

Velocity dependence of the excimer rotational alignment in the reactions of Xe* with halogenated methanes

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Using a beam-gas time-of-flight technique, the XeX* (X=Cl, Br, I) rotational alignment from the reactions of Xe(³P_{2,0}) with CH₃I, CH₂I₂, CH₂Br₂, CHBr₃, CBr₄, CHCl₃, and CCl₄ are reported. The degree of product alignment varies markedly between these systems, decreasing with collision energy, halogen mass, and number of halogens per molecule. At the lowest collision energies studied, a transition from positive to negative polarization was found for CBr₄, CHCl₃, and CCl₄. The negative polarization corresponds to the preferential alignment of the product rotational angular momentum vector parallel to the relative velocity vector.

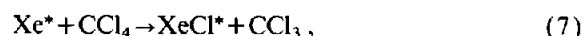
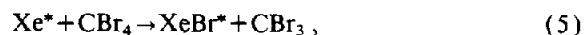
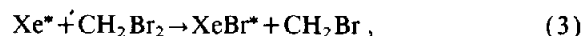
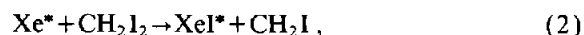
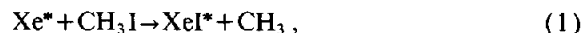
1. Introduction

The study of product rotational alignment provides insight into the disposal of angular momentum in reactive collisions. A number of molecular beam studies of product alignment produced in atom transfer reactions have been reported. The first such experiments were done by Herschbach and co-workers using the electric deflection technique [1–3]. More recently, chemiluminescent reactions have been used to study product alignment as a function of collision energy [4–10], reactant internal state [11], reactant alignment [12], and product vibrational level [13].

Previously we have reported on the polarized emission from the xenon halide excimers produced in the reactions of Xe(³P_{2,0}) with a series of hydrogen halides and halogen molecules [9]. Since the sum of the orbital angular momentum, *L*, and the molecular angular momentum, *J*, has to be conserved, the hydrogen halide reactions are kinematically constrained. As a consequence of these kinematic con-

straints, the product angular momentum distribution is close to the reagent orbital angular momentum distribution, i.e. perpendicular to the relative velocity vector. In contrast, in the Xe* + Br₂, Cl₂ reactions at low collision energies we observed preferential alignment of the angular momentum vector *parallel* to the relative velocity vector. In general, the low collision energy regime (small *L*) has the potential for revealing much of the reaction dynamics that may be masked by kinematic effects at higher collision energies. Our experimental approach allows measurement of product polarization at thermal as well as subthermal collision energies.

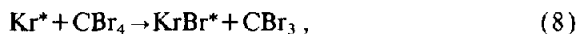
In the present work, we have extended our rotational alignment studies to include the XeX* and KrBr* excimers formed in the following atom transfer reactions:



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With the possible exception of reaction (1), these systems have the mass combination "heavy-heavy-heavy"; thus the kinematic constraints are relaxed and the resulting product rotational alignment may be expected to reflect some of the dynamics of the reactive collision.

2. Experimental

The apparatus used in these experiments has been described in detail previously [9,10]. In brief, a rare-gas beam from an effusive source passes through the plates of a cold cathode discharge, in which metastables are formed. Ions and Rydberg atoms formed in the discharge are removed by sweeper plates downstream. The metastable rare-gas beam is pulsed at 200 Hz. After a 30 cm flight path the pulsed beam passes through the interaction cell containing the target gas at pressures on the order of 10^{-4} Torr. Two photomultiplier tubes view the XeX^* chemiluminescent radiation through broad band pass filters at right angles to beam. A polaroid thin-film polarizer is placed in front of each phototube, oriented such that light is transmitted with polarization parallel to the atomic beam for one detector and perpendicular for the other. The relative response of the two phototubes is measured periodically during the experiment by aligning the polarizers parallel to each other.

The rare gas source is operated at two temperatures, 500 and 170 K. Chemiluminescence is measured as a function of flight time after the pulser, which can be transformed into a signal as a function of rare-gas velocity. Data are accumulated over many sweeps at each beam temperature into 20 μs channels. Since the velocity distributions at the two temperatures overlap, comparison of the results in this overlap region serves as an internal check on the reproducibility of the results.

