Dynamics of the reaction of O\textsuperscript{-} with D\textsubscript{2} at low collision energies: reagent rotational energy effects

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The effects of reagent rotational excitation on the dynamics of the O\textsuperscript{-} + D\textsubscript{2} particle transfer reaction are investigated in a crossed molecular beam experiment. Vibrational-state-resolved angular distributions are measured at collision energies of 0.22, 0.25, and 0.37 eV as a function of the rotational temperature of the D\textsubscript{2} reactant gas, which ranges between 58 and 425 K. When the rotational temperature of the D\textsubscript{2} is lowered, the angular distributions become more strongly backward scattered with a tighter, more intense peak at 180°. In addition, the relative amounts of forward and sideways scattering are decreased. We interpret these product angular distributions as reflecting specific geometries required for passage through the critical transition state region of the potential energy surface where the particle transfer and electron detachment channels compete. Reagent rotational motion correlates to motion in the transition state that is selectively coupled to electron detachment. The more rotational energy present in the reagents, the smaller the probability that the complex remains linear and produces backward-scattered OD\textsuperscript{-}. The product vibrational-state distributions change by only a few percentage points with the variation in rotational energy. While the small difference in the amount of rotational energy present in this system strongly influences the mechanism of particle transfer, it may not significantly alter the number of trajectories leading to that channel. The dynamics of this system are discussed in terms of a local complex potential describing nuclear motion in the critical region of the potential surface.

1. Introduction

The role of reagent rotational energy in reactive collisions has been the focus of considerable experimental and theoretical research.\(^{1,2}\) The vast majority of these studies have been concerned specifically with the influence of rotation on chemical reactivity. It has been shown that the magnitude of the rotational effect depends greatly on the overall characteristics of the potential energy surface on which the collision event occurs and, to a lesser extent, the pre-collision conditions.\(^{3}\) If an optimum transition geometry exists for the reaction, increased reactant rotation may disrupt the preferred orientation, thus lowering the reactive cross section. Conversely, rotational energy can be transformed into translational energy along the reaction coordinate, enhancing the probability for crossing the barrier. The full effect of rotational energy on the reactive cross section may be interpreted as resulting from the competition between these orientation and energy effects. Early molecular beam experiments by Bernstein and co-workers\(^{4,5}\) examined the influence of reagent rotational energy on the reactivity of alkali exchange reactions involving an intermediate. Reactive branching functions were measured using reagent beams with different rotational state distributions for the endothermic reaction CsF + K ⇄ [CsFK] → Cs + KF and the exothermic reaction RbF + K ⇄ [RbFK] → Rb + KF. First, an effusive oven was used to produce a “thermal” molecular beam with a Boltzmann distribution of rotational states. When desired, an electrostatic quadrupole focusing field was switched on to focus those molecules with low rotational states creating a “low-J” beam. This rotational state selection effectively removed 2.4 kcal mol\(^{-1}\) of energy from the collision system in the CsF + K experiments\(^6\) and 2.0 kcal mol\(^{-1}\) in the RbF + K experiments.\(^7\) Decreasing the reagent rotational energy inhibited the decomposition of the intermediate complex in the CsF + K system but promoted its decomposition in the RbF + K system. While rotational energy was significantly less effective than relative translational energy at promoting reactive decay for CsF + K, the magnitude of the rotational energy effect was comparable to the effect for a similar reduction in translational energy in RbF + K. In a recent study, the effect of reagent rotation on total reactivity in the Cl + H\(_2\) system was investigated by Lee et al.\(^8\) State-specific excitation functions were obtained for the reaction by employing different sources for the Cl reagent and both normal and para-H\(_2\). For reactions with ground state Cl(\(^2\)P\(_{1/2}\)), the rotation of the H\(_2\) reagent has little impact on the reactivity of the system at low collision energies (\(\leq 3.5\) kcal). At higher energies, however, rotation plays a significant role in promoting the reaction. Far fewer studies have examined the effect of reagent rotation on the specific dynamics of a reaction. There have been some examples of rotational energy effects on isotopic branching ratios in ion-molecule systems. One particularly interesting example concerns the O\textsuperscript{+} + HD reaction and the effect of the HD rotational temperature. A rotationally adiabatic capture theory by Dateo and Clary\(^2\) evaluates the branching ratio for OH\textsuperscript{+} to OD\textsuperscript{+} production by considering the rate of passage over a J-dependent centrifugal barrier and the orientation of HD with respect to O\textsuperscript{+} at the barrier maximum. The center-of-mass and the center-of-polarization for the HD molecule do not coincide; thus the approach of an O\textsuperscript{+} ion creates a torque on a static or slowly rotating molecule. This torque tends to align the hydrogen atom end of the molecule toward...
the incoming ion, which favors the production of OH\textsuperscript{+}. As rotation in the HD molecule increases, the anisotropic of the potential averages out and the product branching ratio approaches 50\%. Guided ion-beam experiments by Sunderlin and Armentrout\textsuperscript{9} and drift tube studies by Viggiano et al.\textsuperscript{9} have separately confirmed these predictions. Another rotational energy effect based on the asymmetry of the mass distribution in HD was predicted in a set of trajectory studies on the F + HD system by Muckerman.\textsuperscript{6,11} Nonrotating reagents form DF more readily than HF since the larger mass of the D atom results in a wider and less skewed product channel. Rotation in the HD molecule causes the lighter hydrogen atom to sweep out a much larger volume than the deuterium atom because the center-of-mass lies toward the deuterium end. This shields the deuterium atom from the incident fluorine atom and leads to increased reactivity for the hydrogen end. The effect of reagent rotation on the partitioning of energy among the product degrees of freedom has not been widely investigated. In a pump–probe experiment on O(\textsuperscript{1}P) + HCl, Zare et al.\textsuperscript{13} found that product energy disposal was independent of reagent rotational state and excess rotational energy was nearly equipartitioned among the product degrees of freedom.

