

Chemical Stereodynamics underlying the $F+HCl \rightarrow HF+Cl$ reaction

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Abstract

Using the quasiclassical trajectory (QCT) method, we theoretically study the reaction $F+HCl \rightarrow HF+Cl$ on the DHTSN potential energy surface (PES). The distributions of product rovibrational state and the distributions of $P(\phi_r)$ and $P(\theta_r)$ are calculated. The results show that the most populated product states are $v'=3, j'=0-2$ at the collision energy of 6kcal/mol; the product is aligned and oriented at this collision energy.

1. Introduction

Both the scalar properties and the vector properties should be studied for an extensive understanding of a chemical reaction. Vector properties of velocities and angular momentum possess magnitude directly relating to translational and rotational energies and scattering directions, which can offer the fullest picture of the scattering dynamics information.

In 1993, the quasiclassical trajectory (QCT) method has been firstly applied to the chemical stereodynamics area. The trajectories have been run on attractive and repulsive

potential energy surfaces of chemical reactions with different mass combination, and obtained the vector information such as the differential cross-sections, the distributions of $P(\theta_r)$ and $P(\phi_r)$ [1-4].

In recent years, there are growing experimental and theoretical interest in the reaction of $F+HCl \rightarrow HF+Cl$. For instance, Polanyi [5] and co-workers constructed a London-Eyring-Polanyi-Sato (LEPS) potential energy surface (PES) with a small classical barrier of 1.1 kcal/mol, Sayos et al. [6] fitted an ab initio PUMP2/6-311G (3d2f,3p2d) PES with a barrier height of 0.174

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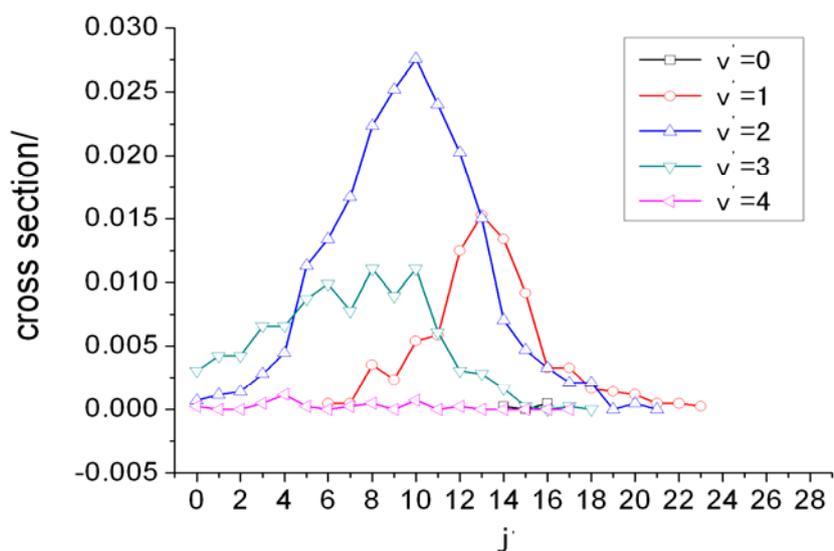


Figure 1. The product rovibrational state distribution at the translational energy of 6kcal/mol.