In a beam-gas arrangement the average relative velocity vector, \mathbf{k} , lies along the molecular beam axis, \mathbf{z} , at all velocities, allowing the use of the TOF method. Prisant et al. [14] and Johnson et al. [15] have demonstrated that polarization data from a beam-gas experiment can be used to obtain product alignment data in the center-of-mass coordinate sys-

tem (c.m.) without loss of information due to averaging over the isotropic velocity distribution of the target gas. The lab to c.m. transformation uses second-order Legendre polynomials as follows:

$$\langle P_2(\hat{\mathbf{J}}' \cdot \hat{\mathbf{z}}) \rangle = \langle P_2(\hat{\mathbf{J}}' \cdot \hat{\mathbf{k}}) \rangle \langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}) \rangle.$$

Here $\langle P_2(\hat{\mathbf{J}}' \cdot \hat{\mathbf{k}}) \rangle$ is the quantity of interest, since it contains $\langle \cos^2 \alpha \rangle$ where α is the average angle between the product angular momentum, $\hat{\mathbf{J}}'$, and $\hat{\mathbf{k}}$. $\langle P_2(\hat{\mathbf{J}}' \cdot \hat{\mathbf{z}}) \rangle$ is obtained from the measurements, and $\langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{z}}) \rangle$ is computed for each beam velocity using a Monte Carlo calculation which averages over all target gas velocities. We express our results in terms of a center-of-mass alignment parameter A , defined as:

$$A = -2 \langle P_2(\hat{\mathbf{J}}' \cdot \hat{\mathbf{k}}) \rangle.$$

The limiting values for A are +1 for complete perpendicular alignment of \mathbf{J}' with respect to \mathbf{k} , and -2 for complete parallel alignment. For an isotropic \mathbf{J}' distribution, $A = 0$.

3. Results

Fig. 1 compares the degree of product rotational alignment resulting from reactions (1)–(7). Table 1 compares the data at a few fixed collision energies with those from previous alignment studies. Direct comparison with the results of Hennessy et al. [5,6] is possible in the $\text{Xe}^* + \text{CH}_3\text{I}$, CCl_4 reactions. In the range of collision energies common to both experiments, the agreement is good. This is also true for the analogous reactions of Cs with CH_3I and CCl_4 [1,2].

A number of trends are immediately apparent from fig. 1:

(a) All systems studied show a strong collisional energy dependence of the XeX^* alignment, which rapidly increases with increasing collision energy.

(b) The magnitude of the XeX^* rotational alignment decreases in the order: $\text{XeI}^* > \text{XeBr}^* > \text{XeCl}^*$.

(c) For a given halogen, the polarization decreases with increasing number of halogen substituents.

The decrease in the XeX^* product rotational alignment with decreasing mass of the transferred halogen is opposite from the trend found in the re-

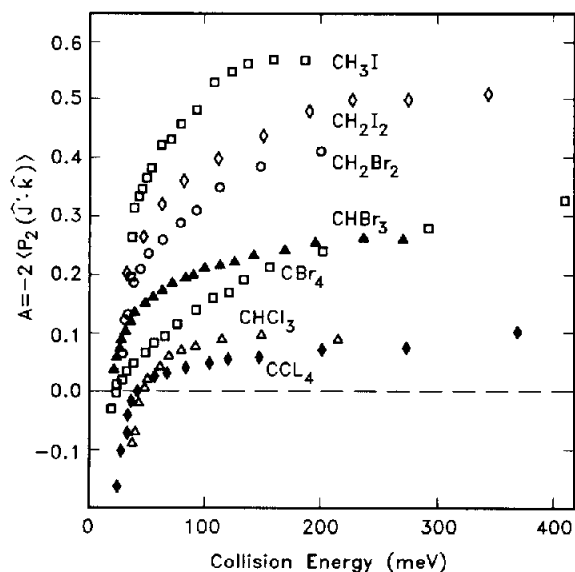


Fig. 1. Collisional energy dependence of the excimer product rotational alignment produced in the reactions of $\text{Xe}(^3P_{2,0})$ with a series of halomethanes.

actions of Xe^* with the homonuclear diatomics [9]. It is of interest to note that the $\text{Xe}^* + \text{CH}_2\text{I}_2$ system, which has almost the same mass combination as $\text{Xe}^* + \text{I}_2$, produces XeI^* which is roughly twice as polarized as that found in the I_2 reaction. Since the additional degrees of freedom in the CH_2I product

might be expected to lower the alignment of the XeI^* excimer in the methylene iodide reaction, the larger excimer polarization is somewhat counterintuitive.

