

Indirect Information on Reactive Transition States from Conservation of Angular Momentum

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By choosing a kinematically constrained bimolecular reaction of the type $H + H'L \rightarrow HH' + L$, where H and H' are heavy atoms and L is a light atom, the orbital angular momentum, L , of the reagents appears almost exclusively as HH' product rotation, J . It follows that the magnitude of J is given by $|L| = \mu v_{\text{rel}} b$, where μ is the reduced mass of the reagent collision partners, v_{rel} is their relative velocity and b is the impact parameter, *i.e.* the distance of closest approach if the reagents moved in undeflected straight-line paths. Hence, by measuring both the product rotational distribution and the relative velocity distribution of the reagents, it is possible to deduce the range of impact parameters resulting in specific vibrational levels of the HH' product. A prototype system is $Ba + HI \rightarrow BaI + H$. Experimental results for BaI ($v = 0$) are presented for this kinematically constrained reaction showing that the range of b is restricted, peaking at or near the energetic cut-off.

Obtaining real-time information on the transition state of a bimolecular reaction, $A + BC \rightarrow AB + C$, is a daunting task that challenges chemists. We present indirect measurements of the approach geometry that leads to a reaction resulting in a specific product state. In particular, we are able to estimate the impact parameter distribution which describes the entrance way to the transition state leading to formation of a specific product. The impact parameter is defined as the distance of closest approach if the reagents were to move in undeflected straight-line paths.¹ Currently, little experimental evidence is available about which values of impact parameter lead to a specific product state. This lack of information is largely because the impact parameter cannot be controlled in reactive scattering experiments.

The observed reaction cross-section, $\sigma(v_{\text{rel}})$, as a function of the relative velocity of the reagents, v_{rel} , is given by

$$\sigma(v_{\text{rel}}) = \int_0^{\infty} \int_0^{\pi} P(b, v_{\text{rel}}, \gamma) f(\gamma) d\gamma 2\pi b db \quad (1)$$

where the impact parameter, b , and the reagent orientation, γ , are each averaged over the appropriate distribution function, $2\pi b$ and $f(\gamma)$, respectively. $P(b, v_{\text{rel}}, \gamma)$ is known as the total opacity function.

This fundamental dependence of reactivity on impact parameter is usually concealed in an average over the impact parameter in state-to-state experiments where there is no angular distribution analysis. However, as first suggested by Herschbach² in a 1962 Faraday Discussion, the dependence of the reaction probability on the impact parameter, b , can be determined if a kinematically constrained reaction of the type $H + H'L \rightarrow HH' + L$ is chosen, where H and H' are heavy atoms and L is a light atom. The special combination of masses in this class of reaction systems means that the reagent orbital

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angular momentum, L , is channelled almost exclusively into product rotational angular momentum, J :

$$L \approx J. \quad (2)$$

The magnitude of the reagent orbital angular momentum is given by:

$$|L| = \mu v_{\text{rel}} b \quad (3)$$

where μ is the reduced mass of the reagents. Hence we obtain:

$$|J| \approx \mu v_{\text{rel}} b. \quad (4)$$

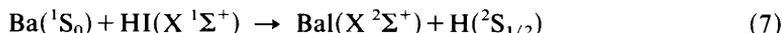
The reduced mass, μ , is known. Thus, by measuring the rotational distribution of the HH' product at a known relative velocity of the reactants, the reactive impact parameter distribution can be deduced. In particular, the specific opacity function, $P_v(b, v_{\text{rel}}, \gamma)$ describing the probability of obtaining products in a vibrational level, v , can be determined. The total opacity function is a sum of the individual specific opacity functions:

$$P(b, v_{\text{rel}}, \gamma) = \sum_v P_v(b, v_{\text{rel}}, \gamma). \quad (5)$$

The shape of $P_v(b, v_{\text{rel}}, \gamma)$ provides the dependence of the final-state distribution on the initial approach geometries of the reactants. When there is no experimental control over the orientation of the reactants an orientation-averaged specific opacity function is obtained:

$$P_v(b, v_{\text{rel}}) = \int_0^\pi P_v(b, v_{\text{rel}}, \gamma) f(\gamma) d\gamma. \quad (6)$$

We have chosen the kinematically constrained reaction



for our studies. By measuring the rotational distribution of product BaI molecules formed in $v=0$ and by measuring the velocity of the reagents, Ba and HI, we aim to determine $P_{v=0}(b, v_{\text{rel}})$ for this reaction.

