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Molecular Frame Coordinates and the Analysis of Scattering from Oriented Molecules

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Molecule-fixed coordinates (MOL coordinates) are introduced for the analysis of reactive scattering from oriented molecules. By transforming the data to the MOL frame one can experimentally determine the orientational configuration from which the products emerge. As an illustration, reactive scattering data from previously published experiments for \( K + CF_3I \rightarrow KI + CF_3 \), where \( CF_3I \) was initially oriented with respect to the incoming \( K \) atom, were transformed to this coordinate system. The experimental angular distribution in the MOL frame is compared with that calculated from the initial distribution of molecular axes and found to be very similar, which suggests that the breakup of the initially oriented molecule occurs in time less than a rotational period.

I. Introduction

Scattering experiments are conducted in the laboratory and normally interpreted in the center-of-mass system (CM) by using Dudley Herschbach's "Newton" diagram named for Sir Isaac Newton, whose laws of motion govern the asymptotic behavior of our reacting species. Analysis in the CM is most appropriate for collisions with central forces. But most molecules are not spherically symmetric, chemical forces are decidedly not simply central forces, and other coordinates might be more illustrative.

In order to probe these angle-dependent forces, a number of studies have recently been conducted with molecules that have been oriented prior to reaction.\(^{1}\) In almost every case studied, reactivity is enormously dependent on the orientation of the molecule. For reaction \( K \) with \( CF_3X \), this dependence has been interpreted\(^2\) in terms of an electron transfer or "harpoon" mechanism, whereby the incoming alkali donates an electron to the oriented molecule, which promptly dissociates,\(^3\) ejecting \( R \) and \( X^- \). Even though the trajectory of the \( X^- \) is greatly perturbed by Coulomb interaction with the \( K^+ \), insight into the reaction mechanism has been gained because the scattered \( KX \) has been found at completely different lab angles, depending on the initial orientation of the \( RX \) molecule. The large difference in angle allowed us to suggest that the molecule essentially exploded along the direction it was pointing, in a manner reminiscent of photodissociation.

More recent studies have explored the harpoon mechanism itself by studying collisional ionization of oriented molecules. In these experiments, \( K \) atoms with \( \approx 5-10 \) eV of kinetic energy collide with an oriented \( RX \) molecule to form \( K^+, R, \) and \( X^- \). The \( K^+ \) product intensity is observed to be enormously dependent on orientation. Interpretation of these experiments (see ref 2a) requires explicit consideration of the Coulomb force between the product ions. This force clearly dominates the exit channel, and the nascent ions will recombine to give a neutral salt unless they have sufficient energy to overcome the Coulomb attraction, in which case they escape as charged particles.

Consideration of the Coulomb forces between the nascent ions (and the complications this introduces into the ionic trajectories) has caused us to consider the motion of the uncharged radical. Useful reaction models can be constructed with these considerations, but the presence of three products (\( K^+, R, \) and \( X^- \)) constrains us to models of ionization, not a direct analysis of the experimental data. But for neutral reactions that form two products (\( KX \) and \( R \)), information about the angular distribution of \( R \) can be directly extracted from the experimental data. This angular distribution can be viewed in any coordinate system, of course. But since the harpoon mechanism is usually viewed in terms of an impulsive dissociation of the intermediate molecular ion, it is useful to view the ejection of the radical in the reference frame of the molecule (MOL coordinates). The uncharged radical is expected to be less perturbed in the exit channel and therefore potentially very informative about the reactive collision.

In this paper, we describe how the angular distribution of \( MX \) in reactions \( M + RX \rightarrow MX + R \) may be transformed into an angular distribution of \( R \) radicals in the reference frame of the molecule (MOL coordinates) before reaction.\(^4\) (The reference frame is located on the molecule with polar axis along the relative velocity between the reacting species.) Information about the radical product follows, of course, from the \( MX \) product by the conservation of energy and momentum. Although the impulsive-harpoon reaction model has inspired this experimental transformation to the MOL system, the transformation is not model dependent and directly produces a result that allows us to think about the attack on the molecule. This result can be compared with a model, and we compare it with the distribution of molecular orientations that obtained before reaction. For \( K + CF_3I \) we find reasonable agreement between the experimental fragment distribution and the distribution of molecular axes before collision. Thus the direction of the \( CF_3I \) molecule does not change much between the approach of the \( K \) and the ejection of the \( CF_3 \), suggesting that the dissociation of the intermediate anion is prompt, with a lifetime less than a rotational period.

