Differential Cross Sections for the H+D_2O → HD+OD Reaction: a Full Dimensional State-to-State Quantum Dynamics Study

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The time-dependent wave-packet method was employed to calculate the first full-dimensional state-to-state differential cross sections (DCS) for the title reaction with D_2O in the ground and the first symmetric (100) and asymmetric stretching (001) excited states. The calculated DCSs for these three initial states are strongly backward peaked at low collision energies. With the increase of collision energy, these DCSs become increasingly broader with the peak position shifting gradually to a smaller angle, consistent with the fact that the title reaction is a direct reaction via an abstraction mechanism. It is found that the (100) and (001) states not only have roughly the same integral cross sections, but also have essentially identical DCS, which are very close to that for the ground state at the same total energy of reaction. The reaction produces a small fraction of OD in the v=1 state, with the population close to the relative reactivity between the ground and vibrationally excited states, therefore confirming the experimental result of Zare et al. and the local mode picture [J. Phys. Chem. 97, 2204 (1993)]. Unexpectedly, the stretching excitation reduces the rotation excitation of product HD at the same total energy.

Key words: State-to-state, Differential cross section, Time-dependent wave-packet method

I. INTRODUCTION

H+H_2O and its isotopically substituted reactions are the prototype for tetra-atomic reactions, in much the same way that the H+H_2 reaction served as the prototype for triatomics. Theoretically, because three of the four atoms are hydrogens, the system is an ideal candidate for high quality ab initio calculation of a potential energy surface (PES), as well as for accurate quantum reactive scattering calculations. Schatz and Elgersma fitted the first analytic PES, known as the WDSE PES [1]. After that, a number of new PES have been constructed with increasing level of accuracy for the reaction system [2–5]. Extensive quantum reactive scattering calculations have been performed on these PES to study dynamics of this benchmark four-atom system.

The H+H_2O→H_2+OH is also considered as the simplest system in which different vibrational modes in the reactant can play an important role in the reaction dynamics. In the past decades, substantial efforts have been devoted to understanding the dependence of reactivity on initial vibrational excitation for the title reaction and its isotopic analogies. Crim, Zare, and co-workers carried out a serial of experimental studies and observed strong mode specific reactivity in the H+H_2O/D_2O reactions with H_2O/D_2O in overtone or fundamental vibrational excitations [6–8]. Bond selectivity has also been demonstrated in the H+HOD reaction with a preferential cleavage of the HOD vibrationally excited bond [9–11]. Theoretically, besides the quasiclassical trajectory (QCT) studies of Schatz et al. [12–14] there have been a number of quantum dynamics studies [15–19], which are in qualitative agreement with the experimental observations. Recently, Fu et al. calculated the exact coupled-channel (CC) integral cross sections (ICS) for H_2O and HOD initially in the first and second stretching excited states and simultaneous excitations of both bending and stretching modes on the YZCL2 PES, and observed strong mode specific and bond selected reactivity as discovered in the experiments [20, 21].

Another important question of mode specificity is how the initial vibrational excitation influences the product state distribution. The Crim group observed that the reaction of water molecules excited to the [04]^− overtone state predominantly produces OH(v=0) while reaction from the [13]^− state produces mostly OH(v=1) [7]. Zare group showed that for the D_2O asymmetric stretch fundamental states (001) and (011), the OD product is produced with little vibrational excitation (OD(v=1):OD(v=0)≈1:20) [8]. At first glance, such an
OD(OH) product vibration distribution might seem surprising. In a normal mode picture, both OD bonds in D$_2$O are equally excited in the symmetrically or asymmetrically excited state. Breaking one OD bond by the incoming H atom should leave the other OD in vibrationally excited state. Zare and coworkers postulated a local mode picture in which the D$_2$O asymmetric stretch state is thought as a linear combination of local mode stretches with the H atom reacting preferentially with the excited OD bond, leaving the other OD group in its vibrational ground state. Until recently, we report the first full-dimensional state-to-state study for the H+H$_2$O→H$_2$+OH reaction with H$_2$O in the ground and the first symmetric and asymmetric stretching excited states [22]. It is found that the (100) and (001) initial excited states both lead to the OH product mostly in its ground vibrational state, confirming the local mode picture of H$_2$O vibration, and revealing the spectator nature of the non-reacting OH bond.

