Quantum mechanical cross sections for the isotopic reactions H+X₂O, X=H,D: A comparison with experiment and with other calculations

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In this work are presented 3-mathematical-dimensional quantum mechanical-energy-dependent cross sections for the two isotopic reactions H+X₂O→Products; X=H,D. The results are compared with experiment and with other calculations. The comparison between theory and experiment leads to two contradictory conclusions regarding the application of the Walch–Dunning–Schatz–Elgersma (WDSE) potential energy surface: (a) The WDSE surface seems to adequately describe the abstraction process; (b) however, the WDSE barrier for the exchange process seems to be too high and therefore yields small cross sections in contrast to those found in the experiment. © 1999 American Institute of Physics. [S0021-9606(99)00525-5]

I. INTRODUCTION

The quantum mechanical (QM) study of tetra-atom systems has recently become one of the major subjects in molecular dynamics. A whole series of systems has been considered and it seems that the only obstacle to extending these studies further is the lack of reliable potential energy surfaces (PES). Among the tetra-atom systems, the most studied ones are the HHOH and its isotopic analogs. The reason for that is threefold: (a) there is available a reasonably good PES which presents correctly the various asymptotic arrangement channels (AC) and seems to describe reasonably well the corresponding close interaction region; (b) three hydrogen atoms are involved in the interaction, a fact which reduces significantly the numerical effort required in order to obtain the results and (c) experimental results with which the theoretical outcomes can be compared are available. In the present study we shall concentrate on two atom–triatom systems, namely, the two isotopic reactions:

\[
\begin{align*}
\text{H+H}_2\text{O} & \rightarrow \text{products} \rightarrow \text{HH}^\prime + \text{OH} \\
\text{H+D}_2\text{O} & \rightarrow \text{products} \rightarrow \text{HD} + \text{OD} \\
\end{align*}
\]

with the aim of obtaining integral cross sections.

These two systems have been subjected to a series of numerical and experimental studies. The numerical treatments are of two kinds: quantum mechanical (QM) calculations and quasiclassical trajectory (QCT) calculations. The majority of these calculations were made on the Walch–Dunning–Schatz–Elgersma (WDSE) potential energy surface (PES) in some cases a modified version was used. Experimental energy-dependent integral cross sections were measured mainly by the Heidelberg group, and they can be summarized as follows: For reactions (1), obviously, only the abstraction process was considered and five cross sections at the energies: E=1.0, 1.5, 1.8, 2.2, and 2.5 eV were measured, for reactions (2) the abstraction and the exchange processes were measured independently: for the abstraction process, cross sections were measured at four energies, namely, E=1.5, 1.8, 2.2, and 2.5 eV and for the exchange process, cross sections were measured at two energies, namely, E=1.5, 2.2 eV and two others, at E=1.8, 2.5 eV were calculated using the line-of-centers excitation function formula derived from the hot H atom reaction/relaxation measurements.

In the present publication we shall report on QM integral cross sections for reactions (1) and (2). Since our approach is based on considering only the reagents AC, the calculations will yield the integral cross sections for the sum of the two types of products. While such results may not be detailed enough, they still provide, as will be shown, an important probe for the relevance of theory to experiment and vice versa. QM cross sections for reactions (1) have already been published by us, although only in the low energy range (they were presented, erroneously, as being cross sections for abstraction only whereas, in fact, they are for the sum of both the abstraction and the exchange). The QM cross sections for reaction (2) are presented here for the first time.

The paper is arranged in the following way: In the next section a few comments are made on the theoretical approach to atom–triatom systems, in the third section results are presented concerning the H+H₂O and the H+D₂O reactions, in the fourth the results are analyzed and discussed and conclusions are given in the fifth section.

