Three-Dimensional Study of Reactive Diatom–Diatom Systems: Quantum Mechanical State-to-State Cross Sections for the H₂ + OX → H + XOH (X = H, D) Reactions

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A detailed quantum mechanical study is made of the three-dimensional tetraatom systems H₂(ν₂) + OX(ν₀) → XOH(ν', j', v) + H (X = H, D). The study is limited to the case where the overall final rotational state K of the product XOH molecules is zero. The calculations are carried out using the negative imaginary arrangement decoupling potentials. The quasi-breathing-sphere approximation is employed for the reagent arrangements and the j₀ approximation for the product arrangements. State-to-state and state-selected cross sections are calculated for the (translational) energy range 0.1–0.7 eV.

I. Introduction

In the present work we consider the two isotopic diatom–diatom reactions

\[ H_2(\nu_2) + OX(\nu_0) \rightarrow HOX(\nu', j', v) + H \quad (X = H, D) \quad (I) \]

with the aim of calculating state-to-state reactive cross sections (CS). Numerous experimental and numerical studies of those reactions and of the reverse reactions

\[ H + HOX(\nu', j', v) \rightarrow H_2 + OX \quad (II) \]

have been published in the last 15 years. At the beginning of the 1980s Zellner and Steinert1 and Chaturvedi and Glass2 made experimental studies of reaction I. More detailed experiments on reaction II were carried out at the beginning of the 1990s by Sinha et al.3a and by Bronikowski and Zare.3b. Most of these experiments emphasized the effect of the vibrational excitation on the reaction rate. It was found that whereas exciting the reactive bond (namely, the H₂ bond in reaction I or the OH bond in reaction II) strongly enhances the reaction process, exciting the nonreactive bond (the OX bond in both cases) has hardly any effect.

Numerical studies of processes I and II have employed quasi-classical trajectories (QCT)4a,b,6 and variational transition-state,5c semiclassical,2c and quantum mechanical (QM) treatments. Most of these treatments were applied on a potential energy surface calculated by Walch and Dunning4a and fitted by Schatz and Elgersma.2a,c Whereas the QCT calculations were carried out without approximations, the QM calculations employed (sometimes even drastic) approximations to reduce the number of internal degrees of freedom. The results of all theoretical treatments to date supported the experimental outcomes; i.e., they indicated that, in the reaction process, there is a strong involvement of the broken bond and a much weaker involvement of the unbroken bond.

We herewith propose a novel three-dimensional (3D) QM treatment of the above tetraatom reactive system. In this treatment the calculations are performed without ignoring any of the six internal coordinates, and in this sense the treatment is fully 3D.

The theory involves an approximation regarding the potential when the reagent molecules are in the region of close proximity. The reagents are assumed to stay in that region for a very short time, so short that the angular part of the potential is hardly allowed to vary. For that short time the behavior of the potential is that of a breathing sphere (namely, not dependent on any angle);

\[ \lambda = \psi_{\lambda} - \psi_{\lambda_0} \quad (2) \]

the approximation is therefore termed the quasi-breathing-sphere (QBS) approximation. The breathing-sphere potential is formed from the ordinary potential by treating the three reagent Jacobi angles as parameters which are randomly selected by the Monte-Carlo method.4 The calculations are repeated several times, each time for a different set of three angles. The final outcome follows from an averaging procedure, as will be discussed in the next section.

In addition we employ the negative imaginary potentials (NIP)5 in order (a) to convert the problem into a bound system problem and permit the application of L¹ basis sets6 and (b) to decouple unnecessary arrangement channels (AC)6a,b,d,e (the tetraatom system in general contains seven open ACs) so that we can consider only the two relevant arrangement channels without the final numerical results being affected.

In this paper we present the detailed theory of our approach. In order to save time, space, and confusion, the theory is carried out for the ground rotational case, namely

\[ AB(\nu_j) + CD(\nu_j) \rightarrow ABC(\nu_j)\lambda |K=0\rangle + D \]

where K is the total rotational quantum number of the product triatom. The same holds for the numerical study; namely, we will report and analyze cross sections (CS) for K = 0 only. From preliminary calculations that were carried out for K ≠ 0 cases, it was found that the state-to-state CSs for K ≠ 0 are very similar to those of the K = 0 case so that the physical content of the K = 0 study is quite representative for the general case.

II. Theory

The relevant Schrödinger equation to be considered is

\[ (E - H_1)\psi_\lambda = V_\lambda \psi_{\lambda_0} \quad (1) \]

where E is the total energy, \( \psi_{\lambda_0} \) is the \( \lambda \) unperturbed part of the total wave function (henceforth \( \lambda \) designates the atom–triatom AC), \( V_\lambda \) is the relevant perturbation potential, \( H_1 \) is the full Hamiltonian (which contains the relevant NIPs) defined in the \( \nu \) AC (henceforth \( \nu \) designates the diatom–diatom AC), and \( \chi_\lambda \) is the function which stands for the perturbed part of the overall wave function \( \psi_\lambda \). Thus

\[ \chi_\lambda = \psi_\lambda - \psi_{\lambda_0} \quad (2) \]

The aim of the numerical treatment is to obtain the state-to-state S matrix element

\[ S(\nu \rightarrow \lambda) = \langle \psi_{\lambda_0} | V_\lambda | \psi_\lambda \rangle = \langle \psi_{\lambda_0} | V_\lambda | \chi_\lambda \rangle = \langle \psi_{\lambda_0} | V_\lambda + \psi_{\lambda_0} \rangle \quad (3) \]

where \( \psi_{\lambda_0} \) is the \( \nu \) unperturbed wave function and \( V_\lambda \) is the relevant perturbation potential in this AC.

