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Quantum reactive scattering with a deep well: Time-dependent calculation for H+O\textsubscript{2} reaction and bound state characterization for HO\textsubscript{2}

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We show in this paper a time-dependent (TD) quantum wave packet calculation for the combustion reaction H+O\textsubscript{2} using the DMBE IV (double many-body expansion) potential energy surface which has a deep well and supports long-lived resonances. The reaction probabilities from the initial states of H+O\textsubscript{2}(\Sigma\text{v}) (\nu=0-3, j=1) for total angular momentum j=0 are obtained for scattering energies from threshold up to 2.5 eV, which show numerous resonance features. Our results show that, by carrying out the wave packet propagation to several picoseconds, one can resolve essentially all the resonance features for this reaction. The present TD results are in good agreement with other time-independent calculations. A particular advantage of the time-dependent approach to this reaction is that resonance structures—strong energy dependence of the reaction probability—can be mapped out in a single wave packet propagation without having to repeat scattering calculations for hundreds of energies. We also report calculations of some low-lying vibrational energies of the hydperoxyl radical HO\textsubscript{2}(^2A^\text{b}) and their spectroscopic assignments. The vibrational frequencies of HO\textsubscript{2}(^2A^\text{b}) on the DMBE IV potential energy surface are lower than experimental values, indicating the need to further improve the accuracy of the potential energy surface.

I. INTRODUCTION

Time-dependent (TD) quantum wave packet methods\textsuperscript{1-3} are emerging as powerful computational tools for studying reactive scattering problems, in particular, for reactions involving polyatomics.\textsuperscript{4-6} The primary computational advantage of the TD approach is that the computational time (CPU) scales as \(N^3\) (\(<\alpha<2\)) with the number of channels \(N\) compared to the \(N^6\) scaling of the time-independent (TI) close-coupling (CC) methods. This is because the TD methods only solve for one solution (one column) at a time, while the standard time-independent (TI) methods solve for all solutions (matrix) in a single calculation. Alternatively, iterative methods could be used in the TI calculation to solve for one column of the solutions at a time, in which case, the CPU time will be proportional to \(N^2\). However, it is generally believed that the TD approach has difficulties to extend to reaction systems involving long-lived resonances. Therefore, most TD calculations have been carried out only for "direct" reactions for which converged results can be obtained within a relatively short propagation time.\textsuperscript{11} For many gas-phase reactions with attractive potential wells, the lifetime of the collision complexes are generally on the order of subpicoseconds. Our recent study for the H\textsubscript{2}+OH reaction shows that the TD approach, using the energy projection technique, is fully capable of resolving resonances of subpicosecond lifetime.\textsuperscript{5} In this paper, we report a TD calculation for the combustion reaction H+O\textsubscript{2}, which has a deep well and supports bound states of the hydperoxyl radical HO\textsubscript{2}. Thus the dynamics calculation for the H+O\textsubscript{2} reaction provides a real challenge to the TD wave packet approach to quantum reactive scattering involving long-lived resonances.

The endothermic reaction \(H(\Sigma)+O(\Sigma)+O(\Pi)\rightarrow OH(\Pi)+O(\Pi)\) plays a central role in combustion chemistry.\textsuperscript{12,13} It is responsible for the chain branching in the oxidation of hydrogen and is a dominant molecular oxygen consuming step in hydrogen–oxygen and methane–oxygen combustion mechanisms.\textsuperscript{14,15} The reaction is endothermic by 0.71 eV and can only proceed at high temperature flames. In addition, through third body collision, the reaction can form intermediate species: the HO\textsubscript{2} radical, which is an important intermediate for many chemical reactions in atmospheric and other areas of chemistry.\textsuperscript{16-20} Considerable amount of experimental works have been carried out to measure the reaction rate coefficient\textsuperscript{21-28} and absolute reaction cross sections.\textsuperscript{29-33} Quasiclassical trajectory (QCT) calculations\textsuperscript{34-36} for the reaction cross sections and rate constants have been carried out using the Melius–Blint potential energy surface (PES)\textsuperscript{37} and the new DMBE IV (double many-body expansion) PES.\textsuperscript{38} Until the end of 1993, however, no rigorous quantum dynamics calculations had been reported for this reaction.