II. THEORETICAL COMMENTS

The present QM calculation is considered as a 3-mathematical-dimensional (3MD) calculation on the ‘‘MD-scale,’’ namely, only the three radial coordinates: r, the nonreactive O–X, (X=H,D) distance; ρ, the distance be-
between the reactive X-atom and the center-of-mass of the OX system; and \( R \), the distance between H and the center-of-mass of the \( \text{X}_2\text{O} \) system, serve as ordinary variables (see Fig. 1). The other three internal coordinates, namely, the three Jacoby angles, are treated as follows: The angle \( \theta \) \((=\cos^{-1}(\hat{r} \cdot \hat{R}))\) is held fixed during the whole calculation; its value is derived from the equilibrium bending angle of the \( \text{X}–\text{O}–\text{X} \) molecule.\(^1\) The angle \( \gamma \) \((=\cos^{-1}(\hat{r} \cdot \hat{R}))\) is held fixed during a single calculation but is then varied from one calculation to the other. In other words, \( \gamma \)-fixed cross sections are calculated and the final result is obtained following a weighted integration (by \( \sin \gamma \)) over \( \gamma \). As for \( \varphi \) (the out-of-plane angle), we do the following: For each set of coordinates \((r_\theta, r_\gamma, \theta, \varphi, \gamma)\), we calculate a \( \varphi \)-averaged potential, which then is used in the actual calculations.\(^{1,6}\) Since in this way no explicit dependence on \( \varphi \) is encountered, the relevant \( \varphi \)-dependent part of the total wave function can be obtained analytically and we are left with a reduced 3MD problem. In case only integral cross sections are required, the \( \varphi \)-dependent part of the wave function can be ignored altogether. This type of approximation—regarding the \( \varphi \)-angle—was checked by us by comparing reactive probabilities obtained in this way with those obtained by considering \( \varphi \) explicitly within the 3MD calculation, i.e., by repeating the calculations for different \( \varphi \)-values. For all practical purposes the two kinds of results were found to be reasonably close. (In fact the previous cross sections for \( \text{H}+\text{H}_2\text{O} \), presented in Ref. 2, were also obtained with the angle \( \varphi \) explicitly considered within the Monte Carlo treatment.) Thus our calculations are 3-physical dimensional calculations carried out in a 3MD framework. We shall not elaborate further on the theoretical aspects of our approach, because it has already been presented several times.\(^{1,4,5,15}\) It is almost redundant to mention that the feasibility of this type of calculation is guaranteed by the application of the arrangement decoupling (linear) negative imaginary potentials (NIP), as introduced by Neuhauser and Baer a decade ago.\(^{1,6}\)

![FIG. 1. The atom–triatom Jacoby system of coordinates.](Image)

**III. RESULTS**

**A. Integral cross sections for the \( \text{H}+\text{H}_2\text{O} \rightarrow \text{products} \) reactions**

This set of reactions has been studied several times, numerically, applying the QM and the QCT approaches. Various PESs were used in these studies, but we shall only refer to two of them, namely, the WDSE\(^{4(a)–4(c)}\) and its modified version.\(^{6(d)}\) Our previous 3MD cross section calculation was performed on the original WDSE PES and the results were published some time ago.\(^2\) We repeated (and extended) these calculations twice, employing the two above mentioned PESs. The two PESs were found to yield identical results. The energy-dependent cross sections are presented in Fig. 2, where they are compared with the more recent 6MD coupled states (CS) cross sections of Zhang and Light (ZL),\(^3\) for the abstraction process. It is noticed that at the low energy range the two treatments yield very similar results and only at the higher energy range are the 3MD cross sections somewhat larger than the CS results. The differences can be interpreted as being due to the contributions of the exchange processes which are included in the present calculation but not in the CS one. The fact that these differences are relatively small implies that the exchange process is weak compared to abstraction. This subject will be discussed further in Sec. IV.

