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Analysis of the experimental orientation dependence of the reaction $CH_3I + Rb \rightarrow RbI + CH_3$

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Experiments by Parker *et al.* (1981), deconvoluted for the precession effect by Stolte *et al.* (1982), yielded the dependence of reaction probability upon the "angle of attack" γ for the $CH_3I + Rb$ reaction. Inversion of these results is carried out via the kinetic theory model of reactive collisions of rigid nonspherical molecules of Evans *et al.* (1985), yielding the angle dependence of the activation barrier as well as an estimate of the colliding-pair anisotropy (asphericity) parameter.

I. INTRODUCTION

Following upon the development of the electrostatic hexapole focuser, which provides orientable symmetric top molecules in focused molecular beams,[1] Brooks and Jones[2] and Beuhler *et al.*[3] exploited this technique to study the orientation dependence of the reactions of alkyl halides with alkali atoms. Later, detailed results on the reactive (and nonreactive) asymmetry of the reaction $CH_3I + Rb \rightarrow RbI + CH_3$ were reported by Beuhler and Bernstein,[4,5] followed recently by a definitive investigation of the same reaction by Parker *et al.*[6] A detailed computational study of the focusing, rotational state selection, and orientation of seeded CH_3I beams was carried out by Chakravorty *et al.*[7] This made is possible for Stolte *et al.*[8] to deconvolute (from the experimental reactive asymmetry data) the effect of the precessional motion of the CH_3I molecules, making use of the quantitative knowledge of the distribution of orientations of CH_3I with respect to the incident Rb beam.

For RbI backscattered in the c.m. system, the reaction probability (i.e., the orientational opacity function) as a function of the so-called "angle of attack" γ was deduced. The best fit to the data could be expressed in the form of a truncated Legendre expansion up to $P_4(\cos\gamma)$. Alternative but somewhat less satisfactory fits included a linear function of $\cos\gamma$ as well as a step-function ("painted sphere", $\sim 50\%$ reactive). All of these concur in the existence of a significant, physically reasonable "cone of nonreaction" for unfavorable orientations. Recently, Engel and Levine[9] used maximal entropy considerations to obtain a more compact representation of the Legendre fit of Ref. 8, using only a $P_1(\cos\gamma)$ constraint. Their opacity function, however, does show finite reactivity in the unfavorable configuration and so is deemed less realistic than those of Ref. 8.

An opacity model for the steric requirements in elementary chemical reactions utilizing the orientation dependence of the activation barrier was developed by Levine and Bernstein (LB).[10] This treatment, which uses the actual γ dependence of the barrier, is more general than the "modified simple collision theory" model of Smith,[11] which assumes a linear dependence of the barrier height upon the cosine of the angle of attack (strictly valid only in the limit $\cos\gamma \cong 1$). Blais *et al.*[12] have tested the applicability of the LB model to describe the orientation dependence of the reaction cross section σ_R upon the angle of attack for the reaction $H + D_2 \rightarrow HD + D$ at collision energies of 0.55 and 1.3 eV (those of the experiments of Gerrity and Valentini[13] and Rettner *et al.*[14]). Quasiclassical trajectory calculations,[12] based on the procedure of Blais and Truhlar,[15] of the orientation dependence of this reaction were well approximated by the angle-dependent barrier, line-of-centers LB model.

Recently, Evans *et al.*[16] developed a simple kinetic theory model of reactive collisions of rigid nonspherical molecules, incorporating the angular momentum and convex shape of the colliding molecules as well as the dependence of barrier height upon mutual orientation. This dependence could be either the linearized ($\cos\gamma$) form of Smith[11] or the more general form of Levine and Bernstein.[10]

The present study uses the result of the Evans model in the near-spherical limit to analyze the Legendre-expansion opacity function of Stolte *et al.*[8] for the title reaction at 0.13_5 eV (the mean collision energy of the experiments of Parker *et al.*[6]).

II. METHOD AND RESULTS

The inversion of the orientation-dependent differential reaction cross section $d\sigma_R/d\cos\gamma \equiv d\sigma(z)/dz$ ($z = \cos\gamma$), is carried out utilizing the results of Evans *et al.*[16] for the collision of a spherical atom with an ellipsoidal diatom. For the limiting case of an ellipsoid of small eccentricity, a simple formula for $d\sigma(z)/dz$ has been obtained in terms of the colliding-pair anisotropy parameter[16] λ (assumed small compared to unity). The "reduced" differential orientational cross section (scaled to unity at its peak $\gamma = 0$) is defined

$$p(z) \equiv \frac{d\sigma(z)/dz}{[d\sigma(z)/dz]_{z=1}}. \tag{1}$$

It can be expressed in the form

$$p(z) = f(z)[(1 + \lambda z^2)/(1 + \lambda)], \tag{2}$$

where $f(z)$ is the orientation dependence of the cross section in the spherical limit, i.e., that calculated via the LB[10] model from the angle dependence of the activation barrier, or by the Smith[11] "linearized barrier" model, scaled to unity at its peak: $f(1) = 1$. The second factor is the correction for nons-

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phericity, associated with the dependence of the surface area element upon z. The pair anisotropy parameter λ is indentified with the eccentricity factor of the appropriate equipotential,[16] for small values of λ.

