$$\bar{j}' \simeq \rho\alpha\langle l\rangle \qquad (28)$$

The distribution of final rotational states (27) is characterized by two parameters, $\bar{j}'$ and the width $\sigma^2(1-\rho^2)$. If l and j' are strongly correlated (as, e.g., in H + Cl_2), $\rho \to 1$ and the cutoff in the rotational distribution will be due to the exponential part in (27) and not due to the energy cutoff in the prior distribution $P^o(v'j')$. The larger is $\langle(\Delta j')^2\rangle$, the larger is σ^2 and the weaker is the correlation ($\rho \to 0$) between l and j'. The limit of large $\langle(\Delta j')^2\rangle$ is the limit where the behavior of $P(v'j')$ is dominated by the prior distribution.

The mass effect is due to $\alpha \propto \sin^2\beta$, cf. (18) and (28). The lighter is the atom exchanged, the lower is the value of $\sin^2\beta$ and hence the lower is the value of $\bar{j}'$. For $\bar{j}' \to 0$ we obtain a one parameter representation

$$P(v'j') = P^o(v'j')\exp(-j'^2/2\sigma^2(1-\rho^2)) \qquad (29)$$

This is the functional form typically employed[17] for H-atom exchange, as in Cl + HI. At higher collision energies when $\langle l\rangle$ is larger and/or for such reactions as D + H_2 (where $\sin^2\beta = 2/3$), one cannot quite put $\bar{j}' = 0$ and (27) provides a more realistic representation.

For the X + HY family of reactions (X,Y halogens), it is observed[17] that $P(v'j')$ is not a function of $E'_j \propto j'^2$ but of $E'_j/(E - E'_v)$. The qualitative reason is clear. The width $\sigma^2 \propto \langle(\Delta j')^2\rangle$ should increase, cf. (8), with the energy in the translation. This is not quantitatively obvious in the kinematic model since it conserves the kinetic energy and not the total energy. If we impose the conservation of total energy, as in section 5, by putting $E'_T = E - E'_v - E'_j$, then we can understand the increase by invoking detailed balance. Note incidentally the prediction that as the initial translational energy increases, σ^2 will increase and the final rotational state distribution will be closer to the prior limit.

7. Concluding Remarks

There is a well-known tendency of heavy-atom-transfer reactions to polarize product rotational angular momenta along the direction of the initial orbital angular momentum. We show that this tendency is marked also for reactions taking place via collinear transition states, even when the transferred atom is not relatively heavy, as is the case for H + H_2. Thus, the polarization of product rotation can be predicted for reactions with collinear transition states with relatively moderate to heavy transferred atoms. In such cases, experiments starting with rotationally and vibrationally cold reactants may be analyzed according to the formulas given here. The measured distribution of product rotational quantum numbers can be used to estimate the opacity function giving the probability of reaction as a function of impact parameter.

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Superthermal Widths of the Collision Energy Distributions in Hot Atom Reactions

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Analytical expressions are presented for the collision energy distribution and its width in hot atom reactions. These expressions are adapted from those derived previously by Chantry [*J. Chem. Phys.* **1971**, *55*, 2746] for the related context of ion–molecule reactions. Although the spread in the collision energy distribution arises solely from the thermal motions of the reagents, its width exceeds the average thermal energies of the reagents, often substantially.

In 1973, Dick Bernstein published a perceptive comment[1] on the Doppler broadening effect on collision cross sections resulting from the thermal motions of target molecules in many different collisional experiments. He stressed the comprehensive treatment of this problem which Chantry had originally derived[2] in the context of ion–molecule reactions, and the generality of this effect in all forms of scattering for both ions and neutral particles.