To obtain $S(\rightarrow \lambda)$, it is necessary to carry out the following steps.

II.1. Derivation of the Unperturbed Wave Functions $\psi_{\alpha \beta} (\alpha = \lambda, \nu)$. To derive $\psi_{\alpha \beta}$ (where $\alpha = \lambda, \nu$), we consider the unperturbed Hamiltonian $H_{\alpha \beta}$ and the relevant Schrodinger equation (SE)

$$ (E - H_{\alpha \beta}) \psi_{\alpha \beta} = 0 \quad (\alpha = \lambda, \nu) \quad (4) $$

$H_{\alpha \beta}$ is written in the form

$$ H_{\alpha \beta} = T_{\alpha} + W_{\alpha} \quad (\alpha = \lambda, \nu) \quad (5) $$

where $T_{\alpha}$ is the kinetic energy and $W_{\alpha}$ is the unperturbed potential. Since different clusters are encountered in the two ACs, we discuss each equation (and solution) separately.

II.1.1. Reagent Equation ($\alpha = \nu$). Here two diatoms are encountered, and consequently $T_{\nu}$ takes the form

$$ T_{\nu} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_2^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \mathbf{R}_{\nu}^2} + \frac{\hbar^2}{2\mu} \frac{j_1(j_1+1)}{r_1^2} + \frac{\hbar^2}{2\mu} \frac{j_2(j_2+1)}{r_2^2} + \frac{j_\nu^2}{2\mu} \quad (6) $$

Here $\mu, r_1$, and $j_1$ are the reduced masses, the vibrational coordinates, and the internal rotational quantum numbers, respectively, of the two diatomics, $\mu$ is the $\nu$th reduced mass, $R_\nu$ is the $\nu$th translational coordinate, and $I_\nu$ is the orbital angular momentum operator. If $\mathbf{J}$ is defined as

$$ \mathbf{J}_\nu = J_1 + J_2 $$

and if $\mathbf{J}$ is the total angular momentum (operator) of the system, then $I_\nu$ is written as

$$ I_\nu = \mathbf{J} - \mathbf{J}_\nu \quad (8) $$

Henceforth we shall employ the body-fixed (BF) framework, in which the $z$ axis is assumed to be along $R_\nu$. Next, we introduce the $j_1$ approximation, and consequently the scalar representation of $I_\nu^2$ is

$$ I_{\nu \nu}^2 = \hbar^2(J(J+1) - 2\Omega^2) + \mathbf{J}_\nu^2 \quad (9) $$

where $\Omega$ is the projection of both $J$ and $J_\nu$ along $R_\nu$. To evaluate $J_{\nu \nu}^2$, we apply once more the $j_1$ approximation, i.e., $J_{\nu \nu}^2$ will be presented as

$$ J_{\nu \nu}^2 = \hbar^2(j_1(j_1+1) - 2\Omega j_\nu + j_\nu^2) \quad (10) $$

where $m_\nu(i = 1, 2)$ are the projections of $j_\nu(i = 1, 2)$, respectively, along $R_\nu$. It can be seen that

$$ \Omega = m_1 + m_2 \quad (11) $$

As for $W_{\nu}$, it is assumed to be of the form

$$ W_{\nu}(r_1r_2R_\nu, \gamma_1\gamma_2) = v_1(r_1) + v_2(r_2) + w_\nu(R_\nu) \quad (12) $$

where $v_1(r_1)$ and $v_2(r_2)$ are the asymptotic vibrational potentials of the two diatomics, $w_\nu(R_\nu)$ is the $\nu$th distortion potential (assumed to increase once $R_\nu$ is small enough and decreases), $\gamma_1(i = 1, 2)$ are two Jacobi angles defined as

$$ \gamma_1 = \cos^{-1}(\hat{R}_\nu \hat{r}_1) \quad (i = 1, 2) $$

and $\hat{r}_1$ is the angle between the $(\hat{R}_\nu, \hat{r}_1)$ and $(\hat{R}_\nu, \hat{r}_2)$ planes. The potential $w_\nu(R_\nu)$ is usually taken as

$$ w_\nu(R_\nu) = U(r_1, r_2, R_\nu, \gamma_{10}, \gamma_{20}) \quad (14) $$

where $U$ is the full potential expressed in terms of the $\gamma$th coordinates, $r_{10}$ and $r_{20}$ are diatomic asymptotic equilibrium distances and $\gamma_{10}$ and $\gamma_{20}$ are three fixed angles to be discussed later.

