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Effect of the reagent vibration on stereodynamics of the reaction $O(^1D)+HF\rightarrow F+OH$*

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This paper studies the influence of the reagent vibration on the reaction $O(^1D)+HF\rightarrow HO+F$ by using a quasi-classical trajectory method on the new *ab initio* $^1A'$ ground singlet potential energy surface (Gómez-Carrasco *et al* 2007 *Chem. Phys. Lett.* **435** 188–193). The product angular distributions which reflect the vector correlation are calculated. Four polarization-dependent differential cross sections (PDDCSs) which are sensitive to many photoinitiated bimolecular reaction experiments are presented in the center of the mass frame, respectively. The differential cross section indicates that the OH product mainly tends to the forward scattering, and other PDDCSs are also influenced by the vibration levels of HF.

Keywords: vector correlation, polarization-dependent differential cross section, vibration of the reactant molecule, quasi-classical trajectory

PACC: 3450L, 8220K

1. Introduction

As the potential laboratory sources of FO radical, the reactions of excited oxygen atoms with fluorides have been paid much attention for our further understanding of the mechanisms of small molecule reactions in recent years. To date, on the experimental side only two works, the kinetic room temperature experiments by Wine *et al* [1] and by Sorokin *et al*,[2] related to the activity of singlet OHF have so far been published. Sorokin *et al* have investigated the reactions of $O(^1D)$ atoms with fluorides by time-resolved laser magnetic resonance, while the former is endowed with a large uncertainty.

The stable intermediate HOF existing on the $^1A'$ potential energy surface is of central importance for the dynamics of the O+HF reaction. Recently, the accurate potential energy surfaces of the ground singlet state of the $O(^1D)$+HF reaction have been calculated by Gómez-Carrasco *et al*.[3] About 20000 multireference configuration interaction (MRCI) single point energies for the $O(^1D)+HF\rightarrow F(^1P)$ +OH reaction have been calculated and fitted to obtain the ground $^1A'$ potential energy surface. Based on the new MRCI potential surface, the reaction probability as a function of collision energy has also been calculated with a wavepacket and quasi-classical trajectory (QCT) method by Gómez-Carrasco, and the results are coincident with each other.[3]

With the rapid development of reaction dynamics during the past few decades,[4−8] the stereodynamics of chemical reaction has attracted many people's attention. Since vector properties, such as velocity and angular momentum, possess not only magnitudes which can be directly related to translational and rotational energies, but also well-defined directions, they can provide valuable information about chemical reaction stereodynamics.[9−15] To shed more light on the state-to-state dynamics, in this paper we employ QCT calculations to study the stereodynamics of the title reaction, and analyse the influence of the reagent vibration on the stereodynamics of this reaction.

2. Theory

2.1. Product rotational polarization

The theory of the product rotational polarization applied here is the one established by Han *et al*.[16−21] For the sake of brevity, only the part relevant to the present work is summarized here. In the centre-of-mass (CM) frame shown in Fig.1, the reagent relative

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velocity vector $\boldsymbol{k}$ is parallel to the z-axis and x–z plane is the scattering plane containing the initial and final relative velocity vectors, $\boldsymbol{k}$ and $\boldsymbol{k}'$. θ_t is the angle between the reagent relative velocity and product relative velocity, namely, scattering angle. θ_r and ϕ_r are the polar and azimuthal angles of the final rotational momentum $\boldsymbol{j}'$.

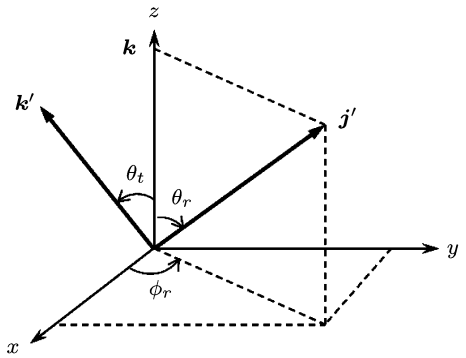


Fig.1. The centre-of-mass coordinate system used to describe the $\boldsymbol{k}$, $\boldsymbol{k}'$ and $\boldsymbol{j}'$ distribution.