Subsequently, it appears that ion–molecule practitioners have remained keenly aware of this treatment of such averaging effects,[3,4] but a similar familiarity seems to have been lacking in the recently expanding field of "hot atom" reactions studied by photolyzing precursor molecules in the presence of other target molecules.[5]

Such an experiment may be represented by a two-step scheme:

$$AB + h\nu \to A + B$$

$$A + C \to \text{products}$$

The purpose of this note is to stress the relevance of the earlier work of Chantry, Bernstein, and others to this type of experiment. Isotropic thermal motions of AB and C are present in almost all practical cases, and they can have a (perhaps surprisingly) dra-

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matic effect on the distribution of A···C collision energies. In particular, this distribution can have a very substantial *width*. This effect has been identified in the hot atom context,[6-9] but we are not aware of any publications in which Chantry's exact treatment of the problem[2] has been adopted. Valentini and co-workers have described a Monte Carlo method for obtaining the collision energy distribution.[7] Bersohn and colleagues have successfully derived expressions for the moments of the distribution.[8,9] In this paper we represent the relevant equations that may be found in Chantry's work,[2,10] briefly outlining the derivation of these expressions using a notation easily applied to hot atom experiments. We also demonstrate the very significant width of the distribution in some typical illustrative cases and emphasize that this can be crucial to the correct interpretation of experimental results.

The *average* collision energy in a hot atom reaction is readily estimated and is only slightly affected by thermal motions of precursor and target molecules.[5-9] However, as explained by Bernstein and others,[1,2,8,11,12] the elementary but critical realization concerning the *width* of a distribution in energy is that it depends (linearly) on *both* the width of the corresponding velocity distribution *and* the absolute average velocity. Therefore, the higher the recoil velocity of A following photolysis, the greater the spread in laboratory-frame kinetic energies of A, E_A^{lab}, caused by the precursor thermal velocities, v_{AB}. Similarly, higher values of E_A^{lab} lead to a greater range of A···C collision energies, E_{coll} (the quantity ultimately of most interest), for a given distribution of target velocities, v_C.

We omit from this brief treatment any additional contributions to the spread in collision energies caused by the finite bandwidth of the photolysis source (often negligible for laser photolysis), by multiple channels in the photolysis (i.e., excitation of internal states of A or B), or by thermal rotational motions of the precursor AB.

The laboratory-frame velocity v_A is the vector sum of v_{AB} and u_A, the recoil velocity of A relative to the center of mass of AB. The distribution of magnitudes of v_A is found by integrating over the Maxwell–Boltzmann distribution of v_{AB}. (Various mathematical procedures have been adopted.[2,13-15]) In terms of energies, the resulting probability density function is

$$P_1(E_A^{lab})\,dE_A^{lab} = \left(\frac{m_{AB}^2}{4\pi kTm_Am_BE_{exc}}\right)^{1/2} \times \left\{\exp\left[-\frac{m_{AB}}{m_AkT}\left(\left(\frac{m_B}{m_{AB}}E_{exc}\right)^{1/2} - (E_A^{lab})^{1/2}\right)^2\right] - \exp\left[-\frac{m_{AB}}{m_AkT}\left(\left(\frac{m_B}{m_{AB}}E_{exc}\right)^{1/2} + (E_A^{lab})^{1/2}\right)^2\right]\right\} dE_A^{lab} \quad (1)$$

where m_i is the mass of species i, T is the common temperature of AB and C, and k is the Boltzmann constant. The total excess energy in the photolysis step, E_{exc}, is equal to $(m_Am_{AB}/2m_B)u_A^2$ by momentum conservation. For a rotationless precursor molecule, E_{exc} is simply the difference between the photon energy and the bond dissociation energy.

TABLE I: Calculated Collision Energy Spreads, w_3, for Some Representative Hot Atom Reactions, A + C, Carried Out at a Temperature of 300 K for the Average Collision Energy $\langle E_{coll}\rangle$[a]

A + C	AB	λ/ nm	E_{exc}/kT	$\langle E_{coll}\rangle/kT$	w_3/kT	representative refs
$H + H_2$	HI	276	55.6	37.3	11.8	7
$H + D_2$	HI	266	62.2	49.6	10.6	6, 7
$H + O_2$	HBr	193	103.1	98.8	6.8	18
$H + CO_2$	HI	285	50.0	48.6	4.0	21
$D + H_2$	DBr	210	81.2	40.4	15.0	19
O + HBr	NO_2	355	14.7	8.7	6.4	20

[a] The lowest states of A and B are generated by photolysis of AB (assumed rotationless) at wavelength λ with an excess energy E_{exc}. Energies are expressed as multiples of kT, where T = 300 K.