Since the $W_{\nu}$ potential is separable in terms of all variables, the solution of eq 4 can be written as

$$ \psi_{\nu \beta}(r_1r_2R_\nu, \gamma_1\gamma_2) = \phi_{\nu \beta}(r_1, r_2) \phi_{\nu \beta}(R_\nu, \gamma_1, \gamma_2) \quad (15) $$

where $\phi_{\nu \beta}(r_1, r_2)$ are the $\nu$th vibrational eigenfunctions, $\phi_{\nu \beta}(R_\nu)$ are the respective spherical harmonics, $\phi_{\nu \beta}(r_1, r_2)$ is the corresponding translational function, and $t_\nu$ stand for the three quantum numbers $n_\nu, j_\nu, m_\nu$. Here $n_\nu$ and $j_\nu$ are vibrational and rotational quantum numbers and $m_\nu$ is the $z$ component of $j_\nu$ with respect to $R_\nu$ (the $\nu$th BF $z$ axis). As for $t_\nu$, the final results will depend only on $\delta = \delta_2 - \delta_1$ (the Jacobi coordinates for the two interacting diatomics are shown in Figure 1a).

II.1.2. Product Equation ($\alpha = \lambda$). In the case of $\alpha = \lambda$ one encounters an atom and a triatom, and consequently $T_\lambda$ becomes

$$ T_\lambda = -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial \rho^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \mathbf{R}_\lambda^2} + \frac{J^2}{2mr} + \frac{(\hat{K} - J_0)^2}{2\mu} \quad (16) $$

Here $m$ and $\mu$ are the reduced masses of one reagent diatom (say AB; see Figure 1) and of the triatom (ABC), respectively, $r$ is the vibrational coordinate of AB ($r = r_1$), $\rho$ is the corresponding...
The HHOH system

<table>
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<td>0.0</td>
<td>(0,0)</td>
<td>(0,0)</td>
</tr>
</tbody>
</table>

The HHOD system

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>H+HOD</th>
<th>H₂+OD</th>
</tr>
</thead>
<tbody>
<tr>
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<td>(0,1)</td>
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</tr>
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</tr>
<tr>
<td>0.0</td>
<td>(0,0)</td>
<td>(0,0)</td>
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</tbody>
</table>

Figure 2. Eigenstates for the HHOH and the HHOD systems.

"translational" coordinate of the triatom, \( \mu_1 \) is the reduced mass of the atom–triatom system, \( R_0 \) is the corresponding translational coordinate, \( \vec{j} \) is the rotational angular momentum of AB with respect to C, \( \vec{K} \) is the total angular momentum of the triatom, and \( \vec{J}_k \) is the corresponding orbital angular momentum. Again the \( j_k \) approximation is employed twice. First \( \rho \) is considered to be the BF \( z \) axis for the triatom system, and consequently the scalar representation of \( (\vec{K} - \vec{j})^2 \) is

\[
(\vec{K} - \vec{j})^2 = \hbar^2 \left[ J(J + 1) + K(K + 1) - 2 \Omega_0^2 \right]
\]

where \( \Omega_0 \) is the projection of \( \vec{K} \) and \( \vec{j} \) along \( \rho \). Next \( \vec{R}_0 \) is considered to be the BF \( z \) axis for the atom–triatom system, and consequently the scalar representation of \( \vec{J}_k^2 \) is

\[
\vec{J}_k^2 = \hbar^2 \left[ J(J + 1) + K(K + 1) - 2 \Omega_0^2 \right]
\]

where \( \Omega_0 \) is the projection of both \( K \) and \( J \) along \( \rho \). As for \( W_\lambda \) it is assumed to be of the form

\[
W_\lambda(r_\rho, \theta, \beta, \gamma) = v(r_\rho) + w_\lambda(R_\rho) \tag{19}
\]

where \( v(r_\rho) \) is the potential of the isolated triatom, \( w_\lambda(R_\rho) \) is the \( \lambda \)th distortion potential which is assumed to increase once \( R_\rho \) is small enough and decreases, \( \theta \) and \( \beta \) are the spherical angles relating \( R \) to \( \rho \); in particular \( \theta \) is defined as

\[
\theta = \cos^{-1}(\rho_R^{(R)}). \tag{20}
\]

The potential \( w_\lambda(R_\rho) \) is usually taken as

\[
w_\lambda(R_\rho) = U(R_\rho, \rho_\rho, \rho_\gamma) \tag{21}
\]

where \( U \) again is the full potential, this time expressed in terms of \( \lambda \) coordinates, and \( \rho_\rho, \rho_\rho, \text{ and } \rho_\gamma \) are the equilibrium coordinates for the triatom. \( \beta \) and \( \gamma \) are two spherical coordinates relating \( \rho \) to \( R_\rho \); in particular \( \gamma \) is the angle between \( R_\rho \) and \( \rho \), namely

\[
\gamma = \cos^{-1}(\rho_R^{(R)}). \tag{22}
\]

\( \beta \) and \( \gamma \) are fixed angular values which serve as parameters, and the final results are expected not to be dependent on them (the same as for \( \rho_\rho, \rho_\rho, \text{ and } \rho_\gamma \)). The Jacobi coordinates for the interacting atom–triatom system are shown in Figure 1b.