Fig. 2 compares the excimer product alignment for the reaction of Kr^* with CBr_4 with that from Xe^* with CBr_4 . The KrBr^* alignment is found to be less than that of XeBr^* (except at the lowest velocities), and displays a weaker dependence on the collision energy.

4. Discussion

Many of the alignment effects observed in this work can be readily understood on the basis of kinematics. A strong polarization results when large initial orbital angular momentum, L , is effectively transferred into excimer rotation, J' . Since the magnitude of L increases with increasing collision energy, one would expect a corresponding increase in product alignment with increasing collision energy. This is consistent with our observations. In addition, the masses of the excimer and polyatomic fragment will affect the amount of angular momentum available for rotation of the excimer product. Increasing the mass of the polyatomic leaving group lessens the kinematic constraints because the larger product orbital angular momentum leaves less of the total angular momentum to be partitioned into J' . This will,

Table 1

Summary of product alignment data from atom transfer reactions involving alkyl halides

Detection method	Reactants	Collision energy (meV)	Alignment ^{a)} (A)
electric deflection ^{b)}	$\text{Cs} + \text{CH}_3\text{I}$	≤ 60	0.24
	$\text{Cs} + \text{CCl}_4$	≤ 60	0.12
cross-beam chemiluminescence ^{c)}	$\text{Xe}^* + \text{CH}_3\text{I}$	60	0.42
	$\text{Xe}^* + \text{CCl}_4$	180	0.48
beam-gas chemiluminescence ^{d)}	$\text{Xe}^* + \text{CCl}_4$	60	0.03
	$\text{Xe}^* + \text{CCl}_4$	430	0.18
	$\text{Xe}^* + \text{CH}_3\text{I}$	60	0.39
	$\text{Xe}^* + \text{CH}_3\text{I}$	200	0.57
	$\text{Xe}^* + \text{CCl}_4$	60	0.03
	$\text{Xe}^* + \text{CCl}_4$	200	0.06

^{a)} See text for definition of the alignment parameter A .

^{b)} Data taken from refs. [1,2].

^{c)} Data taken from refs. [5,6].

^{d)} Results from this work.

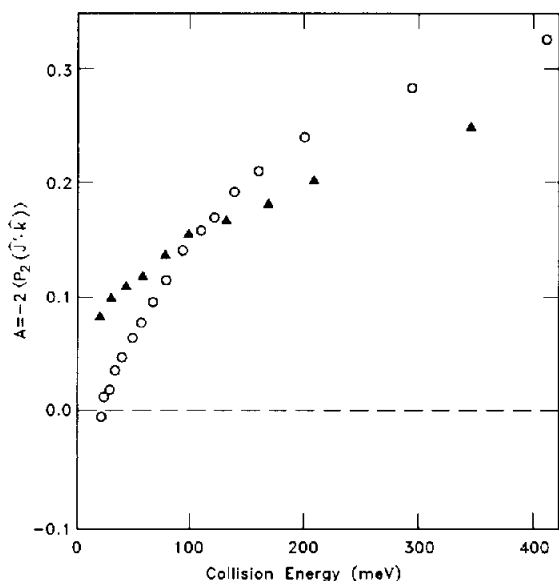


Fig. 2. Comparison of the excimer rotational alignment produced in the reaction of $\text{Xe}^* + \text{CBr}_4$ (O) with the excimer alignment produced in the reaction of $\text{Kr}^* + \text{CBr}_4$ (▲).

in general, lead to less alignment of the excimer rotation. Also, increasing the moment of inertia of the polyatomic radical might allow more rotational angular momentum to be partitioned to the fragment thereby leaving less internal angular momentum available for the excimer. Indeed, for the formation of XeBr^* from reactions (3)–(5), the degree of product alignment decreases as the mass of the polyatomic radical increases. This trend is also observed in the formation of XeI^* from the $\text{Xe}^* + \text{CH}_3\text{I}/\text{CH}_2\text{I}_2$ reactions.