From a dynamical point of view, the H+O\textsubscript{2} reaction presents a real challenge to accurate quantum dynamics calculations. Current \textit{ab initio} electronic structure calculations show no barrier along the reaction path,\textsuperscript{38,39} put a deep well of about \(-2.38\) eV relative to the minimum of the H+O\textsubscript{2} asymptotic potential. The deep well, which corresponds to the hydperoxyl radical HO\textsubscript{2}, supports hundreds of bound states. Most recently, accurate 3D quantum reaction probabilities have been reported by Pack \textit{et al.}\textsuperscript{40} and the cumulative reaction probabilities by Leforestier and Miller\textsuperscript{41} for the H+O\textsubscript{2} reaction using the DMBE IV (double many-body expansion) PES. Numerous resonance features have been reported in these time-independent (TI) quantum dynamics calculations.\textsuperscript{40,41}

In this paper, we present a TD quantum calculation to compute total reaction probabilities as a function of scattering energies. In addition, some bound state energies and their spectroscopic assignments for the hydperoxyl radical
HO\(_2(\tilde{A}^3\Pi)\) on the DMBE IV PES are also presented. The main purpose of the paper is to demonstrate how one can use the TD method to compute reaction probabilities for reactions with numerous resonances of picosecond or subpicosecond lifetime. Our calculation shows how the results converge with respect to the wave packet propagation time and how the long-range force in the exit channel influences the reaction probabilities. The TD scattering calculation for the polyatomic reaction \(H_2 + OH\) shows that subpicosecond resonances could be easily resolved through wave packet propagation.\(^5,6\) As should be mentioned, TD wave packet methods have been recently applied to study resonances based on direct spectroscopic analysis of the autocorrelation function of the TD wave function.\(^5,7\)

This paper is organized as follows: Section II gives a brief review of the TD method for reactive scattering. Section III shows details of our numerical calculation and reports energy dependence of the reaction probabilities for the \(H + O_2\) reaction. We also show how the results converge with respect to the total propagation time of the wave packet and how the results are influenced by the long-range force in the exit channel. A bound state calculation has also been carried out to obtain spectroscopic information of the \(H_2\) radical in the ground state \((\tilde{A}^3\Pi)\). Section IV gives a summary of the present work.

II. THEORY

The theory presented here is for calculating initial state-specific total reaction probabilities for the \(H + O_2\) reaction. Most of the discussions are simply specializations of a previous 6D treatment for diatom–diatom reactions.\(^4,5\) The Hamiltonian expressed in the reactant Jacobi coordinates for a given total angular momentum \(J\) can be written as

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

where \(\mu_r\) is the reduced mass between the center of mass of \(H\) and \(O_2\), \(j\) is the total angular momentum operator, \(j\) is the rotational angular momentum operator of \(O_2\), and \(\mu_j\) is the reduced mass of \(O_2\). The diatomic reference Hamiltonian \(h(r)\) is defined as

\[
h(r) = -\frac{\hbar^2}{2\mu_j} \frac{\partial^2}{\partial r^2} + V_r(r),
\]

where \(V_r\) is a diatomic reference potential.

The time-dependent wave function satisfying the Schrödinger equation \(i\hbar \frac{\partial}{\partial t}\Psi(t) = H\Psi(t)\) can be expanded in terms of the body-fixed (BF) rovibrational eigenfunctions defined using the reactant Jacobi coordinates as

\[
\Psi^{J\mu}_{n_o,j_o,K_o}(R, r, t) = \sum_{n_o,j_o,k_o} F^{J\mu}_{n_o,j_o,K_o}(t) \phi_n(R) \phi_j(r) \chi^{J\mu}_{j_k}(\hat{R}, \hat{r}),
\]

where \(n\) is the translational basis label, \((v_o, j_o, K_o)\) denotes the initial rovibrational state, and \(\epsilon\) is the parity of the system defined as \(\epsilon = (-1)^{J+L}\) with \(L\) being the orbital angular momentum quantum number. Since it is well known that the closed channel components of the wave function are essentially zero in the asymptotic region, we only need to include “open” vibrational channels in the asymptotic region. However, both open and “closed” vibrational channels are needed in the interaction region. We thus employ different grids in the \(R\) coordinate to define the translational basis \(u^{\epsilon}_{n}(R)\) for different vibrational channels. We refer the readers to Refs. 5 and 6 for the explicit form of the nondirect product basis \(u^{\epsilon}_{n}(R)\). The reference vibration eigenfunction \(\phi_n(r)\) for \(O_2\) satisfies the equation

