Quantum wave-packet studies on ion-molecule reaction \( \text{O}^+(4S) + \text{D}_2(X^1\Sigma^+_g) \) with and without Coriolis-coupling effect

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Quantum wave-packet studies on ion-molecule reaction

$\text{O}^+(^4\text{S}) + \text{D}_2(X^1\Sigma_g^+) \text{ with and without Coriolis-coupling effect}$

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Abstract: The time-dependent quantum scattering calculation with Chebyshev wave packet propagation scheme has been carried out based on an accurate electronic potential energy surface of $\text{H}_2\text{O}^+(X^4\text{A}^-)$. Due to the influence of the deep potential well, the reaction probability of $\text{O}^+(^4\text{S}) + \text{D}_2(X^1\Sigma_g^+) \rightarrow \text{OD}^+(X^1\Sigma_g^+) + \text{D}(^2\text{S})$ shows resonance structures regardless of the Coriolis-coupling (CC) effect or centrifugal sudden (CS) approximation. In the range of collision energy 0.0-1.0eV, the integral cross section obtained by the CS approximation calculation is smaller than that by the CC calculation, which indicates that CC effect play a significant role in the title reaction.

Keywords: Chebyshev wave packet propagation, Coriolis-coupling effect, centrifugal sudden approximation, potential energy surface, $\text{O}^+ + \text{D}_2$

1. Introduction

Due to the important role in the interstellar media, plasmas and combustion processes, the ion-molecule reactions have attracted a great deal of attention in recent decades [1-6]. And as a three-atom system, $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$ has been regarded as a typical ion–molecule reaction. To help better understand this kind of reaction, a large number of experiments and theoretical simulations about the $\text{O}^+ + \text{H}_2 (\text{D}_2) \rightarrow \text{OH(D)}^+ + \text{H(D)}$ reactions have been performed worldwide.

On the experimental side, Ng [7] measured the total integral cross section (ICS) of the $\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}$ reaction by a unique triple-quadrupole double-octopole photoionization mass spectrometer, which testified that the reaction proceeds via
predissociation mechanism of the charge transfer. Gillen et al. [8, 9] reported the product velocity vector-distributions of the title reaction, which demonstrated the reaction proceeds from ground state reactants to predominantly ground state products via a direct interaction on the $^4\Sigma^+ - ^4A^1 - ^4A_2$ surfaces.

Theoretically, an accurate potential energy surface (PES) [10,11] of the H$_2$O$^+$ (X$^4A^+$) was reported by Martínez et al.[12] Based on this PES, the ICS and the rate constants (200–1400K) for the O$^+$+D$_2$→OD$^+$+D reaction were obtained using quasi-classical trajectory (QCT) method [13,14]. The results are in agreement with experimental results taken from Burley et al. [15] Klos et al. [16] have calculated the reaction probabilities, ICS and the rate constants for the O$^+$+H$_2$ reaction using centrifugal sudden (CS) approximation on the PES by Martínez et al. Considering the Coriolis-coupling (CC)[17,18,19,20], the reaction O$^+$+H$_2$ including its isotopic variants reaction has been investigated by Xu et al. [21] and the results demonstrated the CC effects play a key role in the O$^+$+H$_2$ (D$_2$)→OH(D)$^+$+H(D) reaction system. To get more information on the related reactions, in 2015, Song et al. [22] constructed a more accurate PES of H$_2$O$^+$ (X$^4A^+$) by fitting 2690 ab initio points. Based on this PES, Wang et al. [23] have obtained the dynamic information of the title reaction by the time-dependent quantum scattering method [24], which is in agreement with experimental results [25].

The CC, an intramolecular effect which influences the accuracy of related dynamical calculation, has been a subject for many collision dynamical researches. Chu et al. [17] have examined the role of CC effect in the ion-molecule reaction by the time-dependent wave-packet scattering method [26-28], and illustrated that it can influence dynamical properties of poly-atomic molecular reactions. Gao et al.[18] have performed the quantum dynamic calculation of the H+Li$_2$ reaction on a globally PES, and indicated that the CC effect should be included in the accurate dynamic study without considering computational cost. For reaction O$^+$+D$_2$→OD$^+$+D, as a typical ion-diatomic molecule system, its further research may give new dynamical information after considering the CC effect based on a novel PES [22].

