Adiabaticity of the Nonreactive Bond in Atom-Triatom Reactions: A Quantum Mechanical Study of the H + H2O → OH + H2 System

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This work is a quantum mechanical study of the four-atom process H + H2O → H2 + OH and its isotopic analogs. State-to-state reactive probabilities were calculated for the collinear configuration. The adiabatic behavior with regard to the nonreactive bond, as established by Sinha et al. (J. Chem. Phys. 1991, 94, 4298), was confirmed for the H + H2O system but not for the H + H2O one. Enhancement of the reaction process due to vibrational excitation as was established by Sinha et al. and Bronikowski et al. (J. Chem. Phys. 1991, 95, 8645) was fully confirmed for the H + HOD system and for the H + H2O system. The calculations were carried out employing negative imaginary potentials to form absorbing boundary conditions.

I. Introduction

Confidence in the reliability of applying negative imaginary potentials (NIPs) to study time-independent scattering processes in general and exchange processes in particular has been steadily growing.1-10 These potentials were applied not only to collinear1,4,5 and other frozen configurations but to three-dimensional systems as well.5,7 In case of the process D + H2(e') → HD (e') + H, state-to-state reactive probabilities were calculated6 and the results compared with the results from more established approaches;11 very encouraging fits were obtained. Other groups have studied NIPs.8,10 In a detailed study, Seideman and Miller,10 confirmed that accurate reactive transition probabilities are well reproduced employing these potentials. These authors reported, moreover, that different types of potentials, e.g., the Woods-Saxon potential and/or power-law potentials, also yield accurate results, for a wide range of parameters.

The present work extends these treatments to four-atom systems. We report on state-to-state reactive transition probabilities for the three isotopic reactions:

\[
\begin{align*}
H + H_2O(v_0,v') &\rightarrow H_2(v_f) + OH(v_o) \quad (I) \\
H + DHO(v_0,v') &\rightarrow HD(v_f) + OH(v_o) \quad (II) \\
H + HDO(v_0,v') &\rightarrow H_2(v_f) + OD(v_o) \quad (III)
\end{align*}
\]

These processes were the subject of two interesting "bond-oriented chemistry" experiments by Sinha et al.12 and Bronikowski et al.13 In fact the possibility of eventually being able to compare experimental results with theoretical results was the main incentive for the present study. As will be seen, a number of interesting conclusions were reached.

Our collinear study is, to a certain extent, similar to that carried out by Bowman and Wang,14 except that they chose to study a noncollinear frozen configuration. They also used hyperspherical coordinates whereas, as will be shown, we applied Jacobi coordinates.

A number of studies on these systems (but less relevant to our present study) are available.15-17 Among these are the experimental study of Kleinermanns and Wolfrum15 and the detailed classical trajectory calculation of Schatz et al.16 The potential energy surface employed in our work is a modified version18 of the Schatz–Elgersma–Walch–Dunning surface.16-18

We would like to remind the reader that this is our second study of a four-atom system employing NIPs.20 In the previous

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study we considered H2 + H2+ system for which we calculated state-selected probabilities for the reactive process:

\[
H_2(v_i) + H_2^+(v_o) \rightarrow H_2^+(v_f) + H \quad (IVa)
\]

and state-to-state probabilities for the charge-transfer process:

\[
H_2(v_i) + H_2^+(v_o) \rightarrow H_2^+(v_o') + H_2(v_f') \quad (IVb)
\]

The calculations were carried out for various frozen configuration and led finally to state-selected reactive and charge-transfer cross sections.

The paper is organized in the following way: the theory related to the four-atom system is presented in section II, results are shown in section III, the analysis is given in section IV, and the summary in section V.