The distribution function $P(\theta_r)$ describing the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation can be expanded in a series of Legendre polynomials, and the expanding coefficients are called orientation (k is odd) and alignment (k is even) parameter. The dihedral angle distribution function $P(\phi_r)$ describing $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation can be expanded in Fourier series. In this calculation, $P(\theta_r)$, $P(\phi_r)$ and $P(\theta_r, \phi_r)$ are expanded up to $k = 18$, $n = 24$, $k = 7$, respectively, which shows good convergence.

The fully correlated CM angular distribution is written as the sum

$$P(\omega_t, \omega_r) = \sum_{kq} \frac{[k]}{4\pi} \frac{1}{\sigma} \frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t} C_{kq}(\theta_r, \phi_r)^*, \qquad (1)$$

where $(1/\sigma)(\mathrm{d}\sigma_{kq}/\mathrm{d}\omega_t)$ is a generalized polarization-dependent differential cross section (PDDCS). Many photoinitiated bimolecular reaction experiments will be sensitive to only those polarization moments with k=0 and k=2. In the present work, $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ are calculated. The PDDCSs are expanded up to $k_1 = 7$, which is sufficient for good convergence. The computational method used here was developed by Han and coworkers.[12,16–18,22]

2.2. Quasiclassical trajectory calculations

In this work, the calculation method of QCT is the same as the one used in Refs.[12], [16]–[20]. The conventional quasiclassical algorithm, which is a sixth order symplectic routine with energy conservation checked, is employed for the numerical solution with Hamilton's classical equations.[20] The accuracy of the numerical integration is verified by checking the conservation of the total energy and total angular momentum for every trajectory. The vibrational and rotational levels of the reactant molecule are taken as v=0–2, and j=0, respectively. The collision energy is 0.2 eV. In the calculation, batches of 10000 trajectories are run for each reaction and the integration step size is chosen as 0.1 fs. The trajectories are started at an initial distance of 10.0 Å (1 Å=0.1 nm) between the O atom and the center of the HF.

3. Results and discussions

Figure 2 shows the calculated $P(\theta_r)$ distribution of OH product from the reaction O(^1D)+HF (v=0–2, j=0) at a collision energy of 0.2 eV, respectively. It represents the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation. The $P(\theta_r)$ distribution is symmetric about $\theta_r = 90°$. It is obvious that the excitation of the initial HF vibration has a high impact on the stereodynamics. From the plot, we can see that the distribution of $P(\theta_r)$ of the products OH changes dramatically when the HF molecule vibrations are excited to the v=1, 2 energy levels.

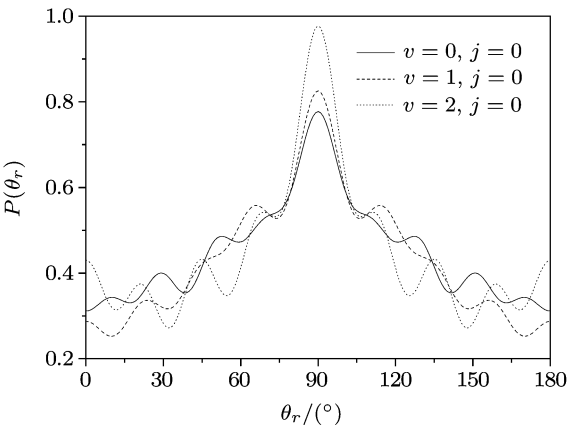


Fig.2. The distribution of $P(\theta_r)$, reflects the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation. Solid line indicates O(^1D)+HF (v=0, j=0)→HO+F; dashed line indicates O(^1D)+HF (v=1, j=0)→HO+F; dotted line indicates O(^1D)+HF (v=2, j=0)→HO+F.

The distribution of $P(\theta_r)$ becomes higher when the reagent vibration is in the v = 1, 2, indicating the product rotational alignment effect becomes stronger when the reagent is in the excited vibration states. This may be explained from the expectation values of

$\langle P_2(\cos\theta_r)\rangle$ which are −0.092, −0.104 and −0.342, respectively. As we know, $P_2(\cos\theta_r)$ is very important, because when the values are close to −0.5, it suggests that $\boldsymbol{j}'$ is preferentially polarized and perpendicular to the reagent relative velocity.

