Effect of isotope substitution on the stereodynamics for O+H(D)Br→OH(D)+Br reactions

Hong Li, Bin Zheng, Ji-Qing Yin, and Qing-Tian Meng[*]

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

Abstract. The influence of the isotope substitution on the dynamics of the title reactions is investigated using the quasi-classical trajectory method based on the potential energy surface for the X^1A' ground singlet state of HOBr system. Apparent differences on the stereo-dynamic properties are discovered between the title reactions. These discrepancies are mainly due to the unequal reduced masses of the reactants and different zero-point energies of the transition state, which affect the vector properties of the title reactions.

1 Introduction

Over the past decade, some significant achievements have been made on the side of theoretical and computational chemistry. One of the progresses is that the quasi-classical trajectory (QCT) method has been widely carried out to analyze the dynamics of chemical reactions, especially for the reaction systems with large mass [1, 2]. Meanwhile, Han *et al.* [3] developed the stereo-dynamics QCT method to cope with the product rotational polarization. So far, many chemical reactions [4–12] have been studied for their product rotational polarization. Moreover, this kind reaction of O + HX → OH + X (X = F, Cl, Br, I) not only is the elementary reaction with Heavy-Light-Heavy (HLH) mass system that makes the product rotation strongly aligned about the direction of the relative velocity, but also contains the important atom shift process about H [13].

Recently, for the reaction O + HBr → OH + Br, many studies for the presented interesting dynamical features have been done, theoretically and experimentally. On the experimental side, Ruscic and Berkowitz have successfully ciphered the heat of formation of HOBr and the dissociation energy of HO–Br [14]. From the theoretical point of view, Tang *et al.* [15] have

---

[*]Corresponding author. *Email address:* qtmeng@sdnu.edu.cn (Q. T. Meng)

successfully employed the three-dimensional time-dependent quantum wave packet method to study the scalar properties of the reaction such as initial state-selected reaction probabilities, reactive cross sections and thermal rate constant. Additionally, the potential energy surface (PES) for the X^1A' singlet state of HOBr system was recently constructed by Peterson [16].

In our previous work, we have studied the vector properties of reaction O + HBr → OH + Br. It is well known that the isotope effect plays key roles in the deduction of the chemical reaction mechanics and the research of intermolecular interaction. To the best of our knowledge, few studies are reported yet for the isotope substitution of the title reactions. Such an inquiry is the subject of this paper. In order to realize the isotope effect on the reaction, we utilize the QCT calculations to investigate O + HBr reaction and its isotope variant on the same singlet PES.

This paper is organized as follows. In Section 2, the QCT calculation is briefly outlined. The results which will be an important consideration are presented and discussed in Section 3. In Section 4, the discussion and its implications are presented.

2   Computational method

The X^1A' ground singlet PES applied to this paper was determined by Peterson employing the method of highly correlated MRCI and explicit basis set [17]. The detailed information such as *ab initio* data and analytical function form of the PES can be referred to in Ref. [18].

The computational method of QCT in this study is the same as the one adopted in Ref. [19, 20]. In the calculations, the classical Hamilton's equations are integrated in three dimensions. According to the product rotational polarization, we mainly concentrate on discussing the isotope effect on the reaction. We set the initial rotational quantum j=0 and initial vibrational quantum v=0. The collision energy of the title reactions is chosen as 0.3 eV. Each reaction runs 10000 trajectories and the integration step size is set as 0.1 fs to guarantee the conservation of the total angular momentum and total energy.

The product polarization calculations we carry out is well-rounded by Han and coworkers [21]. Here we just introduce the details connected with our existing work. In the center-of-mass(CM) frame shown in Fig. 1, the relative velocity vector $\mathbf{k}'$ of the reactant is parallel to the z-axis and the x-z plane which is the scattering plane contains the initial and final relative velocity vectors, $\mathbf{k}$ and $\mathbf{k}'$. The scattering angle θ_t is the angle between the reactant relative velocity and product relative velocity. θ_r and ϕ_r represent, respectively, the polar and azimuzal angle of the product rotational angular momentum $\mathbf{j}'$.

