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THE DYNAMICS OF NONREACTIVE INELASTIC ION-MOLECULE COLLISIONS

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ABSTRACT

A tandem electrostatic energy analyzer molecular beam apparatus has been built for studying low energy inelastic 180° scattering of alkali ions from molecules. A beam of essentially monoenergetic ions is produced by a first analyzer and is focussed on the center of a scattering cell containing essentially stationary molecules. Ions which are not significantly deflected in their laboratory motion after collisions with the molecules are energy analyzed with a second analyzer. The scattered beam intensity detected at a particular final laboratory energy is attributable to collisions resulting in a distinct amount of inelasticity.

The $\text{Na}^+ - \text{H}_2$, HD, D_2 scattering was studied in the relative energy range of 0.74 - 30. eV. The $\text{Na}^+ - \text{D}_2$ system shows predominantly vibrationally elastic scattering below 8 eV relative energy. Above 8 eV the most probable inelasticity observed increases monotonically with the initial collision energy and is comparable to excitation to higher vibrational levels. At 17 eV this inelasticity is 3.92 eV.

Classical trajectory calculations are used to study the contribution of different collision orientations to the scattering spectra. It is found that collisions in which the projectile approaches the molecule along the bisector of its bond yield the most significant contribution to the backscattering spectra. It is shown that all backscattering can be accounted for by considering only zero impact parameter collisions. The results of trajectory calculations using a dumbbell repulsive ion molecule interaction potential on collisions restricted to zero impact parameter are fit to the experimental data. Through the discrepancies in the fit it is found that the ratio of the stiffness of the interaction potential along the collinear axis to that in the molecular bisector plane is greater than that ratio for the dumbbell potential.

I. INTRODUCTION

The physical and chemical behavior of molecules in many phenomena is strongly dependent upon their internal energy. For example, the reaction coordinate for almost every chemical reaction includes vibration on at least either the side of the reactants or the products. The significance of this simple fact is greatly enhanced by the added complication that energy transfer between translational and vibrational degrees of freedom is slow relative to the molecular collision rate. From a classical viewpoint the primary reasons for this are twofold: often only a small fraction of the possible collision orientations result in a significant amount of vibrational excitation, and from the kinematics of the colliding system, often only a small fraction of the total energy available in a collision can be transferred; even in the most favorable orientation. The consequence of these facts is that the rate at which the reactant molecules appear in the appropriate vibrational state for reaction can play an important part in determining the overall rate of reaction. Thus, understanding the dynamics of vibrational excitation through collisions is a problem which is basic to the field of chemical kinetics.

More generally, however, the simple lack of efficiency in the conversion of translational energy into vibrational energy suggests the need for a detailed understanding of the dynamics of the transfer in understanding physical processes involving vibrational relaxation. Transition probabilities can be determined from experiments involving

the measurement of vibrational relaxation times, but these results do not offer any knowledge of the dynamics of the individual molecular encounters. In molecular beam experiments the inelasticity and angular deflection of the particles engaged in a collision are measured. The distribution of these quantities resulting from collisions of all initial orientations can lead to an understanding of the dynamics of the collisions. The experimental studies of the dynamics of vibrational excitation undertaken in this work were performed using molecular beam techniques.

In the particular technique used in these experiments, alkali ions are created and accelerated to the desired laboratory energy. The target molecules, typically molecular hydrogen, are essentially stationary in the laboratory and are hit by the projectile ions. The total energy available in the collision, the relative energy, is less than the laboratory energy of the projectile ions and is given simply by

$$E_r = \frac{m_t}{m_p + m_t} E_l \quad , \quad (I-1)$$

where m_p and m_t are the mass of the projectile and target, respectively, and E_l is the laboratory energy. Only projectiles which are heavier than the target molecules are used so every projectile is left with some forward translation after a collision. In addition, only ions which are deflected very slightly or not at all in the laboratory are capable of being detected. This assures that only the ions which either miss by a large distance or make very direct contact with the

molecules are observed. By measuring the final laboratory energy of the ions, the amount of energy transferred in collisions is determined. In direct or head-on collisions it is assumed that rotational excitation must be largely suppressed, allowing the problem of translational-vibrational energy transfer to be studied directly.

It is obviously advantageous in studying any particular intermolecular process to start with the most simple systems. In these studies of the dynamics of collisional vibrational excitation of molecules the alkali ion - hydrogen molecule system has been chosen for that reason. Molecular hydrogen is the simplest diatomic molecule and alkali ions are the simplest charged particles that are more massive than the target molecule. The charge on the projectiles makes their physical properties (velocity and position) relatively easy to select and analyze. The fact that the electronic structures of the colliding particles are closed shell precludes the transfer of energy into anything but rotational and vibrational excitation and dissociation below initial relative energies of about 10 eV.

In recent years significant experimental molecular beam studies have been made on alkali ion - hydrogen molecule systems. Toennies et.al.¹⁻⁴ have studied the $\text{Li}^+ - \text{H}_2, \text{D}_2$ systems at relative energies ranging from 0.6 to 60 eV, Dittner and Datz⁵ have studied the $\text{Na}^+, \text{K}^+ - \text{H}_2, \text{D}_2$ systems in approximately the same range, and van Dop, Boerboom, and Los⁶ have examined the $\text{K}^+ - \text{H}_2, \text{D}_2$ systems at energies up to 200 eV. All of these studies, which are primarily concerned with measuring the inelasticity of head on or near head on collisions,

show an increasing fraction of the relative energy appearing as internal energy as the collision energy is increased. This follows the trend expected for simple collisional excitation. Above a relative energy of about 27 eV the Li^+ and K^+ scattering show evidence of a second process of greater inelasticity than the simple collisional excitation which, above some lower energy, has become collisional dissociation. For the Li^+-H_2 system² this second process has been interpreted as being a spectator knock out mechanism where the projectile collides with essentially only one of the atoms of the molecule, leaving the motion of the other atom predominantly unchanged. The second process of the K^+ data has been interpreted both as resulting from the spectator mechanism⁶ and as resulting from simple collisional dissociation with one of the hydrogen atoms ending in its first excited electronic state.⁵ At lower energies, $E_r < 10$ eV, in the Li^+-H_2 studies individual vibrational³ and even rotational⁴ quantum transitions have been resolved.

Theoretical work in the field of vibrational energy transfer, which has been compiled in review articles⁷ in the past decade, has been concentrated on studying the dependence of excitation on the initial collision energy, resulting primarily from the collinear collision orientation. In this orientation the centers and the motion of all atoms involved lie along a common axis. The extensive treatment of this configuration is presumably a consequence of its apparent simplicity and the intuitive feeling that it leads to large energy transfer. Molecular beam studies of nonreactive systems, however,

yield results which are most representative of the most probable collision orientation. For the system of a projectile A colliding with a diatomic molecule BC, this most favorable orientation is one in which the internuclear axis of BC lies perpendicular to the axis defining the approach of atom A. Many articles have been concerned with the adoption of a steric factor⁸ which gives the ratio of the energy transferred averaged over all collision orientations to that transferred in a collinear collision. Calculation of such a factor requires the supposition of an orientation function which relates the energy transfer at a given orientation back to the energy transfer of the collinear orientation. Kelley and Wolfsberg⁹ have shown through classical trajectory calculations that, in general, a simple form for this orientation function does not exist. Their studies show that for some systems the energy transfer is a very sensitive function of initial collision orientation, thus obscuring any relation to the collinear orientation. The direct consequence of this is that the majority of the past theory on vibrational energy transfer is not directly applicable to molecular beam studies as described here.

In this thesis the apparatus is described which was used to study the head-on scattering of alkali ions from, in most cases, diatomic molecules. The data obtained from the systems studied are presented, and finally an approximate three dimensional classical trajectory analysis of the systems studied is developed, in light of the above discussion, for the interpretation of the data.

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II. EXPERIMENTAL

A. Introduction and General Description

The apparatus used in performing the experiments has been adapted from one designed originally to perform electron scattering experiments. In its original form, the apparatus was similar to the double electrostatic analyzer apparatus used by Schultz¹ in experiments which examined vibrational excitation of molecules through collisions with electrons. The only components retained in adapting the apparatus for the work presented here are the electrostatic analyzers, and these were modified slightly.

A schematic diagram of the apparatus in its present form is shown in Fig. II-1. Basically, it consists of three main parts: a source which prepares a focused beam of monoenergetic ions, a scattering region which contains stationary molecules, and a detector which scans the energy distribution of ions exiting the scattering region and records the intensity of scattered ions at each energy.

In the source a beam of sodium or lithium ions is produced by indirectly heating a surface coated with a fused mixture of M_2O , Al_2O_3 , and SiO_2 , where M_2O is the oxide of the alkali required. These ions are focused on the entrance slit of a 127° cylindrical electrostatic energy analyzer which is used to narrow the thermal energy distribution of the alkali ion beam. The energy selected beam is accelerated to the desired energy and is focused on the scattering region. This region is contained by a scattering cell which is cooled by liquid nitrogen and contains a light diatomic gas (H_2 , D_2 , or HD).

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Fig. II-1. General schematic of apparatus used for studying the energy distribution of ions backscattered from molecules.

A Ion source	E Beam flag
B Liquid nitrogen cooled copper clamp	F Channeltron detector
C Energy analyzer	G Scattering cell
D Faraday cup	H Beam energy selector

Since the impinging ions are heavier than the target molecules, each ion continues with a positive velocity component in its original direction of travel after a collision with one of the approximately stationary molecules. Ions which have not been deflected more than about 2° exit the scattering cell and enter the detection system. These ions are focused on the entrance slit of a second 127° energy analyzer. The potential between the scattering cell and the analyzer is scanned so that ions of all energies may successively pass through the analyzer into the detector. In this way a spectrum of intensity versus energy may be obtained with each energy being accepted with the same absolute resolution. The detector used is a continuous channel electron multiplier. The pulses from the detector, corresponding to individual scattering events, are recorded both by digital and analog devices.

A more detailed description of the individual components and their operation follows. For ease of description the horizontal plane is defined such that it contains the path of the ion beam. The scattering kinematics and their relevance to interpreting the spectra are also discussed in this chapter.

B. Apparatus

1. Alkali Ion Beam

a. Ion source. Various designs of ion emitters were used. All incorporate the method of directly or indirectly heating a thermionic emitting material. Only the final design used is described, as the majority of the experiments reported here were run after its incorporation.

The thermionic emitting material used is an aluminosilicate of an alkali metal. These were recognized as early as 1927² as being a possible source of alkali ions. More recently their thermal emission behavior has been studied as a function of composition and temperature.³ Basically, it is understood that the alkali ions are loosely held within the aluminosilicate crystal lattice. This allows them to migrate freely within the lattice. Ions which migrate to the surface are easily emitted as a result of the low work function of the material.

The emitting material was prepared by a procedure modified from one reported by Allison and Kamegai.⁴ A mixture of powdered M_2CO_3 , where M is lithium or sodium, Al_2O_3 , and SiO_2 in the ratio of 1:2:1 was mixed thoroughly and fused at about 1500°C in a platinum crucible. The powdered SiO_2 was obtained by grinding quartz in an agate mortar, and the carbonates of the respective 6Li and 7Li isotopes were purchased as 99.30% and 99.99% pure. The fused mixture was repowdered in an agate mortar and a small amount, $\sim 1 \text{ mm}^3$, was fused on the surface of 0.0005 in. platinum foil.

The platinum is spot welded to the center of a filament at a point directly below the adhering emitting material, and the excess platinum is trimmed away. The filament, cut to about 0.1x1.5 cm from 0.001 in. high purity tungsten foil, is spot welded between two tantalum leads prior to the attachment of the platinum foil. These leads, as shown in Fig. II-2 which represents a cross section of the emitter assembly, are welded to kovar-glass feedthroughs which are mounted parallel to one another in a 1/8 in. thick tantalum disk.

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Fig. II-2. Cross section of emitter assembly

- A Tantalum disk
- B Stainless steel housing
- C Tantalum leads
- D Tungsten filament
- E Platinum foil
- F Emitting material
- G Tantalum foil
- H Tantalum foil heat shielding
- I Kovar-glass feedthrough

This disk is made to friction fit into a stainless steel housing. The housing and filament assembly are matched in length such that the emitting material just protrudes through a 2 mm diameter hole in the center of a piece of 0.003 in. tantalum foil spot welded to one end of the housing. Additional pieces of tantalum foil are spot welded around the filament as heat shielding.

The filaments are typically heated by a direct current of about 2.5 amps. The ion emission is very sensitive to this current and a constant voltage transformer is used to eliminate the fluctuations in the line voltage which runs the filament power supply. The average potential of the filament leads is floated at the potential of the emitter housing and is assumed to be the rest potential of the ions formed.

Prior to installment in the apparatus, each emitter is tested in a constant magnetic field mass spectrometer capable of resolving ${}^6\text{Li}^+$ from ${}^7\text{Li}^+$.

b. Ion gun. In order to obtain a high intensity, low energy ion beam a multistage lens system is used. The design of this ion gun is based on one reported by Haskell, Heinz, and Lorents⁵ and is shown in Fig. II-3. The principle of the gun is to accelerate ions extracted from the emitter to a high energy in order to decouple thermal energy and space charge effects from the formation of a beam, and then to decelerate them to the low energy required. Vertical and horizontal deflection plate pairs were added just after the focus in the acceleration stage of the gun. The purpose of these is to compensate for

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Fig. II-3. Cross section of ion gun

- A Emitter
- B Grid
- C Deflection plate
- D Aluminum gun support
- E Energy selector entrance
- F Decelerating region
- G Accelerating region
- H Extracting region

loss in intensity from irregularities in the beam by training the maximum intensity of the beam image on the energy selector entrance slit. The lens and aperture elements of the gun, taken from a kit produced by a firm which is now International Ion Systems Corporation are square plates of stainless steel with 1/16 in. alignment holes in the corners. The emitter and elements of the gun are held in alignment by 1/16 in. diameter alumina rods, the elements being separated by hollow alumina spacers which fit over the rods. The rods are held rigidly at one end by an aluminum support mounted securely to the entrance slit face of the energy selector.

c. Energy selector. A singly charged ion moving perpendicular to an attractive radial electric field at distance r from its center experiences a force equal to $e\mathcal{E}$ toward the center of the field, where e is the electronic charge and $\mathcal{E}$ is the strength of the field at the distance r . If the ions velocity v is such that the centrifugal force experienced by the ion just matches the force of the field acting on the ion, then

$$e\mathcal{E} = \frac{mv^2}{r} \quad (\text{II-1})$$

since the ion will execute a circular path about the center of the field. Substituting the expression for the particles kinetic energy T and rearranging yields

$$T = \frac{e\mathcal{E}}{2} r \quad (\text{II-2})$$

From this equation it is clear that only ions of the appropriate energy will pass through a radial field at a constant distance from its center. Therefore, such a field can be used for the selection and analysis of the energy of charged particles without needing to know their mass.

The selection and analysis of the energy of the beam in the apparatus is done with fields of cylindrical radial symmetry. The focusing effects on charged particles of the cylindrical electrostatic field were originally studied by Hughes and Rojansky and Hughes and McMillen.⁶ In their studies they found that ions entering the field at radius r , but not exactly perpendicular to the field, and having the energy given by Eq. (II-2), would be refocused best on that radius after passing through 127.17° of arc about the field center. In addition they found that the theoretical resolution is simply proportional to the energy at which the particles enter the field and given by $\Delta T = \Delta r T / r$, where Δr is the width of slits at radius r where the particles enter and exit the field.

The design of the energy selector used here and shown in Fig. II-4 makes use of the 127° angle and is essentially identical in design and size to the electron selector reported by Marmet and Kerwin.⁷ Ions which enter the selector are deflected by concentric cylindrical grids made from 200 lines per inch 60% transparent tungsten mesh. Those ions which have the proper energy are refocused on and pass through the exit slit of the selector. Ions whose trajectories pass through either cylindrical grid are electrostatically drawn toward

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Fig. II-4. Energy selector design

A Entrance slit (hidden)	E Top vertical focusing grid
B Exit slit	F Bottom vertical focusing grid (hidden)
C Inner bending grid	G Inner stray ion collecting plate
D Outer bending grid	H Outer stray ion collecting plate

cylindrical plates and collected there. Grids above and below the volume between the cylindrical grids hold a repelling potential and supply vertical focusing. The entrance and exit aperture slit widths are both set to 0.37 mm and the mean trajectory radius is 12.5 mm, making the full width of the primary beam at half maximum about 3% of the energy at which the beam is selected.

The outer cylindrical plate is fitted with a removable shielded Faraday cup in line with the axis of the beam path through the ion gun. When all the elements of the selector are held at the potential of the plate containing the entrance and exit slits of the selector, the ions drift through the outer deflecting grid and into the Faraday cup. This allows finding the optimum focusing conditions of the ion gun. With the Faraday cup removed, the ion path leading to the selector may be viewed, facilitating the alignment of the ion gun with the selector entrance slit.

2. Scattering Cell

The energy selected beam is refocused on the interior of the scattering cell by a three-aperture electrostatic lens⁸ designed by Read and Imhof (see Fig. II-1). This lens allows the recreation of an ion focus at a new potential by the adjustment of the potential on the middle aperture. The scattering cell, shown in vertical cross section in Fig. II-5, was machined from stainless steel. It has 1 mm diameter entrance and exit holes along the axis of the beam. The beam path length through the cell is 17 mm. The scattering gas is leaked from a reservoir through a variable leak into a 0.15 in. I.D.

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Fig. II-5. Vertical cross section of scattering cell

- A Ceramic lens alignment rod
- B Scattering gas inlet
- C Stainless steel cell
- D Ion beam axis
- E Nickel plated copper clamp
- F Copper sleeve
- G Liquid nitrogen reservoir
- H Sandwiched indium foil

stainless steel tube which connects with the top of the cell. The pressure on the inlet line 18 in. above the cell is monitored by a capacitance manometer.

The thermal motion of the scattering gas is the greatest limitation to the resolution of the apparatus. For this reason a cold-clamp assembly was constructed about the cell to cool the scattering gas. The four sides of the cell which are parallel to the beam axis make thermal contact with a copper clamp by sandwiching indium foil between them. The lower portion of this clamp is circular in cross section and fits into a copper sleeve which is cooled directly by liquid nitrogen. The clamp is nickel plated to aid in thermal insulation to radiation. The temperature of the copper clamp is monitored by a copper-constantan thermocouple, and within two hours of initiating the cooling procedure, it settles at a temperature of -177°C .

A second three-aperture Read lens immediately after the cell focuses ions emerging from the cell on the entrance slit of a second 127° energy selector. This lens arrangement, which is symmetric about the scattering cell, is beneficial to calibrating the lenses and is discussed in Section C. The lens apertures are from the same kit as those of the ion gun, and they are held in alignment with the cell in a similar fashion.

3. Beam Analysis and Detection

a. Energy analyzer. The second energy selector is used to analyze the energy distribution of the ions emerging from the scattering cell. The design is identical to that of the first energy selector except

for two modifications.

Scattered and unscattered ions which exit the scattering cell are accelerated or decelerated by the potential of the analyzer aperture plate. The concentric cylindrical deflecting plates hold potentials such that only ions, having the predefined energy after entering the analyzer, may pass through and be focused on the exit slit. Thus, by scanning the potential of the aperture plate, ions corresponding to different final laboratory energies pass successively through the analyzer into the detector. Since the region of the spectrum which is of primary interest is of lower energy than the primary beam, when that region is being observed by the detector the primary beam is passing through and colliding with the outer deflecting grid. The collisions result in scattering which is partially picked up by the detector, creating an unwanted background. The solution used in overcoming this problem was to cut a rectangular hole in the outer grid 0.1 in. high along the region with which the primary beam was able to make contact. This region is about 1 in. in length and is shown in Fig. II-1. The distortion of the deflecting field due to the hole is reduced by adjusting the potential on another concentric cylindrical grid of larger radius.

The outer cylindrical plate is fitted with a removable Faraday cup as with the first selector. This second Faraday cup is used to detect the beam during calibration of the lenses situated on either side of the scattering cell. Removal of the cup allows visual alignment of the scattering cell and its lenses with the exit from the energy selector and the entrance to the energy analyzer.

All surfaces with which the ions can come in contact between the emitter and the detector are coated by painting with a colloidal graphite dispersion to reduce the effects of surface charge build-up.

b. Detector. Ions which pass through the exit slit of the analyzer are accelerated by about 2 kilovolts into a Bendix model 4028 Channeltron Electron Multiplier. A 100 line per inch nickel mesh is supported about 3 mm behind the exit slit to reduce penetration of the accelerating field into the analyzer. The Channeltron is mounted with epoxy at the lip of the cone to a boron nitride insulating disk. This assembly is held in place in a cylindrical stainless steel can by stainless steel screws. The can is supported by four 1/16 in. diameter ceramic rods which are held by a cylindrical stainless steel support, mounted to the exit aperture plate of the energy analyzer. The detector can and support are made to telescope together without making electrical contact although they are generally held at the same potential. The electrical input and signal output leads of the Channeltron pass through 1/4 in. diameter Teflon insulators in the can wall. The Channeltron operating voltage is supplied by a Bendix miniature high voltage power supply type OPS-0301N contained within the vacuum system. The Channeltron operated well with the minimum voltage from the supply and the signal processing electronics discussed in the next section. Viewing the primary beam directly with the detector caused it to overload and the output to drop. Repeated viewing resulted in an increasing noise level, possibly the result of sensitization to thermal emission by an alkali metal coating. This

was remedied by flushing the Channeltron with acetone⁹ which restored it to its original performance.

So that the primary beam can be viewed directly after passing through the analyzer, an insulated beam flag was installed which can be moved between the exit slit of the analyzer and the Channeltron by means of a mechanical feedthrough leading into the evacuated apparatus chamber. The beam flag is connected to an electrometer when it is intercepting the beam.

c. Signal processing electronics. The output from the Channeltron, which is operated with the collector separated from the end of its capillary coil, is connected to ground through a $20K\Omega$ resistor to create voltage pulses. Each pulse corresponds to the detection of an individual ion. These pulses are fed into a high input impedance AC amplifier operated with unity gain to act as a voltage follower. A schematic diagram of the circuit is shown in Fig. II-6. This circuit is located close (~ 2 in. length wire) to the collector to reduce dissipative capacitances which reduce the voltage of single event pulses from the detector. The output of the follower passes out of the vacuum chamber and is fed simultaneously into an oscilloscope, a digital to analog converter, and a scalar.

The pulses, as viewed by the oscilloscope, are all approximately $0.5 \mu\text{sec}$. FWHM and between 0.5 and 1.0 volt in height. The ion detection rate is converted to an analogous voltage by the D to A converter, and that voltage is used to drive the ordinate of an X-Y recorder. The scalar, manufactured by Harshaw Chemical Company, is

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Fig. II-6. Voltage follower circuit for amplifying the current of single event pulses from the Channeltron. The integrated circuit, National Semiconductor Corporation LM 302, is an epoxy encapsulated high gain operational amplifier.

programmed to repeatedly record counts for a designated period of time, reset, and start again. In addition, the scalar is equipped with a teletype interface which permits the accumulated counts to be typed out after every cycle.