In this paper we present evidence that specific features of the potential energy surface for the reaction of O\textsuperscript{+} + D\textsubscript{2}, the subject of ongoing study in our laboratory, lead to a strong dependence of the differential cross section on reagent rotational energy. A rate constant study by Viggiano et al.\textsuperscript{13} on the hydrogenated system in which the rotational temperature of H\textsubscript{2} was varied failed to reveal any significant effect on the rate or the branching ratio of particle transfer to electron detachment. However, the present study demonstrates that rotational effects manifest themselves in the differential cross section, particularly in the product angular distribution. The correlation of reagent rotational motion to motion in the transition state that is selectively coupled to electron detachment is primarily responsible for the effects we observe.

In our previously published work on this system,\textsuperscript{14,15} we measured the differential cross sections for the particle transfer reaction (1):

\[ \text{O}^+ + \text{D}_2 \rightarrow \text{OD}^- + \text{D} + 0.26 \text{ eV} \] (1)

over the collision energy range from 0.25 to 1.20 eV and resolved the angular distributions for individual vibrational states of OD\textsuperscript{−}. As a continuation of that study, we have extended the collision energy range down to 0.22 eV and carried out experiments in which the rotational temperature of the molecular reactant gas was varied by controlling the conditions of the supersonic expansion forming the beam. Collision energies of 0.22, 0.25, and 0.37 eV have been chosen for the rotational temperature experiments because the effect of reagent rotational energy is most readily observable at low energies, where the system is more sensitive to features of the potential energy surface. We have measured the product translational energy distributions again and observed structure corresponding to the formation of OD\textsuperscript{−} in specific vibrational states. We report product angular distributions that reflect the specific geometries required for passage through critical regions of the potential energy surface where particle transfer and electron detachment compete.