\[
h(r)\phi_n(r) = \epsilon_n\phi_n(r).
\]

\[
\Omega_{jK}^{J\mu} \text{ in Eq. (2.3) is the BF total angular momentum eigenfunction defined as}
\]

\[
\Omega_{jK}^{J\mu} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \times [D^j_{\mu,K,M}(\Omega)\Psi]\psi_{jK},
\]

where \(D^j_{\mu,K,M}(\Omega)\Psi\) is the Wigner rotation matrix\(^{44}\) with three Euler angles \((\Omega)\Psi\) and \(\psi_{jK}\) are spherical harmonics.

The potential matrix elements in the angular momentum basis \(\Omega_{jK}^{J\mu}\) for any fixed \((r, \theta)\) can be evaluated as

\[
\langle \Omega_{jK}^{J\mu} | V_{j'K'}^{J'\mu} \rangle = 2\pi \delta_{KK'} \langle \Omega_{jK}^{J\mu} | \psi_{j'K'} \rangle \delta_{JJ'}
\]

\[
+ \delta_{KK'} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi P_{jK}(\theta) P_{j'K'}(\theta)
\]

\[
= 2\pi \delta_{KK'} \int_0^\pi \sin \theta d\theta P_{J\mu}(\theta)\psi_{j'K'},
\]

where \(P_{jK}(\theta) = (\sqrt{2\pi})^{1/2} \psi_{jK}(\theta, 0)\). The centrifugal potential, which is not diagonal in the BF representation, is given by

\[
\hbar^2 \langle j'K' | (J - j)^2 | jK \rangle
\]

\[
= \frac{\hbar^2}{2\mu_r R^2} \delta_{J,j'} \left[ (J(J+1) + j(j+1) - 2K^2) \delta_{K,K'} - \lambda^+_J \lambda^+_K (1 + \delta_{K0})^{1/2} \delta_{K+1,K'} - \lambda^-_J \lambda^-_K \delta_{K-1,K'} \right],
\]

and the quantity \(\lambda\) is defined as

\[
\lambda^+_A = [A(A + 1) - B(B + 1)]^{1/2}.
\]

We employ the split-operator method\(^{45}\) to carry out the wave-packet propagation

\[
\Psi^{J\mu}(R, r, t + \Delta t) = e^{-iH_0\Delta t}\Psi^{J\mu}(R, r, t) - e^{-iV\Delta t/2}\Psi^{J\mu}(R, r, t),
\]

where the reference Hamiltonian \(H_0\) is defined as

\[
H_0 = \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial R^2} + h(r),
\]

and the effective potential operator \(U\) in Eq. (2.9) is defined as

\[
U = \frac{(J - j)^2}{2\mu_r R^2} + \frac{j^2}{2\mu_j r^2} + V(R, r).
\]
The matrix version of Eq. (2.9) for the expansion coefficient vector \( F \) is then given by

\[
F(t+\Delta) = e^{-i\hbar\Delta/2}Te^{-i\hbar t}F(t).
\]  
(2.12)

The time-dependent wave function is absorbed at the edges of the grid to avoid boundary reflections.

The initial wave function is chosen as the product of a specific rovibrational eigenfunction and a localized translational wave packet

\[
\Psi_i(0) = \phi_{\kappa_0}(R) \phi_{\nu_0}(r) \phi_j \phi_{\kappa_0}(\tilde{R}, \tilde{r}),
\]  
(2.13)

where the wave packet \( \phi_{\kappa_0}(R) \) is chosen to be a standard Gaussian function

\[
\phi_{\kappa_0}(R) = \left( \frac{1}{\pi \sigma^2} \right)^{1/4} \exp\left[-(R-R_0)^2/2 \sigma^2\right] e^{-i\kappa_0 R}.
\]
(2.14)

The exact rovibrational function \( \phi_{\nu_0}(r) \) of \( \text{O}_2 \) is expanded in terms of the reference vibrational functions \( \phi_{\nu}(r) \) to generate the coefficient vector of the wave function at \( t=0 \).