Figure 3 shows the dihedral angle distribution $P(\phi_r)$ which describes the correlation of $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$. It can be found that $P(\phi_r)$ tends to be asymmetric with respect to the scattering plane, which directly reflects the strong polarization of angular momentum. The product rotational angular momentum vector $\boldsymbol{j}'$ is not only aligned, but also slightly oriented along the y-axis on the reaction. There are two peaks at $\phi_r = 90°$ and $\phi_r = 270°$, which might suggest that the reaction proceeds preferentially when the reactant velocity vector lies in a plane containing all three atoms. The peak at $\phi_r = 270°$ is stronger than that at $\phi_r = 90°$ when the reagent HF is in vibration ground state, which reflects that the $\boldsymbol{j}'$ is preferentially oriented along the negative direction of y-axis. This trend becomes stronger as the reagent vibration is v=1. However, the oriented direction changes in v=2 energy level. In this case, the peak at $\phi_r = 90°$ is stronger than that at $\phi_r = 270°$. This fact reflects that the $\boldsymbol{j}'$ is oriented along the positive direction of y-axis. With the enhancement of the reagent vibrational excitation, the product rotational polarization becomes stronger, and the direction of orientation changes in v=2 energy level. It can be seen also that the degree of orientation is unconspicuous. This may be due to the deep well on the potential energy surface. The $P(\phi_r)$ distribution is asymmetric, which is probably attributed to the effect of the repulsive energy between H–F atoms. In Ref.[23], Han *et al* developed an "Impulsive Collision Model" of the atom and molecule, A+BC→AB+C reaction, in which an expression has been derived to calculate the angular momentum of product. For the reaction $O(^1D)$+HF→F+OH, the angular momentum $\boldsymbol{j}'$ of the product HF can be expressed as[19,23,24]

$$\boldsymbol{j}' = \boldsymbol{L}\sin^2\beta + \boldsymbol{j}\cos^2\beta + \boldsymbol{J}_1 m_{\mathrm{H}}/m_{\mathrm{HO}}, \quad (2)$$

$$\cos^2\beta = \frac{m_{\mathrm{O}}\cdot m_{\mathrm{F}}}{(m_{\mathrm{O}}+m_{\mathrm{H}})(m_{\mathrm{H}}+m_{\mathrm{F}})}, \quad (3)$$

$$J_1 = \sqrt{\mu_{\mathrm{HF}}R}\,(\boldsymbol{r}_{\mathrm{OH}}\times\boldsymbol{r}_{\mathrm{HF}}), \quad (4)$$

where $\boldsymbol{L}$ and $\boldsymbol{j}$ denote the reagent orbital and rotational angular momentum, respectively, μ_{HF} is the reduced mass of HF molecule and R is the repulsive energy between H and F, $\boldsymbol{r}_{\mathrm{OH}}$ and $\boldsymbol{r}_{\mathrm{HF}}$ are unit vectors where H points to O and F, respectively. During the chemical-bond forming and breaking for the O+HF reaction, the term $\boldsymbol{L}\sin^2\beta + \boldsymbol{j}\cos^2\beta$ in the equation is symmetric, while the term $\boldsymbol{J}_1 m_{\mathrm{H}}/m_{\mathrm{HO}}$ shows a preferring direction because of the effect of the repulsive energy, which leads to the OH product rotation in planes parallel to the scattering plane.[19]

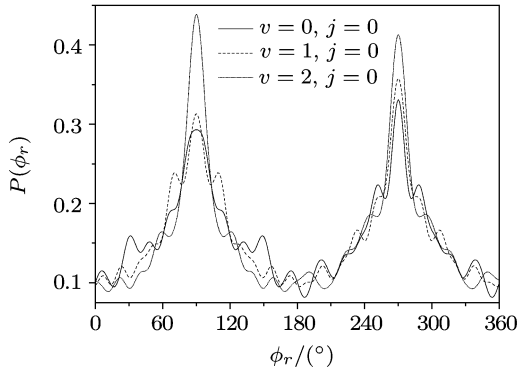


Fig.3. The dihedral angle distribution of $P(\phi_r)$ with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ plane. Solid line indicates $O(^1D)$+HF (v=0, j=0)→HO+F; dashed line indicates $O(^1D)$+HF (v=1, j=0)→HO+F; short dotted line indicates $O(^1D)$+HF (v=2, j=0)→HO+F.

In order to obtain more detailed information of the reaction dynamics, we calculate the distribution of $P(\theta_r,\ \phi_r)$ which is given in Fig.4. There are two peaks at (90°, 90°) and (90°, 270°). It is in good accordance with the distribution of $P(\theta_r)$ and $P(\phi_r)$.

