Theoretical study of stereodynamics for reaction $O(^3P)+HCl^*$

Zhu Tong(朱 通), Hu Guo-Dong(扈国栋), Chen Jian-Zhong(陈建中), Liu Xin-Guo(刘新国), and Zhang Qing-Gang(张庆刚)†

College of Physics and Electronics, Shandong Normal University, Jinan 250014, *China*

(Received 24 June 2009; revised manuscript received 23 November 2009)

The vector correlation between products and reagents for reaction $O(^3P)+HCl\rightarrow OH+Cl$ is studied using a quasi-classical trajectory (QCT) method on the benchmark potential energy surface of the ground $^3A''$ state [Ramachandran and Peterson, *J. Chem. Phys.* **119** (2003) 9550]. The generalised differential cross section $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$ is presented in the centre of mass frame. The distribution of dihedral angles, $P(\phi_r)$, and the distribution of angles between k and j', $P(\theta_r)$, are calculated. The influence of the collision energy and the influence of the reagent rotation and vibration on the product polarization are studied in the present work. The calculated results indicate that the rotational polarization of the product molecule is almost independent of collision energy but sensitive to the reagent rotation and vibration.

Keywords: product rotational polarization, vector correlations, differential cross sections, quasi-classical trajectory

PACC: 3450L, 8220K

1. Introduction

The stereodynamics in the chemical reaction process A+BC→AB+C has attracted much attention in recent decades.[1] It basically deals with vector properties that characterize reactive molecular collisions and are contrary to scalar properties such as integral cross sections, energy requirements for reaction, product disposal of energy, population of quantum states, etc.[2−4] Vector properties, such as velocities and angular momenta, possess not only magnitudes that can be directly related to translational and rotational energies, but also well-defined directions. Only by understanding both the scalar and the vector properties, as well as possible correlations between them, can the fullest pictures of the scattering dynamics emerge.

With the developments of the laser and other experimental techniques, the study of the correlation of vectors in a reaction has become possible. Several experimental methods, such as polarization-resolved chemiluminescence, polarized laser-induced fluorescence, electric deflection methods, REMPI, etc., have been developed to study vector properties in chemical reaction under molecular-beam and bulb conditions.[5−14] In a theoretical respect, substantial progress has been made in recent years in using quasi-classical trajectory methods, quantum-scattering or wave packet propagation techniques to establish unified means for describing the different vector correlations.[15−25] Hijazi and Polanyi used a quasi-classical trajectory (QCT) method on two potential energy surfaces, attractive and repulsive, to investigate the effects of different mass combinations of reactants on the distribution of angles between product rotational angular momentum and reactant relative velocity.[18,19] Han *et al.* reported on the product rotational alignments of several mass combination reactions as a function of collision energy on attractive and repulsive potential surfaces.[15,19−25] And a unified semiclassical treatment of the centre-of-mass correlated (k, k', j') angular distribution was described.

The reaction of ground state oxygen atoms with hydrogen chloride plays an important role in the atmospheric chemistry and serves as a classic example of reaction with heavy-light-heavy (HLH) dynamics and a small skew angle. For this reason it attracted a great deal of attention from theoretical and experimental communities.[23−36] However, most of the previous studies dealt basically with the scalar proper-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10474060 and 10504017), and the Natural Science Foundation of Shandong Province, China (Grant No. 2007A05).

†Corresponding author. E-mail: zhangqg@sdnu.edu.cn or qinggzhang@gmail.com

© 2010 Chinese Physical Society and IOP Publishing Ltd

ties. To shed more light on the stereodynamics of HLH mass combination reaction and gain more insight into the detailed dynamics of the O(^{3}P)+HCl reaction, we carry out a quasi-classical trajectory calculation for the title reaction, and study the vector correlations. The remainder of the present paper is organized as follows. In Section 2, a brief review of the theoretical methodologies is provided. In Section 3, the calculated results are presented and discussed. Finally, the conclusions are drawn in Section 4.

2. Theoretical and computational methods

2.1. Rotational polarization of the product

The centre-of-mass (CM) frame is utilized in the calculation, which is shown in Fig. 1. The z-axis lies in the direction of the reagent relative velocity k, whereas the y-axis is perpendicular to the xz plane containing k and k'. Parameter θ_r is the angle between the reagent relative velocity and product relative velocity (so-called scattering angle), corresponding to the angle between k and k'. Parameter ϕ_r is the azimuthal angle of the final rotational angular momentum j'.

