	SQUARE ERROR. TO STOP THE LEAST SQUARES FIT AFTER CHI SQUARE IS	INPUT.162
C	CHANGING BY LESS THAN 1 PER CENT, SET FTOL=.01	INPUT.163
C		INPUT.164
C	XTOL- SIMILAR TO FTOL EXCEPT THIS IS THE RELATIVE VARIATION IN	INPUT.165
C	THE PARAMETERS THEMSELVES. THE LEAST SQUARES ROUTINE WILL TERMIN-	INPUT.166
C	ATE WHEN THE RELATIVE CHANGE IN THE PARAMETERS IS LESS THAN	INPUT.167
C	XTOL PER CENT.	INPUT.168
C		INPUT.169
C	FACTOR- CONTROLS THE LENGTH OF THE FIRST PARAMETER STEP. 100 IS	INPUT.170
C	THE SUGGESTED VALUE. IT SHOULD LIE IN THE RANGE .1-100.	INPUT.171
C		INPUT.172
C	EPSFCN-THE RELATIVE ACCURACY OF THE DERIVATIVES. MAKE THIS	INPUT.173
C	SEVERAL ORDERS OF MAGNITUDE SMALLER THAN FTOL,XTOL.	INPUT.174
C		INPUT.175
C		INPUT.176
C	IRPT IS READ IN THE MAIN PROGRAM UNIT TEST. ITS FUNCTION IS AS	INPUT.177
C	FOLLOWS	INPUT.178
C	IRPT=1 , THEN A NEW SET OF POTENTIAL PARAMETERS A(I) IS READ,	INPUT.179
C	AND THE CALCULATION REPEATED WITH THE EXPERIMENTAL AVERAGING	INPUT.180
C	PARAMETERS REMAINING UNCHANGED FROM THEIR PREVIOUS VALUE.	INPUT.181
C	IRPT=2, THEN A COMPLETE NEW DATA SET IS INPUT, BEGINNING WITH	INPUT.182
C	CARD 1.	INPUT.183
C	IRPT=0, OR A BLANK CARD WILL TERMINATE PROGRAM.	INPUT.184
C	*****	INPUT.185
C		INPUT.186
C		INPUT.187
C	COMMON/TRIG/DETSIN(100),DETCOS(100)	INPUT.188
	COMMON/VOL/X(5),Y(5),Z(5),WX(5),WY(5),WZ(5)	VOL.2
	COMMON/SAVE/IDIN(5),PHOZ(5),SNOZ(5),NTA(5),DTA(5),ID(5),NCX(5),	SAVE.2
	\$NCY(5),NCZ(5),IIRR(5),ISIMAX(5),IPIMAX(5),NBP(5),NBS(5),HT(5),	SAVE.3
	\$WD(5),MAGL(5),DRD(5),ALM1(5),ALM2(5),BLM1(5),BLM2(5),NPRIM1(5),	SAVE.4
	\$VELO1(5,10),VLWT1(5,10),VELO2(5,10),VLWT2(5,10),CCI(7,5),XCV(5,5)	SAVE.5
	\$YCV(5,5),ZCV(5,5),WXCX(5,5),WYCV(5,5),WZCV(5,5),ANGUN(3,100),	SAVE.6
	\$ERRPT(3,100),DATUM(3,100),DTSN1(3,100),DTCN1(3,100),NSETS	SAVE.7
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR	PTNL.2
	COMMON/LST/EINV(300),INDEX(15),UPAR(15),RM,FTOL,XTOL,MAXFEV,FACTORLST.2	LST.3
	\$EPSFCN	
	COMMON/BEAM/VPRI(10),VSEC(10),WPRI(10),WSEC(10),NPRI,MSEC,IPRIM,	BEAM.2
	+ISECON	BEAM.3
	COMMON/GEOMTY/PRINOZ,SECHOZ,PRISPD,SECSPD,XCOL,YCOL,ZCOL,NPRI,	GEOMTRY.2
	INSEC,SNDD,CSDT,MOPT,NPRI1	GEOMTRY.3
	\$NPRI2,MAXIT	GEOMTRY.4
	REAL NPRI,MSEC,MTOT	GEOMTRY.5
	COMMON/TM/TIME(10),ICH,INTS,SPHAX,SPHIN	TM.2
	COMMON/INTEG/IINT	INTEG.2

COMMON/ETA/STHE(8000),CTHE(8000),META,BETA,IDENT	ETA.2
%IBOSE	ETA.3
COMMON/MH/C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,MTOT	MH.2
COMMON/EN/ENERGY(125),CNTH1(125),CNTH2(125),WGHT1(125),WGHT2(125),EN	EN.2
1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
COMMON/RNG/RANGE(5)	RNG.2
COMMON/AA/BETWD,BETHT,DETRAD,E	AA.2
COMMON/LIMITS/ALIN(2),BLIN(2)	LIMITS.2
COMMON/BAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF	BAT.2
DIMENSION VB(20),A(15)	INPUT.204
DIMENSION TITLE(20)	INPUT.205
RANGE(1)=1.	INPUT.206
C	INPUT.207
C READ PROGRAM PARAMETERS AND TRANSLATE THEM INTO THEIR APPROPRIATE	INPUT.208
C VALUES WHERE NECESSARY	INPUT.209
C	INPUT.210
MN=0	INPUT.211
4100 CONTINUE	INPUT.212
READ(5,2)(TITLE(I),I=1,20)	INPUT.213
READ(5,1000) NPRI,BETA1,VZRO1,PRINOZ	INPUT.215
READ(5,1000) MSEC,BETA2,VZRO2,SECNOZ	INPUT.216
IDENT=1	INPUT.217
IF(NPRI.EQ.MSEC) IDENT=2	INPUT.218
READ(5,1000)XL,YL,ZL,ALIN(1),BLIN(1),ALIN(2),BLIN(2),DETRAD	INPUT.219
C	INPUT.220
C ALIN,BLIN SETS LIMITS FOR DETECTOR SLIT INTEGRALS	INPUT.221
C	INPUT.222
DETHT=BLIN(2)-ALIN(2)	INPUT.223
DETW=BLIN(1)-ALIN(1)	INPUT.224
READ(5,1000) RANGE(2),RANGE(3),RANGE(4),RANGE(5)	INPUT.225
READ(5,1001) NCOLX,NCOLY,NCOLZ,NPRI,MSEC,NANG,IINT,IAPPRX	INPUT.226
READ(5,1001) META,NSKP,NPRI1,NSETS,NOPT,MLST,NFAR,NITER	INPUT.227
READ(5,1001) NPRI2,MAXIT,IBOSE	INPUT.228
IF(IDENT.EQ.1) IBOSE=1	INPUT.229
READ(5,1000) XSTART,XSTEP,RNPHAS,ERROR	INPUT.230
DETA=FLOAT(NSKP)	INPUT.231
READ(5,1000)'A(I),I=1,15)	INPUT.232
IF(MLST.NE.0) READ(5,1001)(INDEX(I),I=1,MLST)	INPUT.233
IF(MLST.NE.0) READ(5,1000) FTOL,XTOL,FACTOR,EPSFCN	INPUT.234
C	INPUT.235
C WRITE OUT INFORMATION ON THE PROGRAM PARAMETERS	INPUT.236
C	INPUT.237
MAXFEV=NITER	INPUT.238
WRITE(6,1002)	INPUT.239
WRITE(6,1003)	INPUT.241
WRITE(6,1004)XL,YL,ZL	INPUT.243
WRITE(6,1005)DETW,DETHT,DETRAD	INPUT.245
WRITE(6,1006)NCOLX,NCOLY,NCOLZ	INPUT.248
WRITE(6,1007) IINT	INPUT.251
WRITE(6,1012) META,DETA	INPUT.253
IF(IAPPRX.EQ.2) WRITE(6,1017)	INPUT.256
IF(XSTART*XSTEP*RNPHAS*ERROR.NE.0.) WRITE(6,1018) XSTART,XSTEP,	INPUT.259
% RNPHAS,ERROR	INPUT.260

IF(IAPPRX.E9.1) WRITE(6,1013)	INPUT.263
WRITE(6,13)	INPUT.264
C	INPUT.267
C READ IN DATA OR ANGULAR RANGE	INPUT.268
C	INPUT.269
IF(NOPT-2) 800,810,820	INPUT.270
C	INPUT.271
C NO DATA	INPUT.272
C	INPUT.273
800 READ(5,1000) ANG1,DANG	INPUT.274
ANG1=ANG1-DANG	INPUT.275
DO 1110 I=1,NANG	INPUT.276
EDAT(I)=1.	INPUT.277
ANG1=ANG1+DANG	INPUT.278
1110 ANGLE(I)=ANG1	INPUT.279
WRITE(6,30)	INPUT.280
WRITE(6,1009)(ANGLE(I),I=1,NANG)	INPUT.283
MVOL=NCOLX*NCOLY*NCOLZ	INPUT.284
GOTO 2222	INPUT.285
C	INPUT.286
C DATA, NO ERRORS	INPUT.287
C	INPUT.288
810 READ(5,1000)(ANGLE(I),SDAT(I),I=1,NANG)	INPUT.289
DO 1120 I=1,NANG	INPUT.290
1120 EDAT(I)=1.	INPUT.291
GOTO 830	INPUT.292
C	INPUT.293
C DATA AND ERRORS	INPUT.294
C	INPUT.295
820 READ(5,1000)(ANGLE(I),SDAT(I),I=1,NANG)	INPUT.296
READ(5,1000)(EDAT(I),I=1,NANG)	INPUT.297
830 CONTINUE	INPUT.298
C	INPUT.299
C WRITE OUT DATA AND ANGULAR RANGE	INPUT.300
C	INPUT.301
WRITE(6,1008) NANG	INPUT.302
WRITE(6,1009)(ANGLE(I),SDAT(I),I=1,NANG)	INPUT.304
IF(NOPT.NE.3) GOTO 831	INPUT.306
WRITE(6,13)	INPUT.307
WRITE(6,1019)	INPUT.308
WRITE(6,1021)(EDAT(I),I=1,NANG)	INPUT.310
831 MVOL=NCOLX*NCOLY*NCOLZ	INPUT.314
C	INPUT.315
C CONVERSION OF ERRORS APPROPRIATE FOR LOG SCALING	INPUT.316
C	INPUT.317
IF(NOPT.EQ.2) GOTO 2223	INPUT.318
DO 1039 I=1,NANG	INPUT.319
EDAT(I)=ALOG(1.+EDAT(I)/SDAT(I))	INPUT.320
C	INPUT.321
1039 CONTINUE	INPUT.322
2223 CONTINUE	INPUT.323
WRITE(6,13)	INPUT.324
C	INPUT.325

C	CONVERT DATA TO LOG SCALE	INPUT.326
C		INPUT.327
	SMAX=ALOG(SDAT(1))	INPUT.328
	SMIN=SMAX	INPUT.329
	DO 1022 I=1,NANG	INPUT.330
	SDAT(I)=ALOG(SDAT(I))	INPUT.331
	SMIN=AMIN1(SDAT(I),SMIN)	INPUT.332
	SMAX=AMAX1(SDAT(I),SMAX)	INPUT.333
1022	CONTINUE	INPUT.334
C		INPUT.335
C	THESE ARE THE SCALE FACTORS FOR THE LINE PRINTER PLOTS OF THE	INPUT.336
C	ANGULAR DISTRIBUTIONS	INPUT.337
C		INPUT.338
	SPMAX=SMAX*1.05	INPUT.339
	SPMIN=SMIN*.95	INPUT.340
	WRITE(6,1023)	INPUT.341
	WRITE(6,1009)(ANGLE(I),SDAT(I),I=1,NANG)	INPUT.344
	IF(NOPT.EQ.2) GOTO 2222	INPUT.345
	WRITE(6,1019)	INPUT.346
	WRITE(6,1021)(EDAT(I),I=1,NANG)	INPUT.347
2222	CONTINUE	INPUT.348
C		INPUT.349
C	CHECK THAT DIMENSIONS ARE O.K.	INPUT.350
C		INPUT.351
	IF(NANG.LE.100) GOTO 9	INPUT.352
	WRITE(6,11)	INPUT.353
	GOTO 5000	INPUT.355
9	IF(NVOL.LE.125) GOTO 10	INPUT.356
	WRITE(6,11)	INPUT.357
	GOTO 5000	INPUT.360
10	IF(NETA*NVOL.LE.8000) GOTO 18	INPUT.361
	WRITE(6,12)	INPUT.362
	GOTO 5000	INPUT.365
C		INPUT.366
C	INITIALIZE PARAMETERS	INPUT.367
C		
18	DO 499 I=1,9	INPUT.368
499	TIME(I)=0.	INPUT.369
	ICM=0	INPUT.370
	INTS=0	INPUT.371
	RM=MSEC*NPRI/(MSEC+NPRI)	INPUT.372
	RM1=RM	INPUT.373
C		INPUT.374
C	CALCULATE QUADRATURE WEIGHTS FOR NEWTON DIAGRAMS AND PHASE SHIFT	INPUT.375
C	ROUTINE	INPUT.376
C		INPUT.377
	CALL WEIGHTS(XL,YL,ZL,NPRI2)	INPUT.378
C		INPUT.379
C	THESE ARE CONSTANTS NEEDED IN CMANG	INPUT.380
C		INPUT.381
	MTOT=NPRI+MSEC	INPUT.382
	C1=2.*PRIMOZ	INPUT.383
	C2=PRIMOZ*PRIMOZ	INPUT.384

	C3=2.*SECNOZ	INPUT.385
	C4=SECNOZ*SECNOZ	INPUT.386
	C5=MSEC*HSEC/MTOT/MTOT	INPUT.387
	C6=.601408*HPRI*HTOT/MSEC*1.98717E-03	INPUT.388
	C7=MSEC/MTOT	INPUT.389
C		INPUT.390
C	SET UP PRIMARY BEAM NEWTON DIAGRAMS	INPUT.391
C		INPUT.392
	WRITE(6,13)	INPUT.393
	WRITE(6,1010)	INPUT.394
	N=HPRI	INPUT.397
	CALL NOZZLE(N,VB(1),VB(11),VZRO1,BETA1)	INPUT.398
	IPRIM=0	INPUT.399
	PMAX=0.	INPUT.400
	DO 1014 I=1,N	INPUT.401
	VPRI(I)=VB(I)	INPUT.402
	WPRI(I)=VB(10+I)	INPUT.403
C		INPUT.404
C	FIND MOST PROBABLE VELO "Y	INPUT.405
C		INPUT.406
	IF(WPRI(I).LT.PMAX) GOTO 1014	INPUT.407
	PMAX=WPRI(I)	INPUT.408
	IPRIM=I	INPUT.409
1014	CONTINUE	INPUT.410
	WRITE(6,1011) HPRI,BETA1,VZRO1,PRINOZ	INPUT.411
C		INPUT.414
C	SET UP SECONDARY BEAM NEWTON DIAGRAMS	INPUT.415
C		INPUT.416
	WRITE(6,13)	INPUT.418
	WRITE(6,1016)	INPUT.419
	N=MSEC	INPUT.422
	CALL NOZZLE(N,VB(1),VB(11),VZRO2,BETA2)	INPUT.423
	PMAX=0.	INPUT.424
	ISECON=0	INPUT.425
	DO 1015 I=1,N	INPUT.426
	VSEC(I)=VB(I)	INPUT.427
	MSEC(I)=VB(I+10)	INPUT.428
C		INPUT.429
C	FIND MOST PROBABLE VELOCITY	INPUT.430
C		INPUT.431
	IF(VSEC(I).LT.PMAX) GOTO 1015	INPUT.432
	PMAX=VSEC(I)	INPUT.433
	ISECON=I	INPUT.434
1015	CONTINUE	INPUT.435
	WRITE(6,1011) MSEC,BETA2,VZRO2,SECNOZ	INPUT.436
	CALL PREPDT(A,RH)	INPUT.437
C		INPUT.438
C	CALCULATE THE SIN, COSINE ARRAYS FOR THE DETECTOR'S POSITION	INPUT.439
C	TO SAVE FUNCTION EVALUATIONS IN THE DFCS ROUTINE	INPUT.440
C		INPUT.441
	DO 5 II=1,NANG	INPUT.442
	DET=ANGLE(II)*3.14159/180.	INPUT.443
	DETSIN(II)=SIN(DET)	INPUT.444

	BETCOS(II)=COS(BET)	INPUT.445
5	CONTINUE	INPUT.446
C		INPUT.447
C	THIS SECTION COPIES THE INPUT PARAMETERS WHEN MORE THAN ONE	INPUT.448
C	DATA SET IS TO BE FIT SIMULTANEOUSLY IN THE LEAST SQUARES ROUTINE	INPUT.449
C		INPUT.450
	IF(NSETS.LT.1) GOTO 4000	INPUT.451
	NN=NN+1	INPUT.452
	BETRD=BETRAD	INPUT.453
	IBIN(NN)=IINT\$PHOZ(NN)=PRINOZ\$SNOZ(NN)=SECOZ\$ONTA(NN)=META	INPUT.454
	BTA(NN)=BETA\$ID(NN)=IDENT\$NCX(NN)=NCOLX\$NCY(NN)=NCOLY\$NCZ(NN)=	INPUT.455
	\$NCOLZ \$ IIRR(NN)=IAPPRX\$ ISIMAX(NN)= ISECON \$IPIMAX(NN)=IPRIM	INPUT.456
	NBP(NN)=NPRIS\$NBS(NN)=NSEC\$HT(NN)=DETHT\$WD(NN)=DETHD\$HAGL(NN)=HANG	INPUT.457
	DRB(NN)=DETRD\$ALM1(NN)=ALIM(1)\$ALM2(NN)=ALIM(2)\$BLM1(NN)=BLIM(1)	INPUT.458
	BLM2(NN)=BLIM(2)	INPUT.459
	NPRIM1(NN)=NPR11	INPUT.460
	DO 4020 I=1,NPRI	INPUT.461
	VELO1(NN,I)=VPRI(I)	INPUT.462
	VLWT1(NN,I)=WPRI(I)	INPUT.463
4020	CONTINUE	INPUT.464
	DO 4025 I=1,NSEC	INPUT.465
	VELD2(NN,I)=VSEC(I)	INPUT.466
	VLWT2(NN,I)=WSEC(I)	INPUT.467
4025	CONTINUE	INPUT.468
	CC1(1,NN)=C1	INPUT.469
	CC1(2,NN)=C2	INPUT.470
	CC1(3,NN)=C3	INPUT.471
	CC1(4,NN)=C4	INPUT.472
	CC1(5,NN)=C5	INPUT.473
	CC1(6,NN)=C6	INPUT.474
	CC1(7,NN)=C7	INPUT.475
	DO 4030 I=1,NCOLX	INPUT.476
	XCV(NN,I)=X(I)	INPUT.477
	WXCV(NN,I)=WX(I)	INPUT.478
4030	CONTINUE	INPUT.479
	DO 4035 I=1,NCOLY	INPUT.480
	YCV(NN,I)=Y(I)	INPUT.481
	WYCV(NN,I)=WY(I)	INPUT.482
4035	CONTINUE	INPUT.483
	DO 4040 I=1,NCOLZ	INPUT.484
	ZCV(NN,I)=Z(I)	INPUT.485
	WZCV(NN,I)=WZ(I)	INPUT.486
4040	CONTINUE	INPUT.487
	DO 4050 I=1,NANG	INPUT.488
	ANGUM(NN,I)=ANGLE(I)	INPUT.489
	ERRPT(NN,I)=EDAT(I)	INPUT.490
	DATUM(NN,I)=SDAT(I)	INPUT.491
	DTSN1(NN,I)=DETSIN(I)	INPUT.492
	DTCN1(NN,I)=DETCOS(I)	INPUT.493
4050	CONTINUE	INPUT.494
	IF(NN.EQ.NSETS) GOTO 4000	INPUT.495
	READ(5,1000) IRPT	INPUT.496
	GOTO 4100	INPUT.497

4000	CONTINUE	INPUT.498
	RETURN	INPUT.499
5000	STOP	INPUT.500
C		
C		
C	FORMAT STATEMENTS	
C		
C		
2	FORMAT(20A4)	INPUT.214
1002	FORMAT(/)	INPUT.240
1003	FORMAT(1H1,45X,*I N P U T P A R A M E T E R S *,/)	INPUT.242
1004	FORMAT(5X,*COLLISION VOLUME DIMENSIONS (X,Y,Z)*,3F10.3,/)	INPUT.244
1005	FORMAT(5X,*DETECTOR WIDTH, HEIGHT, AND DISTANCE FROM COLLISION CEN	INPUT.246
	1TER*,3F10.3,/)	INPUT.247
1006	FORMAT(5X,*NUMBER OF POINTS IN X,Y,Z DIRECTIONS USED IN APPROXIMATE	INPUT.249
	1ING COLLISION VOLUME INTEGRATION*,3I5,/)	INPUT.250
1007	FORMAT(5X,*DETECTOR IS TREATED AS A *,I3,2X,*DIMENSIONAL SLIT*,/)	INPUT.252
1012	FORMAT(5X,*NUMBER OF PHASE SHIFTS=*,I5,2X,* PHASE SHIFT INCREMENT	INPUT.254
	=*,F5.1)	INPUT.255
1017	FORMAT(10X,*ALL NEWTON DIAGRAMS HAVE THE SAME PHASE SHIFTS-IAPPRX=	INPUT.257
	\$2*,/)	INPUT.258
1018	FORMAT(5X,*FOR NUMEROV INTEGRATION, XSTART,XSTEP,RNPHAS,ERROR=*,	INPUT.261
	\$ 4(2X,F9.4))	INPUT.262
1013	FORMAT(5X,*ONLY ONE SET OF PHASE SHIFTS CALCULATED PER NEWTON DIA	INPUT.264
	1GRAM*,/)	INPUT.265
30	FORMAT(10X,* INPUT OPTION 1- ANGLES WHERE DFCS WILL BE CALCULATED*	INPUT.281
	1,/)	INPUT.282
1008	FORMAT(45X,*I N P U T D A T A F O R *,I3,2X,*A N G L E S *,/)	INPUT.303
1009	FORMAT(10(2X,F10.3))	INPUT.305
1019	FORMAT(/,55X,*E R R O R S *,/)	INPUT.309
1021	FORMAT(5(12X,F10.3))	INPUT.311
1000	FORMAT(8F10.3)	INPUT.312
1001	FORMAT(8I10)	INPUT.313
1023	FORMAT(30X,*I N P U T D A T A C O N V E R T E D T O L O G S C I N P U T.	INPUT.342
	- A L E *,/)	INPUT.343
16	FORMAT(1X,*TOO MANY ANGLES*,/)	INPUT.354
11	FORMAT(10X,*NUOV EXCEEDS DIMENSION FOR ARRAYS IN COMMON BLOCK EN*	INPUT.358
	1,/)	INPUT.359
12	FORMAT(10X,*TOTAL NUMBER OF PHASE SHIFTS EXCEEDS DIMENSIONS IN	INPUT.363
	+PHASE SHIFT ROUTINE. CURRENT VALUE IS 8000*,/)	INPUT.364
1010	FORMAT(/,40X,*P R I M A R Y B E A M N E W T O N D I A G R A M	INPUT.395
	1S*,/)	INPUT.396
1011	FORMAT(1X,*MASS=*,F10.3,2X,*BETA=*,F10.3,2X,*VZRO=*,F10.3,5X,*	INPUT.412
	\$NOZZLE DISTANCE FROM COLLISION CENTER=*,F10.3)	INPUT.413
13	FORMAT(/////)	INPUT.417
1016	FORMAT(/,35X,*S E C O N D A R Y B E A M N E W T O N D I A G R	INPUT.420
	1A M S*,/)	INPUT.421
	END	INPUT.501

SUBROUTINE INTENS(TOTAL)

INPUT.502
INTENS.2

COMMON/TH/TIME(10),ICH,INTS,SPHAX,SPHIN	TH.2
COMMON/ETA/STHE(8000),CTHE(8000),META,BETA,IDENT	ETA.2
*,IBOSE	ETA.3
COMMON/EN/ENERGY(125),CHTH1(125),CHTH2(125),WGHT1(125),WGHT2(125),	EN.2
1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
DIMENSION P(1000)	INTENS.6
INTS=INTS+1	INTENS.7
CALL SECOND(BG)	INTENS.8
C	INTENS.9
C FUNCTION- GIVEN THE PHASE SHIFTS AND CENTER OF MASS SCATTERING	INTENS.10
C ANGLES, THIS SUBROUTINE EVALUATES THE LEGENDRE EXPANSION	INTENS.11
C TO OBTAIN THE SCATTERING AMPLITUDE. THE MODULUS	INTENS.12
C OF THE SCATTERING AMPLITUDE IS USED TO FIND THE SCATTERED	INTENS.13
C INTENSITY.	INTENS.14
C	INTENS.15
C PARAMETERS- ON INPUT, THE COMMON BLOCK ETA CONTAINS THE SIN AND	INTENS.16
C COSINE FUNCTIONS OF THE PHASE SHIFTS WHICH ARE INDEPENDENT OF	INTENS.17
C THE SCATTERING ANGLE. THE COSINE OF THE CENTER OF MASS SCATTERING	INTENS.18
C ANGLES ARE CONTAINED IN THE ARRAYS CHTH1,CHTH2 FOR THE TWO	INTENS.19
C POSSIBLE INTERSECTIONS WITH THE NEWTON SPHERE.	INTENS.20
C ON OUTPUT, THE PARAMETER TOTAL CONTAINS THE SCATTERED INTENSITY	INTENS.21
C FROM EACH OF THESE CENTER OF MASS ANGLES.	INTENS.22
C	INTENS.23
C SUBPROGRAMS- FLOAT,SECOND,VECPRO	INTENS.24
C	INTENS.25
C AUTHOR-M.F. VERNON	
C	INTENS.27
C	
C LAST REVISION DATE-FEBRUARY 16,1983	
C	
C TOTAL=0.	INTENS.28
C NVOL=NCOLX*NCOLY*NCOLZ	INTENS.29
C DO 100 II=1,NVOL	INTENS.30
C	INTENS.31
C CALCULATE STARTING INDEX FOR THE NEXT SET OF PHASE SHIFTS, STORED	INTENS.32
C SEQUENTIALLY IN STHE AND CTHE ARRAYS.	INTENS.33
C META IS THE NUMBER OF PHASE SHIFTS.	INTENS.34
C	INTENS.35
C ITEMF=META*(II-1)	INTENS.36
C	INTENS.37
C IF THERE IS NO INTERSECTION WITH NEWTON SPHERE, SKIP TO BACK SIDE	INTENS.38
C	INTENS.39
C IF(WGHT1(II),EQ.0.) GOTO 110	INTENS.40
C X=CHTH1(II)	INTENS.41
C	INTENS.42
C INITIALIZE SUMS OF THE REAL AND IMAGINARY CONTRIBUTIONS	INTENS.43
C FROM THE L=0,1 PARTIAL WAVES.	INTENS.44
C	INTENS.45
C	INTENS.46
C SET UP INITIAL VALUES FOR LEGENDRE RECURSION FORMULA.	INTENS.47
C	INTENS.48
C P(1)=1.	INTENS.49
C P(2)=X	INTENS.50

	P0=1.	INTENS.51
	P1=X	INTENS.52
	IDEL=3	INTENS.53
C		INTENS.54
C	PARTIAL WAVE LOOP	INTENS.55
C		INTENS.56
	DO 50 I=3,META	INTENS.57
C		INTENS.58
C	LEGENDRE RECURSION FORMULA.	INTENS.59
C		INTENS.60
	P2=(FLOAT(IDEL)*X*P1-FLOAT(I-2)*P0)/FLOAT(I-1)	INTENS.61
	P(I)=P2	INTENS.62
C		INTENS.63
C	UPDATE RECURSION FORMULA INITIAL VALUES.	INTENS.64
C		INTENS.65
	P0=P1	INTENS.66
	P1=P2	INTENS.67
	IDEL=IDEL+2	INTENS.68
50	CONTINUE	INTENS.69
C		INTENS.70
C	TOTAL INTENSITY IS SUM OF SQUARES OF REAL AND IMAGINARY PARTS.	INTENS.71
C	THE WEIGHT FACTOR INCLUDES THE VOLUME INTEGRATION WEIGHT, THE	INTENS.72
C	INVERSE ENERGY WEIGHT FROM THE SCATTERING FORMULA, AND THE	INTENS.73
C	INVERSE VELOCITY WEIGHT FOR THE ELECTRON BOMBARDMENT DETECTOR.	INTENS.74
C		INTENS.75
C	IDENT ACCOUNTS FOR SYMMETRIC NUCLEI	INTENS.76
C	IF IBOSE=1 (2), SUM ONLY OVER EVEN (ODD) PARTIAL WAVES WHEN	INTENS.77
C	NUCLEI ARE IDENTICAL.	INTENS.78
C		INTENS.79
	ITH=ITEMP+IBOSE	INTENS.80
	NPROD=META/IDENT -(IBOSE-1)	INTENS.81
	TP=VECPRO(NPROD,CTHE(ITH),IDENT,P(IBOSE),IDENT,0.)	INTENS.82
	SP=VECPRO(NPROD,STHE(ITH),IDENT,P(IBOSE),IDENT,0.)	INTENS.83
	TOTAL=TOTAL+(TP*TP+SP*SP)*WGHT1(II)	INTENS.84
C		INTENS.85
C	BACK SIDE OF NEWTON SPHERE	INTENS.86
C	THE LOGIC AND PARAMETERS ARE DEFINED AS ABOVE	INTENS.87
C		INTENS.88
C		INTENS.89
C	IF THERE IS NO INTERSECTION WITH THE BACK SIDE OF THE NEWTON	INTENS.90
C	SPHERE, GO TO THE NEXT COLLISION VOLUME POINT.	INTENS.91
C		INTENS.92
110	IF(WGHT2(II).EQ.0.) GOTO 100	INTENS.93
C		INTENS.94
C	INITIALIZE VALUES OF THE L=0,1 PARTIAL WAVES FOR THE LEGENDRE	INTENS.95
C	RECURSION FORMULA.	INTENS.96
C		INTENS.97
	X=CMTH2(II)	INTENS.98
	P(1)=1.	INTENS.99
	P(2)=X	INTENS.100
	P0=1.	INTENS.101
	P1=X	INTENS.102
	IDEL=3	INTENS.103

C		INTENS.104
C	LEGRENDRE RECURSION LOOP	INTENS.105
C		INTENS.106
	DO 60 I=3,META	INTENS.107
	P2=(FLOAT(IDEL)*X*P1-FLOAT(I-2)*P0)/FLOAT(I-1)	INTENS.108
	P(I)=P2	INTENS.109
	P0=P1	INTENS.110
	P1=P2	INTENS.111
	IDEL=IDEL+2	INTENS.112
60	CONTINUE	INTENS.113
C		INTENS.114
C	IDENT ACCOUNTS FOR SYMMETRIC NUCLEI	INTENS.115
C	IF IDOSE=1 (2), SUM ONLY OVER EVEN (ODD) PARTIAL WAVES WHEN	INTENS.116
C	NUCLEI ARE IDENTICAL.	INTENS.117
C		INTENS.118
	ITH=ITEMP+IBOSE	INTENS.119
	NPROD=META/IDENT -(IDOSE-1)	INTENS.120
	TP=VECPRO(NPROD,CTHE(ITH),IDENT,P(IBOSE),IDENT,0.)	INTENS.121
	SP=VECPRO(NPROD,STHE(ITH),IDENT,P(IBOSE),IDENT,0.)	INTENS.122
C		INTENS.123
C	SQUARE REAL AND IMAGINARY PARTS OF THE SCATTERING AMPLITUDE TO	INTENS.124
C	OBTAIN THE OBSERVED INTENSITY.	INTENS.125
C		INTENS.126
	TOTAL=TOTAL+(TP*TP+SP*SP)*WGHT2(II)	INTENS.127
100	CONTINUE	INTENS.128
	CALL SECOND(ED)	INTENS.129
	TIME(4)=TIME(4)+ED-BG	INTENS.130
	RETURN	INTENS.131
	END	INTENS.132
		INTENS.133
	SUBROUTINE DFCS(A,SCAT,CHI,RH)	DFCS.2
C		DFCS.3
C	FUNCTION- SUM THE SCATTERING INTENSITY FOR ALL NEWTON DIAGRAMS	DFCS.4
C	OVER ALL ANGLES TO OBTAIN THE COMPUTED SCATTERING INTENSITY	DFCS.5
C	APPROPRIATE FOR THE EXPERIMENTAL CONDITIONS.	DFCS.6
C		
C	PARAMETERS-A, ON INPUT THE POTENTIAL PARAMETERS	DFCS.7
C	RH- THE REDUCED MASS IN AMU.	DFCS.8
C	SCAT- ON OUTPUT, THE CALCULATED SCATTERING INTENSITY FOR THE SET	DFCS.9
C	OF ANGLES SPECIFIED IN THE ARRAY ANGLE.	DFCS.10
C	CHI- THE CHI SQUARE ERROR IN THE FIT OF THE CALCULATED DATA TO	DFCS.11
C	THE OBSERVED DATA, IF GIVEN.	DFCS.12
C	IF IAPPRX=2, ALL NEWTON DIAGRAMS HAVE THE SAME PHASE SHIFT.	DFCS.13
C	IAPPRX=1, ALL COLLISION VOLUME POINTS HAVE THE SAME PHASE SHIFT	DFCS.14
C	FOR EACH NEWTON DIAGRAM	DFCS.15
C	IAPPRX=0, ALL COLLISION VOLUME POINTS HAVE THEIR OWN PHASE SHIFTS	DFCS.16
C		DFCS.17
C		DFCS.18
C	IF NOPT=1, THEN CALCULATED DISTRIBUTION IS SCALED TO A MAXIMUM	DFCS.19
C	VALUE OF 10000, AND CHI SET TO 1.	DFCS.20

C		DFCS.21
C	SUBPROGRAMS CALLED-CHANG,PHSFT,FINT,FILL,MULSNP,SCALE, SORT,	DFCS.22
C	SECOND	DFCS.23
C		DFCS.24
C	AUTHOR-M.F. VERNON	
C	LAST REVISION DATE-FEBRUARY 16,1983	
C		DFCS.26
C		DFCS.27
C	COMMON/TRIG/DETSIN(100),DETCOS(100)	DFCS.28
C	COMMON/GEOMTY/PRINOZ,SECOZ,PRISPD,SECSPD,XCOL,YCOL,ZCOL,NPRI,	GEOMTRY.2
C	1MSEC,SNDT,CSDT,NOPT,NPRI1	GEOMTRY.3
C	\$,NPRI2,MAXIT	GEOMTRY.4
C	REAL NPRI,MSEC,MTOT	GEOMTRY.5
C	COMMON/DAT/ANGLE(100),SDAT(100),EDAT(100),NANG,SF	DAT.2
C	COMMON/BEAM/VPRI(10),VSEC(10),MPRI(10),MSEC(10),NPRI,MSEC,IPRIM,	BEAM.2
C	+ISECON	BEAM.3
C	COMMON/TH/TIME(10),ICH,INTS,SPMAX,SPMIN	TH.2
C	COMMON/INTEG/IINT	INTEG.2
C	COMMON/EN/ENERGY(125),CHTH1(125),CHTH2(125),WGHT1(125),WGHT2(125),EN.2	
C	1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
C	COMMON/AA/DETRAD,DETH,DETRAD,E	AA.2
C	COMMON/LIMITS/ALIM(2),BLIM(2)	LIMITS.2
C	DIMENSION SCAT(1),A(1)	DFCS.37
C	EXTERNAL FINT	DFCS.38
C	ISUG=NPRI2	DFCS.39
C	MAXI=MAXIT	DFCS.40
C	NVOL=NCOLX*NCOLY*NCOLZ	DFCS.41
C		DFCS.42
C	IF IAPPRX=2, THEN ONLY ONE SET OF PHASE SHIFTS IS USED FOR ALL	DFCS.43
C	NEWTON DIAGRAMS	DFCS.44
C		DFCS.45
C	IF(IAPPRX.NE.2) GOTO 15	DFCS.46
C	SECSPD=VSEC(ISECON)	DFCS.47
C	PRISPD=VPRI(IPRIM)	DFCS.48
C		DFCS.49
C	GET COLLISION ENERGY FOR THIS MOST PROBABLE NEWTON DIAGRAM	DFCS.50
C		DFCS.51
C	CALL SECOND(BG)	DFCS.52
C	IOPT=0	DFCS.53
C	XL=DETRAD/SQRT(2.)	DFCS.54
C	YL=XL	DFCS.55
C	ZL=0.	DFCS.56
C	CALL CHANG(XL,YL,ZL,IOPT)	DFCS.57
C		DFCS.58
C	GET PHASE SHIFTS FOR THIS MOST PROBABLE NEWTON DIAGRAM	DFCS.59
C		DFCS.60
C	CALL PHSFT(A,RH,NPRI1)	DFCS.61
C		DFCS.62
C	COPY SAME SET OF PHASE SHIFTS INTO REMAINING PHASE SHIFT ENTRIES	DFCS.63
C	FOR EACH COLLISION VOLUME POINT	DFCS.64
C		DFCS.65

	CALL FILL	DFCS.66
	CALL SECOND(ED)	DFCS.67
	TIME(2)=TIME(2)+ED-BG	DFCS.68
15	CONTINUE	DFCS.69
C		DFCS.70
C	ZERO CALCULATED SCATTERING INTENSITY AT EACH ANGLE	DFCS.71
C		DFCS.72
	DO 10 I=1,NMAG	DFCS.73
	SCAT(I)=0.	DFCS.74
10	CONTINUE	DFCS.75
	DO 200 NM=1,NPRI	DFCS.76
C		DFCS.77
C	CHOOSE PRIMARY SPEED	DFCS.78
C		DFCS.79
	PRISPD=VPRI(NM)	DFCS.80
	DO 200 NM=1,NSEC	DFCS.81
C		DFCS.82
C	CHOOSE SECONDARY SPEED	DFCS.83
C		DFCS.84
	SECSPD=VSEC(NM)	DFCS.85
	CALL SECOND(BG)	DFCS.86
	IF(IAPPRX.EQ.2) GOTO 16	DFCS.87
C		DFCS.88
C	IOPT=0 CALLS CHANG FOR COLLISION ENERGIES ONLY	DFCS.89
C		DFCS.90
	IOPT=0	DFCS.91
	XL=DETRAD/SQRT(2.)	DFCS.92
	YL=XL	DFCS.93
	ZL=0.	DFCS.94
	CALL CHANG(XL,YL,ZL,IOPT)	DFCS.95
C		DFCS.96
C	CALCULATE PHASE SHIFTS FOR COLLISION ENERGIES AT EACH POINT IN	DFCS.97
C	VOLUME GRID.	DFCS.98
C		DFCS.99
	CALL PMSHFT(A,RM,NPRI1)	DFCS.100
C		DFCS.101
C	IAPPRX=1, THEN ALL POINTS IN THE COLLISION VOLUME HAVE THE SAME	DFCS.102
C	PHASE SHIFTS, SO ONLY NEED ONE SET OF PHASE SHIFTS FOR THIS	DFCS.103
C	WHOLE NEWTON DIAGRAM	DFCS.104
C		DFCS.105
	IF(IAPPRX.EQ.1) CALL FILL	DFCS.106
16	CONTINUE	DFCS.107
	CALL SECOND(ED)	DFCS.108
	TIME(2)=TIME(2)+ED-BG	DFCS.109
C		DFCS.110
C	CALCULATE INTENSITY AT EACH DETECTOR ANGLE	DFCS.111
C		DFCS.112
	DO 20 II=1,NMAG	DFCS.113
	DETANG=ANGLE(II)	DFCS.114
	SNDT=DETSIN(II)	DFCS.115
	CSDT=DETCOS(II)	DFCS.116
C		DFCS.117
C	MULSMP INTEGRATES INTENSITY OVER DETECTOR AREA.	DFCS.118

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C                                     DFCS.119
C                                     DFCS.120
C      CALCULATE SCATTERING ACCURATE TO 1 PERCENT OR 1/10 OF DATA ERROR. DFCS.121
C                                     DFCS.122
C      ER=.01                                     DFCS.123
C      IF(EDAT(II).NE.1.) ER =EDAT(II)/10.       DFCS.124
C      CALL MULSMP(IINT,MAXI,ER,FINT,VALUE,IXIT,IBUG) DFCS.125
C      IF(IXIT.NE.1) WRITE(6,501)IXIT,MM,MM,DETANG DFCS.126
C                                     DFCS.131
C      ADD THE NEWTON DIAGRAM WEIGHT.             DFCS.132
C                                     DFCS.133
C      SCAT(II)=SCAT(II)+VALUE*#PRI(MM)*#SEC(MM) DFCS.134
20  CONTINUE                                     DFCS.135
200 CONTINUE                                     DFCS.136
C                                     DFCS.137
C      NORMALIZE FOR DETECTOR AREA,COLLISION VOLUME,NUMBER OF NEWTON DFCS.138
C      DIAGRAMS                                   DFCS.139
C                                     DFCS.140
C      RNORM=DETHD                                DFCS.141
C      IF(IINT.EQ.2) RNORM=RNORM*DETHT           DFCS.142
C      RNORM=1./RNORM                             DFCS.143
C      DO 21 II=1,NANG                             DFCS.144
C      SCAT(II)=SCAT(II)*RNORM                     DFCS.145
21  CONTINUE                                     DFCS.146
C      IF(NOPT.NE.1) GOTO 4900                    DFCS.147
C                                     DFCS.148
C      SCALE CROSS SECTION TO HAVE A MAXIMUM OF 10000 DFCS.149
C                                     DFCS.150
C      CALMAX=SCAT(1)                              DFCS.151
C      DO 30 I=1,NANG                              DFCS.152
C      CALMAX=AMAX1(CALMAX,SCAT(I))                DFCS.153
C      SCAT(I)=ALOG(SCAT(I))                       DFCS.154
30  CONTINUE                                     DFCS.155
C      DO 31 I=1,NANG                              DFCS.156
C      SCAT(I)=SCAT(I)-ALOG(CALMAX)+4.*ALOG(10.) DFCS.157
31  CONTINUE                                     DFCS.158
C      CHI=1                                         DFCS.159
C      GOTO 5000                                    DFCS.160
4900 CONTINUE                                    DFCS.161
C                                     DFCS.162
C      SCALE CROSS SECTION TO DATA TO MINIMIZE CHI SQUARE DFCS.163
C                                     DFCS.164
C      CALL SCALE(SCAT,CHI)                         DFCS.165
5000 RETURN                                     DFCS.166
C
C
C      FORMAT STATEMENTS
C
C
501  FORMAT(10X,*MULSMP ROUTINE (INTEGRATES OVER DETECTOR AREA) DID NOTDFCS.127
*TERMINATE PROPERLY- EXIT PARAMETER= *,I5,/,10X,*CALCULATION IS COND*DFCS.128
*TING, BUT RESULTS MAY LACK DESIRED ACCURACY*,/,10X,*ERROR OCCURDFCS.129
*ED FOR NEWTON DIAGRAM*,2I5,10X,*AT ANGLE*,3X,F10.5,/) DFCS.130

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END

DFCS.167

		DFCS.168
SUBROUTINE CHANG(XD,YD,ZD,IPT)		CHANG.2
COMMON/GEOMTY/PRIMOZ,SECNOZ,PRISPD,SECSPP,XCOL,YCOL,ZCOL,NPRI,		GEOMTRY.2
1MSEC,SNDT,CSDT,NOPT,NPRI1		GEOMTRY.3
%,NPRI2,MAXIT		GEOMTRY.4
REAL NPRI,MSEC,MTOT		GEOMTRY.5
COMMON/WH/C1,C2,C3,C4,C5,C6,C7,C8,C9,C10,MTOT		WH.2
COMMON/EN/ENERGY(125),CMTH1(125),CMTH2(125),WGHT1(125),WGHT2(125),EN.2		EN.2
1NCOLX,NCOLY,NCOLZ,IAPPRX		EN.3
COMMON/VOL/X(5),Y(5),Z(5),WX(5),WY(5),WZ(5)		VOL.2
COMMON/TH/TIME(10),ICH,INTS,SPMAX,SPMIN		TH.2
ICH=ICH+1		CHANG.8
CALL SECOND(BG)		CHANG.9
		CHANG.10
FUNCTION- GIVEN A POINT ON THE DETECTOR LOCATED AT (XD,YD,ZD) IN		CHANG.11
THE LABORATORY, FIND THE CENTER OF MASS SCATTERING ANGLES FOR		CHANG.12
EACH NEWTON DIAGRAM REPRESENTING THE DIFFERENT POINTS IN THE		CHANG.13
COLLISION VOLUME TO THIS POINT ON THE DETECTOR. ADDITIONALLY,		CHANG.14
DETERMINE THE GEOMETRICAL WEIGHT FACTORS TO ACCOUNT FOR		CHANG.15
1. THE COLLISION VOLUME WEIGHT,		CHANG.16
2. THE INVERSE LABORATORY VELOCITY DEPENDENCE OF THE IONIZER		CHANG.17
DETECTOR EFFICIENCY,		CHANG.18
3. THE INVERSE ENERGY DEPENDENCE OF THE ELASTIC SCATTERING CROSS		CHANG.19
SECTION,		CHANG.20
4. THE RELATIVE VELOCITY FACTOR FOR THE TOTAL SCATTERING		CHANG.21
PROBABILITY, AND		CHANG.22
5. THE TRANSFORMATION JACOBIAN FROM THE CENTER OF MASS TO THE		CHANG.23
LABORATORY FRAME APPROPRIATE FOR ELASTIC SCATTERING.		CHANG.24
		CHANG.25
THE WEIGHT FACTORS COMPUTED HERE ARE USED IN THE SUBROUTINE		CHANG.26
INTENS.		CHANG.27
		CHANG.28
PARAMETERS		CHANG.29
XD,YD,ZD- ARE THE INPUT LABORATORY COORDINATES FOR THE POINT ON		CHANG.30
THE DETECTOR WHERE THE SCATTERING INTENSITY IS TO BE FOUND.		CHANG.31
IPT=0, THEN ONLY THE COLLISION ENERGIES ARE FOUND FOR THE		CHANG.32
DIFFERENT POINTS IN THE COLLISION VOLUME. THIS IS USED TO FIND		CHANG.33
THE ENERGIES AT WHICH THE PHASE SHIFTS ARE TO BE COMPUTED.		CHANG.34
IPT=1, FIND COLLISION ENERGIES, SCATTERING ANGLES, AND WEIGHT		CHANG.35
FACTORS.		CHANG.36
		CHANG.37
ON OUTPUT, THE COMMON BLOCK EN CONTAINS THE COLLISION ENERGIES		CHANG.38
IN THE ARRAY ENERGY, THE CENTER OF MASS SCATTERING ANGLES AND		CHANG.39
WEIGHTS FOR THE FORWARD SIDE SCATTERING IN THE ARRAYS CMTH1,WGHT1		CHANG.40
AND THE SCATTERING ANGLES AND WEIGHTS FOR THE BACK SIDE NEWTON		CHANG.41
SPHERE SCATTERING IN THE ARRAYS CMTH2,WGHT2		CHANG.42
IF THE BACK SIDE SCATTERING IS AWAY FROM THE DETECTOR, OR THE		CHANG.43
DETECTOR DOES NOT INTERSECT THE NEWTON SPHERE, THEN THE WEIGHT		CHANG.44
FACTORS FOR THAT POINT ARE SET TO ZERO. IF THE DETECTOR IS		CHANG.45