In what follows we assume that \( \vec{K} = 0 \) and consequently also \( \Omega_0 = \Omega_0 = 0 \). Since the \( W_\lambda \) potential is separable, the solution of eq 4 can be written as

\[
\psi_\lambda(R_\rho, \theta, \beta, \gamma | \rho_\rho, \gamma_\gamma) = (1/r_\rho R_\rho) \phi_\lambda(r_\rho | \rho_\rho, \gamma_\gamma) \zeta_\lambda(R_\rho | \rho_\rho, \gamma_\gamma) \tag{23}
\]

where \( \phi_\lambda(r_\rho | \rho_\rho, \gamma_\gamma) \) are the eigenfunctions of the equation

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_\rho^2} - \frac{\hbar^2}{2\mu_\rho^2} \frac{\partial^2}{\partial \rho_\rho^2} - \frac{\hbar^2}{2\mu_\gamma^2} \frac{\partial^2}{\partial \gamma_\gamma^2} + \frac{j^2}{2(m \rho_\rho^2 + 1/\mu_\rho^2)} + \omega(R_\rho) - \epsilon(\rho_\rho, \gamma_\gamma) \right] \phi_\lambda(r_\rho | \rho_\rho, \gamma_\gamma) = 0 \tag{24}
\]

and \( \zeta_\lambda(R_\rho | \rho_\rho, \gamma_\gamma) \) are the solutions of the equation

\[
\left[ -\frac{\hbar^2}{2\mu_\lambda} \frac{\partial^2}{\partial R_\lambda^2} + \omega(R_\rho) + \frac{\hbar^2}{2\mu_\lambda} \left( J(J + 1) - \frac{1}{R_\lambda^2} \right) - \frac{\hbar^2}{2\mu_\lambda} k^2(\rho_\rho, \gamma_\gamma) \right] \zeta_\lambda(R_\rho | \rho_\rho, \gamma_\gamma) = 0 \tag{25}
\]

Here \( \epsilon(\rho_\rho, \gamma_\gamma) \) are eigenvalues and \( k(\rho_\rho, \gamma_\gamma) \) is defined as

\[
k(\rho_\rho, \gamma_\gamma) = ((2\mu_\lambda/\hbar^2)(E - \epsilon(\rho_\rho, \gamma_\gamma)))^{1/2} \tag{26}
\]

The eigenvalues for this (the product) AC as well as for the reagent AC are presented in Figure 2.

In the general case when \( K \neq 0 \), the expression in eq 23 should be multiplied by \( d_\lambda^2(\rho_\rho, \gamma_\gamma) \), the representation of the rotation matrix with respect to the \( R_\rho, \gamma_\gamma \) axis.13

II.2. Derivation of the Perturbed Function \( \chi_\lambda \). The function \( \chi_\lambda \) is derived by solving eq 1 in the \( \nu \) AC (the AC of the two interacting diatoms). For this sake the \( \nu \) AC is enlarged significantly by extending the range of the reagent vibrational coordinate(s) into the corresponding reactive AC(s). In our particular case only one reactive bond is encountered, namely, the \( H_2 \) bond; consequently, as will be seen, the calculations are carried out for an extended range of the \( H_2 \) vibrational coordinate \( r_\nu \), i.e., \( 0.4 \leq r_\nu \leq 3.2 \) Å.

The Hamiltonian \( H_\nu \) in eq 1 will be written in the form

\[
H_\nu = T_\nu + U(R_\rho, \gamma_\gamma) \tag{27}
\]

where \( T_\nu \) is the kinetic energy operator, \( U \) is the QBS potential expressed in terms of the \( \nu \) coordinates, and \( V(R_\rho, \gamma_\gamma) \) is the required NIP to be discussed later. Henceforth we assume \( U(R_\rho, \gamma_\gamma) \) to be dependent on only the three Jacobi distances \( R_\rho, \gamma_\gamma \).
A potential like this one is obtained by treating the three internal Jacobi angles $\gamma_1$, $\gamma_2$, and $\delta$ as parameters and not as variables. Consequently,
\[
U(R, r_1, r_2) = U(R, r_1, r_2)\gamma_1 = \gamma_{10} - \gamma_{20}\delta = \delta_0
\] (28)

It follows that each calculation is to be carried out for fixed values of these angles but that the overall numerical treatment is to be done for several Monte-Carlo randomly selected sets of these angles. As for $T_m$, it is assumed to be identical to that presented in eq 6, with the additional definitions given in eqs 9–14. It is important to emphasize that within the QBS the two quantum numbers $j_1$ and $j_2$ do not change and remain identical to their asymptotic values.

As already mentioned, the third term in eq 27 is the NIP. The NIP is made up of several terms. They number three internal Jacobi angles $y_1$, $y_2$, and $\delta_2$ as parameters and not as variables. Consequently, the Hamiltonian: a vibrational term $V_{19}$, and the translational term $V_{29}$.

\[
V_1(R_1, r_1, r_2) = -i(v_{19}(r_1) + v_{29}(R))
\] (29)

The potentials are assumed to be the Neuhauser–Baer (BN) linear ramp potentials:
\[
V_1(x) = \left\{ \begin{array}{ll}
\frac{\varepsilon - x_1}{\Delta x_1} & ; x_1 \leq x \leq x_1 + \Delta x_1 \\
0 & ; \text{otherwise}
\end{array} \right.
\] (30)

Here $x_1$ is a point in the asymptotic region, $\Delta x_1$ is the range along which $V_{19} \neq 0$ and $V_{29} = 0$. The potential is the height of the potential. The two parameters $\Delta x_1$ and $V_{29}$, are determined according to the BN inequalities.

Returning to eq 1 (and eq 3), it is noticed that $V_{19}$ ($V_29$) must still be presented explicitly. In both cases $V_{19} (\alpha = \lambda > 0)$ is defined as

\[
V_{19} = U - W_{19} \quad (\alpha = \lambda, \nu)
\] (31)

where $W_\lambda$ and $W_\nu$ are given in eqs 12 and 19, respectively.