A similar treatment applies to the effect of the thermal velocity v_C on the A···C collision energy, E_{coll}. For a *fixed* value of the laboratory energy, E_A^{lab}, the distribution of E_{coll} is found to be

$$P_2(E_{coll}|E_A^{lab})\,dE_{coll} = \left(\frac{m_{AC}^2}{4\pi kTm_Am_CE_A^{lab}}\right)^{1/2}\left\{\exp\left[-\frac{m_{AC}}{m_AkT}\left(\left(\frac{m_C}{m_{AC}}E_A^{lab}\right)^{1/2} - (E_{coll})^{1/2}\right)^2\right] - \exp\left[-\frac{m_{AC}}{m_AkT}\left(\left(\frac{m_C}{m_{AC}}E_A^{lab}\right)^{1/2} + (E_{coll})^{1/2}\right)^2\right]\right\} dE_{coll} \quad (2)$$

Finally, to combine the effects of the thermal motions of AB and C, eq 2 must be integrated over the distribution of E_A^{lab} described by eq 1. The result, as also given by Chantry,[2] is

$$P_3(E_{coll})\,dE_{coll} = \left(\frac{m_{AB}^2m_{AC}^2}{4\pi kTm_Am_Bm_Cm_{ABC}E_{exc}}\right)^{1/2}\left\{\exp\left[-\frac{m_{AB}m_{AC}}{m_Am_{ABC}kT}\times\left(\left(\frac{m_Bm_C}{m_{AB}m_{AC}}E_{exc}\right)^{1/2} - (E_{coll})^{1/2}\right)^2\right] - \exp\left[-\frac{m_{AB}m_{AC}}{m_Am_{ABC}kT}\left(\left(\frac{m_Bm_C}{m_{AB}m_{AC}}E_{exc}\right)^{1/2} + (E_{coll})^{1/2}\right)^2\right]\right\} dE_{coll} \quad (3)$$

The second of the exponential terms in eq 3 is effectively negligible when $E_{exc} \gg (m_{AB}m_{AC}/m_Bm_C)kT$ (i.e., loosely, when the excess energy in photolysis is substantially greater than typical thermal energies). The first term describes a slightly skewed, near-Gaussian form that peaks at $(m_Bm_C/m_{AB}m_{AC})E_{exc}$ and has a full width at half-maximum

$$w_3 = 4\left[\frac{m_Am_Bm_Cm_{ABC}}{m_{AB}^2m_{AC}^2}kTE_{exc}\ln 2\right]^{1/2} \quad (4)$$

A true Gaussian with the same width and peak energy

$$P_3(E_{coll})\,dE_{coll} \simeq \left[\frac{m_{AB}^2m_{AC}^2}{4\pi kTm_Am_Bm_Cm_{ABC}E_{exc}}\right]^{1/2} \times \exp\left[-\frac{m_{AB}^2m_{AC}^2}{4m_Am_Bm_Cm_{ABC}kTE_{exc}}\left(E_{coll} - \frac{m_Bm_C}{m_{AB}m_{AC}}E_{exc}\right)^2\right] dE_{coll} \quad (5)$$

is also a reasonable approximation in this high E_{exc} limit.[2,16,17]

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Kinematic effects play a very important role in determining the width of the collision energy distribution. Generally, w_3 has a global maximum of $1.665(E_{exc}kT)^{1/2}$ for all mass combinations for which $m_A = m_B m_C/m_{ABC}$, requiring $m_A < m_B, m_C$. However, the energy spread in the photolysis step is maximized when $m_A = m_B$ and the spread in the collision step maximized when $m_A = m_C$; these conditions maximize the overall spread when either C or B, respectively, is relatively massive. Note that $P_3(E_{coll})\,dE_{coll}$ describes the probability of finding an A···C particle pair with the relative energy E_{coll}. The rate of collisions between A and C has a probability further weighted by the collision velocity, proportional to $(E_{coll})^{1/2}$.