C	RELATIVE VELOCITY VECTOR=(RELUX,RELUY,RELVZ)	CHANG.98
C		CHANG.99
	RELUX=UX1-UX2	CHANG.100
	RELUY=UY1-UY2	CHANG.101
	RELVZ=VZ1-VZ2	CHANG.102
C		CHANG.103
C	CENTER OF MASS VELOCITY VECTOR=(CMVELX,CMVELY,CMVELZ)	CHANG.104
C		CHANG.105
	CMVELX=(MPRI*UX1+MSEC*UX2)/HTOT +XCOL	CHANG.106
	CMVELY=(MPRI*UY1+MSEC*UY2)/HTOT +YCOL	CHANG.107
	CMVELZ=(MPRI*VZ1+MSEC*VZ2)/HTOT +ZCOL	CHANG.108
C		CHANG.109
C	CALCULATE RADIUS OF NEWTON CIRCLE	CHANG.110
C		CHANG.111
	RDNWT2=C5*(RELUX*RELUX+RELUY*RELUY+RELVZ*RELVZ)	CHANG.112
	RELVEL=SQRT(RDNWT2/C5)	CHANG.113
C		CHANG.114
C	CENTER OF MASS COLLISION ENERGY =E	CHANG.115
C		CHANG.116
	E=C6*RDNWT2	CHANG.117
	ENERGY(INDEX)=E	CHANG.118
C		CHANG.119
C	IF IOPT=0 THEN ONLY WANT TO KNOW THE COLLISION ENERGY TO COMPUTE	CHANG.120
C	PHASE SHIFTS.	CHANG.121
C		CHANG.122
	IF(IOPT.EQ.0) GOTO 100	CHANG.123
	RR=C7/RDNWT2	CHANG.124
C		CHANG.125
C	CALCULATE LINEAR EQN. PARAMETERS FOR Y AND Z COMPONENTS OF	CHANG.126
C	INTERSECTION BETWEEN DETECTOR RAY AND NEWTON CIRCLE.	CHANG.127
C		CHANG.128
	TEMP=XCOL-XD	CHANG.129
	SLPY=(YCOL-YD)/TEMP	CHANG.130
	BY=(XCOL*YD-XD*YCOL)/TEMP	CHANG.131
	SLPZ=(ZCOL-ZD)/TEMP	CHANG.132
	BZ=(XCOL*ZD-XD*ZCOL)/TEMP	CHANG.133
C		CHANG.134
C	A,B,C ARE DEFINED BY THE EQN.	CHANG.135
C	A*XMWT*XMWT+B*XMWT+C=0.	CHANG.136
C	THE TWO SOLUTIONS (XMWT1, XMWT2) ARE THE X COORDINATES OF THE TWO	CHANG.137
C	POINTS ON THE NEWTON CIRCLE.	CHANG.138
C		CHANG.139
	A=1.+SLPY*SLPY+SLPZ*SLPZ	CHANG.140
	B=-2.*(CMVELX+SLPY*(CMVELY-BY))+SLPZ*(CMVELZ-BZ))	CHANG.141
	C=CMVELX*CMVELX+(BY-CMVELY)*(BY-CMVELY)+(BZ-CMVELZ)*(BZ-CMVELZ)	CHANG.142
	1-RDNWT2	CHANG.143
	TEMP=B*B-4.*A*C	CHANG.144
	T5=1./2./A	CHANG.145
	IF(TEMP) 100,40,30	CHANG.146
C		CHANG.147
C	EDGE OF NEWTON CIRCLE	CHANG.148
C		CHANG.149
40	XMWT1=-B*T5	CHANG.150

	XNWT2=XNWT1	CHANG.151
	WRITE(6,31)	CHANG.152
	GOTO 100	CHANG.154
C		CHANG.155
C	TWO DISTINCT ROOTS	CHANG.156
C		CHANG.157
30	TEMP=SQRT(TEMP)	CHANG.158
	XNWT1=(-B+TEMP)*TS	CHANG.159
	XNWT2=(-B-TEMP)*TS	CHANG.160
C		CHANG.161
C	Y,Z COORDINATES DETERMINED BY THE LINEAR EQNS. DEFINED ABOVE.	CHANG.162
C		CHANG.163
35	YNWT1=SLPY*XNWT1+BY	CHANG.164
	YNWT2=SLPY*XNWT2+BY	CHANG.165
	ZNWT1=SLPZ*XNWT1+BZ	CHANG.166
	ZNWT2=SLPZ*XNWT2+BZ	CHANG.167
C		CHANG.168
C	CHECK THAT THE LAB VELOCITY WILL SCATTER PRODUCT INTO THE DETECTOR	CHANG.169
C		CHANG.170
	IF((XNWT1-XCOL)*XD.LT.0.) GOTO 45	CHANG.171
	IF((YNWT1-YCOL)*YD.LT.0.) GOTO 45	CHANG.172
	VCNTX1=(XNWT1-CHVELX)	CHANG.173
	VCNTY1=(YNWT1-CHVELY)	CHANG.174
	VCNTZ1=ZNWT1-CHVELZ	CHANG.175
C		CHANG.176
C	CALCULATE COSINE OF THE CENTER OF MASS SCATTERING ANGLE	CHANG.177
C		CHANG.178
	CHANG1=(VCNTX1*RELVLX+VCNTY1*RELVLY+VCNTZ1*RELVLZ)*RR	CHANG.179
	CHTH1(INDEX)=CHANG1	CHANG.180
C		CHANG.181
C	CALCULATE LABORATORY SPEED OF PRODUCT	CHANG.182
C		CHANG.183
	VLAB1=SQRT((XNWT1-XCOL)**2+(YNWT1-YCOL)**2+(ZNWT1-ZCOL)**2)	CHANG.184
C		CHANG.185
C	CALCULATE LAB CARTESIAN COMPONENTS OF PRODUCT VELOCITY VECTOR	CHANG.186
C		CHANG.187
	VLAB1X=XNWT1-XCOL	CHANG.188
	VLAB1Y=YNWT1-YCOL	CHANG.189
	VLAB1Z=ZNWT1-ZCOL	CHANG.190
C		CHANG.191
C	CALCULATE CENTER OF MASS SCATTERING VECTOR	CHANG.192
C		CHANG.193
	CH1X=XNWT1-CHVELX	CHANG.194
	CH1Y=YNWT1-CHVELY	CHANG.195
	CH1Z=ZNWT1-CHVELZ	CHANG.196
C		CHANG.197
C	CALCULATE THE ABSOLUTE VALUE OF THE COSINE OF THE ANGLE BETWEEN	CHANG.198
C	THE LAB PRODUCT VELOCITY VECTOR AND THE CENTER OF MASS SCATTERING	CHANG.199
C	VECTOR	CHANG.200
C		CHANG.201
	T1=CH1X*VLAB1X+CH1Y*VLAB1Y+CH1Z*VLAB1Z	CHANG.202
	COSUV1=SQRT(T1*T1/RDNWT2)/VLAB1	CHANG.203
C		CHANG.204

C	CALCULATE JACOBIAN FACTORS	CHANG.205
C		CHANG.206
	FJAC1=VLAB1*VLAB1/COSUV1/RDNWT2	CHANG.207
	WGHT1(INDEX)=WX(I)*WY(J)*WZ(K)*RELVEL/VLAB1/ENERGY(INDEX)	CHANG.208
	WGHT1(INDEX)=WGHT1(INDEX)*FJAC1	CHANG.209
C		CHANG.210
C	CHECK THAT THE LAB VELOCITY WILL SCATTER PRODUCT INTO THE DETECTOR	CHANG.211
C		CHANG.212
45	IF((XNWT2-XCOL)*XD.LT.0.) GOTO 100	CHANG.213
	IF((YNWT2-YCOL)*YD.LT.0.) GOTO 100	CHANG.214
	VCNTX2=XNWT2-CHVELX	CHANG.215
	VCNTY2=YNWT2-CHVELY	CHANG.216
	VCNTZ2=ZNWT2-CHVELZ	CHANG.217
C		CHANG.218
C	CALCULATE COSINE OF THE CENTER OF MASS SCATTERING ANGLE	CHANG.219
C		CHANG.220
	CHANG2=(VCNTX2*RELVLX+VCNTY2*RELPLY+VCNTZ2*RELVLZ)*RR	CHANG.221
	CNTH2(INDEX)=CHANG2	CHANG.222
C		CHANG.223
C	CALCULATE LABORATORY SPEED OF PRODUCT	CHANG.224
C		CHANG.225
	VLAB2=SQRT((XNWT2-XCOL)**2+(YNWT2-YCOL)**2+(ZNWT2-ZCOL)**2)	CHANG.226
C		CHANG.227
C	CALCULATE LAB COMPONENTS OF PRODUCT VELOCITY VECTOR	CHANG.228
C		CHANG.229
	VLAB2X=XNWT2-XCOL	CHANG.230
	VLAB2Y=YNWT2-YCOL	CHANG.231
	VLAB2Z=ZNWT2-ZCOL	CHANG.232
C		CHANG.233
C	CALCULATE CENTER OF MASS SCATTERING VECTOR	CHANG.234
C		CHANG.235
	CH2X=XNWT2-CHVELX	CHANG.236
	CH2Y=YNWT2-CHVELY	CHANG.237
	CH2Z=ZNWT2-CHVELZ	CHANG.238
C		CHANG.239
C	CALCULATE THE ABSOLUTE VALUE OF THE COSINE OF THE ANGLE BETWEEN	CHANG.240
C	THE LAB PRODUCT VELOCITY VECTOR AND THE CENTER OF MASS SCATTERING	CHANG.241
C	VECTOR	CHANG.242
C		CHANG.243
	T2=CH2X*VLAB2X+CH2Y*VLAB2Y+CH2Z*VLAB2Z	CHANG.244
	COSUV2=SQRT(T2*T2/RDNWT2)/VLAB2	CHANG.245
C		CHANG.246
C	CALCULATE JACOBIAN FACTORS	CHANG.247
C		CHANG.248
	FJAC2=VLAB2*VLAB2/COSUV2/RDNWT2	CHANG.249
	WGHT2(INDEX)=WGHT1(INDEX)*VLAB1/VLAB2	CHANG.250
	WGHT2(INDEX)=WGHT2(INDEX)*FJAC2/FJAC1	CHANG.251
100	CONTINUE	CHANG.252
C		CHANG.253
C	IF IAPPRX=1, THEN FIND THE POINT IN THE COLLISION ZONE WITH THE	CHANG.254
C	LARGEST WEIGHT FACTOR AND COMPUTE PHASE SHIFTS FOR THIS ENERGY	CHANG.255
C	ONLY. THE CANONICAL ENERGY IS STORED IN ENERGY(1).	CHANG.256
C		CHANG.257

```

70 IF(IAPPRX.EQ.0) GOTO 80                                CHANG.258
   RMAX=0.                                                  CHANG.259
   DO 50 I=1,INDEX                                         CHANG.260
   IF(WGHT1(I).LT.RMAX) GOTO 55                            CHANG.261
   RMAX=WGHT1(I)                                           CHANG.262
   IMAX=I                                                  CHANG.263
55 IF(WGHT2(I).LE.RMAX) GOTO 50                            CHANG.264
   RMAX=WGHT2(I)                                           CHANG.265
   IMAX=I                                                  CHANG.266
50 CONTINUE                                                CHANG.267
   ENERGY(1)=ENERGY(IMAX)                                CHANG.268
80 CALL SECOND(ED)                                         CHANG.269
   TIME(3)=TIME(3)+ED-BG                                   CHANG.270
   RETURN                                                  CHANG.271

C
C
C   FORMAT STATEMENTS
C
C
31 FORMAT(10X,'DETECTOR TANGENT TO NEWTON SPHERE.')
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CHANG.153

CHANG.272

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END

C
C
C   FUNCTION FINT(X)
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CHANG.273

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C   FINT.2
C   FINT.3
C   FINT IS THE FUNCTION WHICH RETURNS THE VALUE OF THE SCATTERED FINT.4
C   INTENSITY AT A POINT ON THE DETECTOR LOCATED AT (XD,YD) IN THE FINT.5
C   LAB FRAME, FROM EACH POINT IN THE COLLISION VOLUME GRID FINT.6
C   PARAMETERS FINT.7
C   X- ON INPUT CONTAINS THE (X,Y)=(X(1),X(2)) POSITION ON THE FINT.8
C   DETECTOR WHERE THE SCATTERING INTENSITY IS TO BE CALCULATED. FINT.9
C   X(1) MEASURES HORIZONTAL DISPLACEMENT FROM THE DETECTOR MIDPOINT FINT.10
C   X(2) MEASURES VERTICAL DISPLACEMENT FINT.11
C   FINT.12
C   SUBPROGRAMS CALLED- INTENS, CHANG FINT.13
C   FINT.14
C   FINT.15
C   COMMON/INTEG/IINT FINT.16
C   COMMON/GEOMTY/PRINOZ,SECONOZ,PRISPD,SECSPD,XCOL,YCOL,ZCOL,NPRI, FINT.17
C   1HSEC,SNDT,CSDT,NOPT,NPRI1 FINT.18
C   %,NPRI2,MAXIT FINT.19
C   REAL NPRI,MSEC,MTOT FINT.20
C   COMMON/AA/DETWD,DETH,DETRAD,E FINT.21
C   DIMENSION X(2) FINT.22
C   FINT.23
C   TRANSLATE FROM DETECTOR COORDINATES TO LAB COORDINATES FINT.24
C   FINT.25
C   XD=DETRAD*CSDT+X(1)*SNDT FINT.26
C   YD=DETRAD*SNDT-X(1)*CSDT
C   ZD=X(2)
```

C	IF ONLY INTEGRATING IN -PLANE SCATTERING, THEN SET Z COORDINATE	FINT.27
C	OF DETECTOR TO ZERO.	FINT.28
C		FINT.29
	IF(IINT.EQ.1) ZD=0.	FINT.30
	IOPT=1	FINT.31
C		FINT.32
C	FIND C.M. ANGLES WHERE INTENSITY IS TO BE EVALUATED	FINT.33
C		FINT.34
	CALL CHANG(XD,YD,ZD,IOPT)	FINT.35
C		FINT.36
C	COMPUTE THE INTENSITY AT THESE ANGLES	FINT.37
C		FINT.38
	CALL INTENS(F)	FINT.39
	FINT=F	FINT.40
	RETURN	FINT.41
	END	FINT.42
		FINT.43
	SUBROUTINE FILL	FILL.2
C		FILL.3
C		FILL.4
C	FUNCTION- WHEN ALL THE COLLISION VOLUME POINTS HAVE THE SAME	FILL.5
C	PHASE SHIFTS, THIS ROUTINE COPIES THE ONE SET OF PHASE SHIFTS	
C	THAT ARE CALCULATED INTO THE PHASE SHIFT ARRAYS FOR THE	
C	REMAINING POINTS. THE COLLISION ENERGY ARRAY IS ALSO COMPLETED	
C	WITH THE ENERGY CORRESPONDING TO THAT OF THE CALCULATED PHASE	
C	SHIFTS.	FILL.9
C		FILL.10
C	SUBPROGRAMS- NONE	FILL.11
C		FILL.12
C	REFERENCE M.F. VERNON, MAY 1982.	FILL.13
C		FILL.14
C		FILL.15
	COMMON/ETA/STHE(8000),CTHE(8000),META,DETA,IDENT	ETA.2
	\$,IBOSE	ETA.3
	COMMON/EN/ENERGY(125),CHTH1(125),CHTH2(125),WGHT1(125),WGHT2(125),	EN.2
	1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
	NVOL=NCOLX*NCOLY*NCOLZ	FILL.18
	DO 50 II=2,NVOL	FILL.19
	ENERGY(II)=ENERGY(1)	FILL.20
	ITEMP=(II-1)*META	FILL.21
	DO 25 J=1,META	FILL.22
	CTHE(ITEMP+J)=CTHE(J)	FILL.23
	STHE(ITEMP+J)=STHE(J)	FILL.24
25	CONTINUE	FILL.25
50	CONTINUE	FILL.26
	RETURN	FILL.27
	END	FILL.28

	FILL.29
SUBROUTINE MULSHP(N,MAXI,E,FINT,VALUE,IXIT,IBUG)	MULSHP.2
C	MULSHP.3
C SIMPSON'S RULE MULTIPLE INTEGRATION FROM SKY SOURCE LIBRARY AND	MULSHP.4
C MODIFIED SLIGHTLY BY M. VERNON.	MULSHP.5
C N = MULTIPLICITY OF THE INTEGRATION. N .LE. 5.	MULSHP.6
C	MULSHP.7
C IF N.EQ.0 THEN VALUE IS RETURNED WITH THE INTENSITY AT THE CENTER	MULSHP.8
C OF THE DETECTOR.	MULSHP.9
C	MULSHP.10
C ALIM = NAME OF FUNCTION ROUTINE DEFINING THE LOWER LIMITS.	MULSHP.11
C BLIM = NAME OF FUNCTION ROUTINE DEFINING THE UPPER LIMITS.	MULSHP.12
C THE CURRENT VERSION OF THE PROGRAM ASSUMES RECTANGULAR	MULSHP.13
C DETECTOR SLITS. THE ALIM, BLIM VALUES ARE CONSTANTS. IF THE	MULSHP.14
C BOUNDARIES DEPEND ON THE COORDINATES, THEN THE ALIM, BLIM	MULSHP.15
C CALLS MUST BE REPLACED BY FUNCTIONS, WITH ARGUMENTS BEING THE	MULSHP.16
C DIMENSION AND XNEW VALUES. NOTE THAT THE LIMIT FUNCTIONS MUST BE	MULSHP.17
C DEFINED SO THAT LOWER DIMENSION LIMITS DEPEND ONLY ON THE HIGHER	MULSHP.18
C DIMENSIONAL COORDINATES.	MULSHP.19
C	MULSHP.20
C MAXI = THE MAX. NO. OF ITERATIONS THE ROUTINE MAY DO.	MULSHP.21
C	MULSHP.22
C FOR ANY DIMENSION, BY THE NTH ITERATION, A TOTAL OF	MULSHP.23
C $2*N + 2*N*(N-1) + \dots + 2*N^2 + 2*N + 3$ FUNCTION EVALUATIONS	MULSHP.24
C WILL HAVE BEEN NECESSARY. IF $N > 3$, AN 8 POINT GAUSS- LEGENDRE	MULSHP.25
C QUADRATURE MAY BE MORE EFFICIENT.	MULSHP.26
C	MULSHP.27
C E = FRACTIONAL ERROR, MEANING	MULSHP.28
C IF $V(I)$ =VALUE OF THE INTEGRAL ON THE ITH ITERATION,	MULSHP.29
C THEN THE PROBLEM IS CONSIDERED SOLVED WHEN	MULSHP.30
C $E \leq \text{ABS}(V(I)) \cdot \text{GT. ABS}(V(I)-V(I+1))$.	MULSHP.31
C FINT = NAME OF FUNCTION ROUTINE DEFINING THE INTEGRAND.	MULSHP.32
C VALUE = LAST APPROXIMATION TO THE INTEGRAL.	MULSHP.33
C IXIT = 1 MEANS NORMAL RETURN	MULSHP.34
C 2 MEANS NO CONVERGENCE	MULSHP.35
C 3 MEANS LOWER .GT. UPPER LIMIT.	MULSHP.36
C IBUG = 1 MEANS PRINT EACH APPROXIMATION TO INTEGRAL.	MULSHP.37
C	MULSHP.38
C SUBPROGRAMS- ABS,FINT	MULSHP.39
C	MULSHP.40
C REFERENCE- M. F. VERNON, 1982	MULSHP.41
C	MULSHP.42
C DIMENSION A(5),B(5),FA(5),FB(5),XH(5),XIR(5),XHA(5),XJ(5),INDEX(5)	MULSHP.43
X ,XNEW(5),FNEWX(5),XI(5),S(5),XE(5),K(5),XIP(5)	MULSHP.44
C COMMON/LIMITS/ALIM(2),BLIM(2)	LIMITS.2
C	MULSHP.46
C IF(IBUG.NE.0) WRITE(6,100)	MULSHP.47
C I=N	MULSHP.50
C	MULSHP.51
C IF DIMENSION IS ZERO, RETURN VALUE AT CENTER OF DETECTOR	MULSHP.52
C	MULSHP.53
C IF(N.EQ.0) GOTO 2001	MULSHP.54
C	MULSHP.55

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C      LOAD LOWER LIMITS, BEGINNING WITH THE HIGHEST DIMENSION FIRST      MULSMP.56
C      IN CASE THE LOWER DIMENSIONAL LIMITS DEPEND ON THESE COORDINATES MULSMP.57
C                                                                              MULSMP.58
C      SET LIMITS FOR THE NEXT PASS AT THE INTEGRAL. K IS USED TO DECIDE MULSMP.59
C      THE STAGE OF THE INTEGRATION OVER THE HIGHER DIMENSIONS (SEE MULSMP.60
C      BELOW) MULSMP.61
C                                                                              MULSMP.62
C      3 DO 1 L=1,I MULSMP.63
C          J=I + 1 - L MULSMP.64
C          K(J)=1 MULSMP.65
C          A(J)=ALIM(J) MULSMP.66
C      1 XNEW(J)=A(J) MULSMP.67
C                                                                              MULSMP.68
C      BEGIN INTEGRATION OVER LOWEST DIMENSIONS WITH NEW VALUES OF MULSMP.69
C      HIGHER DIMENSIONAL COORDINATES MULSMP.70
C                                                                              MULSMP.71
C      2 I=1 MULSMP.72
C                                                                              MULSMP.73
C      GET VALUE OF INTEGRAND AT THE LOWER LIMIT OF LOWEST DIMENSION MULSMP.74
C                                                                              MULSMP.75
C      XNEW(1)=A(1) MULSMP.76
C      FA(1)=FINT(XNEW) MULSMP.77
C                                                                              MULSMP.78
C      GET VALUE OF INTEGRAND AT UPPER LIMIT OF LOWEST DIMENSION MULSMP.79
C                                                                              MULSMP.80
C      B(1)=BLIM(1) MULSMP.81
C      XNEW(1)=B(1) MULSMP.82
C      FB(1)=FINT(XNEW) MULSMP.83
C                                                                              MULSMP.84
C      1000 XH(I)=B(I)-A(I) MULSMP.85
C          IF (.25 * XH(I) .EQ. 0.) GO TO 4 MULSMP.86
C          IF (XH(I) .LT. 0.) GO TO 5 MULSMP.87
C                                                                              MULSMP.88
C      XIR,XHA,XJ ARE CONSTANTS NEEDED TO INITIALIZE ADAPTIVE SIMPSON'S MULSMP.89
C      INTEGRAL. AT THIS POINT, INTEGRAL IS APPROXIMATED USING 2 POINTS MULSMP.90
C      , THE VALUES OF THE INTEGRAND AT THE UPPER AND LOWER LIMITS OF MULSMP.91
C      THE LOWEST DIMENSION MULSMP.92
C                                                                              MULSMP.93
C      XIR(I)=0.5*XH(I) MULSMP.94
C      XHA(I)=XIR(I)/3. MULSMP.95
C      XJ(I)=XIR(I)*(FA(I)+FB(I)) MULSMP.96
C      INDEX(I)=0 MULSMP.97
C                                                                              MULSMP.98
C      NOW BEGIN HALVING STEP SIZE MULSMP.99
C                                                                              MULSMP.100
C      XNEW(I)=A(I)+XIR(I) MULSMP.101
C                                                                              MULSMP.102
C      1006 IF (I .EQ. 1) GO TO 14 MULSMP.103
C                                                                              MULSMP.104
C      IF NOT INTEGRATING LOWEST DIMENSION, THEN MUST DO SO. AT THIS MULSMP.105
C      POINT, A NEW POINT INVOLVING A CHANGE IN THE HIGHER DIMENSIONAL MULSMP.106
C      COORDINATES IS NEEDED, SO MUST BEGIN AT THE LOWEST DIMENSION AND MULSMP.107
C      INTEGRATE UP TO THE DIMENSION WHERE THE NEW MESH POINT IS NEEDED MULSMP.108

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C		MULSMP.109
15	I=I-1	MULSMP.110
	GO TO 3	MULSMP.111
14	FNEWX(1)=FINT(XNEW)	MULSMP.112
C		MULSMP.113
1001	IF (INDEX(I) .GT. 0) GO TO 1003	MULSMP.114
C		MULSMP.115
	FIRST APPROXIMATION,XI, IS 3 POINT SIMPSON'S RULE	MULSMP.116
C		MULSMP.117
1002	INDEX(I)=INDEX(I)+1	MULSMP.118
	XI(I)=XHA(I)*(FB(I)+FA(I)+4.*FNEWX(I))	MULSMP.119
C		MULSMP.120
C	XJ CONTAINS THE CONTRIBUTION TO THE NEXT APPROXIMATION WHICH	MULSMP.121
C	DEPENDS ON THE POINTS ALREADY CALCULATED IN THE ADAPTIVE	MULSMP.122
C	SIMPSON'S INTEGRAL.	MULSMP.123
C		MULSMP.124
1004	XJ(I)=0.25*(XJ(I)+3.*XI(I))	MULSMP.125
	INDEX(I)=INDEX(I)+1	MULSMP.126
	IF (INDEX(I) .GT. MAXI) GO TO 1011	MULSMP.127
C		MULSMP.128
C	HALVE STEP SIZE FOR NEXT APPROXIMATION	MULSMP.129
C		MULSMP.130
1010	XH(I)=0.5*XH(I)	MULSMP.131
	IF (.5 * XH(I) .EQ. 0.) GO TO 7	MULSMP.132
C		MULSMP.133
C	XNEW IS THE FIRST POINT AT THE NEW STEP SIZE. NOTE THAT ONLY	MULSMP.134
C	THE POINTS WHICH ARE AN ODD MULTIPLE OF THE CURRENT STEP SIZE	MULSMP.135
C	ARE CALCULATED, AND THESE ARE OBTAINED BY STARTING AT XNEW AND	MULSMP.136
C	INCREMENTING BY TWICE THE CURRENT STEP SIZE.	MULSMP.137
C		MULSMP.138
	XNEW(I)=0.5*XH(I)+A(I)	MULSMP.139
C		MULSMP.140
C	S= THE SUM OF THE INTEGRAND VALUES AT ALL ODD MULTIPLES OF THE	MULSMP.141
C	CURRENT STEP SIZE, I.E. THE VALUES OF THE INTEGRAND AT POINTS	MULSMP.142
C	NOT PREVIOUSLY CALCULATED.	MULSMP.143
C		MULSMP.144
	S(I)=0.0	MULSMP.145
C		MULSMP.146
C	CHECK IF CURRENT MESH POINT EXCEEDS UPPER LIMIT. IF IT DOES,	MULSMP.147
C	THEN CURRENT MESH SIZE IS FINISHED.	MULSMP.148
C		MULSMP.149
1005	IF (XNEW(I) .LT. B(I)) GO TO 1006	MULSMP.150
C		MULSMP.151
C	CURRENT DIMENSION INTEGRATED, ITS VALUE GIVEN BY XIP.	MULSMP.152
C		MULSMP.153
1007	XIP(I)=(XJ(I)+XH(I)*2.*S(I))/3.	MULSMP.154
C		MULSMP.155
C	CHECK FOR CONVERGENCE	MULSMP.156
C		MULSMP.157
	XE(I)=ABS (E*XIP(I))	MULSMP.158
	IF (IDUG.NE.0) WRITE(6,101)I,INDEX(I),XIP(I),XE(I),XIP(I)-XI(I)	MULSMP.159
	IF (ABS(XIP(I) - XI(I)) .LE. XE(I)) GO TO 1009	MULSMP.161
C		MULSMP.162

C	NOT CONVERGED, SO CURRENT APPROXIMATION NOW BECOMES THE LAST	MULSMP.163
C	APPROXIMATION, AND INTEGRATION CONTINUES BY DECREASING THE	MULSMP.164
C	STEP SIZE	MULSMP.165
C		MULSMP.166
C	1008 XI(I)=XIP(I)	MULSMP.167
C	GO TO 1004	MULSMP.168
C		MULSMP.169
C	SUM UP S WITH CURRENT VALUE OF INTEGRAND, AND INCREMENT TO NEXT	MULSMP.170
C	MESH POINT	MULSMP.171
C		MULSMP.172
C	1003 S(I)=FMENX(I)+S(I)	MULSMP.173
C	XNEW(I)=XNEW(I)+XH(I)	MULSMP.174
C	GO TO 1005	MULSMP.175
C		MULSMP.176
C	4 XIP(I) = 0.	MULSMP.177
C		MULSMP.178
C	1009 IF (I .EQ. N) GO TO 16	MULSMP.179
C		MULSMP.180
C	BEGIN INTEGRATION OVER THE NEXT DIMENSION	MULSMP.181
C		MULSMP.182
C	17 I1=I+1	MULSMP.183
C	J=K(I1)	MULSMP.184
C	GO TO (11,12,13),J	MULSMP.185
C		MULSMP.186
C		MULSMP.187
C	VALUE OF INTEGRAND AT LOWER LIMIT OF NEXT DIMENSION IS THE	MULSMP.188
C	CURRENT VALUE OF XIP.	MULSMP.189
C		MULSMP.190
C	11 FA(I1)=XIP(I)	MULSMP.191
C		MULSMP.192
C	SET K SO THAT AT COMPUTED GOTO WILL BRANCH TO UPPER LIMIT	MULSMP.193
C	(STATEMENT 12) .	MULSMP.194
C		MULSMP.195
C	K(I1)=2	MULSMP.196
C		MULSMP.197
C	SET COORDINATES TO UPPER LIMIT OF CURRENT DIMENSION.	MULSMP.198
C		MULSMP.199
C	B(I1)=BLIN(I1)	MULSMP.200
C	XNEW(I1)=B(I1)	MULSMP.201
C		MULSMP.202
C	NOW BEGIN INTEGRATION OVER ALL LOWER DIMENSIONS WITH THE HIGHEST	MULSMP.203
C	DIMENSION SET AT ITS UPPER LIMIT	MULSMP.204
C		MULSMP.205
C	GO TO 3	MULSMP.206
C		MULSMP.207
C		MULSMP.208
C	SAVE VALUE OF INTEGRAND AT UPPER LIMIT OF CURRENT MAXIMUM	MULSMP.209
C	DIMENSION.	MULSMP.210
C		MULSMP.211
C	12 FB(I1)=XIP(I)	MULSMP.212
C		MULSMP.213
C	SET K TO BRANCH TO STATEMENT 13 ON COMPUTED GOTO TO BEGIN	MULSMP.214
C	SIMPSON'S INTEGRATION FOR CURRENT DIMENSION, NOW THAT THE UPPER	MULSMP.215

C	LOWER LIMITS OF THE INTEGRAND ARE DEFINED.	MULSMP.216
C		MULSMP.217
	K(I1)=3	MULSMP.218
	I=I1	MULSMP.219
	GO TO 1000	MULSMP.220
C		MULSMP.221
C		MULSMP.222
C	FNEWX CONTAINS THE VALUE OF THE INTEGRAND AT CURRENT MESH POINT.	MULSMP.223
C	STORE IT AND CONTINUE INTEGRATION OVER ALL LOWER DIMENSIONS TO	MULSMP.224
C	ACHIEVE INTEGRAND VALUE AT NEXT MESH POINT.	MULSMP.225
C		MULSMP.226
	13 FNEWX(I1)=XIP(I)	MULSMP.227
	I=I1	MULSMP.228
	GO TO 1001	MULSMP.229
C		MULSMP.230
C	INTEGRAL COMPLETED WITH CONVERGENCE OBTAINED.	MULSMP.231
C		MULSMP.232
	16 VALUE=XIP(N)	MULSMP.233
	IXIT = 1	MULSMP.234
	1014 RETURN	MULSMP.235
C		MULSMP.236
C	ERROR EXITS	MULSMP.237
C		MULSMP.238
C		MULSMP.239
C	NO CONVERGENCE WITHIN SPECIFIED NUMBER OF ITERATIONS	MULSMP.240
C		MULSMP.241
	1011 CONTINUE	MULSMP.242
	WRITE(6,1013)	MULSMP.243
	WRITE(6,1012) I,INDEX(I)	MULSMP.244
	VALUE=0.	MULSMP.247
	IXIT = 2	MULSMP.248
	GO TO 1014	MULSMP.250
C		MULSMP.251
5	CONTINUE	MULSMP.252
C		MULSMP.253
C	UPPER BOUND LESS THAN LOWER BOUND	MULSMP.254
C		MULSMP.255
	WRITE(6,1013)	MULSMP.256
	WRITE(6,6) I,A(I),I,B(I)	MULSMP.257
	VALUE = 0.	MULSMP.260
	IXIT = 3	MULSMP.261
	GO TO 1014	MULSMP.262
C		MULSMP.263
7	CONTINUE	MULSMP.264
C		MULSMP.265
C	STEP SIZE IS ZERO	MULSMP.266
C		MULSMP.267
	WRITE(6,1013)	MULSMP.268
	WRITE(6,8) I,INDEX(I),I,A(I),I,B(I)	MULSMP.269
	XIP(I) = XI(I)	MULSMP.273
	GO TO 1009	MULSMP.274
C		MULSMP.275
C	RETURN VALUE AT THE CENTER OF THE DETECTOR COORDINATES FOR	MULSMP.276

C	POINT DETECTOR APPROXIMATION	MULSMP.277
C		MULSMP.278
	2001 XNEW(1)=(ALIM(1)+BLIM(1))/2.	MULSMP.279
	XNEW(2)=(ALIM(2)+BLIM(2))/2.	MULSMP.280
	VALUE=FINI(XNEW)	MULSMP.281
	IXIT=1	MULSMP.282
	GOTO 1014	MULSMP.283
C		
C	FORMAT STATEMENT	
C		
C		
	100 FORMAT(10X,*DIMENSIONS*,10X,*ITERATIONS*,10X,*APPROXIMATION*,10X,*SERIAL*	MULSMP.48
	\$ROR*,10X,*DIFFERENCE*)	MULSMP.49
	101 FORMAT(10X,I5,I5,I5,I11,E14.7,5X,E14.7,10X,E14.7)	MULSMP.160
	1012 FORMAT (4H0THE,I3,34H INTEGRAL HAS NOT CONVERGED AFTER ,I3,	MULSMP.245
	X 11H ITERATIONS)	MULSMP.246
	1013 FORMAT(10X,* ERROR FROM MULSMP INTEGRATION ROUTINE*)	MULSMP.249
	6 FORMAT (///12H NOTE.....A(I2,2H)=1PE20.8/	MULSMP.258
	61 10X2HB(I2,2H)=E20.8)	MULSMP.259
	8 FORMAT (///23H THE STEP SIZE FOR THE I1,21H INTEGRAL = 0 ON THE	MULSMP.270
	81 I5,11H ITERATION.//3H A(I1,3H) =1PE15.4/3H B(I1,3H) =	MULSMP.271
	82 E15.4)	MULSMP.272
	END	MULSMP.284
	SUBROUTINE WEIGHTS(XL,YL,ZL,NPRI1)	MULSMP.285
		WEIGHTS.2
C		WEIGHTS.3
C	FUNCTION- DETERMINE QUADRATURE POINTS AND WEIGHTS FOR THE	WEIGHTS.4
C	COLLISION VOLUME INTEGRATION AND THE SEMI-CLASSICAL PHASE SHIFT	WEIGHTS.5
C	INTEGRATION.	WEIGHTS.6
C		WEIGHTS.7
C	ARGUMENTS- XL,YL,ZL ON INPUT ARE THE X,Y,Z DIMENSIONS OF THE	WEIGHTS.8
C	COLLISION VOLUME.	WEIGHTS.9
C	NPRI1 =1, THEN THE COLLISION VOLUME GRID IS PRINTED	WEIGHTS.10
C	=0, NO PRINTING	WEIGHTS.11
C	ON OUTPUT, THE COMMON BLOCK VOL CONTAINS THE INTEGRATION POINTS	WEIGHTS.12
C	AND WEIGHTS FOR THE COLLISION VOLUME INTEGRATION	WEIGHTS.13
C	THE COMMON BLOCK PHSWTS CONTAINS THE INTEGRATION POINTS AND	WEIGHTS.14
C	WEIGHTS FOR THE SEMICLASSICAL PHASE SHIFT INTEGRALS	WEIGHTS.15
C		WEIGHTS.16
C	SUBPROGRAMS- NONE	WEIGHTS.17
C		WEIGHTS.18
C	REFERENCE- M.F. VERNON	WEIGHTS.19
C		WEIGHTS.20
	COMMON/EN/ENERGY(125),CNTH1(125),CNTH2(125),WGHT1(125),WGHT2(125),EN,2	
	1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
	COMMON/PHSWTS/XQ(10),WQ(10),NXQ	PHSWTS.2
	COMMON/VOL/X(5),Y(5),Z(5),WX(5),WY(5),WZ(5)	VOL.2
	DIMENSION SXQ(10),GWQ(10)	WEIGHTS.24
	DATA(GXQ(I),I=1,7)/.20119,.39415,.57097,.72442,.84821,.93727,.9879	WEIGHTS.25

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19/                                     WEIGHTS.26
DATA(GWQ(I),I=1,7)/.19843,.18416,.16427,.13957,.10716,.07037,.0307/WEIGHTS.27
15/                                     WEIGHTS.28
C                                     WEIGHTS.29
C SET UP GAUSSIAN QUADRATURE POINTS AND WEIGHTS FOR THE SEMI- WEIGHTS.30
C CLASSICAL PHASE SHIFT ROUTINE WEIGHTS.31
C                                     WEIGHTS.32
NXQ=7 WEIGHTS.33
DO 5 I=1,NXQ WEIGHTS.34
XQ(I)=1.-5*XQ(I)*GXQ(I) WEIGHTS.35
WQ(I)=2.*GXQ(I)*GXQ(I)*GWQ(I) WEIGHTS.36
5 CONTINUE WEIGHTS.37
C                                     WEIGHTS.38
C THIS COMPUTES THE POSITIONS AND WEIGHTS USED IN THE INTEGRATION WEIGHTS.39
C OVER THE COLLISION VOLUME. CURRENTLY THE MAXIMUM NUMBER OF POINTS WEIGHTS.40
C IN ANY ONE DIMENSION IS FIVE, IF A LARGER VALUE IS TRIED, IT IS WEIGHTS.41
C SET TO THIS MAXIMUM VALUE AND A MESSAGE PRINTED. WEIGHTS.42
C                                     WEIGHTS.43
NMAX=5 WEIGHTS.44
IF(NCOLX.LE.NMAX) GOTO 10 WEIGHTS.45
NCOLX=NMAX WEIGHTS.46
WRITE(6,1) NMAX WEIGHTS.47
10 IF(NCOLX-2) 11,12,13 WEIGHTS.49
C NCOLX=1 WEIGHTS.50
11 X(1)=0. WEIGHTS.51
WX(1)=1. WEIGHTS.52
GOTO 19 WEIGHTS.53
C NCOLX=2 WEIGHTS.54
12 CONTINUE WEIGHTS.55
X(1)=-.577 GX(2)=-X(1)*WX(1)=1.*WX(2)=1. WEIGHTS.56
GOTO 19 WEIGHTS.57
13 IF(NCOLX-4) 14,15,16 WEIGHTS.58
C NCOLX=3 WEIGHTS.59
14 CONTINUE WEIGHTS.60
X(1)=-.775GX(2)=0.*X(3)=-X(1)*WX(1)=5./9.*WX(2)=8./9.*WX(3)=WX(1) WEIGHTS.61
GOTO 19 WEIGHTS.62
C NCOLX=4 WEIGHTS.63
15 CONTINUE WEIGHTS.64
X(1)=-.9619GX(2)=-.339GX(3)=-X(2)*X(4)=-X(1)*WX(1)=.3489WX(2)=.652 WEIGHTS.65
1*WX(3)=WX(2)*WX(4)=WX(1) WEIGHTS.66
GOTO 19 WEIGHTS.67
C NCOLX=5 WEIGHTS.68
16 CONTINUE WEIGHTS.69
X(1)=-.906GX(2)=-.538GX(3)=0.*X(4)=-X(2)*X(5)=-X(1) WEIGHTS.70
WX(1)=-.2379WX(2)=.4789WX(3)=.5699WX(4)=WX(2)*WX(5)=WX(1) WEIGHTS.71
19 IF(NCOLY.LE.NMAX) GOTO 20 WEIGHTS.72
NCOLY=NMAX WEIGHTS.73
WRITE(6,2) NMAX WEIGHTS.74
20 IF(NCOLY-2) 21,22,23 WEIGHTS.76
C NCOLY=1 WEIGHTS.77
21 Y(1)=0. WEIGHTS.78
MY(1)=1. WEIGHTS.79
GOTO 29 WEIGHTS.80

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C	NCOLY=2	WEIGHTS.81
22	CONTINUE	WEIGHTS.82
	Y(1)=-.5778Y(2)=-Y(1)*WY(1)=1.*WY(2)=1.	WEIGHTS.83
	GOTO 29	WEIGHTS.84
23	IF(NCOLY-4) 24,25,26	WEIGHTS.85
C	NCOLY=3	WEIGHTS.86
24	CONTINUE	WEIGHTS.87
	Y(1)=-.7758Y(2)=0.*Y(3)=-Y(1)*WY(1)=5./9.*WY(2)=8./9.*WY(3)=WY(1)	WEIGHTS.88
	GOTO 29	WEIGHTS.89
C	NCOLY=4	WEIGHTS.90
25	CONTINUE	WEIGHTS.91
	Y(1)=-.8618Y(2)=-.3408Y(3)=-Y(2)*Y(4)=-Y(1)*WY(1)=.2378WY(2)=.478	WEIGHTS.92
	WY(3)=WY(2)*WY(4)=WY(1)	WEIGHTS.93
	GOTO 29	WEIGHTS.94
C	NCOLY=5	WEIGHTS.95
26	CONTINUE	WEIGHTS.96
	Y(1)=-.9068Y(2)=-.5388Y(3)=0.*Y(4)=-Y(2)*Y(5)=-Y(1)	WEIGHTS.97
	WY(1)=.2378WY(2)=.4798WY(3)=.5698WY(4)=WY(2)*WY(5)=WY(1)	WEIGHTS.98
29	IF(NCOLZ.LE.NMAX) GOTO 30	WEIGHTS.99
	NCOLZ=NMAX	WEIGHTS.100
	WRITE(6,3) NMAX	WEIGHTS.101
30	IF(NCOLZ-2) 31,32,33	WEIGHTS.103
C	NCOLZ=1	WEIGHTS.104
31	Z(1)=0.	WEIGHTS.105
	WZ(1)=1.	WEIGHTS.106
	GOTO 39	WEIGHTS.107
C	NCOLZ=2	WEIGHTS.108
32	CONTINUE	WEIGHTS.109
	Z(1)=-.5778Z(2)=-Z(1)*WZ(1)=1.*WZ(2)=1.	WEIGHTS.110
	GOTO 39	WEIGHTS.111
33	IF(NCOLZ-4) 34,35,36	WEIGHTS.112
C	NCOLZ=3	WEIGHTS.113
34	CONTINUE	WEIGHTS.114
	Z(1)=-.7758Z(2)=0.*Z(3)=-Z(1)*WZ(1)=5./9.*WZ(2)=8./9.*WZ(3)=WZ(1)	WEIGHTS.115
	GOTO 39	WEIGHTS.116
C	NCOLZ=4	WEIGHTS.117
35	CONTINUE	WEIGHTS.118
	Z(1)=-.8618Z(2)=-.3408Z(3)=-Z(2)*Z(4)=-Z(1)*WZ(1)=.3498WZ(2)=.652	WEIGHTS.119
	WZ(3)=WZ(2)*WZ(4)=WZ(1)	WEIGHTS.120
	GOTO 39	WEIGHTS.121
C	NCOLZ=5	WEIGHTS.122
36	CONTINUE	WEIGHTS.123
	Z(1)=-.9068Z(2)=-.5388Z(3)=0.*Z(4)=-Z(2)*Z(5)=-Z(1)	WEIGHTS.124
	WZ(1)=.2378WZ(2)=.4798WZ(3)=.5698WZ(4)=WZ(2)*WZ(5)=WZ(1)	WEIGHTS.125
C		WEIGHTS.126
C	CONVERT FROM UNIT INTERVAL TO ACTUAL COLLISION VOLUME DIMENSIONS	WEIGHTS.127
C		WEIGHTS.128
39	DO 40 I=1,NCOLX	WEIGHTS.129
	X(I)=X(I)*XL/2.	WEIGHTS.130
40	CONTINUE	WEIGHTS.131
	DO 45 I=1,NCOLY	WEIGHTS.132
	Y(I)=Y(I)*YL/2.	WEIGHTS.133
45	CONTINUE	WEIGHTS.134