4. Vacuum System

All the components of the apparatus shown contained in the vacuum system in Fig. II-1 are mounted on the inside of 10 in. diameter stainless steel Varian ConFlat blank flange as shown in the photograph of Fig. II-7. All the electrical inputs required to run the apparatus enter the system via a hermetically sealed, multipin plug welded in the flange. The output from the Faraday cups and the Channeltron is connected to a single, shielded, hermetically sealed feedthrough also welded in the flange. The flange itself caps the top of an 8 in. O.D. $\times$ 1/16 in. wall stainless steel tube forming the tank in which all the components mounted to the flange fit. The blank flange mates with a flange at the top of the tube and makes a bakeable seal using an OFHC copper ConFlat flange gasket. The tank, which is 12 in. long, is mounted directly on the top of a 6 in. Granville Phillips Series 251 Cryosorb Cold Trap. The liquid nitrogen cooled cold trap is mounted directly on top of a CVC 6 in. oil diffusion pump, Type PMC 6B. The forepump, a Kinney model KTC-21, is connected to the exhaust port of the diffusion pump by 10 ft. of 2 in. I.D. copper bellow tubing to reduce mechanical vibrations of the apparatus by the forepump.

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Fig. II-7. Photograph showing vacuum tank and flange on which the apparatus components are mounted.

- A Detector output line
- B Scattering gas inlet line
- C Emitter housing
- D Copper clamp about scattering cell
- E Liquid nitrogen cooled copper sleeve
- F Main vacuum tank
- G Flange for liquid nitrogen reservoir
- H Channeltron housing
- I Input cable

The apparatus is baked out for 12 hours prior to running experiments. The upper limit in the bakeout temperature, 125°C is determined by the environmental specifications of the Channeltron power supply contained within the system. After returning to room temperature the pressure is generally in the range of 10^{-8} Torr. This is measured by a Veeco RG75K ionization gauge mounted on a side port in the tank containing the apparatus.

5. Operation

So that the performance of the apparatus in part and as a unit may be understood, a description of the general procedure for running an experiment follows. Although the scattering cell is at ground potential, all potentials mentioned are referenced to the emitter potential unless otherwise specified. Thus a primary ion with a single positive charge entering a region of -20 volts potential will have a translational energy of 20 eV. Figure II-8 shows a schematic representation of the potential division scheme for supplying the various regions and apertures with the appropriate potential, and it may be followed as the operation of the apparatus is described.

After the clamp on the scattering cell has attained its cooled temperature the current through the emitter filament is turned up to about 2 amps. Within 30 seconds an ion current is detected at the Faraday cup mounted on the energy selector. Potentials on the "grid", accelerating aperture system, and the deflection plates are adjusted to maximize the intensity monitored at the first Faraday cup. The potential of the selector aperture plate is held constant to define the energy at which the beam is selected. This energy must be greater

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Fig. II-8. Potential division scheme. The potentiometer at A is used to adjust the initial laboratory ion energy of an experiment. The potentiometer at B is used to scan the final laboratory energy of the scattered beam. The rectangular boxes denote power supplies for the noted function.

than 10% of the energy of the primary ions when they enter the scattering cell to assure the lens between them of having an adequate transmission. In addition, although the selector is capable of passing a beam of 2 eV, the ion gun intensity drops off sharply below 4 eV, presumably due to space charge, thus limiting the narrowest attainable resolution of the beam emerging from the selector to 0.12 eV FWHM (see Sec. 1.c.).

After one hour of operation the beam is stable to within 10% per half hour. At that time the deflecting potentials are applied to the cylindrical grids of the energy selector, and the beam is allowed to pass through the void scattering cell and be collected by the second Faraday cup, which is mounted on the energy analyzer. The potential difference between the emitter and the scattering cell defines the laboratory energy at which scattering events will take place. This energy may be varied without altering the focus of the beam emerging from the selector. This is done by floating the base potential of the power supply and associated potentiometers, which define the relative potentials of the elements from the emitter to the aperture after the exit of the selector, at the appropriate potential. This base potential is connected directly to the emitter as shown in Fig. II-8, and therefore its value in volts defines the initial laboratory energy in eV.

The potentials on the selector grids and the middle aperture of the Read lenses are adjusted to maximize the current detected at the second Faraday cup. This current is typically 5% of that obtained at the first cup and is just as stable.

The beam is next led through the analyzer by applying the deflecting potentials to its cylindrical grids. A maximum current of twice that received by the second cup and 10% of that received at the first cup is collected by the beam flag after adjusting these potentials.

The transmission of a Read lens drops off sharply if the difference in the beam energies on either side is greater than an order of magnitude. In the higher energy experiments, $E_q > 50$ eV, this effect is significant because it imposes a lower limit on the selection and analysis energies and therefore also a limit on the resolution. Since the backscattered ions emerge from the scattering cell at a lower energy than the primary ions enter, an analysis energy of about 75% of the beam selection energy is used in the high energy experiments.

The potential between the scattering cell and the aperture plate of the analyzer added to the energy at which the ions are analyzed defines the energy which ions emerging from the scattering cell must have to be detected. This final laboratory energy, E_q' may be varied without altering the relative potentials on the beam analysis components in a similar manner to the way in which the initial laboratory energy is varied. A second base potential is generated such that its value in volts is equal to the energy of the ions accepted into the detector. Although no component directly uses this potential, it is used to float the potential of the power supply and associated potentiometers, which supply the detection train, above the grounded scattering cell. This potential is also monitored by a digital voltmeter to give a direct indication of the final laboratory collision energy of results being detected.

After the primary beam has been led through the apparatus, the scattering gas is introduced into the cell to a pressure of about 1.5μ , which attenuates the beam approximately 10%. The final-energy potentiometer is set in the region in which scattering is expected for the system being studied, and the beam flag is removed. When the exact position of the maximum of the backscattered peak is found, the potential on the middle aperture of the Read lens after the cell is adjusted to maximize the count rate detected by the Channeltron. This focus is not appreciably sensitive over the region to be examined and is not changed until a new initial energy or scattering gas is used. The energy spectrum of the scattered primary beam is scanned by a 1/5 RPM motor which drives the 10 turn potentiometer supplying the final-energy-base potential. This potential is used to drive the abscissa of the X-Y recorder which is simultaneously recording the analog output from the Channeltron. The digital voltmeter displaying this potential is interfaced with the Harshaw scaler so that, after every counting cycle, the teletype prints out the accumulated counts and the voltage proportional to the energy corresponding to the beginning of the next cycle.

The scattering intensity and beam stability generally allow a single backscattered spectrum to be scanned in fifteen minutes.

C. Apparatus Calibration

Although the design of the ion optical components in the apparatus is taken directly from the literature, there are some differences in their performances from those reported. Still, tabulated focusing

conditions of the various lenses are not generally needed, because focusing the beam in the first and last stages of leading the beam through the apparatus requires adjusting only one or two potentials. Finding the beam at the second Faraday cup, however, requires three simultaneous adjustments: the bending potentials on the selector grids and the potential on the middle aperture of each of the Read lenses. For this reason, on some occasions it is difficult to find the focusing conditions required to pass the beam through to the second cup. Therefore, focusing conditions for the Read lenses were measured and tabulated.

The lens system on either side of the scattering cell is symmetric to reflection through the plane passing through the center of the cell parallel to the lens plates. By using this fact, by applying potentials symmetrically to the plates as shown in Fig. II-9, and by focusing the beam through the selector, the number of parameters governing the intensity at the second cup are reduced to one. That parameter is the potential applied to the middle aperture of the Read lenses.

The potential of the middle aperture V_2 was varied for different ratios of the potential on the cell V_3 to that on the selector and analyzer aperture plates V_1 , where V_1 , V_2 , and V_3 are measured with respect to the emitter. Two distinct maxima observed in the beam intensity at the second cup were presumably due to the two possible focusing conditions with the same symmetry as the lens system. As shown in Fig. II-9, these correspond to the beam crossing itself and forming an "image" in the center of the cell and to it passing parallel through the cell, being focused on infinity in that region.

Case A: Parallel Focus

Case B: Crossed Focus

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Fig. II-9. Read lens system showing symmetry of potentials applied to apertures in calibrating the lenses.

Figure II-10 shows the positions of the maxima in terms of the ratios V_2/V_1 and V_3/V_1 compared to two curves reported by Imhof and Read. Because the topmost curve corresponds to the shorter focal length, it is assumed that the higher row of data points corresponds to the focus which crosses in the center of the cell. Although the beam should ideally enter parallel into the cell minimizing the range of angular deflection acceptable to the detector, this crossing focus is used in running all the scattering experiments. This is done because the crossing focus results in an intensity at least 5 times greater than the parallel focus.

D. Scattering Kinematics

Certain spatial restrictions are imposed on a system of interacting particles by the laws of conservation of momentum and energy. In the two particle system studied in these experiments, it is these restrictions which allow the calculation of the inelasticity of an interaction from the final translational energy of one of the particles. To aid in visualizing this relationship it is helpful to construct a velocity vector or Newton diagram as in Fig. II-11. In the experiments the projectile ion has a laboratory velocity shown by vector $\mathbf{x}$, and the target molecule has no initial laboratory velocity. Therefore, the laboratory center of mass velocity vector $\mathbf{y}_{cm}$ is given by

$$\mathbf{y}_{cm} = \frac{m_p}{m_p + m_t} \mathbf{x} \quad (\text{II-3})$$

XBL 737-1512

Fig. II-10. Focusing properties of Read lens; reported (curves) and experienced in the apparatus (data points). P and Q are the object and image distances of the lens respectively. The unit of these distances is the aperture diameter and separation of the center lens plates (vertical and horizontal scales are different in lens sketch). P and Q are both 6 for the lenses in the apparatus when the beam crosses in the center of the cell.

XBL 737-1516

Fig. II-11. Vector diagram of projectile velocities resulting from scattering from a lighter, stationary target molecule. The cone surrounds the volume containing vectors which are acceptable to the detector. The large circle represents the elastic sphere.

where m_p and m_t are the masses of the projectile and target, respectively. This vector locates the origin of velocities for an observer moving with the center of mass, so the projectile and target velocity vectors would be given by $\underline{u} = \underline{v} - \underline{v}_{cm}$ and $-\underline{v}_{cm}$, respectively, in this center of mass reference frame. After a collision, from conservation of momentum, the velocity of the center of mass of the system is unchanged. If the collision is inelastic, the final projectile center of mass velocity has a magnitude $u' < u$ defined by the inelasticity so that energy is conserved. The locus of all such velocities is the surface of a sphere of radius u' about the center of mass origin and represents the family of laboratory velocities $\underline{v}'$ associated with a given inelasticity. Thus, the inelasticity of an event may be calculated from the measured final laboratory energy and the deflection of a projectile. An elastic collision results in no change in the center of mass speed u and its locus defines the so-called elastic sphere within which all final projectile velocities of inelastic events fall.

Final projectile velocities which fall to the left of the center of mass origin result from relatively head on collisions and therefore the corresponding projectiles are referred to as being backscattered. Those to the right result from more grazing collisions and those projectiles are forward scattered. Since $m_p > m_t$ for all of the systems studied here, the elastic sphere lies entirely to the right of the laboratory origin. Hence, all the scattered projectiles have a forward velocity component after collision.

The apparatus described is designed to only detect ions which have been scattered within a small laboratory deflection angle $\delta\theta$. This criterion defines a cone about $\underline{y}$ with its vertex at the laboratory origin. The volume common to this cone and the elastic sphere defines the portion of scattering examined by the apparatus. Thus, essentially only nearly head-on collisions and very grazing collisions are sampled in an energy spectrum.

E. Data Analysis

A spectrum obtained directly from an experiment is in two forms: an X-Y recorder plot of intensity versus the final laboratory energy and a teletype produced table of counts accumulated over each equal time interval into which the scan is divided along with the final laboratory energy associated with the end of each interval. The recorder plots have a small inherent error as a result of the time constant involved in the digital to analog conversion and generally are used only to monitor the experiment while in progress. The energy column of the teletype produced table is adjusted so that each energy corresponds to the middle of the associated time interval.

The column of adjusted energies actually corresponds to the electrical potential measured between the scattering cell and the final energy base (See Sec. . . . The energy analyzer is adjusted to pass ions with the energy of the final energy base by adjusting the potentials on its bending grids. This is done at the beginning of an experiment such that the current collected at the beam flag from the

primary beam entering the analyzer at the energy of the final energy base is a maximum. It was found that the energy which the analyzer passes changes through the course of an experiment. This fact and the presence of contact potentials caused the potential measured between the scattering cell and the final energy base to be slightly different from the final laboratory energy of the ions being detected. The final energy of the elastic backscattering from helium, which can be calculated from the initial collision energy, is used to adjust the recorded potential to correspond to the actual final laboratory energy. It was found that the behavior of the data was most reasonable if the initial setting of the ion energy was assumed to be correct and the recorded final energy potential was simply shifted by the amount the elastic helium scattering was displaced.

Analyzing the spectra in these experiments requires a detailed knowledge of the function which describes the resolution dependent spreading of the scattered signal. This apparatus function may be determined analytically or empirically. An analytic form requires the analysis of the contributing factors. These factors are the velocity spread in the energy selected primary beam and in the scattering gas and the energy and angular resolution of the scattered beam energy analyzer. The resolution of the selector and analyzer is determined by their slit widths and the selection and analysis energies. The spread in the distribution of velocities of the target gas is characterized by the Boltzmann distribution and the gas temperature.

In parts of the data analysis an analytic form of the apparatus function is used. This function utilized the resolution contributing factors in a one dimensional analysis of the resulting shape and breadth of the function. In comparing this function to the elastic scattering of the $\text{Na}^+\text{-He}$ system it is found that, in general, the FWHM of the peaks agrees well, but the data tend to have a greater intensity trailing toward higher energy. A typical example of this is shown in Fig. II-12. This discrepancy appears to become greater for higher energy experiments and the empirical form of the apparatus function is used in all the final analyses.

The empirical form of the apparatus function is obtained simply by smoothing the elastic scattering data from He. The smoothing operation¹⁰ sequentially adjusts the intensity of each data point to fit a third order polynomial which fits that point and the nearest four other points. Three iterations of this procedure are adequate to remove large fluctuations between adjacent points without altering the overall shape of the curve.

This empirical apparatus function is essentially exact at the final laboratory energy corresponding to that of the backscattering from helium. The shape and width of the actual apparatus function are, however, dependent on the final laboratory energy, and the empirically derived function does not take this into account. Nevertheless, the inelastic scattering spectra are generally entirely contained within a region near the appearance of the He scattering, and the changes in the apparatus function are assumed to be insignificant.

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Fig. II-12. Comparison of the analytical apparatus function (curve) and the elastic scattering of $\text{Na}^+ - \text{He}$ (data points).

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III. DATA

A. Introduction

The extent to which a particular system was studied is a function of both the ability with which that system can be studied with the apparatus, and the amount of information available by studying that system. The ability of the apparatus to examine the scattering from a system depends largely on the ratio of the masses of the projectile ion to the target molecule. If the ion is very much heavier than the molecule, a collision between them cannot significantly change the laboratory velocity of the ion. Hence, it is difficult to resolve the distribution of the scattered ion beam from the primary beam. At the other extreme, where the ion is only slightly heavier than the molecule, only a very small fraction of the total backscattering is accepted by the detector, resulting in very weak intensity. Among the systems studied $\text{Na}^+ - \text{D}_2$ was found to be the best suited for viewing. This fact, coupled with the convenience of comparison with the totally elastic scattering of the identical mass $\text{Na}^+ - \text{He}$ system, led to its being studied the most extensively.

Sodium ion backscattering was also observed from H_2 , HD, CH_4 , and CD_4 . Some data were taken from the backscattering of Li^+ from H_2 . All these data are presented in this chapter.

B. Scattering of Sodium Ion from Hydrogen Molecule

1. $\text{Na}^+ - \text{D}_2$

The scattering of Na^+ from D_2 was examined in the relative energy range of 0.74 to 16.9 eV. This system has been studied previously by Datz and Dittner¹, but at a somewhat higher energy. Schöttler has also studied this system and in an energy range extending into that studied here.² The following are the observations made in this work.

Below 3 eV there is no significant difference from the single elastic scattering peak observed from He. As the initial energy is increased, the side of the peak corresponding to inelastic excitation gradually becomes broader. Above about 5 eV relative energy, the position of the maximum gradually begins to shift toward greater inelasticity. The low laboratory energy side of the peak always remains relatively steep, even at the highest energies studied where the peak maximum is well shifted from the position of elastic scattering. These general trends can be seen in the spectra of Fig. III-1 which give a sample of equally spaced energy studies of the range examined. The $\text{Na}^+ - \text{He}$ backscattering spectra are shown to the right of the spectra they are used to calibrate. The vertical line through the peaks shows the position expected for elastic scattering as determined by the $\text{Na}^+ - \text{He}$ spectra. The suspended tick marks show the expected positions of vibrational excitation from the ground state to the successive vibrational states. The inelasticity which these correspond to was computed from the formula

Fig. III-1. $\text{Na}^+ - \text{D}_2$ and $\text{Na}^+ - \text{He}$ backscattering spectra (data points). The curves are the result of smoothing. The abscissas are labeled in the final laboratory appearance potential. The corrections for converting to final laboratory energy E_{lab} are shown. The backgrounds and amplitudes have been adjusted for ease of comparison.

Fig. III-1. (Cont.)

Fig. III-1. (Cont.)

Fig. III-1. (Cont.)

$$\Delta E(v) = [\bar{\omega}_e v - \bar{\omega}_e x_e v(v+1)]/8067 \quad . \quad (\text{III-1})$$

Here, $\Delta E(v)$ is given in electron volts; v corresponds to the final vibrational quantum number; and $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ have their usual meaning, are used in cm^{-1} , and have been taken from Herzberg.³ The right most tick mark corresponds to the dissociation energy D_0^0 taken from the same source. To facilitate the comparison of spectra of different energies the horizontal scale has been adjusted such that the right border of each graph corresponds to the position at which totally inelastic scattering would fall.

The most obvious feature of these data which characterizes the general trend of increasing inelasticity with increasing energy is the shift in the position of the maximum relative to that from the elastic scattering from He. This is tabulated in Table III-A in the form of the corresponding inelasticity for many of the spectra taken on the Na^+-D_2 system. The few points measured by Schöttler which extend into the range of these studies are in agreement with these data.

2. Na^+-H_2

A few spectra were taken on the Na^+-H_2 system in the relative energy range of 2.4 to 4.8 eV. The single peak observed in this system does not drop below 20% of the intensity at the maximum before it joins with the tail of the primary beam. This intensity in the region between the primary and backward peaks is

Table III. Inelasticities ΔE corresponding to the shift in the sodium ion - hydrogen molecule backscattering peak maximum from the position of elastic backscattering.

(A) $\text{Na}^+ - \text{D}_2$				(B) $\text{Na}^+ - \text{H}_2$			
Experiment Number	E_g (eV)	E_r (eV)	ΔE (eV)	Experiment Number	E_g (eV)	E_r (eV)	ΔE (eV)
77a	20.	2.96	0.00	51	30.	2.40	0.23
41	20.	2.96	0.00	53	40.	3.20	0.08
42	25.	3.70	0.00	54	50.	4.00	0.22
77b	30.	4.44	0.00	55	60.	4.80	0.11
38	30.	4.44	-0.01				
37	30.	4.44	0.03				
45	35.	5.19	-0.01				
77c	40.	5.93	0.07	(C) $\text{Na}^+ - \text{HD}$			
64a	40.	5.93	0.14	Experiment Number	E_g (eV)	E_r (eV)	ΔE (eV)
46	40.	5.93	0.11	71	70.	8.08	0.68
64b	45.	6.67	0.20	72	80.	9.23	0.38
64c	50.	7.41	0.23	73	90.	10.38	0.62
49	50.	7.41	0.00	74	100.	11.54	0.69
64d	55.	8.15	0.27	75	110.	12.69	1.22
59	60.	8.89	0.24	78	130.	15.00	2.11
64e	60.	8.89	0.42	79	150.	17.31	2.81
60	70.	10.37	0.63	81	190.	21.92	5.79
62	80.	11.85	1.10	80	200.	23.08	7.48
68	85.	12.59	1.20	82	250.	28.85	12.78
63	90.	13.33	1.69				
69	90.	13.33	1.53				
70	95.	14.07	2.07				
65	100.	14.81	2.74				
66	110.	16.30	3.46				
67	114.	16.89	3.92				

presumably the result of the poor center of mass angular resolution. The entire elastic sphere falls within 5° of the primary beam axis, and the lightness of the H_2 target allows its thermal motion to produce a very significant smearing of "off-angle" scattering into the center line studies.

The shape and broadening of the H_2 curves is similar to those obtained for D_2 at comparable relative energies. Table III-B shows the computed inelasticities for four of the spectra. The error in these is assumed to be quite a bit larger than for the D_2 data since there is no feasible way of obtaining pure elastic scattering from a target of mass 2. These four spectra are shown in Fig. III-2 plotted in the same manner as the Na^+-D_2 data. The Na^+-He spectra used to calibrate them are not shown.

3. Na^+-HD

Na^+ scattering from HD was studied to determine whether a resolvable inelasticity difference would appear in collisions with either end of the molecule. In some recent results on the nonreactive center line backscattering of O^+ from HD measured by Drs. John Winn and Keith Gillen with a different apparatus, two peaks are observed. These are clearly resolved at 20 eV and correspond approximately to an impulsive mechanism, each peak associated with an O^+ interacting impulsively with one atom of the diatomic. Subsequent H-D interactions serve to broaden the peaks, but the single atom (knock-out) scattering is still easily evident.⁴ Only one peak, however, is observed in the Na^+-HD scattering which was studied up to a relative energy of 29 eV.

$\text{Na}^+ - \text{H}_2$

Fig. III-2. $\text{Na}^+ - \text{H}_2$ backscattering spectra. For additional information refer to Fig. III-1.

The single peaks observed from HD are similar to those of the scattering from the homonuclear diatomic molecules. There is, however, a difference between them on the high energy side at comparable relative energy. Although the shift in the maximum and the broadening are about the same, the $\text{Na}^+\text{-HD}$ peak exhibits a tail leading toward greater inelasticity which is significantly more pronounced. Figure III-3 shows spectra from the $\text{Na}^+\text{-HD}$ and $\text{Na}^+\text{-D}_2$ systems taken at about 9 eV relative energy, and it displays the differences in the shape. Table III-C gives the inelasticities for the $\text{Na}^+\text{-HD}$ data as done for $\text{Na}^+\text{-D}_2$ and four of these spectra are plotted in Fig. III-4 as done for the other data.

C. Other Systems Studied

Very little data was taken on the $\text{Li}^+\text{-H}_2$ system as it has been extensively studied by Toennies et.al.⁵ The few spectra measured are in agreement with, but not as well resolved as, Toennies', which were made using a time-of-flight method of measuring the scattering spectra.

The apparatus here was not capable of detecting Li^+ backscattered from D_2 or He.

The backscattering of Na^+ from CH_4 and CD_4 was examined at a few energies up to 32 eV relative energy. Although the target mass is very close to that of the ions, the backscattering was unmistakably observed from these systems. The ability to detect this scattering while Li^+ scattered from mass 4 was not observed is presumed to be

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Fig. III-3. Comparison of smoothed $\text{Na}^+ - \text{HD}$ and $\text{Na}^+ - \text{D}_2$ data of approximately the same relative energy.