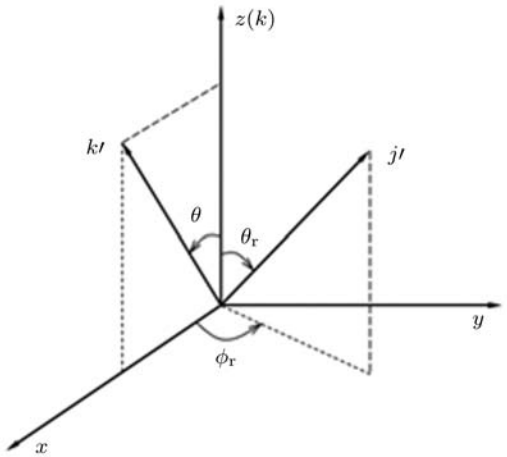


Fig. 1. Centre-of-mass coordinate system used to describe correlation among k, k' and j'.

The full three-dimensional angular distribution associated with k, k', and j' is represented with a set of generalized polarization-dependent differential cross sections (PDDCS) in the CM frame.[37] The fully correlated CM angular distribution is written as

$$\mathrm{P}(\omega_r,\omega_r)=\sum_{kq}\frac{[k]}{4\pi}\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}\mathrm{C}_{kq}(\theta_r,\phi_r), \tag{1}$$

where $[k]=2k+1$, $(1/\sigma)(\mathrm{d}\sigma_{kq}/\mathrm{d}\omega_t)$ is the generalized polarization-dependent differential cross section (PDDCS), and $\mathrm{C}_{kq}(\theta_r,\phi_r)$ are the modified spherical harmonics. The PDDCS is written in the following form:

$$\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq\pm}}{\mathrm{d}\omega_t}=\sum_{k_1}\frac{k_1}{4\pi}S^{k_1}_{kq\pm}\mathrm{C}_{k_1q}(\theta_t,0), \tag{2}$$

where

$$S^{k_1}_{kq\pm}=\langle \mathrm{C}_{k_1q}(\theta_t,0)\mathrm{C}_{kq}(\theta_r,0)[(-1)^q\exp(\mathrm{i}q\phi_r) \pm\exp(-\mathrm{i}q\phi_r)]\rangle. \tag{3}$$

The angular brackets represent an average over all angles, the differential cross section is given by

$$\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{00}}{\mathrm{d}\omega_t}=\mathrm{P}(\omega_t)=\frac{1}{4\pi}\sum_{k_1}[k_1]S^{k_1}_{00}\mathrm{P}_{k_1}(\cos\theta_t). \tag{4}$$

The usual two-vector correlation k–j' is expanded into a series of Legendre polynomials, and the distribution $\mathrm{P}(\theta_r)$ can be written as [19−22]

$$\mathrm{P}(\theta_r)=\frac{1}{2}\sum_k(2k+1)A^{(k)}_0\mathrm{P}_k(\cos\theta_r), \tag{5}$$

where

$$A^{(k)}_0=\int_0^\pi \mathrm{P}(\theta_r)\mathrm{P}_k(\cos\theta_r)\sin\theta_r\mathrm{d}\theta_r=\langle \mathrm{P}_k(\cos\theta_r)\rangle\,. \tag{6}$$

The coefficients $A^{(k)}_0$ are called orientation (k is odd) or alignment (k is even) parameters. $k=2$ indicates the product rotational alignment

$$A^{(2)}_0=\langle \mathrm{P}_2(\cos\theta_r)\rangle=\langle \mathrm{P}_2(\boldsymbol{j'}\cdot\boldsymbol{k})\rangle=\frac{1}{2}\langle 3\cos^2\theta_r-1\rangle. \tag{7}$$

The dihedral angle distribution function $\mathrm{P}(\phi_r)$ describing k–k'–j' correlation can be expanded into Fourier series as

$$\mathrm{P}(\phi_r)=\frac{1}{2\pi}\Big(1+\sum_{\mathrm{even},n>2}a_n\cos n\phi_r+\sum_{\mathrm{odd},n\geq 1}b_n\sin n\phi_r\Big), \tag{8}$$

where

$$a_n=2\langle\cos n\phi_r\rangle \quad\text{and}\quad b_n=2\langle\sin n\phi_r\rangle\,. \tag{9}$$