C	REFERENCE- M.F. VERNON, 1982	NOZZLE.28
C		
C		
	PI=3.1415926	NOZZLE.29
	RNORM=SQRT(PI/SETA)*((1./VZRO**2+1./2./BETA)	NOZZLE.30
	S=1./SQRT(BETA)	NOZZLE.31
	IF(NAL-1) 100,110,120	NOZZLE.32
120	IF(NAL-3) 130,140,150	NOZZLE.33
150	IF(NAL-5) 160,170,180	NOZZLE.34
180	IF(NAL-7) 190,200,210	NOZZLE.35
210	IF(NAL-9) 220,230,240	NOZZLE.36
100	CONTINUE	NOZZLE.37
	WRITE(6,101)	NOZZLE.38
	STOP	NOZZLE.40
C ONE		NOZZLE.41
110	CONTINUE	NOZZLE.42
	VB(1)=VZRO	NOZZLE.43
	FB(1)=VZRO**2/RNORM	NOZZLE.44
	GOTO 250	NOZZLE.45
C TWO		NOZZLE.46
130	CONTINUE	NOZZLE.47
	T=.70718	NOZZLE.48
	VB(1)=VZRO-T	NOZZLE.49
	VB(2)=VZRO+T	NOZZLE.50
	FB(1)=VB(1)**2*.88623/RNORM	NOZZLE.51
	FB(2)=VB(2)**2*.88623/RNORM	NOZZLE.52
	GOTO 250	NOZZLE.53
C THREE		NOZZLE.54
140	CONTINUE	NOZZLE.55
	T=1.22478	NOZZLE.56
	VB(1)=VZRO-T	NOZZLE.57
	VB(2)=VZRO	NOZZLE.58
	VB(3)=VZRO+T	NOZZLE.59
	FB(1)=VB(1)**2*.95409E-01/RNORM	NOZZLE.60
	FB(2)=VB(2)**2*.18164/RNORM	NOZZLE.61
	FB(3)=VB(3)**2*.295409/RNORM	NOZZLE.62
	GOTO 250	NOZZLE.63
C FOUR		NOZZLE.64
160	CONTINUE	NOZZLE.65
	T1=.52468	NOZZLE.66
	T2=.65078	NOZZLE.67
	VB(1)=VZRO-T2	NOZZLE.68
	VB(2)=VZRO-T1	NOZZLE.69
	VB(3)=VZRO+T1	NOZZLE.70
	VB(4)=VZRO+T2	NOZZLE.71
	FB(1)=VB(1)**2*.13128E-02/RNORM	NOZZLE.72
	FB(2)=VB(2)**2*.04914E-01/RNORM	NOZZLE.73
	FB(3)=VB(3)**2*.04914E-01/RNORM	NOZZLE.74
	FB(4)=VB(4)**2*.13128E-02/RNORM	NOZZLE.75
	GOTO 250	NOZZLE.76
C FIVE		NOZZLE.77
170	CONTINUE	NOZZLE.78
	T1=.958578	NOZZLE.79

T2=2.020100S	NOZZLE.00
VB(1)=VZRO-T2	NOZZLE.01
VB(2)=VZRO-T1	NOZZLE.02
VB(3)=VZRO	NOZZLE.03
VB(4)=VZRO+T1	NOZZLE.04
VB(5)=VZRO+T2	NOZZLE.05
FB(1)=VB(1)**201.99532E-02/RNORM	NOZZLE.06
FB(2)=VB(2)**203.93619E-01/RNORM	NOZZLE.07
FB(3)=VB(3)**209.45309E-01/RNORM	NOZZLE.08
FB(4)=VB(4)**20.393619/RNORM	NOZZLE.09
FB(5)=VB(5)**201.99532E-02/RNORM	NOZZLE.90
GOTO 250	NOZZLE.91
C SIX	NOZZLE.92
190 CONTINUE	NOZZLE.93
T1=.4360770S	NOZZLE.94
T2=1.3350490S	NOZZLE.95
T3=2.350600S	NOZZLE.96
VB(1)=VZRO-T3	NOZZLE.97
VB(2)=VZRO-T2	NOZZLE.98
VB(3)=VZRO-T1	NOZZLE.99
VB(4)=VZRO+T1	NOZZLE.100
VB(5)=VZRO+T2	NOZZLE.101
VB(6)=VZRO+T3	NOZZLE.102
FB(1)=VB(1)**204.53001E-03/RNORM	NOZZLE.103
FB(2)=VB(2)**201.57067E-01/RNORM	NOZZLE.104
FB(3)=VB(3)**207.246296E-01/RNORM	NOZZLE.105
FB(4)=VB(4)**207.246296E-01/RNORM	NOZZLE.106
FB(5)=VB(5)**201.57067E-01/RNORM	NOZZLE.107
FB(6)=VB(6)**204.53001E-03/RNORM	NOZZLE.108
GOTO 250	NOZZLE.109
C SEVEN	NOZZLE.110
200 CONTINUE	NOZZLE.111
T1=.816290S	NOZZLE.112
T2=1.673550S	NOZZLE.113
T3=2.651960S	NOZZLE.114
VB(1)=VZRO-T3	NOZZLE.115
VB(2)=VZRO-T2	NOZZLE.116
VB(3)=VZRO-T1	NOZZLE.117
VB(4)=VZRO	NOZZLE.118
VB(5)=VZRO+T1	NOZZLE.119
VB(6)=VZRO+T2	NOZZLE.120
VB(7)=VZRO+T3	NOZZLE.121
FB(1)=VB(1)**209.71781E-04/RNORM	NOZZLE.122
FB(2)=VB(2)**205.45156E-02/RNORM	NOZZLE.123
FB(3)=VB(3)**204.25607E-01/RNORM	NOZZLE.124
FB(4)=VB(4)**208.10264E-01/RNORM	NOZZLE.125
FB(5)=VB(5)**204.25607E-01/RNORM	NOZZLE.126
FB(6)=VB(6)**205.45156E-02/RNORM	NOZZLE.127
FB(7)=VB(7)**209.71781E-04/RNORM	NOZZLE.128
GOTO 250	NOZZLE.129
C EIGHT	NOZZLE.130
220 CONTINUE	NOZZLE.131
T1=.3011070S	NOZZLE.132

	T2=1.157198S	NOZZLE.133
	T3=1.981648S	NOZZLE.134
	T4=2.936448S	NOZZLE.135
	VB(1)=VZRO-T4	NOZZLE.136
	VB(2)=VZRO-T3	NOZZLE.137
	VB(3)=VZRO-T2	NOZZLE.138
	VB(4)=VZRO-T1	NOZZLE.139
	VB(5)=VZRO+T1	NOZZLE.140
	VB(6)=VZRO+T2	NOZZLE.141
	VB(7)=VZRO+T3	NOZZLE.142
	VB(8)=VZRO+T4	NOZZLE.143
	FB(1)=VB(1)##281.99604E-04/RNORM	NOZZLE.144
	FB(2)=VB(2)##281.707798E-02/RNORM	NOZZLE.145
	FB(3)=VB(3)##28.207802/RNORM	NOZZLE.146
	FB(4)=VB(4)##28.661147/RNORM	NOZZLE.147
	FB(5)=VB(5)##28.661147/RNORM	NOZZLE.148
	FB(6)=VB(6)##28.207802/RNORM	NOZZLE.149
	FB(7)=VB(7)##281.707798E-02/RNORM	NOZZLE.150
	FB(8)=VB(8)##281.96604E-04/RNORM	NOZZLE.151
	GOTO 250	NOZZLE.152
C	NINE	NOZZLE.153
230	CONTINUE	NOZZLE.154
	T1=.723558S	NOZZLE.155
	T2=1.468558S	NOZZLE.156
	T3=2.266588S	NOZZLE.157
	T4=3.190998S	NOZZLE.158
	VB(1)=VZRO-T4	NOZZLE.159
	VB(2)=VZRO-T3	NOZZLE.160
	VB(3)=VZRO-T2	NOZZLE.161
	VB(4)=VZRO-T1	NOZZLE.162
	VB(5)=VZRO	NOZZLE.163
	VB(6)=VZRO+T1	NOZZLE.164
	VB(7)=VZRO+T2	NOZZLE.165
	VB(8)=VZRO+T3	NOZZLE.166
	VB(9)=VZRO+T4	NOZZLE.167
	FB(1)=VB(1)##283.96070E-05/RNORM	NOZZLE.168
	FB(2)=VB(2)##284.94362E-03/RNORM	NOZZLE.169
	FB(3)=VB(3)##288.84745E-02/RNORM	NOZZLE.170
	FB(4)=VB(4)##284.32652E-01/RNORM	NOZZLE.171
	FB(5)=VB(5)##287.20235E-01/RNORM	NOZZLE.172
	FB(6)=VB(6)##284.32652E-01/RNORM	NOZZLE.173
	FB(7)=VB(7)##288.84745E-02/RNORM	NOZZLE.174
	FB(8)=VB(8)##284.94362E-03/RNORM	NOZZLE.175
	FB(9)=VB(9)##283.96070E-05/RNORM	NOZZLE.176
	GOTO 250	NOZZLE.177
C	TEN	NOZZLE.178
240	CONTINUE	NOZZLE.179
	T1=.342908S	NOZZLE.180
	T2=1.036618S	NOZZLE.181
	T3=1.756688S	NOZZLE.182
	T4=2.532738S	NOZZLE.183
	T5=3.436168S	NOZZLE.184
	VB(1)=VZRO-T5	NOZZLE.185

	VB(2)=VZRO-T4	NOZZLE.186
	VB(3)=VZRO-T3	NOZZLE.187
	VB(4)=VZRO-T2	NOZZLE.188
	VB(5)=VZRO-T1	NOZZLE.189
	VB(6)=VZRO+T1	NOZZLE.190
	VB(7)=VZRO+T2	NOZZLE.191
	VB(8)=VZRO+T3	NOZZLE.192
	VB(9)=VZRO+T4	NOZZLE.193
	VB(10)=VZRO+T5	NOZZLE.194
	FB(1)=VB(1)*287.6404E-06/RNORM	NOZZLE.195
	FB(2)=VB(2)*281.34364E-03/RNORM	NOZZLE.196
	FB(3)=VB(3)*283.3874E-02/RNORM	NOZZLE.197
	FB(4)=VB(4)*282.40139E-01/RNORM	NOZZLE.198
	FB(5)=VB(5)*284.10842E-01/RNORM	NOZZLE.199
	FB(6)=VB(6)*286.10842E-01/RNORM	NOZZLE.200
	FB(7)=VB(7)*282.40139E-01/RNORM	NOZZLE.201
	FB(8)=VB(8)*283.3874E-02/RNORM	NOZZLE.202
	FB(9)=VB(9)*281.34364E-03/RNORM	NOZZLE.203
	FB(10)=VB(10)*287.6404E-06/RNORM	NOZZLE.204
250	CONTINUE	NOZZLE.205
	WRITE(6,30)	NOZZLE.206
	WRITE(6,40)(VB(I) ,I=1,NVL)	NOZZLE.209
	WRITE(6,40)(FB(I) ,I=1,NVL)	NOZZLE.210
	WRITE(6,41)	NOZZLE.212
	RETURN	NOZZLE.214
C		
C		
C	FORMAT STATEMENTS	
C		
C		
101	FORMAT(5X,NUMBER OF NEWTON DIAGRAMS ZERO*)	NOZZLE.39
30	FORMAT(10X,#VELOCITIES (UNITS OF 10,000 CM/SEC) /RELATIVE WEIGHTS	NOZZLE.207
	1\$,/)	NOZZLE.208
40	FORMAT(10(1X,F11.4))	NOZZLE.211
41	FORMAT(/)	NOZZLE.213
	END	NOZZLE.215
	SUBROUTINE PHSFT(A,RM,NPRI1)	PHASE1.2
C		PHASE1.3
C	JWKB PHASE SHIFTS EVALUATED WITH GAUSS QUADRATURE	PHASE1.4
C	CODED BY CARL HAYDEN	PHASE1.5
C	SQRT(1-X) WEIGHTING FUNCTION	PHASE1.6
C	FOR DETAILS SEE JAMES S. COHEN, JCP,68,PG.1841 (1978).	PHASE1.7
C		PHASE1.8
	COMMON/ETA/STHE(8000),CTHE(8000),META,DETA,IDENT	ETA.2
	*,IBOSE	ETA.3
	COMMON/PHSWTS/XQ(10),WQ(10),NXQ	PHSWTS.2
	COMMON/EN/ENERGY(125),CMTH1(125),CMTH2(125),WGHT1(125),WGHT2(125),EN.2	
	1NCOLX,NCOLY,NCOLZ,IAPPRX	EN.3
	DIMENSION A(15),X(10),V(10),VP(10)	PHASE1.12
	DIMENSION Y(250),YPP(250),Z(250),ZPP(250),W(750)	PHASE1.13

	REAL KR2,KR,KEX,KEX2	PHASE1.14
	NSTEP=INT(DETA)	PHASE1.15
C		PHASE1.16
C	FOR INTERPOLATED PHASE SHIFTS, NEED ADDITIONAL METAS.	PHASE1.17
C		PHASE1.18
	IF(NSTEP.NE.1) META=META+NSTEP	PHASE1.19
	NPHASE=META/NSTEP	PHASE1.20
	ISX=0	PHASE1.21
	NVOL=NCOLX*NCOLY*NCOLZ	PHASE1.22
C		PHASE1.23
C	IAPPRX=1, THEN ALL POINTS IN THE COLLISION VOLUME HAVE THE SAME	PHASE1.24
C	PHASE SHIFT. CALCULATE ONLY ONE SET OF PHASE SHIFTS FOR THIS	PHASE1.25
C	NEWTON DIAGRAM.	PHASE1.26
C		PHASE1.27
	IF(IAPPRX.EQ.1) NVOL=1	PHASE1.28
	IF(NPRI1.NE.1) GOTO 99	PHASE1.29
	WRITE(6,104)	PHASE1.30
	WRITE(6,103)(ENERGY(I),I=1,NVOL)	PHASE1.32
	WRITE(6,105)	PHASE1.33
	WRITE(6,102)	PHASE1.35
99	DO 500 II=1,NVOL	PHASE1.38
C		PHASE1.39
C	ER IS THE REDUCED COLLISION ENERGY	PHASE1.40
C		PHASE1.41
	ER=ENERGY(II)/A(1)	PHASE1.42
C		PHASE1.43
C	ITEMP IS INDEX FOR STORING PHASE SHIFTS AT EACH ENERGY.	PHASE1.44
C		PHASE1.45
	ITEMP=(II-1)*META	PHASE1.46
	ERSR=SQRT(ER)	PHASE1.47
	KR2=20.7481*RM8A(1)*A(2)*2	PHASE1.48
	KR=SQRT(KR2)	PHASE1.49
	CONST=KR*ERSR	PHASE1.50
C		PHASE1.51
C	FIRST GUESS AT TURNING POINT	PHASE1.52
C		PHASE1.53
	XC=0.6	PHASE1.54
C		PHASE1.55
C	AMQN IS THE ORBITAL ANGULAR MOMENTUM	PHASE1.56
C		PHASE1.57
	AMQN=0	PHASE1.58
C		PHASE1.59
C	FOR EACH PARTIAL WAVE	PHASE1.60
C		PHASE1.61
	J=0	PHASE1.62
	DO 60 I=1,META,NSTEP	PHASE1.63
	J=J+1	PHASE1.64
	AM=AMQN+0.5	PHASE1.65
	AM2=AM*AM	PHASE1.66
	L=1	PHASE1.67
C		PHASE1.68
C	CALCULATE CLASSICAL TURNING POINT	PHASE1.69
C		PHASE1.70

DO 10 N=1,199	PHASE1.71
X(L)=XC	PHASE1.72
CALL POT(X,A,U,VP,L,RH)	PHASE1.73
X2=X(L)*X(L)	PHASE1.74
XC=X(L)-((ER-V(L)-(AM2/(KR2*X2)))/((2*AM2)/(KR2*X2*X(L))-UP(L)))	PHASE1.75
IF(ABS(XC-X(L)).LE.1.E-4*XC) GO TO 20	PHASE1.76
IF(N.GE.199) GO TO 50	PHASE1.77
10 CONTINUE	PHASE1.78
20 F=0	PHASE1.79
ETA=0	PHASE1.80
KEX=CONST*XC	PHASE1.81
KEX2=KEX*KEX	PHASE1.82
AMR2=AM2/KEX2	PHASE1.83
C	PHASE1.84
C CALCULATE PHASE SHIFT USING QUAD. SCHEME	PHASE1.85
C	PHASE1.86
PS=0	PHASE1.87
DO 25 K=1,NXQ	PHASE1.88
C	PHASE1.89
C QUAD. POINTS DEPEND ON TURNING POINT.	PHASE1.90
C	PHASE1.91
X(K)=XC/XQ(K)	PHASE1.92
25 CONTINUE	PHASE1.93
C	PHASE1.94
C FIND POTENTIAL AT TURNING POINTS	PHASE1.95
C	PHASE1.96
CALL POT(X,A,U,VP,NXQ,RH)	PHASE1.97
C	PHASE1.98
C SUM UP POTENTIAL CONTRIBUTIONS AT QUAD. POINTS.	PHASE1.99
C	PHASE1.100
DO 26 K=1,NXQ	PHASE1.101
XLT1=XQ(K)	PHASE1.102
AMRX2=AMR2*XLT1**2	PHASE1.103
VR=V(K)	PHASE1.104
TEMP=(1.-AMRX2-VR/ER)/(1.-XLT1)	PHASE1.105
IF(TEMP.LT.0.) GOTO 106	PHASE1.106
F=(SQRT(TEMP)-SQRT(1.+XLT1))/XLT1/XLT1	PHASE1.107
PS=XQ(K)*F+PS	PHASE1.108
26 CONTINUE	PHASE1.109
ETA=KEX*PS+((AM-KEX)*1.5707963)	PHASE1.110
THE=2*ETA	PHASE1.111
T=2*AMQN+1	PHASE1.112
C	PHASE1.113
C CTHE CONTAINS (2*LT+1)*(COS(2*ETA)-1)	PHASE1.114
C STHE CONTAINS (2*LT+1)*SIN(2*ETA)	PHASE1.115
C	PHASE1.116
IF(NSTEP-1) 27,27,28	PHASE1.117
27 CTHE(ITEMP+I)=T*(COS(THE)-1.)	PHASE1.118
STHE(ITEMP+I)=SIN(THE)*T	PHASE1.119
GOTO 29	PHASE1.120
28 Y(J)=T*(COS(THE)-1.)	PHASE1.121
Z(J)=T*SIN(THE)	PHASE1.122
29 CONTINUE	PHASE1.123

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      IF(NPRI1.EQ.1) WRITE(6,100) AMQN,XC,H,ETA
100  FORMAT(10X,F6.1,5X,F10.5,5X,I5,5X,E14.7)
      AMQN=AMQN+ETA
40  CONTINUE
      IF(NSTEP.EQ.1) GOTO 500
      CALL SPLIFT(NSTEP,Y,YPP,NPHASE,W,IERR,ISX,0.,0.,0.,0.)
      ISX=1
      CALL SPLIFT(NSTEP,Z,ZPP,NPHASE,W,IERR,ISX,0.,0.,0.,0.)
      CALL SPLINT(NSTEP,Y,YPP,NPHASE,ITEMP,Z,ZPP)
      IF(NPRI1.NE.1)GOTO 500
      WRITE(6,400)
      WRITE(6,402)
      WRITE(6,401)(CTHE(IJJ+ITEMP),IJJ=1,NETA)
      WRITE(6,403)
      WRITE(6,401)(STHE(IJJ+ITEMP),IJJ=1,NETA)
500  CONTINUE
C
C      RESET NETA IF INTERPOLATED ETA'S USED
C
      IF(NSTEP.NE.1) NETA=NETA-NSTEP
      GOTO 70
102  WRITE(6,101)
      GOTO 51
106  WRITE(6,107) AMQN
      WRITE(6,108) VR,ER
51  STOP
70  RETURN
C
C      FORMAT STATEMENTS
C
104  FORMAT(10X,$COLLISION ENERGIES (KCAL/MOLE)$,/)
105  FORMAT(///)
103  FORMAT(10(2X,E10.4))
102  FORMAT(12X,$L$,11X,$TURNING POINT$,2X,$ITRNS.$,5X,$PHASE$,/)
400  FORMAT(///,10X,$INTERPOLATED PHASE SHIFT FUNCTIONS$,/)
402  FORMAT(///,10X,$CTHE ARRAYS$,/)
401  FORMAT(10(1X,E12.6))
403  FORMAT(///,10X,$STHE ARRAYS$,/)
101  FORMAT(10X,$ XC CALCULATION NOT CONVERGED IN PHASE SHIFT ROUTINE$,)
107  FORMAT(10X,$SORT ARGUMENT NEGATIVE AT AMQN= $,F10.3)
108  FORMAT(10X,$COLLISION ENERGY=$,F8.4,$ POTENTIAL ENERGY=$,F8.4)
      END
C
C      SUBROUTINE BSELF(X(L,ARG,SBJ,SDN)
C      IMPLICIT REAL (A-H,O-Z)
C.....
C** SUBROUTINE TO CALCULATE SPHERICAL BESSEL FUNCTIONS OF THE FIRST AND
C SECOND KINDS, SBJ AND SDN , RESPECTIVELY, OF ORDER L , WITH

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PHASE1.124
 PHASE1.125
 PHASE1.126
 PHASE1.127
 PHASE1.128
 PHASE1.129
 PHASE1.130
 PHASE1.131
 PHASE1.132
 PHASE1.133
 PHASE1.134
 PHASE1.136
 PHASE1.138
 PHASE1.140
 PHASE1.142
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 PHASE1.147
 PHASE1.148
 PHASE1.149
 PHASE1.151
 PHASE1.152
 PHASE1.154
 PHASE1.156
 PHASE1.157

 PHASE1.31
 PHASE1.34
 PHASE1.36
 PHASE1.37
 PHASE1.135
 PHASE1.137
 PHASE1.139
 PHASE1.141
 PHASE1.150
 PHASE1.153
 PHASE1.155
 PHASE1.158

 PHASE1.159
 PHASE2.2
 PHASE2.3
 PHASE2.4
 PHASE2.5
 PHASE2.6

C	ARGUMENT ARG.	PHASE2.7
C		PHASE2.8
	LH=L/2	PHASE2.9
	PH=1.0E0	PHASE2.10
	LE=L	PHASE2.11
	AR1=1.E0/ARG	PHASE2.12
	XQ=SQRT(1.570796326794896E+00*ARG)	PHASE2.13
	AQ=COS(ARG)/XQ	PHASE2.14
	BQ=SIN(ARG)/XQ	PHASE2.15
	XQ=XQ*AR1	PHASE2.16
100	CQ=PH	PHASE2.17
	IF (LE) 110,170,120	PHASE2.18
110	QQ=AQ	PHASE2.19
	RQ=BQ	PHASE2.20
	GO TO 130	PHASE2.21
120	IF (ARG.LT.(1.E0*L)) GO TO 180	PHASE2.22
	QQ=BQ	PHASE2.23
	RQ=AQ	PHASE2.24
130	DO 140 IQ=1,L	PHASE2.25
	PQ=QQ*(CQ+CQ-PH)*AR1-RQ	PHASE2.26
	CQ=CQ+PH	PHASE2.27
	RQ=PQ	PHASE2.28
140	QQ=PQ	PHASE2.29
	PQ=PQ*XQ	PHASE2.30
	IF (PH.LT.0.E+00) GO TO 160	PHASE2.31
	SBJ=PQ	PHASE2.32
150	PH=-1.0E0	PHASE2.33
	LE=-L	PHASE2.34
	GO TO 100	PHASE2.35
160	SBN=PQ	PHASE2.36
	K=L-2*LH	PHASE2.37
	IF (K.EQ.0) SBN=-PQ	PHASE2.38
	RETURN	PHASE2.39
170	SBJ=BQ*XQ	PHASE2.40
	SBN=-AQ*XQ	PHASE2.41
	RETURN	PHASE2.42
C		PHASE2.43
C**	CALCULATE FX OF 1-ST KIND FOR SMALL ARGUMENT BY ASCENDING POWER	PHASE2.44
C	EXPANSION.	PHASE2.45
C		PHASE2.46
180	QQ=1.0E0	PHASE2.47
	DO 190 I=1,L	PHASE2.48
190	QQ=QQ*ARG/(2*I+1)	PHASE2.49
	SBJ=QQ	PHASE2.50
	L4=50	PHASE2.51
	IF (L.GT.12) L4=4*L	PHASE2.52
	CQ=(2*L+1)	PHASE2.53
	QQ=-0.5E0*ARG*ARG	PHASE2.54
	RQ=i.0E0	PHASE2.55
	PQ=RQ	PHASE2.56
	DO 200 I=1,L4	PHASE2.57
	K=I	PHASE2.58
	RQ=RQ*QQ/(I*(CQ+2*I))	PHASE2.59

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      PQ=PQ+RQ                                PHASE2.60
      IF (ABS(RQ/PQ).LT.1.E-10) GO TO 210      PHASE2.61
200  CONTINUE                                  PHASE2.62
      RQ=RQ/PQ                                PHASE2.63
      WRITE (6,1000) L,ARG,L4,RQ              PHASE2.64
210  SBJ=SBJ/PQ                                PHASE2.65
      GO TO 150                                PHASE2.66
1000 FORMAT(10H0  ERROR IN  SBJ,(I3,IH,,E10.5,YH) . AFTER,I4,26H ASCENPHASE2.67
      XDING TERMS  RATIO =,E10.5 )            PHASE2.68
      END                                      PHASE2.69
      SUBROUTINE PMSHFT(A,RH,IWR)              PHASE2.70
C.....PHASE2.71
C*** R.J.LE ROY SUBROUTINE -PMSHFT- , AS OF 16 NOVEMBER, 1978 *** PHASE2.72
C** SUBROUTINE TO CALCULATE THE ABSOLUTE PHASE SHIFT -ADLT- FOR PHASE2.73
C THE POTENTIAL -V(I)- (REDUCED BY THE FACTOR BZ/RSC) AT ENERGY -ZE- PHASE2.74
C AND PARTIAL WAVE -L-. PHASE2.75
C** SOLVE THE RADIAL SCHROEDINGER EQUATION IN THE REDUCED FORM? PHASE2.76
C D2S/DR2--(ZE*BJZ/ESC-V(I)-L*(L+1)*XM2)*S , WHERE XM2=1/X**2 AND PHASE2.77
C S IS THE WAVE FUNCTION. ** USE NUMEROV-S METHOD. PHASE2.78
C** INTEGRATE OUTWARD FROM -XMIN- WITH AN INCREMENT OF -XH- (BOTH PHASE2.79
C IN REDUCED UNITS, I.E. SCALED BY -RSC-), FOR UP TO -N- STEPS. PHASE2.80
C** IF(IWR.GT.0) PRINTS ALL TRIAL PHASE SHIFTS AND NODE POSITIONS. PHASE2.81
C IF(IWR.NE.0) PRINT CONVERGED PHASE SHIFTS AND NODE POSITION* PHASE2.82
C** RADIAL INTEGRATION STOPS WHEN JUKB-CORRECTED VALUES AT 3 PHASE2.83
C SUCCESSIVE NODES AGREE TO WITHIN -PHTST- (RADIANs). PHASE2.84
C-----PHASE2.85
C.....PHASE2.86
      IMPLICIT REAL (A-H,O-Z) PHASE2.87
      COMMON/ETA/STHE(8000),CTHE(8000),META,DETA,IDENT ETA.2
      $,IBOSE ETA.3
      COMMON/EN/ENERGY(125),CHTH1(125),CHTH2(125),WGHT1(125),WGHT2(125),EN.2
      INCOLX,NCOLY,NCOLZ,IAIPRX EN.3
      COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR PTNL.2
      DIMENSION Z(15),X(10),UP(1),A(15) PHASE2.91
      DIMENSION VV(8),RR2(8),XX(8),WW(8),XG(4),WG(4) PHASE2.92
      DIMENSION Y(250),YPP(250),W(750) PHASE2.93
      DATA Z0/0.E0/,ZH/0.5E0/,Z1/1.E0/,Z2/2.E0/,Z3/3.E0/,Z4/4.E0/, PHASE2.94
      X Z5/5.E0/,Z6/6.E0/,PI/3.141592653589793E0/,IFIRST/0/ PHASE2.95
C.....PHASE2.96
C** GAUSSIAN WEIGHTS AND POINTS FOR QUADRATURES. PHASE2.97
C.....PHASE2.98
      DATA XG/-0.8611363115940526E0,-0.3399810435848563E0,1.E0,1.E0/, PHASE2.99
      X WG/0.3478548451374539E0,0.6521451548625461E0,0.E0,0.E0/ PHASE2.100
C.....PHASE2.101
C** ON VERY FIRST ENTRY TO -PMSHFT- ONLY, PREPARE POINTS AND WEIGHTS PHASE2.102
C FOR GAUSSIAN QUADRATURE JUKB EDGE CORRECTION TO MODAL PHASE SHIFT PHASE2.103
C.....PHASE2.104
      IF (IFIRST.GT.0) GO TO 120 PHASE2.105
      IFIRST=1 PHASE2.106
      NGT=4 PHASE2.107
      NGH=2 PHASE2.108
      IF(IWR.GT.0) WRITE(6,1140) PHASE2.109
      IF (IWR.GT.0) WRITE (6,1130) NGT,(XG(I),WG(I),I=1,NGT) PHASE2.111

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DO 110 I=1,MGT	PHASE2.112
J=I	PHASE2.113
IF (I.LE.NGH) GO TO 100	PHASE2.114
J=MGT+1-I	PHASE2.115
XX(I)=ZH*(Z1-XB(J))	PHASE2.116
GO TO 110	PHASE2.117
100 XX(I)=ZH*(Z1+XB(J))	PHASE2.118
110 WW(I)=WB(J)/XX(I)*32	PHASE2.119
IF (IWR.GT.0) WRITE (6,1120) MGT,(XX(I),WW(I),I=1,MGT)	PHASE2.120
C.....	PHASE2.121
C** DEFINE AND INITIALIZE VARIOUS CONSTANTS AND PARAMETERS.	PHASE2.122
C.....	PHASE2.123
X12=Z1/12.E0	PHASE2.124
120 CONTINUE	PHASE2.125
PHTST=ERROR	PHASE2.126
NVOL=NCOLX*NCOLY*NCOLZ	PHASE2.127
IF (IAPPRX.NE.0) NVOL=1	PHASE2.128
NSTEP=INT(DETA)	PHASE2.129
ISX=0	PHASE2.130
C FOR INTERPOLATED ETA'S NEED ADDITIONAL META.	PHASE2.131
IF (NSTEP.NE.1) META=META+NSTEP	PHASE2.132
MPHASE=META/NSTEP	PHASE2.133
C JJ IS THE NUMBER OF COMPUTED PHASE SHIFTS	PHASE2.134
IF (IWR.NE.1) GOTO 99	PHASE2.135
WRITE(6,1150)	PHASE2.136
WRITE(6,104)	PHASE2.138
WRITE(6,103)(ENERGY(I),I=1,NVOL)	PHASE2.140
99 DO 500 IJ=1,NVOL	PHASE2.142
ZE=ENERGY(IJ)*349.757	PHASE2.143
ESC=A(1)	PHASE2.144
XH=XSTEP	PHASE2.145
JJ=0	PHASE2.146
XMIN=XSTART	PHASE2.147
N=INT(RNPHAS)	PHASE2.148
ITEMP=(IJ-1)*META	PHASE2.149
BZ=RM*A(1)*A(2)*A(2)/16.85763	PHASE2.150
DO 60 K=1,META,NSTEP	PHASE2.151
JJ=JJ+1	PHASE2.152
L=K-1	PHASE2.153
T=FLOAT(2*L+1)	PHASE2.154
EJ=L*(L+1)	PHASE2.155
H2=XH*XH	PHASE2.156
E=ZE*BZ/ESC	PHASE2.157
SQE=SQRT(E)	PHASE2.158
MODE=0	PHASE2.159
DLT2=Z0	PHASE2.160
DLT3=Z0	PHASE2.161
COR2=Z0	PHASE2.162
COR3=Z0	PHASE2.163
XND2=-.000001E+00	PHASE2.164
XND3=-.000001E+00	PHASE2.165
IF (IWR.GT.0) WRITE (6,1110)	PHASE2.166
C.....	PHASE2.167


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C** START TESTING FOR PHASE SHIFT CONVERGENCE AT NODES PAST THE      PHASE2.161
C MESH POINT -ILK- WHERE  $E = L*(L+1)/R**2$                                PHASE2.165
C.....PHASE2.170
      XLK=SQRT(Z1/E)                                                    PHASE2.171
      IF (L.GT.0) XLK=SQRT(EJ/E)                                        PHASE2.172
      ILK=(XLK-XMIN)/XH+1                                              PHASE2.173
      IF (ILK.GT.N) GO TO 320                                           PHASE2.174
C.....PHASE2.175
C** IF HAVE POTENTIAL (SUCH AS EXP-6) WITH NEGATIVE V(R) AT VERY    PHASE2.176
C SMALL R, OR IF (V(I)-E) SO HIGH THAT -XH- IS (LOCALLY) MUCH TOO    PHASE2.177
C LARGE, THEN SHIFT INNER STARTING POINT OUTWARD.                     PHASE2.178
C.....PHASE2.179
      IST=1                                                              PHASE2.180
130  IST=IST+1                                                          PHASE2.181
      IF (IST.GE.(N-8)) GO TO 310                                       PHASE2.182
      GI=H2*(V(IST)+EJ*XM2(IST)-E)                                     PHASE2.183
      IF ((GI.LE.Z0).OR.(GI.GT.11.E0)) GO TO 130                       PHASE2.184
      IF ((IMR.GT.0).AND.(IST.GT.2)) WRITE (6,1000) L,ZE,IST          PHASE2.185
      GN=H2*(V(IST-1)+EJ*XM2(IST-1)-E)                                PHASE2.186
      IF (GN.LE.0) GO TO 130                                           PHASE2.187
      IST=IST+1                                                         PHASE2.188
C.....PHASE2.189
C** INITIALIZE WAVE FUNCTION FOR OUTWARD INTEGRATION.                PHASE2.190
C.....PHASE2.191
      IF ((XMIN+(IST-3)*XH).LE.Z0) GO TO 140                           PHASE2.192
C.....PHASE2.193
C** IF INTEGRATION STARTS AT R.GT.0, INITIALIZE WAVE FUNCTION (S      PHASE2.194
C THE EXPONENTIALLY INCREASING JWKB SOLUTION.                        PHASE2.195
C.....PHASE2.196
      SRTGI=SQRT(GI)                                                    PHASE2.197
      SRTGN=SQRT(GN)                                                    PHASE2.198
      SB=Z1                                                              PHASE2.199
      SI=SQRT(SRTGN/SRTGI)*EXP(ZH*(SRTGN+SRTGI))                      PHASE2.200
      IF (SI.GE.SB) GO TO 150                                           PHASE2.201
      WRITE (6,1040) L,ZE,SB,SI                                         PHASE2.202
140  SB=Z0                                                              PHASE2.203
      SI=Z1                                                              PHASE2.204
150  Y1=SB*(Z1-GN*X12)                                                  PHASE2.205
      Y2=SI*(Z1-GI*X12)                                                  PHASE2.206
      RATIN=SI                                                           PHASE2.207
C.....PHASE2.208
C** INTEGRATE OUT TO MESH POINT -ILK- OR CLASSICALLY ALLOWED REGION  PHASE2.209
C.....PHASE2.210
      DO 200 I=IST,N                                                    PHASE2.211
      II=I                                                              PHASE2.212
      SC=SB                                                              PHASE2.213
      SB=SI                                                              PHASE2.214
      Y3=Y2+Y2-Y1+GI*SB                                                PHASE2.215
      GI=H2*(V(I)+EJ*XM2(I)-E)                                         PHASE2.216
      SI=Y3/(Z1-GI*X12)                                                 PHASE2.217
      IF (SI.LE.1.E+30) GO TO 160                                       PHASE2.218
C.....PHASE2.219
C** NORMALIZE IN CASE OF OVERFLOW FROM WAVE FUNCTION GROWTH UNDER POTENTPHASE2.220

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C.....PHASE2.221
    SP=Z1/SI                                PHASE2.222
    IF (ABS(RATIN).GT.1.E-40) RATIN=RATIN*SP    PHASE2.223
    SC=SC*SP                                PHASE2.224
    SB=SB*SP                                PHASE2.225
    SI=Z1                                    PHASE2.226
    Y3=Y3*SP                                PHASE2.227
    Y2=Y2*SP                                PHASE2.228
140  Y1=Y2                                    PHASE2.229
    Y2=Y3                                    PHASE2.230
C.....PHASE2.231
C** TEST FOR AND COUNT MODES                PHASE2.232
C.....PHASE2.233
    IF (SB) 170,180,170                    PHASE2.234
170  IF ((SB*SC).GE.Z0) GO TO 190          PHASE2.235
180  MODE=MODE+1                          PHASE2.236
190  IF ((GI.LT.Z0).AND.(I.GE.ILK)) GO TO 210 PHASE2.237
200  CONTINUE                             PHASE2.238
    GO TO 320                              PHASE2.239
C.....PHASE2.240
C** AT THIS POINT, NORMALIZE BEFORE PROCEEDING PHASE2.241
C.....PHASE2.242
210  SP=Z1/(ABS(SI)+ABS(SC))              PHASE2.243
    IF (ABS(RATIN).GT.1.E-40) RATIN=RATIN*SP    PHASE2.244
    SC=SC*SP                                PHASE2.245
    SB=SB*SP                                PHASE2.246
    SI=SI*SP                                PHASE2.247
    Y1=Y1*SP                                PHASE2.248
    Y2=Y2*SP                                PHASE2.249
    IF (IWR.GT.0) WRITE (6,1090)          PHASE2.250
C.....PHASE2.251
C** NUMERICAL INTEGRATION CALCULATING TRIAL PHASE SHIFTS STARTS HERE PHASE2.252
C.....PHASE2.253
    ILK1=II+1                              PHASE2.254
    DO 200 I=ILK1,N                      PHASE2.255
        Y3=Y2+Y2-Y1+GI*SI                PHASE2.256
        GI=H2*(V(I)+EJ*XM2(I)-E)         PHASE2.257
        SN=Y3/(Z1-GI*XI2)                 PHASE2.258
C.....PHASE2.259
C** LOOK FOR WAVE FUNCTION NODE             PHASE2.260
C.....PHASE2.261
    IF (SI) 220,230,220                    PHASE2.262
220  IF ((SB*SI).GE.Z0) GO TO 270          PHASE2.263
230  MODE=MODE+1                          PHASE2.264
C.....PHASE2.265
C** EVALUATE NODAL PHASE SHIFTS AND TEST FOR CONVERGENCE. PHASE2.266
C.....PHASE2.267
    JN=I                                    PHASE2.268
    XJN=XMIN+(JN-1)*XH                    PHASE2.269
    XJC=XJN-Z3*XH                         PHASE2.270
    XND1=XND2                              PHASE2.271
    XND2=XND3                              PHASE2.272
    XND3=XJN+XH*(SN*SB*SC/((SI-SN)*(SI-SB)*(SI-SC))+Z2*SN*SI*SC/ PHASE2.273

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X ((SB-SN)*(SB-SI)*(SB-SC))+Z3*SN*SI*SB/((SC-SN)*(SC-SI)*(SC-SB)) PHASE2.274
X ) PHASE2.275
IF ((XND3.GT.XJC).AND.(XND3.LT.XJN)) GO TO 240 PHASE2.276
WRITE (6,1100) NODE,L,ZE,JN,XND3 PHASE2.277
XND3=XJN-XH*(Z1+SI/(SI-SB)) PHASE2.278
IF ((XND3.GT.XJC).AND.(XND3.LT.XJN)) GO TO 240 PHASE2.279
WRITE (6,1000) NODE,L,ZE,JN,XND3 PHASE2.280
GO TO 270 PHASE2.281
240 ARG=XND3*SDE PHASE2.282
CALL BSELF(X,L,ARG,SBJ,SN) PHASE2.283
DLTX=ATAN(SBJ/SN) PHASE2.284
DLT1=DLT2 PHASE2.285
DLT2=DLT3 PHASE2.286
DLT3=DLTX PHASE2.287
C..... PHASE2.288
C** ADD JNKB PHASE SHIFT CORRECTION DUE TO POTENTIAL TAIL BEYOND -XND3- PHASE2.289
C..... PHASE2.290
COR1=COR2 PHASE2.291
COR2=COR3 PHASE2.292
C..... PHASE2.293
C** START QUADRATURE CALCULATION OF TRUNCATION CORRECTION PHASE2.294
C** FIRST EVALUATE POTENTIAL AT APPROPRIATE GAUSSIAN POINTS PHASE2.295
C..... PHASE2.296
DO 250 IK=1,NGT PHASE2.297
250 RR2(IK)=XND3/XX(IK) PHASE2.298
CALL POT(RR2,A,VV,VP,NGT,RH) PHASE2.299
C..... PHASE2.300
C** NOW PERFORM ACTUAL QUADRATURE PHASE2.301
C..... PHASE2.302
PSC=Z0 PHASE2.303
DO 260 IK=1,NGT PHASE2.304
260 PSC=PSC+WW(IK)*(SORT(E-VV(IK)-EJ*RR2(IK)) - SORT(E-EJ*RR2(IK))) PHASE2.305
X } PHASE2.306
COR3=PSC*ZH*XND3 PHASE2.307
DLT3=DLT3+COR3 PHASE2.308
SMRH=Z1/SN PHASE2.309
C..... PHASE2.310
C** TEST FOR PHASE SHIFT CONVERGENCE PHASE2.311
C..... PHASE2.312
IF (IMR.GT.0) WRITE (6,1050) NODE,XND3,DLTX,DLT3,COR3 PHASE2.313
IF ((ABS(DLT2-DLT3),LT.PHTST).AND.(ABS(DLT1-DLT2),LT.PHTST)) GO PHASE2.314
X TO 290 PHASE2.315
270 SC=SB PHASE2.316
SB=SI PHASE2.317
SI=SN PHASE2.318
Y1=Y2 PHASE2.319
280 Y2=Y3 PHASE2.320
C..... PHASE2.321
C** END OF INTEGRATION LOOP WHICH CALCULATES NODAL PHASE SHIFTS PHASE2.322
C..... PHASE2.323
WRITE (6,1070) DLT3,COR3,DLT2,COR2,DLT1,COR1,XND3,XND2,XND1 PHASE2.324
C..... PHASE2.325
C** GET ABSOLUTE PHASE SHIFT USING EQ.(9.2.29) OF ABRAHONWITZ AND STEGUN PHASE2.326

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C.....PHASE2.327
290 ZU=Z44EJ+Z1PHASE2.328
R4=Z44NR8PHASE2.329
SIR4=Z1/R4882PHASE2.330
TH=NR8-ZM8LPI+(ZH+SIR48((ZU-Z5.E0)/Z6+SIR48((1073.E0-ZU8(114.E0-
X ZU))/Z5-SIR48(375733E0-ZU8(54703.E0-ZU8(1535.E0-Z58ZU)))/14.E0)))PHASE2.332
X 8(ZU-Z1)/R4PHASE2.333
XNDT=(TH+BLTX)/PIPHASE2.334
NDT=(XNDT+ZH)PHASE2.335
ADLT=BLT3+(NDT-NDT)*PIPHASE2.336
RATIN=RATIN$NRHPHASE2.337
IF (ABS(RATIN).GT.1.0E-10) WRITE (6,1040) L,ZE,RATINPHASE2.338
IF (IMR.EQ.0) GO TO 300PHASE2.339
WRITE (6,1020) L,ZE,ADLT,XND3,COR3PHASE2.340
300 CONTINUEPHASE2.341
THE=2.*ADLTPHASE2.342
IF(NSTEP-1) 27,27,28PHASE2.343
27 CTHE(ITEMP+K)=T8(COS(THE)-1.)PHASE2.344
STHE(ITEMP+K)=T8SIN(THE)PHASE2.345
GOTO 60PHASE2.346
28 Y(JJ)=THEPHASE2.347
60 CONTINUEPHASE2.348
IF(NSTEP.EQ.1) GOTO 500PHASE2.349
CALL SPLIFT(NSTEP,Y,YP,NPHASE,W,IERR,ISX,0.,0.,0.,0.)PHASE2.350
ISX=1PHASE2.351
CALL SPLINT (NSTEP, Y, YP, NPHASE, ITEMP)PHASE2.352
IF(IMR.NE.1) GOTO 500PHASE2.353
WRITE(6,404)PHASE2.354
WRITE(6,402)PHASE2.356
WRITE(6,401)(CTHE(IJJ+ITEMP),IJJ=1,NETA)PHASE2.358
WRITE(6,403)PHASE2.360
WRITE(6,401)(STHE(IJJ+ITEMP),IJJ=1,NETA)PHASE2.362
500 CONTINUEPHASE2.363
IF(NSTEP.NE.1) NETA=NETA-NSTEPPHASE2.364
400 RETURNPHASE2.365
310 WRITE (6,1010) L,ZE,ISTPHASE2.366
GOTO 400PHASE2.367
320 WRITE (6,1030) L,ZE,ILKPHASE2.368
GOTO 400PHASE2.369

C
C
C
C
C
1140 FORMAT(1H1)PHASE2.110
1150 FORMAT(//)PHASE2.137
104 FORMAT(10X,8COLLISION ENERGIES*)PHASE2.139
103 FORMAT(10(2X,E10.4))PHASE2.141
404 FORMAT(//,10X,8INTERPOLATED PHASE SHIFT FUNCTIONS*,//)PHASE2.355
402 FORMAT(//,10X,8CTHE ARRAYS*,//)PHASE2.357
401 FORMAT(10(1X,E12.6))PHASE2.359
403 FORMAT(//,10X,8STHE ARRAYS*,//)PHASE2.361
1000 FORMAT(13H0 FOR L =,I3,7H E =,F9.3,70H POTENTIAL SUCH THAPHASE2.370