$\text{Na}^+ - \text{HD}$

Fig. III-4. $\text{Na}^+ - \text{HD}$ data plotted as done for $\text{Na}^+ - \text{D}_2$ data in Fig. III-1. Calibrating $\text{Na}^+ - \text{He}$ spectra are not shown.

the consequence of a much larger differential backscattering cross section for the heavier systems.

The energy calibration of these data was done by performing elastic scattering from He or Ne. Neither of these were very satisfactory because the elastic peak from He falls far from the region of the inelastic scattering, and the elastic peak from the Ne was so weak that absolute determination of its position was impossible. The scattering from CH_4 and CD_4 was not intense enough to characterize a well defined peak shape, but the estimated maximum in the peaks correspond to an inelasticity less than that observed for Na^+-D_2 at equivalent relative energies. Between 20 and 30 eV relative energy it appears as though CH_4 begins to show significant excitation. At 32.5 eV CD_4 shows an inelasticity of about 12 eV.

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IV. PERPENDICULAR BISECTOR VERSUS COLLINEAR COLLISION MODEL

A. Introduction

The rigorous solution to the problem of atoms and molecules scattering from one another requires the exclusive use of quantum mechanics in simultaneously solving for the motion of the nuclei and electrons of the system. If such a solution were feasible for a particular system, the only benefit obtained by experimentally studying that system would be to measure the capability of an empirical technique in analyzing more complicated systems. Rigorous solutions to the scattering of only the most simple systems have been obtained, however, and scattering studies play a key part in determining the validity of approximations made in reducing the exact problem to one solvable by the present available techniques.

Perhaps the greatest simplification of the problem is offered by the Born-Oppenheimer principle. This principle, based on the fact that the electron mass is much less than any nuclear mass and hence can move much more rapidly and adjust adiabatically to nuclear motion, allows the separation of the nuclear and electronic motion. The consequence is that the nuclei can be assumed to be moving in a potential determined only by their spatial arrangement. The quantum mechanical solution of electronic distribution about the fixed nuclei is still too complicated a problem to be generally useful in determining an a priori potential in which the nuclei move. Still, a potential energy surface may be guessed, and quantum, semi-classical, or classical mechanics may be used in calculating the nuclear motion.

An estimate of the validity of classical mechanics in describing the motion of the particles is obtained by calculating their de Broglie wavelength. If this is much smaller than the range over which the particles interact, classical mechanics may be assumed to be valid. Since the experiments presented here are in the energy range of ~ 10 eV and the lightest particle concerned is a hydrogen molecule, the de Broglie wavelength is on the order of hundredths of an Angstrom. The range over which the interaction of the particles is significant compared to 10 eV is two orders of magnitude greater. Hence, classical mechanics is considered as a reasonable approach to describe the translational motion of the systems studied. The vibrational de Broglie wavelength of molecular hydrogen, however, is more significant, and the use of classical mechanics can only be justified if many vibrational levels are accessible in a collision.

In applying classical mechanics to the inelastic, nonreactive scattering of a projectile from a diatomic target, there are additional considerations. Classically a predefined set of initial conditions results in a definite amount of energy transferred to the molecule in both vibration and rotation. The quantum mechanical solution of the motion of a system with the same initial conditions results in a set of probabilities that the system will end up in the accessible quantum states of internal excitation. A method of determining the agreement between the exact classical and exact quantum mechanical solutions is to compare the phase averaged energy transfer of classical collisions of initial energy E to the quantum mechanical expectation value of the

energy transfer for collisions of the same initial energy. Heidrich, Wilson, and Rapp¹ compared these quantities from exact classical calculations and the exact quantum mechanical calculations of Secrest and Johnson.² The calculations, done on the collinear collision of a projectile with a harmonic oscillator, show surprisingly good agreement well below the correspondence principle limit. Since the data of Chapter 3 clearly do not show resolved vibrational transitions, it is apparent that classical mechanics has a good chance of being adequate to explain them.

In this chapter, exact classical trajectory calculations are done on the system of projectile A colliding at zero impact parameter with diatomic molecule BC in order to understand the dependence of energy transfer on initial orientation. Special consideration is given to the collinear and perpendicular bisector orientations in understanding their relation to the backscattering data.

B. Method of Trajectory Calculations

Once some form for the interaction potential between each pair of atoms has been chosen, the classical equations of motion are obtained easily from the equations of Hamilton or Lagrange. The three body problem, however, does not have a closed form solution, and the equations must be integrated numerically. Such a solution, although straight forward in technique, requires countless repetitive steps and is only feasible for this problem if a digital computer is used.

A system of N point particles free to move in M dimensions is described by $M \times N$ coordinates and their conjugate momenta. In the absence of external fields, the motion of the center of mass of the system is independent of the relative motion of the particles and may be separated leaving $M(N-1)$ coordinates and their conjugate momenta to describe the relative motion of the system.

It is shown in Chapter V that calculation of the three body system in only two dimensions is adequate to duplicate the observed scattering. Therefore, eight variables are required to describe the system completely. The method used in setting up the corresponding equations is essentially identical to that presented by Kelley and Wolfsberg,³ and the following description is largely duplicated from their work. The four coordinates chosen to define the positions of the three particles in two dimensions are shown in Fig. IV-1. R is the distance of A from the B - C center of mass; θ' is the angle between R and an arbitrary fixed axis z ; r is the distance from C to B ; and θ is the angle between r and the z axis.

Fig. IV-1

The Hamiltonian for the system can then be written

$$\mathcal{H} = \mathcal{H}(R, \theta') + \mathcal{H}(r, \theta) + V_I(R, r, \theta', \theta) ,$$

$$\mathcal{H}(R, \theta') = E(R, \theta') = (p_R^2 / 2\tilde{m}) + (p_{\theta'}^2 / 2\tilde{m}R^2)$$

$$\mathcal{H}(r, \theta) = E(r, \theta) = (p_r^2 / 2\mu) + (p_{\theta}^2 / 2\mu r^2) + V_{BC}(r) . \quad (IV-1)$$

The p's are momenta conjugate to the coordinates; $\tilde{m}$ is the reduced mass for motion of A relative to B-C, and μ is the reduced mass for motion of B relative to C. These are given by

$$\tilde{m} = m_A(m_B + m_C) / (m_A + m_B + m_C) \quad (IV-2)$$

and

$$\mu = m_B m_C / (m_B + m_C) , \quad (IV-3)$$

where m_j is the mass of atom j. $V_{BC}(r)$ is the B-C molecular potential and $V_I(R, r, \theta', \theta)$ is the interaction potential of A with B and A with C. Hamilton's equations

$$\partial \mathcal{H} / \partial q_1 = - \dot{p}_1$$

and

$$\partial \mathcal{H} / \partial p_1 = \dot{q}_1 , \quad (IV-4)$$

where q_i and p_i are the i^{th} coordinate and its conjugate momentum respectively, give eight simultaneous linear differential equations of motion for the three body system. The Lawrence Berkeley Laboratory CDC 7600 was employed in solving these equations for the p's and q's as a function of time.

Trajectory calculations are characteristically started at time $t=0$ with A and BC moving toward one another from an initial position where their interaction potential is negligibly small. The particles are allowed to interact until the A-BC interaction is again negligible. At that time any dynamical quantity of interest from the scattered particles may be obtained from the final values of the p's and q's. These results are the consequence of the values initially assigned to those variables.

The initial q's define the orientation of the colliding system. If the z axis is chosen to be parallel to the asymptotic incoming path of A, the initial perpendicular distance of A from this axis defines the impact parameter b of the projectile on the molecule BC. This is given in terms of R_0 and θ'_0 as

$$b = R_0 \sin \theta'_0 \quad (\text{IV-5})$$

where the naughts denote initial values. Conversely, once R_0 has been chosen so that the initial A-BC interaction is negligible, the value of θ'_0 can be determined for a collision from the assigned impact parameter. r_0 is always chosen to be the equilibrium internuclear separation of the diatomic molecule. This leaves the initial orientation of the colliding system completely defined by b and the BC orientation angle θ .

The initial p's define the energy of the system. In these calculations the diatomic molecule was always assumed to have no initial energy, thus p_{r_0} and p_{θ_0} are chosen to be zero. Neglecting

the zero point vibration of the molecule greatly reduces the number of calculations required, because phase averaging does not have to be done. The remaining momenta $p_{\theta'}$ and p_R are initially defined by the initial relative velocity of the collision v_o and the initial coordinates by

$$\begin{aligned} p_{R_o} &= -\tilde{m} v_o \cos \theta'_o \\ p_{\theta'_o} &= \tilde{m} R_o v_o \sin \theta'_o \end{aligned} \quad (\text{IV-6})$$

The integrations are done using fourth-order Adams Moulton Predictor-corrector method with a starting procedure based on Zonneveld's formulas. The time interval of the method is variable within each trajectory. The minimum time interval is generally a function of the initial relative energy of the collision. This interval is generally small enough so that the total energy is conserved to within 0.01% at the end of the trajectory. Each trajectory takes an average of 3/4 seconds to calculate with the computer used.

C. Form of the Potential Used

The ability of the trajectory calculations to duplicate the laboratory observations rests on the shape of the potential surface used. It is therefore imperative to choose a realistic form for the potential, so that, by manipulating the parameters which define the resultant surface shape, a reasonable approximation to the actual surface may be obtained. A form containing many adjustable parameters

has the capability of very accurately duplicating the actual potential, but it also presents the difficulty of simultaneously finding the values of the parameters which define the best fit. Consequently, a form which has the capability of giving a reasonable fit with the manipulation of as few parameters as possible is sought.

The particular family of systems under consideration is that of an alkali ion and a hydrogen molecule in their ground state colliding to yield a vibrationally excited or dissociated hydrogen molecule and a ground state ion:

In view of the above consideration and in following common practice,⁴ the potential used in these calculations to describe the interaction of the ion with the hydrogen atoms is an exponential repulsion between the ion and each atom:

$$V_I(R, r, \theta', \theta) = A' [\exp(-r_{AB}/L) + \exp(-r_{AC}/L)] , \quad (\text{IV-7})$$

where

$$r_{AB} = \left\{ R^2 + \left[\frac{m_C}{m_B + m_C} r \right]^2 - 2 \frac{m_C}{m_B + m_C} R r [\cos(\theta - \theta')] \right\}^{1/2}$$

$$r_{AC} = \left\{ R^2 + \left[\frac{m_B}{m_B + m_C} r \right]^2 + 2 \frac{m_B}{m_B + m_C} R r [\cos(\theta - \theta')] \right\}^{1/2} .$$

Here r_{AB} and r_{AC} are the A,B and A,C distances, and in Eq. (IV-7) L and A' are, respectively, parameters characterizing the steepness and maximum height of the potential between the projectile and each atom. The equipotential locus about B and C appears as two spheres for large B-C separations or high potential energies. Hence, Eq. (IV-7) is referred to as the "dumbbell" potential.

For large separations of B and C the true potential affecting the motion of A relative to B and C is clearly independent of the B, C distance as is the case in Eq. (IV-7). As B and C are brought closer together, the factors which give rise to the ion atom repulsion are altered as a bond is formed, making the repulsion an inseparable function of all three internuclear distances. Since the form of the repulsion chosen does not account for this, these facts are acknowledged as possibly contributing to the greatest weakness in the model. In order to understand the possible discrepancies, it is useful to examine potential energy hypersurfaces which have been calculated for systems containing fewer electrons. He- H_2 interaction potentials have been calculated⁵ by approximate quantum mechanical methods for a range of H_2 internuclear separations. From these potentials it is evident that the initial force experienced along the vibrational coordinate, resulting from He approaching along the perpendicular bisector, is one which compresses the hydrogen atoms. The dumbbell repulsive potential, however, always gives rise to a force acting to spread the molecule from this configuration. Still, this system was studied

for interactions ranging up to only ~ 2 eV and the $\text{Li}^+ - \text{H}_2$ hyper-surface, which has also been calculated,⁶ shows characteristics more closely related to the dumbbell potential.

All attractive potentials, the strongest of which is the charge-induced-dipole attraction, are omitted. This is done because the experiments are performed at an energy considerably higher than the potential well depth resulting from such an attraction, and it is assumed that the transfer of energy in a nonreactive collision is mostly dependent upon the shape of the potential at the turning point and not the presence of a well.⁷ In addition, the polarizability of the hydrogen molecule, which defines the attractive potential between that molecule and an ion, is not simply the sum of the polarizabilities of two isolated hydrogen atoms.⁸ Thus, it is somewhat ambiguous as to how the ion - induced-dipole attraction should be included.

In most of the calculations the B-C molecular potential is taken to be the Morse potential

$$V_{\text{BC}}(r) = D[1 - \exp[-\beta(r-r_0)]]^2, \quad (\text{IV-8})$$

where D , β , and r_0 are chosen as 4.748 eV, $1.944\text{\AA}^{-1}$, and $0.7417\text{\AA}$ to attempt to duplicate the true H_2 potential. A harmonic potential

$$V_{\text{BC}}(r) = \frac{1}{2} k(r-r_0)^2 \quad (\text{IV-9})$$

is used for comparison in some cases. Here k is chosen as 5.725×10^5 dynes/cm and the Morse value of r_0 is retained to duplicate the

position and curvature of the bottom of the Morse potential well.

D. Orientation Dependence of Inelasticity

If only zero impact parameter collisions are considered, the only remaining parameter defining the initial orientation of A to BC is the angle θ of Fig. IV-1. In the past it had been assumed that the energy transferred in a head-on collision is always the greatest for the collinear orientation where $\theta=0^\circ$. Functions^{4,9} were derived which describe the energy imparted into vibration as monotonically decreasing to zero as θ increases from 0° to 90° . Kelley and Wolfsberg¹⁰ showed this behavior to be generally valid only when $m_A \ll m_B=m_C$, and they improved¹¹ on an orientation inelasticity function, obtaining a function to be considered valid when those conditions are met. The expression at which they arrived by an approximate procedure is

$$f(\theta) = \left(\frac{\cos\theta \tanh[(r/2L)\cos\theta]}{\tanh(r/2L)} \right)^2 \quad (IV-10)$$

Still, their function drops to zero when $\theta=90^\circ$ and is independent of the A' parameter. From these treatments and the general disregard for the orientation where $\theta=90^\circ$, the common consensus appears to be that the energy transfer resulting from this perpendicular bisector orientation is either negligibly small or nonexistent.

Figure IV-2 shows the total inelasticity as a function of initial orientation for zero impact parameter collisions at 5 and 10 eV

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Fig. IV-2. Excitation - orientation functions for zero impact parameter collisions. Here $\lambda = 384$ m μ and $L = 0.247\lambda$.

relative energy for the $23+2-2^*$ system. The A' and L values of the repulsive potential of Eq. (IV-7) have been chosen to be 384 eV and $0.247\text{\AA}$, respectively. This choice is based on the A and L values for a spherically symmetric exponential repulsion of Na^+ from the center of a deuterium molecule reported by Dittner and Datz¹² as being predicted by Amdur. The A' value used between the ion and each atom is half that predicted by Amdur for the spherically symmetric potential. This is because at ion-molecule separations which are large compared to the diatomic bond distance, the two centered repulsion converges on the form of a single centered exponential repulsion with a coefficient twice as large as that for the two centered potential,

i.e.

$$\lim_{\frac{R}{r} \rightarrow \infty} A' [\exp(-r_{AB}/L) + \exp(-r_{AC}/L)] = 2A' \exp[-R/L]. \quad (\text{IV-11})$$

The potential predicted by Amdur was reported to be correct to within 25% in the range $1.23 \leq R \leq 2.22\text{\AA}$.

At the energy of these calculations it is evident from Fig. IV-2 that, in addition to the great sensitivity in the excitation - orientation function in the region of collinear collisions, there is a significant amount of inelasticity in the perpendicular bisector orientation. In examining the actual trajectories which give rise to these curves, it is evident that there are three regions of orientation which correspond to distinctly different types of encounters. These encounters are most easily understood in the high energy limit. In this limit the atoms involved act as hard spheres and a distinct

* This notation, $x+y-z$, is used to stand for $m_A=x$, $m_B=y$, and $m_C=z$, where the masses are all in atomic mass units.

sequence exists in collisions between atom pairs. The sequence for the three types of encounters is pictured in a hard sphere representation in Fig. IV-3. The first results, in its purest form, from an exact collinear orientation. In the high energy limit the process resolves itself into three distinct collisions. Here, projectile A collides with atom B; B collides with C transferring all its newly gained momentum to C; and finally A collides again with B. If $m_A \gg m_B = m_C$, as in this case, the motion of A is changed only very slightly in each collision with B. The second collision with B, therefore, imparts again to B nearly the amount of momentum which B lost to C, leaving B and C with approximately no relative motion and with their equilibrium separation. Initial orientations in the range of $25^\circ \lesssim \theta \lesssim 30^\circ$ correspond to a second type of double collision of the projectile. In this case, however, the second collision is with the far atom of the molecule. Here A collides initially with B, with a fraction of the total force going toward compressing the molecule, the rest toward rotation. Then B grazes off C, allowing C to pass and collide with A. This collision of A with C acts to remove most of the rotational energy initially imparted to BC. The result is a relatively large amount of vibrational excitation roughly proportional to the square of the fraction of the force acting to excite vibration since the energy transfer depends on the square of the force.⁴ As the initial orientation angle θ increases, the compressing force acting to excite the molecule is decreased, hence, the excitation becomes less. Finally the third distinct type of

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Fig. IV-3. Hard sphere representation of distinct processes exhibited by classical trajectories calculated on the 23+2-2 system. Velocities are represented qualitatively by arrows.

encounter is that corresponding to A approaching BC along its bond bisector. The mechanism of excitation in this orientation is simply the spreading of the atoms of the diatomic molecule by the projectile simultaneously colliding with B and C.

A simplistic picture of the meaning of the curves in Fig. IV-2 may be constructed using a distribution function derived for the computation of a steric factor. The angular dependence of the inelasticity of the second type of encounter may be equated with one of these functions. In Fig. IV-4 the amplitude of Eq. (IV-10), representing the most sophisticated form of these functions, is adjusted to fit the 10 eV curve of Fig. IV-3 in the region $20^\circ < \theta < 30^\circ$. To a first approximation the discrepancy in the trajectory curve in the region of $\theta=0^\circ$ may be thought of as the result of a second deexciting collision. Likewise, the extra height in the $\theta=90^\circ$ region may be thought of as excitation resulting from a spreading impulse imparted in a broadside collision. At lower energies the vibrational period of the molecule is significant compared to the duration of the collision. Similar calculations by Kelley and Wolfsberg³ done at lower energies show additional structure which is presumably due to a stronger coupling of the collision with the vibrational motion of the oscillator.

It is important in comparing the results of the trajectory calculations to the laboratory data to understand the contribution of an initial orientation to the backscattered energy spectrum. Considering a sphere of radius R about the center of mass of BC, the

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Fig. IV-4. Steric factor orientation function $f(\theta)$ amplitude fit to 10 eV orientation - excitation function of Fig. IV-2. at $\theta = 25^\circ$.

area of an element on the surface of that sphere corresponding to an angle θ is $2\pi R^2 |\sin\theta| d\theta$. The relative contribution to scattering from an orientation defined by θ is proportional to the area of that element. Thus, that contribution is proportional to $|\sin\theta|$. In past publications¹²⁻¹⁴ the inelasticity corresponding to the position of the maximum of the backscattered peak for alkali ion - hydrogen molecule systems has been directly compared to exact classical¹⁵ and quantum mechanical calculations² of a projectile scattering collinearly from a harmonic oscillator. This treatment appears to be poorly chosen because it uses the scattering result of the least favorable orientation to predict a result which is predominantly the consequence of an entirely different process, i.e. broadside scattering. Indeed, the fact that the backscattering data and exact collinear harmonic oscillator calculations agree up to a relative energy of 20 eV in the systems compared has been acknowledged as being coincidental.¹⁶

The following sections of this chapter are aimed at closely examining the two extreme collision orientations: the collinear and the perpendicular bisector collision approach. The collinear orientation is studied to show and explain the striking differences of replacing the harmonic potential with the more realistic Morse potential. The bisector orientation is studied as possibly offering a direct, meaningful comparison to backscattering data.

E. Collinear Collision Orientation

1. Skewed Coordinate Representation

There is a particularly illustrative manner in which trajectories of the collinear collision configuration can be represented. The following is a short derivation of that representation so that its significance may be understood in its subsequent use.

Assume particles A, B, and C are restricted to move only along a single axis. The relative position of the particles is completely defined in terms of the A, B separation r_{AB} and the B, C separation r by coordinates X and Y as shown in Fig. IV-5. X , the distance of A from the BC center of mass, is given by

$$X = r_{AB} + \lambda r, \quad (\text{IV-12})$$

where $\lambda = m_C / (m_B + m_C)$, and Y , the B-C separation, is simply equal to r . The total kinetic energy is given as a function of these coordinates by

$$T = \frac{1}{2} \tilde{m} \dot{X}^2 + \frac{1}{2} \mu \dot{Y}^2. \quad (\text{IV-13})$$

If still another pair of coordinates is chosen such that

$$x = X \quad (\text{IV-14})$$

$$\text{and} \quad y = Y/a, \quad (\text{IV-15})$$

where

$$a^2 = \frac{\tilde{m}}{\mu}, \quad (\text{IV-16})$$

the kinetic energy expression reduces to

$$T = \frac{1}{2} \tilde{m} (\dot{x}^2 + \dot{y}^2) \quad . \quad (\text{IV-17})$$

This equation also expresses the kinetic energy of a point of mass $\tilde{m}$ moving in two dimensions defined by the orthogonal coordinates x and y . This treatment, originally done by Wigner in the paper of Eyring and Polanyi,¹⁷ greatly enhances the qualitative understanding of the motion of the particles by equating their motion to that of a mass point sliding without friction on a potential energy surface. The height of the surface, given by the potential energy of the system, $V(r_{AB}, r)$, can be found in terms of x and y by following through the transformations made.

Fig. IV-5

Returning to the original coordinates r_{AB} and r , the new coordinates result in the $r_{AB} = 0$ and $r = 0$ axes being skewed to one another at an angle β less than 90° (See Fig. IV-6). A general expression for the

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Fig. IV-6. Skewed original coordinates (r_{AB}, r) and mass weighted coordinates (X, Y) of two dimensional representation of collinear system.

slope of the $r_{AB} = 0$ axis is given by y/x , where x and y are expressed in terms of r_{AB} and r for $r_{AB} = 0$:

$$\tan \beta = \left(\frac{y}{x} \right)_{r_{AB}=0} = \frac{1}{\lambda a} \quad (IV-18)$$

Substituting the mass expressions for λ and a yields

$$\beta = \tan^{-1} \left(\frac{m_B M}{m_A m_C} \right)^{1/2} \quad (IV-19)$$

where $M = m_A + m_B + m_C$. In the original treatment the skewing angle used was the complement of this angle. This error was corrected in a later paper.¹⁸

This mass weighted or skewed coordinate representation is used here for plotting and interpreting trajectories and studying the system behavior in the high energy limit. Once the motion of the point moving on the surface is understood, it can be interpreted in terms of the motion of the three particle system. As a guideline, rebounding off the potential wall parallel to the $r_{AB} = 0$ axis is equivalent to A colliding with B, and any motion along the y coordinate corresponds to vibration of the BC oscillator.

