Quasiclassical Trajectory Studies of H + H_2O and H + D_2O Reactions on a New ab Initio Potential Energy Surface†

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Received: March 20, 2000; In Final Form: June 20, 2000

We present the results of quasiclassical trajectory studies of the H + H_2O → OH + H_2, H + D_2O → OD + HD, and H + D_2O → D + HOD reactions. The new potential energy surface of Ochoa and Clary (*J. Phys. Chem. A.* **1998**, *102*, 9631) derived from ab initio calculations has been employed. Absolute reaction cross sections as a function of collision energy have been calculated and compared with previous experimental and theoretical results. Our calculations are in qualitative agreement with the experimental determinations. Additionally, vibrational and rotational distributions have been calculated and compared with experimental measurements. The calculations reproduce the low vibrational excitation for OH and OD products and the relatively cold rotational distributions for OH, OD, and HD products observed in the experiments.

I. Introduction

The reaction

$$\mathrm{H} + \mathrm{H_2O} \rightleftharpoons \mathrm{OH} + \mathrm{H_2} \quad \Delta H_o = 63.1 \text{ kJ/mol} \tag{1}$$

and its isotopic variants is recognized nowadays as a prototypic four-atom reaction that has been studied both experimentally and theoretically for already two decades (see refs 1 and 2 for review). This system provides an excellent benchmark for understanding the dynamics of reactions of polyatomic molecules and the influence of vibrational or translational excitation on these dynamics. Usually, one would like to know how the reaction rate or the production of a particular product depends on the particular vibrational mode or bond that is excited prior to the reaction taking place. Reaction 1 has been investigated thoroughly by means of hot H atom experiments using translationally energetic H atoms produced by photolysis of a precursor.[3−8] These experiments have provided information on the reaction cross sections as a function of translational energy and the OH rotational and vibrational energy distribution. It was found that the reaction occurs by an abstraction mechanism of the H atom, and the nonreactive OH plays the role of a "spectator" with very little rotational excitation and no vibrational excitation. These features of the reaction were confirmed by theoretical calculations on the Walch−Dunning−Schatz−Elgersma potential energy surface (WDSE-PES)[9,10] using the quasiclassical trajectory (QCT) method,[11−13] approximate quantum mechanical (QM) methods,[14−17] and accurate QM methods.[18,19]

Several experimental studies have been reported for the H + D_2O reaction by the groups of Zare[20,21] and Wolfrum,[22−25] in which the following reaction channels can be distinguished:

$$\begin{aligned} \mathrm{H} + \mathrm{D_2O} &\rightarrow \mathrm{OD} + \mathrm{HD} \quad \Delta H_o = 68.9 \text{ kJ/mol} \\ &\rightarrow \mathrm{OH} + \mathrm{D_2} \quad \Delta H_o = 68.7 \text{ kJ/mol} \\ &\rightarrow \mathrm{HOD} + \mathrm{D} \quad \Delta H_o = 7.9 \text{ kJ/mol} \end{aligned} \tag{2}$$

Absolute reactive cross sections at several collision energies have been measured for these reactions. Another set of experiments have been performed for the reaction

$$\begin{aligned} \mathrm{H} + \mathrm{HOD} &\rightarrow \mathrm{OD} + \mathrm{H_2} \quad \Delta H_o = 62.9 \text{ kJ/mol} \\ &\rightarrow \mathrm{HD} + \mathrm{OH} \end{aligned} \tag{3}$$

Crim et al.[26,27] demonstrated that reaction of thermal H atoms with HOD prepared with 4 quanta of OH or 5 quanta of OD local vibrational excitation yields exclusively OD or OH product, respectively, thus providing the first striking examples of a bond-selective bimolecular reaction. Analogously, Bronikowski et al.[21] showed that the selective enhancement of the cross sections of these two channels of reaction 3 can be achieved with just 1 quanta of local vibrational excitation. The corresponding QCT studies of H + HOD(100 and 001) reaction performed by Kudla et al.[28−30] and QM calculations of Zhang et al.[31] on the WDSE PES showed qualitative agreement with these observations.

Very recently, Smith and co-workers[32] have reported experimental rate coefficients for reaction and relaxation of H_2O excited to the vibrational levels $|04\rangle^-$, $|13\rangle^-$, $|03\rangle^-$, $|12\rangle^-$, and $|02\rangle^-$. They observed that the rate coefficients increase with the number of quanta in the excited OH streching local mode. At the same time QCT reactive and QM nonreactive scattering calculations of collisions of H with vibrationally excited H_2O were carried out by the group of Schatz[33,34] on the I5 PES[35] and the newly developed PES by Ochoa and Clary (OC PES).[36] It was noted that the reaction cross sections for H_2O vibrational levels above the energetic threshold do not show translational energy threshold and they increase very fast with decreasing collision energy. Therefore, the calculated rate coefficients for reaction are very large, being a significant fraction of the gas kinetic rate coefficients. Finally, we would like to mention that

† Part of the special issue "C. Bradley Moore Festschrift".

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10.1021/jp001059v CCC: $19.00
Published on Web 08/15/2000

reaction 1 has also been the subject of study for its vector properties, that is, polarization-dependent differential cross sections and angular momentum alignment parameters, experimentally[37,38] and theoretically.[13,39]

As mentioned before, the great bulk of dynamical calculations have been performed on the WDSE PES. Unfortunately, this PES suffers from several deficiencies, such as a spurious well in the entrance channel for the OH + H_2 reaction, an incorrect geometry for the transition state, an incorrect force field for the H_2O molecule and, worst of all, it is not symmetric to the exchange of H atoms. The new OC PES is free from these defects and thus it should be more appropiate for dynamical studies. Very recently Progebnya et al.[40,41] have performed accurate (six-dimensional) QM, approximate QM, and full-dimensional QCT calculations for the OH + H_2 reaction on this PES, demonstrating that it gives good agreement with the experiments for rate constants, differential cross sections, and the simulated photodetachment spectra from H_3O^- that probes the transition state of the reaction.