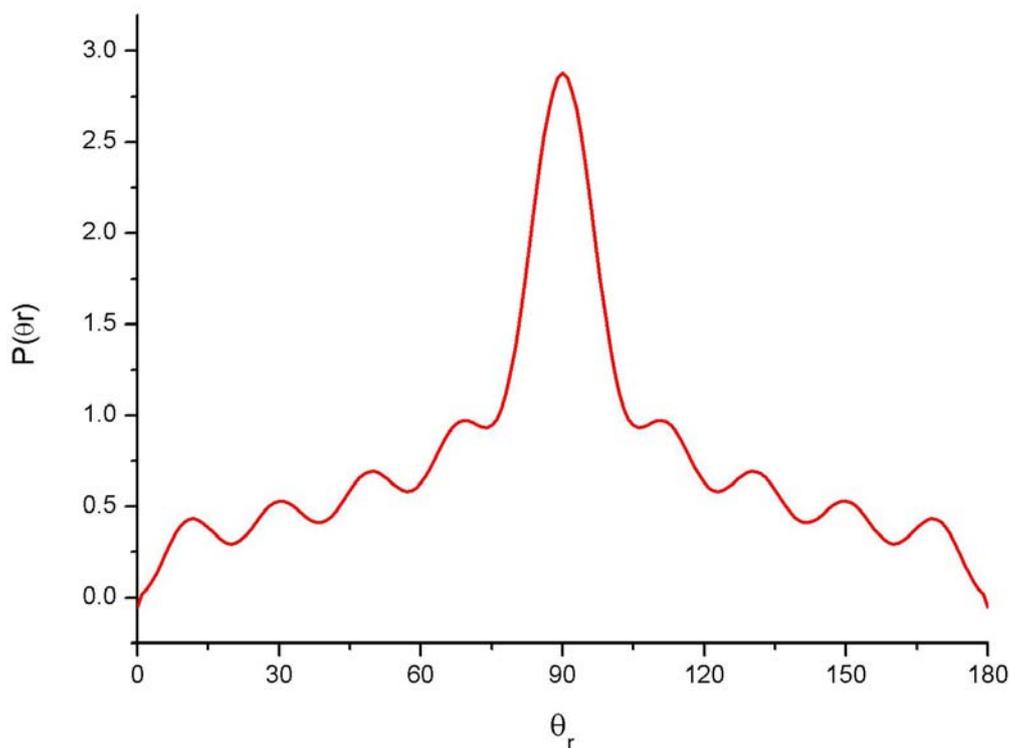


Figure 2. The $P(\theta_r)$ distribution at the translational energy of 6kcal/mol.

eV.(4.013kcal/mol). Deskevich et al. [7] formed a new PES for the ground $1^2A'$ state

of the triatomic FHCl system (DHTSN PES), which has become the basis of a number of recent dynamics calculations.

On the experimental sides, the earliest study of this reaction appeared in 1973 where the experimental rovibrational distribution of the products HF was obtained for temperatures of 300 and 1700 K. In a recent work, Zolot [8] and Nesbitt studied this reaction at a collision energy of 4.3 kcal/mol (0.186 eV) and measured the rovibrational level populations of the HF products, for the vibrational states $v'=0, 1, 2,$ and $3,$ populations were 14%, 34%, 44%, and 8%, respectively.

Most of these studies reported only the scalar properties of the product. Here, we use the QCT method to study the title reaction to provide some vector information. In the following section, we give an outline of the theories and methods we used. Section 3 presents the calculation results and discussions.

2. Theories and methods

2.1 Product rotational polarization

In the center-of-mass (CM) frame, the reagents initial relative velocity vector k is parallel to the z -axis while k' is the relative velocity vector of product. θ_i is the angle between k and k' (so-called scattering angle). ϕ_r and θ_r are the polar and azimuthal angles of the final rotational angular momentum j' . The correlation of two vectors (k - j') can be expanded into a series of Legendre Polynomials,

$$P(\theta_r) = \frac{1}{2} \sum_k (2k+1) a_0^{(k)} P_k(\cos \theta_r) \quad (1)$$

with the coefficient being

$$a_0^{(k)} = \int_0^\pi P(\theta_r) P_k(\cos \theta_r) \sin \theta_r d\theta_r = \langle P_k(\cos \theta_r) \rangle \quad (2)$$

The dihedral angle distribution function $P(\phi_r)$

describing k - k' correlation can be expanded in Fourier series,

$$P(\phi_r) = \frac{1}{2\pi} \left(1 + \sum_{\substack{nevme \geq 2}} a_n \cos n\phi_r + \sum_{\substack{nodd \geq 1}} b_n \sin n\phi_r \right)$$

(3)

where $a_n = 2 \langle \cos n\phi_r \rangle$ and

$$b_n = 2 \langle \sin n\phi_r \rangle \quad (4)$$

2.2 Calculation details

The Quasi-classical trajectory (QCT) method is the same as those used previously [3,4]. The translational energy we investigate is 6kcal/mole. In this calculation, the number of the trajectories is 30,000. The calculation are based on the DHTSN PES and the integration step size is 0.1fs. The initial state of the reagent HCl is chosen to be its ground state.

3. Results and discussions

3.1 Product rovibrational state distribution

The rovibrational distribution of product HF at the translational energy of 6kcal/mol is show in Fig.1. We can see that there is no distribution on $v'=0$ or 1 and few on $v'=4$. The final state $v'=3$ is the dominant channel with a range of rotational levels $j'=0-12$. We also noted that the distribution of $v'=2$ is well-populated.