Earlier work in this laboratory³ was involved with rotational distributions of BaI ($v=8$) product molecules formed in the same reaction by using selectively detected laser-induced fluorescence. In that work, a thermal Ba beam reacted with background HI gas. As the range of collision energies was large, the shape of a velocity-averaged opacity function could be estimated but not uniquely determined. The opacity function was found to be a maximum at close to 2.6 Å with a full-width at half-maximum (FWHM) of 1.0 Å. In the experiments presented in this paper a beam-beam study of the reaction Ba + HI is described in which the translational energy spread of the reactants is narrower than that in the earlier beam-gas study.

Experimental

There have been studies of other kinematically constrained reactions, but none has been able to resolve rotational product states. This is mainly because one of the essential features of these reactions is that the product diatomic molecule must contain two heavy atoms. This means the reduced mass of the product is large and consequently the rotational constant is small. This results in very congested spectra which can only be rotationally resolved with narrow-band lasers and sub-Doppler techniques. Such techniques are used in our experiment.

Fig. 1 shows a schematic cross-section through the apparatus. A full description of this experiment has been given elsewhere⁴ so only a brief summary follows. A Ba beam from an oven source (1300 K) intersects at right angles a supersonic HI beam. The

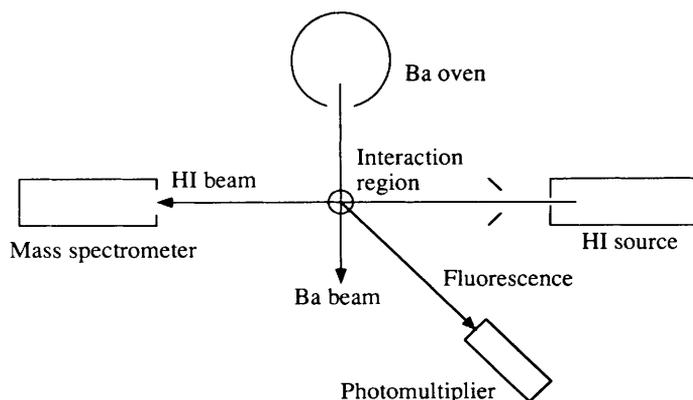


Fig. 1 Schematic horizontal cross-section through the apparatus. The laser beam is directed perpendicular to the plane of the diagram and passes through the interaction region

nascent product BaI molecules are probed by a laser beam which is perpendicular to both molecular beams. Laser-induced fluorescence is used to measure the rotational distribution of the BaI $X^2\Sigma^+$ products formed in $v=0$. The velocity of the Ba beam is determined by Doppler spectroscopy and the velocity of the HI beam is measured by time-of-flight mass spectrometry.⁵

A beam from a continuous-wave single-mode ring dye laser (Coherent 699-29) containing rhodamine 560 dye is used to excite the BaI $C^2\Pi-X^2\Sigma^+$ transition. The total fluorescence from the $C^2\Pi$ state is collected using a photomultiplier as the laser is scanned. One rotational branch (either P_{12} or P_2) is measured to determine the relative populations of the different J states resulting from the reaction. To obtain accurate rotational distributions, the laser is actively power-stabilised as it is scanned using a servo-locked acousto-optic modulator. In addition, a Keplerian telescope/spatial filter collimates the light at the same time as converting any movements of beam position into amplitude fluctuations which are therefore compensated for by the power stabilisation. Attenuation of the laser beam is carried out by two polarisation cubes to reduce the power to 5 mW. This prevents saturation of the BaI transitions.

The HI beam is formed by expansion of a mixture of 6% HI in N_2 at a stagnation pressure of 250 kPa through a 100 μm diameter nozzle. The beam then passes through a 1 mm diameter skimmer before entering the main reaction chamber. The distance from the nozzle to the interaction region is *ca.* 20 cm. The HI beam is directed into a quadrupole mass spectrometer which is used to obtain a time-of-flight spectrum of the HI beam for determining the velocity distribution for a particular set of expansion conditions. When carrying out the time-of-flight measurement a chopper inside the vacuum system is moved to intersect the HI beam.

A Ba oven consisting of a steel crucible heated to 1300 K is used as a source for a beam of ground-state Ba atoms. The Ba beam emerges from the crucible through a 0.8 mm diameter orifice and is collimated by several apertures before entering the main reaction chamber. The velocity of the Ba beam is measured using Doppler spectroscopy of the two-photon transition $^3D_2-^1S_0$ at 36 200.42 cm^{-1} .⁶ A sub-Doppler spectrum is measured with the laser beam vertical, and hence perpendicular to the Ba beam (as in Fig. 1) and a Doppler-limited spectrum is recorded by bringing the laser beam in horizontally, at an angle of 45° to the Ba beam. The laser-induced fluorescence is collected using single-photon counting of the emission through the $^3D_2-^3P^o$ transition at 440 nm which is isolated using a narrow-bandpass interference filter placed in front of the photomultiplier.

