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A new mechanism for the enhancement of activated bimolecular reactions by rotational excitation

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The kinematic mass model (KMM), which has been developed to examine the dynamics of activated bimolecular reactions, has here been adapted to examine how orientational effects associated with reagent rotation influence the rotational state dependence of reaction cross-section. It is shown that, for reactions where the critical dividing surface (CDS) and the equipotential contours near to the CDS are ''prolate,'' i.e., elongated in the direction of the longitudinal molecular axis, rotation favors impact on the CDS near collinear geometries where the barrier to reaction is least, with the result that reaction cross-sections are enhanced with increasing reagent rotation. In the case of the rotational velocity being comparable with, or greater than, the relative translational velocity, this enhancement can greatly exceed that due to part of the rotational energy being available for barrier crossing. The KMM model, allowing for this orientational effect, has been applied to the reactions O+HCl (DCl) and O+H_2 on well-known model potential energy surfaces (PESs) where both the CDSs and the equipotential contours near the CDS are prolate. The results agree well with those from trajectory calculations. The role of the above effects of reagent rotation in the case of surfaces of nonprolate shapes is discussed qualitatively. © *2000 American Institute of Physics.* [S0021-9606(00)02120-6]

I. INTRODUCTION

The measurement and understanding of how reaction cross-sections depend on the energy present in different motions of the reagents is a crucial element of the field of molecular reaction dynamics.[1,2] For direct activated bimolecular reactions, the relative importance of translational and vibrational energy has been quite well-understood, at least for three-atom systems of the $A+BC\rightarrow AB+C$ type, for many years via the ''Polanyi rules.''[3] Reagent vibrational excitation selectively enhances the reaction cross-section in the case of a ''late'' barrier on the potential energy surface (PES), a situation which is expected for an endothermic reaction,[3] whereas translational energy selectively promotes reaction where the barrier is ''early,'' as is usually found for exothermic reactions.[3] In each case, the effect is easily understood, since the effective motion is the one which most effectively couples to the motion along the reaction coordinate which carries the system over the potential energy barrier.

The situation with respect to the effects of reagent rotational excitation is less satisfactory. However, a corollary may be that such effects provide a more sensitive probe of the PES for any particular reaction, or at least of that part of the PES leading to and including the critical dividing surface[1] (CDS) between reagents and products. Extensive reviews of the effects of reagent rotation on reaction cross-sections have been given by Sathyamurthy[4] and Grote *et al.*[5] As they point out, the experimental data base on rotational energy effects is quite sparse, reflecting the difficulty of preparing molecules in defined rotational states and of maintaining that selectivity in the face of facile collisional relaxation. The most successful experiments, which are cited in the review by Grote *et al.*,[5] employ pulsed laser pumping to excite HF or HCl to specific rotational levels in their first vibrational level and observe the reaction of these excited molecules with metal atoms to yield the metal fluoride and H atoms.

The great majority of information about the effects of reagent rotation on chemical reactivity comes from quasi-classical trajectory (QCT) calculations. Nevertheless, there has been no systematic effort to unravel the separate effects, for example, of the form of the PES and of the kinematics or mass combination for the reaction. Most QCT studies have aimed to quantify the rotational effects for a particular reaction. The dependence of the reaction cross-section on the rotational level (j) of the molecular reagent has often been found to be quite complex. Moreover, it has not proven easy from QCT calculations to identify the crucial elements of the collision dynamics and it remains a challenge to theory to explain how reaction cross-sections depend on j.

Broadly speaking, the explanations that have been put forward to explain reagent rotational effects can be classified as either ''energetic'' or ''orientational.'' Sathyamurthy[3] pointed out that, as the reagent rotational energy is increased, more product states become accessible so, at least in the phase space limit, the reaction cross-section might be expected to increase. However, direct reactions rarely, if ever, obey phase space theory, so more dynamical explanations should be sought. One such explanation would be that rotational motion in the (BC) reagent assists the system to surmount the potential energy barrier to reaction. Although, as pointed out previously,[6] on a simple basis it is difficult to see reactivity can be enhanced in this manner for a reaction dominated by a collinear minimum energy path, since rotational motion would be orthogonal to the motion along the reaction coordinate, rotational energy might assist in those many nonlinear collisions that lead to reaction, even in those cases where the lowest barrier to reaction is for a collinear geometry.