2. Review of Pertinent Developments in Classical Collinear Collision Theory

The classical theory of translational - vibrational energy transfer was originally completed in 1936 by Landau and Teller.¹⁹ The qualitative implication of their argument is that the efficiency of leaving the available energy of a collision in vibration

after the collision is proportional to the ratio of the vibrational period to the duration of the collision. In the limiting case of a very slow collinear collision the atoms adiabatically adjust to equally distribute the force of the collision between the two pairs of colliding particles. The outgoing motion of the system after the turning point is identically opposite to the incoming motion. Hence, the oscillator returns to its initial state and no net vibrational excitation is experienced. The other extreme is a fast impulsive collision where the interaction of the projectile A with atom B is over before the BC bond has compressed significantly to affect the motion of C. Hence, the maximum relative motion of B and C results.

Much later, Rapp²⁰ reformulated the theory in making a comparison with a quantum mechanical treatment. In his paper the energy transferred to the oscillator in a collision is expressed as

$$\Delta E = \frac{1}{2\mu} \left| \int_{-\infty}^{\infty} F(t) e^{-i\omega t} dt \right|^2, \quad (\text{IV-20})$$

where ω is the angular frequency of the oscillator's assumed harmonic potential. $F(t)$ is the oscillator driving force, which is found by solving the equation of A scattering from B rigidly bonded to C. The limiting cases of the Landau - Teller argument are readily seen from Eq. (IV-20). If the A, B collision is fast relative to the vibrational period given by $T = 2\pi/\omega$, then the exponential term is constant over the period that the force is finite. The resulting energy transfer is just proportional to the square of the impulse. If the collision

is slow, the exponential term makes many oscillations over the period in which the force acts, averaging the net energy transfer to zero.

Kelley and Wolfsberg²¹ performed exact classical calculations on numerous systems in the collinear configuration. In comparing the exact harmonic oscillator results to the conventional classical theory, they found large differences for some combinations of masses. In addition, they pointed out that, in the high energy limit, the existing theory allowed the oscillator to receive more energy than was available in the collision. This was remedied recently by Mahan,²² who explained that B should not be considered as being bonded rigidly to C in the high energy limit, but rather B should be entirely free from C. This refinement causes the energy transfer of Eq. (IV-20) to converge at high energy on the value expected by A and B colliding once as hard spheres. Still this model does not work when $m_B \ll m_A, m_C$ as then multiple A-B encounters may be experienced.

Secrest²³ solved several cases of the problem of a body colliding with an oscillator fixed to a wall, which he and Johnson² had shown to be equivalent to the collinear three body system. In the equivalent representation, shown in Fig. IV-7, the colliding body has a mass given by

$$m = \frac{m_A m_C}{m_B} \quad (\text{IV-21})$$

and the oscillator has a unit force constant and a unit mass. Since the corresponding formalism is equivalent to the A - BC problem, it is evident that the behavior of a system, especially in comparison

with that predicted by approximate techniques, can be given in terms of m . Referring back to the discrepancies found by Kelley and Wolfsberg,²¹ it is found that the conventional theory is well behaved when $m \ll 1$. Secrest observed in his calculations that in systems where $m \gtrsim 0.5$ the change in the fraction of the energy transferred in a collision as the relative energy is increased is not a smooth monotonic increase. He explained this in terms of multiple collisions in the high energy limit. In general, the behavior of the systems studied by Secrest is understood by the following argument. At low energy the Landau - Teller argument is qualitatively valid for all systems. Hence, as the energy is increased, the fraction of the energy appearing as vibration increases. At high energy, however, the particles act as hard spheres, and, above a limiting value of m , multiple collisions take place as discussed in Section D and shown in case 1 of Fig. IV-3. In the case where $m = 1$, there are two collisions between A and B and the second collision exactly removes all the relative motion initially imparted to B and C. Thus, for that particular case the excitation as a function of energy rises from zero to a maximum and returns to zero as the hard sphere limit is reached.

Fig. IV-7

In the high energy limit, where all three particles act as hard spheres, the energy transfer can be expressed exactly. If A has an initial velocity v_0 relative to B and C, which are initially stationary in the laboratory, then the initial velocity of B relative to the AB center of mass is $v_0 m_A / (m_A + m_B)$. The AB collision is elastic, so after that collision the change in the velocity of B and its laboratory velocity are $2v_0 m_A / (m_A + m_B)$. Since C is still stationary the final relative motion of B and C corresponds to a vibrational energy of $\Delta E = \frac{1}{2} \mu [2 v_0 m_A / (m_A + m_B)]^2$. The fraction of the total relative energy of the initial motion of A on BC is given by

$$\frac{\Delta E}{E_r} = \frac{4m_A m_B m_C M}{(m_A + m_B)^2 (m_B + m_C)^2} \quad (\text{IV-22})$$

where $E_r = \frac{1}{2} \tilde{m} v_0^2$. This quantity can also be obtained readily by considering the skewed coordinate representation developed in the previous subsection. In the hard sphere limit the potential surface is accurately represented by vertical walls on a flat plane as shown in Fig. IV-8a. A projectile A impinging collinearly on the unexcited oscillator BC corresponds to the mass point moving from right to left parallel to the x-axis. As stated before, a collision with the skewed wall is analogous to A colliding elastically with B. The angle at which the mass point rebounds relative to the incoming path determines the component of the initial velocity v_0 which goes toward determining the vibrational energy. This angle, determined through the law of reflection and geometrically related back to β , is $\pi - 2\beta$. Therefore,

(a) $\beta \geq 60^\circ$

(b) $45^\circ \leq \beta < 60^\circ$

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Fig. IV-8. Skewed coordinate representation of hard sphere collinear collisions for (a) $m \approx 1/3$ and (b) $1/3 \leq m < 1$.

the energy ending in vibration is $\frac{1}{2} \tilde{m} [\sin(\gamma-2\beta) v_0]^2$, and the fraction of the initial relative energy in vibration is

$$\frac{\Delta E}{E_r} = \sin^2 2\beta . \quad (\text{IV-23})$$

By use of trigonometric identities Eq. (IV-19) may be substituted into this equation, and it can be shown that Eq. (IV-23) is identical to Eq. (IV-22).

It is evident, as shown in Fig. IV-8b, that if $\beta < 60^\circ$ the mass point, after rebounding off the horizontal wall, will collide with the skewed wall again. The collision with the horizontal wall is equivalent to B and C colliding elastically and results only in reversing the direction of their vibration. The second collision with the skewed wall, however, reduces the energy in vibration. The fraction of the initial relative energy left in vibration is determined as in Fig. IV-8b and is

$$\frac{\Delta E}{E_r} = \sin^2 4\beta . \quad (\text{IV-24})$$

If Eqs. (IV-23) and (IV-24) are compared with the high energy limit of the exact classical calculations of Secrest,²³ differences are found for $m > 1/3$. The ratio of the masses used in determining β in Eq. (IV-19) is just the reciprocal of m . Therefore, the relative inelasticity can be plotted as a function of m for both the total hard sphere case and the high energy limit of the exact calculations.

This has been done in Fig. IV-9 for $0 \leq m \leq 1$. If the molecule being hit is heteronuclear, m can assume values greater than unity. As m becomes larger, and hence β becomes smaller, additional A-B collisions can take place. These are not considered here but can be understood easily by extending the multiple reflection argument in the skewed coordinate representation. The discrepancy of the exact calculations, which is apparent in Fig. IV-9, arises from the use of a harmonic potential for the oscillator. With this potential the horizontal repulsive wall of the skewed coordinate representation remains soft. Therefore, the angle β , which determines the limiting case for which a second collision occurs, is that angle which allows the sinusoidal trajectory of vibration to be tangent to the skewed wall. This case is shown in Fig. IV-10. Solving for β yields

$$\beta = \tan^{-1} (1-2\cos\delta)^{1/2} \quad (\text{IV-25})$$

where δ , the phase of the oscillation at which the second contact is made, is given by the first positive nonzero solution of the equation

$$\delta = \tan\delta \quad (\text{IV-26})$$

This equation, obtained by equating the slope of the skewed wall and the first derivative of the trajectory at the point of tangency, gives δ as approximately 4.49. This corresponds to a β of $\sim 51^\circ$, which is about 9° less than the limiting angle for the total hard sphere model.

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Fig. IV-9. Relative fraction of inelasticity vs. m for A colliding collinearly with BC in the high energy (hard sphere) limit.

Fig. IV-10

In the high energy limit the more realistic Morse potential, in which both repulsions are exponential, converges on the total hard sphere model. In contrast, an unrealistic consequence of the harmonic potential is that, at moderately high energies, the atoms of the oscillator actually pass through one another.

Attermeyer and Marcus²⁴ performed calculations in the adiabatic approximation for comparison to the existing approximate theory and exact calculations. In the adiabatic approximation the forces acting on the system are a function only of the separation of A from the BC center of mass. The equilibrium or adiabatic A-B and B-C distances are found from the A-BC separation, and the forces of that equilibrium configuration are allowed to act on the particles in their actual position. Solutions obtained in the adiabatic approximation must be evaluated by numerical integration and, therefore, require a computer

as do the exact solutions. Still, some useful facts are found from the criteria for good agreement between those solutions. In general, it is found that the agreement is best when the actual trajectory is close to that of an adiabatic collision. It is therefore assumed that the degree of the agreement defines the adiabaticity of a collision or the divergence from a totally impulsive collision. In terms of the skewed coordinate representation, the adiabatic path is the locus of the points of tangency of vertical lines corresponding to constant A-BC separation to the equipotential contours. This path is most readily followed when the potential-energy surface has a well-defined ascending trough. This is the case when the surface is most highly skewed as for large values of m . Thus, the hard sphere limit is approached more slowly with the initial relative energy as m increases.

3. Comparison of Morse and Harmonic Oscillator Results

Collinear trajectory calculations were performed on the 23+2-2 system using both a harmonic and Morse potential so that the difference resulting from the more realistic potential could be estimated and understood. Figure IV-11 shows a plot of inelasticity ΔE versus the initial relative energy E_r for one pair of potentials. The lower curve is for the same system plotted in Fig. IV-2, and the upper curve is for that system with the harmonic potential of Eq. (IV-9) in place of the Morse potential. The harmonic potential calculation results are essentially identical with the exact classical calculations of Secrest.²³ The refinement of these calculations induced by

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Fig. IV-11. Plot of inelasticity vs. the relative energy for the collinear orientation showing the difference experienced from using a Morse and harmonic BC potential. Here, $A' = 384$ eV and $L = 0.247\text{\AA}$.

incorporation a more realistic Morse potential has caused a remarkable difference as observed also by Kelley and Wolfsberg²¹ and Cheng and Wolfsberg.²⁵ To aid in understanding this difference, 10 eV relative energy trajectories for both these systems have been plotted in the skewed coordinate representation in Fig. IV-12. A striking feature in these trajectories is the different degrees with which they vary from the adiabatic path shown by a dashed line. The Morse oscillator trajectory is clearly much closer to that path. This is easily understood, however, through the argument of Attermeyer and Marcus²⁴ that the more well-defined the trough is about the adiabatic path, the more adiabatic the collision is apt to be. The Morse oscillator trajectory, being more adiabatic, would be less inelastic, thus explaining the difference observed in Fig. IV-11. This description is consistent with the interpretation that the inelasticity of the total collision results from the difference in the forces on atoms B and C. When the Morse oscillator is compressed, this difference diminishes greatly due to the stiffness of the repulsive B-C wall. This force increases less rapidly for a harmonic oscillator, hence a greater differential force on B is possible and the inelasticity is greater.

The general criterion for a near adiabatic collision is that the vibrational period of the oscillator is much shorter than the lifetime of the collision. This criterion is usually expressed as

$$\omega L/v_0 \gg 1 \quad (\text{IV-27})$$

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Fig. IV-12. Skewed coordinate representation of 10 eV 23+2-2 trajectories in the collinear orientation for the Morse BC potential ($\Delta E = 0.17$ eV) and the harmonic BC potential ($\Delta E = 2.07$ eV). A' and L are the same as in Fig. IV-11. The potential contours sketched in the background are labeled in eV from the bottom of the BC potential well.

where $\omega = (k/\mu)^{1/2}$ is the angular frequency of the oscillator and v_0 is the initial relative velocity of the collision. The quantity $\omega L/v_0$ is 0.66 for these collisions if the harmonic force constant k is used in computing ω . Since this quantity is closer to satisfying the criterion for an impulsive collision, $\omega L/v_0 \ll 1$, it is evident that an alternate method of computing the critical factor $\omega L/v_0$ should be sought. If one considers the high energy oscillations of a Morse oscillator, it is easily recognized that the period of the motion from the equilibrium separation to the compression turning point and back out again is significantly shorter than half of a full oscillation period. Therefore, it is reasonable to assume that the duration of the relatively hard collision between B and C should be used in arriving at a frequency to characterize a collision in which a realistic molecule is compressed. This treatment also has the correct qualitative effect on the value of $\omega L/v_0$. It can be seen from Fig. IV-9 that for $m \ll 1/3$, the maximum fraction of the initial relative energy capable of being transferred into vibration in a single collision, is small. Thus, the harmonic potential is an adequate representation of the potential which the oscillator samples, and the harmonic frequency may be used as before. For larger values of m , for which significantly anharmonic portions of the oscillator potential are sampled, the frequency must be increased to correspond to the faster oscillation of BC in its compression. It is not absolutely clear how ω should be determined. The oscillator could be assumed to be compressed to a potential equal to the inelasticity

of a single hard collision given by Eq. (IV-23) and corresponding to some turning point r_t . Then the interval of compression from the BC equilibrium separation v_0 is given by

$$\tau = \left(\frac{\mu}{2}\right)^{1/2} \int_0^{r_t} \frac{dr}{(E_r - V(r))^{1/2}} \quad (\text{IV-28})$$

where $V(r)$ is the potential between B and C. This interval could be associated with an appropriate frequency by $\omega = \pi/2\tau$. An alternate method is to regard the frequency as a function of the oscillator coordinate as done by Mahan²² and simply to use the frequency corresponding to r_t .

F. Perpendicular Bisector Approach

1. Direct Applicability of Perpendicular Approach

If one considers the shape of the orientation - excitation function $\Delta E(\theta)$ as plotted in Fig. IV-2, it is possible to obtain a qualitative feeling for the relative contribution of each orientation to the inelasticity spectrum obtained in the experiments. The contribution of an orientation defined by θ to a particular inelasticity is proportional to $\sin\theta$ as mentioned in Section D and inversely proportional to the sensitivity of inelasticity to changing the orientation. If $\Delta E(\theta)$ is relatively insensitive to small changes in the impact parameter b , then the zero impact parameter curves of Fig. IV-2 are suitable for estimating the sensitivity of $\Delta E(\theta)$. The sensitivity can be expressed simply as $d\Delta E(\theta)/d\theta$, and the inelasticity spectrum

can be qualitatively represented for perfectly resolved classical backscattering from homonuclear diatomic molecules as

$$S(\Delta E) \propto \frac{2\pi \sin\theta}{\frac{d\Delta E(\theta)}{d\theta}} \quad , \quad (IV-29)$$

where the right hand side, given in steradians per unit energy is directly proportional to the number of orientations contributing to the inelasticity ΔE of interest (4π steradians corresponding to all possible A-BC zero impact parameter orientations). This equation behaves in an analogous manner to a differential scattering cross section. A differential cross section exhibits a maximum at a rainbow angle where the sensitivity of deflection to changing the impact parameter drops to zero. In addition more than one impact parameter can contribute to its size at a particular deflection. Similarly, an inelasticity spectrum shows a maximum when $d\Delta E(\theta)/d\theta$ goes to zero and multiple orientations may contribute to the intensity at a given inelasticity. Since the slope of $\Delta E(\theta)$ is always zero when $\theta = \pi/2$ for homonuclear diatomic molecules, and since $\sin\theta$ has its maximum value at that same orientation, the highest maximum in the spectrum will ideally appear at the inelasticity resulting from A approaching BC along the perpendicular bisector of its bond. Therefore, it is assumed that, by fitting the results of trajectory studies on this one orientation to the position of the maximum of experimental studies, the parameters which best characterize the interaction potential in the region studied can be found.

2. Comparison to Na^+-D_2 Data

In collinear studies the inelasticity is independent of the A' parameter since it only determines the position of the turning point and not the stiffness of the interaction. In the perpendicular bisector orientation the interaction is dependent on both the L and A' parameters since atom A makes an oblique collision with atoms B and C, thus being affected by their sizes represented partially by A' . Hence, such studies have the capability of predicting suitable values for both parameters.

It is impossible to directly invert scattering results to find the particular parameters which give rise to a certain trend in inelasticity. Therefore, the values of the parameters must be chosen by trial and error to find the potential which best reproduces the trend in inelasticity. So that the effort of this procedure can be minimized, the A' and L dependence of the inelasticity were studied separately prior to searching for a fit.

Increasing A' of Eq. (IV-7) primarily has the effect of increasing the relative sizes of B and C to A. Increasing their sizes reduces the depth with which A penetrates between them in a bisector collision of given initial energy. If A does not penetrate as deep, a smaller component of the collision force acts to spread the molecule and less excitation results. This effect is apparent in Fig. IV-13a where the inelasticity is shown as a function of initial energy for four values of A' and one value of L .

(a) A' dependence

(b) L dependence

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Fig. IV-13. Curves showing the shape dependence of ΔE vs. E_r on the A' and L parameter for collisions in the bisector orientation.

The dependence on L is somewhat more complicated. Increasing L has the general effect of making the interaction softer; however, if A' is held constant it also makes B and C appear larger to A . As a crude approximation, though, the energy transfer in a bisector collision of energy E is primarily dependent on the size of the equipotential contour about BC given by Eq. (IV-7). Therefore, A' and L pairs can be chosen to give an identical equipotential contour at energy E , and the dependence on L can be learned by examining the inelasticity for those potentials at different initial energies. These curves are shown in Fig. IV-13b in an oversimplified representation of the interdependence of A' and L . The L dependence is qualitatively correct, however, and it appears reasonable. For a larger L or softer interaction a lower energy equipotential bounds a larger volume than for a smaller L , causing less force to act in exciting the molecule in a bisector collision.

By making use of the influence of A' and L on the shape of the excitation curve, values have been obtained for those parameters from calculations on the perpendicular bisector orientation to fit the $\text{Na}^+ - \text{D}_2$ data given in Table III-a. These data and the curve corresponding to $A' = 150 \text{ eV}$, and $L = 0.40 \text{ \AA}$, which represent the best fit obtained, are shown in Fig. IV-14.

As a test of the validity of the perpendicular bisector model and, in general, for a better understanding of the breakdown of each individual backscattering spectrum, it is worthwhile to examine the general three-dimensional classical analog to the scattering experiments

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Fig. IV-14. Fit of the results of calculations on the $23+2-2$ system (curve) to the Na^+-D_2 data of table III-A. The curve corresponds to $A' \approx 150$ eV and $L \approx 0.40\text{\AA}$.

using the potential parameters obtained from the perpendicular bisector approach. This is considered in the following chapter, but an important consequence applicable to the present discussion is that the maximum in the peak of the data corresponds to a greater inelasticity than that of the most probably observed process. This means that, for poorly resolved data, the potential, fit solely by using the bisector approach, corresponds to values of A' and L which result in a curve that is too high.

3. Possible Approximations

a. Comparison of Morse and harmonic oscillator results. So far the analysis of data using the perpendicular bisector approach has required the numerical integration of the equations of motion. Therefore, it is desirable to assess the validity of feasible approximations so that the inelasticity may be reduced to an explicit function of the potential parameters A' and L .

Perhaps the most useful approximation if it is valid is the replacement of the Morse potential with a harmonic potential. This modification substantially simplifies the equations of motion and allows an approximate solution of the type derived by Landau and Teller to be pursued. A comparison of the results using the harmonic and Morse potentials of Eqs. (IV-9) and (IV-8) are shown in Fig. IV-15 for calculations on the perpendicular bisector orientation. The repulsive potential used is that of Amdur used in the collinear orientation comparison of Section E(3). In the energy range plotted the harmonic oscillator results show approximately 73% as much

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Fig. IV-15. Inelasticity vs. the initial relative energy for bisector collisions showing the effect of using a harmonic potential in place of the Morse potential. Here, $A' = 384$ eV and $L = 0.247\text{\AA}$.

inelasticity as the Morse calculations.

To aid in understanding the discrepancy between the Morse and harmonic calculations it is useful to plot trajectories in an equivalent two dimensional representation as done for the collinear orientation. If one defines coordinates X and Y as in Fig. IV-16, then Eq. (IV-13) is also applicable to the perpendicular bisector orientation, and the subsequent transformation can be made again. The result is the same as for the collinear case where $x=R$ and $y=r/a$ except that the potential on which the mass point slides has significant differences. Instead of appearing skewed, the equipotential contours elliptically skirt the origin. The mass point sliding into and back out of these contours corresponds to the projectile A colliding simultaneously with atoms B and C. Rebounding from the contours which are parallel to the x -axis is equivalent to B and C compressing and returning as in the skewed representation.

Also the coordinates x and y only remain orthogonal throughout the collision if the atoms of the molecule are identical. Therefore, this single particle representation is applicable only when $m_B = m_C$.

Fig. IV-16a

Fig. IV-16b

HARD SPHERE TURNING POINT

In Fig. IV-17 perpendicular bisector trajectories are plotted for the 10 eV cases of Fig. IV-15. In the region of strong interaction there does not appear to be a significant difference in the trajectories. If, however, one considers the curvature of the oscillator potentials at the turning points of the A-BC motion, it is evident that the Morse curvature is slightly less than that of the harmonic potential. The oscillator frequency, used in determining the critical factor $\omega L/v_0$ discussed in the section on collinear collisions, can be considered to be a function of the oscillator coordinate and is determined by the potential's curvature as discussed by Mahan.²² Since the curvature at the turning point in the x motion is less for the Morse oscillator, those collisions would correspond to a more

(a)

(b)

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Fig. IV-17. Two dimensional representation of 10 eV 23+2-2 collisions in the bisector orientation using the Morse ($\Delta E = 2.72$ eV) and harmonic ($\Delta E = 1.61$ eV) potentials. Here, $A' = 384$ eV and $L = 2.247\text{\AA}$. The potential contours sketched in the background are labeled as eV from the bottom of the BC potential well.

impulsive interaction. Since there is no complication of multiple collisions in this system, a more impulsive collision would result in more excitation. This is what is observed.

b. Hard sphere limit. In the hard sphere limit the configuration in which A just makes contact with both B and C defines a relationship between the coordinates x and y . If d is the sum of the hard sphere radii of A and B then the following relationship holds for the right triangle shown in Fig. IV-16b: $X^2 + Y^2/4 = d^2$. If the transformations of Eqs. (IV-14) and (IV-15) are made this expression becomes

$$\frac{y^2}{(2d/a)^2} + \frac{x^2}{d^2} = 1, \quad (\text{IV-30})$$

which is the equation of an ellipse about the origin in the mass weighted coordinate representation. Just as in the skewed representation, the fraction of inelasticity may be determined geometrically and is given as shown in Fig. IV-18 by

$$\frac{\Delta E}{E} = \sin^2 2\gamma. \quad (\text{IV-31})$$

Here, γ is found from the slope of the ellipse at the point at which the sliding mass point makes contact, and it is obtained from

$$\tan \gamma = -\frac{4}{a} \left(\frac{d^2}{y^2} - \frac{1}{4} \right)^{1/2}, \quad (\text{IV-32})$$

where Y is the separation of the oscillator when A makes contact with BC.