\textit{Ab initio} calculations on the [H\textsubscript{2}O\textsuperscript{−}] potential energy surface by Werner et al.\textsuperscript{16} have been particularly instructive in interpreting the experimental data. The salient results of those calculations are summarized here. The approaching O\textsuperscript{−} and H\textsubscript{2} reagents reactant to OH\textsuperscript{−} (\textit{Σ}\textsuperscript{−}) + H(8\textsubscript{S},2) along a collinear 2\textit{Σ}\textsuperscript{−} surface. This 2\textit{Σ}\textsuperscript{−} surface contains two shallow minima separated by a barrier. The attraction of the approaching reagents leads to the first minimum in which O\textsuperscript{−} is electrostatically bound by an ion–quadrupole interaction to H\textsubscript{2} in a collinear O\textsuperscript{−}−HH geometry. Hydrogen atom transfer occurs over a small barrier to a second local minimum, identified as OH\textsuperscript{−}−H. Decomposition of this second complex, formally a saddle point on the potential energy surface, leads to the OH\textsuperscript{−} + H products. Calculations in non-collinear geometries have determined that bending motion at this saddle point defines the coordinate leading to associative detachment\textsuperscript{15,19} forming H\textsubscript{2}O + e\textsuperscript{−} and no barrier exists along the pathway from OH\textsuperscript{−}−H to the H\textsubscript{2}O + e\textsuperscript{−} continuum. This direct pathway to the H\textsubscript{2}O + e\textsuperscript{−} continuum is consistent with the observation that the associative detachment reaction between OH\textsuperscript{−} and H to form H\textsubscript{2}O + e\textsuperscript{−} occurs at the Langmuir rate.\textsuperscript{19} Therefore, competition between electron detachment and particle transfer takes place in the region of the saddle point of the potential surface. The branching ratio is controlled both by transit time through this region and the nature of the bending motion of the OH\textsuperscript{−}−H species. At the low energy limit, only trajectories that follow the minimum energy reaction path and maintain a collinear geometry will result in particle transfer products.

Associative detachment is the predominant reactive process, especially at very low collision energies. In drift tube measurements at near-thermal energies, Parkes\textsuperscript{20} found the total reaction rate constant of the O\textsuperscript{−} + D\textsubscript{2} system to be 4.9 × 10\textsuperscript{−10} cm\textsuperscript{3} molecule\textsuperscript{−1} s\textsuperscript{−1} and the branching ratio of associative detachment to particle transfer to be 0.98 : 0.02. With increasing collision energy the rate of the associative detachment reaction decreases sharply. However, the total rate of O\textsuperscript{−} destruction is independent of collision energy over the range from thermal to 0.9 eV,\textsuperscript{21} the decrease in the rate of the associative detachment reaction is completely accounted for by a rapid increase in the particle transfer rate. Particle transfer eventually becomes the favored reaction channel at energies above approximately 1.1 eV.\textsuperscript{21}

2. Experimental

A detailed description of the crossed beam apparatus used for this study has appeared in a previous publication,\textsuperscript{22} thus only a brief overview of the experimental method will be provided here. The O\textsuperscript{−} ions were produced by electron impact on N\textsubscript{2}O at a pressure of approximately 0.01 Torr and formed into a beam with a magnetic mass spectrometer. The ion beam laboratory energy distribution was nearly triangular in shape with a full-width at half-maximum of ~0.25 eV. Center-of-mass collision energies ranging from 0.22 to 0.37 eV required lab energy beams ranging from 0.75 to 1.50 eV.

The neutral D\textsubscript{2} beam was produced in three ways in order to provide three different populations of rotational states. The model of Gallagher and Fenn\textsuperscript{23,24} was employed to estimate the rotational temperature of the D\textsubscript{2} gas in the neutral beam. This method estimates the decrease in rotational temperature of the expanding gas, initially at a specific stagnation temperature and pressure, along a flow streamline of the isentropic expansion. The terminal rotational temperature is expressed in terms of the distance downstream from the nozzle exit, the rotational collision number, the heat capacity ratio, and the initial temperature and pressure of the expanding gas, assumed to be ideal. Numerical solutions to the rotational relaxation equation as a function of the properties of the gas and the characteristics of the expansion have been given. Poulson and Miller\textsuperscript{25,26} have incorporated these solutions into a more convenient graphical form. Rotationally resolved photoelectron spectroscopy studies of supersonic molecular beams of D\textsubscript{2} by Pollard et al.\textsuperscript{27} confirmed the Gallagher and Fenn estimates of rotational temperatures for stagnation temperatures over the range 300–700 K. In addition, effective rotational temperatures for D\textsubscript{2} beams with stagnation temperatures down to 78 K have been indirectly determined by Kern et al.\textsuperscript{28} via a pseudo-random time-of-flight technique. At
low \( p_0 d \) values (\( p_0 = \) stagnation pressure; \( d = \) nozzle diameter) the rotational temperatures observed were in good agreement with those determined by the method of Gallagher and Fenn. While the rotational temperatures of the beams in our experiments were not experimentally measured, the operating conditions used, including nozzle diameter, nozzle-skimmer distance, and stagnation pressure, were comparable to those employed in these other experimental studies.