In this work, we report the first full-dimensional (6D) quantum differential cross sections (DCS) for the title reaction with initial nonrotating D$_2$O in (000), (100) and (001) vibrational states to investigate the initial vibrational excitation influences on the product state distribution and DCS, by using the reactant-product decoupling (RPD) scheme based time-dependent wave packet (TDWP) method. Through the development of the TDWP method, it is routine now to calculate fully converged integral cross sections (ICS) without any dynamical approximations for some four-atom reactions [20, 21, 23–27], by only using one set of reactant Jacobi coordinates. However to extract S-matrix elements in a TDWP calculation, one needs to transform the wave function initially prepared in reactant Jacobi coordinates to product Jacobi coordinates, making the calculations much difficult. Up to now, there are basically three state-to-state approaches to deal with the coordinate problem, namely, “reactant coordinates based”, “reactant-product decoupling”, and “product coordinates based” approach. In 2002 and 2006, Zhang calculated the first state-to-state DCS for the H+H$_2$O→H$_2$+OH reaction from the ground initial state in five dimensions with the nonreactive OH bond length fixed [28, 29].

Soon after that, Althorpe and coworkers introduced another coordinate transformation method and applied it to calculate state-to-state reaction probability in full dimensions for the total angular momentum $J=0$ [30–32]. In 2011, the TDWP method was developed to compute full-dimensional DCSs for four-atom reactions and applied to the prototypical HD+OH→H$_2$O+D and D$_2$+OH→HOD+D reactions [33–35]. Excellent agreements were achieved for the first time for a four-atom reaction between the theoretical DCS and high-resolution crossed-molecular beam experimental results, declaring that theory is now able to calculate complete dynamical information for some four-atom reactions.

In this work, we present the theory of the full-dimensional state-to-state quantum dynamics treatment to atom-triatom reactions and some computational details.

II. THEORY

The RPD method, originally introduced by Peng et al. and Huang et al. [36, 37], partitions the full time-dependent wavefunction into a sum of reactant component ($\Psi_r$) and all product components ($\Psi_p; p=1, 2, 3, \ldots$) that satisfy the following decoupled equations,

$$i\hbar \frac{\partial}{\partial t} |\Psi_r(t)\rangle = H_r|\Psi_r(t)\rangle - i\sum_p V_p|\Psi_r(t)\rangle \quad (1)$$

$$i\hbar \frac{\partial}{\partial t} |\Psi_p(t)\rangle = H_p|\Psi_p(t)\rangle + iV_p|\Psi_r(t)\rangle \quad (2)$$

where $-iV_p$ is the negative imaginary potential (absorption potential) employed to prevent the wavefunction $\Psi_r(t)$ from entering the $p$th product arrangement. Then, Althorpe and co-workers employed an exact partitioned version of the split-operator propagator [30], which is more efficient than partitioning the Schrödinger equation. $\Psi_r(t)$ can be propagated in the reactant Jacobi coordinates just as for total reaction probability calculations,

$$\Psi_r(t+\Delta) = e^{-iV_p\Delta/h}e^{-i(H_r/H\Delta)}\Psi_r(t) \quad (3)$$

Every product wave function, $\Psi_p$, can be propagated in its own coordinates as in a normal wave packet propagation except for a source term, $\xi_p$, prepared by Eq.(3),

$$\Psi_p(t+\Delta) = e^{-i(H_p/H\Delta)}\Psi_p(t) + \xi_p(t)$$

$$\quad = e^{-i(H_r/H\Delta)}\Psi_p(t) + (1-e^{-iV_p\Delta/h})\Psi_r(t+\Delta) \quad (4)$$