We continue to describe the derivation of $\chi_\lambda$. Since the whole treatment is to be carried out in the $\nu AC$ for a given fixed set of three Jacobi angles $(\gamma_1, \gamma_2, \delta)$, we shall omit the index $\nu$ and any references to these angles.

Adding the two NIPs to the real potential converts the scattering problem into a bound system problem, and consequently $\chi_\lambda$ can be expanded in terms of square integrable $L^2$ functions.\(^{6,11}\) The ones we chose are localized functions for the translational components and adiabatic basis sets related to the two vibrational coordinates.\(^{12}\)

To continue, we shall refer to a simplified case, where $m_1 = m_2 = 0$. Consequently $\chi_\lambda$ will be written as
\[
\chi_\lambda(R_1, r_2) = \sum_{j_2} \phi_{19}(j_1 | j_2 | q | \nu) g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu)
\] (32)

Here $g(R_{19})$ is the localized Gaussian function:\(^{12}\)
\[
g(R_{19}) = \frac{(\alpha)}{\pi^{1/2}} \exp \left[-\frac{\sigma^2 (R - R_{19})^2}{2} \right]
\] (33)

where $R_{19}$ is the grid size $\sigma = R_{q} - R_{q-1}$.

The potential $f(r_1, r_2 | j_1 | j_2 | q | \nu)$ is an eigenfunction of the equation
\[
\left[ \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_2^2} + U(r_1, r_2) \right] f(r_1, r_2 | j_1 | j_2 | q | \nu) = \frac{\hbar^2}{2\mu} \left( j_1(j_1 + 1) + \frac{j_2(j_2 + 1)}{\mu} \right) - \epsilon |j_1 | j_2 | R_{19} | f(r_1, r_2 | j_1 | j_2 | q | \nu) = 0
\] (35)

where $\epsilon |j_1 | j_2 | R_{19} |$ is the corresponding eigenvalue $(t$ is the integer quantum number related to the eigenstate of eq 35).

The $\sigma^2 |j_1 | j_2 | q | \nu$ coefficients will be obtained following the substitution of eqs 32, 27, and 23 into eq 1 and from the solution of the relevant system of algebraic equations:
\[
(A^j - iB) \psi^j = Z^j
\] (36)

where
\[
A^j = \left\{ \begin{array}{l}
\langle g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu) | E - H(R_{19} | q \nu) \rangle f(r_1, r_2 | j_1 | j_2 | q | \nu) \\
\langle g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu) | d_\nu \rangle f(r_1, r_2 | j_1 | j_2 | q | \nu)
\end{array} \right.
\] (37a)

\[
Z^j = \int \int d_\nu \langle g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu) | \\
| d_\nu \rangle f(r_1, r_2 | j_1 | j_2 | q | \nu) f(r_1, r_2 | j_1 | j_2 | q | \nu)
\] (37b)

and
\[
B_{\psi^j} = \langle g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu) | \psi^j \rangle + \langle \psi^j | g(R_{19}) f(r_1, r_2 | j_1 | j_2 | q | \nu) \rangle
\] (37c)

Here $H$ is the full (real) Hamiltonian, $\psi^j$ is the representation of the rotation matrix with respect to the $R_\nu$ axis,\(^{13}\) and $\Delta$ is the polar angle between $R_\nu$ and $R_{19}$. It is important to mention that in the general case the integrand in eq 37b has to be multiplied by $d_\nu(\Delta)$ where $\Omega_0$ and $\Omega_\nu$ were introduced before (see eqs 11 and 18).

Once $\psi^j$ is calculated, eq 3 is used to calculate the required $S(\nu - \lambda)$ element. For this sake we substitute eqs 15, 23, and 32, integrate over $R_{19}, r_1$ and $r_2$, and sum over all the randomly related sets of three Jacobi angles $(\gamma_1, \gamma_2, \delta)$. The relevant state-to-state cross sections are calculated from the expression
\[
\sigma(vj' \leftrightarrow n_1, n_2j_2) = \left\{ \frac{\pi}{k^2(n_1, n_2j_2)} \sum_{j_1} |S_{j_1}vj' \leftrightarrow n_1, n_2j_2|^2 \right\}
\] (38)

where
\[
k(n_1, n_2j_2) = (2\mu / h^2)(E - \epsilon_{n_1} - \epsilon_{n_2j_2})^{1/2}
\] (39)

Here $\epsilon_{n_2}$ ($i = 1, 2$) are (initial) eigenvalues of the two asymptotic diatoms.

### III. Numerical Details

As specified, the numerical treatment was performed for the exchange process
\[
H_2(v_0) + \text{O}_X(v_0) - \text{HOX}(v_j') + H \quad (X = H, D)
\]

We report on state-to-state cross sections for three different initial states, namely, (0, 0), (0, 1), and (1, 0) and for $\sim 20$ final states where the range of $v_0(\nu)$ is (0, ..., 3) and the range of $J$ is (0, ..., 6). To carry out the calculations, the translational coordinate $R_{19}$ was divided by 30–35 equidistant division points. To each point was attached one exponential as a translational basis function and a set of vibrational adiabatic basis functions. The number of these functions varied from one division point to the other and was determined by a given energy value (see discussion in ref 6c).