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Fig. IV-18. Two dimensional representation of hard sphere limit for bisector collisions. d is the A-B separation at their point of contact.

c. Approximate solution. By comparing Figs. IV-11 and IV-15 it is apparent that the harmonic potential is a better approximation of the Morse potential for broadside collisions than for collinear collisions. This suggests that a similar procedure to the one used in deriving the approximate collinear collision theory can be applied to the perpendicular bisector orientation without having as stringent limits imposed on its validity by the relationship of the masses.

The following approximate solution was derived by Mahan²⁶ and approximately follows the procedure of Landau and Teller¹⁹ and Rapp.²⁰ Their procedure involves the basic assumption that the oscillator coordinate is not significantly perturbed during the collision. This assumption allows the motion along the x coordinate to be solved separately from the motion of the oscillator. This solution provides a time dependent force which can be used in the oscillator equation of motion to define a driven oscillator problem.

If the repulsion of Eq. (IV-7) is used with the harmonic potential between B and C, then the total potential of the system is given by

$$V = 2A'e^{-r_{AB}/L} + \frac{1}{2} k(Y-Y_0)^2, \quad (\text{IV-33})$$

where the coordinates are defined in Fig. IV-16 and Y_0 is the equilibrium B-C separation. Now

$$r_{AB} = (X^2 + \frac{Y^2}{4})^{1/2} = X (1 + \frac{Y^2}{4X^2})^{1/2} \quad (\text{IV-34})$$

and if $4X^2 > Y^2$ at the turning point then a term $(Y^2/8X^2)^2$ may be added to the parentheses without inducing a large error. Then

$$r_{AB} \cong X(1 + \frac{Y^2}{8X^2}) = X + \frac{Y^2}{8X} . \quad (IV-35)$$

So Eq. (IV-33) becomes

$$V = 2A'e^{-(X+Y^2/8X)/L} + \frac{1}{2} k(Y-Y_0)^2 . \quad (IV-36)$$

Now the force acting parallel to the perpendicular bisector axis is given by the negative derivative of the potential, so

$$\ddot{\tilde{m}\tilde{x}} = \frac{2A'}{L} e^{-(X+Y^2/8X)/L} (1-Y^2/8X^2) . \quad (IV-37)$$

If at the turning point $Y^2/8X^2 \ll 1$, then the repulsive potential appears spherical as in Eq. (IV-11), the stiffness of the interaction is everywhere characterized by L , and the $Y^2/8X^2$ term can be omitted from Eq. (IV-37). This approximation is probably good at low energy, but it becomes increasingly worse as the energy is increased.

It is convenient to define X_t as the classical turning point and $\tilde{x} = X - X_t$ and $\tilde{y} = Y - Y_0$. Then Eq. (IV-37) becomes

$$\ddot{\tilde{m}\tilde{x}} = \frac{2A''}{L} e^{-(\tilde{x}+\tilde{y}^2/8\tilde{x})/L} \quad (IV-38)$$

where

$$A'' = A' e^{-(X_t + Y_0^2/8X_t)/L} . \quad (IV-39)$$

A'' is also half the potential energy at the turning point if $Y=Y_0$. Now, if the oscillator coordinate is assumed to be Y_0 throughout the collision then $\dot{\tilde{y}}^2 = 0$ and Eq. (IV-38) becomes

$$\tilde{m} \ddot{\tilde{x}} = \frac{2A''}{L} e^{-\tilde{x}/L} \quad . \quad (\text{IV-40})$$

This may be integrated directly to yield

$$e^{-\tilde{x}/L} = \text{sech}^2(v_0 t/2L) \quad , \quad (\text{IV-41})$$

where v_0 , the initial relative velocity, is related to A'' by $\frac{1}{2} \tilde{m} v_0^2 = 2A''$, because, in the approximation, all the initial kinetic energy is converted into potential energy at the turning point. Equation (IV-41) is identical to the solution of the x motion in the collinear case. This is reasonable, because the solution is dependent only on the stiffness of the potential and v_0 .

For the oscillator equation

$$\mu \ddot{\tilde{y}} = -\frac{\partial V}{\partial Y} = \frac{A'}{2L} \left(\frac{Y}{X}\right) e^{-(X-Y^2/8X)/L} - k(Y-Y_0) \quad , \quad (\text{IV-42})$$

and, if $Y = Y_0$, then

$$\mu \ddot{\tilde{y}} + k \tilde{y} = -\frac{A''}{2L} \left(\frac{Y}{X}\right) e^{-\tilde{x}/L} \quad , \quad (\text{IV-43})$$

where Y/X can be evaluated at the turning point as an approximation. In order to find Y/X at the turning point, consider the hard sphere turning point represented by Fig. IV-16b. From this one can write

$$Y^2/4 + X^2 = d^2 \quad (\text{IV-44})$$

where d is the A-B distance at the turning point. By differentiating one gets

$$\frac{Y}{X} = -4 \frac{dY}{dX} \quad (\text{IV-45})$$

But, from the single particle representation as shown in Fig. IV-18,

$$\frac{d\tilde{Y}}{d\tilde{X}} = \frac{1}{a} \frac{dY}{dX} = \tan \gamma \quad (\text{IV-46})$$

So,

$$\frac{Y}{X} = -\frac{4}{a} \cot \gamma \quad (\text{IV-47})$$

which relates the Y/X term to the parameter γ of the hard sphere case. The equation of y motion is then

$$\mu \ddot{\tilde{y}} + k \tilde{y} = -\frac{2A''}{aL} \cot \gamma e^{-\tilde{x}/L} \quad (\text{IV-48})$$

where the preexponential factors are constants and $\exp(-\tilde{x}/L)$ is given from the solution of the x motion by Eq. (IV-41). Therefore, the equation of y motion has reduced to the driven oscillator problem. Consequently, the energy transfer is given by Eq. (IV-20):

$$\Delta E = \frac{1}{2\mu} \left| \int_{-\infty}^{\infty} F(t) e^{-i\omega t} dt \right|^2 \quad (IV-20)$$

The result of the integration is

$$\Delta E = \left(\frac{8c \tan^2 \gamma}{a^2 \mu v_o^2} \right) (2A'')^2 \left(\frac{\pi \omega L}{v_o} \right)^2 \operatorname{csch} \left(\frac{\pi \omega L}{v_o} \right) \quad (IV-49)$$

and the fraction of the initial energy ending in vibration is

$$\frac{\Delta E}{E_r} = \left(\frac{16c \tan^2 \gamma}{a^2 \mu v_o^4} \right) (2A'')^2 \left(\frac{\pi \omega L}{v_o} \right)^2 \operatorname{csch}^2 \left(\frac{\pi \omega L}{v_o} \right) \quad (IV-50)$$

But $2A''$ is the potential energy at the turning point. At the turning point all the remaining kinetic energy is in a direction parallel to the equipotential of the single particle representation at that turning point. Therefore, the fraction of the initial energy held as potential is the component of the energy perpendicular to that equipotential. As can be determined from Fig. (IV-18), the component of v_o perpendicular to the equipotential at the turning point is $v_o \cos (\gamma - \pi/2)$. Therefore, the corresponding value of the potential is

$$2A'' = \frac{1}{2} \tilde{m} v_o^2 \cos^2 (\gamma - \pi/2) = \frac{1}{2} \tilde{m} v_o^2 \sin^2 \gamma \quad (IV-51)$$

Introducing this expression into Eq. (IV-50), substituting Eq. (IV-16), and using a trigonometric identity yields

$$\frac{\Delta E}{E_r} = \sin^2 2\gamma \left(\frac{\pi \omega L}{v_o} \right)^2 \operatorname{csch}^2 \left(\frac{\pi \omega L}{v_o} \right) . \quad (\text{IV-52})$$

Introduction of the expansion of the hyperbolic cosecant, as done by Mahan²² in the Refined Impulse Approximation, gives

$$\frac{\Delta E}{E_r} = \sin^2 2\gamma \left[1 - \sum_1^{\infty} \frac{2(2^{2k}-1)}{(2k)!} B_{2k} \left(\frac{\pi \omega L}{v_o} \right)^{2k} \right]^2 , \quad (\text{IV-53})$$

where B_{2k} are the Bernoulli numbers. This formulation shows clearly that the energy transfer converges correctly on the hard sphere limit given by Eq. (IV-31) as $\omega L/v_o$ approaches zero.

In order to evaluate Eq. (IV-50) γ must be found. At the turning point, from Eq. (IV-51),

$$E_r \sin^2 \gamma = 2A'' . \quad (\text{IV-52})$$

Using trigonometric identities and substituting Eq. (IV-39) yields

$$\frac{E_r}{1 + \operatorname{ctn}^2 \gamma} = 2A' e^{-X_t} (1 + Y_o^2 / 8X_t^2) / L \quad (\text{IV-53})$$

But Y/X at the turning point is approximated by Eq. (IV-47). Making that substitution, taking the logarithm, and rearranging gives

$$X_t = L \left[\frac{\ln(1 + \operatorname{ctn}^2 \gamma) - \ln \frac{E_r}{2A'}}{1 + \frac{2}{a^2} \operatorname{ctn}^2 \gamma} \right] . \quad (\text{IV-54})$$

The approximations made are most valid when $\sin^2(2\gamma) \ll 1$ or $\text{ctn}\gamma \ll 1$ so

$$X_t = L \left[\frac{\text{ctn}^2\gamma - \ln \frac{E_r}{2A'}}{1 + \frac{2}{a} \text{ctn}^2\gamma} \right], \quad (\text{IV-55})$$

which can be used with Eq. (IV-47) to make successive approximations for γ . The original guess for X_t can be obtained in the limit that γ goes to zero:

$$X_t = -L \ln \frac{E_r}{2A'}, \quad (\text{IV-56})$$

Equation (IV-52) was used to calculate the energy transfer for the system plotted in Fig. IV-15. The γ values were found by successive approximation. The results are plotted in Fig. IV-19 where they are compared to the exact results using a harmonic potential and a Morse potential. The curve of the approximation shows $\sim 30\%$ less inelasticity than the harmonic oscillator curve. This discrepancy is attributed primarily to the fact that, in the exact solution, the atoms of the molecule have separated some when the turning point is reached. At that point in time the force acting to excite the oscillator is the greatest, and, for $\gamma \cong 90^\circ$, any increase in the separation of B and C allows a greater component of the collision force to act along the oscillator coordinate. Comparison with the Morse curve shows that the approximation is really not satisfactory for the system studied, the approximations which were made are less valid as A penetrates deeper between B and C and as the oscillator coordinate

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Fig. IV-19. The approximate bisector collision excitation given by Eq. (IV-52) compared to the exact calculations shown in Fig. IV-15.

distorts significantly during an encounter. This suggests that Eq. (IV-52) is most applicable for low energy impulsive collisions, which would be experienced in a system where $m_A < m_B$.

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V. THREE DIMENSIONAL ANALYSIS OF DATA

A. Introduction

Assuming that the energy transfer and deflection determined from individual classical trajectory calculations are valid, such individual calculations may be combined to duplicate accurately laboratory observations obtained from particle beam scattering experiments. In order to duplicate the intensity v. energy spectra by this method, one must consider both the deflection and inelasticity resulting from a representative array of initial conditions. The deflection is used to determine whether an event is detected. If it is detected, the inelasticity is used to determine at which energy in the spectrum the event should be added to the intensity. In order for the array of initial conditions to be truly representative, the contribution of each trajectory to the final spectrum must be multiplied by a weighting factor. This factor compensates for the difference in the relative density of initial states calculated to the actual density of initial states sampled in the apparatus in the region of that set of initial conditions.

In using trajectory calculations to analyze scattering data it is most valid to consider the above realistic three dimensional analog. The totally general case, however, is inherently the most expensive to compute and it is desirable to reduce the problem by use of valid approximations to one of less complexity. This chapter is devoted to the reduction of the three dimensional analog and using its reduced

form to understand the structure of the Na^+ -hydrogen molecule scattering data and hence the form of the interaction potential governing that system. In reducing the three dimensional problem it is first shown that, for exactly backward scattering, collisions in which the motion of the atoms does not lie in a plane may be neglected. The resulting two dimensional problem is further reduced by showing that only a small range of impact parameters contributes to the backscattering and that it can be simulated by considering only zero impact parameter trajectories.

B. General Three Dimensional Analog

In the most general case the initial conditions of the three particle system can be given completely by 6 coordinates and 6 momenta (See Chapter IV, Sec. B). By making the restriction that the diatomic molecule has no initial internal energy, these twelve parameters may be reduced to four. The four parameters, b, ϕ, θ , and v_0 , which have been chosen to describe the initial conditions for the purposes here, are shown in Fig. V-1. The velocity vector v_0 of A relative to BC is normal to plane P; plane Q contains the nuclei of B and C and is perpendicular to plane P. The impact parameter b is the initial perpendicular distance between the nucleus of projectile A and the axis which passes through the B-C center of mass and is normal to plane P. θ is the angle between this axis and the B-C bond such that an initial condition in which $\theta=0$ corresponds to the AB separation being less than that of AC. ϕ is the angle between the line of intersection of

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Fig. V-1. Parameters describing the initial conditions in three dimensions for A colliding with BC.

the P and Q planes and the line between the point of penetration of plane P by projectile A and the point of penetration of a line parallel to $\underline{v}_0$ which passes through the BC center of mass.

Suppose $S(\theta, E'_\lambda)$ is the intensity of scattering at laboratory deflection angle θ and final laboratory energy E'_λ . If only scattering of initial velocity $\underline{v}_0$ is considered, the intensity at the detector is the integral of this function times an acceptance function over all initial orientations which can give rise to the θ and E'_λ of interest. If the integral is over all possible orientations the acceptance function simply picks out the part of $S(\theta, E'_\lambda)$ which contributes to the scattering viewed by the detector. The total acceptance function should contain two parts; one part to characterize the angular acceptance and another part to characterize the energy acceptance.

First consider the angular part. The apparatus of Chapter II accepts only ions which have experienced little or no laboratory deflection or $\theta(\theta, b, \phi) < \delta\theta$, where $\theta(\theta, b, \phi)$ is the laboratory deflection angle of the projectile A for a collision pair with the initial conditions (θ, b, ϕ) , and $\delta\theta$ is the maximum accepted deflection. Assuming that the probability of detecting a particle that falls within or outside of $\delta\theta$ is one and zero, respectively, the angular acceptance is characterized by a Heaviside function $H[\delta\theta - \theta(\theta, b, \phi)]$ where

$$H(x) = 1 \text{ when } x \geq 0$$

and

$$H(x) = 0 \text{ when } x < 0$$

(V-1)

The energy acceptance also has a finite width but has a shape more closely approximated by a Gaussian curve. It is convenient, for simplicity, to account for this spread equivalently by incorporating it into an apparatus function which is later convoluted with the ideal scattering spectrum. This leaves a Dirac- δ function to account for the energy acceptance function:

$$\delta[E'_L - \epsilon(\theta, b, \phi)] \quad , \quad (V-2)$$

where $\epsilon(\theta, b, \phi)$ is the final laboratory energy of A resulting from the assigned initial conditions and E'_L is the final laboratory energy being viewed by the detector.

The total acceptance function is given by the product of these angular and energy acceptance functions. The intensity at the detector, represented by the integral of $S(\theta, \epsilon)$ times this function over all initial conditions, is given by

$$S(E'_L)_{\theta=0} = \int_0^\infty \int_0^{2\pi} \int_0^\pi S(\theta, \epsilon) \delta[E'_L - \epsilon(\theta, b, \phi)] H[\delta\theta - \theta(\theta, b, \phi)] \sin\theta d\theta db d\phi \quad (V-3)$$

where the factors $\sin\theta$ and b represent the natural density of initial states. This expression gives the ideal center line scattering intensity from collision orientations in three dimensions as observed in the experiments of this work. It does not account for the spread in the initial velocities of the particles or the energy resolution in analyzing the resulting spectrum. These will be considered after the desired simplified form is obtained.

C. Reduction of the Problem to Two Dimensions

In order to understand how Eq. (V-3) may be reduced, it is useful to construct a simplified picture of how the interaction potential contributes to the sensitivity of the deflection to the initial orientation. The equipotential locus of positions of A about BC at its equilibrium separation defines a surface. As a crude approximation, the deflection of the projectile A can be estimated by measuring the deflection of a point, representing A, scattered from a hard surface defined by the relative collision energy equipotential. This surface, given the equation $E_r = A'[\exp(-r_{AB}/L) + \exp(-r_{AC}/L)]$, would appear as a dumbbell at very high energy and as a sphere at very low energies (See Chapter IV, Section C). In the relative collision energies of interest here, 5-20 eV, this surface is somewhere between these two extremes and may be considered to be similar to a prolate ellipsoid of revolution. Figure V-2 shows the "hard ellipsoid" collision model using the coordinate representations of Fig. V-1.

If point projectile A is to be backscattered from BC it must collide normal to the ellipsoid surface. It is evident from Fig. V-2 that this condition can only be met if the incoming path of A lies in the Q plane. Consider, for a given orientation θ , a third plane, constructed to contain the backscattered trajectory of A and to be perpendicular to the Q plane. The radius of curvature of the intersection of this plane with the potential surface at points near the Q plane is roughly independent of the BC orientation given by θ . If

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Fig. V-2. Hard ellipsoid collision model. Point projectile A collides with BC surface. Here the trajectory of A is contained within the plane slicing the BC surface horizontally.

this radius is constant there is some critical perpendicular distance from the Q plane; only if the trajectory is closer to the plane than this critical distance, can the particle fall within the angular acceptance of the detector. Thus, point projectiles which penetrate the P plane and collide with the ellipsoidal surface outside of an area represented by the shaded areas of Fig. V-2 will result in a deflection not acceptable to a center line detector. The border of this ~~area~~ represents an upper boundary on the azimuthal angle ϕ as a function of impact parameter. If d' is the limiting distance of the incoming A trajectory from the Q plane, as shown in Fig. V-3, then, for an impact parameter b , the upper limit on ϕ is given by

$$\phi_m = \sin^{-1} \frac{d'}{b} . \quad (V-4)$$

In the two dimensional scattering of a point from a hard circular potential, the center of mass deflection of a point from a circle of radius ρ is given by geometry in terms of an impact parameter b' as

$$\chi = 2\cos^{-1} \frac{b'}{\rho} . \quad (V-5)$$

Deflection away from the Q plane can be represented by this result if b' is equated with d' :

$$\chi = \pi - \delta\chi = 2\cos^{-1} \frac{b\sin \phi_m}{\rho} \quad (V-6)$$

where ρ now corresponds to the radius of curvature of the potential perpendicular to the Q plane at the point of contact of A and BC.

But

$$\cos^{-1} x = \frac{\pi}{2} - x - \frac{x^3}{6} - \dots \quad (V-7)$$

and for $x \ll 1$

$$\cos^{-1} x \cong \frac{\pi}{2} - x \quad (V-8)$$

Now since $b \sin \phi_m \ll \rho$ for small $\delta\chi$, then $b \sin \phi_m / \rho \ll 1$ and Eq. (V-8) may be substituted into Eq. (V-6) to yield after rearrangement

Fig. V-3

$$\sin \phi_m = \frac{\delta\chi\rho}{2b} \quad (V-9)$$

The limits of the integration of Eq. (V-3) may now be modified so that the ϕ dependence of the angular acceptance function is accounted for by the range of integration over that variable as defined by Eq. (V-12):

$$S(E'_2)_{\theta=0} = \int_0^\pi \int_{-\infty}^\infty \int_{\frac{v'}{u'} \frac{\delta\theta p}{2b}}^{\frac{v'}{u'} \frac{\delta\theta p}{2b}} S(\theta, \epsilon) \delta[E'_2 - \epsilon(\theta, b, \phi)] d\phi H[\delta\theta - \theta(\theta, b)] \sin\theta d\theta db. \quad (V-13)$$

Since the range of ϕ represents only a small displacement with respect to the size of BC, the final energy of backscattered events is, to a good approximation, independent of ϕ in the region of integration. The ϕ dependence of the three dimensional problem may therefore be evaluated yielding

$$S(E'_2)_{\theta=0} = \rho \delta\theta \frac{v'}{u'} \int_0^\pi \int_{-\infty}^\infty S(\theta, \epsilon) \delta[E'_2 - \epsilon(\theta, b)] H[\delta\theta - \theta(\theta, b)] db \sin\theta d\theta \quad (V-14)$$

where $\epsilon(\theta, b)$ and $\theta(\theta, b)$ are computed for $\phi=0$. This two dimensional analog of Eq. (V-3) greatly reduces the effort required in duplicating a spectrum but is less valid at high energies where the assumptions used in arriving at it break down. For its evaluation, however, many more trajectories must be calculated than actually contribute to the result. This is because the acceptance function only selects a fraction of the trajectories which must be calculated to adequately represent the initial orientations from which it samples.

D. Equivalence of Zero Impact Parameter Studies

The fact that the ϕ dependence of the back scattered spectrum may be removed suggests that the b dependence may similarly be removed. In order to examine this possibility, consider first, as done before, the angular acceptance function. This function is strongly dependent on both θ and b . The θ dependence is periodic with a period of π for homonuclear BC target molecules. For zero impact parameter scattering the deflection function $\Theta(\theta, b)$ may be expressed in terms of θ only as

$$\Theta(\theta, 0) = \Theta_m g(\theta) \quad (V-15)$$

where $g(\theta)$ varies between +1 and -1; is symmetric to inversion through $\theta=0$, $\theta = \frac{\pi}{2}$; is zero at $\theta=0$, and $\frac{\pi}{2}$; and has a period of π . Θ_m is the maximum deflection experienced for $b = 0$, and a negative value of $\Theta(\theta, b)$ corresponds to projectile A being deflected with an upward component to its final velocity as viewed in Fig. V-1.

