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Quasi-Classical Trajectory Study of the Effects of Reactant Ro-Vibrational Excitation on the H(^{2}S)+ClO($^2\Pi$) → OH($^2\Pi$)+Cl(^{2}P) Reaction

Chuang Li, Jingmin Kuang, Yujing Zhao and Yanru Huang*

College of science, Liaoning Shihua University, Fushun, 113001, PR China

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Abstract: The quasi-classical trajectory calculations have been performed to investigate the stereodynamics of the reaction H(^{2}S)+ClO($^2\Pi$)→OH($^2\Pi$)+Cl(^{2}P) on the ground electric state $1^1A'$ potential energy surface. The alignment and orientation of the product molecule and the differential cross sections (DCSs) for this reaction at the collision energy 1.0 eV on the different ro-vibrational states of ClO (v=0－2 and j=0－10) are reported. It is found that the product rotational polarization and DCSs are sensitive to the selected initial ro-vibratioanl quantum number. We discuss these phenomena in detail in our work. The calculated results probably indicate that, for this system, the two deep wells of the potential energy surface have a powerful influence on the degree of the product rotational polarization and the product angular distribution.

AMS subject classifications: 68U05, 74F25, 81v55

Key words: Stereodynamics, Quasi-classical trajectory method, Potential energy surface, Rotational alignment and orientation

1. Introduction

In recent years, the hypochlorous acid, HOCl, which corresponds to three dissociation channels, O + HCl, H + OCl, and Cl + OH, has gained considerable attention, since it plays an important role in atmospheric chemistry such as in ozone layer depletion. A lot of works have

* Corresponding author. *E-mail address*: huangganen12@sina.cn (Y.-R Huang)

been performed in experiment and theory. The first experimental value of the rate coefficient for the global deactivation of $O(^1D)$ by HCl was obtained in the measurement of Davidson et al. more than 30 years ago [1, 2]. They reported $k_1=(1.4\pm0.4)\times10^{-10}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ independent of temperature over the range 200–350 K. In 1986, Wine et al. obtained a similar experimental value of $(1.50\pm0.30)\times10^{-10}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 297 K [3]. The experimental investigation of the highly vibrationally and rotationally excited state distribution of OH was carried out by laser induced fluorescence (LIF) [4]. Balucani et al. measured the angular velocity distribution of the ClO product from the reaction $O(^1D)$ + HCl at 12.2 kcal/mol collision energy in a crossed-molecular-beam experiment and estimated the branching ratio $\sigma_{ClO}/\sigma_{OH} \geq 0.34\pm0.10$ [5]. The first pioneering classical trajectory study of the title reaction using an analytical potential energy surface fitted to extensive ab initio calculations was published in 1984, which reveals the reactions proceed via long-living HOCl complexes before breaking up into products [6]. And then a new PES was fitted to the limited ab initio information [7]. Hernandz et al. calculated the potential energy surface of the $O(^1D)$+HCl reaction at an ab initio level[8]. And later, an improved PES was produced by Laganá et al. with supplement of the ab initio points [9].

As mentioned above, most experimental and theoretical studies so far have focused on $O(^1D)$ + HCl→OH + Cl, ClO + H reactions. However, little attention has been paid to the reaction H + ClO→OH + Cl on the single state PES. On other hand, previous investigations deal basically with the scalar properties. In order to gain a comprehensive understanding of the reaction H + OCl→OH + Cl, we should also study the vector properties, such as the velocity and momentum vectors, the rotational alignment and orientation of product molecules. In this paper, the influence of different ro-vibrational excitation states of reagent OCl has been studied. The fitted analytical potential is shown in **Figure 1**.

