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The Effects of Reagent Rotation on the Stereodynamics of $O(^1D)+HCl \rightarrow ClO+H$ Reaction at a Hyperthermal Collision Energy

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Abstract: Usually, the rotation of the product can only result from reagent orbital momentum due to the small rotation of the reagent. And hyperthermal collisions play an important part in the chemistry of extreme environments. In order to study the effects of reagent rotation on the stereodynamics of $O(^1D)+HCl \rightarrow ClO+H$ reaction at a hyperthermal collision energy, we have performed a quasi-classical trajectory calculations on the $^1A'$ state at the collision energy of 60.0kal/mol. The alignment and the orientation of the products have been predicted through the two angular distribution functions __$P(\theta_r)$ and $P(\phi_r)$. A natural generalization of the differential cross section __$PDDCS_{00}$, is also presented to let us have a deeper understanding of the natures of the vector correlation between reagent and product relative velocities and the reaction schemes.

AMS subject classifications: 70E55, 70F07, 80A30

Key words: $O(^1D)+HCl$, Hyperthermal, Stereodynamics, Reagent rotation

As known, $O(^1D)+HCl$ reaction plays an important role in stratospheric chemistry. And there has been an increasing interest in studying this system [1-22]. There are two product channels for the title reaction

$$O(^1D)+HCl(^1\Sigma^+) \rightarrow ClO(^2\Pi)+H(^2S), \qquad \text{(R1)}$$

$$\rightarrow OH(^2\Pi)+Cl(^2P). \qquad \text{(R2)}$$

However, only a few studies are concerned with R1 reaction since R2 is the main product channel. In a crossed-molecular-beam study [2], the angular and velocity distributions of ClO product were presented at the collision energy of 12.2kcal/mol. Also at 12.2kcal/mol

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(collision energy), the product angular distribution and dihedral angle distribution for the ClO forming process were performed through a quasi-classical trajectory (QCT) calculation [8] with the conclusion that proper combinations of insertion and attachment contributions can rationalize the results. Integral cross sections (ICSs) for vibrational states summed over rotational states for ClO, and its translational energy distributions were calculated also at 12.2kcal/mol (collision energy) [9]. Bittererová *et al.* [11] performed a wave-packet calculation to study the effect of reactant rotation and alignment on product branching in the $O(^1D)+HCl \rightarrow ClO+H$ and a striking effect of the initial rotation and rotation (alignment) of HCl on the branching ratio over the collision energy range of 0-0.5eV was found. All these studies are related with low collision energies. Due to its importance in the chemistry of extreme environments [23-26], hyperthermal collisions are necessary to be studied. As is common, the rotation of the reagent (***j***) is small. This causes that the rotational angular momentum (***j***') of the product can only come from reagent orbital momentum (***l***). So we will carry out a theoretical study on the effects of reagent rotation on the stereodynamics of $O(^1D)+HCl \rightarrow ClO+H$ reaction at a hyperthermal collision energy (60.0kcal/mol).

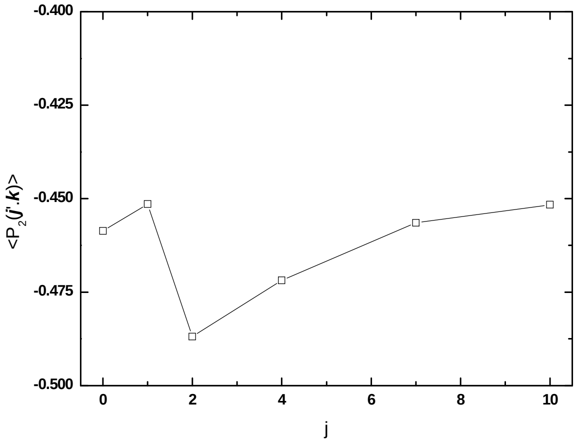

Figure 1: P_2 values for O+HCl (v=0; j=0, 1, 2, 4, 7, 10)→ ClO+H reaction at the collision energy of 60.0kcal/mol.

In present work, a QCT [21, 22, 26-33] calculation is performed on the $^1A'$ PES [12]. $^1A'$ state has a deep well in bent geometry corresponding to stable HClO molecule with the well depth -48.20 kcal/mol. The initial ro-vibrational quantum numbers of the HCl reactant are set as v=0; j=0, 1, 2, 4, 7, 10. 10,000 trajectories are used on the $^1A'$ electronic states at the collision energy of 60.0kcal/mol. The time integral step size is 10^{-4}ps.

As shown in **Figure 1**, the values of alignment parameter__P_2 are approaching to -0.5, indicating that the rotation of ClO is strongly aligned perpendicular to the reagents' relative velocity (***k***). As stated in Ref. [6, 29], this is a typical feature of the Heavy heavy-light (HHL) system. With the increase of the rotational quantum number (j), P_2 has an increasing-then-decreasing-then-increasing trend. The alignment for j=2 is the strongest, which could be proved by $P(\theta_r)$ and $P(\phi_r)$ distributions. Generally, the memory of the complex can be washed out due to the deep well. However, at the hyperthermal collision energy, the O atom tends to overcome the initial barrier, and the trajectories may deviate from the minimum energy path (MEP) and deflect towards the HClO well.