The QCT calculations were performed several times: we shall refer first to the (more recent) ordinary ones by Kudla and Schatz (KS).\(^{13}\) A direct comparison between our calculations and those of KS is possible only for the energy 2.2 eV, for which KS calculated both the abstraction and the exchange cross sections. These authors found that the sum of the two cross sections is \(\sim 3.5\) au (about 0.9 au for abstraction and 2.6 au for exchange), whereas our treatment yields for the sum only \(\sim 0.9\) au, namely a cross section which is four times smaller. It is important to mention that the KS cross sections for abstraction were also much larger than the ZL cross sections. For instance at \(E_{tr}=1.4\) eV the QCT result is \(\sim 0.47\) au versus the ZL result at \(E_{tr}=1.5\) eV of \(\sim 0.24\) au. Recently, new QCT calculations were performed by Bradley and Schatz (BS).\(^{14}\) They are presented in Fig. 3, where they are compared with the older ones due to Kudla and Schatz (KS). It is noticed that the KS cross sections are more than

![FIG. 2. A comparison between QM 3MD (present) and QM-6MD (Ref. 3) cross sections for the assigned reactions.](Image)
two times larger than those of BS. The explanation for the discrepancy is that in the more recent calculations reactive trajectories, not fulfilling zero-point-energy (ZPE) conservation, were eliminated.\textsuperscript{14} These new calculations yielded much smaller cross sections which overlap reasonably well with our and the ZL cross sections.

The comparison with experiment can be made, at this stage, is only with the ZL calculations. For this purpose we consider two measured cross sections, namely, $\sigma(E_{tr} = 1.5 \text{ eV}) = (0.57 \pm 0.18 \text{ au})$ and $\sigma(E_{tr} = 1.8 \text{ eV}) = (0.64 \pm 0.21 \text{ au})$.\textsuperscript{6c} The corresponding CS results are $\sigma(E_{tr} = 1.5 \text{ eV}) \sim 0.25 \text{ au}$ and $\sigma(E_{tr} = 1.75 \text{ eV}) \sim 0.39 \text{ au}$. Thus, the experimental cross section for the lower energy is rather far from the QM result, but for the higher energy this value is reasonably close, considering the size of the experimental error bar. The comparison with our calculations will be done in Sec. IV.

### B. Integral cross sections for the $\text{H} + \text{D}_2\text{O} \rightarrow (\text{products})$ reactions

In this publication we report on the first QM calculation for the $\text{D}_2\text{O} + \text{H}$ reaction. To our knowledge QCT results are available only for the abstraction process, so a limited comparison (at most) can be made with them. However experimental results are available for both the abstraction and the exchange processes, and therefore a comparison with experiment becomes feasible.

In Fig. 4 are compared the total integral cross sections for reactions (1) and (2), as obtained for the original WDSE PES. It is noticed that the isotopic effect is relatively small, $\sim 1.3$, in particular if we recall the isotopic effect encountered in the QCT treatment which, for abstraction, was found to be $\sim 3$. However the large QCT isotope effect could very well be misleading, because the nonconservation of the ZPE which was found to enhance the $\text{H} + \text{H}_2\text{O}$ results by a factor of more than two, is expected to affect the $\text{H} + \text{D}_2\text{O}$ results to a much lesser degree. Therefore, it is probable that, taking into account the ZPE effect, the QCT isotope effect will also be smaller.