II. Theory

As has been frequently shown, the relevant equation to be solved is1-7

\[
(E - H_1)x_\lambda = V_\lambda \Psi_{o\lambda}
\]

where \(E\) is the total energy, \(\Psi_{o\lambda}\) is the \(\lambda\) unperturbed part of the total wave function (here \(\lambda\) and later also \(\nu\) designate arrangement channels (AC)), \(V_\lambda\) is the relevant perturbation potential and \(H_1\) is the full Hamiltonian (which contains the relevant NIPs) defined in the \(\nu\) AC. The aim of the numerical treatment is to obtain the following state-to-state \(S\) matrix elements:21

\[
S(\nu\lambda) = \langle \Psi_{o\lambda} | V_{\nu\lambda} | x_\lambda + \Psi_{o\lambda} \rangle
\]

where \(\Psi_{o\lambda}\) is the \(\nu\)-unperturbed wave function and \(V_{\nu\lambda}\) is the relevant perturbation potential17 in this AC. In the present treatment the \(\lambda\) AC is taken to be the (H,H2O) side whereas the \(\nu\) AC is the (H2,O,H2) side. Consequently the Hamiltonian, \(H_1\), relevant for our case is

\[
H_1 = -\frac{\hbar^2}{2\mu_i} \frac{\delta^2}{\delta r_i^2} - \frac{\hbar^2}{2\mu_2} \frac{\delta^2}{\delta r_2^2} - \frac{\hbar^2}{2M_\nu} \frac{\delta^2}{\delta \nu^2} + U(r_1r_2R) - iv_{\nu\lambda}(r_1) - iv_{\lambda\nu}(r_1)
\]

where \(\mu_i\) and \(\mu_2\), \(i = 1,2\) are the reduced masses and the vibrational coordinates, respectively, of the two diatomics, \(R\) is the translational coordinate, \(M_\nu\) is the \(\nu\) reduced mass of the system:

\[
M_\nu = \frac{(m_1 + m_2)(m_3 + m_4)}{m_1 + m_2 + m_3 + m_4}
\]

\(U(r_1r_2R)\) is the full potential energy surface, \(-iv_{\nu\lambda}(R)\) is the translational NIP, and \(-iv_{\lambda\nu}(r_1)\) is the NIP along the bond to be
broken, namely, the H₂ (or the HD) vibrational coordinate. The two imaginary potentials are assumed to be linear ramp potentials of the kind\(^{22}\)

\[ v_{\text{xi}}(x) = \begin{cases} \frac{x - x_1}{\Delta x_1} & x_1 \leq x \leq x_1 + \Delta x_1 \\ v_{\text{out}} & \text{otherwise} \end{cases} \]  

(5)

where \(v_{\text{out}}\) is the height of the potential, \(\Delta x_1\) its width, and \(x_1\) some \(x\) value outside the interaction region.

Since the \(v\) AC is surrounded by absorbing potentials, the wave function \(\chi_1\) can be expanded in terms of \(L^2\) basis sets.\(^{2,21}\) The ones we chose are the Gaussian functions \(^{22,35}\) for the translational component and the adiabatic\(^{23,24}\) (contracted) basis sets for the internal coordinates (in the following all the coordinates \(R_i\) and \(r_{ij} = i = 1, 2\) are from the \(v\) AC and therefore the index \(v\) will be omitted):

\[ x_i(R_1, r_2|n, m_1) = \sum_{n_q} a(n, m_1|q) g(R|q) f(r, q) \]  

(6)

Here \(n_1\) and \(m_1\) designate eigenstates of the water molecule, \(g(R|q)\) is a Gaussian function of the form

\[ g(r, q) = \left(\frac{\alpha}{\pi \sigma^2}\right)^{1/2} \exp\left[-\frac{\alpha^2}{2} \left(\frac{R - R_q}{\sigma}\right)^2\right] \]  

(7)

where \(R_q, q = 0, ..., N\) are equidistant division points along the interval \([0, R_1 + \Delta R_1]\), \(\alpha\) is a dimensionless parameter, and \(\sigma\) is the grid size:

\[ \sigma = R_q - R_{q-1} \]  