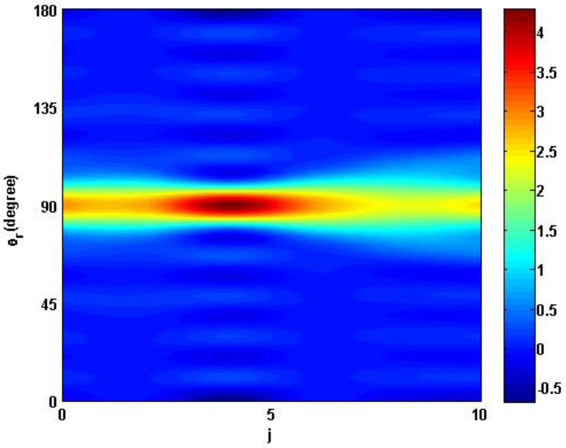

Figure 2: $P(\theta_r)$ distributions for O+HCl (v=0; j=0, 1, 2, 4, 7, 10)→ ClO+H reaction at the collision energy of 60.0kcal/mol.

Reflecting the ***k***-***j***' correlation, $P(\theta_r)$distributions in **Figure 2** are all symmetric with respect to $\theta_r = 90^o$. But they are quite different for different rotational quantum numbers (j). The mass factor for the title reaction is about 0.0086. According to the kinematic limit [28], the product rotation should be strongly aligned along the direction that is perpendicular to reagents' relative velocity vector as shown in Figure 2, since the initial oribital angular momentum almost completely goes into the product rotational angular momentum. The highest and narrowed peak at j=2 state declares the strongest alignment, which agrees well with the alignment parameter.

The dihedral angular distribution__ $P(\phi_r)$ can be used to describe the ***k***-***k***'-***j***' correlation, which can illustrates the polarization of ***j***'. The $P(\phi_r)$ distribution is asymmetric with respect to the ***k***-***k***' scattering plane (*i.e.* at about $\phi_r = 180^o$), which could be explained by the impulse model [28]. **Figure 3** shows that the largest peaks appear around $\phi_r = 270^o$, implying that the ClO molecular axis vector orients along $-y$ axis.

PDDCS$_{00}$ in **Figure 4** can be used to describe the ***k***-***k***' correlation. For the cases of j=0, 2, 4, 7, and 10, obvious forward scattering dominates. This indicates that the impact time is short and that direct reaction is distinct. At j=0, and 2, the largest peaks appear around $\theta_t = 0^o$, declaring dominate direct reactions. As stated in Ref. [26], the distribution is observed to be almost backward-forward symmetric with backward scattering being slightly favoured at the collision energies of 60.0 and 120.0kcal/mol for ClO+H channel. So one can conclude that part of the reaction occurs via a long-lived complex and part via direct abstraction of Cl atom. However, at high collision energies, the intermediate complex usually cannot live long enough to lose memory of its initial orientation. So its alignment/orientation information cannot be washed out.

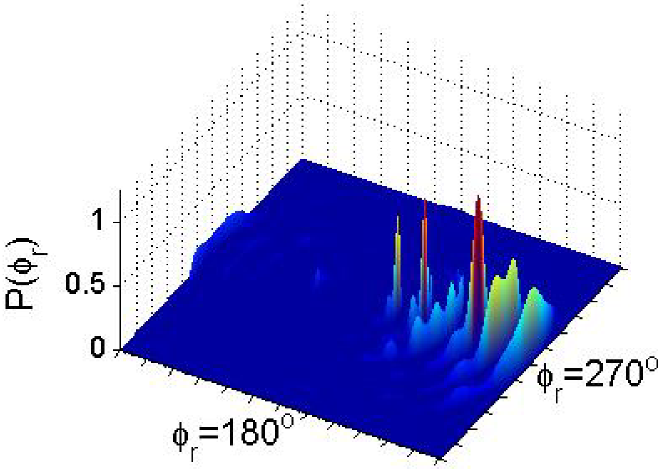

Figure 3: $P(\phi_r)$ distributions for O+HCl (v=0; j=0, 1, 2, 4, 7, 10)→ ClO+H reaction at the collision energy of 60.0kcal/mol.

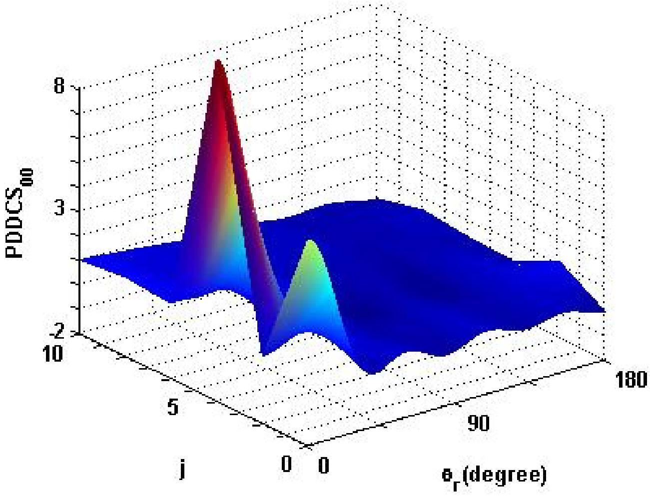

Figure 4: PDDCS$_{00}$ as a function of scattering angle for O+HCl (v=0; j=0, 1, 2, 4, 7, 10)→ ClO+H reaction at the collision energy of 60.0kcal/mol.

For the title reaction, the effects of reagent rotation on the stereodynamics at a hyperthermal collision energy (60.0kcal/mol) have been studied. Both the alignment degree and the orientation direction can vary through the difference in rotation of the reagent. The scattering direction of the product and the reaction scheme can also change under the above condition. So one can deduce that we can control the reaction, partly through varying the reagent rotational state.

Acknowledgements

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