The vector correlation of $\mathbf{k}-\mathbf{j}'$ is the most common. The polar angle distribution function rewriting the correlation of $\mathbf{k}-\mathbf{j}'$ can be expanded in a series of Legendre polynomials and the expanding coefficients are called alignment (k is event) and orientation (k is odd) parameter. The dihedral angle distribution function $P(\phi_r)$ describing $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation can be unfolded in Fourier series. The $P(\theta_r, \phi_r)$ as the function of angles θ_r and ϕ_r of $\mathbf{j}'$ is used to depict the space distribution of the product rotational momentum.
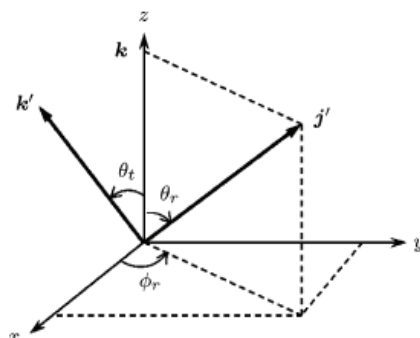
Figure 1: The CM coordinate systerm used to describe the **k**, **k**′ and **j**′ distribution.

The generalized polarization-dependent differential cross sections (PDDCSs) are used to describe the vector correlation of **k**−**k**′−**j**′ and scattering distribution of the product molecule. The fully correlated CM angular distribution function can be written as the sum [22]

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

where $[k] = 2k+1$, $(1/\sigma)(d\sigma_{kq}/d\omega_t)$ is the so-called generalized polarization- dependent differential cross section, and $C_{kq}(\theta_t,\theta_r) = \sqrt{4\pi/(2k+1)}Y_{kq}(\theta_t,\theta_r)$ is the modified spherical harmonic function. In our present work, we utilize the computational method to calculate $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ and $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$.

3   Results and discussion

In order to get a further understanding about the isotopic substitution, we calculate the product angular distribution $P(\theta_r)$ and $P(\phi_r)$ of the title reactions when the collision energy is 0.3 eV. According to the formula $\mathbf{k}\cdot\mathbf{j}' = \cos\theta_r$, we can discover that the correlation of $\mathbf{k}-\mathbf{j}'$ can be described well by the $P(\theta_r)$ distribution. Besides, it can also offer some important information about the product rotational alignment. Thus we plot the $P(\theta_r)$ distribution of the products O(D)H in Fig. 2. It is clear from Fig. 2 that $P(\theta_r)$ distribution is not only symmetric with respect to 90°, but also has a peak near $\theta_r = 90°$, which indicates that the product's rotation angular momentum vector prefers to be perpendicular to the reagent relative velocity. An observation can be made from Fig. 2 that the peak value of $P(\theta_r)$ for the reaction O+HBr is larger than that of the reaction O+DBr, which illustrates that the alignment level of HBr is stronger than that of DBr. On the basis of Refs. [23, 25], two factors are able to affect the $P(\theta_r)$ distribution. One is the character of PES, the other is the mass factor (i.e.,

$\cos^2\beta = m_A m_C / (m_A + m_B)(m_B + m_C)$ for the reaction A+BC→AB+C). However, for the two reactions based on the same PES, the discrepancy of the $P(\theta_r)$ distribution is chiefly attributed to the difference of the mass factor between the reaction O+HBr→OH+Br ($\cos^2\beta = 0.929$) and O+DBr→OD+Br ($\cos^2\beta = 0.866$).
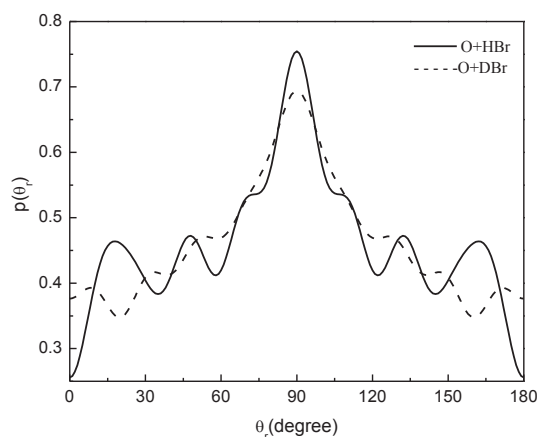

Figure 2: The distribution of $P(\theta_r)$, reflects the $\mathbf{k}-\mathbf{j'}$ coorelation. Solid line represents O+HBr→OH+Br; dotted line represents O+DBR→OD+Br.

