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MASTER

DYNAMIC ISOTOPE EFFECTS IN ION-MOLECULE REACTIONS

Arthur Stephen Werner
(Ph. D. Thesis)

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DYNAMIC ISOTOPE EFFECTS IN ION-MOLECULE REACTIONS

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ABSTRACT

An ion-beam scattering cell apparatus was employed to measure product ion velocity and angular distributions from the reactions of O_2^+ with HD. Five pairs of contour maps of the specific intensity of O_2D^+ and O_2H^+ were measured at collision energies between 2.5 and 8.6 eV. At energies below 4 eV the product distributions are isotropic about and peak at the center-of-mass velocity, indicating that O_2D^+ and O_2H^+ are produced primarily from the decay of a long-lived complex and that these products are highly internally excited. It is also found that most of the system total angular momentum appears as product-ion rotation.

At high collision energies the $O_2^+ \left(\begin{smallmatrix} H \\ HD, D \end{smallmatrix} \right) \begin{smallmatrix} O_2D^+ \\ O_2H^+ \end{smallmatrix}$ reactions are direct. The O_2H^+ is strongly forward scattered and the O_2D^+ is primarily back-scattered. Spectator stripping is invoked and a double head-on impulsive collision model is proposed to account for the high energy dynamic isotope effect. Integrated total cross-sections for O_2D^+ and O_2H^+ formation are calculated, and the O_2D^+/O_2H^+ isotope ratio is found to vary from 5 at low energy to 0.9 at 8.6 eV.

The reactions $\text{O}_2^+ \left(\begin{smallmatrix} \text{HD} & \text{OH} \\ \text{OD} & \text{OH} \end{smallmatrix} \right) \text{OD}^+ / \text{OH}^+$ were investigated in the relative collision energy range from 4.3 to 21.5 eV and are direct at all energies. Both product distributions are extremely broad in the center-of-mass system and most of the available energy goes into product excitation. The OH^+ distributions are forward peaked at all energies. The OD^+ specific intensity spectra are highly symmetric about the center-of-mass velocity, but at large relative energies backscattered product predominates. The OD^+/OH^+ isotope ratio decreases from near unity at low collision energy to 0.07 at 21.5 eV. A double pickup mechanism is devised to partially account for the velocity spectra and isotope effects.

Contour maps of the $\text{O}_2^+(\text{H}_2, \text{O})\text{H}_2\text{O}^+$ reaction were measured at collision energies of 7.3 and 8.9 eV. Product H_2O^+ ions are backscattered at both energies and at 8.9 eV the neutral O atom is formed in an excited electronic state. A two step "rip-off" mechanism is used to explain the dynamics of this reaction.

Quasiequilibrium theory (QET) is used to calculate product ion intensity ratios and lifetimes of the H_2O_2^+ complex formed by low energy collisions of O_2^+ and H_2 . These computations are compared with our previously measured O_2H^+ , OH^+ and H_2O^+ intensity distributions. It is concluded that the large excess of O_2H^+ over the other two products is due to direct formation of this ion at all collision energies. By inclusion of anharmonic contributions and vibration-rotation interactions in the QET rate constant calculations, the H_2O_2^+ decomposition lifetime can be made to agree with measured product ion velocity-angle scattering distributions.

CHAPTER I. INTRODUCTION

A. Ion-Molecule Reaction Dynamics

Experimental studies of gas phase ion-molecule reactions over the past 15-20 years have provided chemists with significant insight into the dynamics of molecular interactions. Recent progress in the ion-molecule reaction field has been the subject of several recent reviews.¹⁻³ Classical theories⁴ of chemical kinetics postulate the existence of an intermediate complex between reactant and product channels, which has been interpreted to mean that chemical reactions proceed via formation of a long-lived intermediate species.

The development of molecular beam techniques permitted the measurement of product velocity and angular spectra. These early experiments showed that, in fact, many reactions proceed directly, even at low collision energies.^{3,5} The most extensively studied ion-molecule reactions, $N_2^+(H_2,H)N_2H^+$ ⁶ and $Ar^+(H_2,H)ArH^+$,⁷ * were found to proceed principally by the spectator stripping model,⁸ that is the ionic projectile

* This shorthand notation will be used throughout the thesis to stand for:

Two reactive channels are abbreviated:

abstracts one hydrogen atom from the neutral without transferring any momentum to the spectator atom. In the N_2^+ reaction,^{6d} as well as in the $N^+(H_2,H)NH^+$ reaction,⁹ the product scattering distributions also indicate a small contribution to the total cross-sections of a mechanism which results in products backscattered in the center-of-mass coordinate system. This type of interaction is peculiar to small impact parameter, or head-on, collisions.

Subsequent dynamic studies have uncovered interesting examples of ion-molecule reactions which do not proceed through formation of long-lived collision complexes.^{10,11} The endothermic reactions of O_2^+ with H_2 ,^{12,13} which are discussed in Chapter III, involve a long-lived intermediate at low energies, but become direct as the relative collision energy is increased.

B. Intramolecular Isotope Effects

Kinetic isotope effects have long been a valuable aid in deducing chemical reaction mechanisms.¹⁴ When an atom of a molecule is replaced by an isotope of the same element the mass dependent molecular parameters, such as vibrational and rotational frequencies, may be substantially altered, yet the potential energy and structure of the molecule are changed only negligibly.¹⁵ The most significant frequency shifts are those accomplished by hydrogen isotopic substitution because the percentage change in mass of the atom of interest is substantial.

Intermolecular isotope studies of ion-molecule reactions were first made by Stevenson and Schlissler¹⁶ to test the Langevin model of ion-

molecule collisions. Later, Friedman and co-workers¹⁷ examined the reactions of rare gas and diatomic ions with HD at low collision energies in an attempt to find evidence for complex formation. The reactions $\text{Ar}^+ \left(\begin{smallmatrix} \text{HD} \\ \text{D} \end{smallmatrix} \right) \begin{smallmatrix} \text{H} \\ \text{D} \end{smallmatrix} \text{ArD}^+ \xrightarrow{18} \text{ArH}^+$ and $\text{N}_2^+ \left(\begin{smallmatrix} \text{HD} \\ \text{D} \end{smallmatrix} \right) \begin{smallmatrix} \text{H} \\ \text{D} \end{smallmatrix} \text{N}_2\text{D}^+ \xrightarrow{6d, 17b, 19} \text{N}_2\text{H}^+$ have been studied thoroughly from thermal energies to collision energies up to 20 eV. For both reaction pairs, approximately equal amounts of XH^+ and XD^+ are produced at low energies (<1 eV), but as the collision energy is increased XH^+ becomes the dominant product. The excess of XH^+ at high energies is in qualitative agreement with the prediction of the ideal stripping model that the XH^+/XD^+ should become infinite above a critical collision energy.

C. Thesis Motivation

In the reaction of O_2^+ with H_2 ,^{10,12,13} the products O_2H^+ , OH^+ and H_2O^+ are formed by a collision complex mechanism at collision energies below 4 eV, and by direct interactions at higher energies. This system provides a unique opportunity to investigate the factors governing long-lived intermediate formation and also to study the effects of a deep potential well between reactants and product channels upon high energy impulsive interactions. By studying the reactions of O_2^+ with HD we are able to uncover details in the reaction mechanisms that are averaged out in the $\text{O}_2^+ - \text{H}_2(\text{D}_2)$ reactions.

The apparatus and experimental techniques employed in this investigation are briefly described in Chapter II. Chapter III is a recapitulation of the $\text{O}_2^+(\text{H}_2)\text{D}_2$ experiments and some new results are presented and

analyzed. In Chapter IV the $O_2^+ \left(\begin{smallmatrix} HD, H \\ D \end{smallmatrix} \right) O_2D^+$ and $O_2^+ \left(\begin{smallmatrix} HD, OH \\ OD \end{smallmatrix} \right) OD^+$ reactions are discussed in detail and two high energy mechanisms are proposed. The low energy reactions of O_2^+ with the pure and mixed hydrogen isotopes are analyzed in Chapter V within the context of statistical unimolecular decay theory.

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CHAPTER II. EXPERIMENTAL

A. Apparatus

The apparatus used for the experiments discussed in this thesis has been described in detail previously.^{1,2} It is displayed schematically in Fig. II-1. Briefly, the apparatus consists of three main parts: a source which prepares and focuses a momentum analyzed beam of ions at a selected energy, a scattering cell containing neutral gas at room temperature, and a detection train consisting of a 90° spherical electrostatic energy analyzer, a quadrupole mass filter, and a semiconductor counter.

Ions are prepared in a Broida-type cavity by means of a 30 GHz diathermy microwave discharge.³ Gaseous oxygen inside this 1-cm diameter tube is kept at a pressure of about 30 μ . Ions extracted from the source, which is floated at a fixed energy, are focused by a series of cylindrical lenses into a magnetic momentum analyzer. A series of lenses focuses the ions emerging from the magnet into a scattering cell consisting of two concentric cylinders. The pressure in the scattering cell is monitored by a capacitance manometer.³ Scattered products enter the detection train which is mounted on a rotatable lid. The angular resolution of the detector is 2.5° full width and the energy analyzer has a resolution of 3 % FWHM.

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Fig. II-1. Schematic representation of the ion-beam scattering cell apparatus.

B. Procedure

After preparation and characterization of a stable primary ion beam, the scattering cell is filled with gas to a pressure $\sim 7 \times 10^{-4}$ torr and the detector mass filter is set to a fixed mass. Centerline spectra are determined by scanning the energy analyzer at the primary beam peak angle. To obtain a contour map, about 15-20 angular scans are made at a series energy analyzer voltages properly spaced to overlap the entire product scattering distribution. At each angle and energy setting signal is counted for 20-30 sec. The background at each point is measured by noting the pressure in the main vacuum tank, emptying the scattering cell of gas, and filling the entire tank to the proper pressure. Except near the primary beam, the background is usually less than one count per second. After each counting period the counting time, energy analyzer voltage, scattering cell pressure, and number of counts are automatically recorded on a teletype. The angle position must be typed in manually.

C. Data Analysis

Each data point is normalized with respect to counting time, pressure, scattering volume, detection volume, and primary beam intensity. The quantity obtained, the specific intensity $\bar{I}$, is defined by Eq. I-1

$$I(\theta) = \int_0^{\infty} \bar{I}(\theta, \phi, u) u^2 du \quad (\text{II-1})$$

where $I(\theta)$ is the barycentric differential cross-section at angle θ and ϕ and u are respectively the azimuthal scattering angle and product

velocity in the center-of-mass coordinate system. The total reaction cross-section σ is just

$$\sigma = 2\pi \int_0^{\pi} I(\theta) \sin\theta d\theta \quad (\text{II-2})$$

The differential and total cross-sections are evaluated numerically from $\bar{I}$.

D. Scattering Dynamics

Figure II-2 is a Newton diagram for scattering of a particle of laboratory velocity v_0 by a stationary target. The position of the center-of-mass of the system is determined by the masses of the colliding particles:

$$v_{cm} = \frac{m_p}{m_p + m_n} v_0 \quad (\text{II-3})$$

where m_p and m_n are the masses of the incident and stationary molecules. The elastic circle represents the loci of possible final velocities of the incident particle after an interaction in which there is no energy or atom exchange between reactant particles. The center-of-mass velocity of the projectile, u , is the same before and after collision. A particle scattered inelastically will have a barycentric velocity, u' , less than its initial velocity. Products are said to be forward scattered if $\theta < |90^\circ|$ and backscattered when $\theta > |90^\circ|$. There are two barycentric angles corresponding to each laboratory scattering angle.

-11-

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Fig. II-2. Newton diagram for collisions between a heavy fast moving particle and a light stationary target. Initial and final velocities and scattering angles of the projectile molecule are shown in both the laboratory and center-of-mass coordinate systems.

E. Contour Maps

The raw data for each experiment are punched on IBM cards and analyzed by a program on a CDC 6600 computer. The program generates a series of graphs of $\bar{I}$ vs. scattering angle at fixed energies and another set of plots of specific intensity vs. velocity at constant angles. Contour maps are derived by drawing smooth curves through these graphs and recording the angle-velocity coordinates of each graph at predetermined intensities. The points chosen are then plotted separately for each intensity: a contour map is produced by superimposing these graphs.

F. Reaction Energetics

From conservation of energy:

$$E_S^O + U = E_S' + U' + \Delta H \quad (\text{II-4})$$

where E_S^O and E_S' are the initial and final relative kinetic energies, U and U' are the internal energies of reactants and products and ΔH is the heat of reaction. We can define the quantity Q , the reaction exoergicity by:

$$Q = E_S' + E_S^O \quad (\text{II-5})$$

or equivalently

$$Q = U - U' - \Delta H \quad (\text{II-6})$$

The Q value is therefore the amount of relative translational energy which is transformed into reaction endothermicity and product excitation.

Measurement of the scattered Q distribution thus enables one to determine the internal state distributions of the collision products. Since the internal energy of the reactants is generally small compared with the other quantities in Eq. II-4 it can usually be neglected. For a reaction which produces a polyatomic ion and a neutral atom, we can set limits on the allowed values of Q :

$$-D(\text{ion}) - \Delta H \leq Q \leq -\Delta H \quad (\text{II-7})$$

The lower limit to Q corresponds to the transfer from kinetic to internal of an amount of energy equal to the heat of reaction plus the strength of the weakest bond in the ionic product.

In a reaction in which the neutral product is polyatomic, large continuous amounts of energy can be put into internal energy of the neutral even in excess of its dissociation limit. Excitation above the neutral dissociation energy appears as relative translation between the neutral fragments. Thus no lower limit to Q can be specified for this type of reaction.

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CHAPTER III. THE REACTIONS OF O_2^+ WITH H_2 AND D_2

Over the past several years the reactive and nonreactive scattering of O_2^+ by H_2 and D_2 has been investigated in some detail in this laboratory.¹⁻⁴ This work will be reviewed in this chapter and some new experiments will be presented and discussed. Since no intermolecular isotope effects were uncovered, H_2 and D_2 will be used interchangeably in the following discussion. The reaction channels which were investigated are:

Reactions (B), (D), and (E) proceed via formation of a persistent collision complex at relative kinetic energies below 4 eV, as evidenced by barycentric product scattering distributions that are very nearly isotropic about the center-of-mass velocity. In this low energy region the cross section for formation of O_2H^+ is about an order of magnitude larger than cross-sections for OH^+ and H_2O^+ production. At higher energies these products are formed by direct mechanisms. Reaction (C) is direct at all energies at which it is observed.

The low energy nonreactive scattering of O_2^+ from D_2 is notable for its large degree of inelasticity and for its small intensity at barycentric angles greater than 135° . The scattering maps of O_2^+ by He have a large amount of signal at all barycentric angles. They also show that the inelasticity of the scattering increases with angle. This inelastic scattering was interpreted in terms of classical theories of vibrational excitation.² A comparison of the low energy nonreactive scattering of O_2^+ by He and by D_2 indicates that the $\text{O}_2^+ - \text{D}_2$ interaction is strongly influenced by chemical forces. The small impact parameter collisions, which would be expected to lead to large angle scattering in Reaction (A), apparently lead to chemical reaction or to highly inelastic scattering with large amounts of excitation of both O_2^+ and D_2 . The strong chemical interactions evident in the non-reactive scattering profiles are consistent with formation of an intermediate complex, O_2D_2^+ .

At collision energies above 6 eV there is a small inelastic secondary maximum in the small angle region. Similar maxima were observed in the nonreactive scattering of N_2^+ by D_2 ⁶ and by CH_4 .⁷ As in the $\text{N}_2^+ - \text{D}_2$ case the amount of inelasticity was found to increase with increasing collision energy, reaching a Q value of about -10 eV at a collision energy of 14.7 eV. Two explanations have been advanced to explain this phenomenon. In the $\text{N}_2^+ - \text{D}_2$ system this feature was explained as the excitation of D_2 to its lowest $^3\Sigma_u$ state by grazing collisions. The $\text{N}_2^+ - \text{CH}_4$ data was rationalized in a similar manner. The same process probably occurs in the $\text{O}_2^+ - \text{D}_2$

collisions, but since this inelastic small angle peaking cannot be separated from the rest of the inelastic forward scattering, it is not possible to test this hypothesis unequivocally.

The instability of O_2D^+ formed by spectator stripping⁶ at energies above 8.6 eV provides a further explanation for this inelastic feature. Since O_2D^+ scattered with the ideal stripping velocity has an internal excitation greater than 2.6 eV, the O_2^+-D bond energy, it will dissociate to O_2^+ and D before reaching the detector. The resulting O_2^+ ions will therefore be traveling at speeds close to the O_2D^+ stripping velocity. Further evidence for this explanation will be given in Chapter IV in connection with the nonreactive scattering of O_2^+ by HD.

The contour maps of Reaction (B) show large degrees of symmetry about the $\pm 90^\circ$ line in the center of mass coordinate system at both high and low collision energies. Since the ionic and the neutral products are identical except for charge, a symmetric spacial distribution can be rationalized as the result of either complex formation or direct interaction in which the oxygen atoms are dynamically equivalent. At high collision energies (above 8.3 eV) where the existence of a long-lived complex intermediate is ruled out, there is a slight degree of asymmetry which probably arises from an interaction in which the oxygen atoms are not dynamically equivalent.

This reaction was not observed at collision energies below 5.55 eV. The cross-section for collisional dissociation increases with energy, as expected, but is only $0.05 \text{ \AA}^2$ at 11 eV. The scattered O^+ distribution is strongly forward peaked, indicating that the dissociation process proceeds by a direct mechanism.

The $O_2^+(D_2, D_2O)O^+$ distributions are similar to those of O^+ formed by the collision of O_2^+ and He,⁵ which suggests that both processes proceed by similar mechanisms. Two mechanisms were proposed to explain the collisional dissociation of O_2^+ by He. Both mechanisms require that the target collides with only one atom of the molecule-ion and that this collision reduces the force between the atoms of the molecule-ion to a negligible value. One mechanism assumes that the collision excites the O_2^+ to a weakly bound state (there are at least four such low-lying excited states of the oxygen molecular ion)⁸ from which the fragments, which are in unspecified electronic states, separate under the influence of weak forces. In the second mechanism, collision of one atom of the projectile with the target is accompanied by adiabatic formation of a complex between O_2^+ and He in which the atoms of the molecular ion are weakly bound. As the interaction occurs, the spectator atom proceeds with its initial velocity only slightly abated, while the other atom slows down. The target atom then leaves the collision region and the O_2^+ is left in its original electronic state, with its atoms separated by a large distance. Since the atoms of the molecular ion are not strongly bound, they continue separating at their new relative velocity.

Reaction (D) is 1.3 eV less endothermic than Reactions (B) and (E) and would, therefore, be expected to have the largest cross-section of the three reactions at low collision energies, particularly if all reactions proceed through an intermediate complex. In fact, H_2O^+ is lower in intensity than either OH^+ or O_2H^+ . This would seem to imply that there is a significant energy barrier to formation of H_2O^+ from the complex; however, Foner and Hudson⁹ by electron bombardment of hydrogen peroxide have found no such barrier. It was alternatively suggested⁴ that the transition state configuration leading to H_2O^+ is highly constrained, perhaps resembling a nonplanar formaldehyde molecule. If this critical configuration for formation of H_2O^+ and O is indeed "tighter" than the transition states for the other channels, then this channel would be expected to be relatively unimportant.

The center-of-mass distribution of scattered H_2O^+ is isotropic at collision energies up to 5.9 eV. This indication of complex formation at high relative energies supports the constrained critical configuration hypothesis, since such a structure could exist for several rotational periods at energies well above the dissociation threshold. These points will be discussed further in Chapter V in connection with the structure and properties of the intermediate complex.

Figure III-1 is a plot of the differential cross sections of scattered H_2O^+ vs. barycentric angle at relative collision energies ranging from 2.93 to 8.89 eV. Within experimental error, the three lower energy plots evince forward-backward symmetry indicative of complex formation. At

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Fig. III-1. Differential cross-sections of scattered H_2O^+ .

7.25 eV $I(\theta)$ has lost its symmetry about $\theta = 90^\circ$, and the product specific intensity is mostly in the backscattered region. The bottom curve in Fig. III-1 shows that at 8.89 eV almost all of the product is scattered beyond 90° and that H_2O^+ is formed principally by zero impact parameter collisions.

Figure III-2 is a contour map of the specific intensity of H_2O^+ at 7.25 eV. The cross in the center of the figure indicates the position of the center-of-mass velocity of the system. The 20% beam profile drawn about the dot representing the velocity of the nominal primary beam velocity encloses 80% of the primary beam angular and velocity spread. Values assigned to the contours are in arbitrary units. The map shows that the distribution is asymmetric with respect to the center-of-mass velocity and that most of the product is backscattered. Apparently at this energy a direct mechanism contributes substantially to the reaction. Figure III-3 shows a similar map at a collision energy of 8.89 eV. The degree of anisotropy of the distribution indicates that the reaction is proceeding entirely by a direct mechanism at this energy. This appears to be the first example of an ion-molecule reaction in which the ionic product is totally backscattered. The velocity distribution is very broad compared to the 20% beam profile, indicating a large distribution of internal energies in the H_2O^+ . The small cross along the 180° line marks the velocity at which H_2O^+ would be found if it were formed by the stripping mechanism (the reverse of the spectator stripping or pick-up model, which is used to explain forward scattering). Most of the H_2O^+ specific intensity is found at slightly larger relative velocities than predicted by the

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Fig. III-2. A specific intensity contour map in the center-of-mass coordinate system of scattered H_2O^+ from the reaction of O_2^+ and H_2 . The $Q = -5.7 \text{ eV}$ circle represents the loci of velocities inside of which the neutral O atom is formed in an excited electronic state.

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Fig. III-3. A contour map of scattered H_2O^+ at a relative energy of 8.89 eV. The $Q = -5.7$ eV circle has the same meaning as in Fig. III-2. The $Q = -8.1$ eV is drawn through the intensity peak. The small cross indicates the velocity at which H_2O^+ formed by stripping is found.

stripping model. This feature is similar to that found in high energy forward spectator stripping reactions such as $N_2^+(D_2, D)N_2D^{+6}$ where the product was found to peak at velocities greater than that predicted by the spectator stripping model. The explanation generally accepted for this phenomenon is that the separating products recoil from each other to produce stable products.