II. Lab-CM-MOL Transformation

Figure 1 shows the standard "Newton" diagram for particles of masses \( m_1 \) and \( m_2 \) colliding at right angles with speeds \( v_1 \) and \( v_2 \). The products of the collision have masses \( m_3 \), \( m_4 \), and laboratory speeds \( v_3 \), \( v_4 \). We assume that particle 3 is detected at laboratory scattering angle \( \phi \) with laboratory speed \( v_3 \).

The origin of the CM system is located at the end of the CM velocity vector defined to conserve momentum by the relations

\[ Mv = m_1v_1 + m_2v_2 = m_3v_3 + m_4v_4 \]  

\[ c = \left( m_1^2v_1^2 + m_2^2v_2^2 \right)^{1/2} / M \]  

\[ M = m_1 + m_2 = m_3 + m_4 \]

The velocity in the lab \((\nu)\) is related to that in the CM \((u)\) by the relations

\[ \nu_i = c + u_i \]

Since (1) conserves momentum, the momenta in the CM sum to

\[ p_1 + p_2 = p_3 + p_4 \]
where the reverse transformation could be used to predict the experimental data. The velocity of particle 1 axis and the final momentum of the product. Exit channel supplement of the principle value of the inverse sine.)

\[ \sin^{-1}(u_1/u_3 - \sin^{-1}(c \sin \alpha/u_1)) \]

where \( \alpha = \phi - \phi_c \) and \( \phi_c \) = lab angle of CM.

The experimental laboratory angular distribution of particle 3 (KI in the K + CF3 reaction) can thus be mapped into a distribution in the CM over \( u_3 \) and \( \chi \). By conservation of momentum the distribution in the CM for particle 4 (CF3) is also determined.

If the molecule is originally oriented with respect to a space-fixed axis, there will be a correlation between that space-fixed axis and the final momentum of the product. Exit channel interactions (say between K+ and I-) may complicate this correlation for one product, and the correlation may be clearer for states because most reactive symmetric top molecules are rather heavy, have small rotational spacing, and have many rotational states populated. Attempts were made in the early experiments to account for this ensemble of states by calculating the distribution of the number of \( \langle \cos \theta \rangle \). This deflection enables one to prepare beams of oriented molecules by first using an inhomogeneous electric field as a state filter to pass only those molecules in states with \( \langle \cos \theta \rangle < 0 \) and then allowing the state-selected molecules to pass adiabatically into a region of uniform electric field. The state-selected molecules are oriented with respect to the local field, and in the region of uniform field, the field direction is specified with respect to the laboratory. The state-selected molecules are thus oriented in the laboratory, and this laboratory orientation may be changed by changing the direction of the uniform field.

Molecules can be prepared in specific JKM states, but most scattering experiments have been performed with a distribution of JKM states because most reactive symmetric top molecules have large rotational spacing, and a high number of rotational states populated. Attempts were made in the early experiments to account for this ensemble of states by calculating the distribution of the number of \( \langle \cos \theta \rangle \). But the distribution of \( \langle \cos \theta \rangle \) is not the same as the distribution over \( \theta \) or, equivalently, of the molecular axes. Here we calculate the distribution of molecular axes to compare with the distribution of fragments experimentally observed.

For a molecule in state JKM, Choi and Bernstein have evaluate the quantum-mechanical distribution function, \( P_{JKM}(\rho) \), as

\[ P_{JKM}(\rho) \, d\rho = 4\pi^2(\Psi^*_{JKM} \Psi_{JKM}) \sin \theta \, d\theta = (2J + 1)/2 \sum_{\rho} C_\rho(JKM)P_{\rho}(\rho) \]

where \( D'_{KM} \) is the rotation matrix and \( \rho = \cos \theta \). This distribution may be expressed in terms of the Legendre polynomials, \( P_{\rho}(\rho) \), as

\[ P_{JKM}(\rho) = (2J + 1)/2 \sum_{\rho} C_\rho(JKM)P_{\rho}(\rho) \]