The dihedral angle distributions $P(\phi_r)$ exhibiting the $\mathbf{k}-\mathbf{k'}-\mathbf{j'}$ correlation are shown in Fig. 3. As seen, the $P(\phi_r)$ is asymmetric with respect to the $\mathbf{k}-\mathbf{k'}$ scattering plane, evidently reflecting the polarization of product rotational angular momentum. The figure shows that the $P(\phi_r)$ distribution has two peaks which are at $\phi_r = 90°$ and 270°, respectively. It implies that the rotational angular momentum vector of HBr is preferentially aligned along the y-axis in the CM frame. And the peak at $\phi_r = 90°$ is stronger than that at $\phi_r = 270°$, which indicates that the rotational angular momentum vector of the product is not only aligned but also oriented along positive y-axis for the title reactions. However, due to the different harmonic zero point energy (ZPE) of the reactant molecules HBr(DBr) which causes the different effective potential well depth of the two reactions, the orientation level of the products OH and DBr is not same with each other. It is obvious that the orientation level of the product OH is stronger than that of OD. Since the reduced mass μ of HBr (DBr) is 0.995 (1.964), in the light of the fundamental vibrational frequency ($\nu = (1/\pi)\sqrt{k/\mu}$), the vibrational frequency of HBr is higher than that of DBr. Therefore, on the basis of the formula of ZPE ($E_0 = (h\nu)/2$), the ZPE of HBr is larger than that of DBr. Consequently, the effective potential well depth of the O+HBr reaction is shallower than that of the O+DBr reaction, which brings about the product OH orienting more strongly than OD.

It is instructive to compare the results of the above analysis. We can outcrop that the $P(\theta_r)$ distribution of the title reactions is symmetric with respect to the relative velocity vector, while the distribution of $P(\phi_r)$ is asymmetric. In line with the heretofore theoretical investigation about the impulsive model of the atom and molecular reaction for the reaction of type A
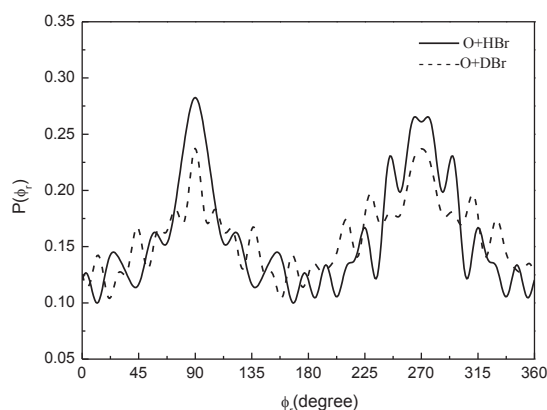
Figure 3: The dihedral angle distribution of $P(\phi_r)$ with respect to the $\mathbf{k}-\mathbf{k}'$ line. Solid line represents O+HBr→OH+Br; dotted line represents O+DBr→OD+Br.

+ BC→ AB+C [19, 23, 24], we obtain $\mathbf{j}'=\mathbf{L}\sin^2\beta+\mathbf{j}\cos^2\beta+\mathbf{J}_1 m_B/m_{OB}$, where $\mathbf{L}$ represents the reactant orbital angular momentum, $\mathbf{J}_1=\sqrt{\mu_{BC}E_R}(r_{AB}\times r_{BC})$, with r_{AB} and r_{BC} standing for unit vectors and B pointing to A and C, respectively, μ_{BC} represents the reduced mass of BC molecule and E_R is the repulsive energy between B and C atoms. During the period of the chemical bond forming and breaking for the two reactions, the term $\mathbf{L}\sin^2\beta+\mathbf{j}\cos^2\beta$ in the equation is symmetric, however, the term $\mathbf{J}_1 m_B/m_{OB}$ presents a preferring direction as a result of the effect of the repulsive energy, which results in the orientation of the product molecules OH or OD.