So in this paper, the dynamics calculation of title reaction is performed using the
time-dependent quantum scattering calculation with the Chebyshev wave packet propagation scheme[29,30] based on the new PES[22]. The role of the CC effect in the reaction is obtained by comparing with the CS dynamic results. This paper is organized as follows: In Section II, a short description of the calculated method is described. The computing results are discussed and analyzed in the Section III. And the conclusions are presented in Section IV.

2. Potential energy surface and dynamical theory

The H2O+(X'4A") PES constructed by Song et al. is employed in the present calculations. The ab initio points are calculated using multireference configuration interaction(MRCI)[31] level and larger basis set aug-cc-pVQZ [32], and the ab initio energies were subsequently corrected by using the double many-body expansion-scaled external correlation (DMBE-SEC) [33] method. The C∞v [OHH]+ minimum locates at R1=2.2950a₀(RHH), R2=2.1209a₀(ROH+) and R3 = 4.4159a₀(ROH+). Compared with the result calculated from analytical PES of Martínez et al. [12], the derivations are only 0.0573a₀, 0.0336a₀, and 0.0237a₀, respectively. The well depth of the present PES is 5.6597eV relative to the O+(4S) + H(2S) + H(2S) asymptote, which is 0.1633eV lower than the results of Martínez et al.[12] The dissociation energy of OH+(X'3Σ-) calculated from the present PES is 5.2972eV, agreeing nicely with the experimental result (5.301eV). Because the electronic ground-state H2O+(X'4A") PES is adiabatic, there is no contribution from the non-adiabatic effects with multiple electronic state [34] involved for this reaction.

In this work, the reactant (O'+D₂) Jacobi coordinates V(R, r, γ) are employed, and the Hamiltonian operator of the system is expressed as,

\[ \hat{H} = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{(\hat{J} - \hat{j})^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_j r^2} + V(R, r, \gamma) \quad (\hbar = 1), \]

(1)

where r and R are the diatomic (D-D) and ion-diatomic (O'+D₂) distances, respectively, with \( \mu_r = m_D \ast m_D / 2m_D \) and \( \mu_R = 2m_{O^+} \ast m_D / (m_{O^+} + 2m_D) \) as the reduced masses corresponding to the radial Jacobi coordinates R and r, and the \( V(R, r, \gamma) \) represents the PES of the corresponding electronic state. J and j are the total
angular momentum operator and the diatomic rotational angular momentum operator, respectively. The modified Chebyshev recursion scheme is applied to propagate the initial wave packet \[29, 30\]

\[
|\psi_{n-1}\rangle = DQ\hat{H}_x c a |\psi_a\rangle - D|\psi_{n-1}\rangle) 
\]

(n > 1),

(2)

with \(|\psi_1\rangle = D\hat{H}_{\text{scaled}}|\psi_0\rangle\), \(D\) being the absorption potential and \(|\psi_0\rangle\) being the initial wave packets.

The time dependent wave function can be expanded in the terms of the body-fixed (BF) translational-vibrational-rotational state \(G(R)\phi(r)Y_{j,l,\Omega}^J\) which can be expressed as follows,

\[
|\psi_{\nu,j,l}\rangle = Ne^{-\frac{E_R}{\epsilon}} Y_{j,\nu}R \chi_{\nu,j,l} \langle j,l,\Omega | \phi_{\nu} \rangle, 
\]

(3)

where the helical quantum number \(\Omega\) is the projection of the total angular momentum \(J\) on the BF z-axis, \(l\) the orbital angular momentum quantum number and \(p\) the system parity. Based on this scheme, the element of the Coriolis-coupling matrix is written as,

\[
\langle Y_{\mu\lambda} | (\hat{j} - \hat{j})^2 | Y_{\nu\nu} \rangle 
= \frac{1}{2\mu_R R^2} \langle Y_{\mu\lambda} | (\hat{j} - \hat{j})^2 | Y_{\nu\nu} \rangle 
= \frac{1}{2\mu_R R^2} [(J(J+1) + \nu(j+1) - 2\Omega^2)] \delta_{\mu\lambda} \delta_{\Omega\Omega'} - 
(1 + \delta_{\Omega,0})(1 + \delta_{\Omega',0})^{1/2} \{ \lambda_{\mu\lambda}^{\pm} \delta_{\Omega\Omega',1} + \lambda_{\mu\lambda}^{\pm} \delta_{\Omega\Omega',1} + p(-1)^1 \delta_{\Omega\Omega',-1}], 
\]