This deflection function may also be expressed as a function only of b if θ is held constant. If Eq. (V-5) for hard sphere scattering is valid as used in Section C, it is equally valid here for expressing the deflection in terms of the impact parameter and the radius ρ' of the potential at the point of contact. That equation together with Eq. (V-11) combine to yield an equation for Θ as a function of b with $\theta=0$:

$$\Theta(0, b) = \pi - 2 \cos^{-1} \frac{u'}{v} \frac{b}{\rho'} \quad (V-16)$$

The backscattering experiments sample collisions of only very small impact parameters so it is safe to assume that in the region of interest $b \ll \rho$. Therefore the $\cos^{-1}$ function may be replaced by the first two terms of its series expansion as done earlier and shown in Eq. (V-8). Thus,

$$\Theta(\theta, b) \cong 2 \frac{u'}{v'} \frac{b}{\rho} \quad . \quad (V-17)$$

If, in fact, the potential is much more spherical than dumbbell shaped, the radius ρ' varies only slightly with θ and as an approximation may be equated with the radius ρ used in Eq. (V-6). If this is valid the b dependence of the deflection function given in Eq. (V-17) is independent of θ and therefore the θ dependence given in Eq. (V-15) is correspondingly decoupled from b . The consequence is that the total deflection function may be written as a simple sum of Eqs. (V-15) and (V-17):

$$\Theta(\theta, b) = \Theta_m g(\theta) + 2 \frac{u'}{v'} \frac{b}{\rho} \quad . \quad (V-18)$$

As a test of the validity of the assumptions used to arrive at this relationship, classical trajectory calculations of $\Theta(\theta)$ have been plotted in Fig. V-5 for $\phi=0$ and $b=0$ to $0.15\text{\AA}$. These curves are for the Na^+-D_2 system at 10 eV relative energy using the parameters of the data fit of Fig. IV-14. It is evident that the behavior is reasonably close to that predicted by Eq. (V-18). The displacement of the curve from the $\theta=0$ axis is linearly proportional to the impact

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Fig. V-5. Laboratory deflection as a function of initial orientation θ for different impact parameters. Here $A' = 150 \text{ eV}$ and $L = 0.40 \text{ \AA}$.

parameter and the deviation from the displacement from that axis is a predominantly unchanged periodic function of θ .

Since the deflection function is well behaved it follows that if the detector accepts events in which $|\theta| \leq \delta\theta$ then, substituting Eq. (V-18) into this inequality,

$$-\delta\theta \leq \theta_m g(\theta) + 2 \frac{u'}{v'} \frac{b}{\rho} \leq \delta\theta \quad (V-19)$$

must define a family of acceptable pairs of initial b and θ 's. This is equivalent to

$$\frac{\rho}{2} \frac{v'}{u'} [\theta_m g(\theta) - \delta\theta] \leq b \leq \frac{\rho}{2} \frac{v'}{u'} [\theta_m g(\theta) + \delta\theta] \quad (V-20)$$

which, for the extreme values of b , defines the limits of the integration over b in Eq. (V-14) imposed by the angular acceptance function. This function may now be removed altogether by writing

$$S(E'_2)_{\theta=0} = \rho\delta\theta \frac{v'}{u'} \int_0^\pi \int_{-\frac{\rho}{2} \frac{v'}{u'} [\theta_m g(\theta) - \delta\theta]}^{\frac{\rho}{2} \frac{v'}{u'} [\theta_m g(\theta) + \delta\theta]} S(\epsilon) \delta[E'_2 - \epsilon(\theta, b)] db \sin\theta d\theta \quad (V-21)$$

From Fig. V-5 it is evident that, for small θ , b does not have to become very large before no more scattering falls within that value. For the case plotted there, no pure backscattering exists after b is 20% of the BC internuclear separation. Within this small range it is reasonable that the orientation - excitation function

$\Delta E(\theta)$ cannot change significantly with respect to b . Figure V-6 shows this function plotted for the same system of Fig. V-5 for $b = 0.0$ to $0.15\text{\AA}$ and it is evident that this assumption is also reasonably valid. Therefore the remaining part of the acceptance function may be removed from the b integral allowing that integral to be evaluated yielding

$$S(E'_L)_{\theta=0} = \rho^2 \delta\theta^2 \left(\frac{v'}{u'}\right)^2 \int_0^\pi S(\epsilon) \delta[E'_L - \epsilon(\theta)] \sin\theta d\theta \quad (V-22)$$

where $\epsilon(\theta)$ is evaluated at $\phi=0$, $b=0$.

This result shows that within the restrictions imposed by the approximations made, inelastic backscattering from three bodied systems in three dimensions may be accurately duplicated by examining two dimensional scattering on that system at zero impact parameter. Intuitively this result appears correct because by counting the zero impact parameter scattering that does not fall within the laboratory acceptance, the collisions that have a finite impact parameter and result in an acceptable deflection are perhaps accounted for. This relationship is easier to see with the aid of a diagram showing the deflection function $\theta(\theta, b)$ as plotted in Fig. V-5. Figure V-7 shows an ideal deflection function conforming to the approximations made in this section for equally spaced values of b . The shaded region corresponds to a hypothetical region of laboratory acceptance and is chosen such that each curve passes through the acceptance zone for different

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Fig. V-6. Orientation - excitation function plotted for different initial impact parameters. Here, $A' = 150 \text{ eV}$ and $L = 0.40 \text{ \AA}$.

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Fig. V-7. Ideal deflection function conforming to Eq. V-18. The shaded regions within the angular acceptance show the actual impact parameter which is responsible for events which are detected with a given initial orientation θ .

values of θ . It is seen that accepting the initial orientations of each impact parameter resulting in an accepted deflection is the same as considering all the orientations from one impact parameter. If the orientation - excitation function does not change significantly over the range of impact parameter needed to represent all orientations, the sum of all of the results of one impact parameter is adequate to represent the backscattering.

It is worthwhile to note that the assumptions made in this section impose a more stringent test of those made in Section C where the problem was first reduced to two dimensions. Therefore the validation of the assumptions made here is sufficient to assert the validity of the model without having to evaluate the more laborious three dimensional trajectories required to validate the earlier assumptions.

The result obtained from Eq. (V-22) holds no consideration for the resolution of an experiment. Before it may correctly be compared to the result of an experiment this must be accounted for. The factors defining the energy resolution in the experiment described in Chapter II are the velocity spread in the energy selected primary beam and in the scattering gas and the energy resolution of the scattered beam analyzer. The total effect of these is expressed by an apparatus function $G(E-E'_2)$ which expresses the relative intensity contributed to the energy spectrum at energy E from a process which ideally results in intensity only at E'_2 . If $S(E'_2)$ expresses the ideal scattering spectrum, then the spectrum observed in the laboratory

$I(E)$ would be given by the convolution of these two functions:

$$I(E) = \int_0^{\infty} S(E'_L) G(E - E'_L) dE'_L \quad (V-23)$$

Since Eq. (V-22) represents the ideal spectrum, the result comparable to the laboratory data is given in light of Eq. (V-23) as

$$I(E) = \rho^2 \delta \theta^2 \int_0^{\infty} \int_0^{\pi} S(\epsilon) \delta[E'_L - \epsilon(\theta)] \sin \theta d\theta \left(\frac{v'}{u'}\right)^2 G(E - E'_L) dE'_L, \quad (V-24)$$

where v'/u' is a function of the initial and final laboratory energies E_L and E'_L and is given by kinematics as

$$\frac{v'}{u'} = \frac{M E_L^{1/2}}{m_A E_L^{1/2} - M E_L^{1/2}} \quad (V-25)$$

E. Comparison to $Na^+ - D_2$ Data

Equation (V-22) may be programmed such that no trajectories are discarded in obtaining a complete backscattered spectrum. This is done by sequentially calculating the inelasticity corresponding to initial orientations defined by equally spaced values of θ and using the calculated inelasticity to direct a count proportional to $\left(\frac{v'}{u'}\right)^2 \sin \theta$ to the appropriate bin of a simulated multichannel analyzer. It was found that initial orientations of BC separated by 2.5° were adequate to give a reasonable convergence of the scattering function.

This orientation spacing requires that 37 trajectories, covering orientations of $0^\circ \leq \theta \leq 90^\circ$, are calculated for one spectrum. The other possible zero impact parameter orientations spaced by 2.5° are reproduced in the original 37 trajectories as a result of the symmetry imposed by the zero impact parameter restriction and offered by the homonuclear molecule. The results of the $0^\circ \leq \theta \leq 90^\circ$ orientations are given twice the weight of those of $\theta=0^\circ$ and 90° since the former each represent four possible orientations and the latter only two. The desired result of Eq. (V-24) is obtained through a computer convolution of the computed histogram and the apparatus function. As discussed in Chapter II, Section E, the apparatus function may be expressed either approximately by the factors which contribute to its width or, more accurately, by the experimental distribution of purely elastic scattering. Initially, for simplicity, an analytic form was used for the apparatus function, but all the final analyses of the data use the empirical form. The computer program used for the calculation of all of the backscattered spectra is given in the Appendix.

In order to obtain a fit between the calculated spectra and the laboratory data, it is advantageous to analyze the association between initial collision orientations and their contribution to the energy spectrum. For this purpose Fig. V-8 shows a typical orientation - excitation function plotted together with its corresponding energy spectrum histogram. These are plotted such that the sought association can be seen by connecting the graphs horizontally. It is readily

Fig. V-8. Association between 10 eV orientation - excitation function of Fig. IV-2 (left) and the corresponding ideal scattering spectrum (right). Shaded regions on the left should be weighted by $\sin \theta$ to be proportional in horizontal length to those in the spectrum. Fluctuations in the spectrum result from the limited number of trajectories (37) used in computing it.

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observable that the position of the maximum is determined by the scattering of the perpendicular bisector orientation and the tail trailing toward greater inelasticity is influenced by the collisions closer to the collinear orientation ($10^\circ < \theta < 40^\circ$). Once this association is ascertained, it is required to know the dependence of the resulting inelasticities of these orientations on the potential parameters. This dependence has already been discussed for the exact collinear and perpendicular bisector orientations in Sections E and F of Chapter IV. The dependence of the inelasticity of the near collinear orientations is understandable by considering the second case of Fig. IV-3. The relative size of A and B determine their ability to deflect off the axis of their original encounter and hence determine their ability to avoid the highly deexciting second collision experienced in the exact collinear orientation. Increasing either A' or L has the effect of increasing the size of A and B. Hence a more direct second A-B deexciting collision is expected, and this change acts to reduce the net energy transfer for the near collinear orientations.

The associations between the initial collision orientations, the dependence of their resulting inelasticities on the repulsive parameters, and their contribution to a scattering spectrum are summarized in Table V-1. With the insight offered by these facts, the repulsive parameters may be adjusted by trial and error until the best fit of the trajectory model to the data is obtained.

In obtaining a fit of parameters to the $\text{Na}^+ - \text{D}_2$ data, it is advantageous to start with those data exhibiting greater inelasticity.

Table V-1

Orientation →		Collinear	Near Collinear	Bisector
Contribution to Spectrum →		Low Energy Tail ↓	High Energy Tail ↓	Position of Maximum ↓
Effect to Contribution	Increase A' →	NO CHANGE	SHIFT TO LOWER ENERGY	
	Increase L (Adjust A' for same bisector i.p.) →	SHIFT TO LOWER ENERGY	DECREASE SIGNIFICANCE

This is because the resulting position of a calculated fit is more sensitive to the manipulation of the repulsive potential parameters the farther the result is from the $\Delta E = 0$ axis. By choosing a value for L and adjusting the value of A' a "best" fit can be obtained for a high energy experiment. The optimum value of A' for the chosen L is then used to determine the fit at a lower energy. If the lower energy experiment does not fit well, a new value of L is chosen and the process is repeated.

Using this procedure with Eq. (V-24) the values 65 eV and $0.55\text{\AA}$ were found for A' and L , respectively. The result of these zero impact parameter calculations is shown compared to the data of Fig. III-1 in Fig. V-9. The ideal scattering histograms of Eq. (V-22) are shown to the right of their resulting convolution. It is evident that below 11.8 eV the maxima of the calculated peaks correspond to greater inelasticity than do the maxima of the peaks of the data. Above 11.8 eV the opposite is true. This suggests that a larger value of L should be chosen. Doing that, however, causes the calculated peaks to narrow and the tail leading toward greater inelasticity to fit less well. The potential used for this fit is, therefore, a compromise in an attempt to fit both the position of the maxima and the high energy tail of the peaks.

Referring back to Fig. V-8 it is clear that the maximum in the peak is most strongly influenced by collisions in or near the bisector orientation, and the high energy tail is determined by more collinear

Fig. V-9. Calculated zero impact parameter spectra (histograms), apparatus functions (smoothed Na^+-He data), resulting convolutions (fits), and Na^+-D_2 data (boxes) for the data plotted in Fig. III-1. The fits are adjusted to match the background and peak height of the data. The histograms are normalized to contain the same area. Here, $A = 65 \text{ eV}$ and $L = 0.55 \text{ \AA}$.

Fig. V-9 (Cont.)

Fig. V-9 (Cont.)

Fig. V-9 (Cont.)

collisions. Since fitting the position of the maximum at all energies requires increasing L , it follows that the potential in the bisector plane is softer than that which has been chosen as fitting best. Similarly, fitting the high energy tail requires decreasing L , corresponding to a harder interaction along the collinear axis. In searching for the best general fit it was found that A' and L values of 300 eV and $0.40\text{\AA}$ give a better fit to the high energy tail but that the fit could be improved by further decreasing L .

Since the general fit appears to become slightly worse at higher energies it was considered that the approximations used in deriving Eq. (V-24) might be breaking down. To check this, a complete two dimensional calculation of Eq. (V-14) was performed and convoluted with the apparatus function to be compared with the 16.3 eV zero impact parameter fit. θ orientations were again chosen at 2.5° intervals and the impact parameter b was increased in steps of $0.02\text{\AA}$. Therefore, 37 trajectories were calculated for $b=0$ and 72 for every $b > 0$. The larger number of trajectories was calculated for $b > 0$ since these orientations must be sampled for $0 \leq \theta < 180^\circ$ to compensate for the loss of symmetry in the orientation - excitation function about $\theta=90^\circ$. The result of each trajectory is again weighted by the number of orientations it represents. The 2.5° spacing resulted in 613 trajectories to be calculated for $b \leq 0.16\text{\AA}$. At $b = 0.16\text{\AA}$ no events fell within the assigned laboratory angular acceptance of $\pm 1^\circ$, and for $b < 0.16\text{\AA}$, 178 trajectories of those calculated fell within the acceptance angle. The result, using the parameters of the best

general fit, is shown in Fig. V-10 compared to the fit and data of Fig. V-9j. At this energy it is apparent that the two curves agree well and the zero impact parameter approximation is still valid.

F. Comparison to $\text{Na}^+ \text{-HD}$ Data

Although these trajectory studies appear to approximately duplicate the observed scattering, it is desirable to obtain further proof that the interpretation of the calculated spectra bears reasonable relevance to the actual scattering processes. A test of this is made by using the model to predict the scattering result of a system which is identical to that already studied except for known differences to which the model is sensitive. The scattering of Na^+ from HD fulfills these requirements, because the interaction potential is essentially identical to that of the $\text{Na}^+ \text{-D}_2$ system despite the differences in the mass of one of the hydrogen atoms.

Figure V-11 shows the result from Eqs. (V-24) and (V-22) for the $23+2-1$ system using the parameters of the best general $\text{Na}^+ \text{-D}_2$ fit. The calculations are done for the energies of the $\text{Na}^+ \text{-HD}$ data of Fig. III-4 and are compared to those data. Thirty seven trajectories per spectrum were used again but, because of the asymmetry of the molecule, orientations of $0 \leq \theta \leq 180$ must be considered. The adjacent initial orientations are therefore spaced by 5° .

Except for the highest energies, the fits are reasonably good. An interesting observation is that the high energy tails of the peaks, which are noted as being slightly more extended than those of the

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Fig. V-10. Zero impact parameter fit of Fig. V-9; compared to the full two dimensional analysis fit.

Fig. V-11. 23+2-1 histograms, apparatus functions, convolution, and $\text{Na}^+\text{-HD}$ data plotted as in Fig. V-11. Any structure existing in the tails of the smoothed $\text{Na}^+\text{-He}$ data apparatus functions is not reproducible and is attributed to random error.

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Fig. V-11 (Cont.)

$\text{Na}^+ - \text{D}_2$ data (See Chapter III, Section 3), are fit better for this system. This ability of the model to duplicate the differences observed between two systems is taken as strong evidence that it is accurately explaining the systems. The origin of the scattering which gives rise to the greater intensity at higher inelasticity is understood by again plotting the orientation - excitation function. This is done in Fig. V-12 for the $E_0 = 100$ eV ($E_T = 12$ eV), 23+1-2 calculation. It is seen here that, while near collinear collisions with the deuterium end of the molecule give a relatively small amount of excitation, near collinear collisions with the hydrogen end lead to a considerable amount of inelasticity. In this case the maximum inelasticity is 4.16 eV. This is 1.67 eV more than the maximum of the $E_0 = 80$ eV calculation on the 23+2-2 system which is of about the same relative energy.

G. Analysis of the Contributions to Rotation and Vibration

It has been ascertained that the zero impact parameter model is capable of explaining the collisions which give rise to the backscattered intensity. Therefore, it is useful to analyze the contribution to vibrational and rotational excitation from those collisions. This analysis should be at least qualitatively correct.

There is some ambiguity as to how exactly the internal energy of a molecule should be separated into rotational and vibrational energy, E_R and E_V , since these motions are coupled in $\mathcal{H}(r, \theta)$ of Eq. (IV-1). Here, the definitions used by Kelley and Wolfsberg

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Fig. V-12. Orientation - excitation function for $23+2-1$ system. Here $A' = 65$ eV and $L = 0.55\text{\AA}$.

(Ref. IV-3) have been adopted, where

$$E_r = (p_\theta^2 / 2\mu r'^2) + V_{BC}(r) ,$$

and

$$E_v = E(r, \theta) - E_r . \quad (V-26)$$

r' is the value of r ($r' \geq r_0$) if the only B-C motion were rotation, and the other symbols are defined in Section B of Chapter IV. This method measures the vibrational energy as the energy from the bottom of the effective vibrational well, given by

$$U_{BC}(r) = \frac{p_\theta^2}{2\mu r^2} + V_{BC}(r) , \quad (V-27)$$

to $U_{BC}(r)$ at the turning points in the B-C vibrational motion. r' is found by using four iterations of Newton's method to locate the appropriate root of the derivative of the effective potential. The equilibrium separation r_0 is used as the initial guess for r' .

Figure V-13 shows the breakdown of four orientation - excitation functions $\Delta E(\theta)$ for the zero impact parameter calculations used to obtain the fit in Fig. V-9. An interesting feature of these is that the maximum vibrational excitation does not become significantly larger than the maximum rotational excitation until the relative energy is greater than about 10 eV. This is a significant consideration if an attempt is made to resolve individual vibrational quantum transitions. However, the maximum rotational excitation is experienced

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Fig. V-13. Contribution to vibration and rotation from zero impact parameter collisions (taken from calculations on Fig. V-9a, d, f and j).

near the collinear orientation and, therefore, results from collisions that are not as probable as those near the bisector orientation. Collisions near the bisector orientation invariably result in more vibrational excitation. Still, it appears that vibrational quantum transitions may be more difficult to resolve at low energies where, as in the case here, the energy resolution of an apparatus may be the best.

The rotational excitation curves show two distinct peaks at all the energies studied. The minimum between the peaks in the ΔE_R curve appears to drop to zero which suggests that it separates clockwise from counter clockwise rotation in the final rotational motion of BC. In a hard sphere picture the peak near the bisector orientation could correspond to A colliding first with B and then with C. The other peak would result from A encountering only B. This interpretation is consistent with the shift of the peaks with energy; as the collision energy is increased, B and C are effectively smaller, hence they can pass one another at smaller initial values of θ so that A can collide with C.

H. The Consideration of Zero-point Vibration

The scattering gas in all of the experiments was at a temperature at which essentially all the target molecules are in their ground vibrational state. The calculations done in the analysis of the data do not account for the zero-point vibrational motion which the molecules still experience in their lowest energy state. Inclusion of this motion to the classical analysis of the spectra was considered

possibly to result in a significant difference from the analysis which neglects that motion. Therefore, some calculations were done incorporating zero-point vibration in the initial conditions in an effort to estimate its effect.

The BC separation can be given approximately for a Morse oscillator in the ground state in terms of the phase δ of the oscillation as

$$r = r_0 - \frac{\ln(1 + \sqrt{\frac{\epsilon_0}{D}} \sin \delta)}{\beta} \quad (V-28)$$

where ϵ_0 is the zero-point energy. The translational energy at r is simply given by $\epsilon_0 - V_{BC}(r)$ and can be used to compute the magnitude of the vibrational momentum p_r . The sign of p_r is given by $\cos \delta / |\cos \delta|$ which determines whether the molecule is expanding or contracting.

Figure V-14 shows the results of zero impact parameter calculations on the 23+2-2 system starting with 0.1951 eV in vibration. Unconvoluted backscattering histograms and orientation - excitation functions are shown for initial relative collision energies of 8.89 eV and 16.3 eV. The six pairs of these for each energy represent calculations done for values of δ spaced by $\pi/3$. Thus the first and sixth are also spaced by the same amount, and together they represent phases of the BC oscillation during the collision which are approximately equally spaced in time. With these exceptions the calculations were performed exactly as they were for Figs. V-9e and V-9j. The most striking property of these results is the tremendous sensitivity to δ which they display. To determine the total effect of the zero-point energy,

Fig. V-14a. Ideal scattering histograms and orientation - excitation functions for 23+2 system plotted in Fig. V-9e and j but starting with 0.1951 eV in vibration. The absolute magnitude of the initial phase δ is arbitrary since it is assigned at the point where the collision is begun.

Fig. V-14b.

however, the histograms must be averaged and compared to those of the $\epsilon_0 = 0$ calculations. Figure V-15 shows the normalized sums of the histograms of Fig. V-14 compared to the $\epsilon_0 = 0$ histogram of Figs. V-9e and V-9j. In addition the average orientation - excitation functions are compared to those for the $\epsilon_0 = 0$ calculations. From the large fluctuations in the phase averaged spectra it is evident that a good comparison requires a much larger sample of initial phases to be calculated. The absence of a distinct trend in the differences of the excitation - orientation functions also suggests this. It is evident, however, that including zero-point vibration will result in a general spreading of the observed scattering spectra and possibly also a shifting toward greater inelasticity. Thus the results of the $\epsilon_0 = 0$ calculations must be considered valid primarily only for the qualitative implications about the dumbbell potential.

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Fig. V-15. Comparison of phase averaged histograms and orientation - excitation functions for the simple average of these curves in Fig. V-14 to those of Fig. V-9e and j. The histograms are normalized to contain the same area.

VI. SUMMARY AND CONCLUSIONS

The main specific contributions of this work are the zero impact parameter (ZIP) method of analysis and a better knowledge of the $\text{Na}^+ - \text{H}_2$ interaction potential. More generally, however, the contribution of greater significance is the insight into the mechanisms of collisional vibrational and rotational excitation found by examining the trajectories which reproduce a spectrum. The descriptions of the mechanisms are by no means completely accurate since the calculations employ classical mechanics in analyzing a system in which the true motion, described by quantum mechanics, must appear somewhat different. Still, the excitation resulting from a given set of initial conditions for a colliding pair can be explained using a classical picture, so it is certainly worthwhile to consider their motion in this more comprehensible manner.

In chapter IV the inelasticity resulting from classical trajectories calculated for only the perpendicular bisector orientation are fit to the data. It is found that these results can give a reasonable fit to the most probable inelasticity observed in the data by choosing the proper value of the A' and L parameters of the dumbbell potential. The more extensive ZIP analysis, when convoluted with the apparatus function, predicts different values for the potential parameters. Therefore, it is assumed that the single orientation analysis is not particularly useful unless the data are more highly resolved.