The PDDCSs of the OH for the O+HF reaction calculated on the new MRCI potential surface at v=0–2, and j=0 are presented in Fig.5. The PDDCSs describe the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation and the scattering direction of the product molecule. The PDDCS of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, which is simply proportional to the differential cross section, only describes the $\boldsymbol{k}$–$\boldsymbol{k}'$ correlation or the scattering direction of the product and is not associated with the orientation and alignment of the product rotational angular momentum vector $\boldsymbol{j}'$. As shown in Fig.5, it is clear that there is a similar trend that the OH product is scattered strongly forward. The values of PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ show a trend which is opposite to the trend for $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$. These may result from the fact that $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ is related to alignment moment $\langle P_2(\cos\theta_r)\rangle$. From Fig.5, it is easy to see that the values are different in the three cases. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ which provides information on ϕ_r is very interesting. At the extremes of forward and backward scattering, the PDDCSs with $q \neq 0$ are necessarily zero. At these limiting scattering angles, the

$\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane is not determined and the values of these PDDCSs must be zero. From Fig.5, we can see that the values of $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ are negative in the whole scope, which suggests the marked preference of product alignment along the y-axis. It is necessary to note that at about 30°, the products display a stronger polarization, which is very important for chemical reaction stereodynamics. Moreover, the degree of polarization is stronger at v=1, 2 than at v=0. The $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ performs different characters in the three cases, reflecting that it is also effected by the reagent vibration.

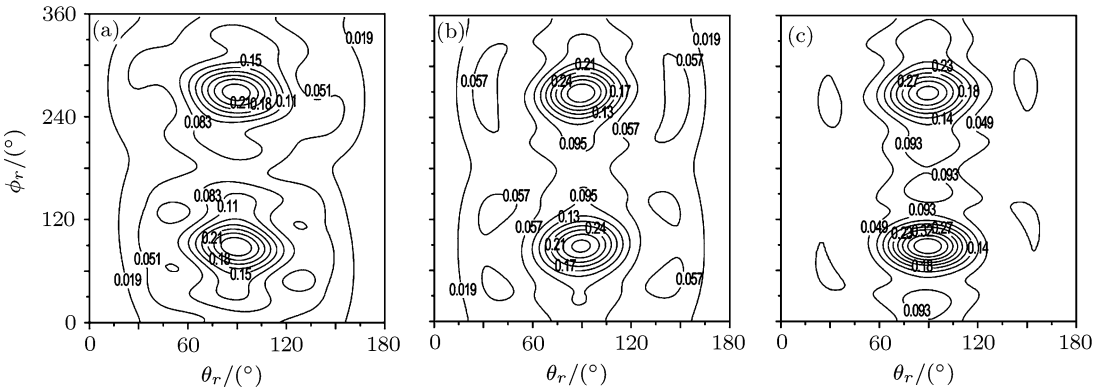


Fig.4. Polar plots of $P(\theta_r,\ \phi_r)$ distribution averaged over all scattering angles. (a), (b) and (c) correspond to O(^1D)+HF (v=0–2, j=0)→HO+F, respectively.

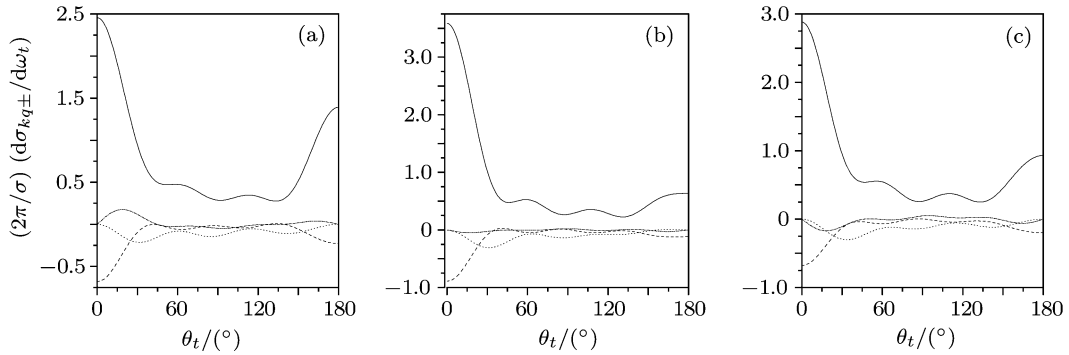


Fig.5. The four polarization-dependent differential cross sections. Solid line indicates $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, dashed line indicates $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, dotted line indicates $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$and short dash-dotted line indicates $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$. (a), (b) and (c) correspond to O(^1D)+HF (v=0–2, j=0)→HO+F respectively.