The Gallagher and Fenn model for estimating rotational temperatures led us to three different sets of expansion conditions. In the first, a \( \text{D}_2 \) beam was prepared by expanding the neat gas at a stagnation pressure of 600 Torr and a temperature of 300 K through a 7 micron nozzle. This will be referred to as our "normal" beam. The estimated rotational temperature is 195 K, corresponding to 0.016 eV of rotational energy in the \( \text{D}_2 \) reagents. A second set of conditions, used to produce what we term "cold" reagents, consisted of a stagnation temperature and pressure of 77 K and 250 Torr, respectively. The rotational temperature of the resultant beam is estimated to be 58 K, corresponding to an average \( \text{D}_2 \) rotational energy of 0.0035 eV. The final set of expansion conditions was used to produce what we term a "hot" reagent beam. The stagnation region was heated to 550 K, while the stagnation pressure was reduced to 450 Torr. The rotational temperature is approximately 425 K, which reflects a rotational energy of 0.035 eV. Fig. 1 shows the rotational population distributions for these three sets of expansion conditions. The effect on the distribution of cooling the nozzle from room temperature to 77 K is fairly dramatic; the population relaxes on the distribution of cooling the nozzle from room temperature of approximately 425 K, which reflects a rotational energy of 0.035 eV. Fig. 1 shows the rotational population distributions for these three sets of expansion conditions. The effect on the distribution of cooling the nozzle from room temperature to 77 K is fairly dramatic; the population relaxes into the first three \( J \) levels, with the majority of the molecules possessing no rotational energy. A less pronounced change in the distribution occurs when the nozzle is heated to 550 K. The maxima in the hot and normal distributions occur for \( J = 2 \), but the \( J = 0 \) and \( 1 \) states for the hot distribution are reduced in population two-fold. In addition, the \( J = 3 \) and \( 4 \) states are enhanced in the hot distribution nearly four-fold and significant population remains in states as high as \( J = 8 \). Although the differences between the hot and normal distributions appear to be subtle, we will show later that significant variations can be observed in the product differential cross sections measured under all three sets of expansion conditions. Following the expansion, the beam was collimated to 2° by a 1.0 mm electroformed skimmer and a 3.5 mm square aperture. A tuning fork chopper modulated the beam at 30 Hz to provide the synchronization for the experiment.

Varying the rotational temperature of the \( \text{D}_2 \) by heating or cooling the nozzle also changed its laboratory translational energy. To maintain a constant relative collision energy, the laboratory energy of the ion beam was adjusted accordingly. Therefore, the ion beam energy was lowered for the experiments with hot reagents, and raised for those with cold reagents.

The beams intersected at a 90° angle in the center of the collision chamber, which was maintained at \( 10^{-7} \) Torr with oil diffusion pumps. The scattered products were energy and mass selected using a rotatable electrostatic energy analyzer with a laboratory resolution of 0.07 eV in conjunction with a quadrupole mass filter. A dual microchannel plate ion detector accomplished actual product detection. Data were collected with a computer-controlled multichannel scalar synchronized with the beam modulation. The energy scale was calibrated at the beginning and end of each experiment by resonant charge transfer from \( \text{NO}^+ \), also produced by electron impact on \( \text{N}_2 \text{O} \) to \( \text{NO} \) expanded supersonically in the crossed beam. This calibration procedure generated a low energy marker at the energy of the NO neutral beam, \( ~0.09 \) eV. All experimental data were duplicated and experiments in which the energy of the primary ion beam drifted by more than 0.05 eV were discarded.