Orientational effects of reagent rotation have largely emphasized the possibility that increased reagent rotational motion will disrupt the progress of a trajectory towards the most favorable, i.e., lowest energy, geometry for reaction. Classical trajectory (CT) studies[7–10] have shown that this is particularly the case for ''oblate'' PESs on which the long-range interactions tend to guide the trajectory towards the lowest energy reaction path, thus increasing the reaction cross-section above the value it would have in the absence of these forces and hence in the case of straight line trajectories. Rotational excitation reduces this funneling effect and causes a decline in reactivity with rotational quantum number in the case of such PESs.

For several reasons, including the ease with which different dynamical effects can be separated out, calculations using simplified models have an important part to play in problems of reaction dynamics. Over the past few years we have developed[11–13] a simple kinematic mass model (KMM) to treat activated bimolecular reactions which is an extension of the angle-dependent line-of-centers (ADLOC) model originally proposed by Smith.[1,14] The KMM, like the ADLOC treatment, assumes straight line trajectories up to the CDS on the PES, and then examines whether the energy associated with some critical component of the velocity of approach exceeds the potential energy at that point on the CDS. However, in contrast to the ADLOC treatment, the effects of the anisotropy of the PES and of BC rotational motion are included in the KMM.

The KMM was first used to calculate opacities, reaction cross-sections, and the effects of reagent rotation for the reactions $O+HCl(DCl)\rightarrow OH(OD)+Cl$ and $O+HBr\rightarrow OH+Br$. Calculations for O+HCl were performed on two PESs,[15,16] one oblate, and one prolate, and the model results were compared with the results of CT calculations[9] run on the same surfaces. When applied to the O+HCl(DCl) reactions on the oblate surface, the cross-sections were about an order-of-magnitude smaller than those obtained from the CT calculation, presumably because of the extensive effects of funneling. However, the same reactions were modeled quite satisfactorily by the KMM applied on the prolate PES. In all cases where a prolate surface was used, both the translational energy and the *j*-dependence of the reaction cross-sections were in fair agreement with the CT results,[9] although at high *j* the model results were lower than those from the trajectories. In view of the success in modeling dynamics on prolate surfaces, only such surfaces have been used in subsequent work including that reported in the present article. It should be noted that, in the CT calculations reported in Refs. 7–9, coplanar collisions were studied, with the vibrational effects on the barriers and these trajectory results therefore appear to be most suitable for comparison with the result of KMM calculations when discussing rotational effects.

In subsequent formulations[12,13] of the KMM, it was extended to include the effects of vibration in the *BC* molecule. In these calculations, the barriers at the CDS were calculated to include not only the electronic energy but also the adiabatic vibrational energy corresponding to the state of the *BC* reagent; i.e., of $v=0$ (Ref. 12) allowing for changes in the zero-point energy in passing from isolated $A+BC$ to the CDS, and of $v=1$ (Ref. 13) to explore the effects of vibrational excitation in the *BC* molecule. These modifications made it possible to compare the KMM results with the numerous results of quasiclassical trajectories. In the case of the O+HCl (DCl) reactions, reasonably good agreement was again obtained in regard to the dependence of the reaction cross-sections on both translational and rotational energy of the reagents, for both $v=0$ and $v=1$, although the agreement was somewhat less good than in the case of the CT calculations. This poorer agreement might be due to additional simplifications introduced in estimating the vibrationally adiabatic barriers and to the neglect of recrossing effects, which become larger the greater the internal excitation of the *BC* reagent, particularly for H atom transfer reactions. Of relevance to the present work was the observation that the reaction cross-sections increased for higher initial *j* levels but the enhancement predicted by the KMM calculations was too weak in all the H atom transfer reactions that were considered.