In the previous studies of Han *et al.*,[38] an "impulse collision model" for the atom and molecule reaction, was developed to calculate the product rotational alignment. According to the model, the rotational angular momentum of the product molecule j' can be expressed as

$$\boldsymbol{j'}=\boldsymbol{l}\sin^2\beta+\boldsymbol{j}\cos^2\beta+\boldsymbol{J}_1 m_{\mathrm{A}}/m_{\mathrm{AB}}, \tag{10}$$

$$\boldsymbol{J}_1=(\mu_{\mathrm{BC}}R)^{1/2}(\boldsymbol{r}_{\mathrm{AB}}\times\boldsymbol{r}_{\mathrm{CB}}), \tag{11}$$

where l is the reagent orbital angular momentum and β is the skew angle. $\boldsymbol{r}_{\rm AB}$ and $\boldsymbol{r}_{\rm CB}$ are unit vectors where B means pointing to A and C, respectively; $\mu_{\rm BC}$ is the reduced mass of the BC molecule and R is the repulsive energy.

2.2. Potential energy surface and QCT calculation

The ground ^{3}A$''$ potential energy surface of the O(^{3}P)+HCl system constructed by Ramachandran and Peterson has been employed in the calculation,[32] whose contour plots for the bent saddle point are shown in Fig. 2. The calculation method of QCT is the same as that in Ref. [39] The quasi-classical algorithm which is the sixth-order symplectic routine with energy conservation checked is employed for the numerical solution with Hamilton's classical equations. The collision energies are 0.6, 0.8, and 1.0 eV, separately. The vibrational and the rotational levels of the reactant molecule are taken as $v = 0$–2 and $j = 0, 1, 3$, respectively. In the calculation, batches of 50000 trajectories are run for each reaction and the integration step size is chosen to be l fs. The accuracy of the numerical integration is verified by checking the conservations of the total energy and the total angular momentum for every trajectory.

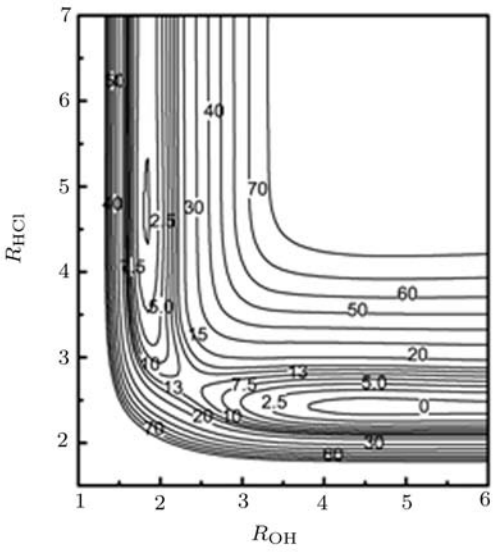


Fig. 2. Contour plots of the ^{3}A$''$ potential energy surface for the bent saddle point (135.9°).

3. Results and discussion

3.1. Influence of collision energy on the stereodynamics

In the calculation, the PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $\mathrm{P}(\theta_r)$ and $\mathrm{P}(\phi_r)$ distributions of product OH molecules for the O(^{3}P)+HCl ($v = j = 0$) reaction calculated at collision energies of 0.6, 0.8, and 1.0 eV have been truncated. The calculated results are shown in Fig. 3. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, which is a simple differential cross section (DCS), describes only the k–k' correlation or the scattering direction of the product. As can be seen from Fig. 3(a), the product molecules are scattered backward at the collision energy of 0.6 eV. When the collision energy increases, the angular distributions shift toward sideway and forward direction.

