

ARTICLE

Influence of Vibrational Excitation on Stereodynamics for $O(^3P)+D_2 \rightarrow OD+D$ Reaction

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Theoretical investigations on the stereodynamics of the $O(^3P)+D_2$ reaction have been calculated by means of the quasi-classical trajectory to study the product rotational polarization at collision energy of 104.5 kJ/mol on the potential energy surface of the ground $3A''$ triplet state. The vector properties including angular momentum alignment distributions and four polarization dependent generalized differential cross-sections of product have been presented. Furthermore, the influence of reagent vibrational excitation on the product vector properties has also been studied. The results indicate that the vector properties are sensitively affected by reagent vibrational excitation.

Key words: Vector correlation, Quasi-classical trajectory, Polarization dependent generalized differential cross-section, Stereodynamics

I. INTRODUCTION

The abstraction reaction between $O(^3P)$ atom and H_2 radical is a major contributor to the production of OH in interstellar environments. This reaction is also important prototypical of atom-molecule reactions [1–3] because it is one of the simplest hydrogen abstractions and it is enough for quantitative theoretical treatments. Therefore, the reaction $O(^3P)+H_2$ has been the topics of a large number of the experimental [4–9] and theoretical investigations [10–19]. The influence of reagent vibrational energy on the rate of the $O(^3P)+H_2$ reaction received much attention because of its importance in modeling radiation in certain rocket plumes [20, 21]. Compared with the very rich information about the dynamics of reaction $O(^3P)+H_2$, which has been provided in detail, the fundamental dynamics of the isotope effect of $O(^3P)+D_2$ reaction is not extremely clear. As we know, the isotope effects have attracted enormous attention because they play significant roles in the deduction of chemical reaction mechanics and the research of intermolecular interaction. And the isotope effects can also provide different dynamic view on the same potential surface. Presser *et al.* reported the rate constant of $O(^3P)+D_2$ by the flash photolysis-resonance fluorescence method [22]. High temperature studies of the rate coefficient of title reaction have been reported by kinetic laser absorption spectroscopy in shock waves [23]. More recently, using crossed-molecular apparatus, Garton *et al.* measured the product angular of the title

reaction and they also performed quasi-classical trajectory (QCT) and trajectory-surface-hopping (TSH) calculation, the results of calculation are in good agreement with their experimental results [24]. In theoretical side, the coupled states distorted wave methods are used to study the quantum reactive collision dynamics of title reaction, reaction probabilities as a function of energy and integral cross sections calculated agreed with experiment results [21]. Based on the accurate potential energy surface constructed by Rogers *et al.* [25], Sultanov *et al.* calculated the cross sections and rate coefficient for OD product by accurate quantum methods as well as J -shifting approximation and the results are coincident with others [12]. Vibrational-rotational energy distributions of the ion-molecule of the title reaction were studied using the crossed molecular beam technique at collision energies of 1.55 and 1.95 eV by Li *et al.* [26].

With the rapid development of reaction dynamics, research of stereodynamics of chemical reaction has received enough attention. As we know, in order to understand the dynamics of an element reaction fully, it's important to explore not only its scalar properties, but also the vector properties. The vector properties, such as velocities and angular momentum, possess not only magnitudes that related to rotational energies, but also the directions. Therefore, it is necessary that the polarization of product angular momentum should be calculated for the title reaction.

In this work, we explored the calculations product rotational polarization and the influence of initial vibrational states of the deuterium molecule on the product's vector correlations for the title reaction on generalized London-Eyring-Polanyi-Sato double-polynomial (GLDP) potential surface. We expect that the anal-

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ysis of the vector properties can reveal more dynamics information that is lost when the directional properties are not explicitly considered.