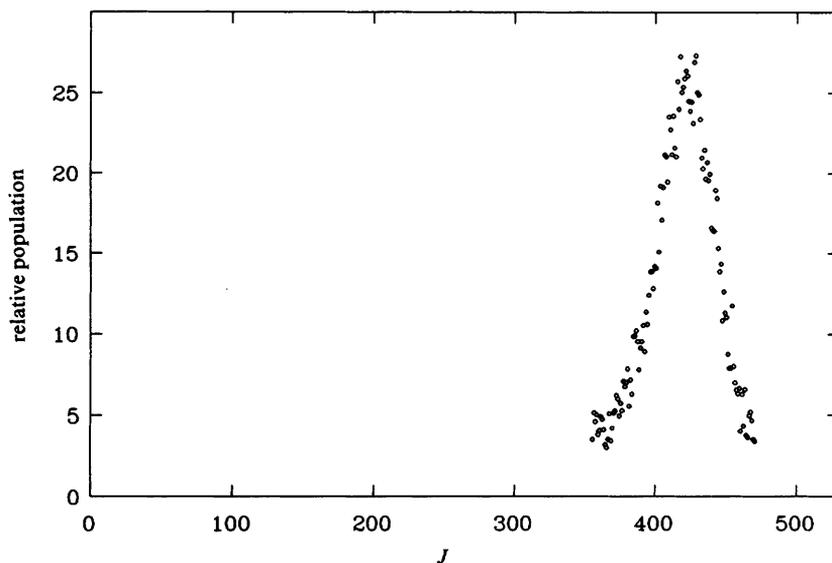


Fig. 2 Rotational distribution of the BaI ($v=0$) product

Results

Both the Ba and HI velocity distributions were modelled to the equation:

$$f(v) = (v - v_0)^2 \exp\left[-\left(\frac{v - v_s}{\alpha_s}\right)^2\right]. \quad (8)$$

Convolution of the known pulse temporal profile of the HI beam with the velocity distribution gives a simulation of the time-of-flight spectrum. Similarly, a convolution of the Doppler-free spectrum with the Ba velocity distribution gives a simulation of the Doppler-limited spectrum. A thermal distribution of the Ba velocities was found to give a very poor simulation; thus eqn. (8) was used.⁴ The values of the parameters, v_0 , v_s and α_s , determined from non-linear least-squares optimisations of the simulations are 183, 282 and 296 m s^{-1} for Ba and 0, 785 and 31 m s^{-1} for HI, respectively. From these results the relative velocity distribution was calculated to have a mean velocity of 976 m s^{-1} and an FWHM of 108 m s^{-1} .

The rotational distribution measured for $v=0$ is found to be very highly excited. A rotational analysis of the BaI $\text{C } ^2\Pi - \text{X } ^2\Sigma^+ (0, 0)$ band has been carried out.⁷ We are able to assign rotational quantum numbers to the lines measured and thus know the rotational angular momentum of the BaI products formed in $v=0$. The resulting rotational distribution is given in Fig. 2. The maximum of the distribution is at $J = 428.5$ and the FWHM is 29. This corresponds to an energy distribution with a maximum at 13.8 kcal mol^{-1} and an FWHM of 1.77 kcal mol^{-1} .

Opacity Function Models

From our experiment we have obtained the rotational distribution for products formed in $v=0$ and the relative velocity distribution of the reagents. We are now in a position to use eqn. (4) to deduce an impact parameter distribution for a particular velocity. To determine the specific opacity function, we choose a number of models for $P(b, v_{\text{rel}})$ and investigate how well they can simulate the experimental rotational distribution. Three models are described.

The principle of conservation of energy constrains all models by providing a velocity-dependent maximum allowed impact parameter, $b_{\max}(v, J)$. As J increases for a given value of v_{rel} , a point is reached when there is no longer enough energy available for products to form. Thus we can write the inequality,

$$E_{\text{rel}} + \Delta E \geq E_{\text{BaI}}(v, J) \quad (9)$$

where E_{rel} is the energy of the reactants, ΔE is the difference between the dissociation energies, D_0^0 of BaI and HI:

$$\Delta E = D_0^0(\text{BaI}) - D_0^0(\text{HI}) \quad (10)$$

and $E_{\text{BaI}}(v, J)$ is the total internal energy of the BaI molecules. The restriction placed on v_{rel} by energy conservation is

$$v_{\text{rel}} \geq \left(\frac{2[E_{\text{BaI}}(v, J) - \Delta E]}{\mu} \right)^{1/2} = v_{\text{min}}(v, J) \quad (11)$$