(4)

where \(\lambda_{ab} = \sqrt{a(a+1) - b(b+1)}\). If we neglect the off-diagonal elements (CS), Eq. (4) can be expressed as,

\[
\langle Y_{\mu\lambda} | (\hat{j} - \hat{j})^2 | Y_{\nu\nu} \rangle 
= \frac{1}{2\mu_R R^2} \langle Y_{\mu\lambda} | (\hat{j} - \hat{j})^2 | Y_{\nu\nu} \rangle 
= \frac{1}{2\mu_R R^2} [(J(J+1) + \nu(j+1) - 2\Omega^2)] \delta_{\mu\lambda} \delta_{\Omega\Omega'} .
\]

(5)

Obviously, we can see that the CS calculation decouples these \(\Omega\) states, so the
calculative cost of the $J>0$ can be reduced greatly.

By analyzing all wave packets that enter the progressive region of the product channel, we can get the reaction probability and ICS, respectively, as

$$P(E) = \frac{1}{\pi \mu |\alpha(E)|^2 (E_{\text{max}} - E_{\text{min}})^2 \sin^2 \theta} \times \text{Im} \left\{ \sum_k -\delta_{\lambda,0} \mathcal{Q} \mathcal{E}^{\mu\nu} \psi_k \right\} \sum_k -\delta_{\lambda,0} \mathcal{Q} e^{-i k \theta} \left[ \delta_{r-r_i} \frac{\partial}{\partial \mathbf{r}} \psi_k \right] \}. \quad (6)$$

$$\sigma_{\nu,J}(E_c) = \frac{\pi}{Q + \hbar k_i^2} \sum_{\mathcal{J} \in \mathcal{S}, m i} \mathcal{Q} \mathcal{J} + \mathcal{R}_{\nu,\lambda}^{bp} (E_c). \quad (7)$$

3. Results and discussion

Table 1 lists the details of the optimized parameters in quantum computation. In the CC calculations, it requires us to include all possible helicity quantum number $\Omega$ to obtain accurate total reaction probabilities. Considering the time-consuming to get the total reaction probabilities with all required $J$, it is necessary to truncate the helical $\Omega$ projection in the calculation. We use $N_\Omega$ to indicate the number of $\Omega$ states in the calculation and test a series of $N_\Omega$ to find the optimal results. The reaction probability of $J = 40$ is depicted in Fig. 1. With the increase of $N_\Omega$, the deviation of the total reaction probabilities from the rigorous CC results becomes smaller. In fact, it is found that the discrepancy in reaction probabilities between $N_\Omega = 11$ and $N_\Omega = 40$ has already been very small. Therefore, we set the $N_\Omega$ value as 11 to perform the accurate quantum dynamic calculations. This value can provide convergent dynamic results which are in agreement with other theoretical works.

Table 1. The optimized parameters employed in the titled reaction.

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<td>Translational basis number</td>
<td>300</td>
</tr>
<tr>
<td>Vibrational basis number</td>
<td>200</td>
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<tr>
<td>Rotational basis number</td>
<td>50</td>
</tr>
<tr>
<td>Center of the initial wave packet</td>
<td>8.0 a.u.</td>
</tr>
<tr>
<td>Width of the initial wave packet</td>
<td>0.10 a.u.</td>
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The calculated reaction probabilities with or without the CC effect at the total angular momentum $J = 10, 20, 30, 40$ are shown in Fig. 2. Due to the existence of a potential well in the PES, the oscillation structure of the reaction probabilities can be found in the collision energy range of 0.0-1.0 eV. Comparing the CC reaction probabilities with the CS ones, we find that the oscillation feature of the CS is stronger than that of the CC. The difference in oscillatory behavior can be attributed to the washing-out effect in the CC calculation by coupling different $\Omega$ states. In addition, the CS approximation slightly underestimates the reaction probabilities. For further examining the role of the CC in the reaction probability, we calculate the reaction probabilities of $J = 45, 50, 55, 60$ which are shown in Fig. 3. From Figs. 2 and 3, it is obvious that due to the existence of the centrifugal barrier, the reaction threshold increases with the increase of $J$. As the increasing of $J$ and the collision energy, the difference of the reaction probabilities between CC and CS becomes smaller.