II. THEORY

A. Potential energy surface and QCT calculations

The product rotational polarization for the title reaction has been calculated on the GLDP surface by means of QCT method. The GLDP PES of the title reaction in the $3A''$ state is best fit to the *ab initio* data calculated by Rogers at collinear abstraction geometry [25]. The classical Hamilton's equations were integrated numerically for motion in three dimensions [27–29]. In our calculations, the trajectories are initiated at an O–D₂ internucleus separation of 10 Å, rotational and vibrational levels of the reactants molecule are taken as $v=0-2$ and $j=0$, respectively, batches of 5×10^4 trajectories are run for each vibrational momentum at the collision energy 104.5 kJ/mol and the integration step size is chosen as 0.1 fs. The accuracy of the numerical integration is verified by checking the conservation of the total energy and total angular momentum for each trajectory.

B. Rotational alignment parameter

We studied the angular momentum \mathbf{j}' of the product molecule through the center-of-mass (CM) frame (Fig.1) orientation or alignment parameters. In this chosen coordinate, the z -axis is parallel to the reagent relative velocity \mathbf{k} , and the y -axis is perpendicular to the xz plane containing \mathbf{k} and \mathbf{k}' . The distribution of \mathbf{j}' of the product molecule is described by a function $f(\theta_r)$, where θ_r is the angle between \mathbf{j}' and \mathbf{k} [30, 31]. The form of $f(\theta_r)$ expanded in a set of Legendre polynomials.

$$f(\theta_r) = \sum_l a_l P_l \cos \theta_r \quad (1)$$

Thus, $l=2$ indicates the product rotational alignment

$$\langle P_2(\mathbf{j}' \cdot z) \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (2)$$

where p_2 is a second Legendre moment, and the brackets indicate an average over the distribution of \mathbf{j}' about \mathbf{k} .

The full angular distribution of the triple vector correlations \mathbf{k} , \mathbf{k}' , \mathbf{j}' of the product molecule can be represented by a set of polarization dependent generalized differential cross-sections (PDDCSs) in the center of mass coordinate. To fully describe the vector correlation of the reaction of atom-diatomic molecule, the correlated center-of-mass function was written as the sum [32, 33].

$$P(\omega_t, \omega_r) = \sum_{kq} \frac{[k]}{4\pi} \frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega_t} C_{kq}(\theta_r, \phi_r)^* \quad (3)$$

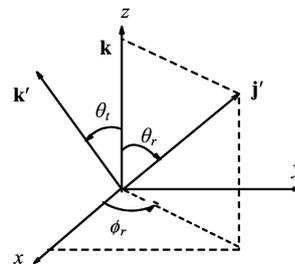


FIG. 1 The center-of-mass coordinate system used to describe the distributions of \mathbf{k} , \mathbf{k}' , and \mathbf{j}' .

where the angles $\omega_t = \theta_t$, ϕ_t and $\omega_r = \theta_r$, ϕ_r refer to the coordinates of the unit vectors \mathbf{k}' , \mathbf{j}' along the directions of the product relative velocity and rotational angular momentum vectors in the CM frame, respectively, while $C_{kq}(\theta_r, \phi_r)$ are modified spherical harmonics. σ is the integral cross section and $[k] = 2k+1$, $\frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega_t}$ is a generalized PDDCS. The functions of PDDCSs are written as follows:

$$\frac{1}{\sigma} \frac{d\sigma_{k0}}{d\omega_t} = 0 \quad (k \text{ is odd}) \quad (4)$$

$$\frac{1}{\sigma} \frac{d\sigma_{kq+}}{d\omega_t} = \frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega_t} + \frac{1}{\sigma} \frac{d\sigma_{k-q}}{d\omega_t} = 0 \quad (5)$$

$(k \text{ even, } q \text{ odd, or } k \text{ odd, } q \text{ even})$

$$\frac{1}{\sigma} \frac{d\sigma_{kq-}}{d\omega_t} = \frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega_t} - \frac{1}{\sigma} \frac{d\sigma_{k-q}}{d\omega_t} = 0 \quad (6)$$

$(k \text{ even, } q \text{ even, or } k \text{ odd, } q \text{ odd})$

The usual distribution function $p(\theta_r)$ describing the two vector \mathbf{k} - \mathbf{j}' correlation is expanded in a series of Legendre polynomials [32, 34, 35].