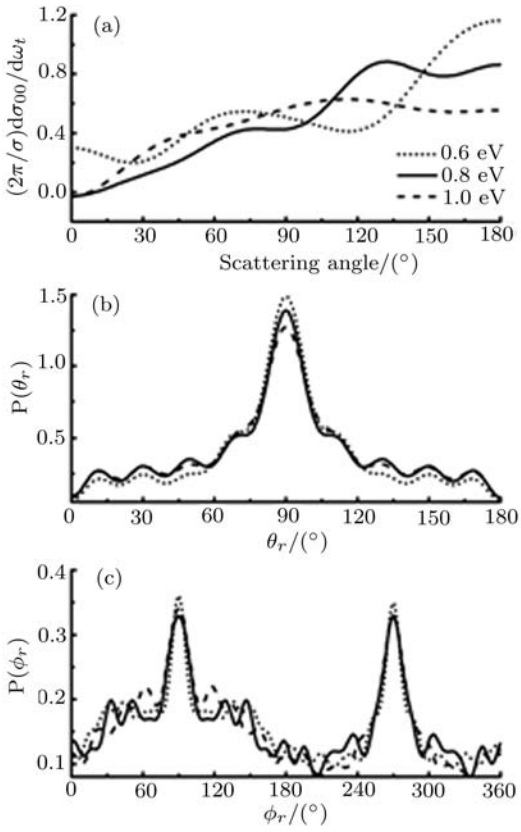


Fig. 3. The calculated results for O(^{3}P)+HCl reaction at different collision energies, showing (a) PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, (b) distribution of $\mathrm{P}(\theta_r)$ for k–j' correlation, and (c) dihedral angle distribution of j', $\mathrm{P}(\phi_r)$, with respect to the k–k' plane.

As shown in Fig. 3(b), the $\mathrm{P}(\theta_r)$ distributions, which represent the k–j' correlation peaked at θ_r angle close to 90° and are symmetric with respect to

90°, which indicates that j' is distributed with cylindrical symmetry in the product scattering frame and the direction of j' is preferentially perpendicular to k direction. The $P(\phi_r)$ distributions shown in Fig. 3(c) describe the k–k'–j' correlation. Those $P(\phi_r)$ distributions tend to be asymmetric with respect to the k–k' scattering plane (or about $\phi_r = 180°$), directly reflecting the strong polarization of angular momentum of the OH product. The peaks of $P(\phi_r)$ distributions that appear at $\phi_r = 90°$ and 270° show that j' is aligned preferentially along y-axis of the CM frame, which also means that the reaction proceeds preferentially when the reactant velocity vector lies in a plane containing all three atoms. We use the term "in-plane" to refer to this preference of product molecule rotation in planes parallel to the scattering plane, and the term "out-of-plane" to refer to the preference of product molecule rotating in planes perpendicular to the scattering plane at the same time. The peak at $\phi_r = 90°$ is apparently higher than that at $\phi_r = 270°$, which means that the product rotational angular momentum vector is not only aligned, but also oriented along the y-axis.

Form Figs. 3(b) and 3(c), one can also see that the peaks of the $P(\theta_r)$ and $P(\phi_r)$ distributions become slightly lower and broader with collision energy increasing, which suggests that the product rotational polarization becomes weaker and the product molecule rotation has a preference of changing from the in-plane reaction mechanism to the out-of-plane mechanism. A similar phenomenon was found in the reaction F+HBr and Cl+H-CH_3.[40−42] However, it is worth while to point out that the change of collision energy has very little influence on $P(\theta_r)$ and $P(\phi_r)$ distributions. This can be explained by the impulse collision model (Eq. (10)). For the O+HCl reaction, the value of $\sin^2\beta$ is so small (0.085) that j' is almost independent of l.

3.2. Influence of reagent rotation on stereodynamics

Figures 4(a), 4(b) and 4(c) show the calculated PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $P(\theta_r)$ distribution and $P(\phi_r)$ distribution of OH product from the reaction $O(^3P)$+HCl ($v = 0$, $j = 0, 1, 3$) at a collision energy of 1.0 eV, respectively. As shown in Fig. 4(a), the angular distributions of the scattered product OH display a preferentially forward scattering tendency with the excitation of the initial HCl rotation increasing. From Figs. 4(b) and 4(c), we can see that the excitation of the initial HCl rotation also has a high effect on $P(\theta_r)$ and $P(\phi_r)$ distributions of the product OH. Both the $P(\theta_r)$ distribution and the $P(\phi_r)$ distribution become broader and lower when the reagent rotation levels are j=1, 3, indicating that the product rotational polarization effect becomes weaker and it is not necessary that the reactant velocity vector lies in a plane containing all three atoms when the reagent is in the excited rotation state. In addition, it can be seen that both the $P(\theta_r)$ distribution and the $P(\phi_r)$ distribution have remarkable change from $j = 2$ to $j = 3$,