Two different types of experiments were performed. In the first, the particle transfer reaction (1) was examined at collision energies of 0.22, 0.25, and 0.37 eV with beams of \( \text{D}_2 \) produced under normal expansion conditions. At each collision energy, laboratory kinetic energy spectra were obtained for a set of 10 to 16 fixed lab scattering angles. Each energy spectrum consisted of either 80 or 120 points, with typical energy bin widths of 0.02 to 0.025 eV. This procedure resulted in data sets consisting of 800 to 1920 data points covering laboratory velocity space. With the exception of the 0.22 eV experiment, these data have been discussed in some detail in a previous report from our laboratory.\textsuperscript{14}

In addition to those experiments, a second set of experiments has been performed in which the rotational temperature of the \( \text{D}_2 \) reagent beam was varied as described above. Cross sections differential in energy and angle were measured at collision energies of 0.22, 0.25, and 0.37 eV with cold \( \text{D}_2 \) reagents and at 0.25 eV with hot reagents. The results of this set of experiments are first reported in the present paper.

### 3. Results and analysis

The objective of the data analysis program is to recover the unique center-of-mass cross section \( I_{\text{lab}}(u, \theta) \) from the laboratory (lab) data. As described in previous publications,\textsuperscript{14} this procedure is accomplished by transforming the laboratory flux distributions into the center-of-mass coordinate system with a pointwise iterative deconvolution procedure.\textsuperscript{29} The energy-independent differential cross section \( I_{\text{lab}}(u, \theta) \) is recovered from the lab data by inverting the transformation relation (2) with concomitant removal of the dispersion in beam velocities:

\[
I_{\text{lab}}(V, \theta) = \sum_{i=1}^{N} f_i \frac{V^2}{w_i} I_{\text{cm}}(u_i, \theta_i) \tag{2}
\]

The summation extends over a grid of \( N \) Newton diagrams that represents the dispersion in beam velocities and intersection angle; the \( i \)th diagram is weighted by the value \( f_i \). A grid of 125 Newton diagrams, composed of five velocities for each beam and five intersection angles, provided a thorough

**Fig. 1** Estimated rotational state distributions for \( \text{D}_2 \) reagent produced under three sets of expansion conditions, see text for details. The normal conditions (A) produce a beam with a rotational temperature of 195 K; the heated nozzle (B), 425 K; the cooled nozzle (C), 58 K.
average over the dispersion in initial conditions. The extracted center-of-mass cross section, transformed into the laboratory coordinate system with appropriate averaging over the initial conditions, recovered the experimental data with an average standard deviation of 6%. The center-of-mass flux distribution \( I_{cm}(u, \theta) \) generated this way is intrinsically non-separable in the variables \( u \) and \( \theta \).

The effects of reagent rotation on the dynamics of the particle transfer reaction are especially evident at the lowest collision energies where reactive trajectories more closely follow the minimum energy path on the potential surface. The center-of-mass flux distribution \( I_{cm}(u, \theta) \) for the OD\(^-\) products is plotted as a function of the polar coordinates \( u \) and \( \theta \) for the 0.22 eV experiment under normal D\(_2\) expansion conditions in Fig. 2. The cross section is biased toward the backward direction (with respect to the direction of the incoming O\(^-\) ion) but extends over the full range of scattering angles. A notable feature is the sharp spike in the backward direction corresponding to the formation of OD\(^-\) in the \( v' = 0 \) state. When the rotational temperature of the D\(_2\) is lowered, the flux distribution becomes more strongly backward scattered with a tighter, more intense peak at 180° as illustrated in Fig. 3. The analysis of the data is aided by an examination of the center-of-mass angular distributions for each collision energy at which the effects of the rotational energy on the particle transfer reaction are more pronounced. Figs. 4 through 6 display the product angular distributions for all experiments completed at each of the three collision energies. At 0.22 eV the cold D\(_2\) product angular distribution is more sharply peaked.

![Collision Energy = 0.22 eV Normal D\(_2\)](image)

\( E_{\text{ref}} = 0.22 \text{ eV} \)

![Total angular distributions for the 0.22 eV experiment with both normal and cold D\(_2\) reagent beams. The lines through the data points are provided only to help guide the eye. Error bars are indicated.](image)
in the backward direction than that of the normal D₂ experiment, as was suggested from the flux distributions. The half-
width of the backward peak is approximately 27° as compared to 35° for the room temperature data. In addition, the relative amounts of forward and sideways scattering are significantly reduced in intensity in the cold distribution. At 0.25 eV the overall distribution is shifted towards the backward direction for cold D₂ with a factor of two decrease in the relative amount of forward scattering. In addition, the hot reagent distribution for this energy is significantly different at higher angles. The number of products scattered at 90° to 120° is a factor of two larger with hot D₂ while the number of products scattered near 180° is a factor of two less than for normal D₂. Finally at the 0.37 eV collision energy the angular distributions for the normal and cold D₂ experiments are very similar in the forward and sideways directions. However, the cold D₂ distribution is again sharply peaked in the backward direction with more than twice the number of products scattered at 180° as in the normal D₂ case.