3.2 Vector information

Figure 2 and Figure 3 plotted the $P(\theta_r)$ and $P(\phi_r)$ distributions at 6kcal/mol for the $F + HCl \rightarrow HF + Cl$ reaction. The distribution of the $P(\theta_r)$ peaks at $\theta_r = 90^\circ$

and is symmetric to the angle of $\theta_r = 90^\circ$.

This calculation result shows that j' of the title reaction has strong alignment perpendicular to k .

The dihedral angular distributions $P(\phi_r)$ of the $F + HCl \rightarrow HF + Cl$ reaction at the same energy is presented in Fig. 4. From the distribution, one can see that $P(\phi_r)$ tends to be asymmetric about $\phi_r = \pi$, directly reflecting the strong polarization of angular momentum. There are two peaks of $P(\phi_r)$, at $\phi_r = 3\pi/2$ and $\phi_r = \pi/2$, suggesting that the

products are strongly oriented and the product angular momentum is aligned along the y-axis. In addition, at the energy of 6kcal/mol, the peak of $P(\phi_r)$ at $\phi_r = 3\pi/2$ is bigger than that at $\phi_r = \pi/2$, which demonstrates that the product HF tends to make anti-clockwise rotation in a plane paralleling to the scattering plane, in other words, the rotational angular momentum vector of the product HF is preferentially oriented along the negative direction of y-axis.

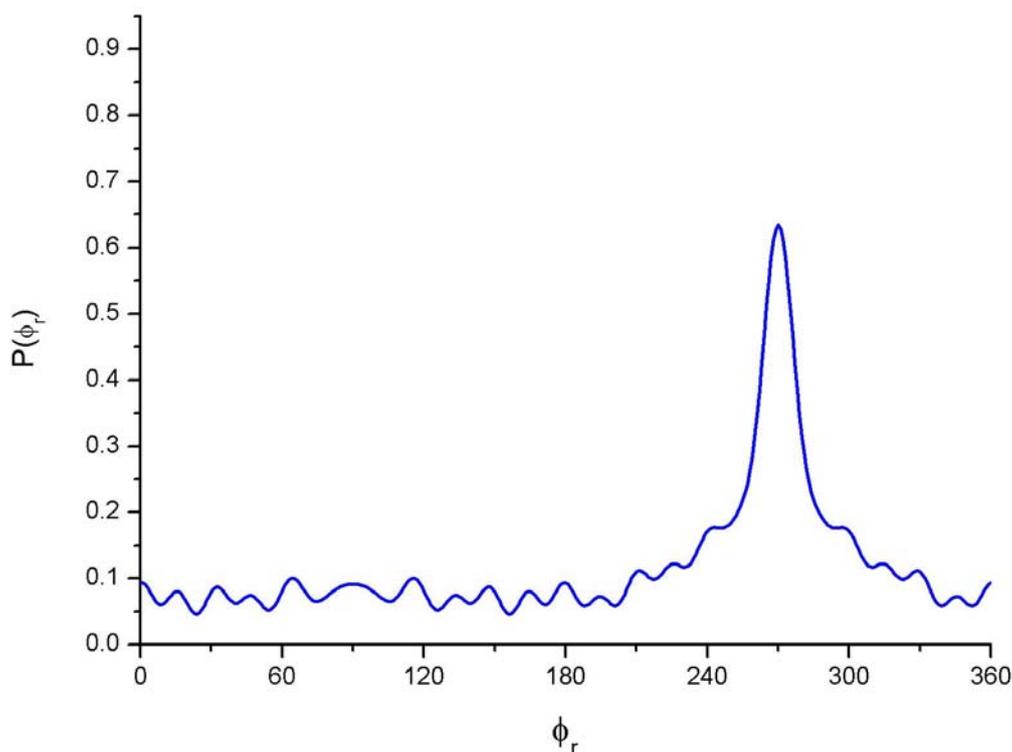


Figure 3. The $P(\phi_r)$ distributions at the translational energy of 6kcal/mol.

4. Conclusion

By employing the DHTSN PES in the present QCT calculation, the chemical stereodynamics have been investigated for the title reaction with a translational energy of 6kcal/mol. The QCT angular distributions of $P(\theta_r)$ and $P(\phi_r)$ suggest that the product

rotational angular momentum j' is not only aligned but also oriented along the direction perpendicular to the scattering plane. The rovibrational state distribution of product HF at 6kcal/mol demonstrates that the $v'=3$, $j'=0-2$ are the most populated product states.

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