This reaction differs from the pick-up reactions in that in this case a large part of the H_2O^+ intensity at 7.25 eV (Fig. III-2) and almost all the intensity at 8.89 eV (Fig. III-3) is inside the $Q = -5.7$ eV circle, which represents the loci of instability of H_2O^+ . For H_2O^+ ions to be found with velocities inside this circle, the neutral O atom must be formed in an excited electronic state. Atomic oxygen has two low lying states, a 1D at 1.97 eV and a 1S at 4.19 eV. The critical value of Q for instability of H_2O^+ if neutral O is formed in the 1D state is -7.7 eV. Therefore, the substantial fraction of H_2O^+ found inside the $Q = -8.1$ eV circle (which corresponds to the peak velocity) must be due to production of O in the 1S state.

This "rip-off" mechanism, which requires that the collision be sufficiently violent to electronically excite the oxygen atom which is kicked out, cannot be satisfactorily described by either of the two mechanisms proposed for collisional dissociation nor by either the knockout or rebound models.⁵ The arguments against the knockout and rebound mechanisms are basically the same as those presented in Ref. 5.

The first mechanism proposed for Reaction (C) requires the collision between the target and one atom of the projectile to leave the molecule-

ion in an excited electronic state from which the ion dissociates. The initial collision must send the target in the forward (initial direction of the projectile) direction and the struck atom in the reverse direction. By the time the atoms of the ion are completely separated, the target, which is very light, will most likely be too far from the struck projectile atom for a bond to be formed.

Mechanism (2) involves the adiabatic formation of a short lived complex between target and projectile in which the unstruck projectile atom is weakly bound. The potential curves for this process as well as those for other possible reaction channels are illustrated in Fig. III-4. The reason that the reaction is unlikely to produce an oxygen atom in an excited electronic state is that the most likely curve crossing is between the lowest two curves, the result of which is the formation of oxygen atom in its ground electronic state.

A more plausible mechanism for the "rip-off" is that the collision between the target and one atom of the projectile electronically excites the O_2^+ to a state asymptotically connected to an oxygen atom in the 1S state. The excited molecule-ion and the hydrogen molecule then adiabatically form a short-lived complex with the force between the oxygen atoms greatly diminished. This process is indicated by the arrows in Fig. III-4. By this mechanism the uncollided oxygen atom leaves the scene with its velocity only slightly abated and the H_2O^+ is scattered backward in the center-of-mass coordinate system. This process is not inconsistent with the velocity distributions for Reaction (C), since, if the charge remains on the spectator oxygen, this atom will be found in the forward direction at a velocity only slightly slower than the original projectile velocity.

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Fig. III-4. Potential curves relevant to the $O_2^+(H_2O)H_2O^+$ reaction at 8.89 eV relative energy. All curves are qualitative but the asymptotes are quantitatively correct. The arrows indicate the path of the "rip-off" mechanism. Dashed lines represent O-O separation and solid lines stand for H₂-O separation.

At relative collision energies below 4 eV O_2H^+ is distributed isotropically about and peaks at the center-of-mass. This isotropic behavior strongly suggests that this reaction occurs via a long-lived collision complex, and that a large fraction of the angular momentum of the complex goes into internal angular momentum of the ionic product. The cross-section for this reaction at low energies, about $2 \text{ \AA}^2$, is about an order of magnitude greater than the cross-sections of Reactions (B) and (D).

The lowest laboratory energy at which product intensity was measured is 25 eV, which corresponds to a relative translational energy of 1.47 eV; diminished primary beam intensity at lower energies prevented a threshold determination. Franck-Condon factors indicate that the $v = 3$ vibrational state of O_2^+ , which has 0.7 eV excitation energy, is the highest significantly populated level of the ions formed in the discharge.⁹ Furthermore, there is an uncertainty in the relative collision energy of ± 0.2 eV due to target motion.⁶ Thus, if the total kinetic and internal energies are available for reaction,¹⁰ an upper limit to the threshold for this reaction can be set at 2.37 eV.

Foner and Hudson¹¹ found a barrier between O_2^+ and H_2 and the hydrogen peroxide complex of 2.5 ± 0.5 eV, which is consistent with our finding. Ding and Henglein,¹² who have also determined the translational spectrum of O_2D^+ from Reaction (E), found a threshold for reactant $\text{O}_2^+(\text{}^2\pi_g)$ ions at a relative energy of about 1.9 eV. Their primary oxygen ions were produced in an electron bombardment source and contained a large fraction of $\text{O}_2^+(\text{}^4\pi_u)$. Ground state oxygen ions produced in such a source would

certainly have at least as much vibrational excitation as those produced in a microwave discharge. Thus, their translational energy threshold value for this 1.97 eV endothermic reaction appears to be somewhat high.

As the relative collision energy of the reactants is increased beyond 5 eV the O_2D^+ product distribution begins to lose its isotropy and forward peaking appears. At a relative energy of 11 eV the product is totally forward scattered and peaks at the ideal stripping velocity. The forward scattered product distribution is broader in both angle and velocity than the high energy product distributions from the $N_2^+(D_2,D)N_2D^+$ and $Ar^+(D_2,D)ArD^+$ reactions.^{6,13} Additionally, in the latter two reactions there is a small but distinct peak at 180° which can be attributed to a separate backscattering mechanism. In the $O_2^+(D_2,D)O_2D^+$ reaction at energies below 9 eV there is also measurable backscattering; however, the scattered specific intensity at angles beyond 90° does not peak at 180° as would be expected from a separate impulsive small impact parameter mechanism, but rather, as illustrated in Fig. III-5, decreases with increasing barycentric angle. At 11 eV there is no observable O_2D^+ scattered beyond 135° . In the $N_2^+(D_2,D)N_2D^+$ and $Ar^+(D_2,D)ArD^+$ reactions the only other channel available is non-reactive scattering. Thus, the small amount of backscattered O_2D^+ is probably best rationalized as a consequence of the increasing importance at high energies of the other reactive channels for small impact parameter collisions.

There is another difference between the high energy $N_2^+(D_2,D)N_2D^+$ and $Ar^+(D_2,D)ArD^+$ reactions and Reaction (E), which indicates that the

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Fig. III-5. A contour map of O_2D^+ scattering intensity at an $O_2^+-D_2$ collision energy of 8.34 eV. Signal outside the $Q = -2$ eV circle is due to apparatus resolution and beam spread. Products found inside the $Q = -4.6$ eV circle are electronically excited. The small cross in the forward direction indicates the position of the spectator stripping (pickup) peak.

mechanisms involved in the latter are more complicated than simple spectator stripping and impulsive backscattering. The high energy N_2D^+ and ArD^+ distributions have large craters about the center of mass positions corresponding to an absence of scattering in the region where either product is unstable with respect to dissociation to N_2^+ and D or to Ar^+ and D. In Fig. III-5 this region is enclosed by the $Q = -4.6$ eV circle (2.6 eV is the estimated upper limit to the dissociation energy of O_2D^+).³ There is a large amount of intensity inside the circle particularly at angles greater than 90° . This intensity can be only partially reduced by a three dimensional deconvolution technique which removes the velocity and angle spread of the measured distribution due to primary beam spread and neutral target motion.¹⁴ Consequently, the intensity which remains in this region must be due to formation of either O_2D^+ or D in an excited electronic state. The lowest excited state of D, the $^2\text{P}^0$, is 10.2 eV above the ground state and hence is not accessible at a collision energy of 8.34 eV. Since an ion formed in the scattering region takes 5×10^{-5} sec to reach the detector, the O_2D^+ must be excited to a state which lives at least this long with respect to dissociation.

Unfortunately, nothing is known about either the symmetry or location of any electronic states of O_2D^+ . Only two low lying states of the DNO molecules, which is isoelectronic with O_2D^+ , have been observed. The higher state ('A') is 1.7 eV above the lower ('A'),¹⁵ which may not be the ground state. There is also a predissociation limit of 2.2 eV above the ('A') state, which probably results from the crossing of a repulsive ($^3\Sigma_g^-$) state with the ('A') state.¹⁶ Thus, the excited state of O_2D^+ , which is formed in the beam experiments, does not correlate with any known states of DNO.

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CHAPTER IV. ISOTOPE EFFECTS

A. Introduction

The experiments discussed in Chapter III, while providing a deep insight into the dynamics of the $O_2^+-H_2$ reactive system, left numerous unanswered questions about the dynamics of the various channels. The mixed isotopic experiments to be discussed in this chapter were undertaken to obtain both a better idea of the nature of the low energy collision complex and a clearer understanding of the high energy impulsive mechanisms. Two intramolecular isotope effects were studied over the relative energy range from 2.5 - 21.5 eV. The channels investigated were:

Replacement of the homonuclear hydrogen by the mixed isotope effectively introduces two additional reaction channels; that is, Reaction (E) of Chapter III is broken down into Reactions (1a) and (1b) above and Reaction (B) of the previous chapter is subdivided into Reactions (2a) and (2b). The electronic potential curves are independent of isotopic substitution, so that it is only the parameters associated with nuclear motion which are being altered.

The qualitative effects of isotopic substitution on the reaction rates and product velocity distributions are different not only for different channels, but also for the high and low energy mechanisms within each channel. For reactions that proceed through formation of a long-lived collision complex, the product barycentric angular distributions, which are always symmetric about the line drawn between $\pm 90^\circ$, are determined solely by the disposal of angular momentum. The high energy isotope effects are derived both from the dynamics of the collision processes and the differences in energetics of the isotopic reactions.

B. Previously Investigated Systems and Models: $\text{Ar}^+ + \text{HD}$ and $\text{N}_2^+ + \text{HD}$

1. Collision Complex Models

The reactions in which intramolecular isotope effects have been most extensively studied are $\text{Ar}^+(\text{HD}, \text{H})\text{ArD}^+$ and $\text{N}_2^+(\text{HD}, \text{H})\text{N}_2\text{D}^+$.¹ These reactions have also been extensively investigated over the past 15 years in the thermal and low collision energy regimes (< 1 eV) in conventional and tandem mass spectrometers, and more recently by means of ion cyclotron resonance.² The isotope ratio in the argon reaction, $k_{\text{ArH}^+}/k_{\text{ArD}^+}$, increases continuously from slightly less than unity at thermal energies³⁻⁵ to greater than three at a collision energy of 4.5 eV.⁵⁻⁷ The nitrogen isotope ratio, which has been measured at collision energies from thermal to 20 eV, similarly favors N_2D^+ in the thermal region^{2,8} and N_2H^+ above about 1 eV.^{7,9}

In an extremely perceptive paper, Klein and Friedman⁴ proposed two mechanisms to account for the thermal and low energy rate gas ion-HD

isotope effect. Moran and Friedman⁸ subsequently extended this analysis to explain the energy dependence of the isotope ratio in diatomic ion-HD reactions. The fact that the $k_{\text{XH}^+}/k_{\text{XD}^+}$ ratio is less than unity at thermal energies was explained on the basis of the formation of an intermediate complex $\text{H} \diagup \text{X} \diagdown \text{D}^+$, whose internal energy is randomly distributed among its vibrational degrees of freedom. This complex then undergoes unimolecular dissociation. The XD^+ product is favored by virtue of its lower zero point energy and higher density of states. At energies above the thermal region Moran and Friedman suggest that the reactants can form a short-lived complex with the XHD^+ or XDH^+ structure; the former is then shown to be favored on the basis of its lower activation energy of formation. This intermediate energy model predicts that the XH^+/XD^+ ratio will be greater than one, in agreement with experimental data.

The first product ion velocity spectra measured by Lacmann and Henglein¹⁰ were those of ArD^+ and ArH^+ from the reactions $\text{Ar}^+ \begin{pmatrix} \text{D}_2, \text{D} \\ \text{H}_2, \text{H} \end{pmatrix} \text{ArD}^+ / \text{ArH}^+$ at collision energies above 1 eV. The reactions were found to proceed by a direct impulsive mechanism. This mechanism, which results in strong forward scattering of the product ion, was shown to agree with the predictions of the spectator stripping model.¹¹ Subsequently, these experiments were extended down to a relative collision energy of 0.1 eV by the Henglein group¹² and by Bailey and co-workers¹³ and by Wolfgang¹⁴ and co-workers. No evidence for complex formation was found by any of these investigators in either the Ar^+ or N_2^+ -hydrogen reaction and the basic concept of spectator stripping was accepted as the principal reactive mechanism at all energies. The lack of evidence for complex formation in

the argon ion reaction has been explained by Mahan¹⁵ as a consequence of the inability of Ar^+ and H_2 to form ground state H-Ar-H^+ .

2. Spectator Stripping Model

In the spectator stripping model the projectile ion collides only with one hydrogen atom of the target without transferring any momentum to the other atom. This is equivalent to a completely inelastic collision between the projectile and the abstracted atom. The internal energy, U' of the product ion is, thus, equal to the relative collision energy between the primary ion and the abstracted atom minus the heat of reaction.

$$U' = \left(\frac{m_a}{m_i + m_a} \right) E_{\text{LAB}} - \Delta H \quad (\text{IV-1})$$

where E_{LAB} is the laboratory energy of the primary ion, ΔH is the heat of reaction, m_a is the mass of the abstracted atom, and m_i is the mass of the incident ion. For the product ion to be stable, U' must be less than the dissociation energy of the ion. The first term on the right hand side of Eq. (IV-1), the kinetic energy of the primary ion relative to the stripped atom, is twice as large for D-atom abstraction as for H-atom abstraction. This equation contains the essence of the high energy isotope effect which strongly favors XH^+ over XD^+ . It predicts an infinite isotope effect XH^+/XD^+ above the energy U' equal to the $\text{X} - \text{D}^+$ dissociation energy. For the $\text{N}_2^+ - \text{HD}$ system this critical energy value corresponds to a relative collision energy between target and projectile of 3.53 eV,⁹ and to 4.83 eV¹⁶ for $\text{Ar}^+ + \text{HD}$. This infinite isotope effect is in fact not observed, indicating that there is stabilization of the stripped ion by recoil of the

products.⁹ In the N_2^+ -HD system the stripped N_2H^+ exceeds the N_2D^+ by a factor of 20 at relative collision energies above 7 eV.⁹

3. Kinematic-Orientation Models

Light and Chan¹⁷ have extended the "modified stripping model" of Wolfgang^{14b} to predict isotopic product distributions of low energy ion-molecule reactions. This direct model breaks down the mechanism into three steps: the incident two-body trajectory under the influence of polarization forces, "reaction" at a particular intermolecular radius and instantaneous velocity, and the trajectory of the separating products under the influence of polarization forces. For the reaction radius, Light and Chan substitute a three-dimensional surface surrounding the HD which is divided into three zones, corresponding to reaction with H, reaction with D, and no reaction. By considering the separation of the center-of-mass from the center-of-charge of HD, and by taking angular momentum into account they calculate reaction probabilities and cross-sections for XH^+ and XD^+ formation.

The predictions of the Light and Chan model agree reasonably well with the experimentally determined isotope ratios for the Ar-HD⁺ and Kr-HD⁺ reactions but fail to explain the isotope effects and total cross-sections of the Ar⁺-HD reaction above a relative energy of a few electron volts. They explain the latter discrepancy as a consequence of the instability of ArD⁺ formed by spectator stripping above a relative energy of 4.8 eV.

The weaknesses of the Light and Chan model are the assumption of decoupling between reactant translational and internal energies and the assumption of unit reaction probability for incident reactant trajectories entering a reaction shell.

Recently, George and Suplinskas¹⁸ applied their kinematic reaction model to the $\text{Ar}^+(\text{HD}, \text{H})\text{ArD}^+ / \text{ArH}^+$ isotope effect. The essence of the kinematic model is: the reactant ion, a hard sphere, approaches a diatomic molecule, two hard spheres in close proximity, under the influence of the ion-induced-dipole potential. The reaction probabilities are functions of relative velocity, impact parameter, and angle of orientation. The actual reaction process may involve a sequence of impacts; the ion may abstract the atom it first hits or it may react with the other atom in a secondary collision. The products then separate in an ion-induced-dipole potential. From this model product angular and velocity distributions, differential cross-sections, and product internal energy partitioning are calculated and compared with experimental results. The predictions of the kinematic model are in reasonable agreement with the specific intensity contour maps of the $\text{Ar}^+(\text{D}_2, \text{D})\text{ArD}^+$ reaction measured in this laboratory.^{18a} George and Suplinskas conclude that in the collision energy range of several electron volts the chemical interaction is dominated by repulsive core interactions and that the description of interactions in terms of stripping and rebound may not be valid.

For the calculation of the isotope effect in the $\text{Ar}^+(\text{HD}, \text{H})\text{ArD}^+ / \text{ArH}^+$ reactions, the kinematic model was modified to account for the separation of the center-of-charge from the center-of-mass of HD. This introduces an orientation effect which causes the lighter H end of the molecule to

rotate toward the incident ion. The calculated isotope ratios agree with the experiments of Henglein et al.⁷ at relative collision energies above 3.8 eV, where the principal controlling factor in the isotope ratio is the instability of ArD^+ . As expected, orientation effects are not very important at these energies.

The orientation-kinematic model qualitatively fails to predict the experimentally determined⁴⁻⁶ energy dependence of the isotope ratio below 2.1 eV. This failure is due to the importance at low energies of the effective potential between the reactants, which is not well understood. Nevertheless, George and Suplinskas were able to demonstrate the significant contribution to reaction cross-section of the torque-orientation effect at low energy.

C. Previous Investigations of the O_2^+ -HD Reactive System

The only other study of the O_2^+ -HD isotope effect is the work of Moran and Friedman.⁸ It is not possible to compare their experiments with those presented here since all their O_2H^+ and O_2D^+ products resulted from the 2 eV exothermic reaction of $\text{O}_2^+(\pi_u)$ with HD. From their total cross-section measurements at relative collision energies up to 0.54 eV they correctly concluded that a significant amount of $\text{OH}^+(\text{OD}^+)$ is formed by the reaction. They also briefly alluded to the effect of collision orientation upon the reaction mechanism. This point will be more fully explored in this chapter.

Some preliminary centerline (0° in the laboratory) velocity spectra of the products of Reactions (1a) and (1b) measured in this laboratory,

were presented by Tsao.¹⁹ By assuming that the sum of the barycentric differential cross-sections at 0° and 180° are proportional to the total reactive cross section, he found that the isotope ratio (σ_{1a}/σ_{1b}) decreases from a value much greater than one at low collision energies to less than 0.2 at a relative collision energy of 8.6 eV. The approximation of the proportionality of the centerline differential cross-section to the total cross-section is reasonable at low energies where the product angular distribution is isotropic in the center-of-mass system (vide infra); but it is not valid at high relative collision energies where the O_2D^+ specific intensity peaks at angles other than 0° and 180° and the O_2H^+ distribution is highly anisotropic. Nevertheless, the energy dependence of the calculated isotope ratios are in good agreement with those computed by integrating over all scattering angles (v.i.). We²⁰ have also published a brief communication on our initial observation of the unique high energy dynamic isotope effect to be discussed in this chapter.

D. Reaction Energetics

Figure IV-1 is a schematic energy level diagram for the reactions of O_2^+ with the three molecular hydrogen isotopic species which have been studied in this laboratory. The thermochemical values for the $O_2^+-H_2$ system were taken from Franklin²¹ and the energies in b) and c) were calculated from the data in a) by correcting for zero point energy differences between the deuterated and dideuterated molecules and the pure hydrogen species. The frequencies used for the zero point energy determinations as well as activation barriers are tabulated in Chapter V. It should be

Fig. IV-1. Reaction energy level diagrams for a) $O_2^+ + H_2$,
b) $O_2^+ + D_2$ and c) $O_2^+ + HD$.

noted that the difference in zero point energy between O_2D^+ and O_2H^+ is 0.07 eV while the difference in energy of formation of $OD^+ + OH$ and $OH^+ + OD$ is only 0.01 eV.

1. General Features of the Reaction Contour Maps

Reactions (1a) and (1b) were studied in the energy range 2.39 - 8.59 eV. Complete contour maps of both reactions were obtained at relative collision energies of 2.51, 3.49, 4.88, 6.45, and 8.59 eV. Centerline (0° velocity) distributions were obtained for the product pairs at 2.39 and 2.93 eV. Maps or centerlines of nonreactively scattered O_2^+ were also measured at these energies. Figures IV-2 - IV-5 show the sets of reactive contour maps determined at 2.51 and 3.49 eV. The product distributions are symmetric about the center-of-mass (represented by the cross in the center of the figure) to within experimental precision. The contour maps are presented in velocity space with the dot in the zero degree direction representing the velocity of the incident ion. The ellipse drawn about the point marking the incident velocity encloses 80% of the primary beam spread. The arrows represent barycentric angles.

As the relative energy is increased the product distributions begin to lose their symmetry about the $\pm 90^\circ$ line. Figures IV-6 and IV-7 show that at a relative energy of 4.88 eV the O_2H^+ begins to evince forward peaking and the O_2D^+ has more intensity in the backward than in the forward direction. The shift to forward peaking of the O_2H^+ continues at 6.45 eV (Fig. IV-9) and is complete at 8.59 eV (Fig. IV-11). The O_2D^+

XBL 712-274

Fig. IV-2. A specific intensity contour map of scattered O_2D^+ from the $O_2^+(HD,H)O_2D^+$ reaction at 2.51 eV relative energy. Signal found outside the $Q = -2$ eV circle is due to apparatus resolution and beam spread. The large cross in the center indicates the position of the center-of-mass velocity.

XBL 712-273

Fig. IV-3. A contour map of scattered O_2H^+ from the $\text{O}_2^+(\text{HD,D})\text{O}_2\text{H}^+$ reaction at 2.54 eV. Because of overlap between masses 32 (O_2^+) and 33 (O_2H^+) product intensity could not be measured in front of the center-of-mass.