$$P(\theta_r) = \frac{1}{2} \sum_k [k] a_0^k P_k \cos \theta_r \quad (7)$$

The dihedral angle distribution of the \mathbf{k} - \mathbf{k}' - \mathbf{j}' three vector correlation is characterized ϕ_r . The distribution of the dihedral angle ϕ_r can be expanded as a Fourier series [34–36].

$$P(\phi_r) = \frac{1}{2\pi} \left(1 + \sum_{n_{\text{even}} \geq 2} a_n \cos n\phi_r + \sum_{n_{\text{odd}} \geq 1} b_n \sin n\phi_r \right) \quad (8)$$

$$a_n = 2 \langle \cos n\phi_r \rangle \quad (9)$$

$$b_n = 2 \langle \sin n\phi_r \rangle \quad (10)$$

The joint probability density function of angles θ_r and ϕ_r , which define the direction of \mathbf{j}' can be written

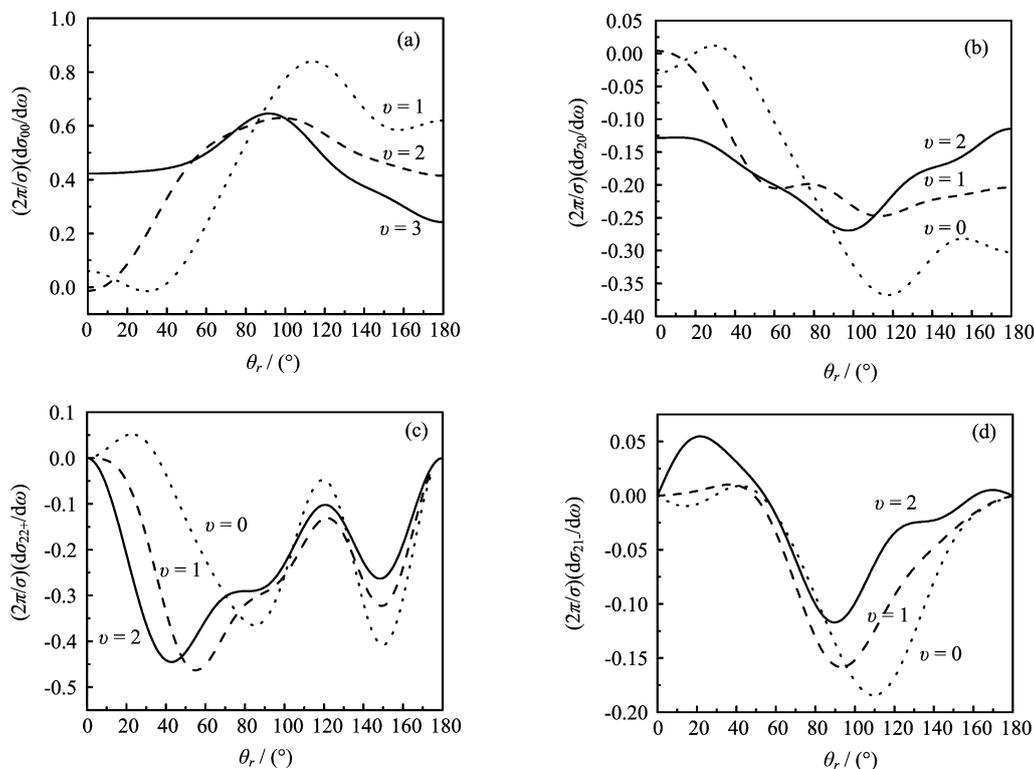


FIG. 2 The four PDDCSs at three reagent vibrational excitations. (a) The PDDCSs with $(k, q)=(0, 0)$. (b)–(d) The PDDCSs with $(k, q)=(2, 0)$, $(2, 2+)$, and $(2, 1-)$, respectively.

as [37]

$$\begin{aligned}
 P(\theta_r, \phi_r) &= \frac{1}{4\pi} \sum_{kq} [k] a_q^k c_{kq}(\theta_r, \phi_r)^* \\
 &= \frac{1}{4\pi} \sum_k \sum_{q \geq 0} (a_{q\pm}^k \cos q\phi_r - \\
 &\quad a_{q\mp}^k i \sin q\phi_r) c_{kq}(\theta_r, 0) \quad (11)
 \end{aligned}$$