For a particular value of J this results in a maximum reactive impact parameter of

$$b_{\max}(v, J) = \frac{J\hbar}{\mu v_{\text{min}}(v, J)} \quad (12)$$

Our experiment is very sensitive to the exothermicity of the reaction, ΔE , as given in eqn. (11). $D_0^0(\text{HI})$ is $70.429 \pm 0.025 \text{ kcal mol}^{-1}$.⁸ We have recently recommended a value of $77.7 \pm 2.0 \text{ kcal mol}^{-1}$ for $D_0^0(\text{BaI})$,⁴ based on our observations of the highest occupied rotational and vibrational levels from the beam-beam reaction $\text{Ba} + \text{HI}$, which gave a lower limit,⁴ and earlier work by Johnson *et al.*,⁹ which used the observation of the onset of predissociation from the $\text{C}^2\Pi$ state to give an upper limit. The models can determine $D_0^0(\text{BaI})$ to better than the uncertainty of $\pm 2.0 \text{ kcal mol}^{-1}$. Thus, $D_0^0(\text{BaI})$ is treated as an adjustable parameter in our simulations of the rotational distribution for the different specific opacity function models.

Model 1: Step Function

In this model all collisions between the reactants below a certain impact parameter are assumed to have the same probability of reacting. The maximum impact parameter is determined by the energy cut-off at each reagent velocity as given in eqn. (12). A non-linear least-squares fit to model this data to the experimental rotational distribution is performed in which $D_0^0(\text{BaI})$ is the only adjustable parameter. Fig. 3 shows the results of this fit. $D_0^0(\text{BaI})$ is determined to be $79.16 \text{ kcal mol}^{-1}$. The insert shows the specific opacity function for the mean relative velocity where the maximum impact parameter is 4.57 \AA .

Model 2: Isosceles Triangle

In this model an isosceles triangle is moved along the energy cut-off with its high- b vertex on the energy cut-off. To keep this model as simple as possible we choose to maintain the width and height of the triangle constant as the relative velocity is changed. There are two fitting parameters in this model, the length of the base of the triangle and $D_0^0(\text{BaI})$. The optimised values of these are 0.036 \AA and $76.59 \text{ kcal mol}^{-1}$. Fig. 4 shows the results of this fit, including an insert showing the impact parameter distribution for the mean relative velocity.

Specific Opacity Function for Ba+HI

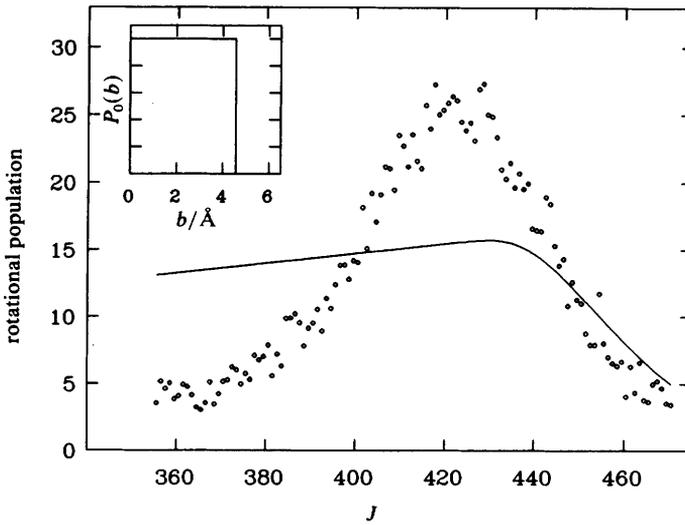


Fig. 3 Simulation of the BaI ($v=0$) rotational distribution using a step function as an opacity function. The insert shows the form of the opacity function for the mean relative velocity