XBL 712-289

Fig. IV-4. A contour map of O_2D^+ specific intensity at a relative energy of 3.49 eV.

XBL 712-287

Fig. IV-5. A contour map of O_2H^+ specific intensity at a relative energy of 3.49 eV.

XBL 712-282

Fig. IV-6. A contour map of O_2D^+ specific intensity at a relative energy of 4.88 eV. The $Q = -4.4 \text{ eV}$ circle is drawn through the side peaks. The isotropy of the distribution begins to disappear at this energy.

XBL 712-281

Fig. IV-7. A specific intensity contour map of scattered O_2H^+ at a relative energy of 4.88 eV. Forward peaking is evident at this energy.

XBL 712-279

Fig. IV-8. A specific intensity contour map of O_2D^+ at a relative collision energy of 6.45 eV.

XBL 712-280

Fig. IV-9. A specific intensity contour map of O_2H^+ at a relative energy of 6.45 eV.

XBL 712-283

Fig. IV-10. A contour map of the specific intensity of O_2D^+ at a relative energy of 8.59 eV. Note the low intensity near the spectator stripping velocity of O_2D^+ , which is marked by a cross.

XBL 712-291

Fig. IV-11. A contour map of O_2H^+ at 8.59 eV. The small cross in the 0° direction indicates the position of the ideal stripping velocity. No scattering is observed beyond 70° .

distributions become increasingly complex as the relative energy increases and the formation of this isotopic species is clearly dynamically different from the formation of O_2H^+ . Figures IV-8 and IV-10 are contour maps of the O_2D^+ distribution at relative energies of 6.45 and 8.59 eV respectively.

2. Low Energy (< 4 eV) Experiments

a. Apparatus Effects. Figures IV-2 - IV-5 are contour maps of the specific intensity of the products of Reactions (1a) and (1b) at relative collision energies of 2.5 and 3.5 eV. These relative energies correspond to laboratory energies of the incident O_2^+ ion of 29.5 and 40.7 eV respectively. Below laboratory energies of about 50 eV the velocity and angular widths of the primary ion beam, represented by the 20% beam profile drawn about the nominal primary beam velocity on each contour map, are significant compared with the size of the product ion scattering distributions. This is evident in Figs. IV-2 - IV-5. Compounding this spread at low energies, are diminished primary ion currents, which, since the scattered signal is proportional to the primary beam intensity, reduce the product ion signal to noise ratio to 3 to 1 for the lowest intensity contours. There is also the additional problem of the overlap between masses 32(O_2^+) and 33(O_2H^+) of about 2%. This overlap factor was determined by scattering O_2^+ from Hc and measuring the O_2^+ signal at quadrupole settings corresponding to peak transmissions of masses 32 and 33. The combination of these factors accounts for the discontinuities in the O_2H^+ contours (Figs. IV-2 and IV-4) in the forward scattering regions.

To correct for the mass overlap, 2% of the net O_2^+ signal at each experimental point is subtracted from the net O_2H^+ signal:

$$N_{O_2H^+} = S_{O_2H^+} - B_{O_2H^+} - 0.02(S_{O_2^+} - B_{O_2^+}) \quad (IV-2)$$

$N_{O_2H^+}$ is the real net O_2H^+ signal, S the gross number of counts and B the number of background counts. At velocities near the primary beam, the scattered O_2^+ signal is so large that it floods the detector to such an extent that the net O_2^+ signal and hence the net O_2H^+ signal cannot be determined.

There is also another reason that nonreactively scattered signal cannot be measured in the neighborhood of the primary beam. For velocity elements falling within the extent of the primary beam spread two processes contribute to the measured signal; scattering of primary ions from other regions into the detected velocity element and scattering out of particles from this velocity element. If more particles are scattered out than in, the number of background counts will be larger than the gross number of counts. This phenomenon is often encountered in our nonreactive scattering measurements even at points in velocity space where the gross signal is not sufficient to flood the detector.

The importance of these apparatus effects increases markedly with decreasing primary beam energy and consequently prevents measurement of O_2H^+ scattering at energies below the lowest energy experiment reported here.

As stated in Chapter III, the $Q = -2$ eV circle represents the loci of center-of-mass product ion velocities outside of which measured scattering intensity is due to a combination of several effects; vibrationally

excited primary O_2^+ ions, velocity-angle spread of the primary beam, thermal motion of the neutral scattering gas, and detector resolution. The broadening due to beam spread, neutral gas motion and detector resolution can be removed or at least significantly reduced by deconvolution. To date, one dimensional iterative and Fourier deconvolution techniques have been applied to ion-molecule product distributions to compensate for one or more of the above effects, and the results are promising.^{22,23} This procedure is described in the appendix. A three-dimensional deconvolution method employing a set of analytical basis functions is currently being developed in this laboratory²⁴ to remove product distribution angular and velocity broadening caused by primary beam spread, neutral gas motion, and apparatus resolution.

Since these procedures have not yet been applied to the experimental data presented here, the product ion distributions of Reactions (1a), (1b) and (3) were measured simultaneously at each energy so that the maps could be directly compared. This was possible at all reactant energies except for the lowest energy set at 29.5 eV laboratory energy, where it was not possible to maintain a primary beam of sufficient intensity for the seven or eight hours necessary to determine three contour maps. Thus, at this energy, only the distributions of O_2H^+ and O_2^+ were measured simultaneously; the O_2D^+ distribution was measured in a separate experiment. The severity of apparatus effects at an energy as low as 29.5 eV render the O_2H^+ map in Fig. IV-3 of only qualitative import.

b. Energy Partitioning. The qualitative features of the O_2D^+ and O_2H^+ distributions at relative energies of 2.5 and 3.5 eV are similar to those

found for the reaction with homonuclear hydrogen below 4 eV. The product specific intensity peaks at or near the center-of-mass velocity and the contours are isotropic about this point in velocity space. This evidence reinforces the hypothesis that the reaction proceeds through the formation of an intermediate complex which lives for several rotations before decaying. Peaking of the specific product intensity near the center-of-mass velocity indicates that the complex has small angular momentum and that the O_2D^+ and O_2H^+ are formed with large internal excitation. Products found exactly at the center-of-mass velocity are formed with zero relative velocity. The apparatus resolution does not permit precise determination of the velocity peak (s), so the partitioning of total reaction energy between internal and translational modes cannot be accurately determined for distributions as broad as those on these low energy maps. The breadth of the velocity distributions can be seen more clearly in Fig. IV-12 which shows the 0° (laboratory) velocity spectra of O_2D^+ and O_2H^+ produced at collision energies of 2.5 and 3.5 eV.

At both 2.5 and 3.5 eV the average Q value, the amount of initial relative kinetic energy transformed into product excitation and heat of reaction, is larger for Reaction (1a) than for (1b). The probability density for Q can be written as:⁹

$$P(Q) = [I(\theta, u)u^3]/[2E'_s I(\theta)] \quad (IV-3)$$

where E'_s is the relative translational energy of the products, u is the product velocity in the center-of-mass system, $I(\theta, u)$ is the specific intensity at u and θ , and $I(\theta)$ is the differential cross-section at the

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Fig. IV-12. Centerline velocity distributions of O_2D^+ and O_2H^+ from the reaction of O_2^+ with ^2HD at collision energies of 2.5 and 3.5 eV.

barycentric angle θ . The average Q value of a scattered distribution is thus:

$$\langle Q \rangle = \frac{\sum Q P(Q)}{\sum P(Q)} \quad (\text{IV-4})$$

The product distributions are nearly isotropic; thus, for computational simplicity, the contours are taken to be circular about the center-of-mass. Unique values of u , Q , and E_s' are then associated with each contour and $I(\theta)$ is independent of angle. Thus, Eq. IV-4 can be simplified to:

$$\langle Q \rangle = \frac{\sum_i \left[I_i Q_i (Q_i + E_s)^{\frac{1}{2}} \Delta Q \right]}{\sum_i \left[I_i (Q_i + E_s)^{\frac{1}{2}} \Delta Q \right]} \quad (\text{IV-5})$$

where I_i and Q_i are the intensity and Q values of the i^{th} contour and E_s is the initial relative energy. The Q_i 's are determined by averaging over all points of the i^{th} contour.

Table IV-1 lists the average Q values and the percent of the total available energy (initial relative energy minus the heat of reaction) which appears as internal excitation of the O_2D^+ or O_2H^+ product for the reaction sets at 2.5, 3.5 and 4.9 eV. While this calculation is admittedly crude, particularly for the O_2D^+ and O_2H^+ product distributions at 4.9 eV shown in Figs. IV-6 and IV-7, where the isotropy has broken down, the qualitative results are most revealing. At all energies the O_2H^+ has a considerably larger internal energy than the O_2D^+ . The average Q values calculated for the 2.5 eV experiments, which are both greater than -2 eV, the maximum physically allowed limit for ground vibrational state reactant ions, should caution us not to overinterpret the results. These lowest

TABLE IV-1

Product Energy Partitioning

Experiment Number	Product	E_s^o (eV)	$\langle Q \rangle$ (eV)	$\langle U' \rangle$ (eV)	$\langle E_s' \rangle$ (eV)	% Total Energy as Internal	$E_s' \text{ (calc)}$ ($\alpha = .44$) (eV)
705	O_2D^+	2.51	-1.66	0.04	.85	4.5%	.22
707	O_2H^+	2.54	-1.82	0.13	.72	15%	.21
702	O_2D^+	3.49	-2.60	0.98	.89	52%	.60
703	O_2H^+	3.49	-3.21	1.52	.28	84%	.57
689	O_2D^+	4.88	-3.35	1.73	1.53	53%	1.12
690	O_2H^+	4.88	-4.26	2.57	0.62	81%	1.09

energy Q values are barely allowed when the average vibrational energy of the primary ions are included in the total available energy, yielding maximum Q limits of -1.69 for O_2H^+ and -1.62 for O_2D^+ . All the calculated Q values are upper limits since the product distributions used to compute these numbers are greatly broadened due to the previously discussed apparatus effects.

The validity of the qualitative conclusion that O_2H^+ is more highly excited than O_2D^+ can be demonstrated by considering the kinematics of the separation of the product pairs. From conservation of momentum the velocity of the product ion with respect to the center-of-mass is:

$$u = g' \left(m_n / (m_i + m_n) \right) \quad (IV-6)$$

where m_i and m_n are the product ion and neutral masses respectively, and g' , the final relative velocity, is equal to $(2E'_0/\mu)^{1/2}$. The measured laboratory energy of the product ion is then

$$E'_{LAB} = \frac{1}{2} m_i (v_{CM} + u)^2 \quad (IV-7)$$

Since $u \ll v_{CM}$ this can be rewritten as:

$$E'_{LAB} \approx \frac{1}{2} m_i v_{CM}^2 \left(1 + \frac{2v_{CM} \cdot u}{v_{CM}^2} \right) \quad (IV-8)$$

$$\text{or} \quad E'_{LAB} \approx \frac{1}{2} m_i v_{CM}^2 \left(1 + \frac{2u \cos \alpha}{v_{CM}} \right) \quad (IV-9)$$

By inserting Eq. IV-6 for u and rearranging we get:

$$E'_{LAB} \approx \frac{1}{2} m_i v_{CM}^2 + v_{CM} \cos \alpha (2E'_0 \mu)^{1/2} \quad (IV-10a)$$

Since at each energy the primary beam parameters are identical for the two isotopic experiments, the distribution of the center-of-mass velocities is the same for both the O_2D^+-H and O_2H^+-D product pairs. Thus, no generality is lost by taking v_{CM} at its nominal value. Equation IV-10a can therefore be written simply:

$$E'_{LAB} - A = B(\mu E'_s)^{\frac{1}{2}} \quad (IV-10b)$$

where A and B are constants. B is the same for both product pairs but A, which is the laboratory energy of a product ion traveling at the center-of-mass velocity, is proportional to the product ion mass. Since the reduced mass of the O_2D^+-H pair is about half that of the O_2H^+-D products, and if both the O_2H^+ and O_2D^+ have the same E'_s distribution, the right hand side of Eq. IV-10b tells us that the barycentric O_2H^+ energy distribution will be $\sqrt{2}$ times broader than the O_2D^+ spectrum. Since the apparatus effects will broaden both distributions in a like manner, the wider spread of the O_2D^+ spectrum cannot be dismissed as the consequence of detector resolution. For identical E'_s functions, Eq. IV-6 similarly predicts that the O_2H^+ velocity distribution will be wider than that of O_2D^+ by $\sqrt{2}$. An examination of Figs. IV-4 - IV-7 indicates that in fact the opposite is true.

From the definition of Q and conservation of energy:

$$Q = U - \Delta H - U' \quad (IV-11)$$

Since the Q values are all upper limits, the product internal energies, U' , and fractions of the total energy appearing as product excitation

listed in Table IV-1 are then lower limits to their actual values. Excluding the 2.5 eV experiments, it is clear that most of the available energy of Reaction (1a) and almost all of the available energy of Reaction (1b) winds up as internal excitation of the ionic product.

The large internal excitation of the products correlates with the qualitative features of the contour maps. As mentioned in Chapter III, the dissociation limit of O_2D^+ is about 2.6 eV; thus, O_2H^+ or O_2D^+ formed with greater than this internal energy will be unstable and will not live long enough to reach the detector. This explains the deviations from centroid peaking evident in Figs. IV-6 and IV-7. The minimum average excitation of O_2H^+ at 4.9 eV listed in Table IV-1 is 2.57 eV, essentially the dissociation limit for this ion.

The specific intensity peaks in the forward direction indicate that another mechanism has become significant for O_2H^+ formation at this energy. It must be emphasized that this forward peaking is not solely from this new direct mechanism, but it does indicate that this new process preferentially scatters the ionic product in the 0° direction.

Similarly, Fig. IV-6 shows that the specific intensity of O_2D^+ produced from 4.9 eV collisions is no longer isotropically distributed about the center-of-mass velocity. Although the minimum average excitation of the O_2D^+ is only 1.73 eV, a substantial fraction of the ions are probably excited beyond the dissociation limit. It is also apparent that some of the O_2D^+ ions at this energy are formed by a mechanism which preferentially backscatters products, but the diffuseness of the distribution makes a more specific definition of this process impossible.

Klotz²⁵ has pointed out that the relative product translational energy is equal to the translational energy in the reaction coordinate plus the energy barrier between the complex and products. This barrier is, for Reactions (1a) and (1b), just the energy necessary to surmount the angular momentum barrier in the product channel. By measuring the kinetic energies of fragments formed by electron bombardment of a series of molecules, having from four to nine atoms, Haney and Franklin²⁶ found that for large excess energy that the translational energy in the reaction coordinate is related to the available energy by:

$$E_t = E^*/\alpha N \quad (\text{IV-12})$$

where E^* is the available or excess energy, N is the number of oscillators of the molecule ($N = 6$ for HOOH^+) and α is an empirical parameter ($\alpha = 1$ corresponds to the high energy limit for a highly constrained complex). More recently, Franklin and co-workers²⁷ applied the quasiequilibrium theory of unimolecular decomposition and the direct count of states method (see Chapter V) to the data of Haney and Franklin and concluded that a "loose" ($N-3$ effective oscillators) transition state is a more appropriate model for the dissociation process.

The Franklin treatment ignores the effective potential barrier, certainly a reasonable procedure, since ions formed by electron bombardment of neutrals at room temperature would be expected to have small angular momentum. As we shall see in the next section, the effective potential barriers in the exit channels of Reactions (1a) and (1b) are negligible compared to the total available energy. The classical treatment, as can be seen from Table IV-1, with $\alpha = .44$ underestimates the

translational energy of O_2D^+ by about 30% and overestimates the O_2H^+ kinetic energy by about a factor of 2. A further analysis of the discrepancy between the O_2H^+ and O_2D^+ excitation energies must await a full deconvolution of the experimental data.

c. Angular Momentum Effects. The total angular momentum of the complex is:

$$\underline{J} = \underline{L} + \underline{j}_O + \underline{j}_H \quad (IV-13)$$

where $\underline{L}$ is the orbital angular momentum of the reactants and $\underline{j}_O$ and $\underline{j}_H$ are the internal angular momenta of the O_2^+ and HD respectively. The most probable value of $\underline{j}_O$ is about $9\hbar$,²⁸ and that for $\underline{j}_H$ is $2\hbar$. Thus the magnitude of the total angular momentum is:

$$J^2 = L^2 + j_O^2 + j_H^2 + 2\underline{L} \cdot \underline{j}_O + 2\underline{L} \cdot \underline{j}_H + 2\underline{j}_O \cdot \underline{j}_H \quad (IV-14)$$

Averaging over all orientations of the $\underline{L}$ and $\underline{j}$ vectors gives:

$$J^2 = L^2 + j_O^2 + j_H^2 \quad (IV-15a)$$

$$J^2 = L^2 + 85\hbar^2 \quad (IV-15b)$$

The initial orbital angular momentum, $\underline{L}$, is equal to μgb , where μ is the reduced mass of the reactants, g is their relative velocity, and b is the impact parameter. To get the average orbital angular momentum at a particular relative collision energy, $\underline{L}$ must be averaged over all impact parameters less than $b_{\max}$:

$$\langle L \rangle = \left(2\pi \int_0^{b_{\max}} \mu g b^2 db \right) / \left(2\pi \int_0^{b_{\max}} b db \right) = \frac{2}{3} \mu g b_{\max} \quad (\text{IV-16})$$

Since $\sigma_{\text{total}} = \pi b_{\max}^2$,

$$\langle L \rangle = \frac{2}{3} \mu g \sqrt{\sigma/\pi} \quad (\text{IV-17})$$

For O_2^+ -HD Eq. IV-17 can be more conveniently written as:

$$\langle L \rangle = 13.87 (E_s^0)^{\frac{1}{2}} \hbar \quad (\text{IV-18})$$

where E_s^0 is the initial relative energy in (eV) and σ is the total cross-section for complex formation in ($\text{\AA}^2$).

Conservation of angular momentum requires that the sum of the internal and orbital angular momenta of the products equals J . The final average orbital angular momentum, L' , can be calculated from Eq. IV-17 by assuming the maximum product impact parameter is equal to $b_{\max}$. This assumption is made more for convenience than from any theoretical justification. However, the maximum incident impact parameter which leads to complex formation is about 1 $\text{\AA}$, which is approximately equal to the perpendicular distance between the H or D atom and the O-O axis. Since, as Mahan et al.²⁸ have shown, the departing hydrogen atom most likely separates from the molecule-ion parallel to the O-O axis, the maximum product impact parameter is also probably not very different than 1 $\text{\AA}$.

Using this value of b' and the maximum final relative kinetic energies listed in Table IV-1, we find, analogous to Eq. IV-18:

$$\langle L' \rangle = 8.25(E'_s)^{\frac{1}{2}} \hbar \quad \text{for } O_2D^+-H \quad (IV-19a)$$

$$\langle L' \rangle = 11.50(E'_s)^{\frac{1}{2}} \hbar \quad \text{for } O_2H^+-D \quad (IV-19b)$$

The magnitude of the internal angular momenta of the products can then be determined from J and L' :

$$J^2 = L'^2 + j'^2 + 2\vec{L}' \cdot \vec{j}' \quad (IV-20a)$$

which upon orientation averaging becomes:

$$J^2 = L'^2 + j'^2 \quad (IV-20b)$$

Solving for j' yields:

$$j' = (J^2 - L'^2)^{\frac{1}{2}} \quad (IV-21)$$

If we treat the separation of the products as a two-body problem with an attractive potential energy $\phi(r)$, then rotation of the transition state creates a maximum in the effective potential V_{eff} for separation of the products:

$$V_{\text{eff}} = L'^2 \hbar^2 / (2\mu r^2) + \phi(r) \quad (IV-22)$$

where ϕ is the ion-induced dipole potential $-C_4/r^4$ and r is the separation of the products. This two-body approximation assumes that the maximum in the effective potential comes at a value of r sufficiently large that the internal motions of the fragments are essentially decoupled from their motion along the reaction coordinate.

The maximum which occurs in the effective potential energy curve can be viewed as a barrier that the transition states must cross in order to become products. In terms of the present discussion it can be pictured

as an ejection potential which supplies part of the final relative kinetic energy to products which have crossed it. The height of this barrier with respect to products is:

$$V_B = L^4/C_4(4\mu)^2 \quad (\text{IV-23})$$

To get $\langle V_B \rangle$ it is necessary to average Eq. IV-23 over b :

$$\begin{aligned} \langle V_B \rangle &= \left(\mu^4 g^4 / C_4 (4\mu)^2 \right) \left[\left(2\pi \int_0^{b_{\max}} b^5 db \right) / \left(2\pi \int_0^{b_{\max}} b db \right) \right] \\ &= (\mu^2 g^4 b_{\max}^4) / (12C_4) \end{aligned} \quad (\text{IV-24})$$

This expression can be written in terms of the final relative energy and the cross-section for formation of the intermediate:

$$\langle V_B \rangle = (E_s'^2 \sigma^2) / (12\pi^2 C_4) \quad (\text{IV-25})$$

The average height of the barrier to formation of the complex from reactants can be found from Eq. IV-25 by substituting the initial relative kinetic energy, E_s^0 , for E_s' and by using the proper potential constant for HD.

Table IV-2 lists the energy barriers and angular momenta in the reactant and product channels along with the relevant parameters, not listed elsewhere in this chapter, used to calculate these quantities.