If \( \phi_{\kappa_0} \) denotes the time-independent (TI) full scattering wave function, where \( i \) and \( E \) are, respectively, initial state and energy labels, the total reaction probability from an initial state \( i \) can be obtained by the formula

\[
P^R_i = \sum_f |S^R_{if}|^2 = \langle \psi^+_i | \hat{F} | \psi^+_E \rangle.
\]
(2.15)

In the above equation, \( \hat{F} \) is the flux operator defined as

\[
\hat{F} = \frac{i}{\hbar} \delta(s-s_0) \hat{u}_s + \hat{u}_d \delta(s-s_0),
\]
(2.16)

where \( s \) is the coordinate perpendicular to a surface located at \( s_0 \) for flux evaluation, and \( \hat{u}_d \) is the velocity operator corresponding to the coordinate \( s \). The scattering wave function \( \psi^+_E \) has the asymptotic form in the product arrangement space

\[
\psi^+_E = \sum_f \rho_f e^{i k_f R_f}.
\]
(2.17)

and is normalized as \( \langle \psi^+_i | \psi^+_E \rangle = 2\pi\hbar \delta(E - E') \). Using Eq. (2.16), Eq. (2.15) can be simplified to yield

\[
P^R_i(E) = \frac{\hbar}{\mu_2} \text{Im} \left[ \left\langle \psi^+_i | \delta(s-s_0) \frac{\partial}{\partial s} | \psi^+_E \right\rangle \right],
\]
(2.18)

where \( \mu_2 \) is the proper mass for the coordinate \( s \).

The TI wave function \( \psi^+_E \) can be obtained easily from the wave packet propagation as follows: Since the TD wave function can be expanded in terms of the TI wave function which forms a complete set

\[
|\psi_i(t)\rangle = e^{-i\hbar t H_{ti}} \psi_i(0) = \frac{1}{2\pi\hbar} \int dE \ e^{-i\hbar t E} |\psi^+_E\rangle a_i(E),
\]
(2.19)

the TI scattering wave function can be obtained by performing a Fourier transform

\[
|\psi^+_E\rangle = \frac{1}{a_i(E)} \int_{-\infty}^{\infty} e^{i t (E - H_{ti})} |\psi_i(0)\rangle dt.
\]
(2.20)

The coefficient \( a_i(E) \) can be easily evaluated from the free asymptotic scattering function as follows:

\[
a_i(E) = \langle \Psi^+_E | \Psi_i(0) \rangle = \lim_{t \to -\infty} \langle \psi^+_E | e^{-i\hbar t H} | \psi_i(0) \rangle = \langle \phi^+_i | \phi^+_E \rangle,
\]
(2.21)

where the last equation holds because the initial wave packet \( \psi_i(0) \) is chosen to be located in the asymptotic region with incoming wave only. The free wave function has the form

\[
\phi^+_i = \frac{\exp(-ik_R i)}{\sqrt{\theta_i}} + \frac{\exp(i k_R i)}{\sqrt{\theta_i}} = \frac{2i}{\sqrt{\theta_i}} \sin(k_R i)
\]
(2.22)

for the zero partial wave and is proportional to the spherical Ricatti-Bessel function for nonzero partial waves. The free function has the same normalization as the full scattering wave function \( \psi^+_E \), namely, \( \langle \phi^+_i | \phi^+_E \rangle = 2\pi\hbar \delta(E - E') \).

III. RESULTS OF CALCULATIONS

A. Bound states of \( \text{HO}_2 \)

Since the ground \( \text{HO}_2(2^2A^\nu) \) PES correlates with the asymptotic \( \text{H}(2^2S)+\text{O}_2(1^2\Sigma^\gamma) \), only odd nuclear rotations \( (j=\text{odd}) \) are included in our calculation.\textsuperscript{40,41,46} We use the standard basis set method to diagonalize the Hamiltonian matrix to obtain bound state energies. The basis functions used in the bound state calculation are the same as those used in the scattering calculation and are defined in the reactant Jacobi coordinates. The minimum energy geometry of \( \text{HO}_2 \) on the DMBE IV PES is bent as shown in Fig. 1 and the well depth is \( D_0=2.3791 \text{ eV} \). The zero is taken to be the minimum of the asymptotic \( \text{H}+\text{O}_2 \) potential. There are two \( \text{HO}_2 \) isomers corresponding to the H atom on either side of the \( \text{O} \sim \text{O} \) bond [cf. Fig. 1(a)]. The barrier height for isomerization of \( \text{HO}_2 \) is 1.766 eV on the DMBE IV PES.\textsuperscript{38}