The ZIP model works reasonably well on the sodium ion - hydrogen molecule system and the values of 65 eV and 0.55Å for A' and L are chosen for the best compromising fit to the data of that system. It is assumed that these values are more reliable in the region of the bisector approach to the molecule since those orientations give rise to the majority of the intensity in the spectra. Since the corresponding potential surface is a compromise to fit the regions influenced by the bisector and near collinear orientations, the actual surface along the bisector plane and collinear axis is assumed to be somewhat different. From the manipulation of the parameter values required to fit the different regions of the curve, it appears that, in relation to the fit, the true potential is softer in the bisector plane and harder along the collinear axis.

If the A' and L values of the fit are used to define a single centered repulsion as given by Eq. (IV-11), the resulting potential is much softer and more extended than that of Amdur (See Chapter IV Section D). The two surfaces cross at a radius of 0.8Å from the geometric center of the molecule and at an energy of 15.1 eV. This radius is smaller than the minimum radius reported for the region of validity of the Amdur potential and the energy is at the high end of the range which these experiments cover.

An important feature in the analysis of the collisions contributions to the spectra is that, above about 10 eV relative energy, the perpendicular bisector approach results in a significant amount of excitation. From the general neglect of this orientation in earlier studies it appears the opinion that this orientation leads primarily

to elastic collisions has been fairly wide spread.

The ability of the ZIP model to explain the Na^+-D_2 system suggests that it is also applicable to the scattering of other alkali ions. The first reduction of the three dimensional problem to a two dimensional one, however, is based on atoms B and C having the same interaction potential with A. This restricts the validity of the model to scattering from diatomic molecules made up of the same atomic species. The derivation of the ZIP model imposes no restrictions on the stiffness of the A-BC potential, so it should be applicable also to systems with a much softer potential. The main drawback to that application is the choice of an A-BC potential which presumably would be significantly different from the dumbbell two centered repulsion.

Since the dumbbell potential does not completely describe the A-BC interaction for the sodium ion - hydrogen molecule system the question arises as to what changes or additions might be made to correct for its weaknesses. A simple exponential attractive potential of the form $V(R') = B' \exp(-R'/L)$, where L is the stiffness parameter of the repulsive dumbbell potential, can be considered to exist between A and the geometric center of BC separated by distance R' . The parameter B' would assume a value $-2A' \ll B' < 0$. This would soften the interaction in the bisector plane without affecting the stiffness of a collinear interaction, and it would only add one more parameter, B' , to be adjusted in finding a fit. An interesting extension to this is that if B' is allowed to vary inversely as the

BC separation the qualitative features of the He-H₂ surfaces calculated by Krauss and Mies and Gordon and Secrest (Ref. IV-5) can be reproduced. On their surfaces H₂ is compressed in collisions in the bisector plane at low energies.

The analysis of the effect of including zero-point vibrational energy in the initial conditions for the ZIP calculations shows that the effect may be fairly dramatic. This suggests that only the qualitative implications about the true potential in comparison to the dumbbell potential should be considered as strictly valid.

It is felt that the analysis by the ZIP method should be expanded to include zero-point vibration before a more sophisticated potential is fit to the data of a system. This would, of course, require the phases of the resulting motion to be adequately represented for each initial orientation. This would demand a significant increase in the number of trajectories required to be calculated in reproducing a spectrum. Consequently, a more efficient method of sampling the initial conditions, such as that of the Monte Carlo technique, is recommended.

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APPENDIX

```

C PROGRAM FOR COMPUTING THE BACKSCATTERING OF THREE BODY SYSTEM (A-BC)
C BY CALCULATING EXACT CLASSICAL TRAJECTORIES. PROGRAM ALSO COMPARES
C RESULTS TO EXPERIMENTAL CENTERLINE SCATTERING DATA
C
C
C      PROGRAM MAIN(INPUT,OUTPUT,PL01,TAPE98,TAPE99-PL01)
C      COMMON/IST/ILA,2*ND
C      COMMON/IRAW/SPACE(100),XMARK,OMARK,BLANK,RMARK,VMARK
C      COMMON/LOGS/EV(91),ER(91),INT(91),FOI(91)
C      COMMON/INT4/2,X(4),Y(4),Z(4)
C      COMMON/VAL/4,MA,MB,MC,MA,MB,MC,AL,BETA,R,D,CC,88,L
C      DIMENSION V(12),R(12),AMP(15),VAP(12)
C      REAL 4,MA,MB,MC,MC,MC,MC,MC,MC,L,LA,LC
C      DOUBLE PRECISION 8*PRINT
C      DATA ERG,G,CM/1.602E-12,1.00E-24,1.00E-8/
C      RAD=3.14159265/180.
C
C      READ SYMBOLS FOR LINE PRINTER PLOTS
C      XMARK = X
C      OMARK = .
C      BLANK =
C      RMARK = R
C      VMARK = V
C
C      READ 107,XMARK,OMARK,BLANK,RMARK,VMARK
107 FORMAT(5A1)
C
C      READ MASSES AND POTENTIAL PARAMETERS
C      VARIABLE      DEFINITION      UNITS
C      MA      - MASS OF ATOM A      AMU
C      MB      - MASS OF ATOM B      AMU
C      MC      - MASS OF ATOM C      AMU
C      R      - EQUILIBRIUM BC SEP      A
C      A      - REPULSIVE PREEXPONENTIAL      EV
C      L      - REPULSIVE RANGE PARAMETER      A
C      BETA    - MORSE EXPONENTIAL PARAMETER      1/A
C      D      - MORSE WELL DEPTH      EV
C
C      READ 101,MA,MB,MC,R,A,L,BETA,D
101 FORMAT(8F10.2)
C
C      READ ITERATION PARAMETERS
C      VARIABLE      DEFINITION      UNITS
C      NN      - NUMBER OF ITERATIONS FOR B=0      TRA-
C      BMAX    - MAXIMUM IMPACT PARAMETER      A
C      DELB    - INCREMENT IN IMPACT PARAMETER      A
C      ANGLE    - HALF LAB ACCEPTANCE ANGLE      DEG
C      FOR (BMAX.GT.0.0) PROGRAM COMPUTES 2D SCATTERING FOR DELB INCRE-
C      MENTS OF 1 UNTIL (B.GT.BMAX) OR UNTIL NO MORE EVENTS FALL WITHIN
C      ANGLE FOR A GIVEN D
C
C      READ 102,NN,IMAX,DELB,ANGLE
102 FORMAT(15,5X,3F10.0)
C      AM=MA
C      BM=MB
C      CM=MC
C      AR=A
C      AL=L
C      CL=L
C      BET=BETA
C      DD=D
C      MA=MA*G

```

```

MH=MB*G
MC=MC*G
BMAX=MAX*CM
DELA=J*LA*CM
R=R*CM
A=A*ERG
BETA=1/TAX*CM
D=D*ERG
L=L*CM
MBC=M1*MC
M=MB*MA
CC=MC/MBC
BB=MB/MBC
AL=A/L
MU=MA*MB*CM
MBC=MB*MC/MBC

```

```

C READ ENERGY, ENERGY-POTENTIAL CONVERSION, AND DECISION PARAMETER
C VARIABLE DEFINITION UNITS
C ELA9 - INITIAL LABORATORY ENERGY EV
C ZERO - ENERGY-POTENTIAL DIFFERENCE VOLT
C C - DECISION PARAMETER
C IF C=0. CALCULATE SCATTERING HISTOGRAM
C IF C=1. CALCULATE HISTOGRAM, CONVOLUTE, AND COMPARE TO
C DATA
C IF C=2. CALCULATE HISTOGRAM, CONVOLUTE, COMPARE, AND PLOT
C (CAL COMP)

```

```

3 READ 101,ELA9,ZERO,C
IF(ELA9.LT.1.)STOP
E=MC*ELA9/M
PRINT 108,ELA9,E,AM,BM,CM
108 FORMAT(17H1ELAB =,F7.2,3H EV/7H EREL =,F7.2,3H EV/5H MA =,F5.1,4H A
1MU/5H MB =,F5.1,4H AMU/5H MC =,F5.1,4H AMU)
PRINT 109
109 FORMAT(12H INTERACTION,8X,5HA(EV),5X,4HL(A),6X,5HD(EV),5X,9HBETA(
11/A))
PRINT 111,AB,BL
111 FORMAT(5X,2HAB,13X,F5.0,4X,F5.3)
PRINT 112,AC,CL
112 FORMAT(5X,2HAC,13X,F5.0,4X,F5.3)
PRINT 113,DD,BET
113 FORMAT(5X,2HBC,13X,F5.3,5X,F5.3,///)
PRINT 114
114 FORMAT(5X,5HERROR,5X,1HQ,9X,4HEVIB,6X,4HEROI,6X,1HB,9X,5HTHE(A,5X,
13HCHI,5X,9HTHETA LAB/)
E=E*ERG
ELA9=ELA9*ERG
DO 100 I=1,60
100 AMP(I)=0.0
BACK=((MA-MBC)/M)**2*ELA9
ECM=(M1/M)**2*ELA9
VCM=SQRT(2.*MA*E/(M*MC))
DELTA=90.*M40/(M-1)
IF(MC-ME.MJIDELTA=DELTA*2.
B=0.0
IF(DELTA.GT..01*RIGO TO 11
DELTA=R*514(DELTA)/2.
ANGLE=20.
11 T=SQRT(MA*MC*((L*ALOG(2.*A/(.0001*E))))**2-B*81/(2.*E*M))
NNN=NN
9 IF(3.GT.BMAX)GO TO 8
KK=0

```

```

DO 10 I=1,2
VA(I)=SQRT(2.*M*U/(M*U**2))
VA(2)=7.
RA(1)=VA(1)*T
RA(2)=-M*U*RA/M
DO 10 I=1,2
10 VAP(I)=VA(I)
THETA=(JJ-I)*DELTA
Z=0.

C
C   DEFINE INITIAL CONDITIONS FOR HAMILTONS EQUATIONS
C   X(1) = A-3C SEPARATION
C   X(2) = 4C SEPARATION
C   X(3) = THETA PRIME OF FIG IV-1 IN THESIS
C   X(4) = THETA OF FIG IV-1 IN THESIS
C   X(5) - X(8) = CONJUGATE MOMENTA OF X(1) - X(4)
C
X(1)=M*SQRT(RA(1)*RA(1)+RA(2)*RA(2))/MBC+R
RABC=X(1)
X(2)=R
X(3)=4*G*IN(8/X(1))
X(4)=THETA
X(5)=-SQRT(2.*M*U*E)
X(6)=7.
X(7)=3*X(5)
X(8)=0.
HPRINT=DALEF(.01*T)

C
C   CALL TRAJECTORY INTEGRATING ROUTINE
C
CALL INTDIB,HPRINT)
6 CALL INT
IF(ABS(X(1)).GT.RABC)GO TO 7
GO TO 6

C
C   COMPUTE DYNAMICAL VARIABLES FROM FINAL X(1) - X(8)
C
7 VA(1)=MBC*(-X(5)*COS(X(3))+X(7)*SIN(X(3))/X(2))/(M*U)
VA(2)=-MBC*(-X(5)*SIN(X(3))+X(7)*COS(X(3))/X(1))/(M*U)
VLAB=VA(1)+VCM
SLAB=SQRT(VLAB**2+VA(2)**2)
GAMMA=ACOS(VLAB/SLAB)/RAD
IF(GAMMA.GT.ANGL)GO TO 1
KK=KK+1
ELABF=.5*M*SLAB**2
IF(ELABF.GT.(ECM+EBACK)/2.)GO TO 1
I=(2*(ELABF-EBACK)/(ECM-EBACK))*50.+10.
IF(I.GT.60)I=60
AMP(1)=AMP(1)+SIN(THETA)
IF(IJ.EQ.1)GO TO 2
IF(IJ.EQ.NN)GO TO 2
AMP(1)=AMP(1)-SIN(THETA)
2 CONTINUE
1 U3C=D*(1.-EXP(-BETA*(X(2)-X(1))**2)
EVIB=(X(6)**2/(2.*M*U*SC)+M*SC)/ERG
EROT=X(6)**2/(2.*M*U*SC*X(2)**2)/ERG
Q=(-(EVIB-EROT)
EF=(-2*ERG*X(5)**2/(2.*M)+X(7)**2/(2.*M)*X(1)**2)-E)/ERG
AP=SQRT(VAP(1)**2+VAP(2)**2)
AD=SQRT(VA(1)**2+VA(2)**2)
ALPHA=ACOS(VAP(1)*VA(1)+VAP(2)*VA(2))/(AD*AP)/RAD
THETA=THETA/RAD
IF(EROT*ERG.GT.D)GO TO 4

```

```

30=2.*PT2/13.*PT2+4*BC*ETA*80*R**4)
PT2=X(1)**2
R1=R*(1.+PT2/13.*PT2+4*BC*ETA*80*R**4)
DO 40 J=1,4
PMR=PT2/(1.+BC*R)**3)
EB=EX*(-BETA*(R1-R))
E2B=E1*EB
R2=R1+(PMR-B0*(EB-E2B))/(1.+PMR/R1-BETA*80*(E3-2.*E2B))
40 R1=R2
V8C=D*(1.-EXP(-BETA*(R1-R)))*2
EROT=(PT2/12.*4*BC*R1**2)+V8C)/ERG*CM
EVIB=-2*EROT
IF(ANGLE.GT.19.)GO TO 4
ERIJJ=ALOG10(EROT)
VIB=EVIB
IF(VIB.LT.-CM)VIB=CM
FOIJJ=-Q*ERG/E
EVIJJ=ALOG10(VIB)
THIJJ=THETA
4 B=B/CM

```

PRINT PERTINENT TRAJECTORY RESULTS

VARIABLE	DEFINITION	UNIT
EF	- FRACTION ERROR IN ENERGY CONSERVATION	
Q	- CHANGE IN A-BC RELATIVE ENERGY	EV
EVIB	- CHANGE IN BC VIBRATIONAL ENERGY	EV
EROT	- CHANGE IN BC ROTATIONAL ENERGY	EV
B	- IMPACT PARAMETER	A
THETA	- INITIAL BC ORIENTATION	DEG
ALPHA	- CENTER OF MASS DEFLECTION	DEG
GAMMA	- LABORATORY DEFLECTION	DEG

PRINT 104,EF,Q,EVIB,EROT,B,THETA,ALPHA,GAMMA

```

70 B=B*CM
104 FORMAT(1X,BF10.5)
NNN=2*(NN-1)
B=B+DELB
IF(ANGLE.GT.19.)GO TO 8
PRINT 103
103 FORMAT(//)
IF(KK.NE.0)GO TO 9
B=BMAX+DELB
8 DELE=(FCM-EBACK)/100.
J=7
IF(B.GT.JMAX)J=1
K=1
SUM=0.0
DO 20 I=1,60
AT=I
EE=(AT-9.5)*DELE+EBACK

```

WEIGHT HISTOGRAM FOR FULL 2D OR 2D, B=0 CASE

```

AMP(I)=AMP(I)*(4*SQR(EE)/(4*SQR(ELAB)-4*SQR(E)))*J
20 SUM=SUM+AMP(I)
DO 30 I=1,60
30 AMPI=170.*AMP(I)/SUM
ELAB=ELAB/ERG

```

CALL ROUTINE FOR LINE PRINTER PLOT OF ORIENTATION-EXCITATION FUNCTION AND ROTATION/VIBRATION SEPARATION

CALL LOGE(NN)

```

C
C CALL ROUTINE FOR LINE PRINTER PLOT OF HISTOGRAM, APPARATUS FUNC-
C TION, BEFORE AND AFTER SMOOTHING, AND FIT TO DATA. IF LOGICAL 51
C CALLS CAL COMP PLOT OF DATA, FIT, AND SMOOTHED APPARATUS FUNCTION
C
CALL GRAPHAMP,C1
GO TO 3
END

SUBROUTINE DERIV
COMMON/INTA/Z,X(8),F(8),X(8,B)
COMMON/VALU/M,MA,M5,MC,M3C,M1,M3BC,AL,BETA,RO,D,CM,PM,L
REAL M,MA,M5,MC,M3C,MU,M3C,L

X(1) = X(4) HAMILTONS Q SUB I
X(5) = X(8) HAMILTONS P SUB I
F(1) = F(4) HAMILTONS P SUB I DOT
F(5) = F(8) HAMILTONS Q SUB I DOT
SEE EQ(IV-4) IN THESIS

X1=X(1)
X2=X(2)
THETA=X(4)-X(3)
X5=X(5)
X6=X(6)
X7=X(7)
X8=X(8)
R2=X1*X1
F(1)=X5/MU
F(2)=X6/MU3C
F(3)=X7/(MU*M2)
F(4)=X3/(MU3C*X2*X2)
SINE=SIN(THETA)
COSINE=COS(THETA)
TB=CM*COSINE
TC=PM*COSINE
X2BC=X2/M3C
X2BC2=X2BC*X2BC
RB=M3C*M3C*X2BC2
RC=M3*M3*X2BC2
RAB=SQRT(R2+RB-2.*TB*X1*X2)
RAC=SQRT(R2+RC-2.*TC*X1*X2)
EAS=EXP(-RAB/L)
EAC=EXP(-RAC/L)
AB1=(X1-TB*X2)/RAB
AC1=(X1+TC*X2)/RAC
F(5)=X7*X7/(MU*X1*X2)+AL*(EAB*AB1+EAC*AC1)
AB2=(CM*M3C*X2-TB*X1)/RAB
AC2=(PM*M3C*X2+TC*X1)/RAC
ER=EXP(-BETA*(X2-RO))
F(6)=-2.*ER*BETA*(1.-ER)+X8*X8/(MU3C*X2*M3)+AL*(EAB*AB2+EAC*AC2)
A31=-CM*X1*X2*SINE/RAB
AC3=PM*X1*X2*SINE/RAC
F(7)=AL*(EAB*AB3+EAC*AC3)
F(8)=-F(7)
RETURN
END

```

SUBROUTINE INT0(NO,HPRO)

[illegible]

```

HPR=HPRD
XX=7.5LF(X)
N=NO
EUS=E'AX
ELB=E'AX/55SR
IP=1
IT=0
NRKS=0
SWIN=SWEX
CALL DERIV
DO 9 I=1,N
T(S,I)=JBLE(Y(I))

```

9 CONTINUE
RETURN
END

```

SUBROUTINE INT
COMMON/INTA/X,Y(8),F(8),T(3,8)
COMMON /INTC/ IPMX,AREF,EMAX,DOOR,R,HFAC,DOAM,DOEX
COMMON /INTP/ NPR,XX,N,ELU,ELB,IP,LI,NRK,DOIN

```

```
LOGICAL SWAM,SWEX,SWJH
LOGICAL SWPR
INTEGER IFAC
DOUBLE PRECISION T,MPR,XX
DOUBLE PRECISION U,H
```

6000 FORM-1 (36H) CANNOT DECREASE H BECAUSE OF HMIN. ,1PE16.0,120)

```

1 CONTINUE
  SWPR=FALSH.
  TEST=0.0
  H=HPR/DBL(FLOAT(IP=24))
  IF ((SWR5-1.3) .GT. (.001*SWR5)) GO TO 220

```

AD445-4 JUL 70 STEP.

```

109 CONTINUE
DO 119 I=1,N
D=0.5*(F(I)+F(I+1))
T(4,I)=D
Y(I)=SQRT(I*(Y(I)+H*(
X 55.707+0.5*(D*(F(I)+F(I+1))-Y(I)+F(I+1)))
109 CONTINUE
X=SQRT(XX+24.0)*H)
CALL JFRIV
DO 119 I=1,N
Y=JRL(I)
D=( F(I)+H*(
X 55.707+0.5*(D*(F(I)+F(I+1))-Y(I)+F(I+1)))
T(5,I)=D
E=495*(SQRT(Y)-Y(I)/24.0)
TEST=A*MAX(1,F(AAXI*(AKF+ABS(Y)-D)),FST)
119 CONTINUE

```

```

C      GO TO 300
C
C      ZUNNEVELD STEP.
200  T(4,1)=0
      DO 219 I=1,N
      D=DRLE(T(1,1))
      T(4,1)=D
C
      Y(1)=SNGL(T(5,1)+H*(
X 12.007*J
      CONTINUE
      X=SNGL(XX+12.007*H)
      CALL DERIV
      DO 219 I=1,N
      D=DRLE(T(1,1))
      T(6,1)=D
C
      Y(1)=SNGL(T(5,1)+H*(
X 12.007*J
      CONTINUE
219  CALL DERIV
      DO 229 I=1,N
      D=DRLE(T(1,1))
      T(7,1)=D
C
      Y(1)=SNGL(T(5,1)+H*(
X 24.007*J
      CONTINUE
229  X=SNGL(XX+24.007*H)
      CALL DERIV
      DO 239 I=1,N
      D=DRLE(T(1,1))
      T(8,1)=D
C
      Y(1)=SNGL(T(5,1)+H*(
X 3.7500*T(4,1)+5.2500*T(6,1)+9.7500*T(7,1)-0.7500*D
      CONTINUE
239  X=SNGL(XX+18.000*H)
      CALL DERIV
      DO 249 I=1,N
      D=DRLE(T(1,1))
      E=ABS(SNGLH*(
X -16.000*T(4,1)-40.000*T(6,1)+40.000*T(7,1)+48.000*T(8,1)
X -128.000*D
      CONTINUE
C
      D=( T(5,1)+H*(
X 4.0000*T(4,1)+8.0000*T(6,1)+8.0000*T(7,1)+4.0000*T(8,1)
X ))
      T(6,1)=D
      TEST=AMAX1(E/AMAX1(ABS(SNGL(D))),TEST)
249  CONTINUE
C
C      BOTH ADAMS-MOULTON AND ZUNNEVELD METHODS CONTINUE FROM HERE.
300  CONTINUE
      X=SNGL(XX+24.000*H)
      IF (TEST.LE. EPS) GO TO 310
      IF (IP*HFAC.GT. IPMX) GO TO 309
C
C      REPEAT STEP WITH SMALLER H.
      NRKS=0
      IP=IP*HFAC
      IT=IT*HFAC

```

```

      DO 305 I=1,N
      Y(I)=SNGLE(T(5,I))
      F(I)=SNGLE(F(4,I))
305  CONTINUE
      GO TO 1

C
C      CANNOT DECREASE H BECAUSE OF HMIN.
309  CONTINUE
      IF (.NOT. SWIN) GO TO 310
      PRINT 6010, X,IP,XX
      SWIN=.FALSE.

C
310  CONTINUE

C
C      ACCEPT CURRENT STEP.
C
C      XX STILL HAS NOT BEEN CHANGED SINCE ENTRY.
C      YY(XX) IS STILL IN T(5, ).
C      F(YY) IS IN T(4, ).
C
      IT=IT+1
      XX=XX+H*PR/DOUBLE(FLOAT(IP),
      NRK5=MIND(NRK5+1,4)
      DO 319 I=1,N
      D=T(6,I)
      T(5,I)=D
      Y(I)=SNGLE(D)
319  CONTINUE
      X=SNGLE(XX)
      CALL DERIV
      IF (IT .LT. IP) GO TO 320

C
C      X IS A MULTIPLE OF H*PRINT.
      SWPR=.TRUE.
      IT=IT-IP

C
320  CONTINUE
      IF (TEST .GE. EL3) GO TO 330
      IF (MOD(IP,H*FAC)+MOD(IT,H*FAC) .NE. 0) GO TO 330

C
C      PROCEED TO NEXT STEP WITH LARGER H, USING ZUNNEVELD METHOD.
      NRK5=0
      IP=IP/H*FAC
      IT=IT/H*FAC
      RETURN

C
C
C      PROCEED TO NEXT STEP WITH SAME H.
330  CONTINUE
      DO 339 I=1,N
      T(1,I)=T(2,I)
      T(2,I)=T(3,I)
      T(3,I)=T(4,I)
339  CONTINUE
      RETURN
      END

SUBROUTINE GRAPHIAMP,C1
COMMON/IST/EL4,ZERO
COMMON/VAL1/M,MA,DIR1,DUM2,MAC