For the purpose of depicting the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation and the scattering direction of
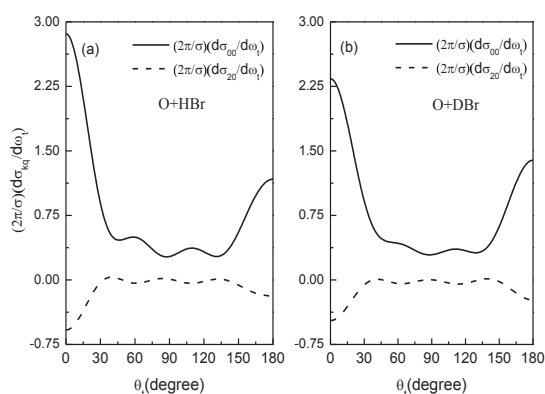

Figure 4: The polarization of dependent generalized differential cross section of the reaction. (a) and (b) correspond to the reaction of O+HBr→OH+Br and O+DBr→OD+Br, respectively. Solid line indicates the PDDCS of $(2\pi/\sigma)(d\sigma_{20})(d\sigma_{00}/d\omega_t)$ and dashed line denotes the PDDCS of $(2\pi/\sigma)(d\sigma_{20})(d\sigma_{20}/d\omega_t)$.

the product molecules O(D)H better, we count the first two PDDCS on the X^1A' PES presented in Fig. 4(a)–(b) corresponding to the two reactions, respectively. The PDDCS of $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$ commonly reflects the $\mathbf{k}-\mathbf{k}'$ correlation or the angular distribution of the product. It is seized from Fig. 4 that the product molecules O(D)H are scattered forward, however, the degree of forward scattering of OH molecule is stronger than that of OD molecule. The PDDCS of $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ is called the average value of the second Legendre moment $\langle P_2(\cos\theta_r)\rangle$. It is conspicuous from the figure that the trend of the $(2\pi/\sigma)(d\sigma_{20}/d\sigma_{20}/d\omega_t)$ is opposite to the trend of the $(2\pi/\sigma)(d\sigma_{20})(d\sigma_{00}/d\omega_t)$, indicating that the product angular momentum $\mathbf{j}'$ is perpendicular to $\mathbf{k}$.

Moreover, it also can be found from Figs. 5 and 6 that the PDDCSs with $q\neq0$ are zero when the scattering angle θ_t is equal to 0° and 180°, respectively. Because the $\mathbf{k}-\mathbf{k}'$ scattering plane is uncertain at these limiting scattering angles, the values of these PDDCSs must be zero. From Fig. 5, it is easy to see that the values of $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ are negative for all scattering angle θ_t, implying that the product alignment is along the y-axis. It is necessary to notice that the products OH and OD display a stronger polarization at about 30° and 150°, respectively, but the polarization degree of the product OH is stronger than that of the product OD. In addition, it can be discovered from Fig. 6 that the trend of PDDCS $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ is similar for the two reactions. The values of the $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ are negative when the scattering angle θ_t is less than 45° and more than 140°, which suggests that the product is aligned along the direction of $\vec{x}+\vec{z}$. The values of the $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ are positive when the scattering angle θ_t belongs to (45°,140°), implying that the product alignment is along the direction of $\vec{x}-\vec{z}$. However, the degree of the product OH polarization is much stronger.
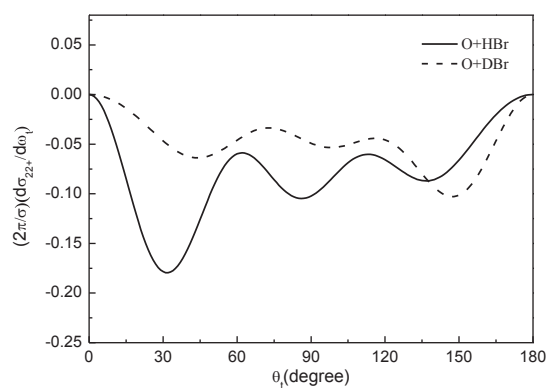

Figure 5: The polarization dependent generalized differential cross-section $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ of the title reactions.
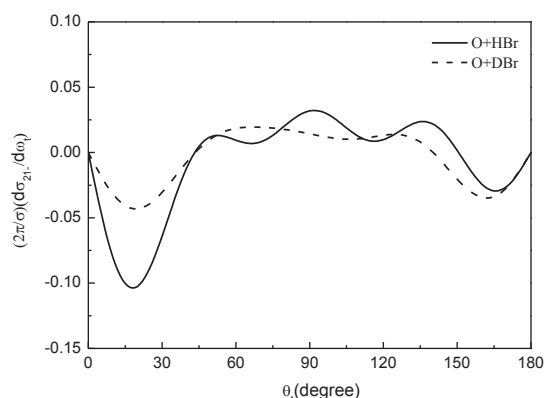
Figure 6: The polarization dependent generalized differential cross-section $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ of the title reactions.