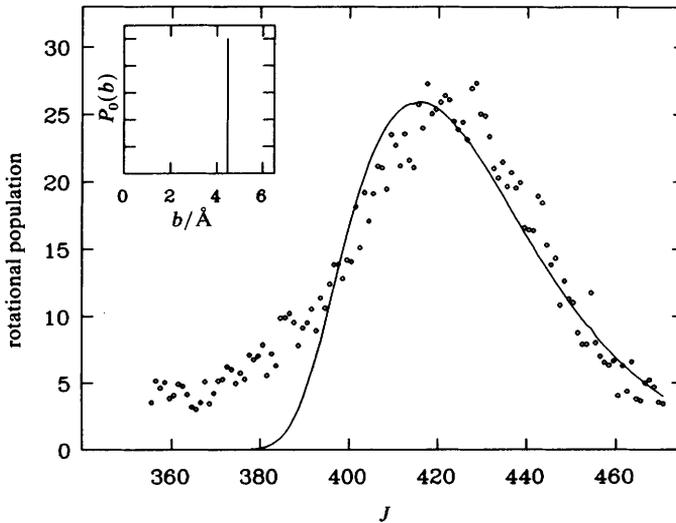


Fig. 4 Simulation of the BaI ($v=0$) rotational distribution using an isosceles triangle as an opacity function. The insert shows the form of the opacity function for the mean relative velocity. The triangle is so narrow that it appears as a line

Model 3: Truncated Gaussian

In this model the opacity function is assumed to be a Gaussian in b of the form:

$$P_{v=0}(b, v_{rel}) = \exp\left[-\frac{1}{2}\left(\frac{b-b_0}{\sigma_b}\right)^2\right] \quad (13)$$

The constraints associated with energy conservation cause this Gaussian distribution to be truncated according to eqn. (12). In this model the parameters which are derived

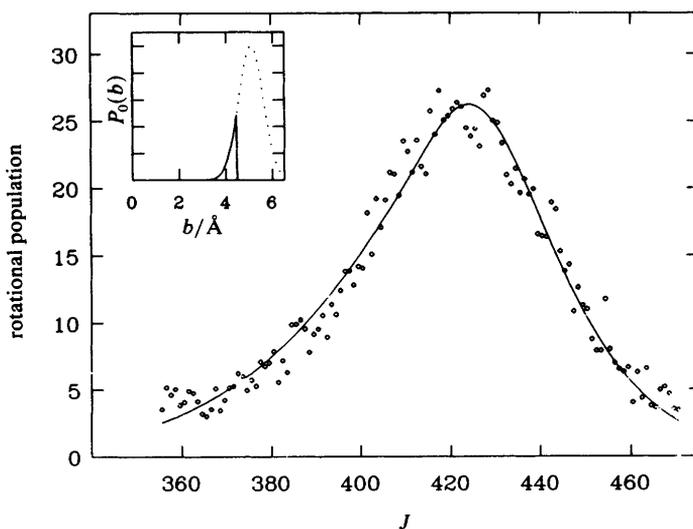


Fig. 5 Simulation of the BaI ($v=0$) rotational distribution using a truncated Gaussian as an opacity function. The insert shows the form of the opacity function for the mean relative velocity. The complete Gaussian is also shown (dotted line)

from a non-linear least-squares fit of the data are the maximum of the Gaussian, b_0 , its width, σ_b , and $D_0^0(\text{BaI})$. The values of these parameters are found to be 5.07 \AA , 0.526 \AA , and $78.42 \text{ kcal mol}^{-1}$. The resulting fit is shown in Fig. 5.

Discussion

As can be seen in Fig. 3 the fit of a step function is very poor. The very narrow, highly excited rotational distribution which we obtain in our experiments can be reproduced only by a model which has a maximum close to the energy limit and has a narrow width. Using a simple model of this type (model 2) improves the fit considerably over the step function, although it still does not closely reproduce the experimental distribution. In particular, it can be seen that the triangular model fails at the rising edge of the rotational distribution. This is because the model does not allow any reactive collisions to happen at impact parameters well below $b_{\text{max}}(v, J)$ and thus restricts the recoil energy to a very narrow range. The fit using the Gaussian distribution is much better (Fig. 5). This model allows for both a sharp maximum close to the energy limit and some reactivity at lower impact parameters.

In models 2 and 3 the specific opacity function is found to have a maximum at or near the energy cut-off and consequently predicts that the most probable impact parameter reacts to give products with (nearly) zero recoil velocity. However, this is not a serious problem because of the uncertainty in the dissociation energy of BaI and the small mass of the H atom relative to the BaI product. If there is just $0.1 \text{ kcal mol}^{-1}$ energy in recoil the H atom escapes from the BaI product at a velocity of 980 m s^{-1} .

Work is underway to carry out a direct inversion of the rotational distribution to find $P_{v=0}(b, v_{\text{rel}})$ and the present simulations should be regarded as preliminary. Nevertheless, we can draw some conclusions about the necessary form of $P_{v=0}(b, v_{\text{rel}})$, namely, that it peaks at or near the energy cut-off and its width is narrow. Thus, spectroscopic study of kinematically constrained reactions can determine the location of the 'door' that opens to the transition state and can provide an estimate of how wide the entrance is.

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