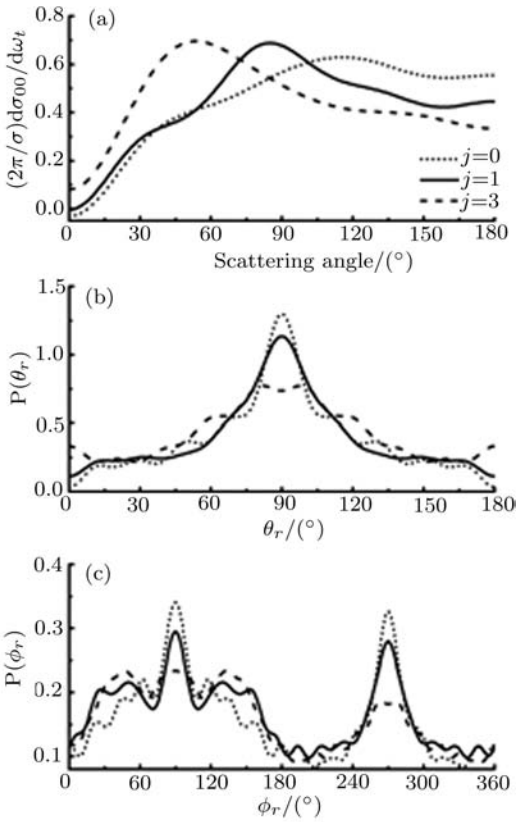


Fig. 4. The calculated results of (a) polarization-dependent differential cross section $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, (b) distribution $P(\theta_r)$ for k–j' correlation, and (c) dihedral angle distribution of j', $P(\phi_r)$, with respect to the k–k' plane, for $O(^3P)$+HCl ($v = 0$, $j = 0, 1, 3$).

while the stereodynamics does not alter significantly from $j = 0$ to $j = 1$. In order to investigate this trend more deeply, we carry out an additional calculation with $j = 5$ and 10. However, the product OH polarization effects are so weak that the calculated $P(\theta_r)$ and $P(\phi_r)$ distributions have no obvious characters. For the O+HCl reaction, the mass factor $\cos^2\beta$ is 0.915, it is easily understood from Eq. (10) that the reagent

rotational momentum j plays an important role in the rotational polarization of product OH. And in the QCT calculations, the reagent rotational momentum j has an initially random orientation. Therefore, an increase of j will reduce the anisotropic distribution of j'. In fact, the product rotational polarization effect is very weak even with $j = 1$, which may be due to the fact that the potential energy surface used in the calculations contains a fairly deep van der Waals well on the product side of the reaction barrier. Generally, the well in the potential energy surface can cause precession of the product angular momentum vector over a wide range of angle. The reactive mechanism, such as the secondary encounter and Coriolis coupling effect[43] may also contribute to a weak product rotational polarization, because it can lead to loss of memory for the angular momentum alignment.

3.3. Influence of reagent vibration on the stereodynamics

The calculated results for reaction O(^{3}P) + HCl (v = 0–2, j = 0) at a collision energy of 1.0 eV are shown in Fig. 5. From the results of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, one can conclude that the products are scattered forward strongly when the reagent vibration is in $v = 1$ level, and the increase of v will enhance this tendency. The distribution of $\mathrm{P}(\theta_r)$ becomes broader and lower when the HCl molecule vibration levels are excited to $v = 1, 2$ energy levels, as shown in Fig. 5(b), indicating that the product rotational alignment effect becomes weaker when the reagent is in the excited vibration state. In Fig. 5(c), the peak at $\phi_r = 270°$ of $\mathrm{P}(\phi_r)$ distribution is apparently smaller than that at $\phi_r = 90°$ when the reagent HCl is in vibration ground state, reflecting that j' is preferentially oriented along the positive direction of the y-axis. However, as the reagent vibration is excited, the peak at $\phi_r = 270°$ becomes higher and narrower, while the opposite tendency is found at $\phi_r = 90°$, that is to say, j' tends to be oriented along the negative direction of y-axis and the product molecule rotation has a preference of changing from the out-of-plane reaction mechanism to the in-plane mechanism. This could be attributed to the repulsive energy between H and Cl atoms, which is important in the case of light atom transfer reaction because of both the high velocity of the light atom and the large mass factor $\cos^2\beta$.[23,26] For O(^{3}P)+HCl (v, $j = 0$) reaction, with the reagent HCl vibration excitation, the repulsive energy between H and Cl atoms increases. In fact, the repulsive energy released in the exit channel can cause precession of the product rotational angular momentum over a wide range of angle. On the other hand, according to Eq. (10), during the forming and breaking of chemical-bond, term $\boldsymbol{l}\sin^2\beta + \boldsymbol{j}\cos^2\beta$ is symmetric while term $\boldsymbol{J}_1 m_\mathrm{A}/m_\mathrm{AB}$ shows a preferential direction, which leads to the orientation of j'. Therefore, the initial vibration excitation of the HCl molecule can lead to the weak alignment but strong orientation of the product rotation.