In accord with the qualitative observations made from the contour maps, most of the angular momentum of the complex goes into internal angular momentum of the molecule ions, about three times the amount which appears as L' . This tells us that the critical configuration of the

TABLE IV-2

Angular Momentum Partitioning and Rotational Barriers

Product	E_s^o (eV)	σ_{TOTAL} ($\text{\AA}^2$)	$\langle V_B \rangle$ (eV)	$\langle L \rangle$ ($\hbar$)	$\langle J \rangle$ ($\hbar$)	$\langle V_B' \rangle$ (eV)	$\langle L' \rangle$ ($\hbar$)	$\langle J' \rangle$ ($\hbar$)
O_2D^+	2.51	3.62	0.122	42	43	0.016	14	41
O_2H^+	2.54					0.012	19	39
O_2D^+	3.49	3.49	0.217	48	49	0.017	15	47
O_2H^+						0.002	11	48
O_2D^+	4.88	3.27	0.372	55	56	0.043	18	53
O_2H^+						0.007	16	53

$$C_4(HD) = 5.78 \text{ eV} - \text{\AA}^4$$

$$C_4(D) = C_4(H) = 4.87 \text{ eV} - \text{\AA}^4$$

complex for dissociation into O_2D^+ and O_2H^+ is very "loose," in accord with the finding of Franklin and co-workers. This point will be discussed further in Chapter V in connection with the choice of normal mode frequencies for the O_2D^+ and O_2H^+ critical configurations.

Mahan et al.²⁸ have discussed the distribution of the total angular momentum between the principal axes of the $D_2O_2^+$ intermediate and concluded that most of the angular momentum resides in the low frequency tumbling rotations about the perpendicular axes rather than in the higher frequency spinning rotation about the unique axis. This explanation is also consistent with the large rotational excitation of the product molecule-ions, since an H or D atom separating from a rapidly tumbling HDO_2^+ (the OOD angle in the equilibrium hydrogen peroxide structure is 105°) would move away in a direction roughly parallel to the O-O bond axis and thereby produce a torque capable of rotationally exciting the product ion. On the other hand, an H or D atom leaving a rapidly spinning hydrogen peroxide ion would separate in a direction more perpendicular to the O-O axis. Rotational excitation of the remaining $H(D)O_2^+$ would be considerably more difficult in this case.

The assumption of statistical equilibrium of the complex, corresponding to a rotational temperature T_r leads to an expression for the probability distribution of quantum numbers, K , for rotation about the unique axis of a prolate top:²⁹

$$P(K) = \exp(-\frac{1}{2}K^2/K_a^2) \quad (IV-26)$$

where

$$K_a = |kT_r I_r / \hbar^2|^{\frac{1}{2}}$$

and

$$I_r = I_B I_A / (I_B - I_A)$$

The total rotational energy of a prolate complex in the transition state is:

$$E_r = (h^2/2) \left[(J^2 - K^2)/I_B - K^2/I_A \right] \quad (\text{IV-28})$$

Assuming that $K^2 \ll J^2$, E_r can be calculated from Eq. IV-28 and T_r can be inserted into Eq. IV-27. The rotation constant, K_a , the moments of inertia of HOOD^+ , and the average quantum number for rotation about the unique axis are listed in Table IV-3 for the experiments at 2.5, 3.5 and 4.9 eV. For all three experiments only 20% of the total angular momentum is concentrated in the unique axis. Those few complexes with large K probably dissociate to products other than O_2H^+ and O_2D^+ since their inability to convert this angular momentum to rotation of the product ion would result in the erection of a high effective potential energy barrier. The effective barrier is much lower for products of more equal mass since the barrier height is inversely proportional to the square of the reduced mass. Further evidence that O_2D^+ and O_2H^+ are formed principally from transition state structures where the angular momentum is concentrated in the tumbling rotations are the negligible exit barriers and consequent independence of the product internal rotation quantum numbers upon reduced mass of the separating partners.

It has been shown²⁹ that the shape of the angular distribution correlates with the mean tilt of $\underline{J}$ with respect to the direction of the final velocity vector. The degree of tilt is represented by the parameter

TABLE IV-3

HOOD⁺ Rotational Constants

E_s^o	E_R	K_a	$\langle K \rangle$	X
2.525	.235	13.0	10	1.6 O ₂ D ⁺ 2.2 O ₂ H ⁺
3.49	.297	14.6	11	1.5 O ₂ D ⁺ 1.1 O ₂ H ⁺
4.48	.379	16.5	13	1.6 O ₂ D ⁺ 1.5 O ₂ H ⁺

$$I_A = 4.35 \times 10^{-40} \text{ g cm}^2 \text{ }^a$$

$$I_B = I_C = 34 \times 10^{-40} \text{ g cm}^2 \text{ }^a$$

$$I_r = 5 \times 10^{-40} \text{ g cm}^2$$

^a J. T. Massey, C. I. Beard and C. K. Jen, J. Mol. Spec.
5, 405 (1960).

$X = L_m/K_a$, where L_m is the maximum product orbital angular momentum. For a prolate top complex with large X the distribution peaks at 0° and 180° . As X decreases the distribution approaches isotropy. The values of X for the experiments discussed in this chapter are listed in Table IV-3. They are sufficiently small that marked forward-backward peaking is unexpected and hence in accord with the nearly isotropic distributions observed in the low energy contour maps.

Further evidence for complex formation is the larger intensity of O_2D^+ than O_2H^+ in the low energy region. This is predicted by RRKM theory on the basis of the lower zero point energy and larger density of states of O_2D^+ . Unimolecular decomposition phenomena will be discussed in detail in Chapter V.

3. Energy Dependence of Total Cross-Sections

The cross-sections and isotope ratios, $(\sigma_{O_2D^+}/\sigma_{O_2H^+})$, for formation of O_2D^+ and O_2H^+ at the five energies at which these quantities were determined are listed in Table IV-4. The cross-sections, except for the O_2H^+ value at 2.5 eV, are precise to within $\pm 30\%$ but the isotope ratios are good to within $\pm 10\%$. Absolute values of the cross-sections were obtained by the following procedure. The cross-section for the reaction $N_2^+(D_2,D)N_2D^+$ at 9.3 eV is measured and normalized to the total cross-section at this energy determined by Hyatt and Lacmann.³⁰ The conversion factor thus determined is used to convert our integrated total to cross-sections to ($\text{\AA}^2$). Since the experiments with O_2^+ were done over a period of several months several such normalizations were performed to account for changing apparatus effects.

TABLE IV-4

Total-Cross Sections and Isotope Effects

Experiment Numbers	Relative Energy (eV)	$\sigma_T(O_2H^+)$ ($\text{\AA}^2$)	$\sigma_T(O_2D^+)$ ($\text{\AA}^2$)	σ_{TOTAL} ($\text{\AA}^2$)	$\frac{\sigma_T(O_2D^+)}{\sigma_T(O_2H^+)}$
705,707	2.52	1.44 (?)	2.48	3.92 (?)	1.72 (?)
702,703	3.49	0.484	2.38	2.86	4.92
689,690	4.88	0.448	2.25	2.70	5.01
686,687	6.45	0.529	2.05	2.58	3.87
669,670	8.59	0.114	0.099	0.21	0.87

The cross-sections for O_2D^+ , O_2H^+ and their sum are plotted vs. relative collision energy in Fig. IV-13. Several interesting observations can be made. The cross-sections decrease extremely slowly with increasing energy in the 2.5 - 6.5 eV range; the relationship $\sigma \propto E_s^{-1/6}$ describes the functionality of the O_2D^+ and the total cross-sections. The flatness of the curves in this energy range is surprising in view of the dynamic changes of the reaction mechanisms evident from the contour maps. The only obvious explanation for this behavior is that while the contribution to the cross-sections from the complex mechanism decreases with energy, the importance of the direct higher energy processes is increasing. Another possible contribution to the constancy of the cross-sections is that even though the cross-section for formation of the intermediate decreases with energy, the dissociation pattern of the complex is such that the O_2D^+ and O_2H^+ channels become more favorable at higher energies.

Between 6.5 and 8.6 eV the O_2D^+ and O_2H^+ cross-sections decrease by factors of 20 and 4.6 respectively. The O_2H^+ map at 8.6 eV (Fig. IV-11) shows that this product is formed by a process akin to spectator stripping, the cross-section for which has been shown to have a steep energy dependence.³⁰ The mechanisms for O_2D^+ formation at 8.6 eV are considerably more complicated, but it is reasonable to assume that a large fraction of the O_2D^+ ions are formed with an internal energy higher than the 2.6 eV required to break the O_2^+-D bond. For example, O_2D^+ ions formed by pure spectator stripping at relative collision energies above 6.9 eV are unstable with respect to dissociation to O_2^+ and D.

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Fig. IV-13. Energy dependence of the total cross-sections of the $O_2^+(HD,H)O_2D^+$ and $O_2^+(HD,D)O_2H^+$ reactions. The $\sigma_{O_2D^+}/\sigma_{O_2H^+}$ isotope ratio is also shown.

4. High Energy Experiments

As noted in Section (2) the symmetry of the scattered O_2H^+ and O_2D^+ distributions about the line connecting $\pm 90^\circ$ begins to disappear at energies above 4.5 eV. The angular distributions of the two ions, as shown in Figs. IV-8 - IV-11 are of drastically different shapes. The differential cross-section curves for scattered O_2H^+ and O_2D^+ at collision energies of 4.88, 6.45 and 8.59 eV are displayed in Fig. IV-14. In accord with the contour map representations, O_2H^+ is scattered mostly into the small angle regions; the degree of forward peaking increases with relative collision energy. At 8.89 eV O_2H^+ is found exclusively in the small angle region. At this highest energy no O_2H^+ was observed beyond 70° .

The O_2D^+ $I(\theta)$ curves have the same shape at all three energies; the curves monotonically increase by a factor of about five between 0° and 90° and then fall to half their peak values as θ goes to 180° . Although the differential cross-section plots conceal the complexity of the O_2D^+ velocity-angle spectra, they indicate that O_2D^+ is preferentially back-scattered at energies above 4.9 eV. The characteristics of the O_2D^+ angular distributions, which differentiate them from previously investigated ion-molecule reactions, are the peaks at barycentric angles other than 0° and 180° , and the diffuseness of the angular distributions.

From the contour maps and differential cross-section curves it is clear that at energies above 4.9 eV stable O_2H^+ and O_2D^+ are formed by mechanisms which are dynamically different. Direct application of the kinematic models of Light and Chan¹⁷ and George and Suplinskas^{18b} to the O_2^+-HD reaction would be inappropriate since neither of these models considers the effect of a deep well in the potential energy surface. However,

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Fig. IV-14. Energy dependence of the center-of-mass differential cross-sections of O_2D^+ and O_2H^+ .

the calculations of these authors point out the degree to which the geometric anisotropy of HD affects reaction probabilities and product trajectories.

The effect of isotopic substitution on reactive collision can also be seen by comparing the maps of the $O_2^+(HD, \frac{H}{D})O_2D^+$ reactions with the $O_2^+(D_2, D)O_2D^+$ map at the same relative collision energy. Figure III-5 shows the velocity angle distribution of the monoisotopic reaction at 8.34 eV relative energy. Comparison of this map with those of the mixed isotope reactions at approximately the same energy (Figs. IV-10 and IV-11) shows that although the $O_2^+(D_2, D)O_2D^+$ map has features in common with both the O_2D^+ and O_2H^+ distributions from O_2^+HD , such as forward peaking (as for O_2H^+) and scattered product at all angles (as for O_2D^+), the homonuclear reaction map is by no means a "weighted sum" of the mixed isotope maps. The major qualitative difference between the $O_2^+-D_2$ map and the mixed isotope distributions is the absence of substantial backward scattering in the $O_2^+(D_2, D)O_2D^+$ reaction.

Figure IV-15 is a specific intensity contour map of the reaction $O_2^+(H_2, H)O_2H^+$ at a relative collision energy of 5.89 eV. This map can be contrasted with Figs. IV-8 and IV-9 which show the scattered O_2D^+ and O_2H^+ distributions from Reactions (1a) and (1b). The O_2H^+ specific intensity from the homonuclear hydrogen reaction lies mostly in the forward hemisphere, but sizeable scattered signal is found at all angles. In the mixed isotope reaction O_2H^+ is forward peaked and O_2D^+ is mostly backscattered. As opposed to the pure isotope reaction, most of the total intensity (sum of O_2D^+ and O_2H^+) is in the backward hemisphere.

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Fig. IV-15. A contour map of the specific intensity of O_2H^+ formed in the reaction $O_2^+(H_2, H)O_2H^+$ at a relative energy of 5.89 eV.

It should be noted at this point that the angular distributions of nonreactively scattered O_2^+ corroborate the observation that most scattered product comes from small impact parameter collisions. Figures IV-16 and IV-17 are contour maps of O_2^+ nonreactively scattered by HD at collision energies of 6.45 and 8.59 eV respectively. The absence of substantial backscattering in both figures implies that small impact collisions lead almost exclusively to reaction or very inelastic nonreactive scattering. A similar conclusion was made for the $N_2^+(D_2, D_2)N_2^+$ system⁹ where charge transfer and dissociative charge transfer are important channels. The large difference between the ionization potentials of O_2 and HD (~ 3.3 eV) and the substantial endothermicity of dissociative charge transfer (~ 6 eV) make these processes less important in the O_2^+ -HD system than in the N_2^+ - D_2 case. The larger amount of backscattered O_2^+ at 8.59 eV than at 6.45 eV is consistent with the much smaller O_2D^+ cross-section at the higher energy.

The difference between the high energy mechanisms by which O_2H^+ and O_2D^+ are formed from O_2^+ -HD can be attributed to a complex combination of geometric and energetic factors. Since these effects favor formation of O_2H^+ over O_2D^+ ,^{9,17,18b} while complex decay preferentially leads to more O_2D^+ than O_2H^+ , the fact that $(\sigma_{O_2D^+}/\sigma_{O_2H^+}) > 1$ at collision energies up to 6.45 eV implies that formation of the $HOOD^+$ intermediate is important even at this relative energy. Complexes formed with O_2^+ and HD nearly parallel to each other and perpendicular to the incident relative velocity vector will, because the center-of-mass of the molecule is closer to the D-atom than to the H-atom, tend to rotate with the H end moving in the initial projectile direction. If the complex dissociates in less than

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Fig. IV-16. A contour map of O_2^+ nonreactively scattered by HD at a relative energy of 6.45 eV.

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Fig. IV-17. A contour map of O_2^+ nonreactively scattered by HD at a relative collision energy of 8.59 eV. The inelastic intensity maximum falls very near to the velocity of O_2D^+ formed by spectator stripping, which is indicated by a cross.

one rotation, O_2H^+ will be primarily scattered in the forward direction and O_2D^+ will appear at large angles. Since vibrational equilibrium occurs on a time scale shorter than or comparable with one rotational period, the intensity of the deuterated product from unimolecular decay will exceed that of O_2H^+ .

As Light and Chan¹⁷ have shown, the separation of the geometric center from the center-of-mass of HD leads to a larger probability that the incident ion will collide with the H end of the molecule. This effect is, of course, most important at energies where complex formation is not the dominant mechanism. Therefore, large impact parameter or grazing collisions are more likely to result in abstraction of a hydrogen atom than a deuterium atom. As Fig. IV-11 shows, O_2H^+ is almost entirely formed by grazing collisions at a collision energy of 8.59 eV.

As noted earlier, O_2D^+ formed by pure spectator stripping at relative collision energies above 6.9 eV is unstable with respect to dissociation to O_2^+ and D. On the other hand, O_2H^+ produced by this mechanism does not have sufficient internal energy to break the O-H bond at collision energies below 13.8 eV. Further evidence for the dissociation of O_2D^+ formed by spectator stripping at energies above 6.9 eV is found on Fig. IV-17. The small angle inelastic peak, enclosed by the 10 K contour line, is located close to the O_2D^+ spectator stripping velocity. This velocity is marked by the small cross. As discussed in Chapter III this intensity maximum can arise in part from dissociation of unstable O_2D^+ .

The insufficiency of this explanation to account for the absence of forward peaking of O_2D^+ is evident in Fig. IV-8, which shows that even at a collision energy below 6.9 eV, O_2D^+ does not display small angle

peaking. The prevalence of backscattering in Reaction (1a) is most likely related to the previously mentioned separation of the center-of-mass from the geometric center of HD. Since the impact parameter is defined with respect to the centers-of-mass of the reactant particles, nearly head on collisions will result in a higher probability of the incident ion reacting with the deuterium atom than with the hydrogen atom. This type of collision is more intimate than a grazing collision and, thus, can more easily achieve product stabilization.

There is another explanation for the absence of backscattered O_2H^+ . Referring to Fig. IV-18, consider the following head-on collision mechanism with the HD internuclear axis parallel to the incident relative velocity vector. In the first step the O_2^+ ion (m_3) having laboratory velocity v_3 collides impulsively with one atom of the diatomic (m_1) which is at rest. The resulting laboratory velocities of the three particles are

$$v_3' = (m_3 - m_1)/(m_3 + m_1)v_3 \quad (IV-29a)$$

$$v_1' = 2m_3/(m_1 + m_3)v_3 \quad (IV-29b)$$

$$v_2' = v_2 = 0 \quad (IV-29c)$$

The struck atom (m_1) then impulsively collides with its partner (m_2) and bounces back. After this second collision the velocities are:

$$v_3'' = v_3' \quad (IV-30a)$$

$$v_1'' = 2\left(\frac{m_1 - m_2}{m_1 + m_2}\right)\left(\frac{m_3}{m_1 + m_3}\right)v_3 \quad (IV-30b)$$

$$v_2'' = \left(\frac{2m_1}{m_1 + m_2}\right)\left(\frac{2m_3}{m_1 + m_3}\right)v_3 \quad (IV-30c)$$

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Fig. IV-18. Schematic representation of the double impulsive collision model. The velocities and in the laboratory frame and are drawn to scale.

The internal energy of the backscattered O_2X^+ ion is then

$$U' = \frac{1}{2} \mu'' g''^2 \quad (IV-31)$$

where

$$\mu'' = \frac{m_1 m_3}{m_1 + m_3} \quad (IV-32a)$$

and

$$g'' = v_3'' - v_1'' = v_3 \left[\frac{m_3 - m_1}{m_1 + m_3} - 2 \left(\frac{m_1 - m_2}{m_1 + m_2} \right) \left(\frac{m_3}{m_1 + m_3} \right) \right] \quad (IV-32b)$$

Using the value of 2.6 eV as the O_2^+ -H and O_2^+ -D dissociation energy and Eqs. IV-31 and IV-32, we find the following upper limits to the initial relative energy, at which product formed by this double impulsive rebound mechanism will be stable:

$$\begin{aligned} O_2^+(HD,H)O_2D^+ &-- 14.85 \text{ eV}, & O_2^+(HD,D)O_2H^+ &-- 4.65 \text{ eV}, \\ O_2^+(D_2,D)O_2D^+ &-- 5.56 \text{ eV}, & O_2^+(H_2,H)O_2H^+ &-- 5.25 \text{ eV}. \end{aligned}$$

These findings are consistent with the persistence of large O_2D^+ signal at 180° from O_2^+ -HD at high relative energies and the lack of substantial backscattering in the other three reactions.

1. Velocity Spectra and Contour Maps

Fifteen pairs of centerline velocity spectra and two pairs of contour maps were determined for Reactions (2a) and (2b) at collision energies between 4.27 and 21.53 eV. As in the O_2D^+ - O_2H^+ experiments, at the same

energy the OD^+ and OH^+ intensities were measured simultaneously so that the apparatus parameters are identical for both the OD^+ and OH^+ distributions. Figures IV-19 - IV-22 show thirteen sets of centerline scans. Several significant observations can be made from these curves. The OD^+ spectra are all very broad and peak near the center-of-mass velocity at each energy. They also display a remarkable degree of symmetry about centroid, but as the collision energy is raised backscattered signal increases relative to 0° barycentric intensity.

The maxima in the OH^+ distributions are always forward of the center-of-mass velocity; the sharpness of the peaking becomes more pronounced with increasing collision energy, but the peak remains close to $v/v_0 = .95$ at all energies. The curves drop off more slowly in the backward than forward direction. This asymmetric behavior increases as the collision energy is raised, showing indications of a shoulder above 12 eV.

Figures IV-23 - IV-26 are specific intensity contour maps of OD^+ and OH^+ formed at relative kinetic energies of 8.55 and 13.30 eV. These maps show that at high energy OH^+ is predominantly forward scattered and OD^+ is mostly backscattered. The product specific intensities, however, are broadly distributed over velocity-angle space.

The dissociation energies of OH and OD are 4.35 and 4.4 eV respectively and are 5.06 and 5.11 for OH^+ and OD^+ .¹⁶ Therefore, in the 8.55 eV experiments, formation of OD^+ or OH^+ ions with center-of-mass velocities inside the $Q = -6.3$ eV circles in Figs. IV-23 and IV-24 may be accompanied by dissociation of the neutral product. At 13.30 eV formation of stable product ions with barycentric velocities within the $Q = -11.3$ eV circles

Figs. IV-19 - IV-22. Centerline velocity distributions of OD^+ and OH^+ formed in the O_2^+ - HD reaction at collision energies from 4.27 - 21.53 eV.

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Fig. IV-19.

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Fig. IV-20.

XBL 713 - 3087

Fig. IV-21.

XBL713 - 3089

Fig. IV-22.

on Figs. IV-25 and IV-26 must result in neutral dissociation or electronic excitation of ion or neutral.

The average Q values for the four complete contour maps have been calculated by the procedure outlined in Section (E) and it is found that almost all of the available energy goes into product excitation. In the 8.55 eV experiments both $\text{OH}^+\text{-OD}$ and $\text{OD}^+\text{-OH}$ product pairs have average internal excitations of 6.55 eV. At 13.30 eV the average internal excitation of both is 11 eV; thus, at this high energy, ion formation is almost exclusively accompanied by neutral dissociation.

2. Cross-Sections and Isotope Ratios

The differential cross-sections at 0° and 180° for both product ions are listed in Table IV-5. While the absolute values of $I(0)$ and $I(180)$ are not particularly interesting, the ratio $[I(180)/I(0)]$ is a sensitive measure of distribution of scattered intensity about the center-of-mass velocity. An examination of the dependence of this parameter upon energy reveals several trends. At collision energies up to about 8.5 eV OD^+ is scattered backward or forward with about equal probability. As the relative energy is raised backscattering becomes increasingly more important, reaching an $[I(180)/I(0)]$ ratio of more than 4 at 21.53 eV relative energy. The OH^+ product, on the other hand, is always primarily forward scattered and the $[I(180)/I(0)]$ ratio is independent of collision energy.