We first report the bound state calculation for the \( \text{HO}_2 \) radical on the DMBE IV PES.\textsuperscript{38} Table I gives a list of 32 bound state energies and their spectroscopic assignments. The symbol \( \nu_1 \) denotes the \( \text{H} \sim \text{O} \) stretch, \( \nu_3 \) denotes the \( \text{H} \sim \text{O} \sim \text{O} \) bend, and \( \nu_2 \) denotes the \( \text{O} \sim \text{O} \) stretch. The energies listed in Table I are relative to the ground state energy \( E_0=2.0158 \text{ eV} \). Thus the zero point energy is \( E_{0z}=E_0-D_0=0.3633 \text{ eV} \) and the dissociation energy is \( D_0=2.11367 \text{ eV} \), where \( E_{2z}=0.09778 \text{ eV} \) is the ground state energy of \( \text{O}_2 \) \((\nu=0, j=1)\). Our calculation shows that the DMBE IV PES supports at least 280 bound states for odd exchange symmetry (odd \( \text{O}_2 \) rotation). No attempt is made to converge highly excited bound state energies at present. The calculated fundamental vibrational frequencies of \( \text{HO}_2 \) on the DMBE IV PES are shown in Table II together with the experimental values. Table II shows that all three theoretical frequencies are below the experimental values ranging from about 30 cm\(^{-1}\) for the \( \nu_3 \) to as high as 93 cm\(^{-1}\) for the bending frequency \( \nu_2 \). This shows that the DMBE IV PES needs to be improved in order to accurately reproduce the spectroscopic data. Our calculated vibrational frequencies are in good agreement with those calculated by Varandas et al.\textsuperscript{20}
B. Reaction probabilities

The numerical parameters for the wave packet propagation are as follows: the grid in $R$ extends from 0.6 to 11.6 bohr and in $r$ from 1.3 to 14 bohr. One hundred evenly spaced grid points are used in the $R$ dimension. A rotational basis with $j_{\text{max}}=69$ is found sufficient to give converged total reaction probabilities at low energies. Reaction probabilities at high energies require up to $j_{\text{max}}=89$ to converge. The interaction region in $R$ is varied from about 6 to 8.5 bohr to obtain convergence. The initial wave packet is chosen to have a narrow width in the $R$ coordinate in order to cover a sufficient range of energies, so that only one wave packet propagation is needed to generate reaction probabilities for all the energies of interest. The wave packet propagation is carried out using a time increment of $\Delta=7.5$ a.u., which is sufficiently accurate for present calculations.

The quantum dynamics calculation for the H+O$_2$ reaction is complicated by two factors. First, the reaction involves long-lived resonances associated with the existence of a deep well corresponding to the bound HO$_2$. This generally requires long propagation time in order to resolve long-lived resonance peaks. Second, the exit channel O+OH has long-range attractive forces that require the use of a large grid. However, if one is interested in only the final state-summed total reaction probabilities, the long-range potential may be cut off so a smaller grid can be used to obtain the total reaction probabilities without any significant loss of accuracy as will be shown later.

Time-independent calculations have recently been reported for the H+O$_2$ reaction on the DMBE IV PES. Pack et al. obtained initial state-selected total reaction probabilities for energies up to 1.42 eV using the hyperspherical coordinate approach.$^{40}$ Leforestier and Miller obtained cumulative reaction probabilities using the reactive flux formalism for energies up to 1.1 eV.$^{51}$ Both results are in general agreement with each other and resonances are found to dominate the reaction probabilities.