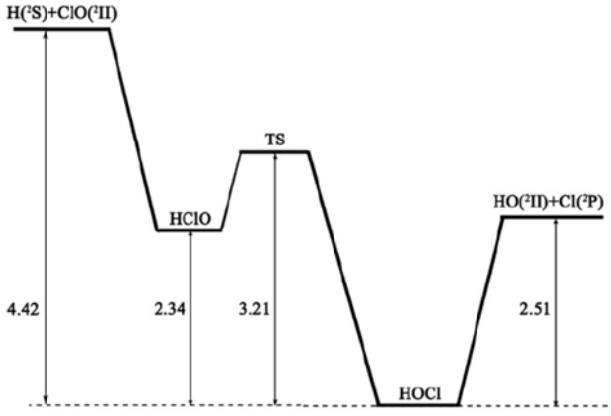

Figure 1: Schematic diagram of the $1^1A'$electronic ground state for the $H(^2S)$+$ClO(^2\Pi)$ reaction

2. Theoretical method

2.1. Rotational polarization of the product

The distribution function $P(\theta_r)$ can be written as [10-12]

$$P(\theta_r) = \frac{1}{2}\sum_k [k] a_0^k P_k(\cos\theta_r), \tag{2.1}$$

where the angular brackets represent an average over all the reactive trajectories. a_0^k are called orientation parameters (k is odd) or alignment parameter (k is even). The distribution of $\phi_r$could be expanded as Fourier series

$$P(\phi_r) = \frac{1}{2\pi}(1 + \sum_{n\ even\geq 2} a_n \cos n\phi_r + \sum_{n\ odd\geq 1} b_n \sin n\phi_r), \tag{2.2}$$

The differential cross section is given by

$$\frac{1}{\sigma}\frac{d\sigma_{00}}{d\omega_t} \equiv P(\omega_t) = \sum_{k_1}\frac{[k_1]}{4\pi} h_0^{k_1}(k_1, 0) P_{k_1}(\cos\theta_t) \ , \tag{2.3}$$

2.2. Computational details

The QCT is a valid and suitable method to investigate chemical stereodynamics [13-17]. In this work, the QCT calculations [18-21] have been carried out for the H(^{2}S)+ClO($^2\Pi$) reaction on a global PES. In the computations, the integration step size is 0.1 fs. Batches of 100 000 trajectories have been run at collision energy 0.5 eV. All the calculations presented in this paper have been obtained using the QCT code developed by Han et al. [11, 22].

3. Results and discussion

3.1 Dependence of the product rotational polarization on initial rotational states of ClO

To obtain a clearer understanding of the dependence of the alignment and orientation of product rotational angular momentum j' on initial rotational states, we have plotted $P(\theta_r)$ and $P(\phi_r)$ at 1.0 eV, with initial states of ClO v=0, j=0, 5 and 10, in **Figure 2**. It is clear that the peak

of $P(\theta_r)$ at θ_r=90° with j=5 is lower and broader than the one with j=0. But as the rotational quantum increases from j=5 to 10, the peak of $P(\theta_r)$ show a very interesting behavior: this peak goes upward by an unnoticeable degree. As shown in **Figure 2**(**b**), the distribution $P(\phi_r)$ describing the $k-k'-j'$correlation is asymmetric with respect to the $k-k'$ plane. Compared with the $P(\theta_r)$ distribution, the behavior of the $P(\phi_r)$ distribution seems more complicate. Furthermore, on the selected initial states of ClO (v=0, j=0, 5, 10), the $P(\phi_r)$ distributions are nearly isotropic and there is no significant peak. This phenomenon implies that the increment of rotational quantum of this system has a very weak effect on the polarization of product rotational orientation.