The total cross-sections for Reactions (2a) and (2b) can be estimated by assuming that they are proportional to I_s , the sum of $I(0)$ and $I(180)$. This quantity is also listed in Table V-5 for each reaction along with the isotope ratio ($I_s(\text{OD}^+)/I_s(\text{OH}^+)$) at each energy. The isotope ratios

TABLE IV-5

Differential Cross-Sections and Isotope Effects

Experiment Number	Product	E_{LAB} (eV)	E_s^O (eV)	$I(0)$ ($\times 10^{-3}$)	$I(180)$ ($\times 10^{-3}$)	I_s ($\times 10^{-3}$)	$\frac{I(180)}{I(0)}$	$\frac{I_s(OD^+)}{I_s(OH^+)}$
538	OD ⁺	49.8	4.27	1.84	1.29	3.13	0.70	1.48
539	OH ⁺			1.57	0.54	2.11	0.34	
582	OD ⁺	68.4	5.86	0.92	0.18	1.10	0.20	1.10
581	OH ⁺			0.98	0.02	1.00	0.02	
541	OD ⁺	75.0	6.43	2.04	2.53	4.57	1.24	1.34
540	OH ⁺			2.76	0.66	3.42	0.24	
578	OD ⁺	79.8	6.84	0.65	0.40	1.05	0.62	0.89
577	OH ⁺			1.12	0.06	1.18	0.05	
565	OD ⁺	88.0	7.54	1.32	1.11	2.43	0.84	0.93
566	OH ⁺			2.35	0.27	2.62	0.11	
572	OD ⁺	90.2	7.73	1.38	1.09	2.47	0.79	0.84
571	OH ⁺			2.60	0.34	2.94	0.13	
576	OD ⁺	99.8	8.55	0.97	1.17	2.14	1.21	0.95
575	OH ⁺			1.97	0.29	2.26	0.15	
544	OD ⁺	100.0	8.57	1.02	1.70	2.72	1.67	1.04
545	OH ⁺			2.14	0.48	2.62	0.22	

TABLE IV-5
(continued)

Experiment Number	Product	E_{LAB} (eV)	E_s^o (eV)	$I(0)$ ($\times 10^{-3}$)	$I(180)$ ($\times 10^{-3}$)	I_s ($\times 10^{-3}$)	$\frac{I(180)}{I(0)}$	$\frac{I_s(OD^+)}{I_s(OH^+)}$
587	OD ⁺	110.2	9.45	1.89	2.13	4.02	1.13	0.66
586	OH ⁺			5.38	0.72	6.10	0.13	
569	OD ⁺	119.7	10.26	1.09	1.81	2.90	1.66	0.73
568	OH ⁺			3.44	0.54	3.98	0.16	
548	OD ⁺	139.9	11.99	0.70	0.96	1.66	1.37	0.54
549	OH ⁺			2.61	0.44	3.05	0.17	
585	OD ⁺	155.1	13.30	1.43	4.17	5.60	2.92	0.66
584	OH ⁺			7.13	1.36	8.49	0.19	
552	OD ⁺	171.0	14.66	0.59	1.04	1.63	1.76	0.32
551	OH ⁺			4.37	0.75	5.12	0.17	
553	OD ⁺	209.2	17.93	0.30	0.65	0.95	2.17	0.16
554	OH ⁺			4.92	0.98	5.90	0.20	
556	OD ⁺	251.1	21.53	0.08	0.34	0.42	4.25	0.07
555	OH ⁺			4.68	1.12	5.80	0.24

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Fig. IV-23. A contour map of the specific intensity of OD^+ at a relative energy of 8.55 eV. Ions found within the $Q = -6.3$ eV circle may be accompanied by dissociation of the neutral product.

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Fig. IV-24. A contour of OH^+ specific intensity at 8.55 eV.
 The $Q = -8.4$ eV circle is drawn with a radius
 equal to the peak velocity.

XBL 712-275

Fig. IV-25. A contour map of OD^+ at a relative collision energy of 13.3 eV. Product ions formed with barycentric velocities within the $Q = -11.3 \text{ eV}$ circle must come from the reaction $\text{O}_2^+ + \text{HD} \rightarrow \text{OD}^+ + \text{H} + \text{D}$.

XBL 712-285

Fig. IV-26. A specific intensity contour map of OH^+ at a relative energy of 13.3 eV.

are also plotted as a function of incident relative energy in Fig. IV-27. The two crosses in Fig. IV-27 represent the isotope effects computed from the ratios of the integrated total cross-sections for OH^+ and OD^+ formation calculated at the energies at which complete contour maps were measured. At these two energies there is excellent agreement between the isotope effects calculated this way and those calculated by the I_s ratio.

3. Discussion

The small cross-sections of Reactions (2a) and (2b) ($\sim .2 \text{ \AA}^2$) and diminished primary beam intensity prohibited meaningful experiments from being carried out at relative collision energies below 4 eV. The lack of symmetry about the center-of-mass velocity of the OH^+ centerline distributions at all energies at which Reaction (2b) was studied indicates that dissociation of a long-lived complex is not the dominant mechanism by which this reaction proceeds at energies above 4 eV. Although the OD^+ velocity spectra are symmetric about centroid at collision energies up to 8.5 eV, the near identity of the OD^+ -OH and OH^+ -OD product pairs precludes one from interpreting a symmetric distribution as implying formation of a persistent complex. Furthermore, it would seem impossible to maintain that a long-lived intermediate exists when the relative energy is as high as 8.5 eV. The same conclusion was reached for the $\text{O}_2^+(\text{H}_2, \text{OH})\text{OH}^+$ reaction,²⁸ in which product ion symmetry at 8.3 eV was observed. This interpretation is consistent with the observation that above a relative energy of 4 eV direct mechanisms become important in the formation of O_2D^+ and O_2H^+ .

XBL714-6705

Fig. IV-27. Energy dependence of the OD^+/OH^+ isotope ratio. Values calculated from total cross-sections are indicated by crosses. The points denoted by open circles were determined from the sum of $I(0^\circ)$ and $I(180^\circ)$.

A comparison of the OD^+ and OH^+ centerline distributions and contour maps indicates that these products are formed at least partially by dynamically different mechanisms at all energies at which Reactions (2a) and (2b) were studied. The geometric factors governing collision probabilities are undoubtedly similar to those involved in O_2D^+ and O_2H^+ formation. As in these latter reactions, the H product is principally forward scattered at all energies where the reaction is direct, but unlike the O_2H^+ distribution, OH^+ scattering is found at all angles, even at a collision energy of 21.5 eV. The OD^+ distribution is similar to the O_2D^+ angular spectra in that product is found at all barycentric angles and scattered intensity is larger in the backward than forward hemisphere, but is different in that the OD^+ velocity spectra peak is very close to the center-of-mass at all angles. There is, of course, an important difference in the energy disposal problems of OD^+ and O_2D^+ in that the former has an essentially continuous energy sink in the form of internal energy of OH and relative translation between O and H, while the latter must transform its excess energy into electronic excitation. Thus, the position of the OD^+ peak is not limited by product recoil.

The observations suggest that at least two mechanisms determine the OD^+ and OH^+ scattering distributions; one which results in the product ion distribution peaking at and symmetric about centroid and which gives OD^+ or OH^+ with about equal probability, and another which is responsible for forward scattering of OH^+ at all energies and which to a lesser degree contributes to OD^+ backscattering. The rapid fall-off of the OD^+/OH^+ isotope ratio (Fig. IV-27) suggests that the second mechanism becomes increasingly dominant as the collision energy is raised.

The second process can be described as a "double pickup" mechanism. In this model the O_2^+ ion approaches the HD molecule with the two internuclear axes parallel to each other and perpendicular to the incident relative velocity vector. Each O atom, with $\frac{1}{2} E_{LAB}$ and velocity v_o picks up an H or D atom. The laboratory velocities of the products after the collision are:

$$v_{OH} = \frac{16}{17} v_o = 0.941 v_o \quad (IV-33a)$$

$$v_{OD} = \frac{16}{18} v_o = 0.889 v_o \quad (IV-33b)$$

where
$$v_{CM} = \frac{32}{35} v_o = 0.914 v_o \quad (IV-33c)$$

The peak OH^+ and OD^+ velocities are plotted in Fig. IV-28 and compared with the predictions of this model. The double pickup mechanism obviously gives poor agreement with the OD^+ peak velocities, which are all very close to the center-of-mass velocity. On the other hand, the OH^+ peak velocities are all larger than that predicted by the model. This latter deviation can be explained as a consequence of forward recoil, which has been used⁹ to explain deviations from the ideal stripping model at energies above which product ions found at the stripping velocity would be unstable. However, since the product ion distributions are so broad, the centerlines may be misleading. The maps show clearly that OD^+ is backscattered, and that there is quite a bit of recoil. Recoil of either product is inconsistent with the simple double pickup model; however, this model may contain the reason why OH^+ is forward and OD^+ backscattered. That is, it shows that the transient high-energy $HOOD^+$ complex rotates

XBL 714-6678

Fig. IV-28. Peak OD^+ and OH^+ velocities plotted as functions of energy. The flatness of the OD^+ velocity spectra at all energies (see Figs. IV-19 - IV-22) makes precise location of the OD^+ peaks uncertain.

with OH moving in the forward and OD in the backward direction. It is also possible that the OH⁺ forward peaking is related to the slight forward peaking observed in the O₂⁺(D₂,OD)OD⁺ reaction at very high energies, which, it was suggested,²⁸ may be caused by the increasing importance of a process in which both O atoms are not equivalent.

We can also calculate the internal energies of the products formed by the double pickup model. If we assume that the energy necessary to break the O₂⁺ and HD bonds comes equally from the O-H and O-D relative kinetic energies and that the exothermic heats of formation of the OH and OD bonds are transformed into excitation of these bonds, we can write the following equations for the internal energies, U', of the OH⁺ and OD⁺ ions.

$$U'_{OD^+} = - \frac{[D(O_2^+) + D(HD)]}{2} + D(OD^+) + \frac{E_{LAB}}{2} \frac{2}{18} \quad (IV-34a)$$

$$U'_{OH^+} = - \frac{[D(O_2^+) + D(HD)]}{2} + D(OH^+) + \frac{E_{LAB}}{2} \frac{1}{17} \quad (IV-34b)$$

The upper limits to the laboratory energies at which OD⁺ and OH⁺ will be stable are 99 and 190 eV respectively. These correspond to relative energies of 9.0 and 17.2 eV. This energy effect, thus, partially explains the steep decrease in the OD⁺/OH⁺ curve in Fig. IV-26 at relative collision energies above 9 eV.

For the O₂⁺(D₂,OD)OD⁺ reaction the double pickup model predicts OD⁺ peaking at the center-of-mass velocity and product stability below 9 eV relative energy, in accord with our experimentally determined²⁸ contour map of the O₂⁺(D₂,OD)OD⁺ reaction at a collision energy of 8.38 eV.

G. Summary

Reactions (1a) and (1b) were studied over the relative collision energy range from 2.5 - 8.6 eV. Below 5 eV both reactions proceed through formation of a persistent complex, with the O_2D^+ cross-section about five times that of O_2H^+ . Most of the available energy of Reaction (1a) and almost all of the excess energy of Reaction (1b) goes into product excitation. Furthermore, the total angular momentum of the system appears chiefly as internal rotation rather than as orbital angular momentum.

Above 5 eV the $O_2^+(HD,H)O_2D^+$ and $O_2^+(HD,D)O_2H^+$ reactions proceed by dynamically different mechanisms. The O_2H^+ distribution, which is almost exclusively forward scattered, is consistent with spectator stripping. On the other hand, the O_2D^+ distribution is very complex but largely backscattered. A binary impulsive collision model is proposed to explain the stability of backscattered O_2D^+ and the absence of backscattered O_2H^+ . It is further concluded that geometric factors strongly influence the observed high-energy isotope effect.

The $O_2^+(HD,OH)OD^+$ and $O_2^+(HD,OD)OH^+$ reactions were investigated at collision energies from 4.3 to 21.5 eV and found to be direct at all energies. Both product distributions are extremely broad and most of the available energy goes into internal excitation. The OH^+ product is forward peaked at all energies and a double pickup model is proposed to partially explain the OH^+ velocity spectra. At all collision energies OD^+ intensity is highly symmetric about the center-of-mass, although at high relative energies backscattered product predominates. It is concluded that Reactions (2a) and (2b) proceed by two processes, the double pickup mechanism and a second mechanism which scatters product ions symmetrically about center-of-mass velocity.

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CHAPTER V. UNIMOLECULAR DECOMPOSITION

A. Introduction

The purpose of this chapter is to analyze the low energy homonuclear and mixed isotope reactions on the basis of statistical unimolecular decay theory. The principal advantage to studying unimolecular decomposition in beam experiments is that each complex formed is a chemically activated species with well known total energy and angular momentum. The short lifetime ($\sim 10^{-12}$ sec) of small excited molecules makes an investigation of their equilibrium decomposition in conventional batch experiments exceedingly difficult because very high pressures are needed to insure statistical equilibrium. Statistical theories have been used successfully¹ to treat the velocity and angular distributions from alkali atom-alkali halide and alkali halide-alkali halide reactions at thermal energies. The ability of unimolecular decomposition models to predict scattering profiles in these three and four atom systems is encouraging evidence for the applicability of these theories to small molecules. The ion-molecule reactions with which we are concerned occur at energies considerably higher than thermal energy. The highest relative collision energy at which all ionic products of the $O_2^+-H_2$ reaction appear to be formed solely through intermediate complex formation is 4.5 eV. Ground state $HOOH^+$ is thermodynamically stable with respect to $O_2^+(^2\pi_g)$ and H_2 by 2.4 eV. Therefore, the intermediate formed by reactants with 4.5 eV relative energy has an internal excitation of 6.9 eV, or 1.15 eV per vibrational mode. There is an additional 2.4 eV barrier to formation of $HOOH^+$ from

$O_2^+(^2\pi_g)$ and H_2 , and therefore, the lowest dissociation path of the intermediate is 3.04 eV to H_2O^+ and O. Since this minimum amount of energy must be located in a particular "reaction coordinate" for the $HOOH^+$ to decompose, it is reasonable to conclude that the excited complex will live long enough to establish vibrational equilibrium.

The plan of this chapter is to discuss briefly the quasiequilibrium theory, examine and apply this theory to the product ion spectrum of electron bombardment of hydrogen peroxide, and then discuss the $O_2^+-H_2$ reaction product ion intensities and isotope effects with particular emphasis on the role of angular momentum.

B. Quasiequilibrium Theory

The quasiequilibrium theory (QET) was developed by Rosenstock et al.² to explain the relative product intensities of ions formed by electron bombardment of polyatomic molecules. The basic underlying premise of the QET is that ionization of a neutral species does not directly lead to ionic fragmentation, but rather, the molecule-ion formed has a certain amount of vibrational and electronic energy with respect to its ground state. Decomposition of the molecule-ion is not immediate but occurs only after several vibrational periods. The assumption is made that an isolated molecule-ion can be represented by a microcanonical ensemble and that within this ensemble systems are uniformly distributed over all states in the region $E, E + \delta E$. Energy exchange between states is assumed to be rapid since the vibrational modes are not purely harmonic. For each possible dissociation product a "reaction coordinate" can be

chosen and an "activated complex" or "transition state" configuration can be selected at a saddle point in the potential energy surface, such that translation past the saddle point corresponds to dissociation. The rate constant for dissociation is just the frequency of crossing the saddle point.

The rate constant for unimolecular dissociation can be derived as follows. Let $\rho(E)\delta E$ be the state density function of the excited molecule. The activated complex has total energy between E and $E + \delta E$, potential energy ϵ_0 , and translational energy ϵ_t in the reaction coordinate. The activated complex energy density is: $\rho^+(E, \epsilon_0, \epsilon_t)\rho_t(\epsilon_t)\delta E\epsilon_t$, where ρ_t is the density of translational states per length r of the reaction coordinate and ρ^+ is the density of states in the remaining degrees of freedom. The one-dimensional translational energy ϵ_t is taken to be the energy of a particle in a one-dimensional box:

$$\epsilon_t = \frac{n^2 h^2}{8mr^2} \quad (V-1)$$

where m is the reduced mass for translation. The translational state density function is given by:

$$\rho_t = \frac{dn}{d\epsilon_t} = \frac{r}{h} \left(\frac{2m}{\epsilon_t} \right)^{\frac{1}{2}} \quad (V-2)$$

The frequency of crossing the barrier, with velocity v along the reaction coordinate, is:

$$f_t(\epsilon_t) = \frac{v}{r} = \frac{1}{2} \left(\frac{2\epsilon_t}{m} \right)^{\frac{1}{2}} \frac{1}{r} \quad (V-3)$$

where the factor $(1/2)$ is inserted to account for outward trajectories only.

The unimolecular rate constant for crossing the barrier is the integral over ϵ_t of the ratio of the activated complex phase space to the molecule-ion phase space times the frequency of crossing the barrier:

$$k(E) = s \int_0^{E-\epsilon_0} \frac{\rho^\ddagger(E, \epsilon_0, \epsilon_t)}{\rho(E)h} d\epsilon_t \quad (V-4)$$

where s is the symmetry number. This equation can be written more conveniently as:

$$k(E) = \frac{s}{h} \frac{W^\ddagger(E-\epsilon_0)}{\rho(E)} \quad (V-5)$$

$W^\ddagger(E-\epsilon_0)$ is the number of states of the activated complex with energy less than or equal to $(E-\epsilon_0)$. The most widely used approximation to the total number of states of a system with energy $\leq E$ is that of Vestal et al.³ The enumeration of the number of states is accomplished by an exact counting of possible assignments of zero quantum number to one or more oscillators and the use of a semiclassical approximation for the remaining excited oscillators.

Buttrill⁴ has written a computer program applying the QET and the Vestal counting of states method to the calculation of unimolecular decomposition product ion intensities. A copy of this program was obtained from the author and was used to compute the rate constants and breakdown curves discussed in the following sections.

C. Electron Bombardment Dissociation

By means of electron bombardment Foner and Hudson⁵ have measured the product ion appearance potentials from hydrogen peroxide. The appearance potentials of O_2H^+ , OH^+ , H_2O^+ , O_2^+ and O^+ relative to the ionization potential of $HOOH^+$ are listed in Table V-1 along with the thermodynamic formation energies of these ions. Corresponding values for the ionic products from $DOOD^+$ and $HOOD^+$, computed from zero point energy differences between hydrogenated and deuterated species, are also listed.

All products are formed at their lowest possible energies except O_2^+ and O^+ . Mahan⁶ has shown that $O_2^+(^2\pi_g)$ and H_2 correlate electronically with an excited planar configuration of $HOOH^+$, rather than with the non-planar ground state. Additionally, dissociation of planar hydrogen peroxide ion to O_2H^+ and H would produce an excited state of O_2H^+ , while the non-planar ground state would yield this ion in its ground electronic state. The barrier to $O_2^+(^2\pi_g)$ formation and the appearance of ground state O_2H^+ therefore suggest that these products are formed from the decay of $HOOH^+$ in its ground electronic state.

The barrier to O^+ formation can be understood as a consequence of Stevenson's Rule,⁷ which states that if the ionization potential of A is greater than that of B, the process

requires an appearance potential greater than the sum of the ionization

TABLE V-1

Thermodynamics of Hydrogen Peroxide Ion Unimolecular Decomposition

Molecule	Products	ΔE_o^a (eV)	Appearance ^b Potential (eV)	$E_{z.p.}$ (eV)	E_s^o (Threshold) (eV)
$HOOH^+$ $E_{z.p.} = .745$ $\Delta E_o^o = 0.0$	O_2H^+, H	4.34	4.34	.388	1.96
	OH^+, OH	4.25	4.25	.415	1.87
	H_2O^+, O	3.04	3.04	.558	0.66
	O_2^+, H_2	2.38	4.78	.389	-
	O^+, H_2O	4.04	~ 6.0	.389	~ 5.55
$DOOD^+$ $E_{z.p.} = .581$ $\Delta E_o^o = 0.0$	O_2D^+, D	4.43	4.43	.315	1.97
	OD^+, OD	4.30	4.30	.302	1.84
	D_2O^+, O	3.06	3.06	.411	0.60
	O_2^+, D_2	2.47	4.87	.310	-
	O^+, D_2O	4.06	~ 6.0	.310	~ 5.55
$HOOD^+$ $E_{z.p.} = .663$ $\Delta E_o^o = 0.0$	O_2D^+, H	4.35	4.35	.315	1.92
	O_2H^+, D	4.42	4.42	.388	1.99
	OD^+, OH	4.28	4.28	.365	1.85
	OH^+, OD	4.27	4.27	.352	1.84
	HDO^+, O	3.03	3.03	.463	0.60
	O_2^+, HD	2.43	4.83	.353	-
	O^+, HDO	4.03	~ 6.0	.353	~ 5.55

$$IP(H_2O_2) = 10.92 \text{ eV}$$

^a J. L. Franklin et al., Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS 25 (1969).

^b Reference 2.

potential of A and the dissociation energy of the AB bond, while the complementary process:

requires an energy greater than or equal to the sum of the ionization potential of B and the AB bond dissociation energy. Since the ionization potential of O is 1 eV greater than that of H₂O, the former will have an appearance potential in excess of its minimum energy of formation.

Foner and Hudson also report the product ion intensity distribution (breakdown curve) for the dissociation of hydrogen peroxide by 50 eV electrons. Table V-2 lists this spectrum and the relative cross-sections of O₂H⁺, OH⁺ and H₂O⁺ produced by the O₂⁺-H₂ reaction at a collision energy of 3 eV, the only energy at which we have complete contour maps of all three products. In the molecular beam experiments oxygen ions arising from complex decay cannot be separated from reactant O₂⁺ scattered elastically and inelastically. Also, no O⁺ is found below 5.55 eV.

The dissociation patterns of H₂O₂⁺ are obviously grossly different for the two types of experiments. The electron bombardment results are qualitatively in accord with the expectations from the product appearance potentials and thus appear to be a better starting point for a test of the QET.