### IV. DISCUSSION

The comparison between QM and experimental cross sections is performed in Table I. The experimental total cross sections were obtained by combining the cross sections for abstraction with those for exchange. It is noticed that the experimental values are two–five times larger (depending on energy and error bars) than the QM ones.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Experiment</th>
<th>QM-3MD</th>
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<tbody>
<tr>
<td>1.25</td>
<td>...</td>
<td>0.10</td>
</tr>
<tr>
<td>1.5</td>
<td>1.17±0.44</td>
<td>0.23</td>
</tr>
<tr>
<td>1.75</td>
<td>...</td>
<td>0.38</td>
</tr>
<tr>
<td>1.8</td>
<td>1.49±0.41</td>
<td>...</td>
</tr>
<tr>
<td>2.0</td>
<td>...</td>
<td>0.54</td>
</tr>
<tr>
<td>2.2</td>
<td>1.72±0.41</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The comparison between our calculations and experiment revealed the fact that the WDSE PES is not accurate enough to yield the experimental sum of the cross sections for the abstraction and exchange for the two above considered isotopic reactions. Our approach allows probing the $\gamma$-regions which contribute to these cross sections and this we shall do, next, in order to reveal the difficulties with the WDSE PES. In Fig. 5 are presented $\gamma$-dependent cross sections, $\sigma(\gamma)$, as calculated for the two reactions at two different energies, namely, at $E_{tr} = 1.25$ and 2.2 eV. It is well noticed that the main region where $\sigma(\gamma)$ is different from zero is the $\gamma=0$ region. To see what kind of reactions take place at this region we refer to Fig. 6, from which it is noticed that the $\gamma=0$ region is probably dominated by abstraction processes, whereas regions with larger $\gamma$ values are more likely to contribute to exchange. We are aware that this distinction cannot be validated on the basis of our present numerical study but it can be supported by findings of other studies. Polanyi and co-workers,\textsuperscript{17} in their detailed QCT study of $\text{H} + \text{HBr}$, established the fact that abstraction takes place when the approaching hydrogen picks the molecular hydro-
from its parent-molecule, in a “face-to-face” situation, namely, from the quasilinear $\gamma \sim 0$ region. As for exchange processes it is well known from numerous QCT and QM studies that these processes are much favored when the approaching atom (or molecule) comes from the back (namely from the quasilinear $\gamma \sim \pi$ region).

Accepting these assertions makes the comparison between the coupled states cross sections for $\text{H}_2\text{O} \rightarrow \text{H}_2\text{OH}$ and our (total) cross sections as shown in Fig. 2 much more interesting. If indeed the present calculation, particularly at the lower energy range, leads primarily to abstraction then the fit between the two QM schemes is very encouraging—because, within both is treated abstraction process only. As the energy increases we expect our calculations to contain contributions due to exchange and indeed at the higher energy range we obtained larger cross sections.

Accepting the above assertions also makes the comparison between theory and experiment much more meaningful. In Table II we compare the experimental energy-dependent cross sections for abstraction with only the present corresponding QM 3MD total cross sections. It is noticed that a very nice fit is obtained for the $\text{H}_2\text{O} + \text{H}$ system (except for one energy value at $E_{\text{r}} = 1.5 \text{ eV}$, where the experimental value is somewhat too large). The fit for the $\text{D}_2\text{O} + \text{H}$ system seems to be less successful because of the significant discrepancy at the high energy region where the QM cross sections are larger than the experimental ones. This discrepancy can be explained, at least to some extent, by considering the $\gamma$-dependent cross sections in Fig. 5. It is noticed that the angular reactive range is larger for the $\text{D}_2\text{O} + \text{H}$ system although the total cross sections for these reactions are $\sim 30\%$ smaller. Since exchange processes are enhanced as $\gamma$ increases, this implies that for $\text{D}_2\text{O} + \text{H}$ as the energy increases, we get QM cross sections with relatively more contributions from exchange than in the $\text{H}_2\text{O} + \text{H}$ case. These enhanced QM exchange cross sections for $\text{D}_2\text{O} + \text{H}$ also explain why our QM isotopic effect is smaller than the experimental one which is based on abstraction only.