It should be noted that the center-of-mass product angular distribution for the 0.37 eV experiment with normal D₂ reagents reported here is slightly different than one reported previously. This experiment, like the other two normal expansion condition experiments, was performed just before the cold D₂ one at the same energy to ensure similar experimental conditions and was repeated to confirm the results. While the overall shape of the center-of-mass flux distribution for the OD⁻ products is similar to that of the earlier experiment, the center-of-mass angular distribution displays somewhat less product scattering in the backward direction. This collision energy accesses a critical region in which a fairly abrupt change in the reaction dynamics takes place. As the collision energy is increased in this regime the reaction changes from one occurring on the time scale of a rotational period to one of more direct dynamics. A slight variation in the energy is likely to be responsible for the differences in the overall scattering distributions between the two experiments.

The vibrational state populations were calculated by integrating the differential cross section determined from the deconvolution of the laboratory data over all center-of-mass scattering angles and over the range of center-of-mass speeds accessible to the specific vibrational state:

$$P(v') = \int_{\theta_{\text{min}}}^{\theta_{\text{max}}} \int_0^{2\pi} I^v_{\text{cm}}(u, \theta) \sin \theta \, d\theta \, du$$

At 0.22 eV two vibrational states are energetically accessible to the OD⁻ products; the slight majority are formed in the ground vibrational state. At 0.25 eV the two product vibrational states are essentially equally populated; however, an increase in collision energy to 0.37 eV results in a shift in population from $v' = 0$ to $v' = 1$. The state populations for the experiments in which reagent rotational energy was varied were calculated in the same manner and compared to the normal state distributions. For the cold 0.22 eV experiment and the hot 0.25 eV experiment only minor deviations from the normal state populations exist and these are within the experimental error. The cold experiments at 0.25 eV and 0.37 eV yield state populations with slightly more products in the ground state than their normal counterparts; however, these differences are right at the limit of the experimental error. Thus, the vibrational state populations appear to be fairly insensitive to the effects of changing the reagent rotational energy.

**4. Discussion**

Changing the reagent rotational excitation of this system results in significant variation in the product angular distributions at collision energies of 0.22, 0.25, and 0.37 eV. In contrast, the product vibrational state distributions change by only a few percentage points with this variation of reagent rotational energy. Under the normal expansion conditions employed for D₂ production, the rotational energy of the reagents is estimated from the model of Gallagher and Fenn to be 0.016 eV. The cold expansion conditions produce a beam of reactants with an estimated rotational energy of 0.0033 eV, whereas the hot conditions yield D₂ with a rotational energy of approximately 0.035 eV. At a collision energy of 0.25 eV, the total energy accessible to products formed from normal D₂ is 0.56 eV. The largest change in the total energy occurs when using rotationally hot reagents, but this corresponds to an increase of less than 0.02 eV. From the point of view of a statistical description of the product state distribution, the small difference in the total energy arising from the enhanced or reduced rotational energy of the D₂ reagents does not result in a perceptible change in the partitioning of
energy into vibration. Since the total angular momentum of the system is dominated by the orbital angular momentum, the small increase in the reagent rotational excitation should not alter the angular momentum partitioning in the products in the absence of a dynamical mechanism. The dramatic change in the product angular distributions with reagent rotational excitation therefore must have a specific dynamical origin.