The parameters necessary for QET calculations are: 1) symmetry number for each reaction, 2) activation energy for each reaction, 3) vibrational frequencies for the molecule-ion, and 4) vibrational frequencies for each transition state. Once the structures of the various transition states are assumed the symmetry numbers are uniquely

TABLE V-2

Relative Product-Ion Intensities

Ion	Foner and Hudson ² (50 eV electrons)	This work 3 eV Relative Energy	Symmetry Number
O_2H^+	0.17	0.85	2
OH^+	0.22	0.08	1
H_2O^+	0.55	0.08	2
O_2^+	0.07	-	1
O^+	0.01	0	2

determined. The activation energies are listed in Table V-1. Since vibrational frequencies have not been measured for ions other than a few diatomics, the frequencies used for the excited molecule are those of neutral hydrogen peroxide, except for the O-O stretch which is taken to be the frequency of the NO stretch in HNO which is isoelectronic with H_2O_2^+ . The vibrational frequencies (ν_1 's) of H_2O_2^+ , D_2O_2^+ and HDO_2^+ are listed in Table V-3.

The problem of determining the transition state configurations is considerably more difficult and involves a large amount of educated guesswork. The choice of reaction coordinates leading to formation of various ions is relatively straightforward; they are assigned as follows: the O-H asymmetric stretch for O_2H^+ , the O-H symmetric stretch for O_2^+ , and the O-O stretch for H_2O^+ and OH^+ .

The transition states are assumed to have the same geometric structure as the H_2O_2^+ ion, but the vibrational frequencies of the critical configurations are modified to account for bond distortions. Several sets of vibrational frequencies chosen for the transition states are displayed in Table V-4. These numbers require some explanation. The labels "rigid" and "free rotation" refer to the torsion about the O-O bond, which is taken to be restricted rotation in all states except two. The choice of frequencies in Table V-4 is somewhat arbitrary but the selection procedure is regulated by a series of empirical rules developed by Wahrhaftig and co-workers⁸ for dissociation of organic molecules. The frequency sets labelled (A) were chosen by this procedure and the other combinations reflect our prejudices.

TABLE V-3

Molecular Parameters

Assignment ^a	Vibrational Frequencies (cm ⁻¹)		
	HOOH ⁺ ^b	DOOD ⁺ ^b	HOOD ⁺ ^c
ν_1	3610	2670	3612
ν_2	1315	1042 ^d	1290
ν_3	1562 ^e	1562 ^e	1562
ν_4	660	480	570
ν_5	3614	2680	2675
ν_6	1266	947	990
	Moments of Inertia ^f (g cm ²)		
	HOOH ⁺	DOOD ⁺	HOOD ⁺
I_A	2.96×10^{-40}	5.60×10^{-40}	4.35×10^{-40}
$I_B = I_C$	34×10^{-40}	34×10^{-40}	34×10^{-40}

^a ν_1 = O-H symmetric stretch

ν_2 = symmetric bend

ν_3 = O-O stretch

ν_4 = torsional bend

ν_5 = O-H asymmetric stretch

ν_6 = asymmetric bend

^b P.A. Giguere and O. Bain, J. Phys. Chem. 56, 340 (1952).

^c Values calculated from H₂O₂⁺ and D₂O₂⁺ frequencies.

^d N. T. Stoichai and V. P. Morozov, Dopov. Akad. Nauk. URSR, 1596 (1966).

^e Taken as the N-O stretching frequency of HNO. F. W. Dalby, Can. J. Phys. 36, 1336 (1958).

^f J.T. Massey, C. I. Beard and C. K. Jen, J. Mol. Spec. 5, 405 (1960).

TABLE V-4

Transition State Frequencies

		ν_1	ν_2	ν_3 (cm^{-1})	ν_4	ν_5	ν_6	
O_2H^+	A	3610	657.5	1562	660	R.C.	1266	} Rigid
	B	3610	657.5	1562	660	R.C.	633	
	C	3610	657.5	1562	170 ^a	R.C.	633	Free Rotation
OH^+	A	3610	329.7	R.C.	660	3614	316.5	Rigid
	B	3610	329.7	R.C.	170 ^a	3614	316.5	Free Rotation
H_2O^+	A	1805	657.5	R.C.	660	1807	633	} Rigid
	B	1805	657.5	R.C.	660	1807	1266	
	C	3610	657.5	R.C.	660	1807	633	
O_2^+	A	R.C.	1315	1562	660	1807	1266	} Rigid
	B	R.C.	1315	1562	660	3614	1266	

^a Free rotation about the O-O bond. R. H. Hunt, R. A. Leacock, C. W. Peters and K. T. Hecht, J. Chem. Phys. 42, 1931 (1965).

Tables V-5 - V-8 display breakdown curves (relative rate constants) calculated from the QET for O_2H^+ , OH^+ , H_2O^+ and O_2^+ . To be precise, since O^+ is formed from the same activated complex configuration as is H_2O^+ , the columns headed by H_2O^+ actually represent both these ions. However, the intensity of H_2O^+ far exceeds the O^+ signal and thus the numbers in these columns can be taken as H_2O^+ relative intensities without introducing significant error. In Tables V-5 - V-8 "Rigid" and "Free Rotation" refer to the fact that the torsional motion about the O-O axis in the molecule ion is taken to be a vibration or a free rotation respectively.

Comparison of the four breakdown curves with the electron bombardment product ion intensity ratios compiled in Table V-2 indicates that the "Rigid 1" system gives the best fit to the data. The calculated product ion distribution is very insensitive to the total energy E of the system; it is therefore impossible to specify the energy at which agreement is closest. An additional complication is the fact that the excitation energy of H_2O_2^+ produced by bombardment with 50 eV electrons is unknown. Nevertheless, since all four transition state structures of the "Rigid 1" system were chosen on the basis of Wahrhaftig's method,⁶ this agreement is impressive evidence for the applicability of QET to molecule-ions as small as HOOH^+ .

D. $\text{O}_2^+ - \text{H}_2$ Reaction Product Ion Ratios

The striking disparity between the product ion ratios in the electron bombardment and beam experiments shows that the mechanism of formation

TABLE V-5

Rigid 1

Transition State Structures

O_2H^+ (A)

OH^+ (A)

H_2O^+ (A)

O_2^+ (A)

Breakdown Curves

E (eV)	O_2H^+	OH^+	H_2O^+	O_2^+
4.000	0.	0.	1.0000	0.
6.000	.0324	.0806	.8748	.0122
8.000	.0681	.1478	.7556	.0286
10.000	.0884	.1804	.6922	.0390
12.000	.1009	.1985	.6548	.0457
14.000	.1093	.2100	.6304	.0504
16.000	.1152	.2177	.6133	.0538
18.000	.1196	.2234	.6007	.0563
20.000	.1231	.2276	.5910	.0584
22.000	.1258	.2309	.5833	.0600
24.000	.1280	.2336	.5771	.0613
26.000	.1299	.2358	.5720	.0624
28.000	.1314	.2376	.5676	.0634
30.000	.1327	.2391	.5640	.0642
32.000	.1339	.2404	.5608	.0649
34.000	.1349	.2416	.5580	.0655
36.000	.1358	.2426	.5556	.0660
38.000	.1366	.2434	.5535	.0665
40.000	.1373	.2442	.5515	.0670
42.000	.1379	.2449	.5498	.0674
44.000	.1385	.2456	.5483	.0677
46.000	.1390	.2461	.5469	.0680
48.000	.1394	.2466	.5456	.0683
50.000	.1399	.2471	.5444	.0686
Electron Bombardment	0.17	0.22	0.55	0.01

TABLE V-6

Rigid 2

Transition State Structures

O_2H^+ (B)

OH^+ (A)

H_2O^+ (B)

O_2^+ (B)

Breakdown Curves

E (ev)	O_2H^+	OH^+	H_2O^+	O_2^+
4.000	0.	0.	1.0000	0.
6.000	.0952	.1312	.7603	.0133
8.000	.1883	.2149	.5720	.0248
10.000	.2344	.2471	.4882	.0303
12.000	.2606	.2627	.4433	.0334
14.000	.2773	.2717	.4156	.0353
16.000	.2889	.2774	.3970	.0367
18.000	.2973	.2814	.3837	.0376
20.000	.3037	.2843	.3736	.0384
22.000	.3087	.2865	.3658	.0390
24.000	.3128	.2882	.3596	.0394
26.000	.3162	.2895	.3544	.0398
28.000	.3190	.2907	.3502	.0402
30.000	.3214	.2916	.3466	.0404
32.000	.3234	.2924	.3435	.0407
34.000	.3252	.2931	.3408	.0409
36.000	.3268	.2937	.3385	.0411
38.000	.3282	.2942	.3364	.0412
40.000	.3294	.2946	.3346	.0414
42.000	.3305	.2950	.3329	.0415
44.000	.3315	.2954	.3315	.0416
46.000	.3324	.2957	.3301	.0417
48.000	.3333	.2960	.3289	.0418
50.000	.3340	.2963	.3278	.0419

TABLE V-7

Rigid 3

Transition State Structures

O_2H^+ (A)

OH^+ (A)

H_2O^+ (C)

O_2^+ (B)

Breakdown Curves

E (ev)	O_2H^+	OH^+	H_2O^+	O_2^+
4.000	.	.	1.0000	.
6.000	.0492	.1219	.8165	.0124
8.000	.1019	.2206	.6520	.0254
10.000	.1308	.2601	.5705	.0326
12.000	.1481	.2907	.5243	.0369
14.000	.1594	.3058	.4950	.0398
16.000	.1674	.3160	.4748	.0418
18.000	.1733	.3232	.4601	.0433
20.000	.1779	.3287	.4490	.0444
22.000	.1815	.3329	.4402	.0453
24.000	.1844	.3363	.4332	.0461
26.000	.1869	.3391	.4274	.0467
28.000	.1889	.3414	.4225	.0472
30.000	.1907	.3433	.4184	.0476
32.000	.1922	.3449	.4149	.0480
34.000	.1935	.3464	.4118	.0483
36.000	.1947	.3476	.4091	.0486
38.000	.1957	.3487	.4067	.0489
40.000	.1966	.3497	.4046	.0491
42.000	.1974	.3508	.4027	.0493
44.000	.1982	.3513	.4010	.0495
46.000	.1988	.3520	.3994	.0497
48.000	.1995	.3527	.3980	.0499
50.000	.2000	.3533	.3967	.0500

TABLE V-8

Free Rotation

Transition State Structures

O_2H^+ (C)

OH^+ (B)

H_2O^+ (B)

O_2^+ (A)

Breakdown Curves

E (eV)	O_2H^+	OH^+	H_2O^+	O_2^+
4.000	0.	0.	1.0000	0.
6.000	.2215	.3007	.4696	.0082
8.000	.3386	.3830	.2669	.0116
10.000	.3819	.4000	.2054	.0127
12.000	.4041	.4054	.1772	.0133
14.000	.4175	.4075	.1612	.0137
16.000	.4266	.4085	.1510	.0139
18.000	.4331	.4089	.1439	.0141
20.000	.4379	.4090	.1387	.0143
22.000	.4418	.4091	.1348	.0144
24.000	.4448	.4091	.1317	.0144
26.000	.4473	.4090	.1291	.0145
28.000	.4494	.4089	.1270	.0146
30.000	.4512	.4089	.1253	.0146
32.000	.4527	.4088	.1238	.0147
34.000	.4541	.4087	.1225	.0147
36.000	.4552	.4086	.1214	.0147
38.000	.4562	.4086	.1204	.0148
40.000	.4572	.4085	.1196	.0148
42.000	.4580	.4084	.1188	.0148
44.000	.4587	.4084	.1181	.0148
46.000	.4594	.4083	.1175	.0148
48.000	.4600	.4083	.1169	.0149
50.000	.4605	.4082	.1164	.0149

of an excited molecule-ion can radically effect the decomposition pattern of that species. In the molecular beam experiments the HOOH^+ is formed with sizeable angular momentum, whereas, electron bombardment ionization leaves the molecule-ion with the same angular momentum as the thermal energy neutral. Marcus⁹ has derived a correction factor to the RRKM rate constant that accounts for the decrease in the product appearance potential due to centrifugal effects. This effect arises from the difference in rotational energies of the molecule-ion and the activated complex due to bond distortions. This correction factor may be significant for molecule-ion excitation energies near product thresholds, but is negligible at the relatively large excitation energies of the HOOH^+ at which the beam experiments were carried out, and, hence, is neglected in the following calculations.

Clearly, the transition state structures proposed in the previous section will not explain the beam product ion ratios listed in Table V-2. From Eq.(V-5) we see that the dissociation rate constant for a particular channel is proportional to the number of states in that channel. The number of states in a molecule increases as the vibrational frequencies are lowered. Thus, to account for the large cross-section of O_2H^+ relative to OH^+ and H_2O^+ in the beam experiments, the O_2H^+ critical configuration must have a considerably larger density of states at a total energy of 5.7 eV than the critical configurations of OH^+ and H_2O^+ . In other words, the O_2H^+ activated complex is "looser" than the "tight" transition state structures of OH^+ and H_2O^+ .

The choice of a "loose" critical configuration for O_2H^+ is consistent with the finding in Chapter IV that this product is highly rotationally

excited. This configuration is assigned large amplitude, low frequency bends which appear as rotation of the product ion. Because of the low appearance potential of H_2O^+ it is necessary to select a "supertight" transition state structure for this ion. The structure used for the critical configuration leading to H_2O^+ resembles a highly constrained formaldehyde molecule. Since the OH^+ and O_2^+ ions have appearance potentials over an electron volt higher than H_2O^+ their transition state configurations need not be as constricted as that chosen for H_2O^+ . The critical configuration chosen for OH^+ has free rotation about the O-O bond. Finally, the transition state structure of O_2^+ is a planar rectangle with the OH bonds weakened with respect to their frequencies in HOOH^+ . The symmetric bend is chosen as the reaction coordinate for this structure.

The frequencies for these "superloose-supertight" (SLST) critical configurations are listed in Table V-9, along with the breakdown curves calculated using these structures. The HOOH^+ frequencies are those listed in Table V-3. The total energy of the molecule-ion, E , in the first column of Table V-9 is the sum of the initial relative collision energy, E_s^0 , and the thermodynamic stability of HOOH^+ with respect to reactants (2.38 eV). The experimental product ion intensity ratios listed in the table were measured at a relative energy of 3 eV, or a total energy of 5.7 eV (taking the O_2^+ primary ion excitation equal to 0.3 eV).

Comparison of the measured product spectrum with that calculated at $E = 5.7$ eV shows remarkable agreement. Since the choice of transition state frequencies was contrived to fit the data, this accord cannot be

TABLE V-9

"Superloose-Supertight" Transition State Frequencies

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
	(cm ⁻¹)					
O_2H^+	3596	141	1562	660	R.C.	141
OH^+	3610	6575	R.C.	170	3614	633
H_2O^+	3610	1315	1562	900	3614	R.C.
O_2^+	1805	R.C.	1562	900	1807	633

Breakdown Curves

E (eV)	O_2H^+	OH^+	H_2O^+	O_2^+
4.200	0.	0.	1.0000	0.
4.400	.0214	.0195	.9585	.0006
4.600	.2527	.0589	.6832	.0053
4.800	.5198	.0779	.3940	.0083
5.000	.6802	.0800	.2303	.0095
5.200	.7668	.0771	.1462	.0100
5.400	.8161	.0732	.1005	.0102
5.600	.8443	.0697	.0737	.0103
5.800	.8661	.0666	.0569	.0103
6.000	.8799	.0641	.0456	.0104
6.200	.8899	.0619	.0378	.0104
6.400	.8975	.0600	.0321	.0105
6.600	.9033	.0584	.0278	.0105
6.800	.9080	.0570	.0244	.0106
7.000	.9118	.0557	.0218	.0106
7.200	.9150	.0547	.0197	.0107
7.400	.9176	.0537	.0180	.0107
7.600	.9199	.0529	.0165	.0107
7.800	.9218	.0521	.0153	.0108

Beam Experiments

5.7

.85

.08

.08

—

taken as proof that the critical configurations are as described. However, this result does indicate that the physical descriptions of the critical configurations may not be unreasonable.

E. Complex Lifetimes

Since the complex must live for several rotations in order for the product ion distributions to be symmetric about the center-of-mass, a calculation of the lifetime of HOOH^+ as a function of relative collision energy would be a direct test of the validity of the SLST configurations. The dissociation rate constants of the molecule-ion to O_2H^+ , OH^+ , H_2O^+ and O_2^+ at total excitation energies up to 7.8 eV are listed in Table V-10. The lifetime of the complex with respect to unimolecular decay to a particular product is simply the reciprocal of the rate constant for formation of that product. For comparison, the rate constants from the "Rigid 1" configurations are displayed in Table V-11.

The lifetimes of the hydrogen peroxide ion intermediate complex with respect to formation of O_2H^+ , OH^+ and H_2O^+ computed from the SLST structures are plotted in Fig. V-1 as functions of relative collision energy. Figure V-2 is a similar graph of the lifetimes calculated from the "Rigid 1" configurations. Also shown on these graphs are the minimum tumbling (τ_B) and spinning (τ_A) rotational periods, calculated by the expression:

$$\tau = 2\pi I / \mu b g \quad (\text{V-6})$$

TABLE V-10

Unimolecular Decomposition Rate Constants for
"Superloose-Supertight" Critical Configurations

E (eV)	$k(\text{O}_2\text{H}^+)$	$k(\text{OH}^+)$ (sec^{-1})	$k(\text{H}_2\text{O}^+)$	$k(\text{O}_2^+)$
3.200	0.	0.	1.7377E+10	0.
3.400	0.	0.	5.3364E+10	0.
3.600	0.	0.	1.1169E+11	0.
3.800	0.	0.	1.9543E+11	0.
4.000	0.	0.	3.0620E+11	0.
4.200	0.	0.	4.4451E+11	0.
4.400	1.3615E+10	1.2389E+10	6.1004E+11	3.9610E+08
4.600	2.9656E+11	6.9153E+10	8.0183E+11	6.1666E+09
4.800	1.3436E+12	2.0124E+11	1.0185E+12	2.1415E+10
5.000	3.7168E+12	4.3725E+11	1.2585E+12	5.1973E+10
5.200	7.9739E+12	8.0129E+11	1.5199E+12	1.0376E+11
5.400	1.4624E+13	1.3125E+12	1.8009E+12	1.8237E+11
5.600	2.4103E+13	1.9851E+12	2.0996E+12	2.9279E+11
5.800	3.6766E+13	2.8288E+12	2.4141E+12	4.3927E+11
6.000	5.2884E+13	3.8495E+12	2.7428E+12	6.2517E+11
6.200	7.2652E+13	5.0495E+12	3.0838E+12	8.5306E+11
6.400	9.6192E+13	6.4283E+12	3.4357E+12	1.1247E+12
6.600	1.2356E+14	7.9833E+12	3.7968E+12	1.4412E+12
6.800	1.5477E+14	9.7100E+12	4.1660E+12	1.8030E+12
7.000	1.8979E+14	1.1602E+13	4.5418E+12	2.2099E+12
7.200	2.2853E+14	1.3653E+13	4.9232E+12	2.6615E+12
7.400	2.7089E+14	1.5856E+13	5.3090E+12	3.1568E+12
7.600	3.1675E+14	1.8201E+13	5.6983E+12	3.6945E+12
7.800	3.6596E+14	2.0680E+13	6.0903E+12	4.2733E+12

TABLE V-11

Unimolecular Decomposition Rate Constants for
"Rigid 1" Critical Configurations

E (ev)	$k_{O_2H^+}$	k_{OH^+} (sec ⁻¹)	$k_{H_2O^+}$	$k_{O_2^+}$
3.200	0.	0.	3.7921E+10	0.
3.400	0.	0.	1.9836E+11	0.
3.600	0.	0.	5.7466E+11	0.
3.800	0.	0.	1.2609E+12	0.
4.000	0.	0.	2.3380E+12	0.
4.200	0.	0.	3.8690E+12	0.
4.400	2.5396E+09	1.0808E+10	5.8981E+12	3.8009E+08
4.600	1.9331E+10	6.3035E+10	8.4523E+12	5.7523E+09
4.800	6.1722E+10	1.8840E+11	1.1543E+13	1.9720E+10
5.000	1.4282E+11	4.1636E+11	1.5171E+13	4.7607E+10
5.200	2.7528E+11	7.7195E+11	1.9325E+13	9.4851E+10
5.400	4.7040E+11	1.2752E+12	2.3987E+13	1.6663E+11
5.600	7.3766E+11	1.9412E+12	2.9133E+13	2.6761E+11
5.800	1.0846E+12	2.7804E+12	3.4737E+13	4.0172E+11
6.000	1.5169E+12	3.7992E+12	4.0768E+13	5.7217E+11
6.200	2.0382E+12	5.0005E+12	4.7196E+13	7.8140E+11
6.400	2.6510E+12	6.3842E+12	5.3989E+13	1.0311E+12
6.600	3.3559E+12	7.9478E+12	6.1116E+13	1.3223E+12
6.800	4.1527E+12	9.6871E+12	6.8546E+13	1.6556E+12
7.000	5.0399E+12	1.1596E+13	7.6250E+13	2.0308E+12
7.200	6.0155E+12	1.3668E+13	8.4198E+13	2.4475E+12
7.400	7.0767E+12	1.5896E+13	9.2364E+13	2.9049E+12
7.600	8.2202E+12	1.8270E+13	1.0072E+14	3.4018E+12
7.800	9.4425E+12	2.0782E+13	1.0925E+14	3.9371E+12

Fig. V-1 Lifetimes of the HOOH^+ intermediate with respect to dissociation to O_2H^+ , OH^+ and H_2O^+ (solid lines), calculated by QET using the "superloose-supertight" transition state set (see text). The dashed lines represent the minimum molecule-ion rotational periods as functions of energy for "tumbling" (τ_B) and "spinning" (τ_A) rotations.

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Fig. V-1.