In the present work we show, using modified KMM calculations, that the orientational effect associated with reagent rotation can give rise to an enhancement of the cross-sections with increasing reagent rotation which can greatly exceed that due to part of rotational kinetic energy being available for barrier crossing. The analysis of the reactions O+HCl(DCl) and $O+H_2$ which we present clearly demonstrates this behavior and leads to a convincing explanation of the strong *j*-dependence of the reaction cross-section.

II. THE KINEMATIC MASS MODEL

The KMM has been described in detail elsewhere.[11–13] Therefore only an outline of the model will be given in the present article emphasizing those aspects which are especially relevant to the present calculations.

In the KMM, attention is focused on relative motion of the reagents within a small element of space at the CDS. It is assumed that the reagents follow straight paths up to this point. This situation is represented in Fig. 1 where some of the parameters which are used in the implementation of the model are illustrated: $\mathbf{v}$ is the relative collision velocity; the coordinates R and γ are the values of the Jacobi coordinates at the point of impact in the collision on the CDS, and $\mathbf{n}$ is a unit vector normal to the equipotential contours at R, γ. Reaction is assumed to occur if the kinetic energy associated with the relative velocity ($\mathbf{v}^*$) perpendicular to the equipotential contours at the point of impact on the CDS exceeds the potential energy barrier or the adiabatic potential energy barrier (E_{bar}) at that point, i.e.,

$$1/2\boldsymbol{\mu}^*\mathbf{v}^{*2}\geqslant E_{\mathrm{bar}}. \tag{1}$$

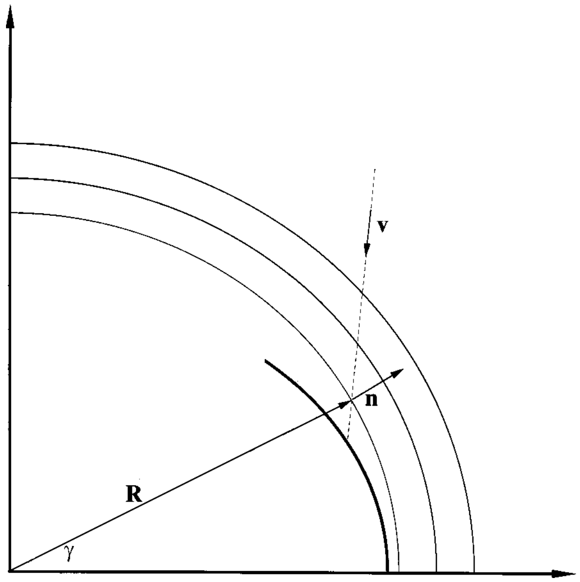

FIG. 1. Schematic representation of an $A+BC$ collision. The heavy line represents part of the critical dividing surface for reaction, the lighter lines represent equipotential contours. R and γ are the coordinates of the point where the straight line trajectory impacts on the critical dividing surface; R being the distance between the centers-of-mass of BC and A at this point, γ the angle between $\mathbf{R}$ and $\mathbf{r}_{BC}$, where the internuclear axis $\mathbf{r}_{BC}$ is assumed to lie along the line defined by $\gamma=0$.

However, a crucial feature of the KMM is that rotational energy effects can be included, because $\mathbf{v}^*$ depends not only on the relative translational velocity but also on the rotational motion of the molecular reagent. It has been shown[11–13] that $\boldsymbol{\mu}^*$ and $\mathbf{v}^*$ are given by

$$\boldsymbol{\mu}^*=\frac{\mu}{1+\frac{\mu(\mathbf{R}\times\mathbf{n})^2}{I}}, \tag{2a}$$

and

$$\mathbf{v}^*=\mathbf{v}_\mathbf{n}-\frac{j(\mathbf{R}\times\mathbf{n})}{I}. \tag{2b}$$

In these equations, μ is the usual reduced mass of the collision partners, I is the moment of inertia of the molecule, j is its rotational angular momentum perpendicular to the plane of the collision, and $\mathbf{v}_\mathbf{n}$ is the component of the relative velocity normal to the equipotential contours. It should be noted that $\boldsymbol{\mu}^*/\mu\leqslant 1$ and the deviation of this ratio from unity reflects the importance of rotational recoil in the system. $\mathbf{v}^*$, on the other hand, can greatly exceed $\mathbf{v}_\mathbf{n}$, depending on the rotational velocity and reflecting the role of rotational energy in facilitating barrier crossing.