(8)

The functions \(f(r, q)\) are eigenfunctions of the equation

\[ \left[ -\frac{h^2}{2m} \frac{\partial^2}{\partial r_1^2} - \frac{h^2}{2m_2} \frac{\partial^2}{\partial r_2^2} + U(r, q) - \epsilon(r, q) \right] \times \]

\[ f(r, q) = \psi_\text{out}(r, q) \]  

(9)

where \(\epsilon(r, q)\) are the corresponding eigenvalues (\(t\) is an integer quantum number related to the \(t\)th eigenstate of eq 9).

The next function to be treated is \(\psi_{\text{out}}(r, q)\) which describes the asymptotic function in the AC. This function is assumed to be a solution of the unperturbed SE (all variables and masses refer to the \(\lambda\) AC):

\[ \left[ -\frac{h^2}{2m} \frac{\partial^2}{\partial r_1^2} - \frac{h^2}{2m_2} \frac{\partial^2}{\partial r_2^2} - \frac{h^2}{2M_\lambda} \frac{\partial^2}{\partial R^2} + W_{\lambda}(r, q) - E \right] \times \]

\[ \psi_{\text{out}}(r, q) = 0 \]  

(10)

where \(r = r_1\) and \(m = \mu_1\) (see eq 3); \(\rho\) is given by

\[ \rho = r_1 + \frac{m_1}{m_1 + m_2} r_1 \]  

(11)

\(\mu\) is the reduced mass of the triatomic molecule:

\[ \mu = \frac{m_1 + m_2}{m_1 + m_2 + m_3} \]  

(12)

\(R\) is the corresponding translational coordinate, and \(M_\lambda\) is the reduced mass of the whole \(\lambda\) system:

\[ M_\lambda = \frac{m_1(m_1 + m_2 + m_3)}{m_1 + m_2 + m_3 + m_4} \]  

(13)

The unperturbed potential \(W_\lambda\) (\(r, q\)) is assumed to be separable with respect to the internal \((r, q)\) and the translational \(R\) coordinates,\(^{23,25}\) i.e.

\[ W_{\lambda}(r, q) = v_{\lambda}(r) + w_{\lambda}(R) \]  

(14)

Here \(v_{\lambda}(r)\) is the potential of the triatomic system and \(w_{\lambda}(R)\) is a potential which decreases as \(R\) increases, defined as

\[ w_{\lambda}(R) = U(r, q) \]  

(15)

where \((r, q)\) is the equilibrium configuration for \(R \rightarrow \infty\).
We start by considering the energy-dependent state-to-state and reactive probabilities for the processes

\[ \text{H} + \text{DOH}(v,0,v') \rightarrow \text{HD}(v_1) + \text{OH}(v_2); \quad (v,v' = 0, 1, 2) \]

The probability curves for \((v = v' = 0); \quad (v = 0, v' = 1); \quad (v = 1, v' = 0); \quad (v = 0, v' = 2); \quad \text{and} \quad (v = 1, v' = 1)\) are shown in Figure 1a–e, respectively. Inspecting the figures it is noticed that as a rule the OH bond does not contribute to nor affect in any way the reaction process. In other words the reaction is adiabatic with respect to this mode of vibration. Thus it is most unlikely that an excited OH starting from \((0,0,0)\) (Figure 1a) or \((1,0,0)\) (Figure 1b) or a deexcited OH starting from \((0,0,1)\) (Figure 1c) can be met. Consequently, the various four-atom reactive