While many of the features of the XeX^* rotational alignment produced in reactions (1)–(7) can be explained on the basis of the kinematic constraints governing the reactions, kinematics alone cannot account for all of the observed effects. Thus, dynamic features of the potential surface governing these atom transfer reactions must also be important. This is particularly true at low collision velocities, where we observed preferential alignment of \mathbf{J}' parallel to \mathbf{k} in a number of cases. In principle, this “negative” polarization can occur in a number of ways: (i) A steric effect can select an angular momentum distribution of the reagent molecules with \mathbf{J} parallel to \mathbf{k} . With small enough L , conservation of angular momentum

can then produce a \mathbf{J}' distribution parallel to \mathbf{k} . As can be seen from fig. 1, this may not be the most attractive explanation since parallel alignment is stronger for the halomethanes with more halogens, which are the more symmetrical molecules. (ii) The angular momentum, j' , of the CH_aX_b product can play a role since both \mathbf{J}' and j' combine to form the total product angular momentum, which – in principle – can have an orientation quite different from \mathbf{J}' . It is, however, hard to evaluate the role of this product without extensive assumptions about the reaction dynamics. (iii) A reaction mechanism involving sideways scattering can cause the plane on which the reaction takes place to tip. In this case the product angular momentum L' is no longer perpendicular to \mathbf{k} , and consequently \mathbf{J}' is no longer necessarily forced to align perpendicularly to \mathbf{k} (see fig. 3).

Since the reaction mechanisms of many of the corresponding alkali-halide systems are well studied by

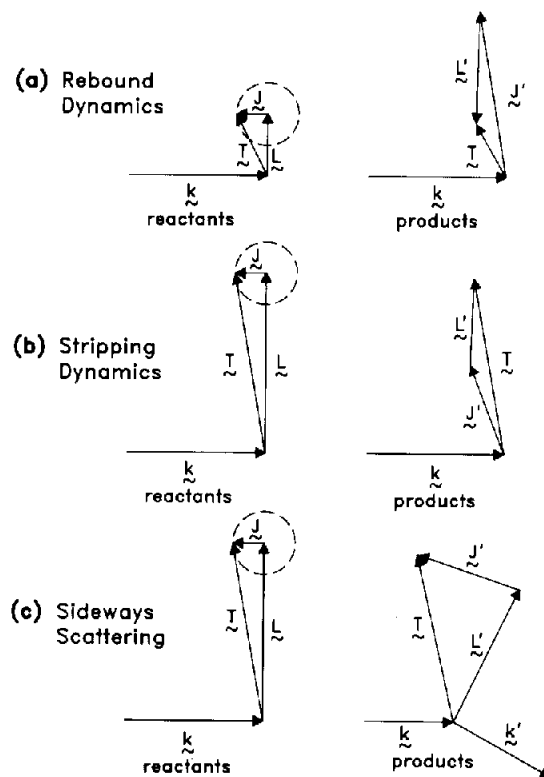


Fig. 3. Graphical representation of the product alignments expected from various reactive scattering mechanisms.

differential scattering, it is particularly instructive to discuss our alignment results in light of the third explanation. Schematic vector diagrams are given in fig. 3 for three cases; rebound, stripping, and sideways scattering. Examples of each mechanism can be found in the I, Br, and Cl reactions, respectively, (vide infra). For the sake of clarity, the reagent angular momentum distribution is drawn small compared to L' , which is certainly not true for the lowest collision energies. Even in that case, however, the average total angular momentum, T , is still perpendicular to k , unless there is a steric effect. Only one product angular momentum is indicated in these diagrams, representing the vector sum of both product angular momenta.

The atom transfer reactions of the alkali-metal atoms with CH_3I are prototypical rebound reactions which proceed over a repulsive potential surface [16–18]. This mechanism is dominated by collisions with small impact parameters (small L) and large repulsive energy release between the products. A large amount of the reaction exoergicity appears as product translational and rotational energy, and relatively little energy is transferred into vibration. In the case of the $\text{Xe}^* + \text{CH}_3\text{I}$ reaction, previous work suggests that formation of the XeI^* excimer may occur via an analogous rebound mechanism. Tamagake et al. report that the cross section for formation of XeI^* is about 4 \AA^2 [19]. Only about 28% of the total available energy is partitioned into vibration. Hijazi and Polanyi [20] found that scattering from a repulsive surface produces a large degree of alignment for the products scattered at 180° . The product relative velocity vector, k' , is opposed to k , and, as shown schematically in fig. 3a, this constrains J' to preferential alignment perpendicular to k . The source of the rotational alignment in this mechanism is not from the initial orbital angular momentum, since for small impact parameters this is small, but rather stems from the repulsive energy release. For this repulsion to be effective in creating rotation in the XeI^* product a significant amount of torque must be exerted in the atom transfer step. If reaction occurs principally through bent configurations then repulsion in the C–I bond can produce a torque in the XeI^* . A bent configuration favors transfer of repulsive energy to product rotation,

whereas a colinear geometry would favor transfer to vibration.