4. Conclusions

We have studied the vector correlations and the PDDCSs for the chemical reaction O(^1D)+HF→F+OH using the QCT method when the reactant molecule is taken as one of v=0–2, and j=0. The collision energy is taken as 0.2 eV. The alignment effect of products becomes stronger with the increase of vibrational quantum numbers and the orientation of the product rotational angular momentum vector $\boldsymbol{j}'$ depends very sensitively on the reagent vibration. The rotational angular momentum vector $\boldsymbol{j}'$ of HF is not only aligned, but also oriented along the y-axis. The direction of orientation is along the negative direction of y-axis when the reagent HF is in v=0, 1 levels while it changes in v=2. Because of the deep well on the potential energy surface, the degree of orientation is small. The PDDCS of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ predicts that the OH product mainly tends to the forward scattering. Furthermore, $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ are clearly influenced by the reagent vibration. In a word, the effect of the reagent vibration on the reaction O(^1D)+HF→F+OH is obvious. We are looking forward to the completion of experimental studies about the

stereodynamics for the O(^1D)+HF reaction system, so that a comparison of high resolution between theory and experiment can be implemented.

References

[1] Wine P H, Wells J R and Ravishankara A R 1986 *J. Chem. Phys.* **84** 1349

[2] Sorokin V I, Gritsan N P and Chichinin A I 1998 *J. Chem. Phys.* **108** 8995

[3] Gómez-Carrasco S, Hernández M L and Alvarino J M 2007 *Chem. Phys. Lett.* **435** 188

[4] Liu X G, Zhang Q G, Zhang Y C, Wang M L and Zhang John Z H 2004 *Chin. Phys.* **13** 1013

[5] Sun G H, Yang X D, Zhu J and Wang C X 2002 *Chin. Phys.* **11** 910

[6] Liu Y F, Zhu Z L, Sun J F, Cong S L and Han K L 2003 *Chin. Phys.* **12** 750

[7] Chu T S, Zhang Y and Han K L 2006 *Int. Rev. Phys. Chem.* **25** 201

[8] Chu T S and Han K L 2008 *Phys. Chem. Chem. Phys.* **10** 2431

[9] Case D A, McClelland G M and Heschbach D R 1978 *Mol. Phys.* **35** 541

[10] Kim S K and Herschbach D R 1987 *Faraday Discuss. Chem. Soc.* **84** 159

[11] Kim H L, Wickramaaratchi M A, Zheng X and Hall G E 1994 *J. Chem. Phys.* **101** 2033

[12] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699

[13] Orr-Ewing A J and Zare R N 1994 *Ann. Rev. Phys. Chem.* **45** 315

[14] Miranda M P and Clary D C 1997 *J. Chem. Phys.* **106** 4509

[15] Brouard M, Gatenby S D, Joseph D M and Vallance C 2000 *J. Chem. Phys.* **113** 3162

[16] Wang M L, Han K L and He G Z 1998 *J. Phys. Chem.* A **102** 10204.

[17] Chen M D, Han K L and Lou N Q 2003 *J. Chem. Phys.* **118** 4463

[18] Wang M L, Han K L and He G Z 1998 *J. Chem. Phys.* **109** 5446

[19] Chen M D, Han K L and Lou N Q 2002 *Chem. Phys. Lett.* **357** 483

[20] Zhang X and Han K L 2006 *Int. J. Quant. Chem.* **106** 1815

[21] Sun C, Liu W W and Ren T Q 2008 *J. Atom. Mol. Phys.* **25** 195

[22] Han K L, He G Z and Lou N Q 1993 *Chin. Chem. Lett.* **4** 517

[23] Han K L, He G Z and Lou N Q 1989 *Chin. J. Chem. Phys.* **2** 323

[24] Li R J, Han K L, Li F E, Lu R C, He G Z and Lou N Q 1994 *Chem. Phys. Lett.* **220** 281