The range of $R_{19}$ was divided into two regions: the one along...
which the NIP was defined (this region is located in the asymptotic part of $R_i$) and the other where the NIP was identically zero. In the present treatment, the whole range of $R_i$ was 1.0-4.5 Å, and the one along which the NIP is different from zero was [$R_i$, $R_i + \Delta R_i$] = [3.8-4.5 Å]. The height of the NIP, namely, $\nu_{\text{NIP}}$, was 0.6 eV.

The following distinction was made for the two vibrational coordinates $r_1$ and $r_2$. The range for the reactive bond was assumed to be 0.4-3.2 Å whereas the range for $r_2$—the nonreactive bond—was taken as 0.5-1.8 Å.

The size of the matrix to be calculated and inverted in each case depended on the total energy and on the mass of the X atom (whether H or D). Usually these sizes were in the range of 300-600.

These inversions had to be done for each value of $J$ and each set of three angles ($\gamma_1, \gamma_2, \delta$). The range from $J_{\text{max}}$ was 30-45, again depending on the energy and the X mass. As for the Monte-Carlo selected angles, the calculations were based on ~40 sets which were distributed among three groups to enhance convergence. Each group was attached to a geometrical region in configuration space. The size of these regions was determined according to their relative contributions to the cross sections (a fourth region, the largest by far, was excluded altogether, as it was found, after a careful study, that no reactions originated from there). For instance, it was realized that in the low-energy region most of the reactive interactions were from quasi-collinear configurations. Contributions from other configurations became more frequent as the energy increased.

A large number of computer runs were performed in order to determine the optimal set of parameters to carry out the calculations (a similar study is described in ref 6e for the triatom system). In the present paper we will refer only to the rate of convergence of the state-to-state cross sections with regard to the number of sets of Jacobi angles ($\gamma_1, \gamma_2, \delta$). This study is presented in Figure 3 and Table 1. In general 40 sets of these angles were required to achieve convergence within 10%.

Before showing and discussing the results, we present in Figure 2 a diagram of the initial and final states for the HHOH and HHOD systems. Its main features are the exothermicities which are ~0.5 eV for the (0,0) initial state and ~1.0 eV for the (1,0) and (0,1) states.

IV. Results and Discussion

Integral cross sections for the two processes

$$\text{XO}(0) + \text{H}_2(0) \to \text{XOH}(\nu'=0) + \text{H} \quad (\text{X} = \text{H, D}) \quad (1a)$$

as a function of translational energy are shown in Figure 4.
3D Study of Reactive Diatom–Diatom Systems

Figure 4. Total reactive cross sections as a function of translational energy for the systems \( \text{H}_2(0) + \text{OH}(1) \rightarrow \text{H}_2\text{O}(K=0) + \text{H} \) and \( \text{H}_2(0) + \text{OD}(0) \rightarrow \text{HDO}(K=0) + \text{H} \).

Figure 5. Relative state-to-state cross sections (%) as a function of translational energy:
(a) \( \text{H}_2(0) + \text{OH}(0) \rightarrow \text{H}_2\text{O}(v''u'|K=0) + \text{H} \),
(b) \( \text{H}_2(0) + \text{OD}(0) \rightarrow \text{HDO}(v''u'|K=0) + \text{H} \).

TABLE 1: Convergence Study with Respect to the Number of Sets of the Three Jacobi Angles \( \gamma_1, \gamma_2, \) and \( \delta \):

<table>
<thead>
<tr>
<th>initial state</th>
<th>( \nu )</th>
<th>( \nu' )</th>
<th>translational energy (eV)</th>
<th>28 sets</th>
<th>33 sets</th>
<th>38 sets</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.700</td>
<td>0.64</td>
<td>0.64</td>
<td>0.70</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.203</td>
<td>0.50</td>
<td>0.52</td>
<td>0.58</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.275</td>
<td>0.18</td>
<td>0.18</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Interestingly, no isotopic effect is detected; the cross sections for the two processes are identical within the accuracy of the calculation. Product distributions for the two systems are shown in Figure 5, as a function of translational energy. As for the HHOH system, with only a few exceptions, no inversion processes are observed; namely, the lower the respective eigenstate, the higher its population. Moreover, hardly any selectivity is seen with respect to the two internal vibrational motions. A somewhat different situation is encountered for the HHOD system. Here the nice order concerning the relative populations of the various states obtained for the HHOH system is not preserved anymore. This is true not only for the highest energy but even for the lower energies. The most prominent case is the (100) state which along the whole studied energy range is much less populated than the (001) and (030) states, although both these states are energetically higher (it is important to emphasize that in the notation \( (v''u'|K=0) \) for the DOH molecule, \( v \) stands for the OD local mode and \( v' \) for the OH local mode, whereas for the HOH molecule, \( v \) stands for the asymmetric mode and \( v' \) for the symmetric one). This fact has to do with adiabaticity of the nonreactive (OD) bond in this system as was discussed previously.

Figure 6. State-to-state cross sections as calculated for \( E_{\text{tot}} = 1.181 \text{ eV} \):
(a) \( \text{H}_2(0) + \text{OH}(0) \rightarrow \text{H}_2\text{O}(v''u'|K=0) + \text{H} \) \( (E_t = 0.700 \text{ eV}) \),
(b) \( \text{H}_2(1) + \text{OH}(0) \rightarrow \text{H}_2\text{O}(v''u'|K=0) + \text{H} \) \( (E_t = 0.203 \text{ eV}) \),
(c) \( \text{H}_2(0) + \text{OH}(1) \rightarrow \text{HOH}(v''u'|K=0) + \text{H} \) \( (E_t = 0.275 \text{ eV}) \).