The appearance of the collisional energy dependence of the XeBr^* alignment from CBr_4 is similar to that from the $\text{Xe}^* + \text{Br}_2$ reaction [9]. It has been found from reactive scattering experiments that the $\text{M} + \text{CBr}_4$, Br_2 reaction products are predominantly scattered into the forward hemisphere, but scattering into wider angles was also observed [21]. Forward scattering is typical of stripping dynamics and is illustrated schematically in fig. 3b. The products are scattered predominantly into the forward hemisphere as a result of large impact parameter collisions and small repulsive energy release. With k' parallel to k (and thus L' parallel to L) a large degree of alignment of J' is expected. The stripping mechanism is similar to rebound in that the reaction tends to proceed on a single plane. It differs, however, from the rebound mechanism in that the product rotation stems from the large amount of initial orbital angular momentum characteristic for large impact parameter collisions. As can be seen from fig. 1 the product alignment decreases at lower collision energies.

The reactions of Xe^* with CCl_4 and CHCl_3 at low collision energies lead to the formation of XeCl^* that is aligned preferentially parallel to the relative velocity vector. A possible explanation for this negative alignment is a mechanism whereby the repulsive energy is released off-axis with respect to k . Evidence for this type of mechanism is found in the reactive scattering of the alkali metals by CHCl_3 and CCl_4 [20,21]. In this earlier work, the product MCl from these reactions showed a marked preference for sideways scattering. Furthermore, the product angular distribution was found to be strongly coupled to the relative velocity, with the favored direction of recoil gradually shifting to the forward hemisphere as the collision energy was increased. The assumption of similar behavior with Xe^* can explain the shift from negative to substantial positive polarization as the collision energy is increased. Fig. 3c illustrates how sideways scattering can lead to product rotational alignment parallel to the relative velocity vector. As the velocity increases and the scattering becomes more forward peaked, as in fig. 3b, alignment more perpendicular to k will result. Consequently the observed alignment in the Xe^* reactions with CCl_4 and

CHCl_3 is consistent with the differential scattering results on the corresponding alkali-metal reactions. In this picture the negative polarization is explained by "tipping" the plane on which the reaction takes place.

The excimer emission from the $\text{Kr}^* + \text{CBr}_4$ shows a weaker polarization than that from the $\text{Xe}^* + \text{CBr}_4$ reaction, except at the lowest velocities. The large differences between the Xe^* and Kr^* reactions are the obvious mass differences and the larger amount of available energy associated with the Kr^* reaction. The lower KrBr^* polarization at the higher velocities can therefore be attributed to the different kinematics. If one assumes the same repulsive energy release and similar reaction dynamics, the larger L of the Xe^* trajectories compared to the Kr^* trajectories would tend to give a larger degree of alignment in the XeBr^* excimer. At the lower velocities, the larger degree of alignment resulting from the KrBr^* excimer must be due to differences in the dynamics governing the atom transfer. Similar observations were made by Hennessy and Simons on the Kr^* , $\text{Xe}^* + \text{Br}_2$ reactions [6]. In these experiments, the KrBr^* alignment was smaller and less dependent on the relative velocity than the XeBr^* alignment.

Finally, it is noted that attempts to fit the data with the direct interaction with product repulsion (DIPR) model [13] resulted in generally poor agreement. This may not be too surprising in view of the assumptions underlying the model, including the omission of internal angular momentum, both in the reagent molecule and in the second product molecule.

5. Summary

The present work shows dramatic differences in rotational alignment resulting from the atom transfer reactions of Xe^* with the halomethanes. These differences cannot be explained by kinematic constraints alone, especially at the lower collision energies. Some of the major trends can be explained by a correlation with the scattering results of the corresponding alkali-metal reactions. The XeI^* excimers are most polarized, even more than in the case of the Xe^*/I_2 reaction, and can be associated with a rebound mechanism. The XeBr^* excimers formed in the reactions of the bromomethanes are less aligned,

and can be associated with a stripping mechanism at the higher velocities. Both the rebound and the stripping mechanism tend to produce substantial positive polarization. On the other hand, the XeCl^* excimers formed from the reactions of Xe^* with chloroform and carbon tetrachloride show very little polarization, which even becomes negative at the lowest energies. This implies alignment preferentially parallel to the relative velocity vector. These reactions can be interpreted as involving sideways scattering, which causes a tipping of the reaction plane.

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