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The Effects of Reagent Rotation on the Stereodynamics of O(^{1}D)+HCl→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(^{1}D)+HCl→ClO+H reaction at a hyperthermal collision energy, we have performed a quasi-classical trajectory calculations on the ^{1}A' 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(^{1}D)+HCl, Hyperthermal, Stereodynamics, Reagent rotation

As known, O(^{1}D)+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

$$O(^1D)+HCl(^1\Sigma^+) \rightarrow ClO(^2\Pi)+H(^2S), \quad (R1)$$

$$\rightarrow OH(^2\Pi)+Cl(^2P). \quad (R2)$$

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).

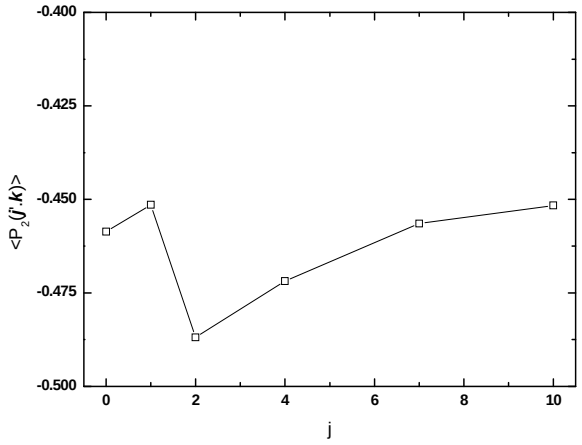

Figure 1: P_2 values for O+HCl (v=0; j=0, 1, 2, 4, 7, 10)→ ClO+H reaction at the collision energy of 60.0kcal/mol.

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