Table I presents the characteristics of the collision energy distributions for some representative hot atom reactions. The spread in collision energies always exceeds the average thermal energies of the reagents; in some cases this difference is extremely substantial.

Many hot atom studies have involved H atoms (and isotopes), generated by photolysis of the heavier hydrogen halides.[5] The overall width of these collision energy distributions will usually depend on the mass of the relatively light target molecule. The worst cases are the reactions H(D) + $H_2(D_2)$, for which the collision energy spread is many times greater than the thermal energy of the $H_2(D_2)$ reactant. However, in terms of relative energy spread, that is w_3/E_{coll}, the worst cases are those such as the O + HBr reaction, in which the masses of A, B, and C are all comparable and E_{exc} is low. For these the relative energy spread can be almost as great as that in a Boltzmann distribution.

The ability to vary the *average* collision energy by changing the photolysis wavelength is a potential virtue of hot atom experiments. However, we must conclude that the inherent *spread* in collision energies will constitute an obvious drawback in the investigation of energy-dependent phenomena, including the partitioning of energy in products,[5-7,9,18-21] and particularly the details of the variation of the cross section with energy, such as the threshold for reaction[8,21] and postulated nonclassical dynamical resonances.[7b,c,22] This drawback afflicts studies done with samples at *ambient* temperature. It can be substantially overcome by using nozzle expansions to produce samples at temperatures of a few degrees kelvin, although cooling cannot remove any inherent distribution in the collision energies caused by multiple channels in the photolysis step. The collision energy spread scales only as $T^{1/2}$, but lowering the temperature from 300 to 5 K, for example, reduces the energy spread by almost a factor of 8. For the reactions listed in Table I this gives w_3 of typically just 1 kcal mol^{-1} and w_3/E_{coll} of only a few percent.

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Dynamics of Ba–Br_2 Chemiionization Reactions

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The formation of $BaBr^+$ ions in reaction of Ba($^1S_0$,$^1P_1$) with Br_2 was studied as a function of laboratory scattering angle and product translational energy in a crossed-beam experiment. The contour map of $BaBr^+$ flux obtained for the ground-state reaction at 1.1-eV collision energy showed a backscattered angular distribution (relative to the barium beam) with a substantial fraction of the available energy appearing in translation. Laser excitation strongly inhibited this channel at 1.1 eV. These experimental observations suggest that for the chemiion reaction head-on, collinear collisions and proximal crossings of the potential energy surfaces are necessary to preclude escape into the dominant neutral pathways. At 1.6-eV collision energy a new laser-dependent source of $BaBr^+$ appeared. This laser-enhanced $BaBr^+$ showed a laboratory angular distribution substantially narrower than for the ground-state reaction, indicating a smaller translational energy release. The angular distribution was ~70% backscattered and displayed a clear dip at the center of mass. This new $BaBr^+$, produced from electronically excited barium at higher translational energy, is ascribed to secondary collisions of BaBr + Br initially formed in low impact parameter collisions. Reaction of electronically excited barium with Br_2 also yielded an associative ionization product $BaBr_2^+$ at both collision energies studied, with a cross section about 1/100th that of the chemiion channel.

Introduction

The reaction of barium with halogen molecules represents an important prototypical case for the study of reaction dynamics in divalent systems.[1-6] Reaction may be initiated with the transfer of one electron via the celebrated "harpoon mechanism",[7-10] but there exist a range of possible product channels owing to the presence of the second valence electron on barium and a second electron-accepting halogen atom. The reaction with ground-state barium is dominated by the production of the ground state, neutral radical pair BaX and X (X a halogen atom).[11,12] In addition,

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