The $J$-dependent partial wave contributions (weighted over a $2J + 1$ factor) to the integral cross section at four given collision energies (0.25 eV, 0.50 eV, 0.75 eV and 1.0 eV) are depicted in Fig. 4. It is clear that the oscillations in the contribution gradually weaken as the collision energy increases regardless of the CC or CS results. Clearly, comparing the CC and CS opacity functions at different collision energies, it is seen that the CC effect can be safely ignored at the high collision energies. For partial waves $J$ of larger numbers, the CC results are a little larger than the CS results. However, they are of comparable amplitudes with $J$ of small numbers. We can also find the fact that, in the CC and CS calculation, the summation of 104 partial wave contributions is enough for the collision energy from 0.0 eV to 1.0 eV.

The ICSs of the title reaction are depicted Fig. 5. It is obviously that the curves of the CC and the CS gradually decline due to the exothermic properties. Oscillatory character can be found also in both the CC and CS results owing to the existence of
the potential well. In the CS calculation, the oscillatory character is more obvious in the low collision energy \((E_c \leq 0.35\text{eV})\) area and the oscillation tends to disappear with the collision energy increasing. From the figure, we can observe that the CS results are a bit lower than the CC ones. And the difference between them decreases gradually with the increase of the collision energy. From the above analysis, we can find that the CC effect has a significant effect on the \(\text{O}^+ + \text{D}_2\) reaction in the low collision energy. This is because the molecular motion of the reactants is slow in the low collision energy, and the \(\text{O}^+\) atom near the \(\text{D}_2\) molecule is more inclined to form the complex and then the \(\text{OD}_2^+\) molecule. However, the reactants move fast and rotate in all directions with the collision energy increasing, which makes the reaction be more prone to a sudden collision, leading to more opportunities to form the \(\text{OD}_2^+\) product molecule directly. In addition, taking into account the experimental error, the experimental results of the title reaction are also displayed in between the maximum and minimum values [25] (Fig. 5). We can find that the ICS of the CS calculation has a good agreement with the experiment results for the high collision energy \((E_c \geq 0.15\text{eV})\), and only for \(E_c < 0.15\ \text{eV}\) the quantum results are under the lower limit of the experimental data. Meanwhile, comparing with the results of Xu et al. [21] for this reaction, we found that the result of our CS is smaller than that of Xu et al. [21] in the low energy region. As the increasing of the collision energy, the difference between the two results becomes smaller.

To supply a better comprehension of the CC effect, the minimum energy path (MEP) of the title reaction is depicted in Fig. 6. The deep potential well in the MEP shows that the reaction is dominated by complex mechanism which usually favors the molecule rotating in different directions. In principle, the rotation of the molecule is isotropic corresponding to different \(\Omega\) states. The CC calculation supposes more possibilities to break the bond of the complex because of the coupling of different \(\Omega\) values, and promote the formation of products. The CS approximation limits the molecular rotation to the plane of three atoms, because only \(\Omega=0\) state is included. This restriction artificially hinders the collision-induced direction changes of angular
momentum vector, and the breaking of the collision complex becomes less favorable of the reaction, resulting in the underestimating of the ICS in the CS calculation.

4. Conclusion

In this paper, we have carried out the time-dependent quantum scattering calculation for the title reaction \( \text{O}^+ + \text{D}_2 \rightarrow \text{OD}^+ + \text{D} \) to obtain the reaction probabilities and the integral cross section. Through the comparison of dynamic results between the Coriolis-coupling effect and the centrifugal sudden approximation calculation, we find that the oscillation feature of the CS is stronger than that of the CC due to the washing-out effect in the CC calculation by coupling different \( \Omega \) states. Comparing with the experimental result, the obtained ICS has a good agreement with the experimental data, especially in the high collision energy region (\( E_c \geq 0.15 \text{eV} \)). Overall, the CC effect has a vital role for the \( \text{O}^+ + \text{D}_2 \) reaction and needs to be included in accurate quantum dynamics studies.

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References


Fig. 1. $N_\Omega$-dependent reaction probabilities of $J=40$ for the titled reaction.

Fig. 2. The reaction probabilities of CC and CS for $J=10, 20, 30, 40$ partial waves.
Fig. 3. The reaction probabilities of CC and CS for $J = 45, 50, 55, 60$ partial waves.

Fig. 4. Weighted the CC and CS partial wave contributions to the ICS at the given collision energy ($0.25\text{eV}, 0.50\text{eV}, 0.75\text{eV}$ and $1.0\text{eV}$).
Fig. 5. Integral cross section of the CC and CS results for the titled reaction.

Fig. 6. Minimum energy path for the $\text{O}^+(\Sigma^+) + \text{D}_2(\Pi_{3/2}) \rightarrow \text{OD}^+(\Sigma^+) + \text{D}(^2\text{S})$