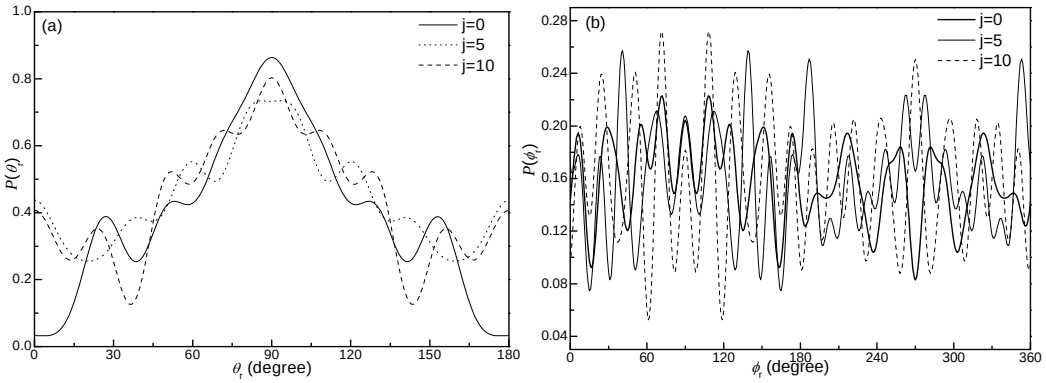

Figure 2: The alignment and orientation of product rotational angular momentum of H+ClO(v = 0,j =0,5,10)→ OH+Cl at collision energy of 1.0 eV. (a) Distribution of $P(\theta_r)$; (b) Dihedral angle distribution of $P(\phi_r)$

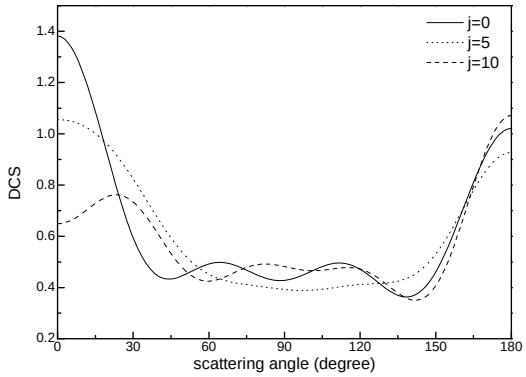

Figure 3: Differential cross sections for H+ClO(v = 0,j =0,5,10) → OH+Cl at collision energy of 1.0 eV.

Figure 3 shows the DCSs for the (v=0, j=0, 5, 10) ro-vibrational states of ClO at the collision energy of 1.0 eV. We found that DCSs present dependence on the rotational excitation of ClO. As the rotational quantum number j increases, the forward peak at 0° become smaller rapidly. It can be noted that the forward peak found for j=0 disappears when

j=10, with a shoulder at about 30°. It can also be seen from **Figure 3** that sideways scattering with angles between 60° and 120° is favored for all rotational quantum number, especially for *j*=5. So, we can conclude that the angular distribution shows a flatting trend with the increasing rotational number *j*. Indeed, when the ClO radical turns more quickly, the chances to obtain a collision between the attacking hydrogen and the target molecule and the interaction with atom O or Cl of ClO are enhanced, and thus it yields a completely randomization of scattering angles. As a result, the product molecules appear in random direction.

3.2. Dependence of the product rotational polarization on initial vibrational states of ClO

We were also interested in the effect of initial vibrational excitation of ClO on the distribution functions $P(\theta_r)$ and $P(\phi_r)$. **Figure 4** displays that the distributions of $P(\theta_r)$ and $P(\phi_r)$ for the (v=0-2, j=0) vibrational states of ClO at the same collision energy as in the j=0—10 case. As can be seen, on the whole, the curves of $P(\theta_r)$ distributions are progressively sharper with increment of vibrational quantum number v, which reflects that the vibrational excitement of the reactant will reinforce the alignment of the product rotational angular momentum. As we know, generally, since the potential energy wells in PES may lead to erase the memory of the product for the angular momentum alignment, the wells can weaken the degree of the product rotational alignment. As a result, the separation of the products will take various directions in space. As shown in **Figure 1**, the reaction H(^{2}S)+ClO(^{2}Π)→OH(^{2}Π)+Cl(^{2}P) is barrierless relative to the entrance channel, and the ground state PES is characterized by two deep wells with the depths of 4.42 eV and 2.08 eV below the H + OCl dissociation asymptote, corresponding to the stable HOCl and HClO molecules in bent geometries. Consequently, the