In implementing the KMM in studies of several reactions occurring on prolate PESs with the molecular reagent in $v=0$[12] and $v=1$,[13] Monte Carlo methods were used to generate the impact parameter and the angles defining the initial orientation of the reagents for individual collisions. The reaction cross-sections were then calculated as if the points of impact on the CDS were reached instantaneously with the translational energy and the rotational angular momentum having the values initially selected. Consequently, any effects of the rotational motion on the distribution of the points of impact were neglected. As pointed out in Ref. 12, such an approximation may not be adequate for reactions where the CDS is nonspherical and the rotational velocity is comparable to, or larger than, the relative translational velocity. This is the case for O+HCl(DCl) at high initial values of j, and even more so for $O+H_2$. This conclusion was reached[12] on the basis of simple model calculations using just one value (1 Å) of the impact parameter and a rotating ellipse as the CDS.

In the present calculations, we have confirmed this crucial hypothesis by analyzing the distribution of points of impact with proper averaging over the impact parameter so that the distributions obtained correspond to those that should occur in calculations of the reaction cross-sections. The main modification to the standard KMM model is that now the approach to the CDS is not assumed to be instantaneous. Rather the reagents approach along straight line trajectories with a relative velocity corresponding to the selected collision energy and assumed to be the same all the way to the CDS. During this time the diatomic species (and therefore the ellipse representing the CDS) rotates with an angular momentum corresponding to the selected rotational state j. In general, the KMM model has been formulated for three-dimensional collisions between an atom (A) and a diatomic molecule (BC).[12,13] For present purposes, the coplanar form was judged to be adequate.[11] Moreover, the forms of the CDS and of the equipotential contours in the vicinity of this surface were assumed to be elliptical, the major and minor axes of these two ellipses being estimated from information about the PESs. The centers of these ellipses which should approximate the shapes of the CDSs and of the equipotential contours in the region relevant for the reactions in question coincide in each case with the center-of-mass of the diatomic reagent, consistent with the requirements of the basic laws of mechanics upon which the model has been developed.

III. RESULTS AND DISCUSSION

For the $O+H_2$ reaction, the parameters of an ellipse, $a=1.59$ Å and $b=0.75a$, approximating the shape of the true CDS, were derived from the analysis[17] (see Fig. 5 in Ref. 17) of the PES used in QCT calculations.[18] To represent the equipotential surface, an ellipse was used with a', the length of the major axis, set equal to a but with $b'=0.92a'$. These parameters were chosen to match the shape of the CDS near the saddle point on the PES for collinear geometries (see Fig. 2 in Ref. 17). Figure 2 displays the distribution of the points of impact on the elliptical CDS. These results clearly demonstrate that, at higher j, this distribution is shifted towards the longitudinal axis where the barrier height is lower thus enhancing the reaction cross-section.

In Fig. 3, the results of standard KMM calculations are compared with those which take into account the change in the distribution of points of impact for each value of j. Both sets of model calculations were performed using the adiabatic barrier heights associated with the reaction of $H_2(v=0)$. That is, the height of the barrier on the CDS included zero-point energy. In Fig. 4, it can be seen that the inclusion