In the original RPD approach, the source term $\xi_p(t)=(1-e^{-iV_p\Delta/h})\Psi_r(t)$ is saved and transformed from reactant to product Jacobi coordinates at every propagation time step. To reduce the computational cost, we use multi-step RPD [32, 38] by saving and transforming the source term at every $M$ time steps in the actual calculation,

$$\Psi_r(t+\Delta) = e^{-V_pM\Delta/h}e^{-i(H_r/H\Delta)}\Psi_r(t) \quad (5)$$

when mod($t+\Delta$)–$t_0$, $M\Delta$=0,

$$\Psi_p(t+\Delta) = e^{-i(H_p/H\Delta)}\Psi_p(t) + (1-e^{-iV_pM\Delta/h})\Psi_r(t+\Delta) \quad (6)$$

where $t_0$ is the starting point for performing wave function transformation. At other time steps, we carried out the standard split-operator propagation [39] for $\Psi_r(t)$ and $\Psi_p(t)$ without the absorption potential, $V_p$, related terms. In this way, we can cut the computational time
for wave function transformation from reactant coordinates to product coordinates by a factor of $M$.

The coordinate systems and wavefunctions representations for both atom-triatom and diatom-diatom scattering studies are outlined here. For details, please refer to Refs. [40, 41]. Figure 1 shows the reagent Jacobi coordinates $(R, r_1, r_2, \theta_1, \theta_2, \varphi)$ for the H+D$_2$O atom-triatom arrangement, and product Jacobi coordinates $(R', r_1', r_2', \theta_1', \theta_2', \varphi')$ for the AB+CD diatom-diatom arrangement. $\Delta$ is the angle between $\vec{R}$ and $\vec{R'}$.

The system Hamiltonian in the H+D$_2$O arrangement for a given total angular momentum $J$ can be written as

$$H = -\frac{\hbar^2}{2\mu R^2} \frac{\partial^2}{\partial r^2} + \frac{(J-j_{12})^2}{2\mu R^2} + \frac{j_1^2}{2\mu_1 r_1^2} + \frac{j_2^2}{2\mu_2 r_2^2} + V(R, r_1, r_2, \theta_1, \theta_2, \varphi) + h_1(r_1) + h_2(r_2)$$  \hspace{1cm} (7)

where $\mu$ is the reduced mass between the center-of-mass of H and D$_2$O, $\textbf{J}$ is the total angular momentum operator of the system, $j_{12}$ is the total angular momentum operator of D$_2$O, $j_1$ is the rotational angular momentum operator of OD, and $j_2$ is the orbital angular momentum of H and D in the OD arrangement. The reference Hamiltonian $h_i(r_i)$ ($i=1, 2$) is defined as

$$h_i(r_i) = -\frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_i(r_i) \hspace{1cm} (8)$$

The time-dependent wave function can be expanded in terms of the translational basis of $R$, the vibrational basis $\phi_{\nu}(r_i)$, and the body-fixed (BF) rovibrational eigenfunction as

$$\Psi_{JMe}(R, r_1, r_2, t) = \sum_{n, v, j, K} F_{n v j K} JMe_{n v j K} (t) u_n^\nu (R) \phi_{\nu}(r_1) \phi_{\nu}(r_2) Y_{JMe}^K (\hat{R}, \hat{r}_1, \hat{r}_2) \hspace{1cm} (9)$$

The BF total angular momentum eigenfunctions can be written as,

$$Y_{j_{12}K}^J = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} [D_{J'M}^{J} Y_{j_{12}K} + e(-1)^{j_1+j_2+j_{12}+J} D_{J'M}^{J+1} Y_{j_{12}K}]$$

$$\equiv D_{J'M}^{J} Y_{j_{12}K} + e(-1)^{j_1+j_2+j_{12}+J} D_{J'M}^{J+1} Y_{j_{12}K} \hspace{1cm} (10)$$

where $D_{J'M}^{J} (\Theta \Phi \Psi)$ is the Wigner rotation matrix [42] with three Euler angles $(\Theta \Phi \Psi)$, $e$ is the parity of the system defined as $e=(-1)^{j_1+j_2+j_{12}+J}$ with $\textbf{L}=\textbf{J}-\textbf{j}_{12}$ being the orbital angular momentum of H and D$_2$O, and $Y_{j_{12}K}$ is the angular momentum eigenfunction of $j_{12}$ defined as,

$$Y_{j_{12}K} = \sum_m D_{K'M}^{K} (\chi, \theta_1, \varphi) \sqrt{\frac{2j_1+1}{4\pi}} \langle j_2 m | j_{12} m \rangle y_{jm} (\theta_2, 0) \hspace{1cm} (11)$$

where $y_{jm}$ are spherical harmonics. Note that in Eq.(10), the restriction $e(-1)^{j_1+j_2+j_{12}+J}=1$ for $K=0$ partitions the whole rotational basis set into even and odd parities. Hence a $K=0$ initial state can appear in one of these two parity blocks. For $K>0$, however, there is no such restriction, the basis set is the same for for even and odd parities. Hence a $K>0$ initial state can appear in both parities.