In the calculation, the polarization parameter

$$a_{q\pm}^k = 2 \langle C_{k|q|}(\theta_r) \cos q\phi_r \rangle \quad (k \text{ even}) \quad (12)$$

$$a_{q\mp}^k = 2i \langle C_{k|q|}(\theta_r) \sin q\phi_r \rangle \quad (k \text{ odd}) \quad (13)$$

For good convergence, the distribution of $P(\theta_r)$, $P(\phi_r)$, and $P(\theta_r, \phi_r)$ are expanded up to $k=18$, $n=24$, $k=7$ in the current work, respectively.

III. RESULTS AND DISCUSSION

The QCT PDDCSs describe the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation and the scattering direction of the OD product molecule for the reaction $O+D_2(v=0-2, j=0) \rightarrow OD+D$ are shown in Fig.2. The distribution of the PDDCSs have been influenced by the value of vibrational momentum, and the effects are different. The PDDCS

$(2\pi/\sigma)(d\sigma_{00}/d\sigma_{\omega_t})$, only describes the $\mathbf{k}-\mathbf{k}'$ correlation or the scattering direction of the product and is not associated with the orientation and alignment of the product rotational angular momentum vector \mathbf{j}' . From Fig.2(a), we found that the scattering direction of the product OD is scattered strongly backward at the level of $v=0$, with increased the number of vibrational quantum, the forward scattering of product becomes stronger and the backward scattering becomes weaker. A trend of $(2\pi/\sigma)(d\sigma_{20}/d\sigma_{\omega_t})$ drawn in Fig.2(b) is opposite to that of $(2\pi/\sigma)(d\sigma_{00}/d\sigma_{\omega_t})$. It is easy to see that the different reagent vibrational excitation has sensitively affected the product angular distributions. The PDDCS $(2\pi/\sigma)(d\sigma_{20}/d\sigma_{\omega_t})$ is the expectation value of the second Legendre moment $\langle P_2(\mathbf{j}' \cdot \mathbf{z}) \rangle$, indicating that \mathbf{j}' is aligned perpendicularly to \mathbf{k} at $\theta_r=0^\circ$ and $\theta_r=180^\circ$ for each case. As can be seen from Fig.2 (c) and (d), the angular distribution PDDCSs with $q \neq 0$ are necessarily zero at the extremities of forward and backward scattering. The PDDCSs $(2\pi/\sigma)(d\sigma_{22+}/d\sigma_{\omega_t})$ at the scattering angles away from extremities forward and backward directions provide information on the ϕ_r dihedral angle distribution and are nonzero at scattering angles away from limiting scattering angles, which indicates that the $(2\pi/\sigma)(d\sigma_{22+}/d\sigma_{\omega_t})$ is not isotropic for sideways and backwards scattering products. From Fig.2(c), we can also see that the values of $(2\pi/\sigma)(d\sigma_{22+}/d\sigma_{\omega_t})$ are negative in the whole scope, which suggests the

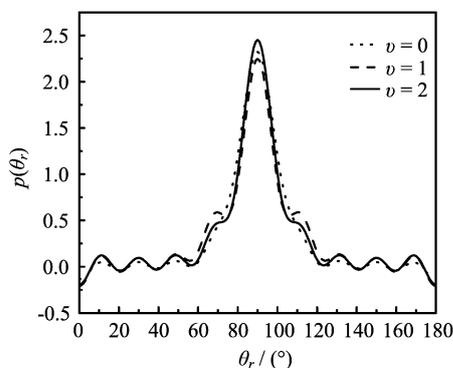


FIG. 3 The $P(\theta_r)$ distributions reflecting $\mathbf{k}\text{-}\mathbf{j}'$ correlation at the collision energy of 104.5 kJ/mol for the three reagent vibrational excitations.

marked preference of product alignment along the y -axis. There are two stronger polarization of the product of the three vibrational momentum, one more or less at about 150° , another at about 85° , 55° , 42° with the increase of reagent vibrational excitation. In Fig.2(d), we can find that the product shows a stronger polarization at about 110° , 92° , and 90° for $v=0-2$, respectively. The $(2\pi/\sigma)(d\sigma_{21-}/d\sigma_{\omega_i})$ performs different characters in the three cases, reflecting that it is considerable influence on the reagent vibrational excitation.