For the present problem, where no information on the angle dependence of the barrier is available *a priori*, the simple "linearized barrier" approximation of Smith[11] is adopted. Thus, following Ref. 16,

$$E_0(z) = E_{th} + E'(1 - z) \tag{3}$$

so that

$$f(z) = 1 - \alpha(1 - z) \tag{4}$$

is linear in z.

Here

$$\alpha \equiv E'/(E - E_{th}), \tag{5}$$

with

$$E_{th} \equiv E_0(1)$$

and

$$E' \equiv -dE_0(z)/dz.$$

It should be recalled that the linearized barrier implies a linear differential cross section in the spherical limit. The nonsphericity factor, however, can introduce significant curvature[16] in $p(z)$, and this will be of importance in the present analysis.

From the work of Wu *et al.*,[17] the value of E_{th} for the subject reaction is taken to be 0.033 ($\pm$ 0.007) eV. E is taken to be the experimental[6] $\bar{E}_{tr} = 0.13_5$ ($\pm$ 0.005) eV.

The Legendre fit[8] to the experimental backscattering data is plotted in Fig. 1. The cutoff value of z, defined by $p(z_0) = 0$, defines the cone of nonreaction.[18,19]

Here, $z_0 = -0.73$ (corresponding to a cone angle of 43°). This determines the value of α in Eq. (4) for $f(z)$; the result is $\alpha = 0.578$. Substituting the above values of E_{th} and E into Eq. (5) yields $E' = 0.059$ eV, so that

$$E_0(z) = 0.033 + 0.059(1 - z). \tag{6}$$

Thus, inversion of such data to yield the angle dependence of the barrier is direct, with E' determined from the cone of nonreaction (via the cutoff z_0).

Using Eq. (4) for $f(z)$ with the above α, Eq. (2) is readily applied to the calculation of a "reduced" differential orientational cross section. Various trial values of λ are assumed until a fit is achieved to the experimental curve of Ref. 8 in Fig. 1. The optimal result, for $\lambda = 0.6_7$, shown as the "calculated" dashed curve in Fig. 1, is a good representation of the Legendre-fit experimental curve. This suggests that both the linearized barrier assumption and the Evans nonsphericity correction are applicable in the present case.

Figure 2 shows the result of the present inversion to yield the angle-dependent potential barrier. The solid line is a plot of Eq. (6), with the cross-hatched zone indicating its uncertainty (based upon the uncertainties in the E_{th} and $\bar{E}_{tr}$). Also shown is a dashed line that is derived by the same procedure, but the less favorable "linear fit" of Ref. 8, *and* neglecting eccentricity (i.e., taking $\lambda = 0$).

III. DISCUSSION

The primary objective of this study was to explore the feasibility of inversion of an experimentally derived orientational opacity function to yield the orientation-dependent barrier to reaction. The results for the $CH_3I + Rb$ system are encouraging, but cannot be considered definitive. However, given a reliable experimental value of the cutoff angle (the cone of nonreaction), the method should yield a fair representation of the overall steepness of the curves of $E_0(z)$ from the threshold energy to the collision energy.

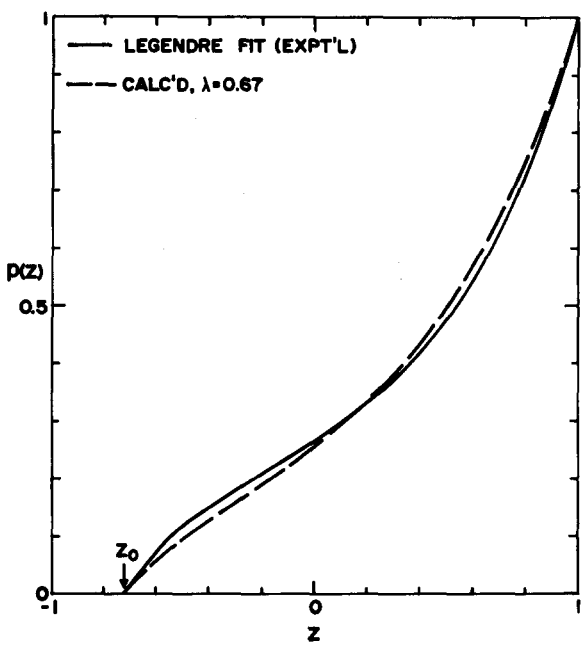

FIG. 1. Orientation dependence of the subject reaction cross section plotted as a scaled reaction probability $p(z)$ vs z, the cosine of the "angle of attack" (i.e., the angle between the relative velocity vector and the dipole axis of the CH_3I). The solid curve is the best experimental result, based upon the Legendre fit of Ref. 8. The dashed curve is the present calculation, using the model of Evans *et al.* (Ref. 16) (for the indicated value of the pair anisotropy parameter λ).