For the the HD+OD arrangement, similarly to the discussion about H+D$_2$O arrangement, we have the same forms of equations, except the quantities with unprimed indices replaced by primed ones. The system Hamiltonian for the HD+OD arrangement, corresponding to Eq.(7),

$$H = -\frac{\hbar^2}{2\mu' R'^2} \frac{\partial^2}{\partial r'^2} + \frac{(J'-j'_{12})^2}{2\mu' R'^2} + \frac{j'_1^2}{2\mu'_1 r'_1^2} + \frac{j'_2^2}{2\mu'_2 r'_2^2} + V(R', r'_1, r'_2, \theta'_1, \theta'_2, \varphi') + h'_1(r'_1) + h'_2(r'_2) \hspace{1cm} (12)$$

where $\mu'$ is the reduced mass between the center of mass of HD and OD, $j'_{12}$ is the total angular momentum operator of HD and OD, which are coupled to form $j'_{12}$

Corresponding to the Eq.(9), we have

$$\Psi_{J'Me}^J (R', r'_1, r'_2, t) = \sum_{n', v', j', K'} \left[ F_{n' v' j' K'}^{J'Me} (t) u_{n'}^{\nu'} (R') \phi_{\nu'}(r'_1) \phi_{\nu'}(r'_2) Y_{J'Me}^{K'} (\hat{R'}, \hat{r}'_1, \hat{r}'_2) \right] \hspace{1cm} (13)$$

It should be pointed out here that the functional form for the product arrangement basis (primed) are different from the one for the reactant arrangement basis (unprimed).

BF total angular momentum basis $Y_{J'Me}^{K'} (\hat{R'}, \hat{r}'_1, \hat{r}'_2)$.
in Eq.(13) are defined as,
\[ Y_{J_iJ_f}^{M_1M_2} = (1 + \delta K_0)^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \left[ D_{KM}^{J_iJ_f} Y_{j_1j_2}^{J_1J_2} + \epsilon(-1)^{J_1+J_2} D_{KM}^{J_1J_2} Y_{j_1j_2}^{J_2J_1} \right] \]
\[ \equiv D_{KM}^{J_1J_2} Y_{j_1j_2}^{J_1J_2} + \epsilon(-1)^{J_1} D_{KM}^{J_1J_2} Y_{j_1j_2}^{J_2J_1} - K_0 \] (14)
where \( \epsilon \) is the parity of the system defined as \( \epsilon = (-1)^{J_1+J_2+N} \) with \( N = J - j_1^2 \) being the orbital angular momentum of HD and OD, and \( Y_{j_1j_2}^{J_1J_2} \) is the angular momentum eigenfunction of \( j_1^2 \).

In our calculations we employ the CXZ PES [5] constructed by using neural network (NN) fitting [43–45] based on 17,000 \( \text{ab initio} \) points calculated at UCCSD(T)-F12a/AVTZ level of theory. It is the best PES available for the system, substantially more accurate and smoother than YZCL2 and XXZ PES. We carry out state-to-state calculations for all the total angular momentum \( J \) up to 40 to converge DCSSs for collision energies up to 1.5 eV for (000) initial state, and for collision energies up to 1.2 eV for (100) and (001) states. The numerical parameters used in reactant atom-triatom coordinates are as the following.