III. Orientation of Molecules

The energy of a symmetric top molecule with dipole moment \( \mu \) in electric field \( E \) is

\[ W = -\mu E J K M / J (J + 1) = -\mu E \langle \cos \theta \rangle \]

where \( J, K, \) and \( M \) are the standard quantum numbers specifying the total angular momentum, the projection on the symmetry axis of the molecule, and the projection on a space-fixed axis and \( \theta \) is the angle between \( \mu \) and \( E \) averaged over the rotational motion of the top. These molecules can be deflected in an inhomogeneous electric field by an amount depending on the sign and magnitude of \( \langle \cos \theta \rangle \). This deflection enables one to prepare beams of oriented molecules by first using an inhomogeneous hexapole field as a state filter to pass only those molecules in states with \( \langle \cos \theta \rangle < 0 \) and then allowing the state-selected molecules to pass adiabatically into a region of uniform electric field. The state-selected molecules are oriented with respect to the local field, and in the region of uniform field, the field direction is specified with respect to the laboratory. The state-selected molecules are thus oriented in the laboratory, and this laboratory orientation may be changed by changing the direction of the uniform field.

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\[ P_{JKM}(\rho) = (2J + 1)/2 \sum_{\rho} C_\rho(JKM)P_{\rho}(\rho) \]
where $C_a(JKM)$ can be written in terms of 3-J symbols as

$$C_a(JKM) = \frac{(2n + 1)(-1)^{M+K}}{2} J_J J M N 0 0 (12)$$

Choi and Bernstein (CB) show probability distribution functions $P_{JKM}(\rho)$ for a few small values of $J, K,$ and $M,$ and those for the [111] and [211] states are shown in Figure 4. The probability distribution for the pure state [211] is included for comparison because it shows a minimum in the distribution, whereas states such as [111] and [222] are monotonically increasing toward $(\cos \theta) = 1.$

For molecules where selection of single $|JKM\rangle$ states is not feasible, the probability distribution, $P(\rho),$ will be a sum over individual states weighted by the population of each state,

$$P(\rho) = \sum_J \sum_K \sum_M P_{JKM}(\rho) f_{JKM}(T) \mathcal{F}_{JKM}(\rho) \quad (13)$$

where $f_{JK}(T)$ is the fraction of molecules in state $J,K$ at temperature $T = T_{\text{rot}}$, $\mathcal{F}_{JKM}(\rho)$ is the probability of transmission through the hexapole electric field, and $P_{JKM}(\rho)$ is defined in (7).

The probability $\mathcal{F}_{JKM}$ that a molecule in state $|JKM\rangle$ is transmitted through the electric field depends on the experimental parameters and on $(\cos \theta)$ and is calculated by using the equations of motion (see Appendix).

Figure 5 shows orientational probability distributions calculated for several different molecules by using different field configurations. The CF$_3$I and CH$_3$I distribution is that for heads/tails using the parameters listed in the Appendix. The distribution for CH$_3$Cl (included for comparison) was calculated for a 1.4-m field with a very small (1.2 mm) exit aperture and temperature of 2 K. The focusing voltage, 5.5 kV, was chosen to approximately maximize the contribution from the [211] state relative to that from the [111] state. The resulting distribution retains a little of the characteristics of the [211] state, but the much more highly populated [111] state has a significant influence and has almost obliterated the minimum near $-0.5.$ As the temperature is increased (and as the apertures become larger) the probability distribution becomes entirely monotonically increasing and insensitive to the assumed temperature or the focusing voltage, although a clear preference for $\cos \theta > 0$ is retained. Because of this insensitivity (and the increasing size of the calculation), we approximate the room temperature orientational distributions for CF$_3$I as that for 10 K, which is virtually indistinguishable from that calculated for 1 K. (At 1 K $\hbar/2kT = 0.07$, and deviations become apparent at much lower temperatures.) The distribution for CH$_3$I was calculated for the same conditions as for CF$_3$I as a comparison to demonstrate that molecular parameters affect the distribution.

IV. Comparison between Experiment and Distribution of Axies

Figures 6 and 7 show the distribution of CF$_3$ fragments in the MOL system for CF$_3$I oriented in the "heads" (1 end) or "tails" (CF$_3$ end) orientations.