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      XT INTEGRATION CANNOT START TILL PAST MESH POINT 8,15)          PHASE2.371
1010 FORMAT(26H0 *** ERROR *** FOR L =,I3,6H E =,F9.3,6SH INTERPHASE2.372
      XATION INTERVAL APPARENTLY CANNOT START TILL MESH POINT 8,15)  PHASE2.373
1020 FORMAT(10H0 AT L =,I3,6H E =,F10.4,23H(1/CH) PHASE SHIFT =,PHASE2.374
      X F12.8,13H FOR X =,F7.4,10H COR3 =,F11.8) PHASE2.375
1030 FORMAT(27H0 *** ERROR *** FOR L =,I3,7H E =,F9.3,9H ILK PHASE2.376
      X =,I5,66H , REACH END OF RANGE BEFORE START LOOKING FOR NODAL PHASE2.377
      XASE SHIFTS ) PHASE2.378
1040 FORMAT(27H0 *** WARNING *** FOR L =,I3,7H E =,F9.3,39H JMKPHASE2.379
      XB INITIALIZATION GIVES SB/SI =,D10.3,1H/,D10.3,17H, SO SET S0PHASE2.380
      X=0. ) PHASE2.381
1050 FORMAT(I6,F15.10,F14.10,F16.10,F14.10) PHASE2.382
1060 FORMAT(20H0 *** CAUTION L =,I3,6H E =,F9.3,47H WAVE FUNCTIONPHASE2.383
      XM MAY BE UNRELIABLE AS RATIO =,D10.3,25H, SO MAKE XM IN SMALLERPHASE2.384
      XR) PHASE2.385
1070 FORMAT(54H *** CAUTION *** NOT CONVERGED BY END OF RANGE DLT =, PHASE2.386
      X 3(F11.8,1H(,F11.8,1H))/46X,8HAT X =,3(F11.8,13X) ) PHASE2.387
1080 FORMAT(1H0,5X,51HINSTABILITY **** IN LINEAR INTERPOLATION AT NODEPHASE2.388
      X =,I3,10H , FOR L=,I3,5H E=,E11.5,12H(1/CH) JN=,I4,8H XND3=PHASE2.389
      X, F10.6) PHASE2.390
1090 FORMAT(62H0 NODE X(NODE) DLT(NODE) DLT(COR3) PHASE2.391
      X COR3 =,2X,30(2H**)) PHASE2.392
1100 FORMAT(1H0,5X,51HINSTABILITY **** IN CUBIC INTERPOLATION AT NODEPHASE2.393
      X =,I3,10H , FOR L=,I3,5H E=,E11.5,12H(1/CH) JN=,I4,8H XND3=PHASE2.394
      X, F10.6) PHASE2.395
1110 FORMAT(/1X,60(2H-- )) PHASE2.396
1120 FORMAT(50H0 POINTS X = RST/R AND EFFECTIVE WEIGHTS FOR, PHASE2.397
      X I3,44H-POINT QUADRATURE FOR PHASE SHIFT CORRECTION,/(3(F22.16, PHASE2.398
      X F20.16))) PHASE2.399
1130 FORMAT(51H0 REGULAR GAUSSIAN POINTS AND WEIGHTS FOR REGULAR, PHASE2.400
      X I3,18H-POINT QUADRATURES,/(3(F22.16,F20.16))) PHASE2.401
      END PHASE2.402

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      SUBROUTINE POT(X,A,U,VP,L,RH) PHASE2.403

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C
C      ESMHSV JNKB POT1.2
C      DEFINITION OF POTENTIAL PARAMETERS- SEE JCP,70,PG. 488 (1979) POT1.3
C      EQUATION 7 AND JCP,59,PG.602 (1973) FOR DETAILS. POT1.4
C      A(1)=EPSILON POT1.5
C      A(2)=RMIN POT1.6
C      A(3)= A POT1.7
C      A(4)=ALPHA POT1.8
C      A(5)=X1 POT1.9
C      A(6)=X2 POT1.10
C      A(7)=X3 POT1.11
C      A(8)=X4 POT1.12
C      A(9)=BETA FOR REPULSIVE WALL MORSE POT1.13
C      A(10)=C6 POT1.14
C      A(11)=C8 POT1.15
C      A(12)=BETA ATTRACTIVE WELL POT1.16
C      POT1.17
C      POT1.18

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C	A(13)=C10	POT1.19
C		POT1.20
	DIMENSION X(10),A(15),V(10),VP(10)	POT1.21
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
	RT=ALOG(2.)	POT1.23
	DO 100 I=1,L	POT1.24
	T1=X(I)-A(5)	POT1.25
	IF(T1)5,5,6	POT1.26
C		POT1.27
C	EXPONENTIAL WALL	POT1.28
C		POT1.29
5	V(I)=A(3)*EXP(-A(4)*X(I)-1.))	POT1.30
	VP(I)=-A(4)*V(I)	POT1.31
	GOTO 100	POT1.32
6	T2=X(I)-A(6)	POT1.33
	IF(T2)7,8,8	POT1.34
C		POT1.35
C	EXPONENTIAL SPLINE	POT1.36
C		POT1.37
7	V(I)=EXP(A1+T1*(A2+T2*(A3+A4*T1)))	POT1.38
	VP(I)=V(I)*A(2+A3*(T1+T2)+A4*T1*(T1+2.*T2))	POT1.39
	GOTO 100	POT1.40
8	T3=X(I)-1.+RT/A(12)	POT1.41
	IF(T3)9,9,10	POT1.42
C		POT1.43
C	FIRST MORSE (RZSIGMA)	POT1.44
C		POT1.45
9	W=(A(9)-RT)/(A(12)-RT)	POT1.46
	E1=EXP(A(9)-X(I)*A(12)*W)	POT1.47
	V(I)=E1*(E1-2.)/W	POT1.48
	VP(I)=2.*E1*A(12)*(1./W-E1)	POT1.49
	GOTO 100	POT1.50
10	T4=X(I)-A(7)	POT1.51
	IF(T4) 11,12,12	POT1.52
C		POT1.53
C	SECOND MORSE	POT1.54
C		POT1.55
11	E1=EXP(-2.*A(12)*X(I)-1.))	POT1.56
	E2=EXP(-A(12)*X(I)-1.))	POT1.57
	V(I)=E1-2.*E2	POT1.58
	VP(I)=-2.*A(12)*E1-E2	POT1.59
	GOTO 100	POT1.60
12	T4=X(I)-A(8)	POT1.61
	T3=X(I)-A(7)	POT1.62
	IF(T4)13,14,14	POT1.63
C		POT1.64
C	POLYNOMIAL SPLINE TO DISPERSION SERIES	POT1.65
C		POT1.66
13	V(I)=B1+T3*(B2+T4*(B3+T3*B4))	POT1.67
	VP(I)=B2+B3*(T4+T3)+B4*T3*(T3+2.*T4)	POT1.68
	GOTO 100	POT1.69
C		POT1.70
C	DISPERSION SERIES	POT1.71

C		POT1.72
14	RR=X(I)*R2	POT1.73
	R4=RR*R3	POT1.74
	R8=RR*R4	POT1.75
	R10=RR*R8	POT1.76
	V(I)=-C6/R4-C8/R8-C10/R10	POT1.77
	VP(I)=6.*C6/R4/X(I)+8.*C8/R8/X(I)+10.*C10/R10/X(I)	POT1.78
100	CONTINUE	POT1.79
	RETURN	POT1.80
	END	POT1.81
		POT1.82
	SUBROUTINE PREPOT(A,RH)	PREPOT1.2
C		PREPOT1.3
C	ESMHSU JMKD	PREPOT1.4
C	DETERMINES THE SPLINE COEFFICIENTS AND REDUCED PARAMETERS FOR	POT1PREPOT1.5
C	SEE THAT SUBROUTINE FOR A LISTING OF THE CORRELATION OF THE	PREPOT1.6
C	PARAMETERS AND THE ENTRIES OF THE A ARRAY	PREPOT1.7
C		PREPOT1.8
	DIMENSION A(15)	PREPOT1.9
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
	ERM6=A(1)*A(2)**6	PREPOT1.11
C		PREPOT1.12
C	REDUCED UNITS FOR DISPERSION COEFFICIENTS	PREPOT1.13
C		PREPOT1.14
	C6=A(10)/ERM6	PREPOT1.15
	C8=A(11)/ERM6/A(2)**2	PREPOT1.16
	C10=A(13)/ERM6/A(2)**4	PREPOT1.17
C		PREPOT1.18
C	SPLINE COEFFICIENTS FOR THE REPULSIVE WALL	PREPOT1.19
C		PREPOT1.20
	A1=ALOG(A(3))-A(4)*A(5)-1.)	PREPOT1.21
	TEMP=EXP(-2.*A(9)*(A(6)-1.))-2.*EXP(-A(9)*(A(6)-1.))	PREPOT1.22
	A2=(ALOG(TEMP)-A1)/(A(6)-A(5))	PREPOT1.23
	A3=-(A(4)+A2)/(A(5)-A(6))	PREPOT1.24
	A4=2.*A(9)*(EXP(-A(9)*(A(6)-1.))-EXP(-2.*A(9)*(A(6)-1.)))*EXP(-(A1	PREPOT1.25
	1+A2*(A(6)-A(5))))-A2-A3*(A(6)-A(5))	PREPOT1.26
	A4=A4/(A(6)-A(5))**2	PREPOT1.27
C		PREPOT1.28
C	SPLINE COEFFICIENTS FOR THE DISPERSION SERIES.	PREPOT1.29
C		PREPOT1.30
	TT=A(12)*(A(7)-1.)	PREPOT1.31
	B1=EXP(-2.*TT)-2.*EXP(-TT)	PREPOT1.32
	TEMP=-C6/A(8)**6-C8/A(8)**8-C10/A(8)**10	PREPOT1.33
	B2=(TEMP-B1)/(A(8)-A(7))	PREPOT1.34
	TEMP=-2.*A(12)*EXP(-2.*TT)+2.*EXP(-TT)*A(12)	PREPOT1.35
	B3=(TEMP-B2)/(A(7)-A(8))	PREPOT1.36
	TEMP=6.*C6/A(8)**7+8.*C8/A(8)**9+10.*C10/A(8)**11	PREPOT1.37
	B4=(TEMP-B2-B3*(A(8)-A(7)))/(A(8)-A(7))**2	PREPOT1.38
	RETURN	PREPOT1.39
	END	PREPOT1.40

		PREPOT1.41
	SUBROUTINE POT(X,A,V,VP,L,RH)	POT2.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C		POT2.4
C	HFD POTENTIAL- SEE JCP,67,P6.152(1977) EDN. (1) FOR DEFINITION OF	POT2.5
C	THE FUNCTIONAL FORM	POT2.6
C	A(1)=EPSILON	POT2.7
C	A(2)=RHIN	POT2.8
C	A(3)=A	POT2.9
C	A(4)=ALPHA	POT2.10
C	A(5)=C6	POT2.11
C	A(6)=C8	POT2.12
C	A(7)=C10	POT2.13
C		POT2.14
	DIMENSION A(15),X(10),V(10),VP(10)	POT2.15
	DO 10 I=1,L	POT2.16
	R=X(I)*A(2)	POT2.17
	RR=R*R	POT2.18
	R6=RR*B3	POT2.19
	F=A(3)*EXP(-A(4)*R)	POT2.20
	G=-C6/R6-C8/R6/RR-C10/R6/RR/RR	POT2.21
	D=1.	POT2.22
	IF(X(I).LE.1.28)D=EXP(-(1.28/X(I)-1.))*2)	POT2.23
	V(I)=(F+G*D)/A(1)	POT2.24
	FP=-F*A(4)	POT2.25
	GP=6.*C6/R6/R+8.*C8/R6/RR/R+10.*C10/R6/RR/RR/R	POT2.26
	DP=0.	POT2.27
	IF(X(I).LE.1.28)DP=2.*1.28*D*(1.28*A(2)/R-1.)*A(2)/R/R	POT2.28
10	VP(I)=(FP+GP*DP+D*G)/A(1)*A(2)	POT2.29
	CONTINUE	POT2.30
	RETURN	POT2.31
	END	POT2.32
		POT2.33
	SUBROUTINE PREPOT(A,RH)	PREPOT2.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C		PREPOT2.4
C	HFD POTENTIAL- SEE POT2 FOR DESCRIPTION OF FUNCTIONAL FORM AND	PREPOT2.5
C	DESCRIPTION AND LITERATURE REFERENCE.	PREPOT2.6
C		PREPOT2.7
	DIMENSION A(15)	PREPOT2.8
	C6=A(5)	PREPOT2.9
	C8=A(6)	PREPOT2.10
	C10=A(7)	PREPOT2.11
	H=EXP(-.28**2)	PREPOT2.12
	T=2.*.28**1.28	PREPOT2.13
	C1=(6.-T)*C6	PREPOT2.14
	C2=(8.-T)*C8	PREPOT2.15

	C3=(10.-T)*C10	PREPOT2.16
	C4=2.8T	PREPOT2.17
	C5=4.81.28-6.81.28*1.28	PREPOT2.18
	D6=C6*(6.8C4-42.-C5)	PREPOT2.19
	D8=C8*(-72.+8.8C4-C5)	PREPOT2.20
	D10=C10*(-110.+10.8C4-C5)	PREPOT2.21
C		PREPOT2.22
C	A MAXIMUM OF 100 ITERATIONS ALLOWED TO FIND RM.	PREPOT2.23
		PREPOT2.24
	DO 10 I=1,100	PREPOT2.25
	RMIN=A(2)	PREPOT2.26
	R=RMIN	PREPOT2.27
	F=A(3)*EXP(-A(4)*A(2))	PREPOT2.28
	RR=RMIN*RRMIN	PREPOT2.29
	R6=RR*23	PREPOT2.30
	G=-C6/R6-C8/R6/RR-C10/R6/RR/RR	PREPOT2.31
C		PREPOT2.32
C	COMPUTE FIRST AND SECOND DERIVATIVES	PREPOT2.33
C		PREPOT2.34
	FP=-A(4)*F	PREPOT2.35
	FPP=-A(4)*FP	PREPOT2.36
	GP=H*(C1+C2/RR+C3/RR/RR)/R/R6	PREPOT2.37
	GPP=H*(D6+D8/RR+D10/RR/RR)/R6/RR	PREPOT2.38
	VP=FP+GP	PREPOT2.39
	VPP=FPP+GPP	PREPOT2.40
C		PREPOT2.41
C	NEWTON'S FORMULA FOR NEW VALUE OF RMIN	PREPOT2.42
C		PREPOT2.43
	RNEW=RMIN-VP/VPP	PREPOT2.44
	A(2)=RNEW	PREPOT2.45
	IF(ABS(RNEW-RMIN).GT.1.E-05) GOTO 10	PREPOT2.46
	A(1)=F+G*H	PREPOT2.47
	A(1)=ABS(A(1))	PREPOT2.48
	GOTO 20	PREPOT2.49
10	CONTINUE	PREPOT2.50
	WRITE(6,15)	PREPOT2.51
15	FORMAT(10X,'PREPOT NOT CONVERGED')	PREPOT2.52
	STOP	PREPOT2.53
20	CONTINUE	PREPOT2.54
	RETURN	PREPOT2.55
	END	PREPOT2.56
		PREPOT2.57
	SUBROUTINE POT(X,A,U,VP,L,RM)	POT3.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C		POT3.4
C	LENNARD-JONES, JMKD	POT3.5
C	DEFINITION OF POTENTIAL PARAMETERS	POT3.6
C	A(1)=EPSILON	POT3.7
C	A(2)=RMIN	POT3.8
C		POT3.9

	DIMENSION A(15),X(10),V(10),VP(10)	POT3.10
	DO 10 I=1,L	POT3.11
	XIN=1./X(I)	POT3.12
	TEMP=XIN**3	POT3.13
	V(I)=4.8TEMP*(TEMP-1)	POT3.14
	VP(I)=24.8TEMP*XIN*(1.-2.8TEMP)	POT3.15
10	CONTINUE	POT3.16
	RETURN	POT3.17
	END	POT3.18
	SUBROUTINE PREPOT(A,RH)	POT3.19
C	BUNNY PREPOT	PREPOT10.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	PREPOT10.3
	DIMENSION A(15)	POTPRE.2
	RETURN	PREPOT10.5
	END	PREPOT10.6
		PREPOT10.7
	SUBROUTINE POT(X,A,V,VP,L,RH)	PREPOT10.8
C		POT11.2
C	HFD POTENTIAL- LEROY PHASE SHIFTS	POT11.3
C	FOR DESCRIPTION OF FUNCTIONAL FORM,LITERATURE REFERENCE AND	POT11.4
C	EXPLANATION OF VARIABLES,SEE POT2	POT11.5
C		POT11.6
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POT11.7
	DIMENSION A(15),X(10),V(10),VP(10)	POTPRE.2
	BZ=RH*A(1)*A(2)*A(2)*349.757/16.85763	POT11.9
	DO 130 I=1,L	POT11.10
	R=X(I)*A(2)	POT11.11
	RR=R*R	POT11.12
	R6=RR**3	POT11.13
	F=A(3)*EXP(-A(4)*R)	POT11.14
	G=-C6/R6-C8/R6/RR-C10/R6/RR/RR	POT11.15
	D=1.	POT11.16
	IF(X(I).LE.1.28) D=EXP(-(1.28/X(I)-1.))*2)	POT11.17
C		POT11.18
C	CONVERT TO REDUCED ENERGY AND WAVENUMBERS	POT11.19
C		POT11.20
	V(I)=BZ*(F+G*D)/A(1)	POT11.21
C		POT11.22
C	SET UP REDUCED CENTRIFUGAL ENERGY	POT11.23
C		POT11.24
	TEMP=1./X(I)	POT11.25
	X(I)=TEMP*TEMP	POT11.26
130	CONTINUE	POT11.27
	RETURN	POT11.28
	END	POT11.29
		POT11.30

	SUBROUTINE PREPOT(A,RM)	POT11.31
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	PREPOT11.2
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RMPPHASE,ERROR	POTPRE.2
	DIMENSION A(15)	PTNL.2
C		PREPOT11.5
C	HFB POT ENT IAL- LEROY EXACT PHASE SHIFTS	PREPOT11.6
C	FOR DESCRIPTION OF FUNCTIONAL FORM,LITERATURE REFERENCE, AND	PREPOT11.7
C	EXPLANATION OF VARIABLES SEE POT2.	PREPOT11.8
C		PREPOT11.9
	XMIN=XSTART	PREPOT11.10
	XH=XSTEP	PREPOT11.11
	N=INT(RMPPHASE)	PREPOT11.12
	C10=A(13)/ERM6/A(2)**4	PREPOT11.13
	C6=A(5)	PREPOT11.14
	C8=A(6)	PREPOT11.15
	C10=A(7)	PREPOT11.16
		PREPOT11.17
C	SELF CONSISTENCY SECTION	PREPOT11.18
C	NEUTON SEARCH FOR RMIN.	PREPOT11.19
C		PREPOT11.20
	H=EXP(-.28**2)	PREPOT11.21
	T=2.*.28**1.28	PREPOT11.22
	C1=(6.-T)*C6	PREPOT11.23
	C2=(8.-T)*C8	PREPOT11.24
	C3=(10.-T)*C10	PREPOT11.25
	C4=2.*T	PREPOT11.26
	C5=4.*1.28-6.*1.28**1.28	PREPOT11.27
	D6=C6*(6.*C4-42.-C5)	PREPOT11.28
	D8=C8*(-72.+8.*C4-C5)	PREPOT11.29
	D10=C10*(-110.+10.*C4-C5)	PREPOT11.30
		PREPOT11.31
C	A MAXIMUM OF 100 ITERATIONS ALLOWED TO FIND RM.	PREPOT11.32
C		PREPOT11.33
C		PREPOT11.34
	DO 10 I=1,100	PREPOT11.35
	RMIN=A(2)	PREPOT11.36
	R=RMIN	PREPOT11.37
	F=A(3)*EXP(-A(4)*A(2))	PREPOT11.38
	RR=RMIN*RMIN	PREPOT11.39
	R6=RR**3	PREPOT11.40
	G=-C6/R6-C8/R6/RR-C10/R6/RR/RR	PREPOT11.41
C		PREPOT11.42
C	COMPUTE FIRST AND SECOND DERIVATIVES	PREPOT11.43
C		PREPOT11.44
	FP=-A(4)*F	PREPOT11.45
	FPP=-A(4)*FP	PREPOT11.46
	GP=H*(C1+C2/RR+C3/RR/RR)/R/R6	PREPOT11.47
	GPP=H*(D6+D8/RR+D10/RR/RR)/R6/R6	PREPOT11.48
	VP=FP+GP	PREPOT11.49
	UPP=FPP+GPP	PREPOT11.50
C		PREPOT11.51

	BZ=RM#A(1)*A(2)*A(2)*349.757/16.85763	POT12.9
	DO 10 I=1,L	POT12.10
	XIN=1./X(I)	POT12.11
	TEMP=XIN**6	POT12.12
	V(I)=4.*TEMP*(TEMP-1.)	POT12.13
	V(I)=V(I)*BZ	POT12.14
	X(I)=XIN*XIN	POT12.15
10	CONTINUE	POT12.16
	RETURN	POT12.17
	END	POT12.18
	SUBROUTINE PREPOT(A,RM)	POT12.19
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR	PREPOT12.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	PTNL.2
	DIMENSION A(15)	POTPRE.2
C	LJ 6-12 "XACT PHASE SHIFTS	PREPOT12.5
C	FOR A DESCRIPTION OF FUNCTIONAL FORM,LITERATURE REFERENCE AND	PREPOT12.6
C	EXPLANATION OF VARIABLES, SEE POT3.	PREPOT12.7
C		PREPOT12.8
C		PREPOT12.9
	XMIN=XSTART	PREPOT12.10
	BZ=RM#A(1)*A(2)*A(2)*349.757/16.85763	PREPOT12.11
	XH=XSTEP	PREPOT12.12
	L=INT(RNPHAS)	PREPOT12.13
	XS=XMIN-XH	PREPOT12.14
	DO 10 I=1,L	PREPOT12.15
	XS=XS+XH	PREPOT12.16
	XIN=1./XS	PREPOT12.17
	TEMP=XIN**6	PREPOT12.18
	V(I)=4.*TEMP*(TEMP-1.)	PREPOT12.19
	V(I)=V(I)*BZ	PREPOT12.20
	XM2(I)=XIN*XIN	PREPOT12.21
10	CONTINUE	PREPOT12.22
	RETURN	PREPOT12.23
	END	PREPOT12.24
		PREPOT12.25
	SUBROUTINE POT(X,A,V,UP,L,RM)	PREPOT12.26
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POT13.2
	DIMENSION A(15),V(10),UP(10),X(10)	POTPRE.2
C		POT13.4
C	EXACT PHASE SHIFT SPHD POTENTIAL	POT13.5
C	JCP,71,PG.2638 (1979).	POT13.6
C	DEFINITION OF A ARRAY	POT13.7
C	A(1)=EPSILON,A(2)=RM,A(3)=A ,A(4)=ALPHA,A(5)=B0,A(6)=B1,	POT13.8
C	A(7)=B2,A(8)=B3,A(9)=XF,A(10)=TAU,A(11)=XD.	POT13.9
C	A(12)=C6,A(13)=C8,A(14)=C10	POT13.10
C		POT13.11
C		POT13.12

	BZ=RM*A(1)*A(2)*A(2)*349.757/16.85763	POT13.13
	DO 10 I=1,L	POT13.14
	Z=X(I)-A(9)	POT13.15
	IF(Z.LT.0.) GOTO 20	POT13.16
C		POT13.17
C	DISPERSION SERIES	POT13.18
C		POT13.19
	XT=X(I)*.86	POT13.20
	XZ=X(I)*.82	POT13.21
	V(I)=- (C6/XT+CB/XT/XZ+C10/XT/XZ/XZ)	POT13.22
	GOTO 30	POT13.23
C		POT13.24
C	SPHD SERIES	POT13.25
C		POT13.26
20	Z=1.-1./X(I)	POT13.27
	H=1./(1.+EXP(A(10)*X(I)-A(11))))	POT13.28
	G=A(5)*Z*Z*(1.+Z*(A(6)+Z*(A(7)+Z*(A(8)))))-1.	POT13.29
	V(I)=H*A(3)*EXP(-A(4)*A(2)*X(I))/A(1)+(1.-H)*G	POT13.30
C		POT13.31
C	CONVERT POTENTIAL TO WAVENUMBERS AND CALCULATE REDUCED	POT13.32
C	CENTRIFUGAL POTENTIAL ARRAY	POT13.33
C		POT13.34
30	X(I)=1./X(I)/X(I)	POT13.35
	V(I)=V(I)*.8Z	POT13.36
10	CONTINUE	POT13.37
	RETURN	POT13.38
	END	POT13.39
		POT13.40
	SUBROUTINE PREPOT(A,RM)	PREPOT13.2
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR	PTNL.2
	COMMON/POTPRE/C6,CB,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
	DIMENSION A(15)	PREPOT13.5
C		PREPOT13.6
C	SPHD EXACT POTENTIAL	PREPOT13.7
C		PREPOT13.8
	BZ=RM*A(1)*A(2)*A(2)*349.757/16.85763	PREPOT13.9
	XMIN=XSTART	PREPOT13.10
	XH=XSTEP	PREPOT13.11
	L=INT(RNPHAS)	PREPOT13.12
	XS=XMIN-XH	PREPOT13.13
C		PREPOT13.14
C	CONVERT DISPERSION CONSTANTS TO REDUCED UNITS	PREPOT13.15
C		PREPOT13.16
	D6=A(12)	PREPOT13.17
	D8=A(13)	PREPOT13.18
	D10=A(14)	PREPOT13.19
	ERN6=A(1)*A(2)*.86	PREPOT13.20
	C6=D6/ERN6	PREPOT13.21
	CB=D8/ERN6/A(2)*.82	PREPOT13.22
	C10=D10/ERN6/A(2)*.84	PREPOT13.23
C		PREPOT13.24

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C      B2,B3 ARE USED TO MATCH DISPERSION SERIES AND ITS FIRST
C      DERIVATIVE AT XF.
C
XF=A(9)
H=1./(1.+EXP(A(10)*XF-A(11))))
H1=-H*H*EXP(A(10)*XF-A(11)))*A(10)
XF6=XF**6
XF2=XF**2
F=-(C6/XF6+C8/XF6/XF2+C10/XF6/XF2/XF2)
F1=(6.*C6/XF6+8.*C8/XF2/XF6+10.*C10/XF2/XF6**2)/XF
G=H*A(3)*EXP(-A(4)*XF)
G1=G*(H1/H-A(4))
RL=1.-1./XF
T=-1.+RL*RL*(A(5)+A(6)*RL)
RL1=1./XF2
CNST1=(F+1.)/RL/RL/A(5)
CNST1=CNST1-1.-RL*A(6)
CNST2=F1/A(5)/RL/RL1
CNST2=CNST2-2.-3.*A(6)*RL
A(7)=(5.*CNST1-CNST2)/RL**2
A(8)=(CNST2-4.*CNST1)/RL**3
DO 10 I=1,L
XS=XS+XH
XM2(I)=XS
Z=XM2(I)-A(9)
IF(Z.LT.0.) GOTO 20

C      DISPERSION SERIES
C
C
XT=XM2(I)**6
X2=XM2(I)**2
V(I)=-(C6/XT+C8/XT/X2+C10/XT/X2**2)
GOTO 30

C      SPHD SERIES
C
C
20 Z=1.-1./XM2(I)
H=1./(1.+EXP(A(10)*XM2(I)-A(11))))
G=A(5)*Z**2*(1.+Z*(A(6)+Z*(A(7)+Z*A(8))))-1.
V(I)=H*A(3)*EXP(-A(4)*A(2)*XM2(I))/A(1)+(1.-H)*G
30 XM2(I)=1./XM2(I)/XM2(I)
V(I)=V(I)*BZ
10 CONTINUE
RETURN
END

SUBROUTINE POT(X,A,V,VP,L,RH)
C
C      ESMHVS-EXACT PHASE SHIFTS
C
C      DEFINITION OF POTENTIAL PARAMETERS? SEE JCP,71,P. 2638 (1979).

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PREPOT13.25
 PREPOT13.26
 PREPOT13.27
 PREPOT13.28
 PREPOT13.29
 PREPOT13.30
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 PREPOT13.65
 PREPOT13.66
 PREPOT13.67
 PREPOT13.68
 PREPOT13.69

 PREPOT13.70
 POT14.2
 POT14.3
 POT14.4
 POT14.5
 POT14.6

C	TRIGONOMETRIC SWITCHING REGION FROM SECOND MORSE TO DISPERSION	POT14.60
C	SERIES	POT14.61
C		POT14.62
	TEMP=EXP(-A(12)*T1)	POT14.63
	RR=X(I)*S2	POT14.64
	R6=RR*S3	POT14.65
	R8=RR*S6	POT14.66
	R10=RR*S8	POT14.67
	B=-C6/R6-C8/R8-C10/R10	POT14.68
	RTT2=3.141592/(A(8)-A(7))	POT14.69
	RTT1=(X(I)-A(7))*RTT2	POT14.70
	S=.5*(COS(RTT1)+1.)	POT14.71
	BS=-RTT2*SIN(RTT1)/2.	POT14.72
	RHORSE=TEMP*(TEMP-2.)	POT14.73
	V(I)=RHORSE*S+(1.-S)*D	POT14.74
	VP(I)=(RHORSE-D)*S+S2.*A(12)*TEMP*(1.-TEMP)	POT14.75
	VP(I)=VP(I)+(1.-S)*6.*C6/R6/X(I)+8.*C8/R8/X(I)+10.*C10/R10/X(I)	POT14.76
	GOTO 100	POT14.77
C		POT14.78
C	DISPERSION SERIES	POT14.79
C		POT14.80
10	RR=X(I)*S2	POT14.81
	R6=RR*S3	POT14.82
	R8=RR*S6	POT14.83
	R10=RR*S8	POT14.84
	V(I)=-C6/R6-C8/R8-C10/R10	POT14.85
	VP(I)=6.*C6/R6/X(I)+8.*C8/R8/X(I)+10.*C10/R10/X(I)	POT14.86
100	CONTINUE	POT14.87
C		POT14.88
C	CONVERT TO WAVENUMBERS AND RETURN REDUCED CENTRIFUGAL POTENTIAL	POT14.89
C		POT14.90
	V(I)=V(I)*BZ	POT14.91
	X(I)=1./X(I)/X(I)	POT14.92
200	CONTINUE	POT14.93
	RETURN	POT14.94
	END	POT14.95
		POT14.96
	SUBROUTINE PREPOT(A,RM)	PREPOT14.2
	DIMENSION A(15)	PREPOT14.3
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RMPHAS,ERROR	PTNL.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C		PREPOT14.6
C	ESMHSV - EXACT PHASE SHIFTS.	PREPOT14.7
C	SEE POT 14 FOR DETAILS ON THE POTENTIAL PARAMETERS. IN THIS	PREPOT14.8
C	VERSION OF THE ESMHSV POTENTIAL, THE TWO MORSE POTENTIALS JOIN AT	PREPOT14.9
C	RM, AND THE DISPERSION SERIES IS SWITCHED ON WITH A TRIGONOMETRIC	PREPOT14.10
C	FUNCTION, NOT A POLYNOMIAL SPLINE.	PREPOT14.11
C		PREPOT14.12
	BZ=RM*A(1)*A(2)*A(2)*349.757/16.85763	PREPOT14.13
	XMIN=XSTART	PREPOT14.14
	XH=XSTEP	PREPOT14.15

5	TEMP=EXP(-A(9)*T1)	PREPOT14.69
	V(I)=TEMP*(TEMP-2.)	PREPOT14.70
	GOTO 100	PREPOT14.71
6	T2=XS-A(7)	PREPOT14.72
	IF(T2) 7,8,8	PREPOT14.73
C		PREPOT14.74
C	SECOND MORSE	PREPOT14.75
C		PREPOT14.76
7	TEMP=EXP(-A(12)*T1)	PREPOT14.77
	V(I)=TEMP*(TEMP-2.)	PREPOT14.78
	GOTO 100	PREPOT14.79
8	T3=XS-A(8)	PREPOT14.80
	IF(T3) 9,9,10	PREPOT14.81
9	CONTINUE	PREPOT14.82
C		PREPOT14.83
C	SWITCHING FUNCTION FROM SECOND MORSE TO DISPERSION SERIES	PREPOT14.84
C		PREPOT14.85
	TEMP=EXP(-A(12)*T1)	PREPOT14.86
	RR=XS**2	PREPOT14.87
	R6=RR**3	PREPOT14.88
	R8=RR**6	PREPOT14.89
	R10=RR**8	PREPOT14.90
	D=-C6/R6-C8/R8-C10/R10	PREPOT14.91
	RTT2=3.141592/(A(8)-A(7))	PREPOT14.92
	RTT1=T2*RTT2	PREPOT14.93
	S=.5*(COS(RTT1)+1.)	PREPOT14.94
	RMORSE=TEMP*(TEMP-2.)	PREPOT14.95
	V(I)=RMORSE*S+(1.-S)*D	PREPOT14.96
	GOTO 100	PREPOT14.97
C		PREPOT14.98
C	DISPERSION SERIES	PREPOT14.99
C		PREPOT14.100
10	RR=XS**2	PREPOT14.101
	R6=RR**3	PREPOT14.102
	R8=RR**6	PREPOT14.103
	R10=RR**8	PREPOT14.104
	V(I)=-C6/R6-C8/R8-C10/R10	PREPOT14.105
100	CONTINUE	PREPOT14.106
C		PREPOT14.107
C	CONVERT POTENTIAL TO WAVENUMBERS AND SET UP CENTRIFUGAL POTENTIAL	PREPOT14.108
C	IN REDUCED UNITS	PREPOT14.109
C		PREPOT14.110
	XN2(I)=1./XS/XS	PREPOT14.111
	V(I)=V(I)*BZ	PREPOT14.112
500	CONTINUE	PREPOT14.113
	RETURN	PREPOT14.114
	END	PREPOT14.115
		PREPOT14.116
	SUBROUTINE POT(X,A,V,VP,L,RH)	POT15.2
C		POT15.3
C	ESMHSV EXACT ETA'S	POT15.4

C		POT15.5
C	DEFINITION OF POTENTIAL PARAMETERS? SEE JCP,70,P. 489 (1979)	POT15.6
C	A(1)=EPSILON,A(2)=RM,A(3)=A,A(4)=ALPHA,A(5)=X1,A(6)=X2,A(7)=X3,	POT15.7
C	A(8)=X4,A(9)=BETA1,A(10)=C6,A(11)=C8,A(12)=BETA2	POT15.8
C		POT15.9
C	THE FOLLOWING ARE THE MAIN DIFFERENCES BETWEEN THIS VERSION AND	POT15.10
C	POT14	POT15.11
C	1. THE OUTER MORSE IS SPLINED TO THE DISPERSION SERIES	POT15.12
C	2. THE TWO MORSE PARTS ARE JOINED AT THE SIGMA POINT.	POT15.13
C		POT15.14
C	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C	DIMENSION X(10),A(15),V(10),VP(10)	POT15.16
C	RT=ALOG(2.)	POT15.17
C	BZ=RM&A(1)&A(2)&A(2)&349.757/16.85763	POT15.18
C	DO 200 I=1,L	POT15.19
C	T1=X(I)-A(5)	POT15.20
C	IF(T1)5,5,6	POT15.21
C		POT15.22
C	EXPONENTIAL REPULSIVE WALL	POT15.23
C		POT15.24
5	V(I)=A(3)*EXP(-A(4)*(X(I)-1.))	POT15.25
C	GOTO 100	POT15.26
6	T2=X(I)-A(6)	POT15.27
C	IF(T2)7,8,8	POT15.28
C		POT15.29
C	EXPONENTIAL SPLINE	POT15.30
C		POT15.31
7	V(I)=EXP(A1+T1*(A2+T2*(A3+A4*T1)))	POT15.32
C	GOTO 100	POT15.33
8	T3=X(I)-1.+RT/A(12)	POT15.34
C	IF(T3)9,9,10	POT15.35
C		POT15.36
C	FIRST MORSE (R< SIGMA)	POT15.37
C		POT15.38
9	W=(A(9)-RT)/(A(12)-RT)	POT15.39
C	E1=EXP(A(9)-X(I)&A(12)&W)	POT15.40
C	V(I)=E1*(E1-2.)/W	POT15.41
C	GOTO 100	POT15.42
10	T4=X(I)-A(7)	POT15.43
C	IF(T4) 11,12,12	POT15.44
C		POT15.45
C	SECOND MORSE	POT15.46
C		POT15.47
11	E1=EXP(-2.&A(12)&(X(I)-1.))	POT15.48
C	E2=EXP(-A(12)&(X(I)-1.))	POT15.49
C	V(I)=E1-2.*E2	POT15.50
C	GOTO 100	POT15.51
12	T4=X(I)-A(8)	POT15.52
C	T3=X(I)-A(7)	POT15.53
C	IF(T4)13,14,14	POT15.54
C		POT15.55
C	POLYNOMIAL SPLINE TO DISPERSION SERIES	POT15.56
C		POT15.57