Another feature to emerge from the calculations is the fact that the relative populations of the (000) state in both systems decrease as a function of energy at the expense of the population of the higher bend states (the relative populations of the two vibrational modes are only slightly affected by the energy increase).

In Figures 6 and 7 are shown the final product state distributions for a fixed total energy (but for different translational (or internal) energies of the reactants). The results for the HHOH system are presented in Figure 6 for \( E_{\text{tot}} = 1.181 \text{ eV} \) and those for the HHOD system in Figure 7 for \( E_{\text{tot}} = 1.026 \text{ eV} \) (the translational energies for the various initial states are given in Table 2). It can be seen that the initial states of the reagents have a strong effect on the product distributions. Whereas when the reagents are in their ground states most of the product molecules are formed in the low bend states (see Figures 6a and 7a), exciting the vibrational states of one of the interacting molecules yields a high percentage of the products in vibrationally excited modes (see Figures 6b,c and 7b,c). These facts are well known for the reagent excited OD molecule and the product DOH molecule. The explanation is based on two features: (a) the OD bond is preserved during the reaction process and (b) the vibrational modes of the DOH molecule are local modes. Consequently the energy, originally
stored in the OD bond, moves smoothly into the OD local mode of the DOH molecule. (Such selectivities were observed also in other kinds of studies.) The situation changes (but only slightly) when it comes to the vibrationally excited OH molecule. Here, like before, the OH bond is preserved during the reaction process, but although the (low) vibrational modes of the HOH molecule are not local (as was explicitly shown in our previous study \(2j\) and also in ref 14), the energy still remains in the vibrational modes, although this time it is distributed between the symmetric and the asymmetric modes of the HOH product molecule. Thus, like in the DOH case, most of the products are formed in vibrationally excited HOH states, but the final distribution between the two modes is determined by statical considerations that follow from Franck-Condon-type models.\(^{16}\)

It is now well accepted that exciting the OD bond will have only a minor effect on the reaction process\(^{1e-h,2}\) and that consequently the distribution of the final bend modes will, at most, be only slightly affected. This is illustrated in Figure 8a, where the relative bend distributions \(P(0,j,0)\) that follow from the reaction \(H_2(0) + OD(0) \rightarrow DOH(0,j,0) + H\) are compared with the sum of the two (relative) distributions \(P(0,j,1) + P(1,j,0)\) that follow from the reaction \(H_2(0) + OD(1) \rightarrow DOH + H\). The two calculations were carried out for the same translational energy, \(E_t = 0.300\) eV.

The calculations for the HHOH system were done for \(E_t = 0.300\) eV; (b) like (a) but for the \(H_2 + OH\) system, calculations were done for \(E_t = 0.275\) eV.

**TABLE 2:** Eigenvalues (eV) and Translational and Total Energies (eV) for the \(H_2 + OX (X = H, D)\) Systems (Numbers Relevant to Figures 6 and 7)

<table>
<thead>
<tr>
<th>(v^*/v')</th>
<th>(\hbar^*/\hbar')</th>
<th>(\hbar^*/\hbar')</th>
<th>(\hbar^*/\hbar')</th>
<th>(\hbar^*/\hbar')</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0</td>
<td>0.481</td>
<td>0.700</td>
<td>1.181</td>
<td>0.413</td>
</tr>
<tr>
<td>0 1</td>
<td>0.906</td>
<td>0.275</td>
<td>1.181</td>
<td>0.726</td>
</tr>
<tr>
<td>1 0</td>
<td>0.978</td>
<td>0.203</td>
<td>1.181</td>
<td>0.910</td>
</tr>
</tbody>
</table>

It is seen that the two distributions are almost identical (note the nice fit for \(j = 3\) in particular). The question is whether this similarity is because the DOH molecule has local modes or whether this is a general feature which results from the adiabaticity of the nonreactive bond. In Figure 8b we show the relevant bend distributions for the \(H_2(0) + OH(v_0) \rightarrow HOH(K = 0) + H\) processes (this time the two calculations were done for \(E_t = 0.275\) eV), and again, as before, the two distributions are similar. This shows that the similarity in the bend distributions results from the adiabaticity of the nonreactive bond.

More about the similarity between the two isotopic reactions is presented in Table 3 where the total cross sections for two different initial vibrational states of the OX \((X = H, D)\) molecules, calculated at the same translational energies (the calculations for the HHOH system were carried out at \(E_t = 0.275\) eV and those for the HHOD system at \(E_t = 0.3\) eV), are compared. In general the four cross sections are similar to each other (the lower cross sections for the HHOH system are due to the lower translational energy and consequently are more markedly affected by the potential barrier).