Accepting our assertion makes even the comparison between the recent QCT cross sections for abstraction and the present QM results quite encouraging. As was discussed earlier once the trajectories which do not conserve the ZPE are eliminated a very good agreement is obtained. However an unpleasant discrepancy is obtained in case of the exchange process. Accepting our assertion means that this PES is hardly capable of yielding the exchange process whereas according to the QCT treatment the exchange cross sections are about three times larger than the ones for abstraction. These large exchange cross sections were obtained without elimi-

### Table II

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\text{H}_2\text{O} \rightarrow \text{H}_2\text{OH}$</th>
<th>$\text{H}_2\text{O} \rightarrow \text{H}_2\text{OH}$</th>
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<tr>
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<td>$\text{H}_2\text{O} \rightarrow \text{H}_2\text{OH}$</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>$0.15$</td>
<td>$0.10$</td>
</tr>
<tr>
<td>1.50</td>
<td>$0.29$</td>
<td>$0.23$</td>
</tr>
<tr>
<td>1.75</td>
<td>$0.50$</td>
<td>$0.38$</td>
</tr>
<tr>
<td>1.80</td>
<td>$0.64 \pm 0.21$</td>
<td>$0.36 \pm 0.11$</td>
</tr>
<tr>
<td>2.0</td>
<td>$0.69$</td>
<td>$0.53$</td>
</tr>
<tr>
<td>2.2</td>
<td>$0.89 \pm 0.25$</td>
<td>$0.39 \pm 0.11$</td>
</tr>
<tr>
<td>2.5</td>
<td>$0.93 \pm 0.32$</td>
<td>$0.39 \pm 0.07$</td>
</tr>
</tbody>
</table>

FIG. 5. QM angular dependent cross sections. Full lines results for $\text{H}_2\text{O} + \text{H}$; dashed lines results for $\text{H}_2\text{D} + \text{D}$; spheres: results for $E_{\text{r}} = 1.25 \text{ eV}$; squares: results for $E_{\text{r}} = 2.2 \text{ eV}$.

FIG. 6. A schematic representation of the two situations for reactions: (a) abstraction: $\text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2\text{OH}$; (b) exchange: $\text{H}_2\text{O} + \text{X} \rightarrow \text{X} + \text{H}_2\text{O}$.
nating the trajectories that do not conserve the ZPE. We contend that if these calculations are repeated without the nonphysical trajectories the cross sections for this process will be significantly smaller and eventually even smaller than those for abstraction.

The experiments indicate that the exchange process in this system is substantial whereas our QM treatment yields only relatively small cross sections for this process. Assuming our treatment is relevant this implies that the potential barrier for exchange in the WDSE PES is too high. If indeed this is the case then this (too) high barrier may be connected with the fact that WDSE PES allows only one of the hydrogens to react.

V. CONCLUSIONS

In this publication 3MD QM energy cross sections for the sum of the two processes, namely, abstraction and exchange [see Eqs. (1) and (2)], are presented for the two isotopic reactions \( H + X_2O \rightarrow \) (products); \( X=H, D \). The results are compared, whenever possible, with QCT (other), QM and experimental results. The comparison with the QCT cross sections for the \( H + H_2O \) system reveals that this approach yields cross sections much larger than the QM ones. However recently new QCT calculations were done, for abstraction, in which reactive trajectories that do not conserve the ZPE were eliminated, as a result of which the fit improved significantly. Unfortunately a similarly modified study was not carried out for exchange. The comparison with the QM 6MD calculations cannot be done directly, unless it is assumed that our calculated cross sections contain only small contributions from exchange (as was discussed in Sec. IV). If this is the case then the fit can be considered as very good. The comparison with experiment is far from being satisfactory but again improves significantly if the assumption is made that our QM cross sections are mainly for abstraction. This applies to both the \( H + H_2O \) and the \( H + D_2O \) reactions. The QM calculations for the total reactive process yield a mild isotopic effect, \( \sim 1.3 \), as compared with the abstraction significant isotopic effect, \( \sim 2 \), found in the experiment. However the weak QM isotopic effect is related to the way the present calculations were done. Doing the calculations for abstraction only will yield a larger isotopic effect bringing the QM results closer to the experimental ones.

The inability of the QM treatment to yield the correct cross sections for the sum of the two processes is attributed to the much too high potential barrier which seems to prevent the exchange process. Still, we have to be somewhat cautious with this final conclusion mainly because our treatment is a frozen-angle-type treatment and therefore the dynamics is restricted to a certain extent.

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