13	V(I)=B1+T3*(B2+T4*(B3+T5*B4))	POT15.58
	GOTO 100	POT15.59
C		POT15.60
C	DISPERSION SERIES	POT15.61
C		POT15.62
14	RR=X(I)*B2	POT15.63
	R4=RR*B3	POT15.64
	R8=RR*R4	POT15.65
	R10=RR*R8	POT15.66
	V(I)=-C6/R4-C8/R8-C10/R10	POT15.67
100	CONTINUE	POT15.68
C		POT15.69
C	CONVERT TO REDUCED UNITS, SET UP CENTRIFUGAL POTENTIAL.	POT15.70
C		POT15.71
	V(I)=V(I)*BZ	POT15.72
	X(I)=1./X(I)/X(I)	POT15.73
200	CONTINUE	POT15.74
	RETURN	POT15.75
	END	POT15.76
		POT15.77
	SUBROUTINE PREPOT(A,RH)	PREPOT15.2
	DIMENSION A(15)	PREPOT15.3
	COMMON/PTNL/V(2001),XM2(2001),XSTART,XSTEP,RNPHAS,ERROR	PTNL.2
	COMMON/POTPRE/C6,C8,C10,B1,B2,B3,B4,A1,A2,A3,A4	POTPRE.2
C		PREPOT15.4
C	ESMHSV- EXACT PHASE SHIFTS	PREPOT15.7
C	MORSE POTENTIALS JOINED AT THE SIGMA POINT	PREPOT15.8
C	POLYNOMIAL SPLINE TO THE DISPERSION SERIES	PREPOT15.9
C		PREPOT15.10
	RT=ALOG(2.)	PREPOT15.11
	BZ=RH*A(1)*A(2)*A(2)*349.757/16.85763	PREPOT15.12
	XMIN=XSTART	PREPOT15.13
	XH=XSTEP	PREPOT15.14
	L=INT(RNPHAS)	PREPOT15.15
	XS=XMIN-XH	PREPOT15.16
C		PREPOT15.17
C	CONVERT DISPERSION CONSTANTS TO REDUCED UNITS	PREPOT15.18
C		PREPOT15.19
	ERM6=A(1)*A(2)*B6	PREPOT15.20
	C6=A(10)/ERM6	PREPOT15.21
	C8=A(11)/ERM6/A(2)*B2	PREPOT15.22
	C10=0.	PREPOT15.23
C		PREPOT15.24
C	CALCULATE SPLINE COEFFICIENTS TO EXPONENTIAL WALL	PREPOT15.25
C		PREPOT15.26
	A1=ALOG(A(3))-A(4)*A(5)-1.)	PREPOT15.27
	TEMP=EXP(-2.*A(9)*A(6)-1.))-2.*EXP(-A(9)*A(6)-1.))	PREPOT15.28
	IF(TEMP.GT.0.) GOTO 20	PREPOT15.29
	WRITE(6,21) A(6),A(9)	PREPOT15.30
21	FORMAT(2X,*IN PREPOT15, SPLINE POINT AND MORSE CURVATURE NOT *	PREPOT15.31
	COMPATIBLE,2(2X,E10.4))	PREPOT15.32

```

STOP PREPOT15.33
20 CONTINUE PREPOT15.34
A2=(ALOG(TEMP)-X1)/(A(6)-A(5)) PREPOT15.35
A3=-(A(4)+A2)/(A(5)-A(6)) PREPOT15.36
A4=2.8A(9)*EXP(-A(9)*A(6)-1.))-EXP(-2.8A(9)*A(6)-1.)))*EXP(-(A1 PREPOT15.37
+ A2*(A(6)-A(5))))-A2-A3*(A(6)-A(5)) PREPOT15.38
A4-A4/(A(6)-A(5))*2 PREPOT15.39
T7=A(12)*A(7)-1.) PREPOT15.40
C PREPOT15.41
C CALCULATE SPLINE CONSTANTS TO DISPERSION SERIES PREPOT15.42
C PREPOT15.43
B1=EXP(-2.8TT)-2.8EXP(-TT) PREPOT15.44
TEMP=-C6/A(8)**6-C8/A(8)**8-C10/A(8)**10 PREPOT15.45
B2=(TEMP-B1)/(A(8)-A(7)) PREPOT15.46
TEMP=-2.8A(12)*EXP(-2.8TT)+2.8EXP(-TT)*A(12) PREPOT15.47
B3=(TEMP-B2)/(A(7)-A(8)) PREPOT15.48
TEMP=6.8C6/A(8)**7+8.8C8/A(8)**9+10.8C10/A(8)**11 PREPOT15.49
B4=(TEMP-B2-B3*(A(8)-A(7)))/(A(8)-A(7))*2 PREPOT15.50
DO 500 I=1,L PREPOT15.51
XS=XS+XH PREPOT15.52
T1=XS-A(5) PREPOT15.53
IF(T1)5,5,6 PREPOT15.54
C PREPOT15.55
C REPULSIVE EXPONENTIAL WALL PREPOT15.56
C PREPOT15.57
5 V(I)=A(3)*EXP(-A(4)*(XS-1.)) PREPOT15.58
GOTO 100 PREPOT15.59
6 T2=XS-A(6) PREPOT15.60
IF(T2)7,8,8 PREPOT15.61
C PREPOT15.62
C EXPONENTIAL SPLINE PREPOT15.63
C PREPOT15.64
7 V(I)=EXP(A1+T1*(A2+T2*(A3+A4*T1))) PREPOT15.65
GOTO 100 PREPOT15.66
8 T3=XS -1.+RT/A(12) PREPOT15.67
IF(T3)9,9,10 PREPOT15.68
C PREPOT15.69
C FIRST MORSE (X<SIGMA) PREPOT15.70
C PREPOT15.71
9 W=(A(9)-RT)/(A(12)-RT) PREPOT15.72
E1=EXP(A(9)-XS 8A(12)*W) PREPOT15.73
V(I)=E1*(E1-2.)/W PREPOT15.74
GOTO 100 PREPOT15.75
10 T4=XS -A(7) PREPOT15.76
IF(T4) 11,12,12 PREPOT15.77
C PREPOT15.78
C SECOND MORSE PREPOT15.79
C PREPOT15.80
11 E1=EXP(-2.8A(12)*(XS -1.)) PREPOT15.81
E2=EXP(-A(12)*(XS -1.)) PREPOT15.82
V(I)=E1-2.8E2 PREPOT15.83
GOTO 100 PREPOT15.84
12 T4=XS -A(8) PREPOT15.85

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	T3=XS -A(7)	PREPOT15.86
	IF(T4)13,14,14	PREPOT15.87
C		PREPOT15.88
C	POLYNOMIAL SPLINE	PREPOT15.89
C		PREPOT15.90
13	V(I)=B1+T3*(B2+T4*(B3+T3*B4))	PREPOT15.91
	GOTO 100	PREPOT15.92
C		PREPOT15.93
C	DISPERSION SERIES	PREPOT15.94
C		PREPOT15.95
14	RR=XS **2	PREPOT15.96
	R6=RR**3	PREPOT15.97
	R8=RR**6	PREPOT15.98
	R10=RR**8	PREPOT15.99
	V(I)=-C6/R6-C8/R8-C10/R10	PREPOT15.100
100	CONTINUE	PREPOT15.101
C		PREPOT15.102
C	CONVERT POTENTIAL TO REDUCED UNITS AND SET UP CENTRIFUGAL POTENT.	PREPOT15.103
C		PREPOT15.104
	XN2(I)=1./XS/XS	PREPOT15.105
	V(I)=V(I)**Z	PREPOT15.106
500	CONTINUE	PREPOT15.107
	RETURN	PREPOT15.108
	END	PREPOT15.109

CHAPTER II. INFRARED VIBRATIONAL PREDISSOCIATION OF
 C_6H_6 , H_2O , and NH_3 CLUSTERS STUDIED BY THE
CROSSED LASER-MOLECULAR BEAM TECHNIQUE

A. INTRODUCTION

Since the observation by Welsh and McKellar of fine structure in the pressure induced infra-red spectra of H_2 with various gases (D_2 , H_2 , Ar, Kr, Xe, N_2 , etc.) at low temperatures,¹ van der Waals molecules and molecular clusters have exhibited a number of intriguing properties which test our understanding of intermolecular forces. One property, in particular, which has been recently studied both experimentally and theoretically, is the vibrational predissociation lifetime of a van der Waals molecule when one of the vibrations of the strong chemical bonds is excited. This vibrational energy is typically 5-50 times the van der Waals bond energy. Early calculations by Child² on the lifetimes of $Ar...HCl(v=1)$ suggested that the vibrationally excited complex was stable to dissociation for times comparable to the infrared radiative lifetime. The spectra of McKellar and Welsh showed that for systems such as $Ar...H_2(v=1)$, the lifetimes are sufficiently long to resolve rotational motions of the H_2 molecule within the complex.

In 1978, Scoles, Gough, and their coworkers³ first observed directly the vibrational predissociation of a van der Waals molecule, $(N_2O)_2$, in the ground electronic state, obtaining a lifetime in the range 10^{-12} - 10^{-4} seconds. The clusters were excited by a diode laser and the predissociation observed as a decrease in signal

at a bolometer which monitored the molecular beam. Since that time, the Waterloo group has studied CO_2 clusters using an F-center laser for excitation.⁴ Levy and coworkers have performed many experiments on the vibrational predissociation of rare gas-iodine clusters in an excited electronic state.⁵ The predissociation was observed in the dispersed fluorescence spectrum of the I_2 fragment produced by the predissociation. Limits to the lifetimes could be determined from the absorption linewidths or by using competing I_2 electronic predissociation or fluorescence rates as an internal clock. From these results, a detailed picture of the propensity rules in vibrational predissociation has been obtained. In addition to earlier work in our laboratory on $(\text{NH}_3)_2$,⁶ Reuss,⁷ Gentry,⁸ and Janda⁹ and their coworkers have observed vibrational predissociation of various clusters with CW or pulsed CO_2 lasers and mass spectrometer detectors. In particular, Janda was able to argue convincingly that on the basis of the observed linewidths and signal strengths, the predissociation was occurring on a timescale of 0.3 – 1.0 picoseconds for ethylene complexes. Current theoretical and experimental studies have considered small clusters as simple model systems for condensed phases. To test the accuracy of cluster models, experimental data for a wide range of compounds with different strengths of intermolecular forces is needed.

In the remainder of this chapter, results are presented on vibrational predissociation studies of C_6H_6 , H_2O , and NH_3 molecular clusters. First, a general description of the experimental techniques and measured quantities is presented. Next, the detailed analyses for

each system are presented. Finally, a summary will generalize the individual results where possible.

B. EXPERIMENTAL ARRANGEMENT

The two experimental methods described below utilize a supersonic expansion to prepare a spatially well defined molecular beam containing molecular clusters, an infrared laser to excite the vibrational motions of interest, and a mass spectrometer to detect the effects on the clusters of laser excitation. One scheme is based on looking for the disappearance of clusters in the molecular beam correlated with the pulsed laser, similar to the method of Janda, et al.,⁹ while a second scheme monitors the appearance of molecular fragments created by the predissociation as in photofragment translational energy spectroscopy.¹⁰

1. Infrared Laser

Tunable, infra-red radiation is generated by a Nd:YAG pumped optical parametric oscillator (OPO) based on the L-shaped cavity design of Byer, et al.²² The far-field pumping arrangement, cavity design, and optics are shown in Fig. 1. The idler frequency easily tunes in the 2800-4000 cm^{-1} range spanning CH, OH, NH, and F-H stretching motions. The repetition rate is 10 Hz, and the output power is 1-4 millijoules/pulse, with 1 joule/ cm^{-2} of Nd:YAG pump energy fluence. The OPO linewidth (the frequency difference between the half power points) in this wavelength range is measured to be 3-4 cm^{-1} . The duration of the OPO pulse is less than 10 nanoseconds.

2. Perpendicular Laser-Molecular Beam Arrangement

An in-plane view of this molecular beam configuration is shown in Fig. 2. In this arrangement, the vibrational predissociation process is observed by the detection of the predissociation products. The laser and molecular beams intersect at right angles, and a rotating mass spectrometer pivots about the intersection point. A series of defining slits restricts the acceptance angle of the mass spectrometer's ionizer to 2 degrees so that only those molecules whose velocities are oriented in the detector's direction and whose positions are within the acceptance cone can be detected. The background pressure in the intersection chamber is 1.0×10^{-7} torr, which ensures that all molecules which enter the detector from events in the intersection region are collision-free, primary products. The molecular beam, produced by a supersonic expansion, is collimated by three apertures to an angular divergence of 1.5° . The cluster distribution of the molecular beam is measured by using the rotating mass spectrometer to directly sample the molecular beam.

The laser is coupled into the vacuum chamber by a BaF_2 lens held in a moveable tube which allows the OPO to be focused at the center of rotation of the detector, where it intersects the molecular beam. An aperture in this tube spatially defines the laser beam diameter to a 2 mm cross section at the intersection point. The laser is linearly polarized perpendicular to the plane defined by the laser and molecular beams. The output energy of the OPO idler frequency is measured with a germanium filter masked power meter placed a few inches beyond

the intersection point. This scheme allows the power dependence of the absorption to be determined, and accounts for frequency variations in the photon number.

The signal produced by OPO photons is recovered from the background by gating a 255 channel, variable channel width, multichannel scaler (LBL 13X3381) with the laser pulse. The time delay between the OPO pulse and the arrival of molecules at the detector which were affected by the OPO photons, is the sum of the neutral molecule flight time from the intersection region to the ionizer, and the ion flight time through the quadrupole mass spectrometer to the ion counting electronics. The ion flight time is independently determined and subtracted prior to analysis.

3. Coaxial Laser-Molecular Beam Arrangement

A cross sectional view of this arrangement is shown in Fig. 3. In this configuration, the laser is colinear with the molecular beam. The electron bombardment ionizer and ion extraction optics are perpendicular to the laser and molecular beams. The quadrupole mass spectrometer directly monitors the molecular beam so the predissociation of clusters appears as a decrease in signal at the ion related to the predissociating parent clusters.

The signal is also gated by the laser and time resolved by the multichannel scaler. The initial delay between the laser pulse and the onset of a change in the time resolved mass spectrometer signal, is the sum of the ion flight time from the ionizer to the counting electronics, and the flight time for the effects of the first cluster

predissociations to reach the ionizer. The 65 cm flight path can detect lifetimes as long as 1.0 millisecond (for the nominal molecular beam velocities of these experiments), while all lifetimes shorter than one microsecond (after correcting for the ion flight time) will appear to be "instantaneous". The power variation of the OPO is measured by monitoring a reflection of the OPO photons from a beam splitter.

C. EXPERIMENTAL OBSERVABLES

From the experimental observations, two quantities are derived: the wavelength dependence of the predissociation cross sections, and the translational energy distributions of the predissociation fragments. The photon energy is sufficient at the wavelengths 2800-3800 cm^{-1} corresponding to the various hydrogen atom stretching frequencies to break the weak intermolecular bond. The perpendicular molecular beam experiment uses the translational recoil velocity of the dissociated fragment clusters (which carries them away from the molecular beam) to detect the absorption of radiation. As shown in Fig. 4, the cluster predissociation fragments must have sufficient recoil energy to reach the detector when it is placed at a fixed angle relative to the molecular beam. Rotating the detector to successively larger angles favors those fragments which have higher translational energy. Through the energy balance equation

$$E'_{\text{int}} = E_{\text{hv}} + E_{\text{int}} - D_0 - E'_t \quad , \quad (1)$$

the internal energy in rotation and vibration of the fragments (E'_{int}) can be obtained from the photon energy (E_{hv}), the initial internal energy of the clusters (E_{int}), the dissociation energy (D_0) and the product recoil energy (E'_t). E'_t can be derived from the measurements of laboratory angular and velocity distributions.

For the measured product yield at a fixed detector angle to be proportional to the photon absorption cross section of the parent cluster, the time scale, τ , for the predissociation process must adhere to two restrictions. First, for the predissociation to be detected, the vibrationally excited clusters must not travel outside the detector's viewing region before dissociating. For the nominal beam velocities 1×10^5 cm/sec, this places an upper limit of 2 microseconds on τ . Secondly, τ cannot vary with the OPD wavelength in such a way as to produce a change in the shape of the laboratory angular distribution. Within the experimental statistical counting error, this has been verified for the systems reported here. Changing the orientation of the laser polarization with respect to the detector-molecular beam plane had no effect on the signals.

The coaxial arrangement directly measures the depletion of the clusters and is not sensitive to the translational energy distribution. As such, it is free from any assumptions regarding the angular shape of the laboratory photofragment distributions, and is limited only by the upper bound on the lifetime given by the 65 cm flight path. It is to be pointed out that, in the colinear experiment, the signal is proportional to the number of polymers dissociating within 1

millisecond after excitation, while in the perpendicular beam experiment only the fragments formed during the first 2 microseconds after the laser pulse may be detected. Both spectra being identical, we can assume that $\tau \leq 2$ microseconds for all wavelengths measured, and that the above assumptions concerning the shape of the laboratory distributions made in the perpendicular arrangement are valid.

D. BENZENE

1. Introduction

Benzene is a natural choice as an experimental model system for learning about intermolecular interactions due to its widespread use in simulations of liquid behavior,^{11,12,13} and the existence of a large body of spectroscopic data in different phases.^{14,15,16} Extensive modeling of the intermolecular potential function for benzene has been done by Evans and Watts¹¹ who have derived a six-centered Lennard-Jones potential which adequately describes the second virial coefficient, the static lattice energy, the solid state crystal structure, liquid phase distribution functions, viscosity, and thermal conductivity. Simpler models have been proposed by Lowden and Chandler¹³ and MacRury, Steele, and Berne,¹² and where comparison is possible, there is qualitative agreement on the interpretation of the results. For example, all have predicted that the local structure in the room temperature liquid should be similar to the solid with a preferred T-shaped nearest neighbor geometry.

In a molecular beam electric resonance study, Janda et al.¹⁷ have shown that benzene dimer is polar, strongly suggesting that the

gas phase dimer is also T-shaped. The similar near neighbor geometry in the dimer and condensed phases is the basis for assuming that a simple model for some condensed phase properties might be found in the small, gas phase clusters.

Two general theories have addressed the vibrational predissociation rate question - the "momentum gap" model of Ewing¹⁸ and the "energy gap" model of Beswick and Jortner.¹⁹ The basic prediction of both theories is that the most efficient predissociation mechanism minimizes the translational energy of the predissociation products. The physical basis for this minimization of the translational energy was shown to be the poor overlap between the continuum translational wavefunction of the products and the initial "bound" state intermolecular wavefunction of the vibrationally excited cluster.

To date, these models have been applied only to binary complexes such as $\text{He} \cdots \text{I}_2$.²⁰ A recent theoretical study of $(\text{N}_2\text{O})_2$ by Ewing²¹ is especially intriguing. According to the momentum gap model, Ewing predicted that the most probable dissociation channel involves a $V \rightarrow V, T$ energy transfer to the $v_1=1$ vibrational state of the N_2O monomer when the $v_3=1$ mode is excited. This product state minimizes the translational energy of the fragments. Using a realistic model function for the intermolecular potential, Ewing also concluded that a dipole-dipole coupling was more consistent with the dissociation lifetime than the Morse coupling of the intermolecular vibrational (and dissociation) coordinate. Beswick and Jortner, using a different dimer geometry and intermolecular potential, predict that the two N_2O monomer products

will be left in the $v_2 = 1$ and $v_1 = 1$ states respectively.¹⁹ The energy gap and product states for this process are different than those predicted by Ewing. Therefore, the theoretical models are sensitive to details of both the intermolecular potential and the physical mechanism which determines the predissociation lifetime. The simplicity of the Ewing and Beswick/Jortner models for a wide range of molecules invites further experimental confirmation. Using benzene as a "large molecule" test case to investigate cluster dissociation, other factors in the intermolecular vibrational energy relaxation might be necessary to understand the product state distributions when more than one vibrational state has a small momentum gap.¹⁹

2. Results

Benzene clusters were formed by bubbling He through room temperature liquid benzene and expanding the gas mixture through a 0.18 mm diameter nozzle heated to 70°C. The distribution of cluster sizes was controlled by changing the He pressure.

In Fig. 6, the off axis predissociation spectra taken at the parent ions of benzene monomer (mass 78) and pentamer (mass 390) using the perpendicular laser-molecular beam configuration are shown. The signals represent the total laser induced signal corrected for background and photon number, and, consequently, are proportional to the absorption cross section. These masses, to have reached the detector, must have originated from a cluster containing at least two or six benzene molecules, respectively. Therefore, the spectra are labeled according to the smallest polymer capable of contributing to that

mass, although fragmentation of larger clusters to these masses either in the predissociation process or by the electron bombardment ionization may also contribute. From Fig. 6, it can be concluded that the frequency shifts of the different polymers are small compared to the laser spectral bandwidth. The atypical beam conditions for these spectra, (Ar carrier gas and a room temperature nozzle), can produce large clusters. The principal spectral change is in the relative intensities of the three bands, showing that a unique spectral identification of the absorbing clusters is not possible at this resolution.

To assign the off-axis predissociation fragment signals to a parent cluster, the pressure dependence of the off-axis signals were compared to the pressure dependence of the polymers in the molecular beam, obtained by rotating the mass spectrometer to 0° along the molecular beam axis. In Fig. 7, the ratios of the off-axis predissociation fragment signals at mass 78, to the parent molecular beam mass 156 and 234 signals with the detector placed at 0° , are plotted as a function of the nozzle stagnation pressure. The 78 (off-axis fragments)/156 (0° molecular beam parent) ratio is flat, while the 78 (off-axis fragments)/234 (0° molecular beam parent) ratio falls sharply. This is consistent with the assumption that the off-axis mass 78 signal comes from the molecular beam cluster detected at 0° at mass 156, presumed to be the dimer. Under these expansion conditions, the signals in the molecular beam which relate to clusters containing more than three monomers are negligible. The ratios of mass 156:mass 234:mass 312 in the molecular beam are 100:3:0.3.

In a molecular beam study on the polarity of benzene polymers,¹⁷ it was concluded that only 1/10 of the benzene dimers were ionized to the parent mass peak. With this known proclivity for fragmentation of the neutral clusters by electron bombardment, other evidence is necessary to show that the mass 78 off-axis signal is indeed that of the monomer photofragment from predissociation dimers, and not the ionization by-product of dimer photofragments originating from the predissociation of trimer and larger clusters. To verify these mass assignments, the coaxial laser-molecular beam configuration is used.

Figure 8 shows two time-resolved signals obtained with the coaxial method, as well as a time-of-flight spectra obtained with the perpendicular method by placing the detector at zero degrees. This simulates the depletion scheme of the coaxial configuration. The increase in sensitivity is dramatic, a consequence of the increased interaction volume between the laser and molecular beams. From the decrease in signal at mass 78 in the coaxial arrangement, it is clear that the clusters are fragmented by electron impact to mass 78 ions. That is, when the laser dissociates the benzene clusters, they are no longer present at the ionizer to fragment by electron bombardment to mass 78. The slight positive signal at mass 50 comes from the increase in the neutral monomer density resulting from the photodissociation of benzene clusters in or near the ionizer. Its shorter time duration is a result of the progressively smaller solid angle of acceptance for cluster photofragments more than a few centimeters from the ionizer. This different temporal behavior from the mass 78 signal shows that

mass 50 ions correlate only to neutral benzene monomers. It also shows that the mass 78 signal cannot be explained as a change in the monomer fragmentation pattern which might occur should the monomer beam component be vibrationally excited by the laser. Since the mass spectra of benzene monomer has prominent peaks at mass 78 and 50-52,²³ one would expect the laser related signals at these masses to extend for a time equal to the neutral monomer flight time from the nozzle to the detector, if the monomer were absorbing radiation. The mass 50-52 signals are inconsistent with this explanation. The experimentally derived partial electron bombardment fragmentation pattern is summarized by

From the preceding analysis, it is clear that if the mass 50-52 angular scan in the perpendicular laser-molecular beam geometry is the same as the mass 78 scan, then the mass 78 data relates to benzene monomer predissociation fragments and not ionization fragments from higher clusters. Figure 9 shows the time-of-flight data taken at the two masses for two laboratory angles, establishing the validity of the previous assumption that the mass 78 off-axis signal results from ionizing monomers. The mass 156 off-axis signal is assigned to the

trimer predissociation based on the strength of the observed signal; the tetramer and larger clusters in the molecular beam are present in negligible amounts.

The angular distributions of the mass 78 and 156 products, shown in Fig. 10, are similar in shape and extend only 10 degrees from the molecular beam. By measuring the beam velocity, V_0 , of the initial clusters using a rotating slotted disk placed at a known distance from the ionizer,²⁴ and if the functional form of the center-of-mass angular distribution is known, the transverse velocity of the pre-dissociation fragments can be computed from the laboratory angle. The observed steep monotonic increase of the dissociation signal with decreasing laboratory angle can only be fit with a translational energy distribution which also has a decrease with increasing translational energy and peaks very near zero translational energy.

An analytical function of the form

$$P(E) = \alpha e^{-\alpha E} \quad (3)$$

was used to quantitatively fit the measured laboratory angular and time-of-flight distributions. This center-of-mass energy distribution is convoluted over the experimental conditions (the finite aperture sizes, initial velocity distribution of the molecular beam, and ionizer length) assuming an isotropic center-of-mass angular distribution. The small range of laboratory angles where product is observed is insensitive to details of the center-of-mass angular distribution. Furthermore, it is shown below that it is reasonable to assume that

the vibrationally excited complex rotates several times before pre-dissociating. An isotropic center-of-mass distribution is appropriate in this case. In Fig. 10, the best fit curves for the mass 78 ($\alpha=5$) (kcal/mole)⁻¹ and 156 ($\alpha=7$) (kcal/mole)⁻¹ signals are compared with the experimental data.

From the measured wavelength dependence of the predissociation cross sections, it is clear that the perturbations of the three monomer vibrational bands in the 3000-3100 cm^{-1} range are small. The resolution of the laser is insufficient to observe rotational fine structure. No additional vibrational bands were observed which could be attributed to different bonding sites in the clusters or to a reduction of D_{6h} symmetry in the monomers. Combination bands involving intermolecular vibrations with an absorption strength greater than 1/5 of the fundamentals were not detected in this wavelength range. The absence of P, R rotational branches in the predissociation spectra limits either the internal temperature of the clusters or the size of the potential barrier hindering individual molecular rotation, as in liquid, room temperature benzene.

The observed signals were all linear in photon number. Additional absorption of photons by the predissociation products was not observed at this photon flux ($\sim 7 \times 10^{17}$ photons/ cm^2 pulse).

3. Discussion

From the results of these experiments, three properties of the vibrational predissociation can be determined: the identification of the main product channels, the lifetime of the vibrationally excited clusters, and the internal energy distribution of the products.

The main product channels established by the pressure dependence and mass spectroscopy of the OPO induced signals for the predissociation of benzene dimers and trimers are

From the consistency of the wavelength dependence of the two predissociation signals measured in the perpendicular and coaxial configurations, it is clear that the clusters are predissociating within several microseconds of the laser pulse. A lower limit to the vibrationally excited state lifetime of 1 picosecond may be deduced by ascribing all of the observed linewidths (neglecting the $\sim 3\text{--}4\text{ cm}^{-1}$ spectral bandwidth of the OPO and the initial internal state distribution of the clusters) to homogeneous broadening caused by the predissociation. This lower limit is consistent with the lack of a polarization dependence for the observed signals in the perpendicular configuration. If the rotational distribution of the dimers is characterized by the same temperature as the molecular beam translational energy distribution (50°K), and can be modeled as a simple diatomic with $5\text{ \AA}$ bond length, the most probable rotational state has a classical rotational frequency of 1 picosecond. A polarization dependence would be expected if the predissociation lifetime was significantly shorter than this rotational frequency and if the transition dipole had a fixed orientation with respect to the intermolecular

axis. Since the intermolecular forces are poorly understood, large amplitude motion of the low frequency vibrations may well preclude such a fixed transition moment. Consequently, the lack of a polarization dependence is consistent with the lower lifetime limit deduced from the linewidth, but does not supply an independent determination of it. Recently, predissociation attributed to benzene dimers near 1040 cm^{-1} has been observed^{25,26} with a linewidth of less than 3 cm^{-1} .²⁵

The translational energy distribution which adequately fits the data peaks at zero translational energy and has a very narrow energy spread. Therefore, the energy in internal excitation of the fragments for the most probable case is

$$E'_{\text{int}} = E_{\text{int}} + E_{\text{hv}} - D_0 \quad (5)$$

For simplicity, the initial internal energy is neglected. The adiabatic cooling in the nozzle expansion is expected to make this term small compared to the errors in the remaining larger contributions to the internal energy.

An estimate for the bond energy between two benzene molecules may be obtained from the crystal sublimation energy at 0°K . Model calculations^{11,12} which reproduce this value give $\sim 750\text{ cm}^{-1}$ for the pair potential zero point binding energy. Therefore, the internal energy of the fragments determined from Eq. (5) is 2300 cm^{-1} .

How is this energy distributed among the available internal states of the monomer and dimer fragments from the trimer predissociation?

If all the excess energy were placed in the dimer fragment, it would be far in excess of the dimer bond energy, and the dimer would be expected to predissociate before reaching the ionizer. The observation of dimer product places a lower limit of 1550 cm^{-1} on the internal energy in the monomer. The rate of energy migration among the three benzene molecules in the trimer, for this unequal energy distribution to be observed, is then slower than the predissociation rate. Likewise, the photon excitation is to a particular monomer, and that is the monomer which is vibrationally excited in the predissociation products. This implies that the benzene monomers are located at distinguishable sites in the trimer. If this were not true, the zeroth order vibrational wavefunction would be delocalized over the three monomers.

One can tentatively generalize this conclusion to the case of dimers; we expect the dissociation to yield one "vibrationally hot" and one "vibrationally cold" molecule. This is consistent with the postulated T-shaped dimer structure where the two molecules are not equivalent.

The above predissociation mechanism qualitatively agrees with the momentum gap model proposed by Ewing. The substantial internal excitation of the products automatically reduces the momentum gap to a small value. The density of internal vibrational states near 2000 cm^{-1} in benzene monomer is sufficient to ensure that there will always be a resonant state within 10 cm^{-1} , even if the rotational excitation is not significant. This high density of states is

advantageous for testing in finer detail the predissociation process, because there are probably several product states with nearly the same momentum gap. Other factors to date not explicitly considered in the momentum gap model, especially the detailed predissociation dynamics, will have to be understood in order to predict the relative vibrational, rotational state populations in the products. Such state distributions are expected to become available in the near future for some of these systems from laboratory measurements. An accurate determination of the ground state binding energy can also be deduced from such measurements from the highest vibrational-rotational state populated in the products.

E. WATER

1. Introduction

Understanding the structure and dynamics of condensed phases from intermolecular potentials is an important problem. Substantial agreement between theory and experiment has been made for the weakly interacting rare gases²⁷ where, due to the domination of pairwise additive potentials in these systems, a single realistic pair interaction potential has been able to accurately fit experimental data of all phases. Conversely, for strongly interacting molecules such as water, no single pair potential has yet been proposed which accurately reproduces the known physical properties of this substance in all phases.²⁸ The strong orientational forces responsible for hydrogen bonding are notoriously difficult to theoretically model.

In 1951 Rowlinson²⁹ proposed the first molecular model aimed at a quantitative prediction of solid state properties, beginning with

known gas phase properties. Subsequently, many different pair potentials have been published. The Ben-Naim Stillinger potential,^{30(a,b)} for example, was an "effective" pair potential for the liquid which partially accounted for many-body effects. An extensive series of ab initio calculations have also been performed by Clementi and co-workers.^{31a-g} Beginning with Hartree-Fock potentials for the water dimer, studies were made of the effects of configuration interaction, empirical dispersion terms, and many-body effects on the structure of the liquid and small polymers predicted by these pairwise additive potentials. The conclusions of these studies were: (a) that the liquid state structural properties were predicted as well as by any other current potential, (b) that the three body interaction accounts for approximately 10 percent of the binding energy and has no strong angular dependence, and (c) that analytical fits to Hartree-Fock calculations, suitably corrected for the dispersion interaction, can reproduce results in an economical form.

When potentials which have been designed to predict liquid state structural properties are used to calculate the properties mainly dependent on the pair interaction potential or vice versa, agreement has not been very satisfactory. The determination of the potential parameters from experimental results is difficult because the available experimental data are largely integral quantities which depend on many different regions of the potential surface. Consequently, errors in the repulsive interaction can be compensated for by errors in the attractive well so that a single experimental observable can always be

fit. Moreover, even when disagreement is observed in the computed properties, it is not clear which region of the potential is responsible, and a trial and error method of adjusting the potential parameters has been the method of choice in improving agreement with experimental data. To better discriminate against potential forms, microscopic data sensitive to well defined regions of the potential energy surface are needed.

Infrared spectra of clusters of water have been experimentally available since the original matrix isolation work of Pimentel and co-workers.³² In these studies, the dependence of infrared absorption linestrengths on the matrix to absorber ratio was used to assign the various absorption bands to specific polymers. The problems of overlapping absorptions bands limited the application of the matrix isolation technique to principally the dimer and trimer. No similarity with the broad, structureless infrared spectrum of liquid water was observed. More recently, Luck³³ has carefully followed the concentration dependence of the infrared matrix absorptions to extend the correlations between bands and polymer sizes.

An additional property sensitive to features of the interaction potential of water clusters is the time scale for predissociation of vibrationally excited clusters containing energy in excess of the hydrogen bond energy. In 1946, Stepanov³⁴ proposed that the broadening of the hydrogen bonded infrared vibrational spectra might be a result of predissociation. More recently, Hagen and Kassner³⁵ have calculated the decay rate for water trimers as a function of temperature based on a Slater type model. Robertson and Coulson,^{36a-c}

Ewing,³⁷ and Beswick and Jortner³⁸ have all calculated predissociation rates for binary complexes using first order time dependent perturbation theory. This current theoretical work has shown that the dissociation rate is intimately connected with the mode of energy disposal.

Experimental studies on relaxation lifetimes in liquid H_2O have included dielectric,³⁹ nuclear quadrupole resonance (NQR),⁴⁰ inelastic neutron scattering,⁴¹ and depolarized Rayleigh scattering (DPRS).⁴² The 2-5 picosecond relaxation times observed in the room temperature dielectric and NQR studies have been related to orientational lifetimes in liquid water. The DPRS experiments measure two lifetimes. The slower component is similar to the reorientational time scale of the NQR and neutron scattering results, while the fast component of 0.6 picoseconds has an Arrhenius temperature dependence with a 3 kcal/mole activation energy. This fast lifetime was interpreted as the time constant for breaking a hydrogen bond, with the activation energy measuring the energy difference between waters oriented in the proper direction for hydrogen bonding and those that are not. The induction period for the other relaxation processes which depend on reorientation suggests that the breaking of a hydrogen bond is the rate-determining step before reorientation can occur. The vibrational predissociation lifetimes would then be expected to be longer than 1 picosecond, depending also on the hydrogen bond breaking rate.

The current work was undertaken to provide infrared spectra of selected clusters of water molecules in order to assign the features

in the vibrational spectra and relate these assignments to current interaction potentials of water. Using the crossed laser-molecular beam technique, the frequency dependence of the predissociation fragment yield is measured, improving spectroscopic assignments as a result of careful control of cluster size distribution and the mass selective detection scheme. Additional measurements of the velocity distributions of the predissociation fragments give directly the translational energy released in the predissociation. From these new observations, an explanation for the discrepancy between the condensed phase water and gas phase pair interactions is given. The infrared spectra are seen to be quite sensitive to the proposed intermolecular potential model and should figure prominently in determining future intermolecular water potentials.

2. Experimental Results

A molecular beam of water (nozzle diameter 0.18 mm, nozzle temperature 125°C) containing a small percentage of water clusters was crossed at right angles by the infrared radiation in the perpendicular laser-molecular beam configuration. Because there is always a distribution of polymer species in the molecular beam, and because of problems associated with ion fragmentation, unique identification of the water clusters in the electron bombardment ionizer is not possible. However, one important feature of the mass selective detection scheme is that it acts as a "high-pass" filter; that is, for a given detected ion mass, only clusters larger than a certain size can possibly contribute to the signal. This represents a significant advantage

over the matrix isolation technique, where strong absorption by monomers and smaller clusters often obscures absorption peaks due to larger clusters.

As an example, suppose we set the quadrupole mass filter to pass $(\text{H}_2\text{O})_3\text{H}^+$ ($m/e = 55$). The smallest water cluster which could produce this ion in the ionizer is $(\text{H}_2\text{O})_4$, and the smallest cluster which could produce $(\text{H}_2\text{O})_4$ by vibrational predissociation is $(\text{H}_2\text{O})_5$. Thus, only pentamers and larger clusters can contribute to the vibrational predissociation signal measured at $m/e = 55$. Contamination from higher polymers can be minimized by carefully controlling the expansion conditions of the molecular beam. For example, in the investigation of $(\text{H}_2\text{O})_3$, the nozzle stagnation pressure was adjusted so that the concentration of the next higher polymer $(\text{H}_2\text{O})_4$ was substantially less than $(\text{H}_2\text{O})_3$. The combination of working on the largest observable clusters in the beam and the mass selective detection scheme, while not able to completely eliminate the contamination, allows the main features and trends in the cluster spectra to be obtained.

Vibrational predissociation spectra were measured using four different nozzle stagnation pressures. For each stagnation pressure, the ion mass detected was chosen to be the largest mass whose signal was 10 times larger than the background after 2000 laser shots at the absorption maximum. The experimental conditions are summarized in Table 1. In all cases, the detector was positioned at a fixed angle of 4° from the molecular beam. At each frequency, the signal was accumulated for at least 2000 laser shots and normalized to the

average laser power. To ensure long-term stability, the spectra were scanned in two directions and checked for agreement within statistical counting error. Also, for each spectrum, the power dependence of the signal was checked at the major peaks to guarantee linearity of the predissociation yield with photon flux. The large error bars near 3550 cm^{-1} result from anomalously low idler power attributed to OH impurity in the LiNbO_3 crystal. For these points, the counting times were extended to $\sim 20,000$ laser shots. Finally, the power normalized signals were divided by frequency to convert from power to photon flux.

To obtain information on the dynamics of the vibrational predissociation process, angular and velocity distributions of the predissociation products were also measured at selected laser frequencies.

In the coaxial configuration, preliminary frequency scans at H_3O^+ and $(\text{H}_2\text{O})_2\text{H}^+$ were taken. The perpendicular configuration does not allow one to measure the water dimer spectrum because of a large monomer background from the molecular beam at small detector angles. Additionally, as shown below, the larger clusters predissociate by loss of a monomer. This latter monomer background is correlated with the laser and can be removed only by reducing the polymerization conditions in the molecular beam. At mild water vapor pressures where there was no detectable signal at H_3O^+ , there was no signal detected at H_2O^+ after 2000 laser shots in the frequency range $3600\text{--}3750\text{ cm}^{-1}$.

A preliminary frequency scan and power dependence was measured in the coaxial configuration for large water clusters. The large clusters

were formed by passing 100 torr of Ar through an 80°C water bath and expanding the mixture from a 0.07 mm, 102°C nozzle. The count rate for all $(\text{H}_2\text{O})_n\text{H}^+$ masses up to $n=19$ were at least 400 kHz from this source. The power dependence was linear up to the maximum energy of 8 mj/pulse.

3. Analysis

The water cluster vibrational predissociation spectra are shown in Fig. 11. The relatively high binding energies of the water clusters compared to the photon excitation energy substantially reduce the possible vibrational predissociation channels. Using four different intermolecular potentials,⁴³⁻⁴⁶ the equilibrium bond energies (D_e) relative to complete dissociation of an n -mer into n water monomers were calculated⁴⁷ and are listed in Table 2.

There are two major energy classifications of the allowed dissociation processes. The lowest energy channel for all polymers includes a monomer fragment and is called monomeric dissociation (MD). It is defined by the equation:

The next energetically accessible dissociation process divides the parent cluster into two smaller clusters. This channel is called cluster dissociation (CD) and is defined by the equation:

The CD channel computed from the D_e bond energies in Table 2 is not always accessible over the frequency range probed. The simplest explanation consistent with the spectral observations discussed here and the dynamic properties presented below, would attribute all dissociations as occurring through the energetically favorable MD channel. The time-of-flight and angular distributions (see below) do not change with frequency within experimental error, as might be expected if a new dissociation channel became energetically accessible.

The electron impact fragmentation behavior of water clusters has recently been analyzed in the literature.^{48,49} Briefly, the exceptional stability of the H_3O^+ ion explains the dominance of the mass peaks $(H_2O)_n H^+$ in the mass spectrum. The electron bombardment ionization of the neutral $(H_2O)_n$ clusters presumably first proceeds by the ionization of a water monomer subunit. A unimolecular ion-molecule reaction follows in which the H_3O^+ ion is formed (solvated by the remaining water molecules) and an OH radical is ejected from the cluster. The dominant ionization mechanism, then, is assumed to be

If this simple picture were complete, each water cluster, $(H_2O)_n$, would be correlated with a single ion, $(H_2O)_{n-1} H^+$, in the mass spectrometer, and assignment of the vibrational predissociation spectra would be straightforward. Unfortunately, in the electron bombardment ionization process, the $(H_2O)_{n-1} H^+$ ion may be formed with substantial

vibrational energy, such that one or more water molecules may evaporate from the cluster ion. Therefore, the mass spectrum of each water cluster, $(\text{H}_2\text{O})_n$, also contains smaller $(\text{H}_2\text{O})_m \text{H}^+$ mass peaks (where $m < n - 1$). This source of contamination is impossible to eliminate by mass spectroscopy alone. The fact that this contamination can potentially be very serious is demonstrated in Figs. 11(a),(e). The two spectra shown were measured by tuning the mass spectrometer to H_3O^+ , nominally assigned to the trimer dissociation by Eqs. (7) and (8), but using very different nozzle expansion conditions. The Fig. 11(a) spectrum was obtained with the water reservoir held at 67.5°C , giving a nozzle stagnation pressure of 209 torr (see Table 1). The H_3O^+ signal amounted to 1.2 counts/laser pulse at 3400 cm^{-1} , with 0.7 counts/pulse at $(\text{H}_2\text{O})_2\text{H}^+$ and much less signal at all higher masses. The spectrum in Fig. 11(e) was obtained with the water reservoir held at 90°C , giving a nozzle stagnation pressure of 526 torr. Under these conditions the water beam was heavily polymerized. The H_3O^+ signal at 3400 cm^{-1} was 5.3 counts/pulse, and at least 1 count/pulse was obtained at all $(\text{H}_2\text{O})_n \text{H}^+$ masses up to $(\text{H}_2\text{O})_6 \text{H}^+$. While we believe that the spectrum in Fig. 11(a) is largely due to predissociation of water trimers, it is clear that the spectrum in Fig. 11(e) is heavily contaminated by fragmentation of the predissociation products of larger water clusters in the ionizer.

However, we can still get some idea of how the water cluster distribution varied with nozzle stagnation pressure, by assuming that $(\text{H}_2\text{O})_n \text{H}^+$ is the major ion fragment of $(\text{H}_2\text{O})_{n+1}$. We list in Table 3

the pressure dependence of the ion ratios $(\text{H}_2\text{O})_n \text{H}^+:\text{H}_3\text{O}^+$, $n = 1-3$, measured by pointing the mass spectrometer directly into the water beam.

Information on the predissociation product energy distributions is obtained from the laboratory angular and time-of-flight distributions of the products. The experimental angular distributions, shown in Fig. 12, exhibit a steep monotonic decrease with increasing laboratory angle, and can only be fit with a center-of-mass energy distribution which peaks at or near zero translational energy and rapidly decreases with increasing product translational energy. A simple analysis relating the laboratory angle, nominal beam velocity, and center-of-mass velocity shows that the recoil energy necessary to scatter fragments to 4° is merely tens of wavenumbers, while the particles scattered 10° have several hundred wavenumbers of translational energy. This means that most of the excess energy is in the internal excitation of the fragment molecules.

The observation of a reasonable signal level (~ 1 count/laser pulse) in the experiment implies an upper limit of ~ 1 microsecond to the vibrationally excited cluster lifetime. If the lifetime of the excited state was longer than the four microsecond residence time of the clusters in the viewing range of the detector, then only a fraction of the predissociated clusters could be detected. For the signal level to be 1 count/pulse, a large fraction of the clusters in the beam must have predissociated within 1 microsecond of the laser pulse.

4. Discussion

a. Spectroscopy

As a first attempt to assign the features of the water cluster spectra, normal mode calculations have been performed using water potentials which allow the intramolecular monomer bonds to distort. For each potential, the configuration of the atoms was varied using a multi-parameter minimization procedure to find locally stable polymer configurations (Fig. 13). For the Watts potential,⁴³ a single minimum was found for the water trimer, a cyclic structure shown in Fig. 13b. Larger polymers had several local minima, but in each case the lowest energy configuration found was cyclic. For the Stillinger central force⁴⁴ and polarization potentials⁴⁵, the minimum energy configurations found beginning at the minimum energy structures of the Watts potential were also cyclic, except for the polarization model where the linear trimer is most stable. At the minima, the harmonic frequencies of the normal modes were calculated using finite differences to obtain the second derivative force constants of the potential. Table 4 contains the normal mode frequencies for several water polymer configurations obtained using the published potential forms. Using the harmonic frequencies, the harmonic zero point energies (HZPE) were also obtained.

The observed absorption spectra are characterized by two features: a sharp, narrow absorption 15 cm^{-1} wide located at 3715 cm^{-1} , and a 600 cm^{-1} broad absorption extending from $3000\text{--}3600\text{ cm}^{-1}$ with an approximate 150 cm^{-1} superimposed fine structure. The sharp peak is

midway between the gas phase monomer symmetric (3657 cm^{-1}) and antisymmetric (3756 cm^{-1}) stretching vibrations, and is representative of an uncoupled, non-hydrogen bonded intramolecular OH stretch. For comparison, the OH stretch in HOD occurs at 3705 cm^{-1} . This narrow band is also what would be expected for the free hydrogens of the equilibrium ring structures determined in the energy minimization calculations. If neither hydrogen atom of a particular water molecule is involved in hydrogen bonding, there should appear two absorption peaks correlating to perturbed symmetric and antisymmetric stretching frequencies for this "hydrogen accepting" monomer. The single sharp peak is taken as evidence that the isolated polymers containing three or more molecules are cyclic with at least one hydrogen atom of each water molecule hydrogen bonded. Additional experimental evidence for the cyclic structures is given by the small to undetectable dipole moments of water polymers in a molecular beam polarity study.⁵⁰

The calculated harmonic normal mode frequencies of the Watts potential show the tight frequency grouping of the free hydrogens, midway between the calculated monomer normal mode frequencies obtained with the same potential model. The Stillinger potential frequencies show a blue shift relative to the Stillinger monomer frequencies with little grouping. This is presumably a result of the compromise the Stillinger model was forced to make when attempting to fit with the same form of the OH interaction potential both the infrared absorption frequencies and electrostatic properties of the monomer. The potential was not sufficiently flexible to enable an exact fit to all of these observables.

The second major feature of the spectra—the broad, hydrogen bonded absorption—is not as easily understood. The broadness of the hydrogen bonded infrared spectra has been experimentally well documented.⁵¹ The theoretical models which have explained the extensive absorption in other systems (such as carboxylic acid dimers⁵²) conclude that a strong coupling picture, involving at least the hydrogen bond and intramolecular stretching coordinates common to the hydrogen bonded hydrogen atom, is necessary. Additional complications may arise from the resonant first overtone of the intramolecular bending frequency near 3200 cm^{-1} .⁵³ The breadth of other hydrogen bonded systems has been explained without resorting to a Fermi resonance picture. Hence, the fundamental coupling mechanism producing the broad water cluster absorptions is taken to involve the $\text{O} \cdots \text{HO}$ group, with Fermi resonance (involving $2\nu_2$) possibly accounting for a portion of the intensity pattern near 3200 cm^{-1} . Even without an exact quantum number assignment of the vibrational bands, the similarity of the frequencies and number of bands for the series of polymers measured, as compared to the matrix isolated dimer,⁵⁴ means that once the cyclic structures are formed, the basic near neighbor interactions dominate. A proper treatment of the large amplitude intermolecular motion is necessary before the strong coupling picture can be adequately tested. If more than one local minimum structure is accessible to the ground state wave function, it is not known how the infrared spectra would be affected.