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Fig. V-2. Intermediate lifetimes calculated using "Rigid 1" transition state set (solid lines). Dashed lines are as in Fig. V-1.

where I is one of the principal moments of the inertia of HOOH^+ , μ is the reduced mass of the reactants (O_2^+-H_2), b is the incident impact parameter, and g is the initial relative velocity.

An examination of Fig. V-1 shows that the calculated lifetimes of the complex with respect to formation of OH^+ and H_2O^+ are consistent with contour map distributions of these ions. Although the HOOH^+ lifetimes for decay to these products become less than one rotation about the perpendicular axis at relative collision energies above 3 eV, the complex can undergo several rotations about the O-O bond at energies in excess of 4 eV. It is possible that those complexes which have their angular momentum residing principally in the high frequency spinning rotation preferably decay to OH^+ and H_2O^+ . As noted in Chap. IV, O_2H^+ is formed mainly from critical configurations in which the angular momentum is concentrated in rotation about the axes perpendicular to the O-O axis. From the H_2O^+ angular distributions it appears that this product is formed by a complex mechanism at collision energies up to 5.9 eV. In accord with this observation, the lifetime of the molecule-ion with respect to H_2O^+ formation via the "supertight" critical configuration is several spinning rotations at energies above 5 eV. Since barycentric symmetry of the OH^+ distribution cannot be taken as evidence for complex formation, we cannot determine the range of collision energies in which this product is formed via a persistent intermediate.

However, the "superloose" O_2H^+ critical configuration clearly fails to explain the symmetry observed in the $\text{O}_2^+(\text{H}_2, \text{H})\text{O}_2\text{H}^+$ reaction at energies up to 4 eV. As shown in Fig. V-1, the lifetime of the molecule-ion with

respect to dissociation by this channel is shorter than a tumbling period at relative energies above 1.8 eV and less than a rotation about the unique axis above 2.7 eV. Since the lifetime of the excited intermediate is governed by the channel with the largest rate constant, the failure of the "superloose" O_2H^+ structure to predict a sufficiently long lifetime for this channel indicates that the agreement between the SLST calculated breakdown curve and the product ion ratios measured in the beam experiments is not very significant.

We can reconcile the breakdown curve agreement and the failure of the lifetime prediction by inspection of Eq. V-5. At a fixed total energy the denominator, the density of states of the molecule-ion at E , is identical for all product channels. The $W^\ddagger(E-\epsilon_0)$ term, the number of states of the activated complex with energy less than or equal to $(E-\epsilon_0)$, is determined by the choice of critical configuration frequencies. Thus, the calculated product ion intensity ratios are functions solely of the relative number of states in each critical configuration. The absolute rate constants, on the other hand, are functions not only of the critical configurations but also depend on the density of states of the excited molecule-ion. In the Vestal³ direct count of states method all oscillators are assumed to be harmonic. Several authors¹⁰ have calculated corrections to the density and totality of states due to anharmonicity. The importance of anharmonicity increases with increasing molecular energy. From the treatment of Haarhoff,^{10a} the anharmonic correction increases the density of states of $HOOH^+$ at a total energy of 5.7 eV by a factor of 4.7. We estimate the correction factors to the totality of states of the activated complexes to be 1.3 for OH^+ and O_2H^+ and 1.8 for H_2O^+ . Thus, at a total

molecule-ion energy of 5.7 eV, the calculated lifetimes with respect to dissociation to O_2H^+ and OH^+ are increased by a factor of 3.5 and that for H_2O^+ is increased by a factor of 2.6. This longer lifetime for decay to O_2H^+ is still too low to be consistent with the O_2H^+ low energy angular distributions.

These anharmonicity corrections are also applicable to the lifetime curves shown in Fig. V-2 computed for the "Rigid 1" configurations. For this frequency set the OH^+ and O_2H^+ lifetimes are in accord with the formation of these ions via a long-lived complex. An increase in the H_2O^+ lifetime (by a factor of three) due to anharmonic corrections raises the calculated curve for this ion to about one rotational period about the unique axis.

The failure of the SLST transition state set to account for the observed O_2H^+ symmetric angular distributions at relative energies up to 4.5 eV can be interpreted in two ways. The large excess intensity of O_2H^+ compared with the cross-sections of the other products at low energies can be explained as a consequence of the contribution of a direct mechanism for formation of this ion at all collision energies. In fact, Mahan⁶ has shown that $\text{O}_2^+(\text{}^2\pi_g)$ can react directly with H_2 via a planar nonlinear intermediate. Since at low energies the O_2H^+ intensity is concentrated at centroid, this direct interaction must lead to highly excited products. Since the apparatus velocity and angular resolution is poor in the low energy experiments, a slight asymmetry of the scattering distributions due to direct interaction could not be detected. If the direct contribution to the O_2H^+ signal were substantial, we would not expect the QET to predict an O_2H^+ intensity

an order of magnitude higher than either the OH^+ or H_2O^+ intensity. In this case, the "Rigid 1" O_2H^+ critical configuration, which at relative energies below 4 eV predicts a decay lifetime greater than a tumbling period, would be an acceptable description of the O_2H^+ transition state. Furthermore, the "supertight" H_2O^+ critical configuration yields lifetimes commensurate with the energy dependence of the H_2O^+ scattering distributions, and either the "Rigid 1" or SLST transition state structure for OH^+ gives reasonable decay times of the molecule-ion to this product. By inspection of the H_2O^+ and OH^+ lifetime curves in Fig. V-1 and the O_2H^+ curve in Fig. V-2, we see that the anharmonic corrections to these three critical configurations at 5.7 eV produces a set of transition states which predict about equal intensities of OH^+ , H_2O^+ and O_2H^+ and lifetimes with respect to dissociation longer than a tumbling period. If these critical configurations are correct representations of the dissociation process all the extra O_2H^+ can be explained by direct formation of this ion.

The disparity between the product ion intensity ratios determined in the beam and electron bombardment experiments can then be explained by noting that direct formation of O_2H^+ does not occur in the electron bombardment dissociation of hydrogen peroxide. It is also possible that part of the H_2O^+ intensity measured by Foner and Hudson is due to the presence of water in their reaction vessel. If this were the case, their H_2O^+ signal would be too high and the "Rigid 1" critical configuration for H_2O^+ would be an inapt description of this transition state.

An alternative explanation for the failure of QET to predict the energy dependence of the product ion distributions in the beam experiments

is that there is strong vibration-rotation coupling in the excited intermediate due to the large angular momentum of the HOOH^+ . Unimolecular decay theory assumes that the density and totality of states of an activated molecule is solely dependent upon the phase space available to internal vibrational motion. However, if at relative energies above an electron volt all the collisional angular momentum becomes rotation about the O-O axis of HOOH^+ the rotational period ($\sim 3 \times 10^{-14}$ sec) would be comparable to the mean vibrational period of the molecule (2.5×10^{-14} sec). Consequently, the vibration-rotation coupling may be strong enough to invalidate density and totality of states calculations based solely upon vibrational motion. The small amount of total angular momentum of excited molecule-ions formed by electron bombardment renders this vibration-rotation interaction relatively unimportant and the enumeration of states methods employed are valid for this type of experiment.

The effect of molecular rotations that are "active" in exchanging energy with vibrational modes can be estimated by writing the expression for the RRKM rate constant as:

$$k \cong \langle \nu \rangle \left(\frac{E - \epsilon_0 + E_{z.p.}}{E + E_{z.p.}} \right)^{s+r/2-1} \quad (\text{V-7})$$

where s and r are respectively the numbers of oscillators and active rotations. If we assume that the rotation about the unique axis and the two tumbling rotations are all active then the "effective" number of oscillators of the molecule-ion is increased by $3/2$. Taking the average bond strength of HOOH^+ as 4 eV, the lifetime of the complex at an excitation energy of 5.7 eV is increased by a factor of

$$\left(\frac{E + E_{z.p.}}{E - \epsilon_0 + E_{z.p.}} \right)^{3/2} = \left(\frac{6.4}{2.4} \right)^{3/2} = 4.4$$

Thus anharmonic effects and inclusion of "active" rotations in the rate constant expression combine to increase the calculated lifetime of the intermediate by a factor of about thirteen. By pushing of statistical unimolecular decomposition theory to its limit we can increase all the proposed critical configuration lifetimes, except the "superloose" O_2H^+ structure, to values of several tumbling rotations at total energies above 4 eV. However, the large excess of O_2H^+ must still be rationalized as a consequence of direct interaction.

In the alkali-atom alkali halide reactions, the moments of inertia of the intermediates are considerably larger than the moment of inertia about the unique axis of $HOOH^+$, and therefore, the rotational periods are considerably longer than the mean vibrational period, and vibration-rotation coupling is less important than in the $O_2^+-H_2$ reactions. The approximate equality of vibrational and rotational periods in the present experiments indicates that barycentric product symmetry does not necessarily prove statistical equilibrium of the intermediate. Since several vibrations are necessary to attain equilibrium between the modes of the molecule-ion, non statistical dissociation can occur even though the complex has undergone several rotations.

F. The Low Energy O_2D^+/O_2H^+ Isotope Effect

Critical configurations analogous to those proposed for formation of O_2H^+ from $O_2^+-H_2$ were used to calculate the O_2D^+/O_2H^+ intensity ratios at collision energies below 5 eV. The transition states leading to O_2D^+ and O_2H^+ differ only in the changes in vibrational frequencies caused by isotopic substitution. For all trial activation state frequency sets the calculated isotope ratios, O_2D^+/O_2H^+ , are between 1.7 and 2, whereas the experimental ratios at both 3.5 and 4.9 eV are about 5 (Table IV-4). The low calculated isotope ratio is not unexpected at excitation energies significantly higher than the product appearance potentials since the frequency differences in the modes which are not identical for the O_2D^+ and O_2H^+ transition states are of the order of $\sqrt{2}$. Only near threshold are the computed isotope effects substantial because in this region the phase space available to each transition state is governed largely by the zero point energy differences between the isotopic products. The vibration-rotation coupling effect upon the two product intensities should be comparable and thus direct interaction must be invoked to explain the large experimental isotope effects. As noted in the discussion of the high energy isotope effects, the relative energy of the projectile with respect to the D atom is twice that with respect to the H atom. Therefore, the threshold for direct D atom abstraction would be expected to be lower than that for H atom abstraction and we would expect a low energy direct isotope effect to favor O_2D^+ .

G. Summary

The angular distributions of O_2H^+ , OH^+ , and H_2O^+ formed by the interaction of $\text{O}_2^+(^2\pi_g)$ and H_2 at low collision energies indicate that these reactions proceed through a persistent collision complex. The intensity of O_2H^+ exceeds the intensities of the other products by about an order of magnitude. These product ion intensity ratios differ significantly from the breakdown curves of hydrogen peroxide determined by electron bombardment, which have a large excess of H_2O^+ .

Using QET and two sets of transition state frequencies we find that one set explains the electron bombardment product distribution and the other agrees with the beam relative cross-sections. Both sets predict lifetimes of the excited intermediate that are too short to be in accord with the product ion angular distributions. Furthermore, neither frequency set explains the observed $\text{O}_2\text{D}^+/\text{O}_2\text{H}^+$ isotope ratio.

There are two explanations for the failure of unimolecular decay theory to predict both the product ion intensity ratios and the lifetime of the intermediate complex in the beam experiments. The large excess of O_2H^+ is rationalized as the result of formation of this ion by direct interaction at all collision energies. To be consistent with the symmetric angular distributions of this product at relative energies up to 4 eV, this direct mechanism must produce O_2H^+ ions with high internal excitation. The high $\text{O}_2\text{D}^+/\text{O}_2\text{H}^+$ isotope effect is also a consequence of this direct interaction, since at low energies both unimolecular dissociation and atom abstraction favor the D product.

The large angular momentum of the HOOH^+ formed in the beam experiments produces a situation in which the rotational period of the intermediate about the unique axis is comparable with the mean vibrational period. There is thus a substantial vibration-rotation coupling which may seriously alter the density and totality of states of the excited molecule-ion and the transition states. Since statistical theory assumes that the density and totality of states functions can be calculated solely from the partitioning of the excitation energy over the normal vibrational modes, QET underestimates these functions. It is therefore suggested that in its present form an RRKM type statistical theory may not be applicable to the decay of the intermediate formed in the beam experiments.

From the beam data in its present form it is not possible to separate the O_2H^+ product distributions into contributions from complex decay and from direct interaction. Deconvolution of these translational spectra might make this possible and would allow comparison between experimental and QET predicted product internal and kinetic energy distributions, which are more sensitive to state density calculations than are product ion intensity ratios. A study of the energy dependence of the experimental breakdown curves should provide further information on the extent of vibration-rotation coupling since this effect becomes more pronounced with increasing energy. These studies might also be extended to DOOD^+ since the moment of inertia about the unique axis is about twice that of HOOH^+ and the vibration-rotation coupling should be correspondingly smaller.

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APPENDIX - DECONVOLUTION

A. Introduction

This appendix describes a one-dimensional numerical deconvolution procedure that has been applied to some of the scattering experiments performed in our laboratory. The deconvolution technique has previously been used in conjunction with scattering data,^{1,2} as well as with radio astronomy aerial distributions,³ spectroscopic line width broadening,⁴ and electron impact ionization.⁵

In a beam experiment one is interested in extracting the scattered product specific intensity as a function of final relative velocity, translational exoergicity, barycentric angle or other basic parameter. What we actually measure in an experiment is the average of the specific intensity over the primary beam velocity and angle spread, the neutral gas velocity distribution, and the detector band width. For the one-dimensional treatment the effects of angular spread and out-of-plane scattering will be ignored. These factors have been taken into account by two and three dimensional analytical techniques developed in our laboratory.⁶

We can represent the measured laboratory output function, h , as the convolution of the ideal scattering function (specific intensity function), f , with the apparatus function g :

$$h(y) = \int_{-\infty}^{\infty} f(t)g(t-y)dt \quad (A-1)$$

This integral is usually abbreviated $h = f \circ g$. The term $g(t-y)$ includes the primary beam and neutral gas spreads and the detector band width. The procedure for inverting Eq. A-1 and extracting $f(t)$ is known as deconvolution.

In an experiment, primary and product ion intensities are measured as functions of laboratory velocity. If we assume that all products are scattered from the center-of-mass with a fixed relative velocity (or energy), the product ion laboratory velocity is:

$$v' = v_{cm} \pm u' \quad (A-2)$$

where

$$v_{cm} = \frac{m_o}{m_o + m_n} v_o + \frac{m_n}{m_o + m_n} v_n \quad (A-3)$$

m_o and m_n are the masses and v_o and v_n are the laboratory velocities of the primary ions and neutrals respectively (v_n is, of course, nominally equal to zero).

Thus the spread in the product ion laboratory velocity due to the width of the primary beam is:

$$\Delta v' = \frac{m_o}{m_o + m_n} \Delta v_o \quad (A-4)$$

and that due to the neutral gas distribution is:

$$\Delta v' = \frac{m_n}{m_o + m_n} \Delta v_n \quad (A-5)$$

The apparatus function, g , is the convolution of Δv_o and Δv_n scaled to the center-of-mass velocity, where Δv_o is the measured primary distribution including the detector band width and Δv_n is a one-dimensional Maxwell-Boltzmann distribution.

B. Smoothing

Before inversion of Eq. A-1 it is necessary to remove both random and non-random fluctuations from the output function. Non-random or compatible noise results from the convolution of the apparatus function with some real function and can only be removed by experimental refinements or mathematical techniques. Examples of this type of contribution to the output signal are mass overlap and out-of-plane scattering. The former is removed by the procedure discussed in Chap. IV, but compensation for the latter is very difficult and is neglected here.

Purely random or statistical noise arises in our experiments mainly from electronic pickup and primary beam fluctuations. The long time average of this type of spurious signal is zero; equivalently, the time average of the convolution of the apparatus function with the random noise function is zero. For the iterative smoothing operation we assume that this identity holds for each measured output function.

The output function can be expanded as⁵

$$h(y) = h_s(y) + n_I(y) \quad (A-6)$$

where $h_s(y)$ is the noiseless or smoothed output function (including the compatible noise) and $n_I(y)$ is the incompatible noise. The convolution of Eq.(A-6) with the apparatus function is

$$g \circ h(y) = g \circ h_s(y) + g \circ n_I(y) \quad (A-7)$$

where the second term on the right hand side is zero. Since the convolution operation is associative,³ Eq.(A-7) can be written as

$$h_{ls} = g \circ h_{obs} = g \circ (h_s + n_I) \quad (A-8)$$

where $(h_s + n_I)$ is the output function actually measured in the lab. Since $g \circ n$ is assumed to be identically zero, h_{ls} is a broadened real noiseless function. A method due to Van Cittert⁴ is commonly used^{1,3,5} to reduce this broadened distribution to the ideal smoothed product distribution.* This procedure takes the broadened product distribution, h_{ls} , and restores it to the ideal smoothed product distribution by the following iterative method:

$$h_{ns} = h_{(n-1)s} + g \circ (h_{obs} - h_{(n-1)s}) \quad (A-9)$$

An advantage of this iterative technique over Fourier smoothing (which will be discussed shortly) is that the Van Cittert procedure is localized, while the Fourier method is long range. The localized nature of the iterative technique can be understood by visualizing the overlap

* For a brief proof that this method does indeed approach the ideal smoothed product distribution see Ref. 3.

of the apparatus function with the output function (see Fig. A-1). Thus excessive noise in one region of the output function will not interfere with the smoothing operation in non-local portions of the output distribution.

C. Fourier Deconvolution

The Fourier method, although less satisfactory in practice than the iterative method, gives a clearer insight into both the smoothing and the deconvolution processes. It can be easily proven that the Fourier transform of the convolution integral:

$$T[h(y)] = T\left[\int_{-\infty}^{\infty} f(t)g(t-y)dt\right] \quad (A-10)$$

is equivalent to:

$$Th(y) = Tf(y)Tg(y) \quad (A-11)$$

Rearrangement of Eq.(A-11) followed by Fourier inversion yields:

$$f = T^{-1}(Tf) = T^{-1}(Th/Tg) \quad (A-12)$$

Although the Fourier method is mathematically straightforward⁷ and easily programmable, there are several constraints on the transforms, which severely limit the utility of this technique. Since the detector used to measure both the primary and product distributions has a finite band width, there is an upper limit to the frequencies which can be detected. That is, if one were to Fourier analyze a particular scattering function, one would in general need an infinite series of frequencies to

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Fig. A-1. Representation of the overlap between a "typical" apparatus function and "typical" output function. In the iterative smoothing and deconvolution procedures successive integrations are performed by placing the apparatus function peak directly above each point on the output curve. Note that each apparatus function positioning overlaps only a small section of the output function.

perfectly describe the function. However, since the apparatus function is insensitive to frequencies higher than some frequency, s_m , the effect of the finite dimensions of the apparatus function is to eliminate a semi-infinite band of frequencies above s_m and alter the relative amplitudes of the lower frequency components.

Bracewell and Roberts³ have shown that the observed distribution is completely determined by measurements spaced at equal intervals at least as small as $1/2 s_m^{-1}$. That is, $1/2 s_m^{-1}$ is the minimum useful sampling interval. From this it follows that no detail finer in width than this interval can be recovered in the scattering function. This resolution limit corresponds to one-half of the full width at half maximum, which in our experiments is equal to 2 to 3% of the primary beam energy.

Since the product distribution is the result of the convolution of the apparatus function with a normalized scattering function, it cannot contain any frequencies higher than s_m . Furthermore, if the transforms of h and g are normalized at $s = 0$, then at all other frequencies $|T(h)| < |T(g)|$. Since the amplitude of the transform of the product distribution can only exceed that of the apparatus function because of the contribution of incompatible noise, if $|T(h)|$ is found to be greater than $|T(g)|$ at any point, $|T(h)|$ is set equal to the value of $|T(g)|$ at that frequency.

Once the smoothed product distribution transform has been constructed, the transform of f , the scattering function transform, can be developed simply by taking the ratio of smoothed product transform to the apparatus function transform at discrete frequencies. The scattering function transform can then be straightforwardly inverted to produce the scattering function.

As noted previously, cutting off the product transform at the critical frequency s_m distorts the relative amplitudes of the lower frequency components of $T(h)$. This high frequency cutoff along with the truncation of $|T(h)|$ to $|T(g)|$ at frequencies where $|T(h)| > |T(g)|$ (this truncation general occurs at high frequencies) discourages convergence of the scattering function transform and usually results in an overly broadened scattering distribution. In actual practice, to produce a sufficiently convergent scattering function it is necessary to include Fourier components beyond s_m . This procedure, however, introduces spurious peaks in f , especially near the baseline. Therefore one must be particularly wary of side peaks in the scattering function which are neither partially visible in the output function nor plausible on physical grounds.

D. Iterative Deconvolution

It is possible to partially overcome the problem of spurious oscillations by the use of an iterative deconvolution operation, similar to the previously described iterative smoothing process. This method was also developed by Van Cittert⁴ in the early 1930's. As in the Fourier method, it is necessary to invert the convolution integral

$$h_s(y) = \int_{-\infty}^{\infty} f(x)g(x-y)dx \quad (A-13)$$

where h_s is the smoothed output function.

Since the only approximation to f available is the smoothed output function, we use h_s as the zero order guess to the inversion solution. The first approximation to the scattering function is:

$$f_1(y) = h_s(y) + [h_s(y) - h_s(y) \circ g] \quad (A-14)$$

We then use the following iterative procedure for f_n until $[h_s - f_{n-1} \circ g]$ becomes smaller than a suitable convergence limit.

$$f_n(y) = f_{n-1}(y) + [h_s(y) - f_{n-1} \circ g] \quad (A-15)$$

A computer program, which is listed at the end of this appendix, has been written to deconvolute one-dimensional distributions by using iterative smoothing and iterative deconvolution. Iterative deconvolution was found to give more acceptable results than Fourier deconvolution for most of the cases studied. This conclusion agrees with that of Ioup and Thomas¹ who correctly point out that the iterative method, by setting negative values of either $h(y)$ or $f(y)$ equal to zero, dampens spurious positive oscillations and hence produces fewer artificial peaks in the ideal scattering function. It was found that for the majority of data analyzed the fold of the ideal scattering function with the apparatus function could be made to converge to within a few percent of the smoothed output function. For these cases the fold is always broader than the output function, indicating that the deconvoluted scattering function gives an upper limit to the spread of the ideal scattering function.