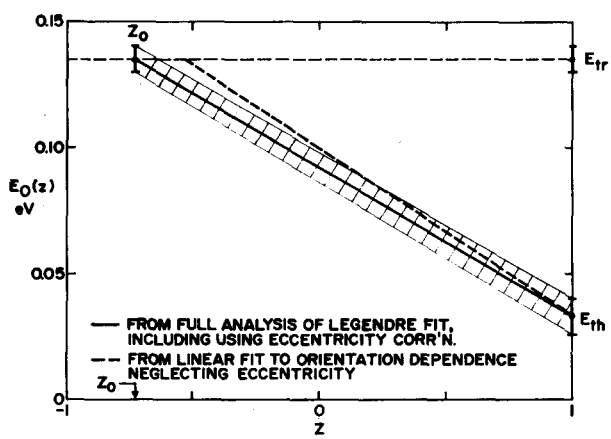

FIG. 2. Orientation dependence of the activation energy barrier for the subject reaction, from the present inversion. The solid straight line represents the best present analysis that, upon taking cognizance of the eccentricity correction of Evans *et al.* (Ref. 16) yields the dashed curve fit of $p(z)$ in Fig. 1. The cross-hatched zone indicates the uncertainty (see the text). The dashed line comes from the less satisfactory, linear fit to the data (Ref. 18), representation of the experiments (see the text). No information is available on $E_0(z)$ above $\bar{E}_{tr}$ (the dashed horizontal line).

The Evans eccentricity equation appears to account for the curvature in the experimentally derived orientation dependence $p(z)$ of Fig. 1, suggesting that it is physically realistic. The deduced value of λ for this system is, however, somewhat larger than "slightly aspherical" (cf. the derivation of Ref. 16). Nevertheless, this value of λ is not unreasonable, based upon the known nonsphericity of CH_3I. The pair anisotropy parameter can be estimated either from steric models or from calculated equipotentials using Eq. (3.30) of Ref. 16 for λ. This can be written

$$\lambda = R^2 - 1, \tag{7}$$

where R is the ratio of the major to the minor axis of the best-fit ellipse. From a steric model[19] for $CH_3I + Rb$, Eq. (7) yields a value of $\lambda = 0.5_4 \pm 0.1$. Using the zero-energy equipotential from a diatomics-in-molecule (DIM)-approximated potential energy surface for the related $CH_3I + K$ system,[20] one finds $\lambda = 0.8 \pm 0.2$. Thus the present value of $\lambda = 0.6_7$ from Fig. 1 is not unreasonable.

A more difficult question is the degree to which the present inversion is unique. It should be recalled that the linear fit of Ref. 8 would imply $\lambda = 0$ (for the linearized barrier case). The corresponding angle-dependent barrier (Fig. 2) is very similar to that derived from the Legendre fit, since only the cutoff angle matters here. This weakens the significance of the conclusions relative to the magnitude of the pair anisotropy parameter and its influence on $d\sigma/dz$. However, the correction for nonsphericity is inherently required in the line-of-centers rigid-body model. Obviously, further experimental orientation-dependence measurements of high accuracy are required to settle this point.

It is also necessary to extend such measurements to cover a wide range of collision energies. It seems likely on physical grounds that the barrier will rise sharply (near z_0) with increasing E. The DIM potential surface[20,21] for $CH_3I + K$ suggests an angle-dependent barrier function that is virtually angle independent, with a near-vertical rise at a cutoff z_0 of -0.24. This is much closer to the "painted sphere" model, with step-function opacity. However, since trajectory calculations[21] on this surface gave only fair results (i.e., they were unable to reproduce all of the "coarse" observations on this system), one has only limited confidence in the details of the surface, such as the shape of $E_0(z)$.

The important question of the deviation from the linearized barrier function must be investigated further. In the application of the LB model to the $H + D_2$ reaction, Blais *et al.*[12] found that the trajectory results confirmed the model-calculated $d\sigma/dz$ [the latter based upon the actual curved, angle-dependent $E_0(z)$ function]. The resulting concave-down $p(z)$ (obviously deviant from the linear form corresponding to a linearized barrier) leads to a very small pair anisotropy ($\lambda \leqslant 0.1$). This is not inconsistent with expectation for the $H + D_2$ system, however.

Finally, it should be noted that the experimental data for the title reaction show a decrease in the reactive asymmetry for forward (c.m.) scattering.[6(b)] Thus, the actual $d\sigma/dz$ (integrated over all scattering angles) will be slightly less "steep" than the Legendre-fit curve of Fig. 1, which refers to backscattering. The subject of the detailed double differential cross section $d^2\sigma(\theta,\gamma)$ requires further analysis (both experimental and theoretical).

IV. CONCLUDING REMARKS

The experimental results on the orientation dependence of the cross section for the $CH_3I + Rb$ reaction have been inverted using the model of Evans *et al.*[16] to yield the angle-dependent activation barrier (for energies $\leqslant 0.13_5$ eV), as well as an estimate of the colliding-pair anisotropy parameter. Further experiments of high accuracy over a range of collision energies are needed before it will be possible to appraise the accuracy of the inversion procedure. Nevertheless, it appears that a rigid-body model incorporating an orientation-dependent barrier may be a good starting point toward a more rigorous inversion, eventually leading from reactive asymmetry measurements to the anisotropic potential surface.

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