### Table I. Bound state energies of HO$_2$(A*) for total angular momentum $J=0$ and for odd exchange symmetry of O$_2$ on DMBE IV PES relative to the ground state energy at $-2.0158$ eV. The minimum of the potential well is $-2.3791$ eV and zero corresponds to the minimum of the H(3S)+O$_2$(X$_2^2$) potential. $\nu_1$ corresponds to the OH stretch, $\nu_2$ corresponds to the HOO bending, and $\nu_3$ corresponds to the OO stretch.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Energy (eV)</th>
<th>($\nu_1$, $\nu_2$, $\nu_3$)</th>
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</thead>
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<tr>
<td>1</td>
<td>0.0000</td>
<td>(0 0 0)</td>
</tr>
<tr>
<td>2</td>
<td>0.1321</td>
<td>(0 0 1)</td>
</tr>
<tr>
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<td>0.1637</td>
<td>(0 1 0)</td>
</tr>
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<td>4</td>
<td>0.2593</td>
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<td>5</td>
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</tr>
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<td>6</td>
<td>0.3121</td>
<td>(0 2 1)</td>
</tr>
<tr>
<td>7</td>
<td>0.3820</td>
<td>(0 3 0)</td>
</tr>
<tr>
<td>8</td>
<td>0.4134</td>
<td>(1 0 0)</td>
</tr>
<tr>
<td>9</td>
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<td>(0 1 0)</td>
</tr>
<tr>
<td>10</td>
<td>0.4256</td>
<td>(0 2 1)</td>
</tr>
<tr>
<td>11</td>
<td>0.4620</td>
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<td>0.6612</td>
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<td>23</td>
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<td>25</td>
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<td>(0 16 5)</td>
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<td>26</td>
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<tr>
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</tr>
<tr>
<td>30</td>
<td>0.7964</td>
<td>(0 21 10)</td>
</tr>
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<td>31</td>
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<td>(0 22 11)</td>
</tr>
<tr>
<td>32</td>
<td>0.8135</td>
<td>(0 23 12)</td>
</tr>
</tbody>
</table>

### Table II. A comparison of the calculated fundamental vibrational frequencies of the hydroperoxy radical (HO$_2$) on the DMBE IV PES (Ref. 38) with experimental measurements. The frequencies are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Calculation</th>
<th>Milligan and Jacob$^*$$^{47}$</th>
<th>Ogiulv$^b$$^{48}$</th>
<th>Paukert and Johnston$^b$$^{49}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>3339</td>
<td>3414</td>
<td>3412</td>
<td>3410</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1297</td>
<td>1390</td>
<td>1395</td>
<td>1390</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1065</td>
<td>1101</td>
<td>1104</td>
<td>1095</td>
</tr>
</tbody>
</table>

$^a$Reference 47.

$^b$Reference 48.

$^c$Reference 49.
Figure 2 shows the calculated total reaction probabilities from the ground state of $O_2(v=0, j=1)$ in the energy range of 0.81–0.89 eV computed at different propagation time. Here the scattering energy is defined as the total energy of the reactant $H+O_2$, and the threshold energy for reaction is 0.8115 eV. As shown in Fig. 2, wave packet propagation up to $t=15000$ a.u. yields essentially zero probabilities at energies below 0.89 eV. Some broad peaks already appeared at $t=30$ K and more peaks are seen at $t=50$ K. Thus the resonance structures grow more pronounced and more peaks appear as propagation time increases. The results at the longest time ($t=150$ K$=4$ ps) are in quite good agreement with the TI calculation of Pack et al.$^{40}$ in this energy range. A few narrow resonances in Ref. 40 are missing in the present calculation, and perhaps even longer propagation time is required to resolve them completely. The reaction probabilities are essentially dominated by resonances, in good agreement with Refs. 40 and 41.