Figure 1. Reactive transition probability as a function of the translational energy for the processes \(\text{H} + \text{DOH}(v,0,v') \rightarrow \text{HD}(v_1) + \text{OH}(v_2)\). \(v'\) refers to the OH mode and \(v\) to the OD mode. (a) Results for \(v = 0, v' = 0\). (b) Results for \(v = 0, v' = 1\). (c) Results for \(v = 1, v' = 0\). (d) Results for \(v = 0, v' = 2\). (e) Results for \(v = 1, v' = 1\).
probability curves are, essentially, characteristic three-atom curves. Such a feature was mentioned by Sun and Bowman who found in their collinear H + HCN studies that the two CN atoms essentially behaved like a single atom. There the adiabaticity was with respect to the CN bond and was attributed to the relatively strong CN bond. Here this is not the case since the OD and OH bonds are of similar strength. There is therefore a different reason. The fact that a heavy oxygen is in between the two light hydrogens seems to decouple the internal collective motion of the three atoms and to form two independent series of modes (local modes) of the motions, each related to one of the light atoms.

A somewhat similar behavior is seen in Figure 2a–e in which we present the reactive probabilities for the processes:

\[ \text{H} + \text{HOD}(v,0) \rightarrow \text{H}_2(v_1) + \text{OD}(v_2) \quad (\text{III'}) \]

Here in case of \( v = v' = 0 \) the reaction product OD(1) is essentially missing (very similar to the previous case) but for \( v = 1, v' = 0 \) and \( v = 0, v' = 1 \) the situation is somewhat different. In the

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**Figure 2.** Reactive transition probability as a function of the translational energy for the processes H + HOD\((v,0,v') \rightarrow \text{H}_2(v_1) + \text{OD}(v_2)\). For notation see Figure 1.
first case (when the OD bond is excited) we got a small amount (<10%) of deexcited OD and in the second case a small amount of excited OD (<10%). Thus the results seem to indicate only a minor intervention of the nonreactive bond in the reaction process.

Thus far, these findings agreed with the experimental results of Sinha et al.\textsuperscript{12} In those experiments, vibrationally excited (HDO) molecules were prepared by laser excitation and allowed to react with slow hydrogen atoms. The study was carried out with local modes [(0,n),0] n = 2, 3, 4 and [(1,3),0]. Reactive products were observed in all four cases but whereas in the first three no excited OH molecules were recorded in the fourth one no ground OH state was observed. This indicated that the reaction process was essentially adiabatic with respect to the nonreacting bond.

To a certain extent the results presented also support the measurements by Bronikowski et al.,\textsuperscript{13} who found that the reactivity of the H + HOD system is enhanced by exciting the relevant bond. It is difficult to make a quantitative comparison but in general the following is found: (a) Exciting the relevant
bond (namely the OD bond to form HD or the OH bond to form H₂) results in lowering the threshold for the reaction (see Figures 1b,d,e and 2c,e); (b) Exciting the nonrelevant bond leaves the threshold almost unaffected (see Figures 1c and 2b).

The situation is unexpectedly different with respect to the reactions

\[
H + H₂O(ν,0,ν') \rightarrow H₂(ν') + OH(ν') \quad (II')
\]

(Here ν stands for the asymmetric mode and ν' for the symmetric one.)

The relevant energy dependent reactive probabilities are shown in Figure 3a–e. In fact the behavior encountered for the reactions from the ground state is not unusual as per the previous discussion namely the main products were H₂(0) and OH(0) and to a lesser extent H₂(1) but no excited OH is obtained. The situation changes once the reactions take place with an excited H₂O. An instance of this is illustrated in Figure 3b which shows results for the symmetric excitation, namely from an initial state (0,0,1). On the basis of the previous two HOD cases no excited OH molecules were to be expected. However not only were the OH molecules
Figure 5. Equi-eigenfunction lines of the collinear \( \text{H}_2\text{O}(v,0,v') \) molecule. \( v \) refers to the asymmetric mode, and \( v' \) to the symmetric mode. a–i and k stand for the numerical values \( 4, 3, 2, 1, -1/2, -1, -2, -3, -4 \). (a) Equi-eigenfunction lines for \( (0,0,0) \). (b) Equi-eigenfunction lines for \( (0,0,1) \). (c) Equi-eigenfunction lines for \( (1,0,0) \). (d) Equi-eigenfunction lines for \( (0,0,2) \). (e) Equi-eigenfunction lines for \( (1,0,1) \). (f) Equi-eigenfunction lines for \( (2,0,0) \).