Liquid water infrared spectra have been quantitatively analyzed by assuming the Badger-Bauer relation between frequency and bond length

to be operative.⁵⁵ Using an empirical curve of frequencies and bond lengths, the distribution of oxygen-oxygen distances in the liquid has been calculated from the infrared spectra. The near Gaussian shape of the liquid infrared spectra does not show any of the fine structure seen in the polymer spectrum, although the existence of four components comprising the broad infrared absorption can be inferred from curve decomposition.⁵⁶ These four bands were then suggested to be characteristic of water molecules bound to different numbers of, or in different ways to, neighboring water molecules.

Additional evidence for distinct water bonding types in the liquid has been derived from the temperature dependence of the first stretching overtones. Using the overtone region to separate the congested fundamental infrared bands, Luck⁵⁷ and others⁵⁶ have performed many experiments which show clear isosbestic behavior in this region, suggesting an equilibrium between at least two species of water molecules. Recently, Sceats⁵⁸ has reinterpreted the overtone region using a quantum mechanical picture, showing that reasonable values for the electrical and mechanical anharmonicities in the liquid phase can explain the observed isosbestic behavior. Consequently, the apparent isosbestic behavior is not a sufficient condition for the mixture model of water.

More recently, Byer et al.⁵⁹ have measured the depolarization CARS spectra of liquid H_2O and have observed spectral structure in the regions of the bands observed here, excepting the free OH stretch. Their experiment shows that the broad liquid absorption is composed of

several overlapping vibrational bands. Despite the fact that the room temperature infrared bands are so overlapped giving the appearance of a single broad band, the depolarization CARS experiment can resolve these features using the different depolarization ratios of the vibrational transitions. The cooling of the water clusters in the molecular beam expansion, and mass selective detection enable the features to be resolved in the work reported here. With this clear evidence for substructure in the liquid phase spectrum, a confident analogy can be drawn between the interactions present in the gas phase clusters and the liquid.

Matrix isolation results beginning with the pioneering work of Pimentel³² have used the concentration dependence of spectral features to assign bands to particular water polymers. Host materials have included Ar, N₂, and D₂.⁵⁴ The dimer has attracted the most attention because the original N₂ matrix work suggested a cyclic structure for the dimer; contrary to later theoretical calculations. Subsequent higher resolution matrix studies have identified the expected number of intramolecular vibrations for a trans-linear structure, the same given by the most extensive quantum mechanical calculations, although the D₂ matrix appears exceptional, supporting only a cyclic structure.⁶⁰ Molecular beam electric resonance spectroscopy⁵⁰ has definitely established that the gas phase dimer is stable in the trans-linear form. The conclusion seems to be that the difference in energy of different water dimer geometries is insufficient to result in one matrix dimer independent of the host material.

The vibrational predissociation spectra obtained in this study disagree with some of the matrix assignments for trimer and multimer spectra. Primarily, the gas phase clusters are all seen to absorb over the same frequency range, principally distinguished by variations in intensity, not frequency. It is difficult for the matrix technique to distinguish between different species absorbing at the same frequency. The molecular beam method with mass selectivity can limit the size of the parent polymers which are measured, and to some degree, circumvents this problem.

For the assignments of the matrix trimer spectra to be correct, the matrix trimer would either have to be trapped in a different intermolecular geometry than exists in the gas phase (such as a linear arrangement), or the contributions from higher polymers in the present molecular beam experiments dominated the signal assigned to the trimer. However, the trend with decreasing beam polymerization (lower nozzle stagnation pressures) in the series of spectra reported here, indicates a decrease in intensity of the 3550 cm^{-1} band relative to the 3200 and 3350 cm^{-1} bands. The $3550\text{--}3700\text{ cm}^{-1}$ frequency range in the matrix studies is assigned to the trimer, with the 3300 cm^{-1} range assigned to tetramer and higher clusters. Thus, the pressure dependence of the H_3O^+ spectrum in the molecular beam study is in the opposite direction to be consistent with the assignments obtained from the matrix studies.

The similarities of the liquid water and cluster spectra allows us to conclude that small, cyclic polymers form an excellent zeroth order model for explaining the infrared absorptions of liquid water.

McDonald and Klein^{61(a)} used the Watts central force model based on fitting known monomer/dimer properties and found a disappointingly poor fit to liquid properties. Similarly, those potentials based on bulk phase properties, most notably the Stillinger-Rahman central force potential, give poor agreement with gas phase properties such as second virial coefficients and dimer geometries.⁶² It has been suggested,²⁸ therefore, that large, non-additive, many body effects in water may preclude the existence of a simple central force model which can explain gas phase and cluster properties as well as liquid/solid behavior.

Perhaps the key to this problem is contained in the cluster spectra shown here. If one takes the known results for the infrared spectra of water dimers from matrix isolation work,⁵⁴ there is observed to be a dramatic spectral change between the matrix dimer and the gas phase trimer of this work. The dimer spectra are confined to a narrower frequency range ($3530\text{--}3715\text{ cm}^{-1}$), and bear little similarity to liquid water. In contrast, the trimer and higher clusters absorb over the complete range that liquid water does. To verify the conclusions of the molecular beam experiments, the water dimer and trimer spectra were measured using the coaxial molecular beam configuration shown in Fig. 1b. The dimer mass peak, H_3O^+ , shows the expected high frequency ν_1 , ν_3 doublet of the perturbed, hydrogen-accepting water monomer. This feature is absent in the trimer spectra, indicating the abrupt change to the cyclic configuration. To concentrate on dimer properties may then be misleading if one wishes to predict liquid properties.

From the sophisticated SCF calculations by Clementi et al.³¹ using large basis sets, it was concluded that within the frozen monomer approximation, the non-additive, three-body interaction is only 10 percent of the pair interaction energy and shows no pronounced directional character. This implies that the Watts potential should show excellent agreement with experiment, predicting the pair interaction properties especially well. Correcting the calculated dimer "intramolecular" frequencies from the Watts model by the previous procedure of insuring that the calculated and observed monomer transitions agree, Table 5 shows the rather remarkable agreement between the Watts model normal mode frequencies and the assigned matrix transitions for the dimer. The cyclic polymers of the Watts model, however, are seen to have normal modes in the same range as the dimer. Therefore, the empirical pair potential does not predict a lowering of the hydrogen-bonded intramolecular harmonic frequency upon forming a cyclic structure. The calculations show, therefore, that changes in the reduced mass cannot account for the experimentally observed red shifts. Nonadditive effects must be quite important for the intramolecular properties, so far unexplored in theoretical calculations within the frozen monomer approximation.

b. Dynamics

The experimental results establish that predissociation is occurring within microseconds of the laser pulse and that most of the excess energy remains as internal excitation of the fragments (based on the negligible amount of energy appearing in fragment translational motion).

The two current theories of vibrational predissociation by Ewing, and Beswick and Jortner have only addressed the case of binary complexes. These are dynamical models, the rate of dissociation being sensitive to the coupling between the wave functions of intermolecular motion and final translational motion. On the other hand, since the coupling is sufficiently strong in the water clusters and there are so many vibrational degrees of freedom, it is possible that a statistical product energy distribution is more appropriate.

In order to understand the dynamics of dissociation, three calculations have been performed using the Watts potential to investigate the predissociation mechanism. The first consists in determining a local, minimum energy dissociation coordinate (LDC). The minimization computer program was modified to allow the distance between two of the oxygen atoms to be fixed at one value while varying the remaining atomic positions to minimize the total energy. Starting at the minimum energy configurations for the dimer, trimer and tetramer, the LDC's are shown in Fig. 14.

The dimer dissociation is straightforward, resembling a simple diatomic molecule. The trimer, however, shows a two-step process to dissociation. First, the ring structure is broken ($R = 2.75\text{\AA}$ to $5.50\text{\AA}$). Afterwards, a monomer dissociates from the cluster as in the dimer. The tetramer indicates more exotic behavior which also should be characteristic of larger clusters. Curve C in Fig. 14 shows the dissociation when two adjacent water molecules of the tetramer are pulled apart. The plateau is again characteristic of the opening of

the cyclic equilibrium structure. However, the dissociation of the linear tetramer does not proceed concertedly with the reforming of the cyclic trimer. The configuration of the trimer subunit near dissociation is extended and far removed from its equilibrium geometry. It is expected, therefore, to contain substantial internal energy. Repeating the calculation in the reverse direction (adding a monomer to a cyclic trimer) results in curve D of Fig. 14. The reverse path has a relative minimum with the approaching water monomer bonded to one of the free OH groups of the cyclic trimer. The energy barrier to adding a water molecule to form a cyclic tetramer from this relative minimum is ~ 0.5 kcal. The "hysteresis" of the two paths is a result of the numerous local minima on the potential surface. Since the LDC is generated by small sequential displacements ($\sim 0.2\text{\AA}$) of the oxygen-oxygen distance, these curves are not global minima.

The LDC's suggest that there are two timescales analogous to the liquid phase relaxation measurements: the hydrogen bond breaking rate; and the cluster dissociation rate. The hydrogen bond breaking rate will nominally be that of the transfer rate of the photon energy from the high frequency, "intramolecular," optically excited vibrations into the intermolecular motions. This process should be describable by the vibrational predissociation theories of Ewing or Beswick/Jortner. The second time scale, that for dissociation of the clusters once the energy has been coupled into the lower frequency intermolecular motions, is not expected to be negligible. The LDC's indicate that the cyclic polymers must undergo substantial configurational changes

before dissociation. This is expected to strongly couple all of the allowed exit channels satisfying energy and angular momentum conservation.

To explore this strong coupling in the exit channels, several molecular dynamics calculations were performed. The tetramer was the first system studied. The initial positions were chosen to correspond to the minimum energy cyclic configuration. When the energy was set equal to the HZPE, the trajectories indicated that the ring structure was preserved with no interchange of the hydrogen-bonded and free OH groups. Therefore, the initial configuration of the polymers could be fixed at the cyclic minimum without substantial error, since the gross bonding topology was satisfied. The velocities were chosen randomly according to a Boltzmann distribution with a temperature of 100°K. The residual velocity components in the zero angular momentum frame were scaled so that this "internal" kinetic energy equaled the sum of the HZPE and the photon energy. The original rotational motion was then replaced, thus allowing the internal vibrational energy to be constant, and independent of the rotational temperature. This accounts for the presumed disequilibrium between the vibrational and rotational degrees of freedom of the polymers produced in the adiabatic beam expansion. The trajectories were integrated using the CLAMPS⁶³ simulation package and displayed on the NRCC interactive graphics system.⁶⁴

Twenty trajectories were followed for 30 picoseconds with no dissociation. Even though the bonding topology changed every few

picoseconds between cyclic, linear, tetrahedral, and similar configurations, and the effective temperature of the cluster was 2200°K, the heat capacity was still sufficiently large to insure that $\tau > 1500$ psecs. Subsequently, three ensembles of fifty, 20 picosecond trajectories were followed for the water dimer. The rotational temperatures for these ensembles were 10°K, 100°K, and 200°K, and the total internal energy fixed at 3000°K (which is the sum of the photon energy and HZPE). The minimum potential energy configuration was chosen as the starting configuration. The decay curves are shown in Fig. 15. Additionally, 50 trajectories were followed in which the hydrogen-bonded proton was initially extended along its OH intramolecular bond axis so that it had 10 kcal/mole of potential energy. This was investigated to determine the time required for the high frequency vibrational energy to couple into the low frequency motions. None of the trajectories for this last set dissociated, even though for several of the trajectories, the energy was seen to be transferred into intermolecular motions. The conclusion from these computer studies is that the lifetime of the clusters is composed of two contributions: the energy transfer time from the optically excited high frequency modes into the intermolecular cluster modes, and the decay time of the excited cluster (in which the energy is distributed progressively throughout the cluster) into products. The primary energy transfer time is expected to decrease with increasing cluster size, since the number of internal energy states resonant with the optically excited state will increase (the energy gaps approach zero), while the

decay time to products after the energy transfers from the optically excited state will increase with cluster size as the effective heat capacity increases.

Finally, RRKM calculations were attempted for a series of points along the LDC, but the results indicated lifetimes too short compared to the classical trajectory calculations. For these small systems in which rotational motions are nearly unhindered in the critical configuration, it is difficult to obtain reasonable values for the vibrational frequencies from simple "normal mode" type analyses. On the other hand, with the level of excitation being not much higher than the fundamental intramolecular vibrational energies and the hydrogen bond dissociation energy, one would expect dynamic factors to be more important than statistical ones.

If extensive energy randomization is occurring, by increasing the cluster size, the predissociation rates could be reduced. A series of experiments was tried in the coaxial configuration to see if the rate could be slowed to a timescale measurable on that apparatus, $\sim 10^6$ sec⁻¹. The results of these measurements indicated that for clusters containing at least 20 water molecules, the time scales were too short to resolve. However, several complications serve to increase the ambiguity of these results. For example, if the photon absorption rate for large clusters is proportional to the cluster size, while the predissociation rate is inversely dependent on the cluster size, the rate of predissociation observed would be independent of cluster size, but possibly power dependent. For the dimer and trimer, we can be

reasonably sure that the predissociation rate is much faster than the rate of sequential photon absorption. If the photon density is sufficiently high to dissociate 50 percent of the trimers, we can expect that on the average, all hexamers will have absorbed at least one photon, while dodecamers will have absorbed two photons, etc. The large clusters may be expected to absorb more than one photon within the ~ 5 nanosecond laser pulse. If they still predissociate faster than 10^6 sec^{-1} , but slower than 10^8 sec^{-1} , one can expect some secondary dissociation. Additionally, for the large clusters, the translational recoil is so small that the products are not scattered out of the beam. What is observed, in the worst case, is a difference in the rate of predissociation from the given cluster, to the rate at which that cluster mass is repopulated by predissociations from larger clusters. Hence, the desired conditions are difficult to verify, namely, a power level where only one photon is absorbed for the large clusters, and a cluster distribution rapidly decreasing in intensity with increasing cluster size in order to minimize repopulation. The experimental data in Fig. 17 show that when the power is reduced, the time dependence of the signal does not change over one order of magnitude in laser power, where signal is observable. Figure 18 shows the absorption spectra for mass 289, corresponding to clusters equal to or larger than $(\text{H}_2\text{O})_{17}$.

F. NH_3

1. Introduction

NH_3 monomer has three strong infrared bands in the 3000-3500 cm^{-1} frequency range - the symmetric (ν_1 , A symmetry) and

antisymmetric (ν_3 , E symmetry) NH stretches, and the first overtone of the antisymmetric band ($2\nu_2$, A+E symmetry). For the monomer, the ν_3 band is well separated to higher frequency and easily assigned, whereas the ν_1 and $2\nu_2$ bands are in Fermi resonance and mixed. For hydrogen-bonded liquids, the monomer bending frequencies are expected to increase, because the preferred hydrogen-bonded geometry has a strong orientational dependence. The stretching frequencies should decrease because electron density is removed from the NH intramolecular bonding orbitals to form the intermolecular hydrogen bonds. These effects have been observed in recent experiments,⁶⁵ and microscopic models have been able to explain their physical origins.⁶⁶ For NH_3 , the ν_1 and $2\nu_2$ bands in condensed phases are reversed with respect to their gas phase ordering. Because the liquid and gas phase ν_1 - $2\nu_2$ regions look similar at first glance, this interchange was noticed only after the combined infrared⁶⁹ and Raman spectra,^{65,68-70} (including polarization dependence) of several isotopic forms of NH_3 were studied. In addition, condensed phases of NH_3 have been studied by x-ray and neutron scattering,⁷² matrix isolation spectroscopy,⁷³⁻⁷⁵ and a molecular beam polarity study.⁷⁶

Recent theoretical work on the NH_3 intermolecular potential has included ab initio studies of the pairwise,⁷⁷ and three-body terms^{78,79,80} of the intermolecular potential, as well as empirical atom-atom potential functions⁸¹⁻⁸³ based on condensed phase properties of NH_3 . These latter potentials have been used in Monte Carlo and molecular dynamics simulations of liquid NH_3 .⁸⁴⁻⁸⁵ Even within

the fixed monomer geometry approximation of these theoretical treatments, non-additive effects appear to be very important, contributing 25 percent of the trimer binding energy at its equilibrium configuration.⁷⁸

The effect of intermolecular forces on the Fermi resonance of the ν_1 and $2\nu_2$ modes, including resonant energy exchange, has been elegantly treated by McHale and Wang.⁶⁶ Using a Mori-Zwanzig projection operator formalism, they have derived expressions relating the observed Raman spectrum to the microscopic potential terms governing the inter- and intramolecular anharmonicity and Fermi resonances. From these results, the nonlinear concentration dependence of portions of the Raman spectra can be understood. No equivalent treatment of the infrared spectra of liquid NH_3 has been reported.

2. Experimental Results

NH_3 polymers were studied using the perpendicular laser-molecular beam configuration. They were formed by expanding pure ammonia vapor through a 0.18 mm diameter, room temperature, glass nozzle. The distribution of clusters was controlled by changing the ammonia pressure behind the nozzle. The predissociation spectra were obtained by measuring the variation in signal with laser frequency at a fixed detector angle of 4° relative to the ammonia beam. The shape of the angular distributions did not change within the 10 percent statistical error of the measurements. The laser power dependence of the signal was measured at the absorption peaks, and the spectra recorded in the linear response region. The spectra then represent

the absorption cross sections for the clusters. Figure 19 shows the spectra recorded at different masses. The angular distributions of the detected masses are presented in Fig. 20. For the spectra in Fig. 19, the next polymer signal was 50 percent that of the recorded mass.

As in the previous cluster studies, the parentage of the detected masses is complicated by fragmentation in the electron bombardment ionization and by multiple vibrational predissociation channels. Unlike water clusters, where the intermolecular bond energies are quantitatively known, the energetics of neutral ammonia clusters are smaller and experimentally poorly determined.⁸⁶⁻⁸⁹ A molecular beam photoionization study⁸⁶ has derived total binding energies of ammonia polymers through the hexamer of -4.6, -13.7, and -17.5 kcal/mole respectively. Two spectroscopic studies^{88,89} have used the quadratic dependence of some absorption features to derive enthalpies of -3.5 kcal/mole and -4.5 kcal/mole for the ammonia dimer. Analysis of imperfect gas properties⁸⁷ deduces a dimer binding energy of -3.2 kcal/mole. Consequently, it is impossible to preclude predissociation by channels involving the breaking of more than one hydrogen bond. Based on analogies to previous work, the most probable product channel contributing to each mass is assigned by the following predissociation-ionization steps:

The separation of different product masses in the angular distributions of Fig. 20 indicates that ion fragmentation is not as severe as for the water clusters. The dominant uncertainty in the ammonia spectra mass assignment is taken to be the predissociation process of Eq. (9).

3. Discussion

a. Spectra

The differences between the ammonia monomer and cluster spectra are smaller than for water. Hence, the strength of hydrogen-bonding in NH_3 is noticeably weaker. The main trends with increasing cluster size are an increase in the intensity of the 3375 cm^{-1} band relative to the 3225 cm^{-1} doublet, and a merging of the low frequency doublet to a single broad peak. The relationship of these spectral changes to the intermolecular forces is complicated by the anharmonicity and Fermi resonance of the ν_1 , $2\nu_2$ and ν_3 bands. These intramolecular couplings are of the order of the intermolecular perturbations. To analyze the observed results, all of these effects must be considered. Such a task is beyond the scope of the work presented here. A theory incorporating these effects has been developed for the Raman spectra of strongly intermolecularly coupled vibrational modes in Fermi resonance,⁶⁶ but no equivalent treatment for the infrared spectra has appeared.

b. Dynamics

The lifetimes of the vibrationally excited ammonia clusters are less than a microsecond, as observed in the other cluster studies.

The well-resolved differences of the angular distribution shapes enable a more detailed treatment of the energy disposal than in the water clusters. Two distinct cases for the vibrational predissociation will be considered.

The first mechanism is a direct predissociation whereby the monomer fragment absorbing the radiation dissociates from the cluster as the energy redistributes into the intermolecular bonds.

In this case, regardless of cluster size, the maximum energy which appears as relative translational motion ($E_{\max}$) of the departing monomer is the same, independent of cluster size. Momentum and energy balance determine the maximum angle where the heavier product is observed for a cluster containing N monomers (monomer mass M) and moving with laboratory velocity v ,

$$\sin(\theta_{\max}^N) = \frac{1}{v} \left(\frac{2E_{\max}}{M} \frac{1}{N(N-1)} \right)^{1/2} \quad (11)$$

The ratio of the maximum scattering angles for sequential cluster sizes is dependent only on the cluster size

$$\frac{\sin(\theta_{\max}^N)}{\sin(\theta_{\max}^{N+1})} = \left(\frac{(N+1)}{(N-1)} \right)^{1/2} . \quad (12)$$

The second model assumes energy randomization over the cluster, and the maximum translational energy is inversely dependent on cluster

size. Momentum and energy balance determine the ratio of maximum scattering angles for adjacent masses as defined above:

$$\frac{\sin(\theta_{\max}^N)}{\sin(\theta_{\max}^{N-1})} = \frac{(N+1)}{N} \left(\frac{N}{N-1} \right)^{1/2} . \quad (13)$$

Table 6 shows the experimental ratios and the predictions of each model. The important point is that the direct model predicts the observed angles of maximum scattering to within experimental error for the mass assignments made according to Eqs. (9) and (10), while the randomization model does not.

Does the direct model have a physical basis, based on the knowledge we have for ammonia and a probable predissociation mechanism? As noted previously, the intramolecular motions in NH_3 are highly coupled. Also, the translational energy distributions indicate that the most probable predissociation will have negligible translational energy. Any mechanism postulated should be consistent with internally excited fragments but not randomization. Analogous to benzene, the ammonia polymers seem to predissociate by first redistributing the energy among lower frequency intramolecular vibrations of the monomer which absorbed the photon. Subsequently, the minimum energy necessary to break the intermolecular bonds is lost from these lower frequency vibrations. This model assumes rapid intramolecular energy redistribution, with a slower rate of energy migration into the intermolecular bond. Most probably, the binding energy for an ammonia monomer is

similar to the lowest frequency intramolecular vibration, $\nu_2 = 950 \text{ cm}^{-1}$. In this case, the intermolecular bond is required to absorb at once sufficient energy to dissociate. The monomer products are predicted to be internally excited by this model, while the cluster fragments should be characterized by the internal temperature of the cluster before photoexcitation.

4. Summary

For the C_6H_6 , NH_3 , and H_2O clusters studied, the rate of vibrational predissociation is greater than 10^6 sec^{-1} . In all cases, the measured translational energy distributions of the fragments indicate no detectable variation with excitation wavelength, partially a consequence of the small amount of energy released into translational motion. The rapid vibrational predissociation rate and small kinetic energy release are in qualitative agreement with the predictions of Ewing and Beswick/Jortner. Although these models have heretofore only been applied to binary clusters, they predict that for predissociation rates of the magnitude observed here, the energy will be concentrated in internal motions of the products.

For the NH_3 and C_6H_6 clusters, where the intermolecular forces do not radically perturb the monomer intramolecular spectrum, the translational energy distributions suggest a rather detailed scenario for the infrared intermolecular energy flow leading to predissociation. After one photon is absorbed into the H atom intramolecular stretching frequencies, the intermolecular perturbations induce this energy to flow into combinations and overtones of the lower frequency intramolecular motions, namely NH or CH bends. Once these lower frequency

motions are populated, the energy can more resonantly flow into the intermolecular modes in units of these low frequency vibrations. As the lowest frequency intramolecular vibrations in C_6H_6 and NH_3 are comparable to the intermolecular binding energy, little energy randomization can occur in the cluster before predissociation. The intermolecular bond is forced to accept at one time an amount of energy which exceeds the intermolecular bond strength, so predissociation occurs before intermolecular energy migration.

The infrared spectra obtained for water clusters containing three or more water monomers show a pronounced similarity with liquid water. This is a result of the cyclic structures of these polymers, where each water monomer is acting as both a hydrogen bond donor and acceptor. This last conclusion has been important in explaining the poor agreement between the potential models based on dimer properties and those based on liquid or solid properties. The modifications to the intramolecular potential based on the work by Sceats shows that physically reasonable models can reproduce the gross red shifts without modifying the intermolecular force fields. This decoupling of the intramolecular and intermolecular forces to first order should enable most properties to be fit in a systematic way.

The analysis presented here for H_2O should also explain the observed features of HF clusters,⁹⁰ which show the same dramatic change between the dimer and trimer and provide additional evidence for the favored cyclic equilibrium structures of small hydrogen bonded clusters containing three or more molecules.

Several issues still remain unsolved. First of all, the reasons for the breadth of the hydrogen bond absorption is unexplained, as well as the exact assignments of the bands observed. The recent classical linear response theory methods of Behrens and Wilson,⁹¹ if extended to handle combination and overtone bands, will enable the larger cluster spectra to be calculated. Although there are uncertainties in the dipole moment and potential functions, the special trends with cluster size outlined in these experiments might be properly accounted for, considering the large amplitude motion of these clusters, by the classically based spectral response theory.

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Table 1. Experimental conditions used to measure the vibrational predissociation spectra in Fig. 1. In all cases the angle between the detector and the molecular beam was 4° , and the nozzle temperature was 125°C .

Temperature of water reservoir	Pressure at nozzle (torr)	Ion mass detected	Fig. 1 label	Smallest water cluster capable of contribution to signal
67.5	209	H_3O^+	a	trimer
72	255	$(\text{H}_2\text{O})_2 \text{H}^+$	b	tetramer
80	355	$(\text{H}_2\text{O})_3 \text{H}^+$	c	pentamer
84	417	$(\text{H}_2\text{O})_4 \text{H}^+$	d	hexamer

Table 2. Water polymer energetics.

$D_e(\text{cm}^{-1})$	Fig. 3 Label	Watts	Owicki	Stillinger (C.F.)	Stillinger (Pol.)
H ₂ O		0.0	0.0	0.0	0.0
(H ₂ O) ₂	a	2122.0	1904.0	1993.0	2388.0
(H ₂ O) ₃	b	5450.0	5183.0	5472.0	3774.0
(H ₂ O) ₃	c	—	—	—	5387.0
(H ₂ O) ₄	d	9187.0	8624.0	7667.0	10147.0
(H ₂ O) ₄	e	7526.0	—	—	—
(H ₂ O) ₅	f	12100.0	12429.0	11980.0	15789.0

Harmonic ZPE (cm^{-1})	Fig. 3 Label	Watts	Owicki*	Stillinger (C.F.)	Stillinger (Pol.)
(H ₂ O)		4723.0	0.0	4739.0	5107.0
(H ₂ O) ₂	a	10224.0	854.0	10320.0	11863.0
(H ₂ O) ₃	b	16088.0	1876.0	18417.0	18870.0
(H ₂ O) ₃	c	—	—	—	18597.0
(H ₂ O) ₄	d	21682.0	3094.0	23897.0	26611.0
(H ₂ O) ₄	e	21406.0	—	—	—
(H ₂ O) ₅	f	27145.0	3941.0	28891.0	36252.0

*Rigid H₂O molecule. ZPE's of (H₂O)_n are only from the motions associated with hydrogen bonding.

Table 3. Pressure dependence of the water cluster distribution in the molecular beam.

Pressure at Nozzle (Torr)	$\frac{(\text{H}_2\text{O})_2 \text{ H}^+}{\text{H}_3\text{O}^+}$	$\frac{(\text{H}_2\text{O})_3 \text{ H}^+}{\text{H}_3\text{O}^+}$	$\frac{(\text{H}_2\text{O})_4 \text{ H}^+}{\text{H}_3\text{O}^+}$
150	0.19	0.02	—
185	0.34	0.10	0.02
235	0.54	0.25	0.08
290	0.66	0.43	0.17
355	0.78	0.46	0.32
435	0.92	0.68	0.48
525	1.0	0.75	0.57

Table 4. High frequency vibrations for potential models. The values in parentheses are the integrated band intensities (using a linear approximation to the dipole moment function) for the normal coordinates, normalized to the most intense free OH transition.

	Watts		Stillinger Central Force		Stillinger Polarization	
Monomer	3951(1.00) 3841(0.52)	1653(0.99)	4283(0.34) 3820(1.00)	1375(1.20)	4354(0.82) 4203(1.00)	1642(5.29)
	Fig. 3(a)		Fig. 3(a)		Fig. 3(a)	
Dimer	3920.(1.00) 3914.(0.87) 3815.(0.45) 3760.(0.73)	1708.(0.90) 1670.(1.12)	4363.(0.95) 4303.(1.00) 3877.(2.68) 3834.(2.74)	1495.(3.09) 1415.(3.53)	4689.(0.25) 4485.(1.00) 4455.(0.25) 4157.(0.28)	1811.(0.25) 1638.(0.32)
	Fig. 3(b)		Fig. 3(b)		Fig. 3(b)	
Trimer	3890.(0.00) 3884.(1.00) 3884.(1.00) 3696.(0.80) 3969.(0.80) 3660.(0.00)	1773.(0.00) 1727.(0.85) 1727.(0.85)	4545.(1.00) 4545.(1.00) 4422.(0.0) 3959.(2.05) 3959.(2.05) 3894.(0.0)	2918.(0.00) 1840.(0.31) 1840.(0.31)	4680.(0.99) 4657.(1.00) 4464.(0.06) 4415.(0.11) 4375.(0.53) 4337.(0.75)	1780.(0.03) 1703.(0.46) 1647.(0.39) 4496.(0.13) 4412.(0.27) 4138.(0.15)

Table 4. Continued.

	Watts				Stillinger Central Force		Stillinger Polarization	
	Fig. 3(d)		Fig. 3(e)		Fig. 3(d)		Fig. 3(d)	
Tetramer	3888.(0.00)	1749.(0.00)	3924.(0.90)	1791.(0.17)	4677.(0.59)	2269.(1.44)	4864.(0.02)	1858.(0.06)
	3884.(1.00)	1733.(1.16)	3892.(0.47)	1748.(1.14)	4636.(0.65)	2138.(1.69)	4766.(1.0)	1772.(0.08)
	3884.(1.00)	1733.(1.16)	3886.(1.00)	1727.(1.27)	4461.(0.81)	1579.(1.12)	4766.(1.0)	1770.(0.08)
	3883.(0.00)	1733.(0.00)	3819.(0.27)	1669.(0.99)	4403.(1.00)	1548.(4.96)	4507.(0.0)	1770.(0.0)
	3741.(0.00)		3779.(1.01)		3994.(1.59)		4483.(0.0)	
	3727.(0.76)		3701.(0.95)		3982.(1.200)		4409.(0.48)	
	3727.(0.76)		3687.(0.69)		3949.(1.29)		4409.(0.48)	
	3704.(0.00)		3653.(0.12)		3911.(1.32)		4384.(0.18)	
Pentamer	Fig. 3(f)		Fig. 3(f)		Fig. 3(f)		Fig. 3(f)	
	3886.(0.02)	1737.(0.10)			4512.(0.0)	1652.(0.13)	4812.(0.12)	2173.(0.00)
	3882.(0.98)	1736.(0.27)			4506.(0.0)	1629.(2.92)	4747.(0.29)	2068.(0.08)
	3882.(1.00)	1736.(0.01)			4463.(1.00)	1627.(2.78)	4672.(1.00)	2059.(0.04)
	3881.(0.10)	1732.(1.31)			4463.(1.00)	1611.(0.14)	4663.(0.77)	2051.(0.04)
	3880.(0.26)	1731.(1.02)			4431.(0.0)	1606.(0.05)	4612.(0.28)	2001.(0.01)
	3744.(0.00)				3959.(1.61)		4408.(1.08)	
	3743.(0.00)				3957.(1.70)		4325.(0.42)	
	3729.(0.91)				3943.(2.14)		4272.(5.99)	
	3728.(0.91)				3943.(2.14)		4248.(7.40)	
	3713.(0.00)				3934.(0.0)		3985.(0.32)	

Table 5. Comparison of assigned matrix $(\text{H}_2\text{O})_2$ transitions with the Watts potential model.

Watts' Harmonic Frequencies	Watts' Scaled Frequencies	Ar Matrix	Diff.	.
(x.951)				
3920.	3729.	3726.	+3	
3914.	3723.	3709.	+14	
3815.	3629.	3634.	-5	
3760.	3577.	3574.	+3	
N ₂ Matrix				
		3715	+19	
		3699	+24	
		3627	+2	
		3550	+22	

Table 6. Comparison of energy disposal mechanisms for direct and random models of NH_3 cluster predissociation.

N Cluster size	Experimental Ratios of Maximum Scattering Angles	Direct Model (Eq. 12)	Energy Randomization Model (Eq. 13)
3	1.41	1.41	1.63
4	1.20	1.29	1.44
5	1.11	1.22	1.34

FIGURE CAPTIONS

- Fig. 1. Schematic diagram of the Nd:YAG pumped OPO. Components indicated are: 1. Telescope, 2. Input coupler (100 transmittance at $1.06\ \mu$, 100 reflectance at $1.4\text{--}2.1\ \mu$), 3. Gold mirror, 4. 30°C temperature stabilized, angle tuned LiNbO_3 crystal, 5. Output coupler (100% transmittance at $1.06\ \mu$, 50% reflectance at $1.4\text{--}2.1\ \mu$), 6. Double pass YAG mirror (100% reflectance at $1.06\ \mu$, 100% transmittance at $1.4\text{--}4.0\ \mu$), 7. BaF_2 lens.
- Fig. 2. In plane view of perpendicular laser molecular beam apparatus. Labeled components are: 1. $0.007''$ quartz nozzle heated to 70°C , 2. First skimmer, 3. Second skimmer, 4. Third skimmer, 5. Power meter, 6. Germanium filter, 7. Ionizer assembly. 8. Quadrupole mass spectrometer. θ measures the angle of rotation of the detector from the molecular beam.
- Fig. 3. Side view of the coaxial laser-molecular beam apparatus. Labeled components are: 1. BaF_2 entrance window for the OPO beam, 2. Quadrupole mass spectrometer, 3. Ionizer assembly, 4. Final molecular beam defining aperture, 5. Second skimmer, 6. First skimmer, 7. Nozzle.
- Fig. 4. Schematic view of the perpendicular arrangement showing how the recoil velocity of the predissociation fragment relates to the detector's laboratory angle, θ , relative to the molecular beam. The insert shows that the angle is

determined from the vector addition of the recoil velocity (dotted arrows) and the initial beam velocity (thick arrow). The final laboratory velocities are the solid arrows, also shown at the intersection point of the OPO and molecular beams.

- Fig. 5. Wavelength dependence of the mass 78 angular distributions. Open circles $\nu_{\text{OPO}} = 3040 \text{ cm}^{-1}$, solid circles, $\nu_{\text{OPO}} = 3095 \text{ cm}^{-1}$. The 3040 cm^{-1} data have been displaced $+0.5^\circ$ relative to the 3095 cm^{-1} data to allow easier comparison.
- Fig. 6. Wavelength dependence of the predissociation cross sections. A) Mass 390, $(\text{C}_6\text{H}_6)_5^+$, at 400 torr Ar with $T_{\text{nozzle}} = 25^\circ\text{C}$, B) Mass 78, C_6H_6^+ , at 250 torr Ar with $T_{\text{nozzle}} = 25^\circ\text{C}$.
- Fig. 7. Pressure dependence of the mass 78 signal in the perpendicular arrangement with the detector angle at $\theta = 4^\circ$. The solid points are the ratio mass 78($\theta = 4^\circ$)/mass 156($\theta = 0^\circ$), the open circles are the ratio mass 78($\theta = 4^\circ$)/mass 234($\theta = 0^\circ$).
- Fig. 8. Comparison of the time resolved mass spectrometer signals of the perpendicular and colinear configurations. A) Mass 78 data taken at $\theta = 0^\circ$ in the perpendicular laser-molecular beam arrangement, B), C), D) are masses 156, 78, and 50 respectively of the colinear configuration.
- Fig. 9. Time of flight spectra at masses 78 (solid points) and 50 (open circles). A) Detector angle $\theta = 4^\circ$, B) Detector angle $\theta = 5^\circ$.

Fig. 10. Angular distribution of predissociation fragments. Solid points are mass 156, open circles are mass 78. The curves are the calculated distributions using the center-of-mass energy distribution given by Eqn. 3. For mass 78 and 156, the best fit values for α are 5 and 7 (kcal/mole)⁻¹ respectively.

Fig. 11. Water cluster and condensed phase spectra. Panels (a)-(d) are spectra observed in the present work for the conditions given in Table I. Panel (e) conditions are described in the text. Panel (f) is taken from Ref. 6, Panel (g) from Ref. (30b), Panel (h) from E. Whalley and J. E. Bertie, J. Chem. Phys. 46, 1264 (1967).

Fig. 12. Laboratory angular distributions for the detected mass $\bigcirc$ - H_3O^+ ; $+$ - $(\text{H}_2\text{O})_2 \text{H}^+$; $\square$ - $(\text{H}_2\text{O})_3 \text{H}^+$; $\bullet$ - $(\text{H}_2\text{O})_4 \text{H}^+$.

Fig. 13. Minimum energy cluster geometries for the Watts potential energy function (a,b,d,e,f), for the polarization model trimer (c), and for the configuration characterizing a transition state for the tetramer dissociating into a trimer and a monomer (g).

Fig. 14. Locally adiabatic dissociation energy curves for
 A. $(\text{H}_2\text{O})_2 \rightarrow 2\text{H}_2\text{O}$, B. $(\text{H}_2\text{O})_3 \rightarrow (\text{H}_2\text{O})_2 + \text{H}_2\text{O}$, C. $(\text{H}_2\text{O})_4 \rightarrow (\text{H}_2\text{O})_3 + \text{H}_2\text{O}$ when adjacent hydrogen bonded waters are separated, D. $(\text{H}_2\text{O})_4 \leftarrow (\text{H}_2\text{O})_3 + \text{H}_2\text{O}$ when it is formed from a monomer adding to a cyclic trimer, E. $(\text{H}_2\text{O})_4 \rightarrow (\text{H}_2\text{O})_3 + \text{H}_2\text{O}$ when opposing nonhydrogen bonded water molecules of the cyclic tetramer are separated.

Fig. 15. The decay curves of the molecular dynamics trajectories for the conditions

- $T_{\text{vib}} = 3000^{\circ}\text{K}$, $T_{\text{rot}} = 0^{\circ}\text{K}$
- + $T_{\text{vib}} = 3000^{\circ}\text{K}$, $T_{\text{rot}} = 100^{\circ}\text{K}$
- $T_{\text{vib}} = 3000^{\circ}\text{K}$, $T_{\text{rot}} = 200^{\circ}\text{K}$
- $T_{\text{vib}} = 5000^{\circ}\text{K}$, $T_{\text{rot}} = 100^{\circ}\text{K}$

Fig. 16. Absorption cross section observed in the coaxial configuration at (A) H_3O^+ and (B) $(\text{H}_2\text{O})_2\text{H}^+$, corresponding to $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ respectively.

Fig. 17. Time resolved signal observed in the coaxial configuration at mass 217(○) and mass 145 (●). The offset of the two peaks is from the different ion delays.

Fig. 18. Absorption cross section observed at mass 289 in the coaxial configuration, corresponding to $(\text{H}_2\text{O})_{17}$.

Fig. 19. Ammonia polymer spectra

- (A) Mass 18 corresponding to $(\text{NH}_3)_3$ predissociation products
- (B) Mass 35 corresponding to $(\text{NH}_3)_4$ predissociation products
- (C) Mass 52 corresponding to $(\text{NH}_3)_5$ predissociation products

Fig. 20. Angular distributions for the ammonia cluster predissociation products.

XBL 815-9910

Fig. 2

DL 015-9994

Fig. 3

XBL 816-9998

Fig. 4

XBL 816-9996

Fig. 5

XBL 815-9992

Fig. 6

XBL 816-9997

Fig. 7

XBL 815-9989

Fig. 8

XBL 815-9993

Fig. 9

XBL 816-9995

Fig. 10

XBL 819-1335

Fig. 11

XBL 819-1333

Fig. 12

XBL 819-1334

Fig. 13

XBL 819-1332

Fig. 14

Fig. 15

XBL 819-1331

Fig. 16

Fig. 17

Fig. 18

XBL 799-11718

Fig. 19

XBL 834-9241

Fig. 20

III. REACTIVE SCATTERING OF $\text{Na}(3^2\text{P}_{3/2}) + \text{HCl}$

A. INTRODUCTION

Since the establishment of the non-relativistic Schrodinger equation in the 1930's, it has been known that the basic principles necessary to explain simple atom-molecule collision phenomena were well-defined. However, the realistic prediction of observations based on these first principles had to await the development of the modern computer, which could solve the large set of equations governing even a simple three body quantum mechanical system. Now that realistic, theoretical treatment of the interparticle forces and dynamics is computationally possible, current interest in the field of reaction dynamics is focused on detailed quantitative comparisons of theory with experiment.¹ The primary goals are to understand how the forces between particles affect the outcome of a collision, and how, through a judicious choice of initial conditions, the chemist can exert control over a collision to produce some desired product.

Although exact quantum treatments are possible for simple collisions (within the Born-Oppenheimer approximation) involving three structureless particles, governed by a single potential energy surface, and with a sparse internal energy level structure,² (i.e., $\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H}_2$), it is clear that such numerical approaches are not of general utility. First, the insight gained from this black box treatment is difficult to generalize. Each reaction appears unique, dominated by its individual parameters. Second, projected computer advancement will not enable substantial progress in the complexity of

the problems approached by ab initio methods much beyond the current level of treatment, i.e., three atom systems. Although the successful ab initio treatment of the forces and dynamics of a collision is important, and will continue to be an active area of study, simplifications of exact treatments through all manners of approximation are equally important. Through cleverly chosen approximations, one hopes to understand the particular details of a reaction as well as the general rules they suggest for other reactions of that type.

The work of Polanyi is an outstanding example of this approach. Using generalized mass combinations and potentials, the classical trajectory method was used to derive product energy distributions and rules which govern the energy disposal of reactant translational, vibrational, or rotational energy. These models have been applied to halogen atom reactions forming hydrogen halides³ as well as many alkali reactions.⁴

The current experimental work was undertaken hoping to stimulate theoretical work on simple three atom reactions where one of the reactants is in an excited electronic state. Previous molecular beam work in this area has been confined mostly to metastable states of the rare gases⁵ or oxygen atoms.⁶ Notable exceptions are the work of Zare and coworkers on $\text{Ca}(^1\text{P})^{7-10}$ and $\text{I}_2^*(^3\pi)^{11}$ reactions, and the work of Hertel, et al. on the nonreactive quenching of $\text{Na}(3^2\text{P}_{3/2})$.¹²⁻²¹

In the present study, a crossed beams, reactive scattering apparatus has been modified to enable scattering studies of $\text{Na}(3^2\text{P}_{3/2})$ atoms. The crossed molecular beams method is a powerful experimental technique

to probe reactions dynamics. Coupled with the selectivity of laser excitation of the reactant atoms, a new class of reactions involving short-lived excited states can now be studied by the crossed beams method.

The structure of this chapter is as follows. First, a short review of pertinent scattering work on excited electronic states created by laser optical pumping is reviewed in order to understand what quantities and features of a reaction can be measured, and to develop the framework within which such features are related to the physics of the scattering process. Second, the experimental method used here to study the $\text{Na}(3^2\text{P}_{3/2}) + \text{HCl} \rightarrow \text{NaCl}(^1\Sigma^+) + \text{H}(^2\text{S})$ reaction is described. Next, experimental data for the $\text{Na}^* + \text{HCl}$ reaction (an asterisk is used to denote the $^2\text{P}_{3/2}$ state) are presented at collision energies of 5.38 and 19.4 kc/m. The data at the lower collision energy are analyzed to obtain the center-of-mass product energy and recoil angle distribution. These derived distributions are subsequently discussed to understand the features of the potential energy surface which might be responsible for the observations, as well as the role of angular momentum conservation in the reaction dynamics. A final section summarizes what we have learned from this study, and the questions raised by it.

B. HISTORICAL REVIEW OF SCATTERING STUDIES OF SHORT LIVED ATOMIC EXCITED STATES

The Hertel group has published three extensive works on the quenching of $\text{Na}(3^2\text{P}_{3/2})$ by H_2 ,^{16,17} CO ,¹⁵ and N_2 .¹²⁻¹⁴ We now briefly

review the main conclusions of these studies which will form the basis for discussion of the "pre-reaction" interaction between $\text{Na}(3^2P_{3/2}) + \text{HCl}$. For each reaction, extensive quantum mechanical structure calculations were included of the relevant potential energy surfaces, and the scattering dynamics were explained in terms of the calculated potential energy surface features.

1. $\text{Na}^* + \text{H}_2$

From the electronic potential energy surface calculations, the $A^2B_2 \text{Na}^* - \text{H}_2$ excited state surface was found to be energetically lowest, favoring a C_{2v} configuration. The location of the crossing seam with the ground state surface occurs at a $\text{Na} - \text{H}_2$ distance of $R = 2.42\text{\AA}$ with an H_2 bond length of $r = 1.15\text{\AA}$. The H_2 (or D_2) bond is elongated at the crossing point and corresponds approximately to that of free $\text{H}_2(v = 2)$ and $\text{D}_2(v = 3)$. The observed vibrational $\text{H}_2(\text{D}_2)$ distributions peak at these values, with a Poisson-like distribution. The fact that the H_2 and D_2 energy transfer spectra are similar means that no special resonance effects are occurring. A projection of the H_2 (D_2) bond length at the crossing seam onto the ground state surface $\text{H}_2(\text{D}_2)$ vibrational basis set is sufficient to explain the observed features. The potential energy surface calculations indicate that the ground state surface is strongly repulsive in the R coordinate at the crossing seam. As the H_2 bond begins to contract after quenching, the Na atom and H_2 molecule rapidly separate. The calculated ground state surface shows negligible R - r coupling. Consequently, the asymptotic H_2 vibrational state distribution is taken to be that formed

at the crossing seam, with negligible H_2 vibrational state interaction as the products separate.

The magnitude of the experimental quenching cross section is large. The A^2B_2 state has a significant attractive well in the quantum calculations. The absorbing sphere model, using the calculated potential parameters, predicts a capture radius, or maximum impact parameter leading to quenching, c. $3.91\text{\AA}$. This is less than the orbiting impact parameter calculated from the attractive well parameters of the excited state potential energy surface. Therefore, orbiting will not affect this result.

The calculated surface is also consistent with the 5 kc/m ($\Delta j = 5$) rotational excitation of H_2 experimentally estimated from the breadth of the final vibrational state distributions. The strong preference for the C_{2v} geometry (the potential surface increases rapidly as the sodium- H_2 angle deviates from 90°) means that the Na^*-H_2 complex will stay locked in a C_{2v} geometry as the reactants approach. Depending on the initial impact parameter, the known location of the quenching seam can be used to calculate the Na^*-H_2 collision complex rotational frequency at the quenching configuration. Since the products recede rapidly from each other, and the departing Na atom exerts little torque on the H_2 molecule, the H_2 rotational energy is given by that at the critical configuration.

2. $Na^* + CO$

The potential energy surfaces (PES) for $Na(3P) + CO$ favor linear quenching configurations. When Na^* approaches the carbon end,

electron density plots indicate 30-60 percent of the Na(3P) electron is transferred to CO. Of the two excited state PESs at the linear configuration, the A state is bound by 24.4 kc/m, while the B state is repulsive. As observed for H₂, the ground state surface at the crossing seam is highly repulsive in R with little R-r coupling. To first approximation, the asymptotic vibrational distributions are taken to be those created by the "Franck-Condon" transfer to the ground state surface at the crossing seam. If Na^{*} approaches the oxygen end, the attraction is not as great, and a larger CO bond extension with a smaller Na*-CO distance is needed to reach the crossing seam.

The experimental results show very large rotational excitation which is explained by the calculated potential energy surface features as follows. If Na^{*} is quenched at the carbon end, the ground state surface prefers the Na-OC configuration by over 24 kc/m. There being no barrier in the calculated ground state surface for achieving this rotated configuration, a large torque is felt by the CO, resulting in substantial rotational excitation.

The presence of two active, distinct quenching sites leads to different internal energy distributions. Quenching at the oxygen produces larger CO vibrational excitation, while the carbon atom causes significant CO rotational excitation.

3. Na^{*} + N₂

This system has been studied at the highest level of resolution. From the experimental energy and angular distributions, forward scattering has significant rotational excitation ($\Delta j > 60$), while vibrational

excitation dominates the backward scattering angles. The final N_2 vibrational distribution is similar to the H_2 results, and the general quenching mechanism is presupposed to be analogous. As the Na^* approaches N_2 , the sodium 3P electron is partially transferred to an anti-bonding orbital of N_2 . Since N_2^- has a longer equilibrium bond length, the N_2 molecule stretches. At the crossing seam between the ground and excited states, the asymptotic N_2 vibrational distribution is obtained by projecting the stretched N_2 bond length onto the free N_2 molecular vibrational wavefunctions. Again, the C_{2v} configuration is favored, with the absorbing sphere model predicting the large quenching cross sections observed.

For this system, the effect of the $Na(3P)$ orbital alignment and orientation on the scattering was measured. When polarized radiation is used to excite the Na atoms, the m sublevels are not equally repopulated due to the different Clebsch-Gordon coefficients coupling the ground state m sublevels by spontaneous decay. Laser excitation for many spontaneous decay cycles redistributes the Na atoms among the m sublevels. As a result, after many spontaneous decays, an anisotropic distribution of the three degenerate 3P orbitals is created. The ratio of the populations of the P orbitals is, at best, 2.5:1:1. The hyperfine structure determines this anisotropy ratio. By directing the k vector of the laser to intersect the collision volume either perpendicular or parallel to the scattering plane, and by rotating the laser polarization vector or circularly polarizing the light, the initial distribution of P orbitals can be selected.

In Fig. 1, the major laser beam, scattering plane configurations are shown. On the left are two different alignments of the linearly polarized electric field vector relative to the scattering plane, when the k vector of the laser is in the scattering plane. When the E -vector is perpendicular to the scattering plane, the $|p_{\pi^{-}}\rangle$ orbital is favored, having negative reflection symmetry relative to the collision plane. When the E vector is rotated into the scattering plane, a mixture of $|p_{\pi^{+}}\rangle$ and $|p_{\sigma}\rangle$ states is made, depending on the angle the E vector makes with the relative velocity vector. When the laser propagates perpendicularly to the collision plane, and the linear polarization rotated, the asymptotic distribution can be predominately $|p_{\sigma}\rangle$ if the E vector is parallel to the relative velocity vector, or $|p_{\pi^{+}}\rangle$ if it is perpendicular. Since the P orbital axis is in the scattering plane, these states have positive reflection symmetry. If the laser is circularly polarized and directed perpendicular to the scattering plane, then the electronic angular momentum of the P orbital is also perpendicular to the scattering plane.