The reaction probabilities at high energies are converged in relatively short propagation time. This is shown in Fig. 3, where total reaction probabilities from the ground $O_2(0,1)$ at energies up to 1.45 eV are plotted at four different propagation time. As shown in Fig. 3, most high-energy results are essentially converged at $t=50$ K a.u. The result at $t=50$ K is
not visibly different from that propagated to three times longer ($t=150$ K). Even at $t=15$ K, the reaction probabilities above 1.2 eV already have the basically correct shape. Similar convergence is also seen for reaction probabilities out of vibrationally excited initial states. Figure 4 shows reaction probabilities from several excited vibration states of $O_2(v,1)$ for $v=0$–3. The trend is that vibrational excitation gradually decreases the amplitude of probability. It should be pointed out, however, that the plotted energy is the total scattering energy (internal energy of $O_2$ plus translational energy). Thus it does not imply that the vibrational excitation decreases reaction probability when measured in kinetic energies. It is also clear from Figs. 3 and 4 that resonances persist all the way to high energies without any significant broadening of the widths. In comparing the present reaction probabilities at high energies with those from Ref. 40, we notice that the results in Fig. 4 of Ref. 40 contain too few points at high energies to allow for a meaningful comparison, but the qualitative trend in reaction probabilities is quite similar in both calculations.

We also show in Fig. 5 the total reaction probability at scattering energies up to 2.5 eV. The experimental measurement of the cross section shows a sharp peak at the scattering energy $\sim 2$ eV$^{29-31}$ The QCT calculation by Varandas$^{36}$ shows a rather broad feature around this energy region. The present quantum calculation shows that the reaction probability continues to climb as energy increases and there is no sign of sharp peak at around $E=2$ eV.

It is worth emphasizing at this point the particular feature of the TD wave packet method. The complicated energy

$$H + O_2(v,1) \rightarrow O + HO$$

FIG. 5. Total reaction probabilities from initial state $H+O_2(v=0, j=1)$ for scattering energies up to 2.5 eV.
dependence of the reaction probabilities shown in Figs. 2–5 are mapped out in a single wave packet propagation for hundreds of energies at only a fractional cost of the total wave packet propagation. This is extremely attractive for systems like H₂O₂, for which several hundreds of close-coupling (CC) calculations need to be repeated in order to map out the resonance structures in the standard propagation approach. Such energy-dependent propagation could be very expensive computationally as the CPU time in each CC propagation scales as \( N^3 \).

Another aspect of the present calculation is related to the long-range attractive forces between O and OH in the product arrangement. Figure 6 shows a plot of the potential energy as a function of the O₂ diatomic distance \( R_{OO} \) minimized with respect to other two internal coordinates. The asymptotic value is 0.58151 eV as \( R_{OO} \) approaches infinity. We have placed absorption potential at as far as \( R_{OO}=12 \) bohr in order to obtain converged results for almost all the energies except a few extremely low energies. Such a calculation requires a quite large grid for the interaction region and is computationally expensive. If we are interested in the total (final state-summed) reaction probabilities only, we could employ a scheme to cut off the PES in the product arrangement to artificially shortened the long-range force. This is shown in Fig. 6 by the dashed line which denotes a modified PES. The modified PES is obtained simply by multiplying the PES by a smooth cut-off function in the product arrangement, so that it reaches its asymptotic value much quickly as shown in Fig. 6. The calculation on the curtailed PES requires a smaller grid and the absorption can start at about 6 bohr. In fact, the results are generally insensitive to cut-off parameters except at very low energies. Thus the computation on the curtailed PES is much smaller compared to that on the original DMBE IV PES. The reaction probabilities on the curtailed PES are compared to those on the original PES in Fig. 7. Although some small deviations are observed, the results on the curtailed PES are generally in excellent agreement with those on the original PES.

IV. CONCLUSIONS AND DISCUSSIONS

A time-dependent quantum dynamics calculation for the combustion reaction H+O₂ on the DMBE IV PES has been presented. The H+O₂ reaction system has a deep well and support numerous resonances. The TD method maps out the resonance structures (energy dependence of the reaction probabilities) from a single wave packet propagation. The H+O₂ reaction is dominated by resonances and our calculated initial state-selected total reaction probabilities are in good agreement with the TI calculation of Pack et al.⁶⁰ Resonances persist all the way to the highest energies in our calculation. The lifetime of most resonances are in subpicoseconds and a few are in picoseconds. The long-range potential in the product arrangement could be artificially shortened for the calculation of total reaction probabilities without any significant loss of accuracy.

Bound state calculation for the HO₂ radical has also been carried out, and the energies of 32 lowest bound states and their spectroscopic assignments are given for the odd nuclear exchange symmetry (odd O₂ rotation). The calculated vibrational frequencies on the DMBE IV PES are lower than the experimental measurements, indicating the need for further improvement of the PES.

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