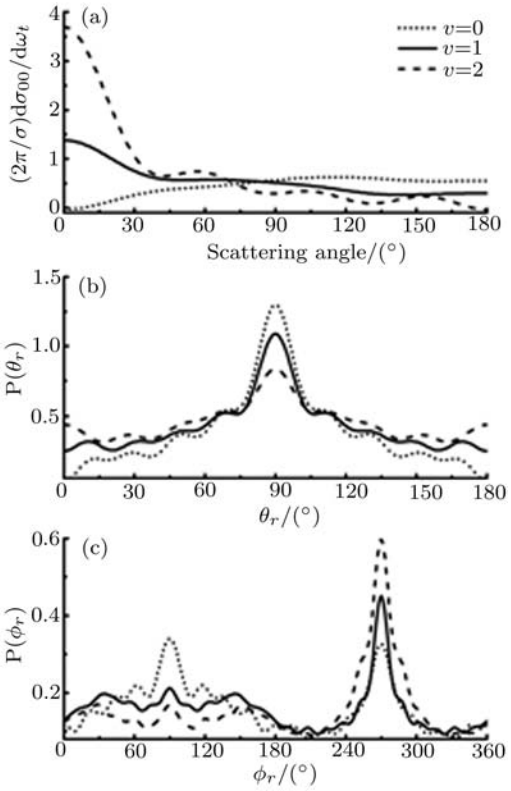


Fig. 5. The calculated results of (a) polarization-dependent differential cross section $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, (b) distribution of $\mathrm{P}(\theta_r)$ for k–j' correlation, and (c) dihedral angle distribution of j', $\mathrm{P}(\phi_r)$, with respect to the k–k' plane, for O(^{3}P)+HCl (v = 0–2, $j = 0$) reaction.

4. Conclusion

In this work we studied the vector correlations for chemical reaction O(^{3}P)+HCl using QCT method at different collision energies and the reactant molecules for levels v = 0–2, and $j = 0, 1, 3$. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ predicts that the HF product tends mainly to forward scattering as collision energy increases and reagent rotation and vibration are excited.

The rotational angular momentum vector j' of product OH is not only aligned, but also oriented along the y-axis. The rotational polarization of product molecule is almost independent of the increase of the collision energy. However, at the same collision energy the alignment and the orientation of the product rotational angular momentum vector j' depend very sensitively on reagent rotation and vibration.