It is clear from these plots that there is a marked asymmetry in the reaction: neither angular distribution is symmetric about $90^\circ$ (which corresponds to sideways orientation). It is also clear that for both orientations some fragments are ejected on the "wrong" side of $90^\circ$ or at angles
V. Discussion

Figures 6–8 show the experimental angular distribution of the $\text{CF}_3$ radical in the reference frame of the molecule, which results from the inversion of the experimental KI angular distribution. This is another, more illustrative view of the experimental data and is not model dependent. These experimental results show directly that the radical is, broadly speaking, ejected in the initial direction of the molecular axes.

The agreement between the experimental angular distributions in the MOL frame and the calculated distribution of initial molecular axes is surprisingly good, especially given the lack of any adjustable parameters. The plots shown in Figures 6–8 represent the first semiquantitative attempt to reconcile the heads/tails scattering data with that taken in the sideways orientation. In every case, heads, tails, and sideways, the experimental results very closely echo the initial distribution of molecular axes. The agreement supports the general conclusion reached earlier that the $\text{CF}_3$ molecule essentially explodes on receiving the harpoon electron, ejecting the fragments in the direction of the molecular axis. If the intermediate molecular ion were to live for times on the order of the rotational period, or if the ejected $\text{CF}_3$ radical were perturbed much in the exit channel, the correlation between angular distribution and distribution of axes would be lost. (The $\text{CF}_3$ must interact a little because it must carry off enough energy to stabilize the nascent KI, so it cannot be an isolated spectator.)

We have chosen to illustrate this method using $\text{CF}_3\text{I}$ not only because it does illustrate the method but also because it is the only molecule for which sideways data are available. In other cases we do not expect the fragment angular distribution to mirror the distribution of axes. Methyl iodide, for example, seems to be only backward scattered, even in the tails orientation. $\text{CF}_3\text{Br}$ shows forward scattering in the tails orientation but with lower intensity than from the heads orientation. Complete interpretation of these other results is particularly tantalizing but must be deferred pending determination of the speed distribution of the products of the oriented molecule reactions.

Note Added in Proof. Loesch and Möller (Loesch, H. J.; Möller, J. J. Chem. Phys. 1992, 97, 9016) have recently used an equivalent coordinate system (called the O frame) for DIPR model calculations to explain the reactivity of K with oriented ICI molecules.

Acknowledgment. I am delighted to dedicate this paper to Dudley Herschbach on the occasion of his 60th birthday. It was great fun and inspiration to be a certified member of the "lunatic fringe", and Dudley's enthusiasm, support, and example have been invaluable to me for many years. Grateful acknowledgement is made to the Robert A. Welch Foundation and to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Appendix


This geometry was initially used to maximize the intensity from an effusive beam source. The molecular beam is initially collimated by focusing from a glass capillary array and could (in principle) be focused to a point by the field. The beam enters the focusing field parallel to the axis and encounters an incident axial beam stop (radius $R = r_0$). If (cos $\theta$) $= M K / J (J + 1)$, a molecule will experience a deflection toward the axis of the field and pass through the exit aperture (also radius $r_0$). The equation of motion inside the field is

$$ r = r_0 \cos \omega t; \quad \omega^2 = \frac{6 \mu V_0 (\cos \theta)}{m r_L^3} \quad (A1) $$

For a field of length $L_2$, a molecule of speed $v$ will pass through the exit aperture if

$$ -R < r_0 \cos (\omega L_2 / v) < R \quad (A2) $$

and molecules are passed by the field if they enter in an annular ring of inner radius $r_L$ and outer radius $r_L$, where

$$ r_L \text{ is the lesser of } \frac{R}{|\cos (\omega L_2 / v)|} \text{ or } r_L \quad (A3) $$

The speed-dependent fraction of molecules entering the field in state (JKM), that pass through the field is then

$$ F_{JKM}(v, V_0) = \frac{r_L^2 - r_L^2}{r_L^2 - r_L^2} \quad (A4) $$

The probability that the state (JKM) appears in the final state-selected beam is then $F_{JKM}(v, V_0)$ integrated over the initial speed distribution, and

$$ F_{JKM}(V_0) = \int_0^\infty F_{JKM}(v, V_0) P(v) dv \quad (A5) $$

For an effusive beam, $P(v)$ is the modified Maxwell–Boltzmann speed distribution.