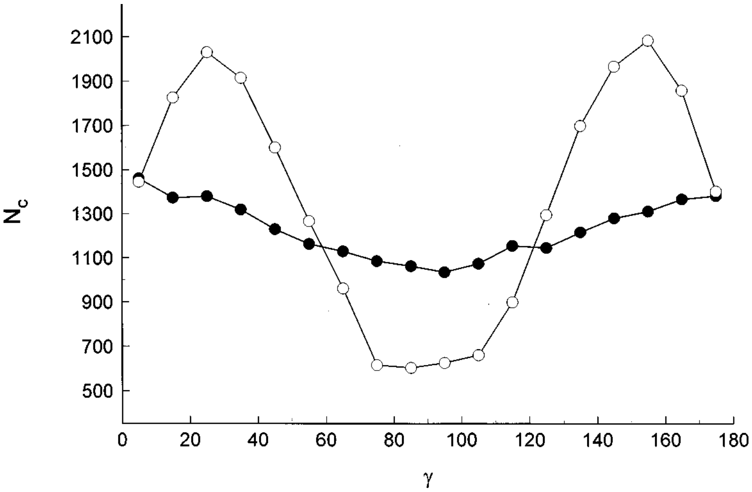

FIG. 2. The distribution of collisions on the critical dividing surface for the $O+H_2$ reaction, for $j=0$ (●) and for $j=10$ (○). The collision energy was $E_{\mathrm{trans}}=12$ kcal/mol in each case. The shape of the critical dividing surface was approximated by an ellipse as described in the text.

of the factor allowing for the modified distribution of impact points over the CDS considerably improves the agreement of the model calculations with those from QCT calculations. Since the coplanar version of the KMM was used, the reaction probabilities were normalized to the QCT cross-section at $j=0$ and with $E_{\mathrm{trans}}=20$kcal/mol, as in Ref. 8.

Similar calculations to those on $O+H_2$ were carried out on O+HCl and O+DCl and the results confirmed the effects of reagent rotation on reactivity. In these cases, the KMM results could be compared directly with those from coplanar CT calculations,[10] that is, with the *BC* vibration ''frozen.'' The energies at the CDS were those from the PES,[12] with no zero-point energies added, and the KMM results required no normalization since both sets of calculations represented the results of coplanar collisions. The CDS and the equipotential surfaces were again modeled by ellipses with $a=2.57$ Å, $b=0.69a$, and $a'=2.57$ Å, $b'=0.84a'$, respectively. The centers of these ellipses coincide with the center-of-mass of the molecule as described at the end of the previous Sec. II. In the CT calculations,[10] the internuclear distance $r_{\mathrm{HCl}}(r_{\mathrm{DCl}})$ was held constant at its value at the saddle point on the collinear PES. The chosen values of a, b, a', and b' should therefore be regarded as describing the anisotropy of the PES at these values of $r_{\mathrm{HCl}}(r_{\mathrm{DCl}})$.

It can be seen from Fig. 5 that the standard KMM treatment reproduces the *j*-dependence of the cross-section for the O+HCl reaction quite well for values of *j* up to about 8 but does not reproduce the steep increase which occurs at higher *j*. However, if the KMM calculations are modified to allow for the effects of rotation on the distribution of collisions on the CDS, the model results agree well with those from CTs over the whole range of *j*. As shown in Fig. 6, the situation is similar for O+DCl, although the *j*-dependence is now much less pronounced, due to the rotational velocity of DCl being less than that of HCl for the same *j*. It should be noted that the γ-dependence of the barrier heights is much steeper for O+HCl than for $O+H_2$ so that in the latter case reactive collisions occur over a much wider range of γ. It is for this reason that the rotational effects only become strong at higher values of *j* in the O+HCl reaction.

IV. SUMMARY AND CONCLUSIONS

The calculations reported in this article indicate that reagent rotational excitation can significantly modify the distribution of points on the CDS of a PES which are reached by potentially reactive trajectories. For the surfaces for which calculations have been carried out in the present work, for which both the CDS and the equipotential contours are prolate in shape, the effect of increasing rotational excitation