The polarization study of $Na^{*} + N_2$ consisted in measuring the effect on the scattering signal of the different initial Na $|p_{\pi^{+}}\rangle$, $|p_{\pi^{-}}\rangle$, and $|p_{\sigma}\rangle$ distributions. Hertel and Hermann²¹ have shown in a detailed way how these polarization dependencies relate to the density matrix representing the collision process. Experimentally, the polarization of the Na resonance fluorescence determines the actual moments of the Na charge distributions created by the optical pumping. Using these parameters, which characterize the initial distribution of P

orbitals, at each detector scattering angle four additional numbers are determined from ratios of the scattering intensity. These are: (a) the difference in the scattering signal with left and right handed circularly polarized light, normalized to their sum, (b) the ratio of the minimum to maximum scattering intensity when the E vector is linear polarized and rotated in the scattering plane, (c) the angle between the relative velocity vector and the laser polarization axis which maximizes the scattering for part (b) above, and finally, (d) the ratio of the scattering intensity with the P orbital perpendicular to the scattering plane to the P orbital axis in the scattering plane, scaled to the value of the scattered intensity of part (b) for the same in-plane polarization angle.

From these four ratios, the complete Na atom density matrix is known, as a function of scattering angle. Physically, these quantities are interpreted and understood by considering the time-inverse quenching process, $\text{Na}(3S) + \text{N}_2(v') \rightarrow \text{Na}(3P) + \text{N}_2(v=0)$. Here, a collision produces an excited Na atom, and the polarization of the fluorescence emitted at a certain angle reflects the different $|p_{\pi}^{+}\rangle$, $|p_{\pi}^{-}\rangle$, and $|p_{\sigma}\rangle$ contributions to the Na atom wavefunction for scattering to that angle. By rotating to a basis which has the Z axis along the laser k vector, and the X axis along the polarization angle producing maximum scattering for linearly polarized light with the polarization vector in the scattering plane, the resulting diagonal density matrix elements are then the length, width, and height of the Na(3P) charge cloud formed in the inverse quenching process at that Na scattering

angle. Alternatively, the height also measures the relative differential cross section for changing the molecular reflection symmetry, while the sum of the width and length gives the relative differential cross section for preserving the molecular symmetry. Of course, the overall symmetry of the total collision is preserved. As a result, these two processes are incoherent. The measurements show that the molecular symmetry changing cross section is a minimum at the peak of the energy transfer. This is interpreted to result from the locking of the Na^* to the body fixed Na^*-N_2 frame. At a distance of $\sim 5.3\text{\AA}$, where the body fixed frame is established (see below), the $\text{Na}^* - \text{N}_2$ complex will have the Na^* symmetry prepared by the optical pumping, i.e. $|\pi^+\rangle$, $|\pi^-\rangle$, or $|\sigma\rangle$. The minimum in the symmetry changing cross section implies that it is difficult to change only the Na^* symmetry, because the tight binding of the $\text{Na}^* - \text{N}_2$ interaction forces the $\text{Na}^* - \text{N}_2$ complex symmetry to change as well.

The variation in the laser polarization angle for maximum quenching with scattering angle reflects which state, $|\pi^+\rangle$ or $|\sigma\rangle$, is more effective at quenching, as a function of the impact parameter. For a given impact parameter, as the Na^* atom approaches the N_2 molecule, Coriolis coupling will cause continuous $|\pi^+\rangle \longleftrightarrow |\sigma\rangle$ transitions. The Na^* atomic wave function at a $\text{Na}^* - \text{N}_2$ separation, R , and impact parameter, b , is composed of both $|\sigma\rangle$ and $|\pi^+\rangle$ states in the mixture

$$|X\rangle = \cos\alpha |\sigma\rangle + \sin(\alpha) |\pi^+\rangle, \quad (1)$$

where $\cos \alpha = \frac{b}{R}$. At some distance, R' , the potential interactions between Na^* and N_2 will split the asymptotically degenerate $|p\sigma\rangle$ and $|p\pi\rangle$ potential surfaces. At this distance, the Na^* will begin to change from a space fixed to body fixed frame. When the $|p\sigma\rangle$ and $|p\pi\rangle$ potential curves are split by the rotational energy of the P orbital, it is said that the body fixed axis now dominates. For a long range potential of the form $V_{\sigma,\pi} \sim C_n R^{-n}$, this locking or merging distance is

$$R_m = \left(\frac{\Delta C}{n\hbar^2} \right)^{1/(n-2)} \quad (2)$$

where $\Delta C = |C_\sigma - C_\pi|$. The angle of maximum quenching shows what direction the P orbital prefers, at the merging distance to the body fixed frame, to maximize quenching. The observations show that this angle is approximately one-half the scattering angle. If the merging distance is approximately independent of the impact parameter, then this observation shows that the P orbital wishes to be tangent to the merging sphere, i.e., $|p\pi\rangle$ states are preferred.

At large Na scattering angles, the polarization asymmetry is small. As large angle scattering corresponds to smaller impact parameters, the locking radius is largest from Eq. (2). Of course, in the limit $b = 0$, the space and body fixed frames are equal. If the Na^* atom spends more time in the mixing region (where the $V_\sigma - V_\pi$ potential separation is comparable to the centrifugal energy of the P orbital), it will have more opportunities to forget its initial, asymptotically prepared

state distribution. An equal mixture of $\bar{A}$ and $\bar{A}'$ $\text{Na}^* - \text{N}_2$ collision complex states will be formed, reducing the observed anisotropy.

Finally, the measurements of the left-right asymmetry when the laser is circularly polarized and propagating perpendicularly to the scattering plane, gives information on the impact parameter dependence of the transfer of the Z component of the electronic orbital angular momentum into the heavy particle, nuclear motion. Quantum mechanically, $|p_\sigma\rangle$ and $|p_\pi^+\rangle$ states have the same overall symmetry, and can be coherently excited in a collision. If we again picture the inverse quenching process, the sign of this transfer will depend on the phase difference between the $|p_\sigma\rangle$ and $|p_\pi^+\rangle$ amplitudes in the final Na^* atom wavefunction. If the measured angular momentum transfer passes through zero at some Na scattering angle, then the phase difference between the $|p_\sigma\rangle$ and $|p_\pi^+\rangle$ states is a multiple of 180° , or the average trajectory has switched from predominately repulsive to predominately attractive in nature.

Additionally, if the cross section is larger for the electronic orbital angular momentum (L^*) aligned antiparallel to the nuclear orbital angular momentum (L), then in a scattering experiment with the products detected in the scattering plane, we can say that the Na^* atom prefers to pass on the left of the N_2 molecule rather than on the right. If the detector samples a cylindrically symmetric distribution about the relative velocity vector, no circular asymmetry can be observed. The observed circular asymmetry in a crossed beam experiment is a result of detecting only a small, biased subset of the scattering angles.

To summarize the results of Hertel, the product distributions from Na(3P) quenching can be understood from the geometry of the collision complex at the crossing seam with the ground state. Polarization studies provide detailed information on the transformation of the Na(3P) atom from a spaced to body fixed basis, and on the efficiency of angular momentum transfer from the 3P orbital motion to the heavy particle, nuclear motion.

4. Ca* + HCl

Rettner and Zare⁷⁻¹⁰ have published the only studies using optical pumping to investigate the effects of alignment on a chemical reaction. They have measured the chemiluminescence for a series of $\text{Ca}(^1\text{P}) + \text{HCl} \rightarrow \text{CaCl}(^2\Sigma, ^2\Pi) + \text{H}$ reactions in a beam-gas experiment, and observed the dependence of the branching ratio between the $^2\Sigma$ and $^2\Pi$ CaCl electronic states on the angle between the Ca atom velocity vector and the laser polarization vector.

For the $\text{Ca}^* + \text{HCl}$ reaction, a large reaction cross section was observed. The total fluorescence was independent of the laser polarization, but the dispersed fluorescence indicated that the product state electronic symmetry correlated with the initial atomic symmetry, i.e., $|\text{p}\sigma\rangle \longleftrightarrow ^2\Sigma$, $|\text{p}\pi\rangle \longleftrightarrow ^2\Pi$. The independence of the total cross section on the laser polarization was interpreted by invoking an electron transfer harpoon mechanism. Reactions with the large cross sections typical of the observed $\text{Ca}^* + \text{HCl}$ magnitudes usually favor such ionic intermediates. The probability of the electron jump was concluded to be independent of the orbital alignment. However, the ion core formed by the electron transfer is aligned, and the different molecular states

coupling to the ion core will decide whether a 2_{π} or 2_{Σ} CaCl^+ state is formed. From the experimental results, the Ca^+ orbital symmetry is preserved (adiabatic behavior), correlating to the Ca^+Cl^- molecular state with the most similar Ca^+ character.

For the reaction $\text{Ca}^* + \text{Cl}_2$, the total fluorescence cross section was dependent on the $\text{Ca}(^1\text{P})$ orbital alignment. The added symmetry of Cl_2 vs. HCl causes some of the Ca-Cl_2 molecular states to not correlate with fluorescent product states. By varying the polarization, the Ca atoms can be preferentially directed on or off these dark potential surfaces.

With this historical background, we have modified a scattering apparatus to study reactive collisions of $\text{Na}(3^2\text{P}_{3/2})$ following the basic design configuration of Hertel, et al.¹²⁻²¹ The major difference between the two apparatus is the scattered product detector. Hertel and coworkers use a hot wire filament, sensitive to alkali atoms, while in this case, an electron bombardment ionization universal mass spectrometer is used. The added flexibility of detecting product at any mass comes with approximately a 10^5 loss in detection efficiency compared to the hot wire filament. HCl was chosen as a scattering partner for the initial reaction because the detector background at $m/e = 58$ is low, and the reaction is 4.68 kcal/mol endothermic in the ground state. The endothermicity enables a test of the experimental procedure with different amounts of competing ground state reaction by simply changing the collision energy. In addition, the kinematics of the reaction restricts all the product to observable

detector angles. The alkali-hydrogen halide family of reactions has been extensively studied by the molecular beam technique, including the efficiency of vibration, rotation and translation for promoting reaction.^{22,23,24} Some ab initio²⁵ and semiempirical²⁶ potential energy surfaces are available and several classical trajectory studies²⁷ of reactions on these surfaces have been reported. Related theoretical studies of the $H + HL$ mass combination have been published.^{28,29}

Finally, Polanyi^{3,30} has reported measurements of the relative reaction cross sections for the $Na + HCl(v,j)$ reaction for $v = 1 - 4$, $j = 5 - 15$. The vibrational enhancement indicated gas kinetic reaction cross sections. The rotational dependence, with a minimum at $j = 10$, was rationalized in terms of the preferred $HCl - Na$ orientations for reaction. Barker and Weston³¹ studied the translational energy dependence of the quenching of $Na(3P)$ atoms by a number of reactive and nonreactive molecules. The absorbing sphere model for the total cross section was consistent with their results.

C. EXPERIMENTAL ARRANGEMENT

In this section, modifications to an already existing crossed molecular beams apparatus which enable scattering studies of $Na(3^2P_{3/2})$ atoms are described. Characteristics of the basic apparatus are given elsewhere.²⁴ Briefly, two sonic beams are crossed at right angles (beam overlap volume $\sim 10^{-3} \text{ cm}^3$) in a liquid nitrogen cooled chamber, under single collision conditions. The collision chamber ambient background pressure is 1×10^{-7} torr. Scattered product is detected with a rotatable mass spectrometer which rotates in the plane defined

by the two reactant beams. The mass spectrometer detector consists of an electron bombardment ionizer, quadrupole mass filter, and a Daly ion counter, enclosed in a triply differentially pumped, ultra-high vacuum chamber. The experimental improvements described below include the development of a stable, seeded, Na atom source and the ability to excite a sizeable fraction of the Na atoms in the collision volume to the $3^2P_{3/2}$ excited state by the method of optical pumping. In addition, the experiment can measure moments of the $Na(3^2P_{3/2})$ charge distribution created by the polarized, exciting laser radiation, and the dependence of the observed scattering on these moments.

1. Sodium Beam

The sodium atom beam is produced by a two chamber stainless steel oven shown in Fig. 2. The main section, of volume 150cc, is the reservoir for the molten sodium metal. It is heated by .090 inch diameter thermal coax heating cable (SEMCO, Inc.) brazed into contact with the oven body. The braze melting point is 1050°C. At the top of the reservoir is a stainless steel gas inlet tube affixed onto a mini-conflat flange and sealed by a .005 inch thick nickel gasket. The gas inlet tube is radiatively heated by a .080 inch wide, 24 inch long tungsten ribbon. The gas inlet tube serves two functions. First, the sodium metal is easily loaded into the reservoir through the mini-conflat flange opening. Second, rare gases, introduced through the inlet tube, enable the velocity of the sodium atoms to be varied over the range $1. - 3. \times 10^5$ cm/sec at a constant nozzle temperature, here chosen to be 740°C. A plug constriction in the inlet tube increases

the local rare gas flow velocity so sodium vapor will not diffuse upstream and clog the inlet tube where the temperature is cooler. Additionally, the radiation heater is kept 50°-100°C warmer than the reservoir temperature to help impede the sodium from diffusing up the inlet tube. The sodium reservoir is the coldest part of the oven and determines the sodium vapor pressure.

The nozzle chamber consists of a 3.0 inch long, .25 inch diameter stainless steel tube, heated by .060 inch diameter thermal coax heating cable, again brazed into contact with the stainless steel tube. The nozzle aperture is formed by drilling a .003-.005 inch diameter hole in a .020 inch thick stainless steel disk, which in turn is welded onto the stainless steel tube. This additional chamber for the nozzle allows the nozzle to be hotter than the reservoir, thus preventing the formation of sodium polymers.

All connections to the thermal coax heating cable follow the design suggestions of Amperex.³² Basically, a precision machined ceramic jacket is used to reduce rotational and bending mechanical stresses to the exposed center conductor at the junction to the electrical power leads. The ceramic piece is brazed to the sheathing on one side and the electrical power connector on the other. This arrangement reduces the heat dissipated at the junction to the power leads because good thermal contact is made with the high thermal conductivity of the copper power cable. Up to 150 watts of power can be delivered to the oven with the lengths of cable chosen. This is sufficient to raise the oven temperature above the melting point of

the braze material before the heating cable itself fails. All ovens are surrounded by two radiation shields.

The reservoir and nozzle heater power supplies are actively controlled to stabilize their temperature to within $\pm 2^{\circ}\text{C}$ of any desired set point. This is necessary to maintain stable intensity and velocity for the sodium beam. For the worst case, He seeding, small changes in the sodium partial pressure changes the average mass of the He/Na mixture, affecting the velocity distribution. With the actively controlled temperatures of both reservoir and nozzle, long term variations in the Na beam's average flow velocity are well within the short time scale velocity spread characterizing the isentropic expansion.

The oven assembly is supported by a water-cooled copper block. It is attached to the nozzle chamber vacuum bulkhead by three screws, which also enable it to be aligned along the beam axis. Except for the skimmer described below, care was taken to remove all obstructions from the nozzle and to maximize gas conductance away from the nozzle-skimmer region. The nozzle tube, with heaters, is approximately 3/8 inch diameter. The nearest support is approximately one inch further away.

The central portion of the Na beam is skimmed by a single piece, heated, stainless steel skimmer. The skimmer aperture is .045 inch diameter and is located .26 - .30 inches from the nozzle. The skimmer is also heated by coax heating cable. A second heated surface is placed to mask the edge where the skimmer fits through the nozzle chamber bulkhead. Without this mask, sodium would condense on the

cooler bulkhead eventually bridging over to the heated skimmer. When this happens, the liquid sodium conducts sufficient heat from the skimmer that it soon becomes clogged by the incident flux of sodium from the nozzle.

The final size of the sodium beam was determined by a rectangular aperture made from razor blades located in the second differential pumping region. The heat radiated from the skimmer is sufficient to keep the defining slit from clogging by the small amount of sodium incident upon it.

Balzers 71 diffusion pump fluid was used in the Na source and differential diffusion pumps. Octoil showed some signs of deterioration with time, as well as depositing thin films on the surfaces of these pumping regions. A full charge of DC704 would completely react to form a white, oilish, crystalline precipitate in less than one Na oven charge. Before loading Na metal into the oven, its oxide coating was removed in an inert atmosphere. Care was taken to clean the nozzle and differential chambers of sodium residue between runs. Also, each new charge of sodium, after evacuation of the source chamber, was held at just above the Na melting point ($\sim 150^{\circ}\text{C}$) for many hours to remove all impurities and vapor trapped in the solid. Ultra high purity rare gases, as well as an all metal, leak tight gas inlet system were found to be necessary to avoid slow clogging of the nozzle.

2. HCl Beam

The HCl beam was formed from a heated tube with an interchangeable nozzle affixed on the end, as shown in Fig. 3. A platinum electron

beam aperture (Ted Pella, Inc.) of 70 micron diameter was used in this study. The nozzle tube slides in a fixture which allows the nozzle-skimmer distance to be changed while the nozzle remains on the beam center-line axis. The nozzle temperature was actively stabilized to 180°C , to prohibit HCl polymer formation. Typically, 350 torr HCl nozzle backing pressure was used. A low pressure regulator, in addition to the standard cylinder regulator, was necessary to stabilize the delivery pressure at these low values. A 150 Hz tuning fork chopper was mounted on a water-cooled copper block attached to the nozzle chamber bulkhead. The cooling block was needed because the heated nozzle, via the alignment fixture, would heat the front of the nozzle chamber sufficient (70°C) to stop the chopper modulation.

The nozzle backing pressure of HCl was optimized at the same time the phase and gate width of the chopper modulation function were measured. The latter were measured by time resolving the signal at the mass spectrometer and displaying several chopping cycles. The gate width was set to the minimum of the chopper open or closed time interval. The phase and pressures were set by optimizing the contrast between the channels with the chopper open and closed.

3. Optical Preparation of $\text{Na}(3^2\text{P}_{3/2})$

The creation of a large, stationary fraction of $\text{Na}(3^2\text{P}_{3/2})$ atoms by optical pumping has been exhaustively and elegantly studied by Hertel and coworkers.¹⁸⁻²¹ Their experimental technique has been adopted here. Briefly, the selection rules on ΔF , the change in total angular momentum, insure that all atoms excited from $^2\text{S}_{1/2}(F=2) \longrightarrow ^2\text{P}_{3/2}(F=3)$ will form an isolated, two level system. The

level structure appropriate to the $3S \rightarrow 3P$ transition is shown in Fig.

4. Spontaneous decay from the $^2P_{3/2}(F=3)$ level can only repopulate the $^2S_{1/2}(F=2)$ level of the ground state. Assuming all ground state levels are equally populated before the atoms enter the laser beam, at most 31.25 percent of the Na beam can be in the $^2P_{3/2}$ state.

Several details are pertinent to achieving this 3P excitation efficiency. Power broadening must be less than 60 MHz, the separation of the $^2P_{3/2}(F=2,3)$ hyperfine levels. If this condition is not met, and the $^2P_{3/2}(F=2)$ level is excited, it can spontaneously decay to the $^2S_{1/2}(F=1)$ ground state HPF level and be lost from further optical pumping cycles. As the power broadening follows the laser profile, it is important to expand the laser beam so that the central portion is not power broadened beyond 60 MHz. Secondly, the sodium beam angular divergence along the laser beam propagation direction produces an associated transverse doppler shift. If this doppler shift is larger than 60 MHz, then some fraction of the sodium beam will be shifted off the $^2P_{3/2}(F=3)$ resonance. For Na seeded in He, this limits the angular divergence to 1° .

At the time this experimental work was performed, it was thought that the published work by Hertel, et al. on the optical pumping of Na had definitely established that 30 percent of the Na atoms are excited to the $3^2P_{3/2}$ state. Recently, unpublished work³⁴ has appeared by this group suggesting that perhaps only 15-20 percent excitation is achieved. The reason for this is thought to be the weak coupling to the $3^2P_{3/2}(F=2)$ hpf level, which removes atoms from the desired

isolated, two level system. Empirically, in the work by Schmidt and coworkers¹² on the scattering of $\text{Na}^+ + \text{Na}(3\text{S}) \longrightarrow \text{Na}^+ + \text{Na}(3\text{P})$ a 12 percent reduction in the inelastic $\text{Na}^+ + \text{Na}(3\text{S}) \longrightarrow \text{Na}^+ + \text{Na}(3\text{P})$ transition was observed when the sodium beam was optically pumped. Unfortunately, in the $\text{Na} + \text{HCl}$ scattering experiments, there is no feature in the angular or velocity distributions which can be assigned only to ground state $\text{Na}(3\text{S})$ scattering. If such a feature can be found, the depletion of it by exciting Na atoms to the excited state would measure the effective Na fraction optically pumped to the $3^2\text{P}_{3/2}$ state. Consequently, in the analysis below, both cases of 15 percent (empirical) and 30 percent (theoretical) excitation efficiency are analyzed. Where the differences are important, they will be noted.

A combination of commercial camera lenses is used to image the sodium fluorescence onto a phototube (RCA IP28). The lenses magnify the fluorescence region tenfold, and in conjunction with a moveable iris aperture, located at an intermediate focal plane, spatially selected regions of the fluorescence can be measured. In this way, any spatial dependence of the fluorescence intensity can be observed, as well as the average polarization characteristics of the fluorescence determined for the entire collision volume.

The signal from the camera phototube, after current amplification (Kiethly Model 427) drives a lock-in stabilizer (Lansing 80-214) which corrects for short term (~ 1 sec) frequency drifts. The necessary reduction of the transverse doppler width noted above causes a 50 percent pumping loss if the laser frequency drifts 20 MHz off line center.

The manufacturer's specifications for the dye laser's drift rate is less than 100 MHz/hour. However, the experimental environment of the molecular beam laboratory is not suited to meet these requirements. Luckily, only a small feedback is needed to correct for these slow drifts.

The commercial lock-in stabilizer produces a DC correction voltage and AC (510 Hz) modulation reference frequency. These are appropriately scaled and summed, then input to the external voltage controlled frequency drive of the CR-599-21 dye laser scan electronics. In this manner, the Fabrey-Perot cavity of the 599-21 is dithered at 510 Hz with ~5 MHz amplitude. The intracavity feedback elements of the dye laser assured the laser frequency exactly tracks this reference cavity. The DC correction voltage (when the lock-in phase is properly set) applied to the reference cavity then maximizes the fluorescence. When properly aligned, the laser stability is sufficient for greater than 24 hour continuous operation.

As will be discussed in detail below, the polarization properties of the laser can be utilized to create oriented or aligned Na(3P) charge distributions. To perform alignment and orientation experiments, all windows and mirrors are anti-reflection coated for 5890Å with measured ellipticities of less than 1/2 percent. This insures that the polarization properties of the laser are preserved at the scattering center. Care was taken to remove oil from windows and mirrors in the vacuum chamber. The final 45° beam stirring mirror, located at the base of the scattering chamber, is heated to 100°C to

prevent oil accumulation. The aligned or oriented 3P orbital can be affected by stray magnetic fields or radiation trapping. Hertel¹⁸ has shown that as long as the magnetic fields are smaller than 1 gauss and the Na atom density $< 10^{11}/\text{cm}^3$, such effects are negligible. The magnetic field was measured and found to be less than 1 gauss. As long as the sodium partial pressure is kept below 10 torr for the 3 inch nozzle-collision volume distance, radiation trapping will be negligible. The actual charge alignment is measured concurrently with the polarization studies by recording the polarization of the fluorescence using the fluorescence monitor.

4. Angular Distribution Measurement Procedure

The laser beam can be directed to the scattering volume from three directions. A 45° crossing relative to the Na beam is used to measure the velocity of the Na atoms by the doppler shift method. Apertures on the entrance flanges to the collision chamber and internal photodiodes allow the laser beam to be positioned within 1 mm of its optimum position without breaking vacuum. After laser induced signal at the mass spectrometer is seen, fine tuning of the laser position to maximize the contrast of the mass spectrometer signal with and without the laser is done. The fluorescence monitor is then positioned to image the central region of the fluorescence onto the phototube for maximum phototube signal.

Most of the data acquisition is computer controlled. Five basic quantities are measured in an angular scan; the laser fluorescence (LF), the mass spectrometer signals with the laser on and HCl beam on

($L_{+}X_{+}$), the laser off and HCl beam on ($L_{-}X_{+}$), the laser on and HCl beam off ($L_{+}X_{-}$), and the laser off and HCl beam off ($L_{-}X_{-}$). With the laser off, the difference

$$(L_{-}X_{+}) - (L_{-}X_{-}) \propto \frac{d\sigma}{d\Omega} (3^2S_{1/2}) \quad (3)$$

is proportional to the 3S ground state scattering. When the laser is on and if the optical pumping is saturated, the signal has contributions of 31.25 percent from $3^2P_{3/2}$ scattering and 68.75 percent from $3^2S_{1/2}$ scattering. The following combination of the four mass spectrometer signals is proportional to the $3^2P_{3/2}$ differential cross section

$$\frac{d\sigma}{d\Omega} (3^2P_{3/2}) \propto (L_{+}X_{+} - L_{+}X_{-}) - .6875 * (L_{-}X_{+} - L_{-}X_{-}) \quad (4)$$

The HCl beam is 100 percent amplitude modulated by the 150 Hz tuning fork chopper mounted in the HCl beam differential chamber. The laser beam is 100 percent amplitude modulated at 6 Hz by a stepping motor controlled beam stop. For 24 tuning fork chopper cycles, the signals are accumulated with the laser on. On the 25th chopper cycle, no signal is obtained to allow time for the laser beam flag to block the laser beam. Then, 24 chopper cycles with the laser blocked are accumulated. On the 25th cycle, no signal is obtained while the laser beam flag unblocks the laser. The above process is then repeated for a preset number of times determined by the user. In this way, once

the phase and gate width of the tuning fork modulation are known, the gating is automatically accomplished without significant loss of duty cycle or computer intervention.

When the laser is blocked, the fluorescence signal is lost. To stop the lock-in from wandering, a 1/6 sec blanking pulse is sent to the error loop of the lock-in. This freezes the lock-in at the frequency present when the blanking pulse arrived for the duration of time the laser is blocked. Feedback then resumes with fluorescence signal at the lock-in input.

The computer accumulates data at each angle for a preset time. When completed, the five signal channels are read, the contents displayed and written to disk. The fluorescence is checked to insure that it has not varied significantly from the maximum value recorded. If it has changed, the experimenter is informed of this fact. If the laser optics had moved, or laser frequency lock lost, these errors can be corrected at this time and the data point repeated. Approximately every 30 minutes, the computer program directs the user to return to a reference angle where the signals are measured for several of the preset time intervals. When the data file is processed, these periodic reference points are used to scale the laser on and laser off channels separately by linear interpolation. This accounts for beam intensity drifts, and changes in detector sensitivity. The scale factors for the laser on and off channels should be equal if only the Na number density is varying. For stable scans, these scale factors empirically varied less than ± 4 percent. For all data presented, the

error bars for the mean are one standard deviation for the statistical error associated with the finite signal count, or the variance of the mean of the actual measurements, whichever is larger. Typically, four separate angular scans are averaged to obtain approximately 10 percent error in the derived 3P distributions. The total counting time at each angle is usually eight minutes.

It is instructive to trace the effect of errors in the five measured angular data signals on the derived Na(3P) scattering cross sections. If we allow each of these signals to have an associated error, and we correct Eq. (4) for the unequal fluxes of Na(3S) and Na(3P) atoms, then the error in the differential cross section corresponding to the hypothetical case of 100 percent optical pumping efficiency is:

$$\Delta \frac{d\sigma}{d\Omega}^* = \frac{\Delta_{on} + (1-P)\Delta_{off}}{P} + \frac{\Delta P}{P^2} S_{on} - S_{off} \quad (5)$$

In Eq. (5), Δ_{on} and Δ_{off} are the statistical errors in the signals observed with the laser on (S_{on}) and the laser off (S_{off}). P and ΔP are the true optical pumping efficiency and error in this efficiency, respectively. The first term in Eq. (5) is the error resulting from statistical fluctuation in the mass spectrometer signals, while the second term is the error from the uncertainty or variation in the optical pumping efficiency. By accumulating data for sufficiently long time intervals, the first term can be made small, assuming, of course, that all source and detector conditions are stable. We note

at this stage that if only 15 percent of the sodium atoms are excited, then compared to a typical ground state scattering experiment, the error is ~ 7 times as large for equal counting times.

The second term in Eq. (5) is proportional to the difference in the laser on - laser off signal. If the laser frequency were to drift, causing a change in pumping efficiency, ΔP , then the variations would be larger at the higher signals. This underscores the need to actively stabilize the laser frequency and operate at saturation to reduce $\Delta P/P \sim .01$, where one can safely assume the second term in Eq.(5) is negligible compared to the statistical data fluctuations.

5. Doppler Shift Measurements of Na Velocity Distributions

At each normalization point, the sodium velocity distribution is measured by monitoring the doppler shifted fluorescence from the 45° laser crossing, and scanning the laser frequency. This can also be performed by the computer. First, a shutter is opened to allow the laser to pass at 45° to the sodium beam. Next, an analog switch changes the computer external frequency drive input from the lock-in amplifier to the computer D/A output. The computer scans the laser, recording the fluorescence intensity and the intensity of the Fabrey-Perot used as a relative frequency standard. The fluorescence intensity has the characteristic patterns shown in Fig. 5. There are four peaks. The two narrow and intense peaks are from the orthogonal Na beam intersection used in the optical pumping. Their separation is the ground state HPF splitting (1.77 GHz) minus a weighted sum of the $3^2P_{3/2}$ HPF structure determined by the fluorescence transition

strengths from the $3^2P_{3/2}$ ($F=3, 2$ and 1) HPF levels. Empirically, this weighting produces a splitting of 1.67–1.70 GHz for the narrow peaks. This separation is consistent with the splitting derived from the fringe spacing (1.5 GHz) of the Fabrey-Perot and with the location of the center-of-mass for the Na + HCl scattering. If only the 1.77 GHz ground state HPF splitting is used, the center of mass shifts 2° towards the Na beam from where it is empirically observed and predicted by the 1.67 GHz spacing.

The two broad, red shifted peaks of Fig. 5 are the doppler shifted analogs of the orthogonal crossing peaks. The separation, in GHz, from the orthogonal crossing and the corresponding 45° crossing transition, Δf , is related to the average flow velocity, v_0 , by the equation

$$v_0(\text{cm/sec}) = 83300. * \Delta f(\text{GHz}) \quad (6)$$

The Na beam velocity distribution is found by fitting the observed fluorescence intensity to the functional form

$$I(v)dv = Cve^{-8(v-v_0)^2} dv \quad (7)$$

appropriate for the number density velocity distribution. The distribution is weighted by $1/v$ in the doppler shift measurements, as the faster moving atoms spend less time in the laser beam, and execute less spontaneous radiation cycles.

6. Product Velocity Measurements

Time-of-flight measurements of the product velocity distributions at selected detector angles are obtained by the cross correlation

method. As for the angular data, two velocity distribution measurements are needed at each angle, with and without laser excitation. These are obtained in two different experiments.

Without laser excitation, the scattered products are correlated by a 255 channel pseudo-random sequence encoded onto a spinning disk placed between the reaction volume and mass spectrometer. The basic details of this procedure are given elsewhere.²⁴ The only major difference here is the use of a digital function module to synchronize the rotation of the disk to the channel advance of the multi-channel scaler (MCS). The digital function module contains 14 bit phase resolution for sin and cosine analog wavefunctions. The channel advance is used to generate the sin and cosine phases. These two analog signals are amplified and used to drive an asynchronous motor (Globe 75A 1003-2). Because every 1/255 of an MCS cycle the phase of the wheel is advanced, the synchronization is nearly exact for the applied restoring force to the motor.

With laser excitation, the laser beam itself is correlated. In this way, the full flight path from the collision zone to the detector of 20 cm is utilized. When the correlation wheel is placed between the detector and the mass spectrometer, as done without laser excitation, the flight distance is only 17 cm. Additionally, the entire signal from the interaction volume is modulated by the laser without the need to reduce the entrance aperture to the detector to match the smallest slit in the pseudo-random sequence. Normally, when the scattered product is modulated, this is done to achieve higher resolution. Using lenses to focus the laser light on the rotating disk, the

resolution is limited only by the slit size variation of the pseudo-random sequence and the uncertainty in the point where the product is ionized in the mass spectrometer. By cross correlating the fluorescence, the modulation function is directly obtained including the variation in slit size and wheel rotation synchronization. In the TOF data analysis, the correlation matrix generated by this measured modulation sequence can be inverted and used to decorrelate to the TOF data as outlined by Comsa, et al.³³

When correlating the laser, the 3P Na population is modulated by the pseudo-random sequence. For every Na atom excited, one is removed from the ground state. Hence, equal densities of 3S and 3P sodium atoms are modulated by the laser correlation. In general, the 3P atoms contribute a positive signal, while 3S atoms contribute a negative signal by the laser modulation.

The different reactivity of the two types of atoms determine the TOF pattern observed. The excited state reactivity, compared to the ground state reactivity, is derived from the angular data for 31 percent excitation efficiency by the equation

$$R(\theta) = \frac{d\sigma^*/d\Omega(\theta)}{d\sigma/d\Omega(\theta)} = \frac{(L_+X_+ - L_+X_-) - .69 (L_-X_+ - L_-X_-)}{.31 (L_-X_+ - L_-X_-)} \quad (8)$$

If $X(t)$ and $Y(t)$ are the observed TOF spectra with and without the laser at the angle θ , normalized to equal areas (i.e. same total signal counts corrected for background), then these signals are related to $P(t)$ and $S(t)$, the 3P and 3S TOF distributions by

$$X(t) = a P(t) - b S(t)$$

$$Y(t) = S(t) \quad (9)$$

Integrating the total signals in X and Y, using Eq. (6) and assuming that X and Y are normalized for unit areas, then

$$a = \frac{R}{R-1}, \quad b = \frac{1}{R-1} \quad (10)$$

If $R = 1$, then the normalization condition in Eq. (10) is undefined.

In performing TOF measurements, overlap of the laser and molecular beam volumes is not as critical as in the angular measurements. For the angular measurements, one must know the actual percentage of Na atoms excited. For TOF measurements, the laser correlated 3S and 3P densities are always equal. Finally, the 3P TOF distribution is given by

$$P(t) = \frac{(R-1)}{R} X(t) + \frac{1}{R} Y(t) \quad (11)$$

For the long term operation necessary for obtaining good signal to noise ratios, a second lock-in scheme for the laser stabilization was needed for the TOF measurements. The 510 Hz reference frequency of the lock-in stabilizer with blanking, used for angular measurements, is in the same frequency range as the laser modulation by the correlation sequence. A second lock-in, operating at 100 Hz, dithered the laser frequency well below the range of the correlation sequence, and

made the TOF measurements easy to perform for many continuous hours. To improve the TOF signals at different collision energies, the sodium beam divergence determined by the defining slits can be adjusted to match the transverse doppler shift.

7. Variation of Total Cross Section with Collision Energy

For fixed collision energy, measurements of the angular and time-of-flight product distributions enable the determination of a center-of-mass frame product flux distribution. A fitted functional form to the product energy and angular distribution in the center-of-mass frame can be integrated to give an estimate of the total cross section for product formation at this energy. However, because absolute reactant densities and detection efficiency are unknown, this estimate is poor.

One method for obtaining total cross sections uses the nonreactive sodium scattering at several collision energies to fit a spherical long range potential that matches the small angle scattering.²⁴ The depletion of the large angle, nonreactive scattering from that predicted by the spherical potential can be used to estimate a maximum impact parameter for reaction. When extensive product ion fragmentation occurs, this method is difficult to apply unless the elastic contribution can be differentiated in the time-of-flight distributions.

A second method²⁴ is based on estimating the relative detection efficiency of Na/NaCl, then using the fitted spherical potential to give the absolute scale. Besides the errors introduced by the spherical potential approximation to the nonreactive scattering, the

estimation of ionization efficiencies and fragmentation patterns usually introduce absolute errors of 100 percent.

To further improve this latter method, the fluorescence signal can be used to very accurately compare cross sections at different collision energies. With different seed gases, the sodium density and speed are different for each collision energy. By measuring the fluorescence (LF), velocity distributions, and the mass spectrometer signals with fixed detector sensitivity and fluorescence photomultiplier gain, an accurate, relative sodium density for each collision energy can be derived. The relative scale factor, β , for data obtained at different collision energies is simply then

$$\frac{n(\text{Na})}{n'(\text{Na})} \frac{g}{g'} = \beta \quad (12)$$

where $g = |v_{\text{Na}} - v_{\text{HC}}|$ is the relative speed of the reactants and $n(\text{Na})$ is the relative sodium density. The primes in Eq.(12) refer to parameters at a different collision energy. The sodium density is proportional to the fluorescence signal and the velocity. (The saturated fluorescence signal is proportional to the time the sodium atoms spend in the laser beam, $1/v_{\text{Na}}$, and the number density of atoms with that velocity.) Hence, Eq. (12) can be written

$$\frac{\text{LF} \cdot v_{\text{Na}}}{\text{LF}' \cdot v_{\text{Na}}'} \frac{g}{g'} = \beta \quad (13)$$

For the He/Ne seeding cases of the data shown below, the relative scale factor is $s = 8.7$, favoring He. Using these accurate relative scale factors, the shape of the total cross section can be established, although an absolute scale must still be provided by comparison with the nonreactive scattering. The advantages now are that all data can be used simultaneously in determining a single detection efficiency, because the relative scale factors are known quite well. Finally, the shape of the total cross section with collision energy is very important when fitting the angle-velocity data and allowing for a distribution of reactant velocities. If the collision cross section changes quickly with energy (for example, near threshold) the weighting of the different velocity groups can have a pronounced effect on the derived product energy and angle distributions.

D. EXPERIMENTAL RESULTS

The Na atom velocity distributions were derived from the doppler shifted fluorescence measurements shown in Fig. 5. The HCl velocity distribution was taken from the previous work of Becker, et al.²⁴ by scaling their measured flow velocity to be consistent with the 180°C nozzle temperature of this experiment. The value obtained, 8.45×10^4 cm/sec, is consistent with 99 percent relaxation of the HCl rotations in the adiabatic expansion. Unrelaxed, the HCl flow velocity would be 7.23×10^4 cm/sec. An independent check of the accuracy of the reactant beam flow velocities is provided by the sodium ground electronic state reactive NaCl angular distribution measured at the 5.38 kcal/m collision energy. At this collision energy, only 0.7

kc/m is available for product translation. The maximum NaCl center-of-mass recoil velocity is then 4×10^3 cm/sec. Consequently, the observed laboratory angular distribution shown in Fig. 6 reflects only the distribution of center-of-mass angles from the velocity dispersion of the reactant beams. The maximum of the NaCl angular distribution located at 40° in the laboratory frame is correctly predicted by these beam velocities. A product flux distribution which is independent of both the recoil angle and energy reproduces the observed angular variation as shown in Fig. 7.

The Newton diagrams corresponding to the two collision energies for which data will be presented are shown in Fig. 8. The full widths at half-maximum for the reactant beam velocities, as well as the distribution of center-of-mass angles generated using the flow velocity of one beam and the half-maximum velocities of the other beam, are shown as hatched areas on the Newton diagrams. The approximate angular broadening caused by these distributions, $\Delta\theta_{cm}$, is also given.

The maximum center-of-mass product velocity allowed in the Na(3P) reaction, U_{NaCl}^* , is determined from the reaction endothermicity of 4.68 kc/m, the photon energy of 48.53 kc/m, and the translational energy corresponding to the flow velocities of each beam. The maximum laboratory scattering angles where product can appear from the excited state reaction are also indicated.

The angular distributions measured at masses 23 and 58 without laser excitation are shown in Fig. 6. As noted above, the reaction $Na(3S) + HCl \rightarrow NaCl + H$ at 5.38 kc/m collision energy is barely

allowed. For the mass combination of this reaction, the product parent mass angular distribution contains no detailed information on the product energy or center-of-mass scattering angle distribution, given the current detector resolution and reactant beams velocity dispersions.

The angular distribution at mass 23 is predominately non-reactive, elastic scattering, with a minor contribution from reactively scattered NaCl detected at mass 23 from fragmentation in the ionization process. As the detection sensitivities for mass 23 and mass 58 in the experiment are approximately equal, the fragmentation ratio for NaCl formed near threshold and ionized by 160 volt electrons can be estimated by subtracting different multiples of the mass 58 angular distribution from the mass 23 angular distribution. The family of curves generated using multiplicative factors in the range 1-2 is shown in Fig. 9. Assuming the depletion of the large angle, non-reactive scattering is negligible for this near threshold collision energy, a fragmentation ratio of 50-55 percent results in a smooth, monotonic mass 23 angular distribution for the corrected, non-reactive sodium scattering.

Varying the electron energy from 50-200 volts did not markedly change the fragmentation ratio. Future measurements of mass 23 ground state reactive and non-reactive time-of-flight distributions at angles where NaCl fragmentation is important can, of course, distinguish the NaCl ion fragment contribution to the Na(3S) elastic scattering by their different, and, distinct laboratory velocities.

A similar analysis of the non-reactive Na(3S) scattering at the 19.4 keV collision energy is ambiguous. Here, the mass 23 data is

dominated by NaCl reaction product fragments. Figure 9 shows the corrected mass 23 non-reactive distribution when fragmentation ratios of 50, 66, and 70 percent are assumed for the NaCl product formed at this collision energy. The large errors on the derived non-reactive scattering distributions indicate that non-reactive scattering contributes very little to the observed intensity. At this energy and for this angular range, no reliable non-reactive distributions can be derived from the angular measurements alone. The strong reactive signal at this collision energy suggests that the large angle, non-reactive scattering should be largely depleted by reaction. Unlike the 5.38 keV mass 23 distribution, there is no obvious pure, non-reactive scattering at large or small angles to enable an interpolation through the angular range dominated by reaction product fragmentation. Again, time-of-flight measurements can resolve the non-reactive contribution at each angle. The conclusion that the reactive NaCl product fragments more at this higher collision energy is firmly grounded. Fragmentation ratios less than 70 percent always leave a residual bump near the center-of-mass. Rainbow or inelastic scattering are physically unlikely to produce such results.

The laboratory differential cross sections observed with and without laser excitation are shown in Fig. 10 for the two collision energies. The Na(3P) angular distributions derived from Eq. (4) for both energies at masses 23 and 58 are shown in Fig. 11. A 50 percent error in the fraction of Na atoms assumed to be in the 3P state significantly affects the derived Na(3P) differential cross sections

for the 19.4 kc/m collision energy data, while the 5.38 kc/m collision energy data is basically unchanged within the stated measurement errors. Figure 12 shows the non-reactive mass 23 distributions derived by assuming several fixed values for the NaCl fragmentation ratio, with an optical pumping efficiency of 30 percent. These fragmentation curves are not qualitatively different if only 15 percent of the atoms are assumed excited to the $3^2P_{3/2}$ state.

Laser correlated time-of-flight (TOF) measurements at selected angles for masses 23 and 58 at the 5.38 kc/m collision energy are shown in Figs. 13-14. The mass 23 data at the laboratory angles 25° and 30° clearly exhibit a fast, Na(3P) elastic peak as well as a slower, broader, reactive ion fragment peak. At all angles, a fluorescence induced signal, not displayed in Figs. 13-14 appears in the first channels. This signal is also observed when the mass spectrometer is set to pass an arbitrary mass well separated from the masses of the products and reactants. This signal is thought to result from scattered fluorescence striking the Daly ion counter photomultiplier. When correlated, this signal appears in the first channel. The magnitude of this artifact is small, and can be separated from the true heavy particle scattering which appears well displaced to longer product arrival times. When the ion flight time is used to displace the laser correlated TOF data, this artifact moves to channels 254-255. The displayed TOF data is then the actual data measured. The only numerical transformation applied was to interpolate the convoluted data over the channels 254, 255, 1, and 2, to correct for the multi-channel scaler reset and synchronization error.

Time-of-flight measurements of the ground electronic state scattering have not been performed to date. To obtain only the Na(3P) contribution to the laser correlated TOFs, they were corrected according to Eq. (8) using computed ground state TOF distributions. As stated above, at this near threshold collision energy, the ground state reactive scattering is severely convoluted by the distribution of center-of-mass angles. The TOF distributions obtained from a fit to the mass 58 ground state angular distribution are expected to closely approximate the true ground state TOFs. The corrected, mass 23 distributions derived differ little from the original laser correlated TOFs. The chief effect is to boost the signal at 35° , 40° , and 45° for the channels near the center-of-mass. As the reactivity is approximately a factor of ten larger in the 3P state, the corrected channels are displaced within the statistical error of the original TOFs.

At this point, it should be stated that the error in the assumed fraction of Na(3P) atoms in the collision volume can have a dramatic effect on the correction of the TOF data. The weighting of the Na(3S) TOF to the laser correlated TOF depends on the ratio of the reactivity of Na(3P) to Na(3S) atoms at that laboratory angle. In turn, this depends on what fraction of the Na atoms we assume cause the difference in the angular distributions when the laser excites the Na beam. At the collision energy 5.38 kcal/m, the laser effect is large compared to the ground state scattering signal. Large errors in the fraction of Na atoms excited do not have significant results on the derived

center-of-mass energy and angle distributions. For the 19.4 kcal/mol collision energy, the ground state signal is comparable to the laser induced signal and the assumed value for the Na(3P) fraction can qualitatively affect the shape of the angular and TOF data used to obtain the center-of-mass product flux distributions.

Polarization measurements performed at laboratory angles of 40° and 55° were independent of the direction of the laser electric field vector in the scattering plane, and on the handedness of the light. From the statistical accuracy of these measurements, the polarization dependence for rotation of the electric field vector in the scattering plane is estimated to be less than 20 percent. The two detector angles were chosen to sample the center-of-mass and back scattered product. For the back scattered product, we expect a limited range of contributing impact parameters. Although velocity resolved polarization studies might show a dependence, we feel that for this particular reaction, the intrinsic polarization dependence is small and is expected for the reaction mechanism postulated below.

Finally, in Fig. 15, the laser induced mass spectrometer signal is plotted against the laser fluorescence. These data were obtained by attenuating the laser power over two orders of magnitude using filters. An "eyeball" fit to the data is drawn, indicating that within the experimental accuracy, a linear dependence is observed. We take this as evidence that the mass spectrometer, fluorescence detector, and optical pumping are properly functioning as a system within the statistical errors of the observed signal strengths.