The interaction region was defined by a rectangular box of [1.0, 6.0] \( a_0 \) in the \( r_1 \) coordinate, and [1.0, 6.0] \( a_0 \) for the \( R \) coordinate. The number of vibrational basis functions used was 65 for \( r_1 \) coordinate. For the \( R \) coordinate, we used 40 sine discrete variable representation (DVR) points. The asymptotic region was defined from 6.0 \( a_0 \) to 12.0 \( a_0 \) with 42 sine DVR points for the \( R \) coordinate and 8 vibrational basis functions for the \( r_1 \) coordinates. The number of vibrational basis functions for the nonreactive OD is 12 for interaction and 7 for asymptotic regions. For the rotational motion, we used \( j^\text{max}=28 \) and \( j_2^\text{max}=60 \), which results in 22475 rotational basis functions for \( K=0 \) and even parity. The number of \( K \) blocks used in the calculation increases with the total angular momentum, from 1 for \( J=0 \), up to 7 for \( J=40 \). The initial Gaussian wave packet was centered at \( R_0=10 \) a.u. for lower total angular momentum, \( J \), we propagated the wave packets for 6000 a.u. of time with a time step of 10 to converge the low energy reaction probability. The absorption potential on the \( r_1 \) coordinate for the MRPD calculation takes the form:

\[ V_p(r_1) = C \left( \frac{r_1 - r_1^0}{\Delta r_1} \right)^n \] (16)
with \( r_1^0 = 4.5 \) a.u., \( \Delta r_1 = 1.5 \) a.u., \( C = 0.2, n = 1.5 \). To minimize the computational cost, the coordinate transformation is carried out at every 8 propagation time steps.

Continuous propagation in the product diatom-diatom coordinates only involves a total number of 120 sine functions for the translational coordinate \( R' \) in a range of [3.0, 15.0] \( a_0 \), 5 vibrational basis functions for HD bond, and 3 vibrational basis functions for OD bond. We used \( j^\text{max}=30, j_2^\text{max}=18 \), resulting in a total of 4750 coupled rotational basis functions for \( K=0 \) with even parity. The number of \( K \) blocks used in the calculation increases from 1 for \( J=0 \), up to 10 for \( J=40 \). A dividing surface is placed at \( R'=10.0 \) a.u. to extract \( S \) matrix elements. Since one OD bond is treated as a nonreactive bond in this work, the reaction probabilities and cross sections should be doubled.

III. RESULTS

Figure 2 shows the total reaction probabilities for the (000), (100), and (001) three initial states as a function of collision energy on the CXZ PES, from the initial state selected wave packet (ISSWP) approach only using reactant Jacobi coordinates, in comparison with those from the RPD state-to-state calculations. As can be seen, for both the ground and excited initial states, the agreements between these two kinds of results are excellent in the entire energy region considered here, indicating the RPD partition of the wave function as well as the continuous propagation in diatom-diatom coordinates is of high accuracy. The reaction probability for the ground state increases steadily with increasing collision energy starting from about 0.9 eV, and is very small in the energy region considered here. The overall behavior of reaction probabilities for the first symmetric stretching excited (100) and asymmetric stretching excited (001) states is quite similar to that for the ground state, although the former is much larger and exhibits some oscillatory structures.

Figure 3(a) shows the ICS for the three initial states as a function of collision energy from the ISSWP approach only using reactant Jacobi coordinates, in comparison with those from the RPD state-to-state calculations. As can be seen, the RPD based state-to-state calculation is also of high accuracy for \( J>0 \). The overall behavior of the ICS is fairly similar to that of the total reaction probabilities shown in Fig. 2, except that the oscillatory structures on the (100) and (001) probability curves vanish on the cross section curves.

The ICS for (000) state is quite small with the value of roughly 0.023 \( a_0^2 \) at \( E_c=1.5 \) eV, which is smaller than the experimental results by a factor of 1.3 to 4.8 (according to the data points in Ref.[46]). In addition, the reaction cross section for \( \text{H}+\text{D}_2\text{O} \) is two to three times smaller than that for \( \text{H}+\text{H}_2\text{O} \), due to less mobility of D atom compared to H atom. We can also see from Fig.3(a) that one-quantum excitations of stretching modes of \( \text{D}_2\text{O} \) substantially enhance the reactivity. The enhancement factors are 37.7 at the collision energy of 1.2 eV. Zare and co-workers have previously

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measured that one-quantum excitation of the asymmetric stretch in D$_2$O (or the combination of one quantum each of bend and asymmetric stretch) increases the cross section by at least a factor of 5 (and possibly a factor of 20) [8]. In the low collision energy region, the (001) state is slightly more reactive than the (100) state because of the higher excitation energy for the (001) state. Figure 3(b) shows the ICS for the three initial states as a function of total energy, which are measured with respect to the energy of the D$_2$O ground rovibrational state. The ICS for (100) state is only slightly larger than that for (001) state in the high total energy region, indicating the first symmetric and asymmetric stretching excitation of D$_2$O have nearly equal efficacy on promoting the reaction.