The ab initio calculation of the potential energy surface for the O\textsuperscript{−} + H\textsubscript{2} system by Werner et al.\textsuperscript{34,35} serves as an important point of reference in the discussion of the dynamical origin of these changes in the product angular distributions. Specifically, it is the correlation of rotational motion in the approaching D\textsubscript{2} molecule with bending motion in the collinear OD\textsuperscript{−} – D species that is of critical importance here. The ab initio calculations show clearly that in the vicinity of this saddle point, bending motion accesses the electron detachment continuum. The dynamics of nuclear motion in this region of the potential surface may be described by a local complex potential\textsuperscript{30} of the form:

\[
V(R) = U(R) - \frac{i}{2} I(R) \tag{4}
\]

where \( R \) denotes the multidimensional coordinates of the polyatomic system and \( I(R) \) is the autoionization width. The lifetime of the transient system against detachment is represented in terms of the autoionization width as \( \hbar I(R) / 2 \). It follows that the probability of electron detachment in the coordinate interval \([R\textsubscript{i}, R\textsubscript{f}]\) is given by the expression:

\[
P(R\textsubscript{i}, R\textsubscript{f}) = 1 - \exp \left( - \frac{2I(R)}{\hbar V_r} \right. \int_{R\textsubscript{i}}^{R\textsubscript{f}} dR \tag{5}
\]

where \( V_r \) is the radial velocity of the nuclei and the integrand compares the transit time of the trajectory to the autoionization lifetime.\textsuperscript{31} As the nuclear velocities increase and the transit time becomes short with respect to the autoionization lifetime this detachment probability decreases.

In the O\textsuperscript{−} + D\textsubscript{2} system, the autoionization line width \( I(R) \) is zero for coordinates that maintain collinearity of the OD\textsuperscript{−} – D configuration but nonzero for bent configurations. In the limit that the transit time through the saddle point region is long in comparison to the autoionization lifetime, i.e. the zero kinetic energy limit, only collinear collisions lead to particle transfer and the OD\textsuperscript{−} products are backward scattered. Reduced rotational excitation in the D\textsubscript{2} reagents increases the likelihood of achieving the collinear geometry necessary for particle transfer and concomitant backward scattering. Equivalently, enhanced reagent rotational excitation correlates to bending excitation in the OD\textsuperscript{−} – D species and reduces the probability of maintaining a collinear geometry on the time scale of particle transfer. The experimental data show precisely such an effect. The angular distributions resulting from the experiments with the normal reagents have products distributed over a wide range in addition to a sharp peak in the backward direction that diminishes in intensity as the collision energy is raised. In contrast, the angular distributions for the experiments with rotationally cold reagents show a sharp backward peak at all three collision energies and a decrease in the relative amounts of forward and sideways scattering. The rotationally hot reagents produce an angular distribution that peaks in the forward direction and plateaus in the angular range from 60° to 180° with an intensity less than 50% of the forward maximum. The sharpening of the backward peak and the deepening of the minimum at sideways angles with decreasing reagent rotational excitation are consistent with the enhanced role that rotational energy of the reagents plays in the competition between particle transfer and electron detachment at low collision energies.

The angular distributions for each experiment have been normalized in a point by point manner to the maximum intensity, providing a description of the relative amounts of scattering in the center-of-mass frame. To determine the absolute change in the angular distribution as a function of reagent rotational energy, the product intensities must be normalized using the total cross section for the reaction. It is extremely difficult to measure the total reaction cross section in a crossed beam experiment, and therefore we cannot discuss anything besides the relative changes in the barycentric distributions that occur upon cooling the D\textsubscript{2} reagent. Much higher resolution experiments are necessary if we want to be exact about the normalization of the angular distributions. However, theoretical works on comparable systems show only a weak dependence of total cross section on reagent rotational energy at low rotational energies.\textsuperscript{32,33} For example, quasiclassical trajectory calculations by González et al.\textsuperscript{33} on the O\textsuperscript{+} + D\textsubscript{2} reaction at 0.25 eV determined that the total cross section changes by approximately 5% when the D\textsubscript{2} rotational state is increased from \( J = 0 \) to \( J = 2 \). The effects of a similar change in the total cross section with rotational energy in the O\textsuperscript{+} + D\textsubscript{2} system would be below the limits of detection in our experiment.