Part of our study was also devoted to the influence of a vibrationally excited \(H_2\) molecule on the reaction process. In Table 4 are given the total cross sections for the processes \(H_2(v_H) + OX(0) \rightarrow XO + H \quad (X = H, D; \nu_X = 0, 1)\) (the calculations for the HHHO system were done at \(E_{tot} = 1.181\) eV and those

---

**Figure 7.** Same as Figure 6 but for \(E_{tot} = 1.026\) eV and the following reactions: (a) \(H_2(0) + OD(0) \rightarrow DOH(0,j,0) + H\) \((E_t = 0.613\) eV), (b) \(H_2(1) + OD(0) \rightarrow DOH(0,j,0) + H\) \((E_t = 0.116\) eV), (c) \(H_2(0) + OD(1) \rightarrow DOH(0,j,0) + H\) \((E_t = 0.300\) eV).

**Figure 8.** Relative cross sections as a function of the bend quantum number \(j\). (a) \((-\quad\) cross sections for \(H_2(0) + OD(0) \rightarrow DOH(0,j,0) + H\) \((E_t = 0.300\) eV); (b) \((-\quad\) cross sections for the two processes \(H_2(0) + OD(0) \rightarrow DOH(0,j,0) + H\) \((E_t = 0.300\) eV).
TABLE 4: Comparison between Cross Sections ($\sigma_0$) Calculated for the Reactions $\text{H}_2(\text{PH}) + \text{O}(0) \rightarrow \text{HOH}(K=0) + \text{H} (X = \text{H}, \text{D})$ at Fixed Total Energies

<table>
<thead>
<tr>
<th>$\text{PH}$</th>
<th>$\text{HOH}$</th>
<th>$\text{HHOD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.70</td>
<td>0.60</td>
</tr>
<tr>
<td>1</td>
<td>0.58</td>
<td>0.66</td>
</tr>
</tbody>
</table>

* The calculations for the HHOH system were carried out at $E_{tot} = 1.181$ eV and those for the HHOD system at $E_{tot} = 1.026$ eV.

for the HHOD system at $E_{tot} = 1.026$ eV). In general the four cross sections are similar to each other.

These two modes affect the final state distribution of the products much more markedly. Whereas in the case of the H$_2$ ground state most of the products are formed in the low bend modes (see Figures 6a and 7a), large fractions of vibrationally excited XOH molecules are obtained in the case of the excited H$_2$. Here we encounter what is known as the $v \rightarrow v'$ transition law, mentioned frequently for atom–diatom systems. In other words although the H$_2$ bond is the reactive bond, most of the energy stored in this bond moves into the vibrational modes of the product XOH molecule. In the case of the HHOH system this energy is stored solely in the newly formed HO bond (this again is due to the adiabaticity of the OD bond), and in the case of the HHOD this energy is mainly stored in the symmetric mode; however, a large fraction of it is also found in the asymmetric mode.

As was mentioned several times throughout this paper, similar studies were performed by other groups. We are not in a stage of conducting systematic comparisons with results obtained from other approaches because, so far, we considered state-to-state calculations: (1) The calculation of $\sigma_0$ for the products—the atom and the triatom. Like $\sigma_0$, the function $\psi_0$ describes an elastic scattering process. (2) The calculation of $\chi_0$, which is the perturbed part of the total wave function calculated in the enlarged reagent (or product) AC.

V. Conclusions

In what follows we summarize the numerical procedure, emphasizing the approximations that were done. Within the numerical treatment we distinguish between three different calculations: (1) The calculation of $\psi_0$, which is the unperturbed (asymptotic) wave function of the reagents—the two diatomics. The function $\psi_0$ describes an elastic scattering process. (2) The calculation of $\psi_0$, which is the unperturbed (asymptotic) wave function of the products—the atom and the triatom. Like $\psi_0$, the function $\psi_0$ describes an elastic scattering process. (3) The calculation of $\chi_0$, which is the perturbed part of the total wave function calculated in the enlarged reagent (or product) AC.

The two functions $\psi_0$ and $\psi_0$ are treated in their full dimensionality (which also means keeping all relevant quantum numbers); namely, the functions are described employing all six internal coordinates. However, to reduce the computational efforts, we did not use the Arthurs–Dalgarro representation but the one within the $j_s$ approximation. The $\chi_0$ function is also expressed in terms of all six coordinates but is treated within the breathing-sphere approximation. Here the three angles $\gamma_1$, $\gamma_2$, and $\delta$ are considered as parameters of the potential rather than variables, and consequently for each separate calculation the potential becomes isotropic. $\Sigma$ matrix elements were obtained for 45 different randomly selected sets of such angles. The final cross sections are calculated, averaging over these angles. Although it was a relatively heavy calculation, we significantly reduced the amount of programming and computer time by applying NIPs to decouple reactive ACs.

The two isotropic reactions which we considered differ in that the two product–triatomic molecules have different vibrational modes: the HOH molecule is characterized by normal modes, whereas the DOH molecule is characterized by local modes. Although their internal structure was different, we could observe no significant isotopic effects on the reaction process. The magnitude of the total cross sections (for $K = 0$) as a function of translational energy were similar, and the overall internal distributions were almost the same. It is true that, in the OD(1) case, the (1,0,0) state was by far the most populated one (hardly any products were detected in the (0,0,1) state), whereas in the case of OH(1) the two vibrational states (1,0,0) and (0,0,1) were almost equally populated. Still, the sum of the transition probabilities of the two vibrationally excited states was equal to those of the DOH molecule. We also studied the effect of a vibrationally excited H$_2$ molecule on the reaction process and were able to establish the (proper) $v \rightarrow v'$ transition law for the tetramoton system in question.

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References and Notes