E. DATA ANALYSIS

In this section, the experimental data is analyzed to find what center-of-mass recoil energy and angular distributions are consistent with the measurements. First, the type of the collision process responsible for the measurements is identified. Next, the data is quantitatively reduced, within the framework of the identified collision process, to the fundamental center-of-mass frame product flux distributions. The effect of the reactant beam velocity dispersions, finite detector apertures, and other experimental broadening mechanisms are taken into account.

The Na(3P) scattering distributions measured at masses 23 and 58 can be reasonably ascribed to one of the following collision processes.

Analogous to the Na(3S) reactive scattering, NaCl product is expected to be favored over NaH. However, unlike the ground state scattering, the mass 23 angular distributions do not have the same shape as the mass 58 distributions. As shown in Fig. 12, the curves derived from the measured 5.38 kc/m collision energy mass 23 distribution correcting for NaCl fragmentation, always have residual intensity in the backward scattered direction peaking at a laboratory angle of 50°. This conclusion is independent of the fraction of atoms assumed in the 3P state. If we followed the logic applied to the Na(3S) scattering,

we would conclude that there is significant Na(3P) scattering which is not attributable to elastic or NaCl reactive scattering. It will now be argued that this conclusion is an artifact of the electron bombardment ionization process and the dependency of the NaCl fragmentation ratio on internal energy.

From the ground state Na(3S) reactive scattering analysis, it was noted that from threshold to 15 kc/m above threshold, the NaCl fragmentation ratio changed from 50 to 70 percent. In this case, the absolute signal levels of the Na^+ ions ascribed to NaCl fragments were within a factor of two of the NaCl parent signal. For the Na(3P) angular distributions, this approximate equivalence no longer holds. The NaCl^+ parent signal is only 1/10 of the mass 23 signal. If we presume the mass 23 signal is from NaCl ion fragments, then the mass 23 angular distribution is a more accurate measure of the true NaCl reactive product distribution, than the comparably weak parent mass distribution. For example, a relative change in the fragmentation ratio of 2 percent will affect the shape of the mass 58 distribution by 20 percent. Since there is sound evidence for a rapid increase in the fragmentation ratio in the ground state reaction, and the NaCl parent mass is a minor ion in the excited state reaction, the mass 23 distribution is taken to reflect the true NaCl product distribution. Of course, corrections for the Na(3P) elastic scattering must be done at small angles.

In the above discussion, it was tacitly assumed that all of the mass 23 data (correcting for elastic scattering) was from NaCl ion

fragmentation, and that NaH formation or quenching were unnecessary to explain any of the mass 23 intensity. The derived energy and recoil angle distributions, to be presented below, are physically plausible and fit the data well. Therefore, our argument is self-consistent. Having assumed the mass 23 distribution is mostly NaCl ion fragments, we could analyze the data without resorting to nonphysical mechanisms. To make the argument definitive, we now reason that quenching or NaH formation cannot account for the observations with the same success without ridiculous constraints on these two processes.

Figure 16 shows the kinematically allowed recoil velocities for different HCl vibrational states if Na(3P) is quenched by HCl. The indicated rotational states are those allowed by energy conservation for that vibrational state. The mass combination of the quenching channel differs markedly from the NaCl reactive channel. Consequently, the quenching channel can scatter product to all laboratory angles. Recalling that the residual mass 23 intensity is at 50° in the laboratory frame for the 5.38 kc/m collision energy, if this signal is assigned to quenching, then the quenching process is extraordinarily resonant. From Fig. 16, not only must HCl be vibrationally excited to scatter Na only in the laboratory range 15° – 70° , but only a narrow range of rotational states are accessible as well. From the experimental results of Na quenching by N_2 , H_2 , and CO measured by Hertel and coworkers, this final state selectivity was never observed. Moreover, when an additional 15 kc/m of translational energy is available at the 19.4 kc/m collision energy, the Na(3P) scattering follows the

kinematic constraints characteristic of the NaCl product. At this higher collision energy, if the mass 23 distribution was from quenching, then the final state distribution is even more restricted than at the 5.38 ke/m collision energy. These absurd conclusions rule out quenching as an important source of the Na scattering for the angular range of these measurements.

A similar argument applies for NaH formation; its mass combination is essentially identical to the quenching channel. Here too, the data at the two collision energies can only be explained by assuming a decrease in the product translational energy at the higher collision energy.

Center-of-mass energy and angular distributions were obtained using the CMLAB program written by R. Buss.³⁵ Two modifications of the program were made. First, the laser correlated TOFs were corrected for any DC offset using the cross correlated data in channels 55-200. Next, the sum of the first 50 channels where the elastic and reactive product is observed, was normalized to the difference between the Na(3P) and Na(3S) angular distributions for that angle. The Na(3P) angular distribution was multiplied by a term to correct for the different number densities contributing to the laser correlated TOFs and angular distributions, assuming 15 percent of the Na atoms are in the excited state. The program then scaled the calculated TOFs to have a total signal count equal to the calculated angular intensity at their respective angles. Trial and error fits to reduce the chi-square error in the TOF data were done to obtain final translational

energy, $P(E)$, and recoil angle, $T(\theta)$ distributions. The manner with which the integration over the beam velocities was performed was changed to a proper quadrature appropriate for nozzle beam speed distributions.

Five different data sets were optimized for best fit, uncoupled $P(E)$ and $T(\theta)$ distributions. These were

- (1) Mass 23 laser correlated TOF's, uncorrected for the $\text{Na}(3S)$, NaCl , mass 23 ion fragment depleted by the laser.
- (2) Same as (1) but corrected for laser depletion of the $\text{Na}(3S)$, NaCl fragment appearing at mass 23. Fifteen percent of the Na atoms were assumed excited by the laser in the collision volume.
- (3) Mass 58 laser correlated TOF's, uncorrected for laser depletion of the mass 58 ground state reactive scattering.
- (4) Same as (3), but corrected for laser depletion of ground state reaction assuming 15 percent of the Na atoms are optically excited.
- (5) The sum of (2) and (4) assuming equal detection efficiencies for masses 23 and 58.

The derived contour maps of the scattered flux, the observed and calculated TOF's, the observed and calculated angular distributions, and the $P(E)$, $T(\theta)$ functions corresponding to the best fits are shown in Figs. 17-24. Some fitted distributions assuming forward-backward symmetry are also shown in Figs. 25-28.

The best center-of-mass scattering distributions derived from the uncoupled recoil angle-translational energy assumption, shown in Fig.

19, provide a good overall fit to the data. Two features of the calculated curves, which are not in accord with the experimental results, are the enhanced intensity of the leading edges of the 25° and 30° laboratory TOF distributions, and a resolved, double peak structure in the 35°, 40° and 45° TOF distributions for channels near the center-of-mass.

The double peak structure is sensitive to the shape of the product translational energy distribution, $P(E)$, in the interval 0-5 kcal/m. Increasing the widths of the reactant velocity distribution by 50 percent also reduces the double peaking without serious alterations to the fit of the remaining angular and TOF data. Additionally, the numerical method used to integrate the product scattering with negligible recoil velocity distorts the calculated distributions for these channels, further enhanced by the Jacobian transformation from the $\text{cm} \rightarrow \text{laboratory frame}$.

With allowance for the above errors introduced by the method of data analysis, the poorer fits to the TOF data near the center-of-mass can also result from the RRK functional form³⁵ used to model the product translational energy distributions. The broad, flat $P(E)$ restricts the shapes allowed for the slow product. Only one parameter in the RRK function describes the rise of the $P(E)$ from $E=0$. To match the product translational energy distribution needed to fit the remaining fast product, this parameter cannot assume any arbitrary value, and a compromise value is assumed.

The fast laboratory product calculated, but not observed, in the 25° and 30° TOF distributions is probably an artifact of assuming an

uncoupled $P(E)$ and $T(\theta)$ distribution for the center-of-mass scattering. The fit to the data indicates that there should be less product with translational energy in the range 35-50 kcal/mol for center-of-mass scattering angles, $\theta < 30^\circ$.

Attempts using a tabular form for the energy and angular distributions, or radically different initial values for the Legendre series and RRK analytical scattering distributions, eventually converged to distributions similar to the best fits shown here. If the mass 58 data was added to the mass 23 data, assuming equal detection efficiencies for both masses, the best fits obtained were within the range found acceptable for the mass 23 data only. The main difference was a further reduction in the scattering intensity at 0° and 180° in the center-of-mass frame.

Fits attempted for the mass 58 data alone were poor. Reaction exothermicities 30 percent above the thermochemical value were needed to obtain even a coarse fit. The calculated and observed data were most in error for the backward scattered, slow product.

In Fig. 19, the range of angular distributions consistent with the best data fits for the mass 23 or combined mass 23 and mass 58 data are shown. The relative variations in the derived $P(E)$ distributions were much less. The indicated allowed variations are based on a reasonable guess of the sensitivity of the data to the fits.

We conclude this discussion of the derivation of the center-of-mass scattering distributions by noting that the energy dependence of the total reaction cross section was neglected. The large reaction

exothermicity diminishes the effect of the spread in collision energies produced by the reactant beam velocity distributions. In addition, the RRK form of the $P(E)$ naturally accounts for the different total energies for each Newton diagram generated in the integration over the beam velocity distributions. There is no need for the product translational energy to extend to values which apparently violate the reaction exothermicity²⁴.

In the derivation of the $P(E)$ distribution, the reaction exothermicity was a free variable. The final value obtained, 45.4 kc/m agrees favorably with the value 43.9 kc/m calculated from the $\text{Na}(3\text{S}) \rightarrow 3\text{P}$ transition energy (48.53 kc/m) and the $\text{Na}(3\text{S}) + \text{HCl} \rightarrow \text{NaCl} + \text{H}$ reaction endothermicity of 4.68 kc/m. The good agreement for the value of the exothermicity obtained from the data analysis is taken as confirmation that the mass 23 data are NaCl product fragments, and that the measured and derived distributions are faithful representations of the true $\text{Na}(3\text{P}) + \text{HCl} \rightarrow \text{NaCl} + \text{H}$ reaction.

F. DISCUSSION

In this section, we strive to understand what detailed reaction mechanism could account for the experimental observations. Any mechanism must successfully explain the four major experimental findings. These are the derived center-of-mass recoil angle and product translational energy distributions, the large enhancement in the reactivity of $\text{Na}(3\text{P})$ compared to $\text{Na}(3\text{S})$, and the lack of an observable laser polarization dependence on the NaCl product scattering. Because there are no reliable potential energy surface calculations for the $\text{Na}(3\text{P}) + \text{HCl}$ reaction, the discussion will be qualitative. We stress that the

collision process is complex, involving several electronic states, and that simple explanations are probably not possible. Even for the simpler reactions $\text{Li}(2\text{S}) + \text{HX} \rightarrow \text{LiX} + \text{H}$, $\text{X} = \text{F}, \text{Cl}$ ²⁴, subsequent trajectory studies²⁷ indicated an involved mechanism which could not be reduced to a simple description.

For the $\text{Na} + \text{HCl} \rightarrow \text{NaCl} + \text{H}$ reaction, with a covalent to ionic bond change, an electron transfer mechanism in the spirit of the alkali-halogen "harpoon" model is a good, first model for the reaction. The electron jump distance, calculated from the -23 kc/m vertical electron affinity for $\text{HCl}(v=0)$ and the 76 kc/m ionization potential of $\text{Na}(3\text{P})$, is $3.5\text{\AA}$. A negative electron affinity indicates the anion is unstable with respect to the neutral molecule and a free electron. The reaction cross section is $38\text{\AA}^2$ for this jump distance. If $\text{Na}(3\text{P})$ interacts at large distances with HCl in an analogous way as Hertel, et al. observed for N_2 , H_2 and CO , then the HCl bond is expected to stretch as the $\text{Na}(3\text{P})$ approaches. The HCl electron affinity is increased as the bond stretches, enlarging the reaction cross section. The large reaction cross section observed is then consistent with our expectations of an electron jump initiating reaction step.

The total reaction cross section is expected to be affected in approximately the same way by either Na electronic energy or HCl vibrational energy.³ This is because the vibrational excitation increases the HCl electron affinity, while electronic excitation reduces the Na ionization potential. To first order, the reaction

cross section will depend only on the energy difference between the ionization potential and electron affinity for Na and HCl, respectively.

The electron transfer mechanism early in the reaction also explains the lack of a polarization dependence in the reaction. As noted by Rettner and Zare,¹⁰ the alignment of the P orbital for the general C_s symmetry of $\text{Na} + \text{HCl}$ is not expected to affect the probability of electron transfer at the crossing point. The $\text{Na}^+ + \text{HCl}^-(^2\Sigma^+)$ state can cross all the $\text{Na}(3P) + \text{HCl}(^1\Sigma)$ states. If the $\text{Na}(3P) + \text{HCl}$ states are not substantially repulsive (<5 kcal/m) at the crossing distance, the lack of an observable effect on the product angular or velocity distributions from the initial P orbital alignment is expected, since each initial molecular collision state must go through the same $\text{Na}^+(^1S) + \text{HCl}^-(^2\Sigma^+)$ intermediate surface to reach the $\text{NaCl}(^1\Sigma^+) + \text{H}(^2S)$ products. The orbital alignment dependence seen by Rettner and Zare¹⁰ for $\text{Ca}(^1P) + \text{HCl}$ resulted from the polarized ion core formed at the electron transfer, and a number of low lying, accessible, excited Ca^+ states. The $\text{Na}^+(^1S)$ core can have no alignment, and only one low lying $\text{Na}^+ + \text{HCl}^-$ ion pair state is accessible.

The large reaction cross section implies that significant initial orbital angular momentum (L) is present. The additional $1h$ of angular momentum from the orbital electronic motion, when circularly polarized light is used in the optical pumping, cannot have a large effect on the differential cross section, as is observed.

The transformation from space to body fixed frames of reference is predicted to occur at substantial distances for the dominating long

range, $1/R^5$, dipole-quadrupole interaction of $\text{Na}(3P) + \text{HCl}$. From Eq. (2), the impact parameter dependence of the body fixed frame locking distance is

$$R_L(\text{\AA}) = 11.2 * b(\text{\AA})^{-1/3} \quad (18)$$

for the 5.38 kc/m collision energy. The $V_\sigma - V_\pi$ splitting was calculated from the formula of Buckingham.³⁶ Even if there is an adiabatic transfer from the space to body fixed axes, the ion pair intermediate will not be sensitive to the P orbital alignment, unless one of the excited potential surfaces is strongly repulsive so that it does not cross the charge transfer curve at the 5.38 kc/m collision energy. Such is not expected, nor observed.

The product energy and angular distributions, containing the most detailed information on the reaction mechanism, are more difficult to relate directly to the electron transfer model. The dominance of backward scattering suggests an early release of the reaction exothermicity. This is opposite that observed for $\text{Li}(2S) + \text{HCl}$ ²⁴, where strong forward scattering was seen. The decrease in the angular distributions at 0° and 180° center-of-mass scattering angles, and the slightly structured, non-monotonic $T(\theta)$ seem to rule out a long lived collision complex or coplanar reaction geometry. The latter might be expected by the mass combination of this reaction, with substantial initial orbital angular momentum and a low product reduced mass. The moderate enhancement at the forward scattering angles near $\theta_{\text{cm}} = 60^\circ$

is also peculiar, especially since this matches the features seen for the $\text{Li}(2\text{S}) + \text{HCl} \rightarrow \text{LiCl} + \text{H}$ reaction²⁴.

The geometry of the transition state is unknown for this reaction. The large cross section, small product reduced mass, and direct mechanism based on the structured $\text{T}(\theta)$ would seem to preclude a tightly-bound, linear geometry. A bent, or loose transition state seems more probable, since sine weighting of $\text{T}(\theta)$ shows broad sideways NaCl scattering. Noting that the $\text{NaCl}(v=0)$ internuclear separation is $2.36\text{\AA}$ and the $\text{HCl}(v=0)$ separation is $1.27\text{\AA}$, for a 90° transition state geometry, product exit parameters of $1.5\text{\AA}$ are reasonable. Taking the average product translational energy of 25 kcal/m , the product orbital angular momentum is $34\hbar$. For $3.5\text{\AA}$ impact parameters at the 5.38 kcal/m collision energy, the total initial angular momentum is $\sim 160\hbar$, implying an average $127\hbar$ must be in NaCl rotations. Neglecting centrifugal distortion, this is an average 8.9 kcal/m of product rotational energy, leaving an additional 15 kcal/m for product vibrational energy. The slower, forward scattered product seen in the 25° and 30° laboratory TOF would be a consequence of larger NaCl rotational excitation, necessary to satisfy angular momentum conservation if the forward scattering correlates with larger impact parameter collisions. For the broad product translational energy distribution observed, the utility of an average product translational energy is dubious.

The early release of the reaction exothermicity is expected, since HCl is known to dissociate by low energy electrons to $\text{H} + \text{Cl}^-$.³⁷ Hence, at the transfer distance, the slow electron will initiate the H

atom departure by dissociate attachment. The extent of the interaction between the forming $\text{Na}^+ \text{Cl}^-$ molecule and departing H atom is not known. The large product translational energy suggests this exit channel coupling is small. Conversely, the forward scattering of the product angular distribution in alkali-halogen reactions has been related to charge migration^{4b}. This involves significant interaction among all three atoms. The current case of a light hydrogen atom leaving is expected to reduce the three particle interaction times considerably.

A more detailed analysis of the $P(E)$, $T(\theta)$ distributions must wait until more is known about the PES of this reaction.

G. CONCLUSION

The crossed-molecular beams technique has measured the NaCl product center-of-mass scattering distribution for the reaction

at a collision energy of 5.38 kcal/m. The enhanced cross section for reaction of Na(3P) vs. Na(3S) atoms and the lack of an observable polarization dependence for the reaction is consistent with the expected electron transfer reaction mechanism. The product energy and angular distributions indicate a predominance of sideways scattering, unlike the $\text{Li}(2S) + \text{HCl} \longrightarrow \text{LiCl} + \text{H}$ reaction²⁴, where forward scattering was observed. The large initial orbital angular momentum does correlate predominately (~80 percent) with product rotation as expected for this mass combination. Significant product translational energy is favored by the repulsive energy release initiated by dissociate attachment of HCl from the transfer of the sodium P orbital electron.

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FIGURE CAPTIONS

Fig. 1. Schematic representation of how different laser beam E and k vector directions relative to the collision plane determine the initial, asymptotic distribution of P orbitals. On the left hand side, the laser propagates in the scattering plane. When the E vector is perpendicular to the collision plane (top), $|p_{\pi}^{-}\rangle$ states are preferred with negative reflection symmetry. With the E vector in the collision plane, a mixture of $|p_{\pi}^{+}\rangle$ and $|p_{\sigma}\rangle$ states are formed, depending on the angle between the relative velocity vector and the laser E vector. On the right hand side, the laser beam propagates perpendicularly to the collision plane. The top (bottom) figure shows that if the E vector is perpendicular (parallel) to the relative velocity vector, $|p_{\pi}^{+}\rangle$ ($|p_{\sigma}\rangle$) states are preferred.

Fig. 2. Cross section of the seeded Na atom source. Components are (a) Main Na reservoir, (b) Reservoir heating cables, (c) gas inlet tube, (d) ceramic support posts for inlet tube radiation heater, (e) flow constrictor, (f) nozzle tube, (g) nozzle tube heating elements, (h) nozzle disk, (i) oven copper support block, (j) nozzle alignment bolts, (k) heated skimmer, (l) skimmer heaters, (m) pre-skimmer, (n) pre-skimmer heaters, (o) defining slits, (p) radiation shields, (q) beam flag, (r) reservoir thermocouple, (s) nozzle chamber bulkhead.

- Fig. 3. Cross sectional view of HCl keyed beam source; (a) nozzle, (b) nozzle heater block, (c) nozzle alignment fixture, (d) gas inlet tube, (e) skimmer, (f) nozzle bulkhead.
- Fig. 4. $\text{Na}(3^2\text{S}_{1/2})$, $\text{Na}(3^2\text{P}_{1/2})$, and $\text{Na}(3^2\text{P}_{3/2})$ electronic state hyperfine structure. The double headed arrow shows the two level system used for optically pumping a steady state fraction of Na atoms to the $3^2\text{P}_{3/2}$ state.
- Fig. 5. Doppler shifted fluorescence for He (top) and Ne (bottom) seeded Na atom beams. Δf measures the $F=2 \rightarrow F'=3$ transition shift. The bottom trace is a relative frequency standard derived from an etalon.
- Fig. 6. $\text{Na}(3\text{S}) + \text{HCl}$ scattering angular distributions measured at the two collision energies at mass 23 (top) and mass 58 (bottom). The signal is measured in units of the experimentally observed count rates.
- Fig. 7. Calculated and observed NaCl product angular distribution for the $\text{Na}(3\text{S}) + \text{HCl}$ reaction. A constant product energy and recoil angle distribution was assumed. The good fit to the data indicates that the recoil velocity is so small, that no information on the structure of the center-of-mass scattering distribution can be obtained of this energy at the current apparatus resolution.
- Fig. 8. Newton diagrams for the $\text{Na}(3\text{P}) + \text{HCl}$ system at the two collision energies measured in the experiment. The hatched areas show the FWHM velocity distributions at each beam, and

the distribution of center-of-mass angles resulting from the reactant beam velocity spreads. The maximal NaCl product velocity is restricted to the circle drawn about the center-of-mass by conservation of energy. The laboratory angles tangent to these circles are the nominal maximum scattering angles for observation of NaCl product.

Fig. 9. Mass 23 angular distributions corrected for fragmentation of NaCl reaction product assuming different fragmentation ratios.

Fig. 10. Angular distributions observed with laser on and off at mass 23 (top) and mass 58 (bottom) at the two experimental collision energies. At mass 23 and 5.38 kc/m collision energy, the enhancement of the signal caused by the laser excitation is clear, while at mass 58 and 19.4 kc/m collision energy, the enhancement is barely observable.

Fig. 11. Na(3P) + HCl scattering angular distributions measured at the two collision energies at mass 23 (top) and mass 58 (bottom). Error bars are 1 standard deviation of the mean. The signal is in units of the observed count rates.

Fig. 12. Na(3P) + HCl mass 23 angular distributions, corrected for NaCl product fragmentation assuming different fragmentation ratios.

Fig. 13. Experimental laser correlated time-of-flight distributions at mass 23 for the indicated laboratory angles. At 25° and 30°, elastic scattering of Na(3P) atoms can be easily seen.

The slow, broader peak at all angles is assigned to NaCl product which fragments in the electron impact ionizer to Na^+ .

Fig. 14. Experimental laser correlated time-of-flight distributions of mass 58 at the indicated laboratory angles.

Fig. 15. Laser induced scattering as a function of the resonance fluorescence intensity. If the experiment is operating correctly, the data should fall on a straight line. The straight line is an "eyeball" fit to the data indicating that, to first order, this is true.

Fig. 16. Newton diagram showing the laboratory angular range accessible to the inelastic $\text{Na}(3P) + \text{HCl}$ quenching channel, or the NaH product reaction channel. The inelastic channel is labeled by the vibrational product state of the HCl, and the maximum HCl rotational level accessible for that vibrational state. The two circles showing NaH product are based on different values for the NaH bond energy.

Fig. 17. Calculated and observed laboratory angular distributions for the 5.38 kc/m collision energy, $\text{Na}(3P) + \text{HCl}$ reaction using a 5 term legendre expansion in the center-of-mass scattering angle and an RRK function for the translational energy.

Fig. 18. Calculated and observed laboratory product arrival distributions for selected laboratory angles for the 5 term legendre expansion of fig 17.

- Fig. 19 Best fit $P(E)$ and $T(\theta)$ distributions for the 5 term legendre series. The shaded areas and hatch marks delimit the allowed range of the functions with essentially no discernable change in the quality of the fit to the data.
- Fig. 20 Contour product flux map for the distributions of fig. 19.
- Fig. 21 Calculated and observed angular distributions for a 7 term legendre series.
- Fig. 22 Calculated and observed TOF data for the 7 term legendre series.
- Fig. 23 Best fit $T(\theta)$ and $P(E)$ functions for the 7 term legendre series.
- Fig. 24 Contour product flux map for the 7 term legendre series.
- Fig. 25 Laboratory angular distributions for the best fit center-of-mass scattering distributions with forward-backward symmetry. The poor quality of the fits show that the reaction is definitely backward scattered.
- Fig. 26 TOF data observed and calculated for the forward-backward symmetric scattering distribution.
- Fig. 27 Best fit $T(\theta)$ and $P(E)$ functions for the forward-backward symmetric scattering distribution.
- Fig. 28 Product flux contour map for the forward-backward symmetric best fit distributions of fig. 27. Note that the symmetric case shows an increase in the intensity near 60° , similar to the 5 and 7 term legendre expansions.

XBL 836-5864

Fig. 1

18- 224 8115

Fig. 2

XBL 834-9474

Fig. 3

Fig. 4

KBL 836-5967

Fig. 5

RHM 856 5814

Fig. 6

Fig. 7

x0L030-3031

Fig. 8

XBL836-3833

Fig. 9

Fig. 10

Fig. 11

XBL836-3832

Fig. 12

Mass 23 Laser Correlated
TOF Distributions

18L 836-3549

Fig. 13

Mass 58 Laser Correlated
TOF Distributions

Fig. 14

XBL 836-5860

Fig. 15

XBL 836-5947

Fig. 16

5 Term Legendre Series

XBL 837-10702

Fig. 17

Fig. 18

XBL 837-10705

Fig. 19

Fig. 20

XBL B37-10703

Fig. 21

Fig. 22

$$E_{\text{col}} = 5.38 \text{ kc/m}$$

7 Term Legendre Series

XBL 837-10698

Fig. 23

$$E_{\text{col}} = 5.38 \text{ kc/m}$$

7 Term Legendre Series

Fig. 24

(Forward/Backward Symmetric Scattering)

XBL 837-10701

Fig. 25

Fig. 26

(Forward/Backward Symmetric Scattering)

XBL 837-10709

Fig. 27

$$E_{\text{col}} \approx 5.35 \text{ kcal/m}$$

(Forward/Backward Symmetric Scattering)

KBL 837-10704

Fig. 28

APPENDIX III. OPTICAL PUMPING STUDIES OF THE $\text{Li } 2\text{S} \rightarrow 2\text{P}$ AND $\text{Na } 3\text{S} \rightarrow 3\text{P}$ TRANSITIONS

A major problem in studying the collision dynamics of excited atomic states is the creation of a large fraction of the atoms in the excited state. Because most atoms have a multiplicity of hyperfine levels in the ground electronic state, a single laser frequency is unable to produce, in general, a steady state fraction of the atoms in the excited state. Usually, the excited state can decay by spontaneous emission to ground state hyperfine levels not resonant with the laser frequency. Consequently, after a few spontaneous emission cycles, initially resonant atoms will no longer be excited by the laser. The usable fraction of excited state atoms in the collision volume will be less than 1 percent.

To study excited state atom reactions for atoms other than sodium, it is necessary to develop optical pumping schemes matched to their ground state hyperfine structure. In this appendix, the results of a preliminary study of the feasibility of creating a steady state excited population of $\text{Li}(2\text{P})$ is presented. Lithium was chosen because its small number of electrons make its reactions attractive for ab initio electronic structure calculations of the reaction potential energy surfaces. Such calculations compare experimental results with basic theory, deepening the understanding of the collision process. As will be shown below, creating excited state Li atoms also represents the next stage in experimental complexity.

Let us begin by reviewing how sodium can be efficiently excited to

the $3^2P_{3/2}$ state. First, the transition intensity is strong and can be saturated with available cw lasers. Second, the frequency of the $3S \rightarrow 3P$ transition is near the peak of the rhodamine 6G dye emission curve. With readily obtained commercial laser hardware and a minimum of effort, the long term stability of the dye laser power and wavelength insured that this component of a molecular beam experiment is dependable. Third, by simply controlling the laser frequency, 30 percent of the sodium beam can be continuously excited when the transition is saturated. As discussed in Chapter 3, this was a consequence of the selection rules on the total angular momentum for spontaneous emission. When the $3S(F=2) \rightarrow 3P(F'=3)$ transition is excited, and the laser bandwidth and power broadening are less than the $3P(F'=2) - 3P(F'=3)$ 65 MHz splitting, an isolated, two-level system results

Now consider the example of optically pumping the $3^2P_{1/2}$ spin orbit level. Figure 1 shows the level structure for this transition. If the laser were tuned to excite the $F=2 \rightarrow F'=1$ transition, and the light linearly polarized, the $|M|=2$ magnetic sublevels of the $F=2$ ground state would not be excited to the $F'=1$ level because of the selection rule $\Delta M=0$. However, spontaneous emission connects the $3^2P_{1/2}$ ($F'=1$), $|M|=1$ magnetic sublevels to these "dark," $3^2S_{1/2}$ ($F=2$), $|M|=2$ magnetic sublevels. Consequently, after a very few spontaneous emission cycles, all of the atoms would be in the $3^2S_{1/2}$ ($F=2$), $|M|=2$ sublevels, even if there were no spontaneous decay to the $3^2S_{1/2}$ ($F=1$) ground state hpf level.

Let us then suppose that both the $3^2S_{1/2}$ ($F=1,2$) $\rightarrow 3^2P_{1/2}$ ($F'=2$) transitions are pumped with two linearly polarized lasers. In this

case, the $3^2S_{1/2}$ ($F=2$), $M=0$ magnetic sublevel is a trap because it has no transition moment to the $3^2P_{1/2}$ ($F'=2$) state for linearly polarized light. An additional laser, tuned to the $3^2S_{1/2}$ ($F=2$) $\rightarrow$ $3^2P_{1/2}$ ($F'=1$) transition, is needed. In this manner, one can show that no combination of two laser frequencies of circular or linear polarization can optically pump a steady fraction into the $3^2P_{1/2}$ spin orbit state.¹

Pritchard² has suggested that the application of a weak magnetic field perpendicular to the laser polarization axis is sufficient to remove the $M=0$ trap. (The Larmor precession frequency, if fast on the time scale of a few spontaneous emission cycles, will mix the M sublevels and stop population accumulation in the $M=0$ sublevel). In a scattering experiment with $\text{Na} + \text{Ar}^2$, a 17 percent reduction in the scattered Na intensity was observed when two laser frequencies were used to excite the $3^2P_{1/2}$ spin orbit state. This was taken as a measure of the fraction of sodium atoms pumped. To create the two frequencies, a molecular beam of sodium atoms was crossed nonorthogonally by a laser beam which was reflected upon itself. These two counterpropagating laser beams, if the angle between the laser and molecular beams is chosen correctly, are doppler shifted by the ground state hpf splitting of 1.77 Ghz, and for some fraction of the atomic beam, the two resonance conditions are met.

The above problem for optical pumping of the $3^2P_{1/2}$ spin orbit level was a consequence of the upper level having less than or equal total angular momentum than the ground state levels, and integral values for the total angular momentum. An additional problem, coherence trapping, can arise when two ground states are connected to a common

upper level by resonant cw radiation even if there are no magnetic sublevel traps. Much theoretical work on coherence trapping has recently appeared,³⁻⁶ as well as some experimental verification.^{3,7} Figure 2a shows the three state level structure called a lambda system. If two monochromatic resonant fields are used to pump both ground states to the excited state, and both are at resonance, then it can be shown that the steady state population in the upper state is zero.³ The two laser fields create a coherence between the two ground state levels, such that the phases between the ground state amplitudes in the complete wavefunction uncouples the system from the driving fields. An alternative view shows that the system executes Raman transitions between the two ground state levels, with the excited level acting as a virtual state.

In an experiment, before the atoms enter the laser fields, there is no coherence between the two ground states. In the presence of the laser fields, two new ground basis states can be formed which are linear combinations of the original states. One of these states is coupled, the other uncoupled, from the laser fields.³ As spontaneous decay occurs, the atoms in the optically coupled state are continuously depleted. Two laser frequencies are no better than one in producing a steady state excited population.

A theoretical study of the effects of laser bandwidth and detuning for a three level lambda system driven by two laser fields has been reported by Knight.⁵ In particular, he examined the effects of phase correlation between the two laser fields on the coherence trapping. The individual laser fields were allowed to have phase fluctuations,

but the field amplitudes (and Rabi frequencies) were assumed constant. In this model, the constant field amplitude approximation enables a final separation of the atomic variables from the field equations. With the inclusion of uncorrelated fluctuations for each of the applied fields, the coherence trapping is reduced by the off-resonant frequency components from the fluctuating phases. If, however, both fields are critically cross-correlated, that is, the phase fluctuations between the two fields are dependent, then the coherence trapping is preserved, even in the presence of the fluctuations from the individual fields.

In this appendix, the model developed by Knight is extended to consider the asymptotic state distributions for a three level lambda system driven by two nearly resonant, phase fluctuating laser fields with variable cross-correlation. This model is applied to experimental observations of fluorescence and ionization yields when the ^6Li isotope is optically pumped by two, cw, single-mode optical fields, one derived from the other by acousto-optic modulation. The acoustic modulation frequency is set equal to the $2^2S_{1/2}$ ($F=1/2$)-(F=3/2), 228 Mhz hpf splitting. The modulator stability is quite high, and since the two frequencies are derived from the same laser, they have precisely the same phase fluctuations. In this way, the two laser fields have a fixed frequency difference which is independent of the laser bandwidth, i.e., they are critically cross correlated. The hyperfine structure of the ^6Li , $2P_{3/2}$ level is shown in Fig. 2(b). Unlike ^{23}Na , the ^6Li hyperfine structure is overlapped within the 6 Mhz radiative linewidth. A single mode, single frequency dye laser is unable to create a steady state $2P_{3/2}$ population, as spontaneous emission will connect the

overlapped $^2P_{3/2}$ levels with both ground state hyperfine levels. However, ^6Li , with half integral total angular momentum, has no M level traps and the $\text{Li}(2S \rightarrow 2P)$ transition is located near the maximum of the DCM dye laser emission. Experimentally, sufficient laser power (80 mW) and stability are readily obtained such that if the intrinsically overlapped excited state hyperfine structure and coherence trapping problems can be solved, $^6\text{Li } ^2P_{3/2}$ scattering experiments should be straightforward.

We now derive the steady state populations of a three level lambda system, beginning with the optical Bloch equations obtained by Knight and Dalton.⁵ These equations were derived from a quantized treatment of the laser fluctuations, which are modeled as a stochastic process. The Bloch equations were obtained by using a reduced density matrix for the atom-laser system, making the usual rotating wave approximation. Lamb shifts of the atomic levels and the variation of the Rabi frequency with the laser coherent states (field amplitudes) are ignored. As we are only concerned with the atomic level populations, irrespective of the state of the laser field, the Bloch equations reduce to a simple set of linear coupled differential equations with constant coefficients.

For the time independent solution to these equations, we follow the method of Stroud.⁸ For ease of computer calculation, we also redefine the off-diagonal density matrix elements into their real and imaginary parts. Additionally, we define two new diagonal elements which are the sum and difference of the populations in the two ground

state levels. As noted by Stroud, the nine differential equations for the density matrix elements are dependent when the time derivative is set to zero. We reduce this to a non-singular set of equations, by defining new variables which are the old variables divided by the sum of the populations in the two ground states. This sum is never zero. The equation involving the sum variable is discarded. The solution is easily provided by available software. The actual equations are given by Eq. (1). In Eq. (1), γ_{12} and γ_{10} are the spontaneous decay rates from level 1 to levels 2 and 0, respectively, δ_a and δ_b are the detunings from resonance for the fields a and b, ζ_a and ζ_b are the Rabi frequencies for the two laser fields, Δ_{aa} and Δ_{bb} are the uncorrelated phase fluctuation bandwidths for the fields a and b, and Δ_{ab} is the cross-correlated bandwidth. D is the difference between the two ground state populations normalized to their sum i.e., $D = (\sigma_{22} - \sigma_{00}) / (\sigma_{22} + \sigma_{00})$. R_{ij} and I_{ij} are the real and imaginary off-diagonal density matrix elements, normalized to the two ground state populations, viz,

$$R_{ij} = \frac{\sigma_{ij} + \sigma_{ji}}{2(\sigma_{00} + \sigma_{22})} \quad , \quad I_{ij} = \frac{\sigma_{ij} - \sigma_{ji}}{2(\sigma_{00} + \sigma_{22})} \quad . \quad (2)$$

Finally, $\sigma_{11}' = \sigma_{11} / (\sigma_{00} + \sigma_{22})$, where σ_{11} is the excited state population.

Figure 3 shows the dependence of the excited state population on the detunings from resonance of each of the fields, on the Rabi frequencies of the applied fields, and on the amount of cross-

$$\begin{bmatrix}
 0 & \frac{y_{12}-y_{10}}{2} & -\epsilon_a/2 & 0 & 0 & \epsilon_b/2 & 0 \\
 0 & -(y_{10}+y_{12}) & -\epsilon_a & 0 & 0 & 0 & 0 \\
 \epsilon_a/2 & \epsilon_a/2 & -(a_{aa} + \frac{y_{10}+y_{12}}{2}) & -a_a & 0 & 0 & 0 \\
 0 & 0 & a_a & -(a_{aa} + \frac{y_{10}+y_{12}}{2}) & -\epsilon_b/2 & 0 & 0 \\
 0 & 0 & \epsilon_b/2 & 0 & -(a_a+a_b) & \epsilon_a/2 & 0 \\
 0 & 0 & 0 & \epsilon_b/2 & -(a_{aa}+a_{bb}-2a_{ab}) & 0 & \epsilon_a/2 \\
 -\epsilon_b/2 & \epsilon_b/2 & 0 & 0 & 0 & -(a_{bb} + \frac{y_{10}+y_{12}}{2}) & -a_b \\
 0 & 0 & 0 & 0 & -\epsilon_a/2 & a_b & -(a_{bb} + \frac{y_{10}+y_{12}}{2})
 \end{bmatrix}
 \begin{bmatrix}
 0 \\
 a_{11} \\
 R_{01} \\
 l_{01} \\
 R_{02} \\
 l_{02} \\
 R_{12} \\
 l_{12}
 \end{bmatrix}
 =
 \begin{bmatrix}
 0 \\
 0 \\
 \epsilon_a/2 \\
 0 \\
 0 \\
 0 \\
 \epsilon_b/2 \\
 0
 \end{bmatrix}
 \quad (1)$$

correlation between the two laser fields. The unit of frequency is taken as the total spontaneous emission rate from the excited state.

The experimental configuration of Fig. 4 was used to investigate the optical pumping of Li. A similar study was done by Baum, et al.⁹ In the present experiment, a heated tantalum oven, similar to that used in a previous molecular beam study,¹⁰ creates a Li atomic beam which is illuminated at right angles by two, coaxial cw laser beams, of spot size 2mm. The two frequencies were obtained by passing the output of a commercial single mode dye laser (operating with DCM dye and tuned to the $2S \rightarrow 2P$ transition at 6709 angstroms), through a commercial acoustic-optic modulator (Intra-Action) set for the 228 MHz ground state hpf splitting. The applied frequency was measured with a microwave counter. The two frequencies were recombined on a Glan-Thompson prism by rotating the polarization of one of the beams. The beams were made coaxial by overlapping them at two points separated by thirty feet, with the molecular beam intersection point approximately midway between the alignment points. The beams are linearly polarized, with their polarizations at right angles to each other. The power in each beam could be adjusted with filters, and the frequency shift changed over the range 200-230 MHz with the acoustic-optic modulator. The laser bandwidth was estimated using a scanning Fabrey-Perot with 1.5 GHZ FSR, finesse 200, and found to be less than 10 MHz.

Measurements consisted of monitoring the fluorescence from the illumination zone and scanning the dye laser frequency. The fluorescence is proportional to the excited state population. As the laser

is scanned, the absolute frequency is not recorded, so the position of maximum fluorescence relative to the transition resonance is not known. To compare with the calculations, we use the maximum seen during the frequency scan. Figure 5 shows typical fluorescence scans with and without the second laser beam. As the fluorescence is polarized, and the photomultiplier views only a small solid angle of the total emission, and the two laser beam's polarizations are orthogonal, the fluorescence induced by each laser is not detected with equal efficiency.

The results of the experiments show that the expected increase from the presence of the second laser was not realized. Given the Li atom velocity and the laser beam diameter, the atoms spend approximately 50 spontaneous lifetimes in the laser beam. If the second beam was able to saturate the three level system as expected, the fluorescence should have increased by at least one order of magnitude. Instead, only a 50 percent non-additive increase was observed. The model calculations would explain this (assuming the maximum possible cross-correlation was present between the two fields) if the laser power in one beam was sufficient to pump both transitions. In Fig. 3, the population in the upper level is shown for different laser powers assuming that only one field drives the transitions. The calculations, with cross-correlation, show that at high power, both the one and two frequency experiments are able to excite near the maximal fraction. However, the two frequency case is ten times more efficient at low powers. In the experiments, no improvement was seen with the second laser frequency at lower powers.

To understand the deviations of the observations from the model predictions, we reconsider the assumptions of the optical pumping model which would invalidate the predictions we have made. First, the model calculations assume that the power broadening is not commensurate with the ground state hpf splitting. This is definitely not the case at the high powers of some of the experiments. In particular, see Fig. 5(a). Second, the phase fluctuation model also predicts a Lorentzian laser lineshape which overestimates the power in the wings of the laser line. The result of this error is to overestimate the effectiveness of the off-resonance pumping. Third, we have assumed the two laser frequencies are critically cross correlated. The experimental results appear closer to the uncorrelated model calculations. If this were the case, the excited state population would be substantial. Finally, the approximation of the ${}^6\text{Li}$, ${}^2\text{S}_{1/2}(F=1/2, 3/2) \rightarrow {}^2\text{P}_{3/2}(F=5/2, 3/2, 1/2)$ level structure as a 3 level lambda system is also incorrect. Instead, there are 18 levels, with several sets of inter-connected lambda systems. The presence of the other, slightly non-degenerate, F levels in the ${}^2\text{P}_{3/2}$ state may effectively dephase the coherence in the individual lambda systems, in effect, uncorrelating the laser fields. A more elaborate density matrix treatment is necessary, incorporating all m sublevels, to ascertain the importance of this approximation.

To check the hypothesis that the three level system was already saturated by one strong field, a second set of experiments was done using a pulsed dye laser in addition to the optical pumping laser. To measure the excited state population without resorting to relative

fluorescence yields, we chose to ionize the 2P population by resonant multi-photon ionization through the 3D intermediate state as outlined by Payne.¹¹ The pulsed laser, of 10 nanosecond duration, takes a "snapshot" of the $2^2P_{3/2}$ population. If this ionization step can be saturated, then the ion yield, as a function of the parameters of the optical pumping cw laser, will provide us with the required information about our pumping scheme.

As an absolute calibration, the pulsed laser can be used to ionize the ground state by the sequence $Li(2S) \rightarrow 3P \rightarrow Li^+ + e^-$. The $2S \rightarrow 3P$ photon is obtained by doubling pulsed, visible light. The residual pulsed visible light is sufficiently energetic to ionize the 3P state. If the ion yield can be saturated with respect to both the visible and doubled wavelengths, then the ion yield from the ground state ionization scheme will measure the density of Li atoms at the crossing of the cw laser. Comparing the ion yield for the ground and excited states will provide directly the fraction pumped.

The ground state signal was ionized and saturated, as shown in Fig. 6. However, no significant signal was seen from the excited state (i.e., <.1 percent of the ground state signal), with one or both cw frequencies present.

As a check, the same experiment was performed for Na, where we know that a large fraction of the atoms can be excited. The results are shown in Fig. 7. Here, the overlap of the cw and pulsed beams was done by maximizing the ion signal from the 3P state. The cw beam was unfocused so it would be larger than the cross section of the pulsed

beam. The pulsed beam was unfocused, and its cross section determined by an aperture. Once the $3P \rightarrow Na^+$ ion signal was maximized with respect to the cw laser beam position, only the dyes were changed in the pulsed laser to measure the ground state signal. Again, all signals were saturated and resonant as expected. (In regard to this last point, care was taken to be sure that the pulsed laser was operating with a low level of amplified spontaneous emission. Initial experiments indicated that the intermediate state (4D or 4P) resonance was quite broad. This was found to be from amplified spontaneous emission and the large oscillator strengths of these transitions.) The absolute determination of the 3P/3S ratio for sodium was very small by this technique. Additionally, no depletion of the ground state ion signal by optical pumping with the cw laser to the 3P state was seen.

If the Rabi frequency of the cw 3S-3P transition is large compared to the time duration of the ionization laser pulse, then it might be possible to so strongly saturate the ionization step, that as the atoms cycle between the 3S and 3P states, they can all be removed by the ionization laser. To check this, the uv power was reduced so the ion signal was several orders of magnitude lower than when saturated. Again, no depletion was obtained. If the Na beam was blocked, the ion signal disappeared.

To explain the results, we are forced to assume either an error in the experiment, or in our naive model for the ionization process. With regard to the former, the apertures in the vacuum chamber near to the

ion collector were efficient at ion production if the pulsed laser was not properly aligned. Back reflections from the optical windows also produced ion signal if the laser beam was not aligned properly. It is known that aromatic compounds are ionized efficiently and sometimes dissociatively by uv light. The silicone pumping fluid could then contribute some signal, but the resonant conditions for the ionizing frequencies cast doubt on this interpretation. Most probably, the total ion yield, which depends on the knowledge of the system for the duration of the pulsed laser excitation, is not simply a matter of our naive view of 30 percent of the population in the 3P state. Instead, it might depend on the amount of 3S character in the wavefunction. More elaborate experiments and models will be needed to check the behavior of Na or Li atoms in the presence of several saturated resonant fields and with access to a continuum decay.

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FIGURE CAPTIONS

- Fig. 1. ^{23}Na hyperfine structure for the $3^2S_{1/2}$ and $3^2P_{1/2}$ electronic states. The solid lines with double headed arrows show the m levels connected by simulated emission by the two, linearly polarized lasers tuned to the $^2S_{1/2} (F=1,2) \rightarrow ^2P_{1/2} (F'=1)$ transitions. The wavy, single headed arrows show which ground state m sublevels are connected to the $F'=1, M=-1$ sublevel by spontaneous emission. It can be seen that the $3^2S_{1/2} (F=2), M = -2$ sublevel is a trap by this optical pumping scheme.
- Fig. 2. (a). Three level lamda system. δ_a and δ_b are the frequency offsets of the two applied fields (whose frequencies are ω_1 and ω_2) from the $0 \rightarrow 1$ and $2 \rightarrow 1$ transition resonances. Γ_{10} and Γ_{12} are the spontaneous emission rates from level 1 to levels 0 and 2 respectively.
- (b). Hyperfine structure of the $2^2S_{1/2}$ and $2^2P_{3/2}$ states for ^6Li .
- Fig. 3. (a). Fraction 1, steady state population in the excited level of the lamda system shown in Fig. 2(a). ζ is the rabi frequency of the fields, in units of the total spontaneous decay rate from state 1. $\Delta_{ab}=1$ and 0 are the limits of full or no cross-correlation between the laser fields. The family of curves on each graph shows the dependence of the excited state population as one frequency is scanned with the other held fixed at different frequency offsets from resonance. The offset frequency is the location of the node in the curves.

(b). Power dependence of the excited state asymptotic population when one laser field is scanned through the lambda system. The $\delta_a - \delta_b$ frequency offset corresponds to the ${}^6\text{Li } 2^2\text{S}_{1/2}$ hyperfine splitting.

Fig. 4. Experimental arrangement used to study the optical pumping and ionization of Li and Na atoms. An Ar ion laser pumps a commercial dye laser, which passes through an acousto-optic modular (AOM). The two output frequencies are recombined on a prism, then orthogonally cross the atomic beam. The fluorescence is imaged onto a photomultiplier by a lens/spatial filter combination.

Fig. 5. Frequency dependence of ${}^6\text{Li}$ fluorescence observed for several different laser powers. The curves on the left hand side are for a single laser frequency. The curves on the right hand side were observed when both laser frequencies derived from the acousto-optic modulator excited the Li beam.

Fig. 6. Li^+ ion yield vs. laser power for the $2\text{S} \rightarrow 3\text{P}$ transition (solid line) and the $3\text{P} \rightarrow 4\text{D}$ transition (dashed line).

Fig. 7. Na^+ ion yield vs. laser power for the $3\text{S} \rightarrow 3\text{P}$ transition (solid line) and the $3\text{P} \rightarrow 4\text{D}$ transition (dashed line).

$^{23}\text{No} (I = 3/2)$

XBL836-5862

Fig. 1

xBL636-3861

Fig. 2

XBL 836-5056

Fig. 3

Fig. 4

Fig. 5

Power

Fig. 6

XBL 836-5050

X01036-5857

Fig. 7

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