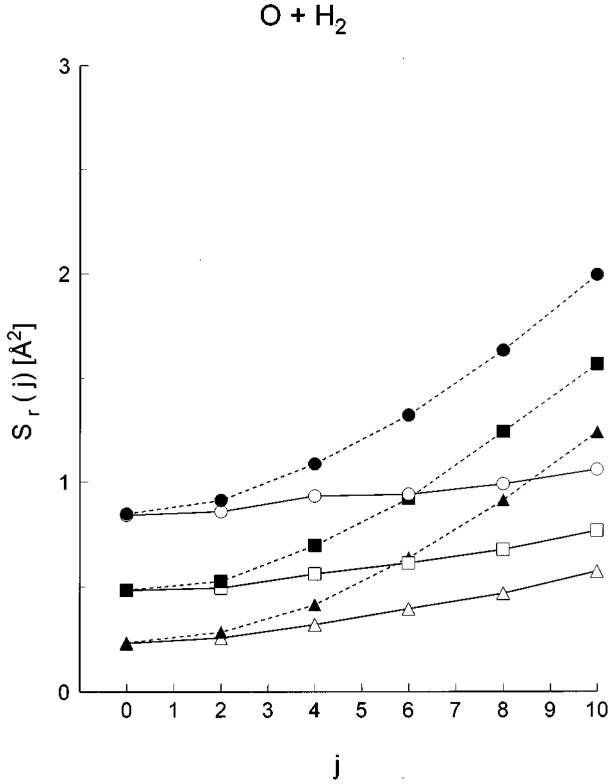

FIG. 3. KMM cross-sections for the $O+H_2$ reaction at three different collision energies: $E_{\mathrm{trans}}=12$ kcal/mol (△,▲), $E_{\mathrm{trans}}=15$ kcal/mol (□,■), and $E_{\mathrm{trans}}=20$ kcal/mol (○,●). Open symbols show the results of standard KMM calculations and therefore include only the energetic effects of reagent rotation; closed symbols show the results which include the efects of the distribution of collisions on the critical dividing surface.

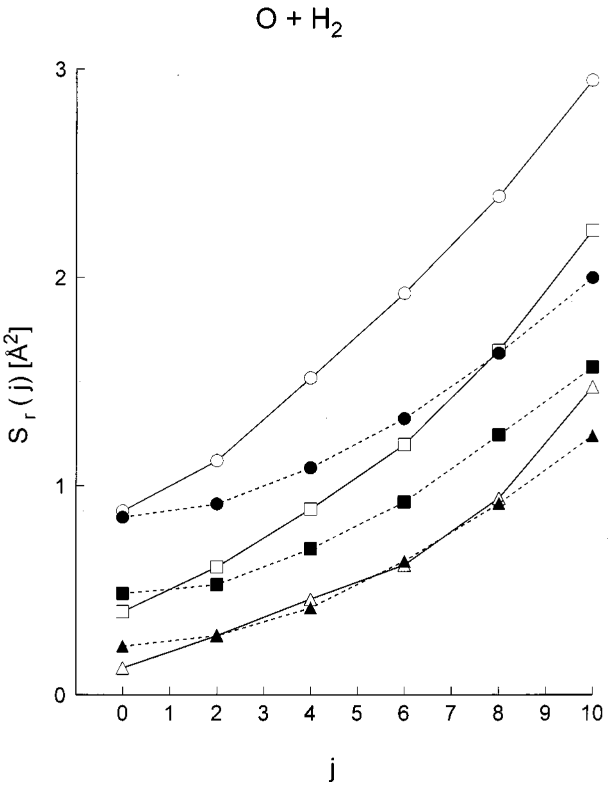

FIG. 4. Comparison of the QCT cross-sections for the O+H_2 reaction (open symbols) with those calculated by the modified KMM treatment (closed symbols). The collision energies are: $E_{\mathrm{trans}}=12$ kcal/mol (△,▲), $E_{\mathrm{trans}}=15$ kcal/mol (□,■), and $E_{\mathrm{trans}}=20$ kcal/mol (○,●).

is to concentrate the points of impact near the collinear arrangement of the three atoms, where the barrier to reaction is least, and therefore to enhance the reaction cross-sections. Qualitatively, this effect can be understood in the following way. When the rotational velocity is much greater than the relative translational velocity, the attacking atom can sample many different molecular orientations as it approaches the diatomic reagent. In the limit where the rotational velocity is very much greater than the collision velocity, the first impact on the CDS will be wherever the separation R on this surface is greatest. In the case of a prolate CDS, R is greatest where the barrier to reaction is least, so reactivity is enhanced. On the other hand, if R is greatest where the barrier to reaction is greatest, which is the case when the CDS is oblate, reactivity is likely to be diminished by increasing reagent rotational excitation. This suggests that information about the actual j-dependence of cross sections for a particular reaction will provide valuable information about the shape of the PES for that system near the configurations critical for reaction.