Although the PDDCSs are influenced by the vibration levels of D_2 , the peak of $P(\theta_r)$ and $P(\phi_r)$ on the $3A''$ PES are not sensitive to the vibrational quantum number as shown in Fig.3 and Fig.4. For three vibrational states, it is clearly that the peaks of $P(\theta_r)$ distribution at $\theta_r=90^\circ$ and symmetric with respect to 90° , which shows that the product rotational angular momentum vector is distributed with cylindrical symmetry in the product scattering plane and strongly aligned along the direction at right angle to the relative velocity direction. It is presented that there is a tiny discrepancy among the distribution of $P(\theta_r)$ of three reactions. The peak of $P(\theta_r)$ distribution of the reaction $O(^3P)+D_2(v=2, j=0)$ is broader and higher than the others, indicating the product rotational alignment effect becomes stronger when the reagent is in the excited vibration states.

The distributions of $P(\phi_r)$ are shown in Fig.4. Those $P(\phi_r)$ tend to be antisymmetric with respect to the $\mathbf{k}\text{-}\mathbf{k}'$ scattering plane, directly reflecting the strong polarization of angular momentum for the reaction $O(^3P)+D_2(v=0-2, j=0)\rightarrow OD+D$. Peaks of angular momentum vectors of products of three vibrational states appear at $\phi_r=270^\circ$ but almost disappear at $\phi_r=90^\circ$, which shows that the rotational angular momentum vector of the product OD is mainly aligned along y -axis of the CM frame. Because the peaks at $\phi_r=270^\circ$ is apparently higher than any other degrees, which implied that the rotational angular momentum vectors is not only aligned, but also preferen-

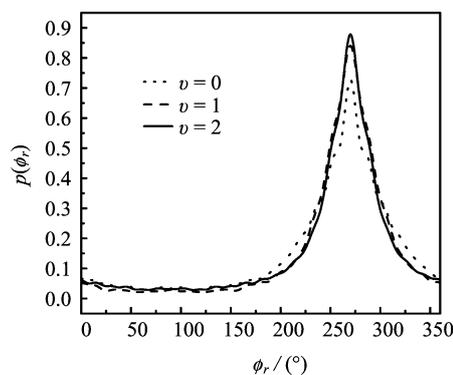


FIG. 4 The $P(\phi_r)$ distribution describing the dihedral angle distribution of \mathbf{j}' with respect to the $\mathbf{k}\text{-}\mathbf{k}'$ plane at three reagent vibrational excitations.

tially oriented along the negative y -axis [38]. The orientation of the products for the reactions is evidently different. With the enhancement of the reagent vibrational excitation, the product rotational polarization becomes stronger, and with respect to the reaction $O(^3P)+D_2(v=0-2)$, the peak at $\phi_r=270^\circ$ is apparently stronger as the vibrational state of D_2 molecule increases. It can also be seen that the degree of orientation is greatly conspicuous. The results seem interesting that the title reactions are symmetric about the relative velocity vector, while the distribution of $P(\phi_r)$ is antisymmetric. The reason is probably that the repulse energy between D–D atoms led to the violation of the symmetry when the reaction occurs. It is said that the impulse model about the molecular reaction for the reaction $A+BC\rightarrow AB+C$ [39], the distribution of \mathbf{j}' , there is

$$j' = L \sin^2 \beta + j \cos^2 \beta + \frac{J_1 m_A}{m_B} \quad (14)$$

$$J_1 = (u_{BC} R)^{1/2} r_{AB} r_{CB} \quad (15)$$

where L is the reagent orbital angular momentum, u_{BC} is the reduced mass of the BC molecular, and R is the repulsive energy. In the reaction of $O(^3P)+H_2\rightarrow OH+H$, the term of $L \sin^2 \beta + j \cos^2 \beta$ is symmetric, while the term $J_1 m_A/m_B$ shows a preferring direction for the effect of repulsive energy, which leads to the orientation of the product OD.