It must be emphasized that in a significant number of cases convergent deconvolution was not possible without introducing oscillations

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Fig. A-2. Comparison of the measured intensity distribution of O_2^+ backscattered by He ($\square$) at 11.12 eV, with the same distribution after iterative smoothing and deconvolution (-). The apparatus function used ($\triangle$) is the convolution of the measured primary ion distribution with a neutral gas Maxwell-Boltzmann distribution. Note that deconvolution removes most of the signal from the forbidden regions: $Q > 0$ and $Q < -6.8$ eV.

Fig. A-3 Comparison of the measured intensity distribution of O_2^+ scattered by He at 5.56 eV through 180° in the center-of-mass system ($-\square-$) with the same distribution after iterative smoothing and deconvolution ($---$) using an apparatus function ($-\triangle-$) determined from the primary ion and neutral gas distributions. Deconvolution removes most of the signal in the forbidden region beyond $Q = 0$.

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Fig. A-3.

so severe as to make the results physically unrealistic. Therefore, numerical deconvolution cannot be used as a black box, but rather each deconvoluted result must be checked against both the physics of the scattering and the deconvoluted results of similar experiments.

Figures A-2 and A-3 are examples of the application of iterative smoothing and deconvolution to centerline velocity spectra of O_2^+ backscattered by He. In the 11.12 eV relative energy experiment (Fig. A-2), deconvolution narrows the measured half-width by 29%, and more significantly this procedure removes almost all the scattering in the energetically forbidden regions where $Q > 0$ and < -6.8 eV. Similarly, in Fig. A-3 the output function is narrowed by 23% and the signal beyond $Q = 0$ is greatly reduced. The side spikes in Fig. A-2 can be attributed to random noise not removed by the smoothing operation.

E. Program VOLUME

```

C VOLUTE PERFORMS A ONE-DIMENSIONAL DECONVOLUTION OF EITHER ENERGY OR
C ANGULAR DISTRIBUTIONS USING ITERATIVE SMOOTHING AND DECONVOLUTION.
C THE PRINTED OUTPUT LISTS IN ORDER - THE MEASURED PRIMARY BEAM DIS-
C TRIBUTION, THE APPARATUS FUNCTION REDUCED TO TO THE CENTER-OF-MASS,
C THE MEASURED OUTPUT FUNCTION, THE SMOOTHED OUTPUT FUNCTION, THE DE-
C CONVOLUTED RESULT, AND AS A CHECK, THE FOLD OF THE RESULT WITH THE
C APPARATUS FUNCTION. ALL FUNCTION AS TABULATED VS. LABORATORY VELOCITY
C IN UNITS OF E6 CM/SEC. THE NUMBER OF REQUIRED ITERATIONS AND THE PER-
C CENT CONVERGENCE ARE ALSO GIVEN FOR BOTH THE SMOOTHING AND DECON-
C VOLUTION OPERATIONS.
C
C A CAL-COMP PLOT OF THE RESULT(NO SYMBOLS), THE MEASURED OUTPUT FUNC-
C TION(SQUARES), AND THE APPARATUS FUNCTION(TRIANGLES) IS ALSO GENERATED.
C
      PROGRAM VOLUTE(INPUT,OUTPUT,TAPE 98,PLOT,TAPE 99=PLCT)
      DIMENSION XG(99),XH(99),G(99),H(99),HS(99),HC(99),HH(99),XE(2),NAM
      IE(8),HR(99),GI(99,99),DEL(99)
      CCOMMON/LABEL/LETTER1(8),LETTER2(8)
      READ 6, NTRS
C NTRS = NUMBER OF DATA SETS TO BE READ IN.
      6 FORMAT(I5)
      1100 READ 110, NEXP,ELAB,EREL,ECM,QPEAK,AMI,AMN,AMP
C NEXP = EXPERIMENT NUMBER, ELAB = PRIMARY BEAM LABORATORY ENERERGY(EV),
C EREL = RELATIVE ENERGY(EV), ECM = CM ENERGY(EV), QPEAK = PEAK Q VALUE(EV),
C AMI = PRIMARY ION MASS(AMU), AMN = NEUTRAL MASS(AMU). AMP = PRODUCT ION
C MASS(AMU). OF THESE CONSTANTSONLY ELAB, AMI, AMN, AND AMP ARE USED IN
C THE CALCULATIONS.
      110 FORMAT ( I5,7F10.5)
      READ 115, NAME
C ALPHANUMERIC FORMAT FOR IDENTIFICATION OF PRINTOUT.
      115 FORMAT(8A10)
      PRINT 111, NEXP
      111 FORMAT (18H1EXPERIMENT NUMBER,I7)
      PRINT 215, NAME
      215 FORMAT(1H0,8A10)
      PRINT 113, ELAB,EREL,ECM
      113 FORMAT (18H0LABORATORY ENERGY,F10.5,3X,15HRELATIVE ENERGY,F10.5,3X
      1,21HCENTER OF MASS ENERGY,F10.5)
      PRINT 114, QPEAK
      114 FORMAT (6H0QPEAK,F10.5)
      READ 1,NPG,NPH
C NPG AND NPH ARE THE INDICES OF THE APPARATUS AND OUTPUT FUNCTIONS
C RESPECTIVELY WHICH WILL BE PLOTTED AT THE SAME ABSCISSA VALUE ON THE
C GRAPHS. NPG IS GENERALLY THE INDEX OF THE APPARATUS FUNCTION PEAK.
      1 FORMAT (2I5)
      READ 3, TEMP,ING
C TEMP = TEMPERATURE CF THE NEUTRAL SCATTERING GAS(DEGK). ING = 0 MEANS
C ENERGY DISTRIBUTIONS. ING = 1 MEANS ANGULAR DISTIBUTIONS.
      3 FORMAT (F10.5,I5)
C PRIMARY AND PEAK DISTRIBUTIONS NORMALIZED TO PEAK VALUES OF UNITY
      DC 8 I = 1,99
      READ 2, XG(I),G(I),NSTOP
C G(I) IS THE EXPERIMENTAL APPARATUS FUNCTION MEASURED AT POINTS XG(I). A 1
C MUST BE PLACED IN COL 30 OF THE LAST CARD. DATA MUST BE ENTERED IN ORDER
C OF INCREASING ABSCISSA VALUE.
      IF (ING.EQ.1) GO TO 1058

```



```

      XG(I) = (AMI/(AMI+AMN))*1.39*SQRT(XG(I)/AMI)
1058 IF(NSTOP.EQ.1) GO TO 58
      8 CONTINUE
      58 NG = I
      2 FORMAT (2F10.5,I10)
      DC 9 I = 1,99
      READ 2, XH(I),H(I),NSTOP
C H(I) IS THE EXPERIMENTAL OUTPUT FUNCTION MEASURED AT POINTS XH(I). A 1
C MUST BE PLACED IN COL 30 OF THE LAST CARD. DATA MUST BE ENTERED IN ORDER
C OF INCREASING ABSCISSA VALUE.
      IF (ING.EQ.1) GO TO 1059
      XH(I) = 1.39*SQRT(XH(I)/AMP)
1059 IF(NSTOP.EQ.1) GO TO 59
      9 CONTINUE
      59 NH = I
      READ 115, LETTER1
      READ 115, LETTER2
C THE LAST TWO CARDS ARE ALPHANUMERIC GRAPH LABELS.
      GMAX = G(1)
      NGM = NG - 1
      DO 290 N=1,NGM
      IF(G(N+1)-G(N))290,292,292
292 IF(G(N+1) - GMAX) 290,293,293
293 GMAX = G(N+1)
290 CONTINUE
      HMAX = H(1)
      NHM = NH - 1
      DO 190 N=1,NHM
      IF(H(N+1)-H(N))190,192,192
192 IF(H(N+1) - HMAX) 190,193,193
193 HMAX = H(N+1)
190 CONTINUE
      PRINT 20
      20 FORMAT (6H1      X,15X,1HG)
      DO 40 I=1,NG
      G(I) = G(I)/GMAX
      40 PRINT 50, XG(I),G(I)
      50 FORMAT (F10.5,6X,F10.5)
      CALL CONVOL (XG,G,AMN,AMI,NPG,NG,TEMP,ING,ELAB)
      GSUM = G(1)*(XG(2)-XG(1))/2. + G(NG)*(XG(NG)-XG(NGM))/2.
      DO 250 K=2,NGM
250 GSUM = GSUM + G(K)*(XG(K+1)-XG(K-1))/2.
      DO 251 K=1,NG
251 G(K) = G(K)/GSUM
      XP = XG(NPG)
      DO 870 IK=1,NG
870 XG(IK) = XG(IK) + XH(NPH) - XP
      DO 300 J=1,NH
      DO 306 L=1,NH
      XLDEL = XH(NPH) - XH(J) + XH(L)
      IF(XLDEL.GT.XG(NG)) GO TO 307
      IF(XLDEL.LE. XG(1)) GO TO 307
      DO 303 I=1,NG
      IF(ABS(XLDEL-XG(I))-0.00001) 304,304,303
303 CONTINUE
      GO TO 302

```

```

304 FF = G(I)
    GO TO 301
302 CALL INTRAX (XLDEL,XG,G,NG,FF)
    GO TO 301
307 FF=0.0
301 GI(J,L) = FF
306 CONTINUE
300 CONTINUE
    GMAX = G(1)
    DO 599 N=1,NGM
        IF(G(N+1)-G(N)) 599,598,598
598 IF(G(N+1)-GMAX) 599,597,597
597 GMAX = G(N+1)
599 CONTINUE
    PRINT 21
    21 FORMAT (6H1      X,15X,4HGCON)
    DO 600 I=1,NG
        G(I) = G(I)/GMAX
600 PRINT 50,XG(I),G(I)
    PRINT 22
    22 FORMAT (6H1      X,15X,1HH)
    DO 41 I=1,NH
        H(I) = H(I)/HMAX
        HR(I) = H(I)
    41 PRINT 50, XH(I),H(I)
C IFN = 1 SMOOTHING OPERATION. IFN = 2 DECONVOLUTION OPERATION.
5001 IFN = 1
    201 NHL = NH - 1
        HSUM = H(1)*(XH(2)-XH(1))/2. + H(NH)*(XH(NH)-XH(NHL))/2.
        DO 1250 K=2,NHL
1250 HSUM = HSUM + H(K)*(XH(K+1)-XH(K-1))/2.
        DO 1251 K=1,NH
1251 H(K) = H(K)/HSUM
        DO 80 MM=1,NH
            80 HC(MM)=H(MM)
                DEL(1)=(XH(2)-XH(1))/2.
                DEL(NH) = (XH(NH)-XH(NHL))/2.
                DO 107 K=2,NHL
107 DEL(K) = (XH(K+1)-XH(K-1))/2.0
                NN= 1
            100 DO 4 J = 1,NH
C INTEGRATION
                IF (IFN.GT.1) GO TO 900
                IF(NN-2)900,1900,1900
            900 SUM = H(1)*GI(J,1)*DEL(1)+H(NH)*GI(J,NH)*DEL(NH)
                GO TO 1000
            1900 SUM=(HC(1)-HH(1))*GI(J,1)*DEL(1)+(HC(NH)-HH(NH))*GI(J,NH)*DEL(NH)
            1000 DO 160 L=2,NHL
                IF(IFN.GT.1) GO TO 901
                IF(NN-2)901,1901,1901
            901 SUM = SUM + H(L)*GI(J,L)*DEL(L)
                GO TO 160
            1901 SUM = SUM + (HC(L)-HH(L))*GI(J,L)*DEL(L)
            160 CONTINUE
                IF(IFN.GT.1) GO TO 2900
                IF(NN-2)700,1700,1700

```

```

700 HS(J) = SUM
   GO TO 4
1700 HS(J) = SUM + H(J)
   GO TO 4
2900 IF(NN.EQ.1) GO TO 2901
   HS(J) = H(J) + HC(J) - SUM
   GO TO 4
2901 HS(J) = 2.*HC(J) - SUM
   4 CONTINUE
   HB = ABS(HS(1))
   DO 90 N=1,NHL
   IF(ABS(HS(N+1))-ABS(HS(N)))90,92,92
92 IF(ABS(HS(N+1))-HB)90,93,93
93 HB = ABS(HS(N+1))
90 CONTINUE
   DO 75 L = 1,NH
   IF(HS(L).GE.0.0) GO TO 75
   HS(L) = 0.0
75 HH(L) = HS(L)
C CONVERGENCE CHECK
   HSUM = 0.0
   CHANGE = 0.0
   DO 81 MK=1,NH
   CHANGE = CHANGE + ABS(H(MK)-HS(MK))
81 HSUM = HSUM + ABS(H(MK))+ABS(HS(MK))
   CHUM = CHANGE/HSUM
C CONVERGENCE LIMIT MAY BE VARIED.
   IF(CHUM-0.00005)82,82,83
82 JKL = 1
   GO TO 85
83 JKL = 2
85 DO 86 L=1,NH
86 H(L) = HS(L)
   IF(JKL-1)101,101,11
11 NN= NN+ 1
C MAXIMUM NUMBER OF ITERATIONS MAY BE VARIED.
   IF(NN-050)100,101,101
101 IF (IFN.EQ.1) GO TO 13
   PRINT 24
24 FORMAT (6H1 X,15X,1HF)
   GO TO 33
13 PRINT 23
23 FORMAT (6H1 X,13X,7HHSMOOTH)
33 HMAX = H(1)
   DO 1033 N=1,NHM
   IF(H(N+1)-H(N)) 1033,1034,1034
1034 IF(H(N+1)-HMAX) 1033,1035,1035
1035 HMAX = H(N+1)
1033 CONTINUE
   DO 34 L= 1,NH
   H(L) = H(L)/HMAX
34 PRINT 50,XH(L),H(L)
   CHUM = CHUM*100.
   PRINT 880, NN,CHUM
880 FORMAT (21HONUMBER OF ITERATIONS,15,7X,19HPERCENT CCNVERGENCE,E10.
13)

```

```

      IF(IFN.EQ.2) GO TO 200
      IFN = 2
      GO TO 201
200  CALL VULCAN (XG,GI,XH,H,NH,NHL,DEL)
      IF(XH(1).LE.XG(1)) GO TO 830
      XE(1) = XG(1)
      GO TO 831
830  XE(1) = XH(1)
831  IF(XH(NH).GE.XG(NG)) GO TO 832
      XE(2) = XG(NG)
      GO TO 833
832  XE(2) = XH(NH)
833  CALL GRAPH (XH,H,NH,XH,HR,NH,XG,G,NG,XE,31HLABORATORY VELOCITY (E6
      1 CM/SEC),9HINTENSITY,16HLABORATORY ANGLE,ING)
4000 NTRS = NTRS - 1
      IF(NTRS) 1101,1101,1100
1101 CONTINUE
      END
      SUBROUTINE CONVOL (X,Y,AMN,AMI,NPG,NG,TEMP,ING,ELAB)
C  CONVOL FINDS THE CONVOLUTION OF THE MEASURED PRIMARY ION DISTRIBUTION WITH THE
C  MAXWELLIAN NEUTRAL SCATTERING GAS DISTRIBUTION AND THEREBY DETERMINES THE
C  ACTUAL APPARATUS FUNCTION
      DIMENSION X(99),Y(99),V(99),DEL(99),YC(99)
      RN = ((AMI+AMN)**2)/(0.000167*TEMP*AMN)
      VB = SQRT(2.*AMI*ELAB)/(AMI+AMN)
      IF(ING.EQ.1) GO TO 20
      DO 1 I=1,NG
1    V(I) = X(I)
      GO TO 25
20   DO 11 J=1,NG
      XC = X(J) - X(NPG)
11   V(J) = VB*TAN(0.01745*XC)
25   DEL(1) = ABS(V(2)-V(1))/2.
      DEL(NG) = ABS(V(NG)-V(NG-1))/2.
      ND = NG- 1
      DO 2 J=2,ND
2    DEL(J) = ABS(V(J+1)-V(J-1))/2.
      DO 3 K=1,NG
      SUM = 0.0
      DO 4 L=1,NG
4    SUM = SUM + Y(L)*EXP(-RN*(V(L)-V(K))**2)*DEL(L)
3    YC(K) = SUM
      DO 5 M=1,NG
5    Y(M) = YC(M)
      YMAX = Y(1)
      DO 7 N=1,ND
      IF(Y(N+1)-Y(N))7,8,8
8    IF(Y(N+1)-YMAX)7,9,9
9    YMAX = Y(N+1)
      NP = N + 1
7    CCNTINUE
      DO 10 J=1,NG
10   Y(J) = Y(J)/YMAX
      NPG = NP
      RETURN
      END

```

```

SUBROUTINE VULCAN (XG,GI,XH,H,NH,NHL,DEL)
DIMENSION DEL(99),XG(99),XH(99),GI(99,99),H(99),HV(99)
DO 1 J=1,NH
SUM = H(1)*GI(J,1)*DEL(1)+H(NH)*GI(J,NH)*DEL(NH)
DO 2 L=2,NHL
2 SUM = SUM + H(L)*GI(J,L)*DEL(L)
1 HV(J) = SUM
HVMAX = HV(1)
DO 3 K=1,NHL
IF(HV(K+1)-HV(K))3,4,4
4 IF(HV(K+1)-HVMAX)3,5,5
5 HVMAX = HV(K+1)
3 CONTINUE
PRINT 6
6 FORMAT (6H1      X,15X,4HFOLD)
DO 7 M=1,NH
HV(M) = HV(M)/HVMAX
7 PRINT 8, XH(M),HV(M)
8 FORMAT (F10.5,6X,F10.5)
RETURN
END
SUBROUTINE INTRAX (XL,X,Y,N,FF)
C INTRAX USES NTPO FOR A 3 POINT LOGARITHMIC INTERPOLATION OR EXTRAPOLA
C TION OF THE APPARATUS FUNCTION.
DIMENSION X(99),Y(99),XU(3),YU(3)
NN = 3
MN = N - 1
IF(XL.LT.X(2)) GO TO 1
IF(XL.GT.X(N-1)) GO TO 3
DO 5 I = 3,MN
5 IF(XL.LT.X(I)) GO TO 6
6 IF((XL-X(I-1)).LE.(X(I)-XL)) GO TO 7
MI = I - 1
GO TO 4
7 MI = I - 2
GO TO 4
1 MI = 1
GO TO 4
3 MI = N - 3
DO 2 I=1,3
XU(I) = X(MI+I-1)
2 YU(I) = Y(MI+I-1)
CALL NTPO (XL,FI,NN,XU,YU)
FF = FI
RETURN
END
SUBROUTINE NTPO (XX,FF,N,X,F)
C MODIFIED VERSION OF NTPO BY DAVID SNYDER LRL BERKELEY 7/14/65
C THIS ROUTINE FITS A (N-1)TH ORDER POLYNOMIAL TO THE N PCINTS (X,F)(I)
C AND EVALUATES THIS POLYNOMIAL AT THE POINT XX.
C XX = INTERPOLANT
C FF = F(XX)
C N = NUMBER OF SAMPLE POINTS (X,F)
C X = ARRAY OF ABSCISSA VALUES (NO TWO THE SAME)
C F = CORRESPONDING ARRAY OF ORDINATE VALUES
DIMENSION X(1),F(1),GY(99)

```

```

      F0 = 0.
CAN USE GENERAL FORMULAS,  XX.NE.ANYX(M)
      DO 1 I=1,N
      IF(F(I).EQ.0.0) GO TO 3
      GY(I) = ALOG(F(I))
      GO TO 1
3     GY(I) = 0.0
1     CONTINUE
      DO 100 I=1,N
      PAK = GY(I)
      XI = X(I)
      DO 50 K=1,N
      IF(K.EQ.I) GO TO 50
      AK = XX - X(K)
      PAK = PAK * AK / (XI-X(K))
50    CONTINUE
      F0 = F0 + PAK
100   CONTINUE
C GIVE ANSWERS TO CALLING PROGRAM AND RETURN
210   FF = EXP(F0)
      RETURN
      END
      SUBROUTINE GRAPH (X,Y,N,X2,Y2,N2,X3,Y3,N3,XE,RX,RY,RZ,ING)
      COMMON/LABEL/LETTER1(8),LETTER2(8)
      COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
      DIMENSION ROUNDX(9),ROUNDY(5),X(1),Y(1),XE(2)
      DATA(ROUNDX(I),I=1,9)/2.,2.5,3.,3.5,4.,4.5,5.,6.,9./
      DATA (ROUNDY(I),I=1,5)/1.,1.1,1.2,1.3,1.4/
      DATA NROUNDX,NROUNDY,PARTX,PARTY/9,5,10.,10./
      CCXMIN=100.$CCXMAX=1100.$CCYMIN=89.$CCYMAX=1089.
      CALL LINEUP(XE,2,ROUNDX,NROUNDX,PARTX,XMIN,XMAX)
      CALL LINEUP (Y,N,ROUNDY,NROUNCY,PARTY,YMIN,YMAX)
      CALL CCGRID (1,10,6HNOLBLS,1,10)
      CALL CCLBL(IFIX(PARTX),IFIX(PARTY))
      CALL CCLOT (X,Y,N,4HJOIN)
      CALL CCLOT (X2,Y2,N2,4HJOIN,7,1)
      CALL CCLOT (X3,Y3,N3,4HJOIN,8,1)
      IF(ING.EQ.1) GO TO 1
      CALL CCLTR (485.,12.,0,2,RX)
      GO TO 2
1     CALL CCLTR (485.,12.,0,2,RZ)
2     CALL CCLTR (23.,530.,1,2,RY)
620   FORMAT (8A10)
      WRITE(98,620) LETTER1
      CALL CCLTR (150.,1000.,0,2)
      WRITE(98,620) LETTER2
      CALL CCLTR(150.,950.,0,2)
      CALL CCNEXT
      RETURN
      END

```

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