4 Conclusions

In this paper we have carried out a QCT calculation to investigate the product polarization for the title reactions at the same collision energy of 0.3 eV. The distributions of $P(\theta_r)$, $P(\phi_r)$ and four PDDCSs are computed. The results suggest that the products O(D)H chiefly tend to be forward scattering but the degree of forward scattering and product polarization is obviously different. These differences are mainly caused by two aspects, i.e. the unequal mass factor of the reactants and different ZPE, which influence the vector correlations of the title reactions, such as four PDDCSs, the product molecules rotational angular momentum alignment and orientation, etc.

References

 [1] K. L. Han, X. G. Zheng, B. F. Sun, *et al.*, Chem. Phys. Lett. 181 (1991) 474.
 [2] M. L. Wang, K. L. Han, J. P. Zhan, *et al.*, Chem. Phys. Lett. 278 (1997) 307.
 [3] K. L. Han, G. Z. He, and N. Q. Lou, J. Chem. Phys. 96 (1992) 7865.
 [4] W. L. Li, M. S. Wang, C. L. Yang, *et al.*, Chem. Phys. Lett. 125 (2007) 445.
 [5] W. L. Li, M. S. Wang, Y. M. Dong, *et al.*, Chem. Phys. 97 (2008) 348.
 [6] W. W. Xu, X. G. Liu, and Q. G. Zhang, Mol. Phys. 106 (2008) 1787.
 [7] Y. Xu, J. Zhao, D. G. Yue, *et al.*, Chinese Phys. B 18 (2009) 1674
 [8] J. Zhao, Y. Xu, and Q. T. Meng, Chinese Phys. B 19 (2010) 0634.
 [9] J. Zhao, Y. Xu, and Q. T. Meng, Can. J. Phys. 87 (2009) 1247.
[10] J. Zhao, Y. Xu, and Q. T. Meng, Sci. China Chem. 53 (2010) 927.

[11] J. Zhao, Y. Xu, D. G. Yue, *et al.*, Chem. Phys. Lett. 471 (2009) 160.
[12] Y. Xu, J. Zhao, J. Wang, *et al.*, Acta Phys. Sin. 59 (2010) 144 (in Chinese).
[13] D. Brandt and J. C. Polanyi, Chem. Phys. 35 (1978) 23.
[14] B. Ruscic and J. J. Berkowitz, Chem. Phys. 101 (1994) 7795.
[15] B. Y. Tang, Q. K. Tang, M. D. Chen, *et al.*, J. Chem. Phys. 120 (2004) 8537.
[16] K. A. Peterson, J. Chem. Phys. 113 (2000) 4598.
[17] S. Skokov, K. A. Peterson, and J. M. Bowman, J. Chem. Phys. 109 (1998) 2662.
[18] K. A. Peterson, S. Skokov, and J. M. Bowman, J. Chem. Phys. 111 (1999) 7446.
[19] M. D. Chen, K. L. Han, and N. Q. Lou, Chem. Phys. Lett. 357 (2002) 483.
[20] Y. F. Liu, Z. Z. Liu, G. S. Lv, *et al.*, Int. J. At. Mol. Phys. 23 (2006) 1145.
[21] K. L. Han, G. Z. He, and N. Q. Lou, J. Chem. Phys. 105 (1996) 8699.
[22] F. J. Aoiz, M. Brouard, and P. A. Enriquez, J. Chem. Phys. 105 (1996) 4964.
[23] R. J. Li, K. L. Han, F. E. Li, *et al.*, Chem. Phys. Lett. 220 (1994) 286.
[24] K. L. Han, G. Z. He, and N. Q. Lou, Chinese J. Chem. Phys. 2 (1989) 323.
[25] M. L. Wang, K. L. Han, and G. Z. He, J. Chem. Phys. 109 (1998) 5446.