The product angular distributions which reflect the vector correlation contain rich information about the angular momentum polarization. In order to validate more information about the product molecule axis polarization, the $P(\theta_r, \phi_r)$ distribution averaged over all scattering angles were plotted in Fig.5. The distributions of $P(\theta_r, \phi_r)$ with a peak at $(90^\circ, 270^\circ)$ are in good accordance with the distributions of $P(\theta_r)$ and $P(\phi_r)$ of the products for three vibrational states, although the shapes exist some differences. The distributions of $P(\theta_r, \phi_r)$ present that the products are preferentially

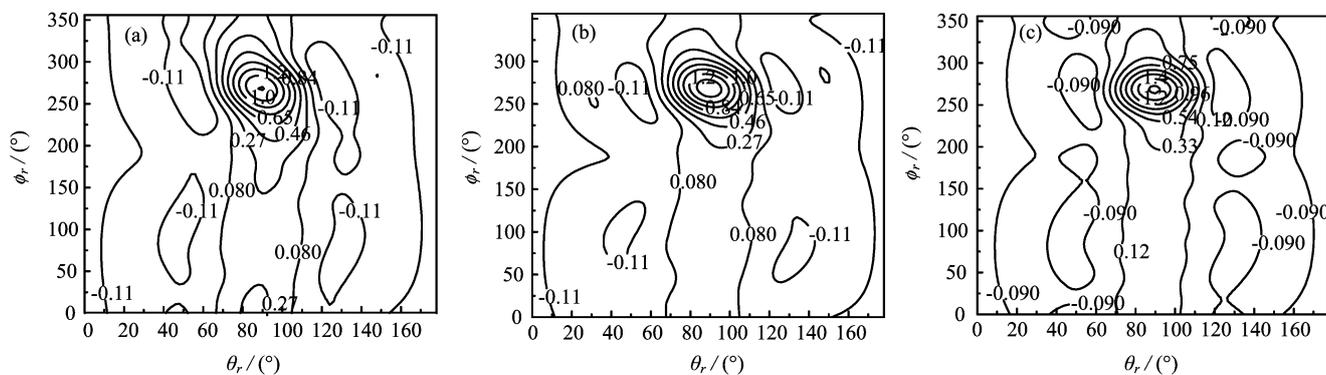


FIG. 5 Polar plots of $P(\theta_r, \phi_r)$ distribution for at three values of v (a) $v=0$, (b) $v=1$, and (c) $v=2$.

polarized perpendicular to the scattering plane and the products of reactions are mainly rotating in planes parallel to the scattering plane [40].

IV. CONCLUSION

The product rotational polarization of title reaction has been calculated by means of the QCT method on the collision energy 104.5 kJ/mol to study the influence of reagent vibrational excitation on the product vector properties. The PDDCSs of the title reaction are computed in CM. The PDDCS $(2\pi/\sigma)(d\sigma_{00}/d\sigma_{\omega_i})$ demonstrates that the OD product mainly tends to the backward scattering, with increasing vibrational quantum numbers, the forward scattering of product becomes stronger, the other PDDCSs present that the product rotational polarization are very sensitive to various initial vibrational states of D_2 . In addition, the distribution of $P(\theta_r)$ and $P(\phi_r)$ of the products for the title reactions $O(^3P)+D_2(v=0-2, j=0)$ were plotted in this work. The $P(\theta_r)$ suggests that \mathbf{j}' are strongly aligned along perpendicular to \mathbf{k} . And the distribution of $P(\phi_r)$ show that the product rotational angular momentum vector \mathbf{j}' is oriented along the negative direction of y -axis of the CM frame and imply a preference for left-handed product rotation. It is well explained by impulse model. The product rotational alignment effect tends to become stronger as reagent vibrational momentum increasing.

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