References

[1] Orr-Ewing A J and Zare R N 1994 *Ann. Rev. Phys. Chem.* **45** 315
[2] Liu X G, Zhang Q G, Zhang Y C, Wang M L and Zhang J Z H 2004 *Chin. Phys.* **13** 1013
[3] Sun G H, Yang X D, Zhu J and Wang C X 2002 *Chin. Phys.* **11** 910
[4] Wang F H, Yang C L, Zhu Z H and Jing F Q 2005 *Chin. Phys.* **14** 317
[5] Hsu D S Y and Herschbach D R 1973 *Faraday Discuss. Chem. Soc.* **55** 166
[6] Li R J, Li F, Han K L, Lu R C, He G Z and Lou N Q 1993 *Proc. Int. Conf. Laser* **92** 456
[7] Li R J, Li F, Han K L, Lu R C, He G Z and Lou N Q 1994 *Chem. Phys. Lett.* **220** 281
[8] Hsu D S Y, Weinstein N D and Herschbach D R 1975 *Mol. Phys.* **29** 257
[9] Ma X G, Yang C L, Gong Y B and Wang M S 2009 *Chin. Phys.* B **18** 5296
[10] Hennessy R J and Simons J P 1982 *Mol. Phys.* **43** 181
[11] Menedez M, Garay M, Verdasco E Castano J and Gonzalez-Urena J A 1993 *Phys. Chem.* **97** 5936
[12] Costen M L, Hancock G and Orr-Ewing A J 1991 *Faraday Discuss. Chem. Soc.* **91** 79
[13] Jonah C D, Zare R N and Ottinger C 1992 *J. Chem. Phys.* **97** 952
[14] van der Zande W, Zhang R, McKendrick K G, Zare R N and Valentini J J 1991 *J. Phys. Chem.* **95** 8205
[15] Han K L, He G Z and Lou N Q 1993 *Chin. Chem. Lett.* **4** 517
[16] Polanyi J C and Wong W H 1969 *J. Chem. Phys.* **15** 1439
[17] Hijazi N H and Polanyi J C 1975 *Chem. Phys.* **11** 1
[18] Hijazi N H and Polanyi J C 1975 *J. Chem. Phys.* **63** 2249
[19] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699
[20] Wang M L, Han K L and He G Z 1998 *J. Phys. Chem.* A **102** 10204
[21] Wang M L, Han K L and He G Z 1998 *J. Chem. Phys.* **109** 5446
[22] Xu W W, Liu X G, Luan S X, Sun S S and Zhang Q G 2009 *Chin. Phys.* B **18** 339
[23] Kong H, Liang J J, Liu X G, Xu W W and Zhang Q G 2009 *Acta Phys. Sin.* **58** 6926 (in Chinese)
[24] Chen M D, Han K L and Lou N Q 2003 *J. Chem. Phys.* **118** 4463
[25] Chu T S, Zhang Y and Han K L 2006 *Int. Rev. Phys. Chem.* **25** 201
[26] Rakestraw D J, McKendrick K G and Zare R N 1987 *J. Chem. Phys.* **87** 7341
[27] Zhang R, van der Zande W J, Bronikowski M J and Zare R N 1991 *J. Chem. Phys.* **94** 2704
[28] Ramachandran B, Senekowitsch J and Wyatt R E 1997 *Chem. Phys. Lett.* **270** 387
[29] Ramachandran B 2000 *J. Chem. Phys.* **112** 3680
[30] Xie T, Bowman J, Duff J W, Braunstein M and Ramachandran B 2005 *J. Chem. Phys.* **122** 014301
[31] Barguen P, Alvarin J M and González-Lezana T 2008 *Eur. Phys. J.* D **47** 181
[32] Koizumi H, Schatz G C and Gordon M S 1991 *J. Chem. Phys.* **95** 6241
[33] Ramachandran B, Schrader III E A, Senekowitsch J and Wyatt R E 1999 *J. Chem. Phys.* **111** 3862
[34] Ramachandran B and Peterson K A 2003 *J. Chem. Phys.* **119** 9550
[35] Brouard M, Lambert H M, Rayner S P and Simons J P 1996 *Mol. Phys.* **89** 403
[36] Guo X M, Han K L, Liu J Y, Wan Y, Wang S F and Xia A D 2009 *Chin. Phys.* B **18** 142
[37] Ju L P, Han K L and Zhang J Z H 2009 *J. Comput. Chem.* **30** 305
[38] Han K L, He G Z and Lou N Q 1989 *Chin. J. Chem. Phys.* **2** 323 (in Chinese)
[39] Zhang X and Han K L 2006 *Int. Quantum Chem.* **106** 1815
[40] Duan Z X, Qi Y and Yang C L 2008 *Mol. Phys.* **106** 2725
[41] Fan K M, Liu Y, Liu S H, Ren W Y and Wang A S 2007 *Chin. Phys.* **16** 1641
[42] Orr-Ewing A J, Simpson W R, Rakitzis T P, Kandel S A and Zare R N 1997 *J. Chem. Phys.* **106** 5961
[43] Chu T S and Han K L 2008 *Phys. Chem. Chem. Phys.* **10** 243