Figure 4 shows the DCS for the three initial states, each at four collision energies, in terms of surface plots for the product translational energy and angle distributions for the reaction. It can be seen at the first glance that the first symmetric (100) and asymmetric (001) stretching excited states have essentially identical DCS. Just like the ground initial state, the DCSs for these two states are strongly backward peaked at the threshold energy. As the collision energy increases, the angular distribution becomes increasingly broader, and the peak position starts to shift gradually to a smaller angle, consistent with the fact that the title reaction is a direct reaction via an abstraction mechanism. At the same collision energy, the DCS for the ground state is very different from those for the vibrationally excited state. However, one may note that the DCS at each column shown in Fig.4 resemble each other somewhat in shape, indicating that the angular distributions for these three states are similar at the same total energy (because the excitation energy for (100) and (001) states are about 0.331 and 0.346 eV, close to the collision energy difference between the ground and vibrationally excited state shown in the figure).

In order to examine the effect of the stretching excitation on the angular distribution in a quantitative manner, we present the total DCS for the three states at collision energies of 0.9, 1.06, and 1.2 eV in Fig.5(a). The behavior of angle distributions for the excited states is quite different from the ground state at the same collision energy, and the former are much broader and have obvious forward scattering components. The DCS for the (100) and (001) states are very close to each other, indicating that one quantum in the symmetric or antisymmetric stretching excitation of D$_2$O has nearly identical effects to DCS.

Figure 5 (b) shows the total DCS for the three states at total energies of 0.9, 1.2, and 1.5 eV. Overall, the angle distributions for (000), (100), and (001) vibrational states are quite similar at the same total energy of reaction, although these two stretch vibrational excitations enhance the cross section by at least 9 times relative to that for the ground state. Therefore, the energy initially deposited in stretching vibrations is much more efficient than the translational energy at promoting the reaction, but has rather similar effects on product angular distribution as the translational energy. In addition, the backward scattering components from the initial excited states decrease more slowly than that from the ground state as the total energy increases, and exhibit some oscillatory structures.

Figure 6 shows the product HD($v$=1) and OD($v$=1) vibrational state populations for the three initial states as a function of total energy. It should be noted that
FIG. 4 Surface plots for the product translational energy and angle distributions for the three initial states (000), (100), and (001) at several collision energies.

FIG. 5 (a) Differential cross sections for the three initial states at collision energies of 0.9, 1.06, and 1.2 eV. (b) Differential cross sections for the three initial states at the total energies of 0.9, 1.2, and 1.5 eV.

the population for (000) state in Fig.6(b) was multiplied by a factor of 20 before plotting. When D$_2$O is in the vibrational ground state, both HD and OD products are vibrationally very cold in the energy region considered here. There is a small fraction of HD($v=1$) produced only for collision energy higher than 1.25 eV with a population of 4.3% at 1.5 eV, and almost no OD($v=1$) produced. The initial vibrational excitations increase the branching ratios of HD($v=1$) and OD($v=1$) channels at the same total energy. The population of
HD(v=1) reaches 10.6% at $E_{\text{tot}}=1.55$ eV. However, the OD vibration excited populations remain small for the initial (100) and (001) states.