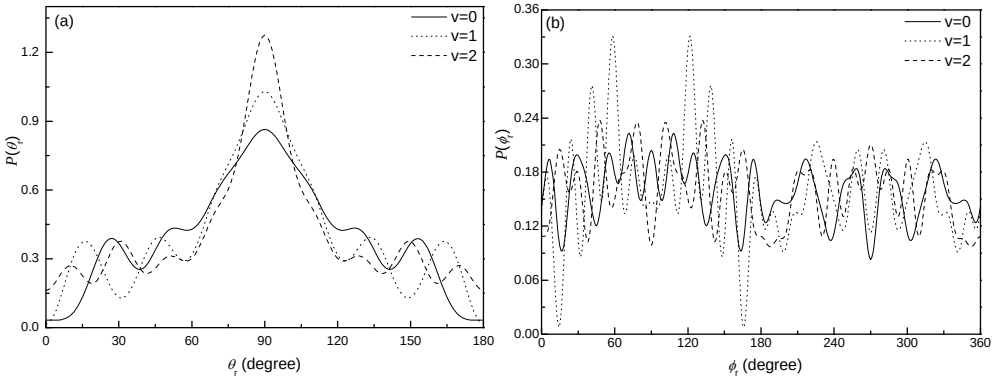

Figure 4: The alignment and orientation of product rotational angular momentum of H+ClO(v = 0,1,2, j =0)→

OH+Cl at collision energy of 1.0 eV. (a) Distribution of $P(\theta_r)$; (b) Dihedral angle distribution of $P(\phi_r)$

intermediate trapped temporarily in these two deep wells will undergo several rotations. The longer the intermediate is trapped, the weaker the degree of the alignment. As the vibrational state of ClO is excited, it is easier for the intermediate complex to break free from the chains of the potential well and be ejected out. In other words, with the increasing vibrational quantum number, the vibrational motion of the intermediate is more intensive, the complex lifetime becomes shorter, which will finally result in stronger rotational polarization of the product. Although the initial vibration state of ClO reactant is found to have an strong effect on the $P(\theta_r)$ distributions, the $P(\phi_r)$ distributions do not change with the increasing vibrational quantum number. As **Figure 4**(**b**) shows, on the whole, there is no obvious peak at $\phi_r = 90^o$ and $\phi_r = 270^o$.

We have also calculated DCSs on the different initial vibrational states. As can be seen from **Figure 5**, the angular distribution of product OH with v=1 shows the similar shape and behavior to those obtained with v=0. However, as the quantum number increase from v=1 to v=2, the intensity of the backward peak decreases significantly. This phenomenon illustrates again that the higher vibrational excitation of reactant could make the lifetime of complex trapped in the wells shorter.

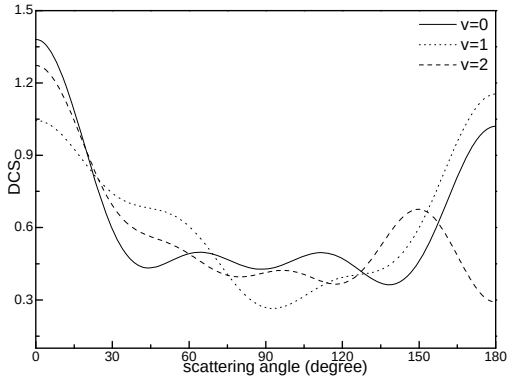

Figure 5: Differential cross sections for H+ClO(v = 0,1,2, j =0) → OH+Cl at collision energy of 1.0 eV.

4 Conclusions

In this work, QCT calculations have been carried out to study the stereodynamics of the H(^{2}S)+ClO($^2\Pi$)→OH($^2\Pi$)+Cl(^{2}P) reaction on the singlet ground state potential energy surface. The theoretical results include the product angular momentum alignment distribution $P(\theta_r)$, the product angular momentum orientation distribution $P(\phi_r)$, and DCSs at the collision energy of 1.0 eV on the ro-vibrational state of ClO (v=0-2, j=0-10). When the ClO radical is rotational excited, the peak of $P(\theta_r)$ becomes lower and broader and DCS shows a flatting trend. On the other hand, with the increasing vibrational quantum number, the peak of $P(\theta_r)$

is found to be enhanced and the rotation of OH has a preference of changing from the "in-plane" reaction mechanism to the "out-of-plane" reaction mechanism.

Acknowledgments

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