B. Full-Wave Geometry.

This geometry is more appropriate for a supersonic source and molecules emerge from a nozzle (point) source located on the axis and can (in principle) be focused back...
Molecular Frame Coordinates

<table>
<thead>
<tr>
<th>TABLE I: Parameters Used in Calculation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>parameter</td>
</tr>
<tr>
<td>$l_1$, source field, cm</td>
</tr>
<tr>
<td>$l_2 = L$ field length, cm</td>
</tr>
<tr>
<td>$r_1$, field radius, cm</td>
</tr>
<tr>
<td>$r_2$, stop radius, cm</td>
</tr>
<tr>
<td>$R$, exit radius, cm</td>
</tr>
<tr>
<td>$\nu_0$ (flow velocity, cm/s)</td>
</tr>
<tr>
<td>$T_0$ (trans temp)</td>
</tr>
<tr>
<td>$V_0$, kV</td>
</tr>
</tbody>
</table>

* Rotational constants and $\mu$. References 5a and 10. $c$ References 5b and 19.

The source is a distance $l_1$ from the hexapole field of length $l_2$, and an axial beam stop of radius $r_2$ is chosen to occlude the exit aperture of radius $R$ so that a molecule must be deflected toward the axis to pass through the exit. The equation of motion inside the field is

$$r = \alpha[l_1 \cos(\omega t) + (\nu/\omega) \sin(\omega t)]$$  \hspace{1cm} (B1)

where $\alpha$ is the angle of injection into the field and $\omega$ is defined in eq A1. Molecules are passed by the field if they are injected between the angle subtended at the source by the stop ($\alpha_0 = r_2/l_1$) and $a_0$, where $a_0$ is the lesser of

$$\frac{R/l_1}{[1/\beta_1 \sin \beta_2 + \cos \beta_2]}$$  \hspace{1cm} (B2)

or

$$\frac{\omega r_1}{\nu(1 + \beta_1)^{3/2}}$$  \hspace{1cm} (B3)

Equation B2 results from requiring $r < R$, and (B3) results from the condition that $r_{\text{max}} < r_1$ and $\beta = \omega l_1/\nu$. The speed-dependent fraction of molecules entering the field in state $JKM$ that pass through the field is then

$$A(V_0,\nu) = (\alpha_m^2 - \alpha_0^2)/\alpha_l^2$$  \hspace{1cm} (B4)

which must be integrated over the speed distribution to yield $F_{JKM}(V_0)$

$$F_{JKM}(V_0) = \int_0^\infty A(V_0,\nu)P(\nu) \, d\nu$$  \hspace{1cm} (B5)

where $P(\nu)$ is the speed distribution characteristic of a supersonic beam (Table 1).

References and Notes

(1) See, for example, the following articles and references cited therein:

(b) Brooks, P. R. Science 1976, 193, 11.

(3) The negative ion that results is expected to be formed either in a reorientation state or high on the negative wall of the state. For the molecular ion will dissociate within one vibration. The ejection of particles from the oriented molecule is thus similar to that which is obtained from photodissociation. This is similar to the DIPR-DIP model introduced many years ago in trajectory studies (Kuntz, P. J.; Mok, M. H.; Polansky, J. C. J. Chem. Phys. 1969, 50, 4623. Herschbach, D. R. Faraday Discuss. Chem. Soc. 1973, 55, 233).

(4) This approach has drawn inspiration from conclusions drawn about reagent attack geometries in studies of H atoms with halogens: McDonald, J. D.; LeBreton, P. R.; Lee, Y. T.; Herschbach, D. R. J. Chem. Phys. 1972, 56, 769.

(5) References 5a and 10.

(6) Notes
(7) References 5a and 10.

(8) This process can be complicated by nonadiabatic passage from the inhomogeneous electric field to the uniform field, although adiabatic passage is normal (see ref 10).

(9) References 5a and 10.

(10) References 5a and 10.

(11) References 5a and 10.

(12) References 5a and 10.

(13) References 5a and 10.

(14) References 5a and 10.

(15) References 5a and 10.

(16) References 5a and 10.

(17) References 5a and 10.

(18) References 5a and 10.

(19) References 5a and 10.

(20) References 5a and 10.