The influence of autodetachment on the dissociation of triatomic negative ions formed by low-energy electron impact was examined by Goursaud et al.\textsuperscript{34,35} through classical trajectory calculations. Ejection of the electron was represented by the unimolecular rate constant \( I(R)/\hbar \), where the value of \( I(R) \) was held fixed while the internuclear distance, \( R \), remained less than a critical length and was taken to be zero otherwise. The competition between dissociation and autodetachment for each trajectory was characterized by a survival probability \( \exp(-\tau_c/\hbar) \), in which \( \tau_c \) defines the time spent in the autodetachment region. The dissociation of H\textsubscript{2}O\textsuperscript{−} was examined on repulsive surfaces which were reasonable approximations to the \( ^2\text{B}_\text{e} \) surface leading to \( \text{H}^+ + \text{OH} \). The process \( \text{H}_2\text{O}^− \to \text{H}^+ + \text{OH} \) was also studied on hypothetical attractive surfaces to determine the influence of the shape of the surface on energy partitioning. On the repulsive surfaces autodetachment was found to act as a suppressor of slow trajectories. As the energy available to the system was increased, the kinetic energy distributions of the fragmentation products broadened. The influence of the autodetachment rate on dissociation was found to be notably weaker on the attractive surfaces. The kinetic energy distributions exhibit a maximum at low energies with a tail or secondary maximum at higher energies. On these attractive surfaces strong coupling is found between translational and rotational energy modes. The dissociation processes that partition excess energy into translational modes are not necessarily the fastest, in contrast to what was observed on the repulsive surfaces. The walls of the potential surface may reflect the trajectories, increasing the time ultimately spent in the autodetachment region. For a realistic value of the autodetachment lifetime, the partitioning of the excess energy in the fragments favors the internal modes to the translational mode by a 3 : 1 ratio. When the amount of excess energy in the system is increased, the average dissociation time decreases and products are formed with higher kinetic energies.

The method of Goursaud et al.\textsuperscript{34,35} may be extended to describe the competition between electron detachment and particle transfer in the O\textsuperscript{−} + D\textsubscript{2} system. Using a similar representation for the ejection of the electron, trajectory calculations performed on a potential energy surface that accurately describes the critical region of the saddle point where bound nuclear motions are embedded in the continuum for electron detachment will provide a more complete understanding of this system. In addition to internuclear distances, the unimolecular rate constant describing the ejection of the electron must depend on the geometry of the intermediate
complex, OD$^-$ - D. While the complex remains collinear the value of $\Gamma(R)$ will be zero since there is no possibility for electron detachment. For any other configurations, the value will depend on the internuclear distances as in the previously described dissociation studies; only when the nuclei are within a critical distance will $\Gamma(R)$ be nonzero. Such a computational effort requires an accurate potential energy surface for the system over a wide range of geometries along with a representation for the imaginary part of the optical potential, $\Gamma(R)$, in terms of the appropriate bending coordinate. A program of study of this kind holds promise for probing, via ab initio methods, critical regions of the potential surface, in addition to providing benchmarks for dynamical calculations on accurate surfaces. The dynamical subtleties examined in terms of the coupling between internal and translational degrees of freedom in restricted regions of the potential surface, as well as the role of these motions in the branching between detachment and particle transfer, should be fruitful areas of inquiry. We hope that the present experimental data stimulate such computations.

5. Conclusion

We have presented experimental evidence that reagent rotational energy strongly affects the dynamics of the O$^-$ + D$_2$ system at low collision energies between 0.22 and 0.37 eV. The center-of-mass product angular distributions display sharp backward scattering for rotationally cold reagents, but shift to the forward and sideways directions as the rotational temperature is raised. This is evidence of the critical role that collinear trajectories play in the saddle point region of the potential surface where electron detachment occurs. The more rotational energy present in the reagents, the harder it is for the complex to remain linear through this region and reach the OD$^-$ + D asymptote, producing backward scattered OD$^-$. Instead, bending motion in the intermediate may lead to electron detachment if the transit time through the critical region of the potential surface is long compared to the autodetachment lifetime. The center-of-mass angular distributions have proven to be most sensitive to the effects of reagent rotational energy on this system. The product vibrational state distributions display only a weak dependence on rotational temperature, and the rate constant and branching ratio are relatively insensitive to temperature.$^{13}$ This suggests that a small change in the amount of rotational energy present in this system strongly influences the mechanism of particle transfer but may not significantly alter the number of trajectories leading to that channel. Detailed dynamical calculations to further investigate the competition between particle transfer and electron detachment are necessary for a complete understanding of this rather complex ion–molecule system.

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