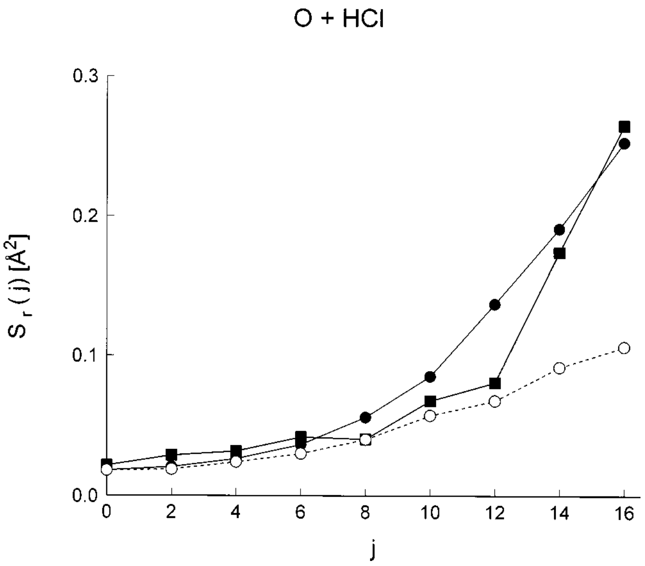

FIG. 5. Rotational dependence of the reaction cross-sections for the O+HCl reaction at $E_{\mathrm{trans}}=10$ kcal/mol calculated from QCTs (●), from the present KMM method (■), and from the standard KMM method (○) in which only the energetic effects of reagent rotation are taken into account.

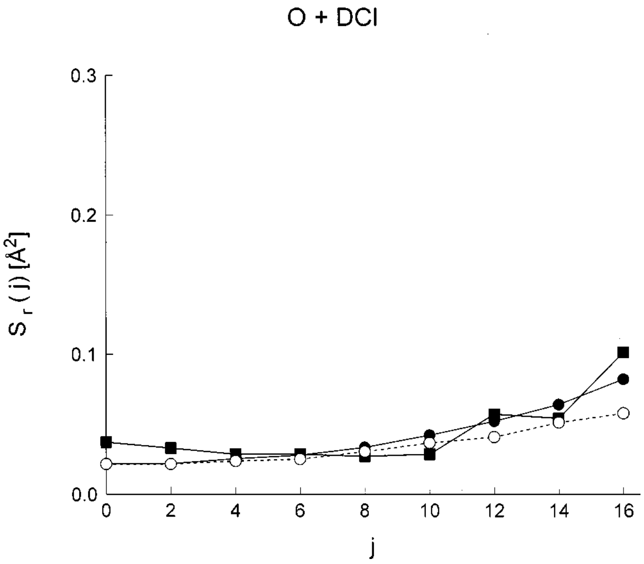

FIG. 6. The same as Fig. 5 but for the O+DCl reaction.

We reiterate that when the equipotential contours are oblate, no simple modeling is possible due to the strong funneling effects which lead to trajectories being reoriented on their approach to the CDS. The following qualitative observations can however be made: when j increases, the favorable reorientation effects may be disrupted, leading to a decrease of the reaction cross-sections. At higher j, the effects discussed here may prevail so that the cross-section would start to increase with j. The variation of the cross-sections with j might then go through a minimum, behavior which has been observed in several cases.[4]

Although the modified KMM reproduces the effects of rotational excitation on reaction cross-sections quite well, as judged by comparison with the results of QCT calculations, the agreement is less than perfect. Any remaining differences might be caused by approximations in the energies and shape of the CDSs used in the KMM calculations. A more interesting possibility is that our model calculations underestimate the effect of rotation because they make no allowance for the fact that the approach of the reagents will become slower as they get close to the CDS and the potential energy rises. It seems likely that the rotational velocity will be affected less by such intermolecular forces. Consequently, the time available for a favorable orientation to be found may be longer than that given by a calculation which assumes that the reagents follow straight line trajectories up to the CDS with their initial relative velocity undiminished by intermolecular forces. If this is correct, the impacts on the CDS will cluster even more strongly about the point where R is greatest and E_{bar} least.

ACKNOWLEDGMENTS

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