```

```

DIFF=ABS(JN-DAT-X(100),DATAY(100),DATX(100),DA:Y(100),YPP(50),YY(50)
REAL V,M,MH
EPAK=((M-M/2)/V)*2*ELAS
EUM=(M/2)*2*LAS
DE=(E-M-DAK)/100
K=1
DO 40 I=1,60
40 IF(AM(I).GT.-4*(K))K=1
XI=EPAK-10*JN
CALL HISTO(X),0.,0.,1.,0.,AMP,K,0,11
IF(C.LT..5)GO TO 1
CALL DAT(NJAT,NIM,YPEA,YBAS,0,1,NIM,2)
DX=(DAT(NIM)-DATX(1))/60
CALL HISTO(DATX,DATY,DX,YPEA,YBAS,0,1,NIM,2)
DO 10 I=1,1
CALL SMJOTH(DATY,NDAT)
10 CONTINUE
CALL HISTO(DATX,DATY,DX,YPEA,YBAS,0,1,NIM,2)
YBAS=DATY(1)
K=1
DO 20 I=1,NDAT
DATY(1)=DATY(1)-YBAS
IF(DATY(1).LT.0.)DATY(1)=0.
20 IF(DATY(1).GT.DATY(K))K=1
A=DATY(K)-DATY(K-1)
B=DATY(K+1)-DATY(K)
XPEA=(A+B)*(DATX(K+1)-DATX(K-1))/((A-B)*4.)+(DATX(K+1)+DATX(K-1))/
12.
CALL DAT(NDAT,NIMP,YPEAK,YBASE,DATX,DATY,SEC)
DX=(DATX(NIMP)-DATX(1))/60.
C
C CONVOLUTE CALCULATED SCATTERING DISTRIBUTION WITH APPARATUS
C FUNCTION
C
DO 50 I=1,60
50 YY(I)=0.0
K=1
DO 30 I=1,60
AI=I
E=DATX(1)+(AI-.5)*DX-ZERO
DO 30 J=1,60
IF(AMP(J).LE.0.0)GO TO 30
AI=J
EPEAK=(AI-.5)*DE+FBACK
XP=XPEA-EPEAK+E
IF(XP.GT.DATX(NIMP))GO TO 30
IF(XP.LT.DATX(1))GO TO 30
DO 70 L=2,NIM
IF(XP.GT.DATX(L))GO TO 70
YY(I)=YY(I)+((XP-DATX(L-1))*(DATY(L)-DATY(L-1))/(DATX(L)-DATX(L-1)
1)*DATY(L-1))*AMP(J)
L=NIM
IF(YY(I).GT.YY(K))K=I
70 CONTINUE
30 CONTINUE
TOP=YY(K)
DO 60 I=1,60
60 YY(I)=YY(I)/TOP
CALL HISTO(DATX,DATY,DX,YPEAK,YBASE,YY,K,NIMP,0)
IF(C.LT.1.5)GO TO 1
CALL PLOT(DATX,DATY,DATX,DATY,YY,NIMP,NIM,YPEAK,YBASE,DX)
1 RETURN
END

```

```

SUBROUTINE HISTO(X,Y,XN,YN,YT,XN,L)
COMMON/IST/ELAB,ZERO
COMMON/DRAW/SPACF(100),XMARK,OMARK,BLANK
COMMON/VALU/M,MA,OMM,MBC
DIMENSION X(1),Y(1),YY(1)
REAL M,MBC,M
PRINT 101
101 FORMAT(17HENERGY,47X,9HINTEGRALS:TY,50X,16HD -Q/EREL FIT)
DO 40 I=1,100
40 SPACE(1)=BLANK
YYI=0.0
KY=1
J=1
DO 10 I=1,60
E2=X(I)+I*DX
E1=E2-DX
IF(L.GT.1)GO TO 3
JY=90.+(YM-YB)*YY(I)/YY(K)+YB)/YM
IF(JY.LT.1)JY=1
IF(JY.GT.100)JY=100
DO 20 JX=1,JY
20 SPACE(JX)=XMARK
IF(L.GT.0)GO TO 4
3 IF(J.GT.N)GO TO 4
IF(X(J).GT.E2)GO TO 4
IF(X(J).GE.E1)GO TO 5
J=J+1
GO TO 3
5 KY=90.+(YJ)/YM
IF(KY.LT.1)KY=1
IF(KY.GT.100)KY=100
J=J+1
SPACE(KY)=OMARK
4 E=E1-ZERO+DX/2.
IF(L.EQ.1)E=E+ZERO
Q=-MBC*ELAB*(1.-((MA-M*SORT(E/ELAB))/MBC)**2)/M
DEE=-Q*M/(MBC*ELAB)
IF(L.LT.2)YYI=YY(I)
POT=E1+DX/2.
PRINT 172,POT,(SPACE(I),I=1,100),Q,DEE,YYI
102 FORMAT(1X,F6.2,2X,100A1,2F7.3,F7.2)
DO 30 I=1,JY
30 SPACF(1)=BLANK
10 SPACE(KY)=BLANK
RETURN
END

```

```

SUBROUTINE SMOOTH(Y,N)
DIMENSION Y(1)
YO=(Y(1)+Y(2)+Y(3))/3.
Y(1)=(17.*Y(1)+12.*(YO+Y(2))-3.*(YO+Y(3)))/35.
Y(2)=(17.*Y(2)+12.*(Y(1)+Y(3))-3.*(YO+Y(4)))/35.
M=N-2
DO 10 I=3,M
10 Y(I)=(17.*Y(I)+12.*(Y(I-1)+Y(I+1))-3.*(Y(I-2)+Y(I+2)))/35.
RETURN
END

```

```

SUBROUTINE DAT(N,N1,X,Y,S)
DIMENSION X(1),Y(1)
READ N,N1,X(1),Y(1)
READ N1,N2,Y2,Y3,Y4
101 FOR MAT(1:5,3:10,0)
  READ N1,N2,(X(1),I=1,N0)
  READ N2,(Y(1),I=1,N0)
102 FOR MAT(3:10,0)
  DO 10 I=1,N1
    X(1)=X(I+1)-(X(I+1)-X(I))* (S/2. - .5+3.4)
  RETURN
END

```

```

SUBROUTINE PLOT(DATX,DATY,DATAX,DATAY,YY,TIME,NIM,YP5X,YBASE,71)
DIMENSION DATX(1),DATY(1),DATAX(11),DATAY(1),XX(60),YY(1)
COMMON/CCPODL/XMIN,XMAX,YMIN,YMAX,D1,D2,D3,D4
L=DATX(1)/5.
XMIN=5.*L
L=DATAX(NIMP)/5.
XMAX=5.*(L+1)
N=XMAX-XMIN+0.5
M=N/5+1
YMIN=0.
YMAX=YPEAK/0.8
DO 10 I=1,60
  YY(I)=YY(I)*(YPEAK-YBASE)+YBASE
  CALL CCGRID(1,N,6HNORLS)
  CALL CCPLOT(DATX,DATY,NIM,4HJOIN)
  CALL CCPLOT(DATAX,DATAY,NIMP,6HJOIN,7,1)
  DO 20 J=1,60
    AI=J
    23 XX(J)=DATAX(1)+(AI-.5)*DX
    CALL CCPLOT(XX,YY,60,4HJOIN)
    MIN=XMIN+0.5
    DO 30 I=1,M
      MY=MIN+(I-1)*5
      AM=(MY-MIN)
      AN=N
      CCX=1000.*AM/AN+31.
      WRITE(6,101)MY
101  FORMAT(I7)
    30 CALL CCLTR(CCX,5),0,3)
    CALL CCNEXT
    CALL CCEND
  RETURN
END

```

```

S'JBROJTIME LOGE(N)
COMMON/DRAW/SPACE(170), MARK,DOT,BLANK,VMARK,VMARK
COMMON/LOGS/EX(91),EP, THETA(91),Q(91)
DO 17 I=1,100
  SPACE(1)=BLANK
  PRINT 132
102 FORMAT(1H1,53X,7H-Q/REL/9H THE I A .0,17X,3H0=1,17X,3H0=2,17X,3H0=3,
1,17X,3H0=4,17X,3H0=5)
DO 17 I=1,4
DO 50 J=1,5
K=(J-1)*20+1

```

```

50 SPACE(K)=D0F
   KK=200.*Z(I)*1.5
   IF(KK.LT.1)KK=1
   IF(KK.GT.100)KK=100
   SPACE(KK)=XMAX
   PRINT 103,THETA(I),(SPACE(J),J=1,100)
40 SPACE(KK)=BLANK
   PRINT 101
101 FORMAT(11H1,40X,1/HINELASTICITY (EV)/12H 1 2 3 4 5 6 7 8 9 10,15X,4H,001,16X
1,3H,01,17X,2H,1,17X,2H,1,17X,2H,1,17X,2H,1,10.)
   DO 20 I=1,4
   DO 30 J=1,5
   K=(J-1)*20+1
30 SPACE(K)=D0F
   KK=100.*(EV(I)+4.1/4.75+0.5
   IF(KK.LT.1)KK=1
   IF(KK.GT.100)KK=100
   SPACE(KK)=VMAX
   JJ=100.*(EV(I)+4.1/4.75+0.5
   IF(JJ.LT.1)JJ=1
   IF(JJ.GT.100)JJ=100
   SPACE(JJ)=RMAX
   PRINT 103,THETA(I),(SPACE(J),J=1,100)
   SPACE(JJ)=BLANK
20 SPACE(KK)=BLANK
103 FORMAT(1X,F5.1,1X,100A1,1H.)
RETURN
E.

```


E19 = 80.00 V
 E21 = 11.45 V
 HA = 23.0 AMU
 HB = 2.0 AMU
 HC = 2.0 AMU

THE ACTION A (V) I (A) D (V) B (AT 1/2 A)

00 65 0.590
 01 65 0.590
 02 4.740 1.944

Page	C	V (V)	R (V)	D	THETA	CHI	THETA LAB
000001	0.00000	0.00000	0.00000	0.00000	0.00000	100.00000	0.00000
000002	0.00000	0.00000	0.00000	0.00000	0.00000	177.13548	0.57725
000003	0.00000	0.00000	0.00000	0.00000	0.00000	174.77197	0.56037
000004	0.00000	0.00000	0.00000	0.00000	0.00000	173.44730	1.21014
000005	0.00000	0.00000	0.00000	0.00000	0.00000	172.42052	1.38226
000006	0.00000	0.00000	0.00000	0.00000	0.00000	171.73572	1.45028
000007	0.00000	0.00000	0.00000	0.00000	0.00000	171.34721	1.55195
000008	0.00000	0.00000	0.00000	0.00000	0.00000	171.21483	1.68761
000009	0.00000	0.00000	0.00000	0.00000	0.00000	171.20121	1.55387
000010	0.00000	0.00000	0.00000	0.00000	0.00000	171.20612	1.65369
000011	0.00000	0.00000	0.00000	0.00000	0.00000	171.44976	1.57508
000012	0.00000	0.00000	0.00000	0.00000	0.00000	171.66639	1.24678
000013	0.00000	0.00000	0.00000	0.00000	0.00000	171.71932	1.61130
000014	0.00000	0.00000	0.00000	0.00000	0.00000	172.20247	1.46540
000015	0.00000	0.00000	0.00000	0.00000	0.00000	172.00000	1.62285
000016	0.00000	0.00000	0.00000	0.00000	0.00000	172.62151	1.37271
000017	0.00000	0.00000	0.00000	0.00000	0.00000	173.14031	1.31941
000018	0.00000	0.00000	0.00000	0.00000	0.00000	173.48230	1.26352
000019	0.00000	0.00000	0.00000	0.00000	0.00000	173.82133	1.20548
000020	0.00000	0.00000	0.00000	0.00000	0.00000	174.14250	1.14472
000021	0.00000	0.00000	0.00000	0.00000	0.00000	174.50764	1.08941
000022	0.00000	0.00000	0.00000	0.00000	0.00000	174.85386	1.02122
000023	0.00000	0.00000	0.00000	0.00000	0.00000	175.19936	0.95732
000024	0.00000	0.00000	0.00000	0.00000	0.00000	175.54665	0.89206
000025	0.00000	0.00000	0.00000	0.00000	0.00000	175.85384	0.82580
000026	0.00000	0.00000	0.00000	0.00000	0.00000	176.24073	0.75892
000027	0.00000	0.00000	0.00000	0.00000	0.00000	176.50526	0.69165
000028	0.00000	0.00000	0.00000	0.00000	0.00000	176.93071	0.62351
000029	0.00000	0.00000	0.00000	0.00000	0.00000	177.22126	0.55491
000030	0.00000	0.00000	0.00000	0.00000	0.00000	177.61478	0.48606
000031	0.00000	0.00000	0.00000	0.00000	0.00000	177.77130	0.41596
000032	0.00000	0.00000	0.00000	0.00000	0.00000	178.10225	0.34766
000033	0.00000	0.00000	0.00000	0.00000	0.00000	178.64349	0.27021
000034	0.00000	0.00000	0.00000	0.00000	0.00000	179.04335	0.20071
000035	0.00000	0.00000	0.00000	0.00000	0.00000	179.32214	0.13526
000036	0.00000	0.00000	0.00000	0.00000	0.00000	180.66118	0.06563
000037	0.00000	0.00000	0.00000	0.00000	0.00000	180.00000	0.00000

Numerical trajectory results.

Excitation - orientation function.

IN	RGV	INTENSITY	G	-G/REL	FIT
37.06	X		2.651	-.224	0.00
37.05	X		2.256	-.155	0.00
37.23	X		2.045	-.174	0.00
37.02	X		1.778	-.150	0.00
37.00	X		1.495	-.126	0.00
37.79	X		1.215	-.103	0.00
37.57	X		.925	-.075	0.00
37.16	X		.646	-.046	0.00
37.30	X		.357	-.023	0.00
37.52	X		.131	-.011	0.00
37.71	X	XX	-.131	.011	19.37
37.65	X	XX	-.385	.033	24.61
47.74	X	XX	-.644	.054	11.46
47.02	X	XX	-.856	.076	7.04
47.05	X	XX	-1.144	.057	9.67
47.03	X	XX	-1.369	.117	6.16
47.11	X	XXXXXXXXXXXX	-1.630	.130	2.67
47.07	X	XXXXXXXXXXXXXXXXXXXX	-1.868	.158	4.85
47.18	X	XXXXXXXXXXXXXXXXXXXX	-2.103	.177	4.82
47.37	X	XXXXXXXXXXXXXXXXXXXX	-2.324	.157	4.33
47.07	X	XXXXXXXXXXXXXXXXXXXX	-2.562	.216	4.55
47.74	X		-2.787	.235	6.46
47.02	X		-3.009	.254	6.00
47.10	X		-3.227	.272	0.00
47.25	X		-3.442	.250	0.00
47.47	X		-3.654	.308	0.00
47.07	X		-3.863	.326	0.00
47.34	X		-4.064	.343	0.00
47.03	X		-4.271	.360	0.00
47.21	X		-4.473	.377	0.00
47.07	X		-4.687	.354	0.00
47.03	X		-4.861	.430	0.00
47.76	X		-5.051	.426	0.00
47.05	X		-5.236	.442	0.00
47.11	X		-5.423	.458	0.00
47.22	X		-5.604	.473	0.00
47.00	X		-5.782	.488	0.00
47.05	X		-5.958	.503	0.00
47.67	X		-6.130	.517	0.00
47.00	X		-6.300	.532	0.00
47.02	X		-6.467	.546	0.00
47.42	X		-6.630	.555	0.00
47.01	X		-6.751	.573	0.00
47.76	X		-6.950	.566	0.00
47.64	X		-7.105	.555	0.00
47.18	X		-7.257	.612	0.00
47.35	X		-7.407	.625	0.00
47.03	X		-7.554	.637	0.00
47.71	X		-7.658	.620	0.00
47.00	X		-7.840	.661	0.00
47.01	X		-7.978	.673	0.00
47.77	X		-8.114	.685	0.00
47.67	X		-8.248	.666	0.00
47.64	X		-8.375	.707	0.00
47.62	X		-8.507	.718	0.00
47.00	X		-8.638	.728	0.00
47.07	X		-8.755	.735	0.00
47.77	X		-8.875	.745	0.00
47.07	X		-8.952	.755	0.00
47.74	X		-9.107	.768	0.00

Ideal scattering histogram.

Raw Na⁺-He data.

37.67
 37.81
 37.95
 38.09
 38.23
 38.37
 38.51
 38.65
 38.79
 38.93
 39.07
 39.21
 39.35
 39.49
 39.63
 39.77
 39.91
 40.05
 40.19
 40.33
 40.47
 40.61
 40.75
 40.89
 41.03
 41.17
 41.31
 41.45
 41.59
 41.73
 41.87
 42.01
 42.15
 42.29
 42.43
 42.57
 42.71
 42.85
 42.99
 43.13
 43.27
 43.41
 43.55
 43.69
 43.83
 43.97
 44.11
 44.25
 44.39
 44.53
 44.67
 44.81
 44.95
 45.09
 45.23
 45.37
 45.51
 45.65
 45.79
 45.93

INTENSITY

Q	-Q/EREL	FIT
4.616	-0.350	0.00
4.374	-0.365	0.00
4.134	-0.385	0.00
3.896	-0.395	0.00
3.660	-0.395	0.00
3.426	-0.285	0.00
3.195	-0.270	0.00
2.965	-0.250	0.00
2.738	-0.221	0.00
2.514	-0.212	0.00
2.291	-0.163	0.00
2.070	-0.175	0.00
1.852	-0.156	0.00
1.636	-0.138	0.00
1.421	-0.120	0.00
1.205	-0.102	0.00
0.989	-0.084	0.00
0.771	-0.067	0.00
0.555	-0.049	0.00
0.339	-0.032	0.00
0.123	-0.015	0.00
-0.093	0.002	0.00
-0.309	0.018	0.00
-0.525	0.035	0.00
-0.741	0.051	0.00
-0.957	0.067	0.00
-1.173	0.083	0.00
-1.389	0.099	0.00
-1.605	0.115	0.00
-1.821	0.130	0.00
-2.037	0.146	0.00
-2.253	0.161	0.00
-2.469	0.176	0.00
-2.685	0.191	0.00
-2.901	0.206	0.00
-3.117	0.220	0.00
-3.333	0.235	0.00
-3.549	0.249	0.00
-3.765	0.263	0.00
-3.981	0.277	0.00
-4.197	0.291	0.00
-4.413	0.304	0.00
-4.629	0.318	0.00
-4.845	0.331	0.00
-5.061	0.344	0.00
-5.277	0.357	0.00
-5.493	0.370	0.00
-5.709	0.383	0.00
-5.925	0.395	0.00
-6.141	0.408	0.00
-6.357	0.420	0.00
-6.573	0.432	0.00
-6.789	0.444	0.00
-7.005	0.456	0.00
-7.221	0.467	0.00
-7.437	0.479	0.00
-7.653	0.490	0.00
-7.869	0.501	0.00
-8.085	0.513	0.00
-8.301	0.523	0.00

Smoothed Na⁺-He data (apparatus function).

CHRCV	INTENSITY	C	-C/REL	FIT
37.00	0000000	4.550	-0.387	0.00
37.05	0000000	4.254	-0.363	0.00
37.10	0000000	4.006	-0.336	0.00
37.15	0000000	3.710	-0.314	0.00
37.20	0000000	3.434	-0.250	0.00
37.25	0000000	3.154	-0.266	0.00
37.30	0000000	2.876	-0.243	0.01
37.35	0000000	2.602	-0.220	0.01
37.40	0000000	2.330	-0.197	0.02
37.45	0000000	2.052	-0.174	0.03
37.50	0000000	1.758	-0.152	0.05
37.55	0000000	1.451	-0.130	0.05
37.60	0000000	1.211	-0.118	0.05
37.65	0000000	1.022	-0.066	0.02
37.70	0000000	0.769	-0.065	0.02
37.75	0000000	0.520	-0.044	0.04
37.80	0000000	0.273	-0.029	0.07
37.85	0000000	0.010	-0.003	0.05
37.90	0000000	-0.211	0.018	0.01
37.95	0000000	-0.448	0.030	0.00
38.00	0000000	-0.693	0.058	0.07
38.05	0000000	-0.914	0.077	0.00
38.10	0000000	-1.143	0.093	0.00
38.15	0000000	-1.365	0.116	0.00
38.20	0000000	-1.552	0.134	0.01
38.25	0000000	-1.812	0.153	0.05
38.30	0000000	-2.025	0.171	0.08
38.35	0000000	-2.244	0.189	0.00
38.40	0000000	-2.445	0.207	0.03
38.45	0000000	-2.644	0.225	0.05
38.50	0000000	-2.810	0.242	0.00
38.55	0000000	-3.014	0.255	0.01
38.60	0000000	-3.278	0.276	0.05
38.65	0000000	-3.472	0.293	0.09
38.70	0000000	-3.647	0.309	0.05
38.75	0000000	-3.800	0.326	0.01
38.80	0000000	-4.090	0.362	0.07
38.85	0000000	-4.237	0.377	0.05
38.90	0000000	-4.421	0.373	0.03
38.95	0000000	-4.603	0.388	0.01
39.00	0000000	-4.763	0.404	0.00
39.05	0000000	-4.960	0.418	0.00
39.10	0000000	-5.134	0.433	0.07
39.15	0000000	-5.365	0.448	0.04
39.20	0000000	-5.474	0.462	0.00
39.25	0000000	-5.641	0.476	0.05
39.30	0000000	-5.800	0.480	0.04
39.35	0000000	-5.966	0.503	0.04
39.40	0000000	-6.125	0.517	0.03
39.45	0000000	-6.282	0.530	0.02
39.50	0000000	-6.436	0.543	0.02
39.55	0000000	-6.566	0.550	0.02
39.60	0000000	-6.737	0.560	0.01
39.65	0000000	-6.884	0.561	0.01
39.70	0000000	-7.028	0.563	0.01
39.75	0000000	-7.110	0.565	0.01
39.80	0000000	-7.312	0.577	0.00
39.85	0000000	-7.447	0.622	0.00
39.90	0000000	-7.582	0.640	0.00
39.95	0000000	-7.715	0.651	0.00

Convolved apparatus function and histogram
compared to raw Na⁺-D₂ data.

Sample of Cal Camp plot of fit to data (convolution), data, and apparatus function.