These small populations of OD(v=1) clearly reveal that D$_2$O fundamental stretching excitations produce vibrationally "cold" OD as the ground initial state, in agreement with the experimental observation of Zare and coworkers [8]. In the normal mode picture, the (100) and (001) state correspond, respectively, to the symmetric and antisymmetric vibrational excitations of D$_2$O with both OD bonds vibrationally excited. Breaking one OD bond by an incoming H atom will leave another OD bond vibrationally hot. However, in the local mode picture, the (100) and (001) states correspond to $|10\rangle \pm 2^{-1/2}|[10] \pm |01\rangle\rangle$, i.e. each OD bond is a superposition of the ground and first excited quantum states. When the incident H comes in, it will react with each quantum state independently without any effect from the non-reacting OD group if the non-reacting OD is a spectator, producing OD in the corresponding quantum state. Because the reactivity of the OD excited state is much higher than the ground state, the incident H atom tends to react with the excited state, producing OD mainly in the corresponding ground state. On the other hand, the H atom also reacts with the ground OD state, producing a small fraction of the OD(v=1) state. The fraction of OD(v=1) should be approximately equal to the relative reactivity between the OD(v=0) and OD(v=1) states. As can be seen from Fig.6(b), the fraction of the OD(v=1) population is very close to the relative reactivity. Therefore, the local mode picture works very well here, and the non-reacting OD bond does act as a spectator.

Figure 7 shows the normalized rotational distributions for HD (a) and OD (b) product for the three initial states at some total energy. For the ground state reaction, the general trend in the change of HD or OD rotational distributions with the increase of collision energy is quite similar: the distribution becomes broader, and the $j_{\text{HD}}=0$ or $j_{\text{OD}}=0$ population declines. The $j_{\text{HD}}=0$ population decreases from 29% at $E_c=0.9$ eV to 2% at $E_c=1.5$ eV, and the $j_{\text{OD}}=0$ population decreases from 26% to 7%. The OD rotation distribution has a maximum at $j_{\text{OD}}=2$ for all the energies shown, except for $E_c=0.9$ eV, for which $j_{\text{OD}}=0$ is marginally larger than $j_{\text{OD}}=2$ because of the oscillatory behavior. In contrast, the most probable rotational state for HD becomes higher with the increase of collision energy, changing from $j_{\text{HD}}=1$ at $E_c=0.9$ eV to $j_{\text{HD}}=7$ at $E_c=1.5$ eV. We can also see from Fig.7(b) that the OD products from the (100) and (001) reactions have essentially the same rotational distribution as the ground state reaction, indicating one-quantum excitations of stretching modes of D$_2$O has little effect on the OD rotational distribution.

This is consistent with the experimental observation of Zare and coworkers [8], and further supports the picture of the non-reacting OD bond as a spectator. Unexpectedly, the HD rotation distribution from vibrationally excited reaction becomes less excited at the same total energy, which is different from the H+H$_2$O reaction [22].

The differences in the vibrational and rotational excitation of HD and OD can also be found from the energy partition information. Figure 8 shows the fraction of total available energy in the product channel going into
FIG. 8 The fraction of the total available energy in the product channel going into the rotation (a) and vibration (b) excitation of HD and OD as a function of the total energy. The corresponding total available energy in the product channel is also shown on the top of each panel. Note the fraction for OD vibration for the ground state was multiplied by a factor of 10 before plotting.

IV. CONCLUSIONS

We employ the TDWP method to calculate the first full-dimensional state-to-state DCS for the H+D2O→HD+OD reaction with D2O in the ground and the first symmetric and asymmetric stretching excited states on the CXZ PES. The calculated DCS for these three initial state are strongly backward peaked at low collision energies, become increasingly broader with the increase of collision energy, with the peak position shifting gradually to a smaller angle, consistent with the fact that the title reaction is a direct reaction via an abstraction mechanism. Our calculations revealed that the stretching excitation is much more efficient at promoting the reactivity than the translational energy, but has a rather similar effect on the angular distribution as the translational energy. Moreover, the DCS for the (100) and (001) states are very close to each other, indicating that one quantum in the symmetric or antisymmetric stretching excitation of D2O has nearly identical effects to DCS as found in the H+H2O reaction [22]. Product vibrational and rotational state distributions and energy partitioning information are also presented. The small populations of OD(ν=1) from (100) and (001) initial states can be explained clearly by the local mode picture of D2O vibration, and reveals that the non-reacting OD does act as a spectator in the reaction. Unexpectedly, the initial vibrational excitation reduces the rotation excitation of HD at the same total energy. The present full-dimensional state-to-state quantum dynamics study for the title reaction is of considerable importance to our understanding of mode-specific chemistry.

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