So far the findings were interesting if not surprising (except these for \( (0,0,0) \) and \( (1,0,1) \)) because the \( \text{H}_2\text{O} \) molecule behaved so differently from its isotopic analogs. It is important to reiterate that the results for \( \text{HOD} \) were all in good qualitative agreement with both the experiments and with other the quantum mechanical calculations. However, the results for the \( \text{H}_2\text{O} \) system are not only novel but also very different and therefore more insight is needed.

IV. Analysis of the Results

To understand the significant difference in the behavior of \( \text{HDO} \) and \( \text{H}_2\text{O} \) we present in Figures 4 and 5, respectively the
eigenfunctions of the two molecules. Each figure shows six eigenfunctions, corresponding to the (0,0,0), (0,0,1), (1,0,0), (0,0,2), (1,0,1), (2,0,0) states. In both figures the eigenfunctions are presented in terms of $r$, an interatomic coordinate (the OH distance in case of DOH), and $\rho$, the associated Jacobi coordinate (see eq II). It is noticed that whereas the eigenfunction (0,0,0) is similar for both molecules, all other cases (0,0,1), (1,0,0), (0,0,2), (1,0,1), (2,0,0) assume different shapes. The HOD molecule is seen to be a typical local-mode-type molecule (each bond is excited "separately") but the H$_2$O is a typical normal-mode-type molecule (for a more extensive discussion on the excited stretching vibrations of water, see ref 27). These differences have strong implications on how the systems behave during a reactive collision.

The H$_2$O behaves like a two-atomic molecule, because the nonreactive bond essentially does not affect the reaction process. The H$_2$O behaves like a triatomic molecule, where all three atoms take part in the reaction process. Consequently strong quasi-selection rules are encountered in the HOD case but are missing in the case of the H$_2$O molecule.

V. Summary

In this work we have presented a new approach to treat reactive four-atom systems. The approach is based on the application of absorbing imaginary potentials (which form absorbing boundary conditions) and the Kohn variational principle to solve for the coefficients of the $L^2$ basis functions.$^{21}$ As a special case we have treated the reactive interaction between a hydrogen atom and a water molecule. The four atoms were assumed to be arranged along a line (collinear arrangement). Three cases were considered, namely, the (H,HOH), (H,DOH), and (H,HOD) systems.

The main difficulty with the collinear configuration was that we were forced to consider a linear H$_2$O. Making the H$_2$O linear affected the endothermicity of the reaction; the change caused it to be $\sim 0.1$ eV rather than $\sim 0.7$ eV. As a consequence only limited information regarding the vibrational enhancement of the reactive process, as was detected experimentally by Sinha et al.$^{12}$ and by Bronikowski et al.$^{13}$ could be obtained.

More detailed and somewhat unexpected results were obtained regarding the adiabaticity of the reaction process with respect to the nonreactive vibrational bond. In this respect we found differences in the behavior of the (H, H$_2$O) system and the two (H, HOD) systems. Whereas the two (H, HOD) systems reacted while the nonreactive bond were kept almost adiabatic and therefore indifferent to the reactive process the (H, H$_2$O) system reacted with the nonreactive bond taking an active part in the reaction process and thus getting excited (or deexcited). The findings regarding the HOD agree with the experiment of Sinha et al.$^{12}$ who established an adiabatic behavior for the (HOD) system.

All these findings are based on the study of the collinear configuration. We do not anticipate significant qualitative changes (in particularly the unexpected behavior of the H$_2$O molecule) while moving to other configurations. We are now in the final stages of modifying our programs, and we hope soon to report on three-dimensional results.

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References and Notes

(19) Schatz, G. C., private communications.