In this work we aim to study reactions 1 and 2 by means of QCT methodology on the OC PES. In particular, we are interested in calculating the excitation functions (that is, the absolute reactive cross sections as a function of translational or collision energy) of these reactions in order to compare with experimental results and previous theoretical studies. Additionally, energy partitioning and some rotational and vibrational distributions are presented. The results obtained here should be another rigorous test of the accuracy of the OC PES.

II. Methodology

The methodology of QCT calculations carried out in this work has been described many times, and extensive recent reviews can be found in the literature.[42] The classical equations of motion have been formulated in space-fixed Cartesian coordinates with the Z-axis lying along the direction of the initial relative velocity. Integration of these equations has been performed with a combined fourth-order Runge−Kutta and sixth-order Adams−Moulton algorithms as implemented in the VENUS96 package.[43] The evaluation of the potential energy derivatives of the OC PES has been done numerically using a finite-difference algorithm given by Ridders.[44] This numerical algorithm has been tested using the WDSE PES for which there are analytical derivatives, and the results agree perfectly. The pseudoquantization of final diatomic products has been performed by equating the square of the modulus of the classical rotational angular momentum to $j'(j' + 1)\hbar$. The vibrational quantum number v' is found by equating the internal energy of the molecule to a rovibrational Dunham expansion in (v' + 1/2) and $j'(j' + 1)$, whose coefficients are calculated by fitting the semiclassical or quantum rovibrational energies given by the asymptotic diatomic limits of the PES.[45] We have checked that this procedure is strictly equivalent to the usual Einstein−Brillouin−Keller (EBK) semiclassical quantization. The noninteger v' and j' values have been rounded off to the nearest integer. In previous QCT studies of the H + H_2O and H + HOD reactions,[12,13] it was proposed to apply a posteriori zero-point energy (ZPE) constrains in order to preserve the zero-point energy in the QCT method. This is achieved just by rejecting trajectories that lead to diatomic products with internal energy below their zero-point energies. It was found that meaningful results were obtained only when these constrains are applied only to the H_2 molecule and not to the OH molecule. The justification of this is based on the fact that the OH is basically a “spectator” bond. Although we find this procedure somewhat arbitrary and not fully justified, we have done calculations employing these types of constrains to see their effect on the cross sections and to compare with previous studies on different PES.

TABLE 1: Vibrational Energies (cm^{-1}) of H_2O

vibrational state	QM[a]	SC[b]	QM-SC
000	4610	4613	−3
010	6204	6182	22
020	7764	7780	−16
100	8234	8254	−20
001	8329	8380	−51

[a] Ref 41. [b] Present results.

Finally, to define the H_2O vibrational initial conditions one has to calculate the corresponding “good” action variables. The method used to obtain the action variables is based on the Sorbie−Handy version[46] of the fast Fourier transform (FFT) approach described by Eaker et al.[47−49] and Martens and Ezra.[50] In this method, the evaluation of the action integrals is performed using a Fourier series representation of normal coordinates $Q_k(t)$ and momenta $P_k(t)$. Basically, the equations of motions for the isolated water molecule are integrated with a fixed time step h. A set of M points equally spaced in time are sampled for each coordinate and momenta at every S time steps for a total integration time of $T = hMS$. The time series have been multiplied by a standard −74 dB Blackman−Harris window function[51] before calculating their FFTs. We have used harmonic actions and angles chosen randomly to define initial conditions for each trajectory. Once a trajectory which produces the desired actions, that is, a quasi-periodic trajectory, has been eventually found it is integrated for a longer time storing the coordinates and momenta at regular intervals for their use as initial conditions for the collision simulations.

III. Numerical Details

As discussed before, the first stage of the dynamical calculations is to determine trajectories whose actions correspond to the desired initial quantum state of the triatom. The computed semiclassical eigenvalues for the first five vibrational states of the H_2O molecule are compared with the available quantum mechanical results for the OC PES[40] in Table 1. The results have been obtained with a time step h = 2 au (≈0.05 fs), M = 1024 points, and S = 40. Note the good agreement between semiclassical and quantum eigenvalues of the (000) state of H_2O which is the initial state of interest in this work. Batches of 25000 trajectories for each relative translational energy have been run for reactions 1 and 2. Up to 10^4 trajectories have been considered for the collision energies, E_{coll}, of 1.4 and 2.2 eV to obtain rotational distributions with a reasonable statistics. A maximum impact parameter b_{max} of 1.5 Å has been selected for E_{coll} up to 2.2 eV and 2.0 Å for E_{coll} = 2.6 eV. The initial distance R_{max} from the H atom to the center-of-mass of the triatomic molecule was chosen to be 8 Å. The Cartesian coordinates and velocities for the H_2O molecule were randomly oriented by rotation through Eurler’s angles within the H_2O space-fixed center-of-mass coordinate frame. An integration time step of 2 au was used which gave a typical conservation of total energy better than 10^{-4} eV. However, some trajectories for which the conservation of energy was worse than 5×10^{-4} eV were rejected.

IV. Results and Discussion

In Figure 1, the present QCT cross sections for the H + H_2O(000) → OH + H_2 are compared with the results of QCT

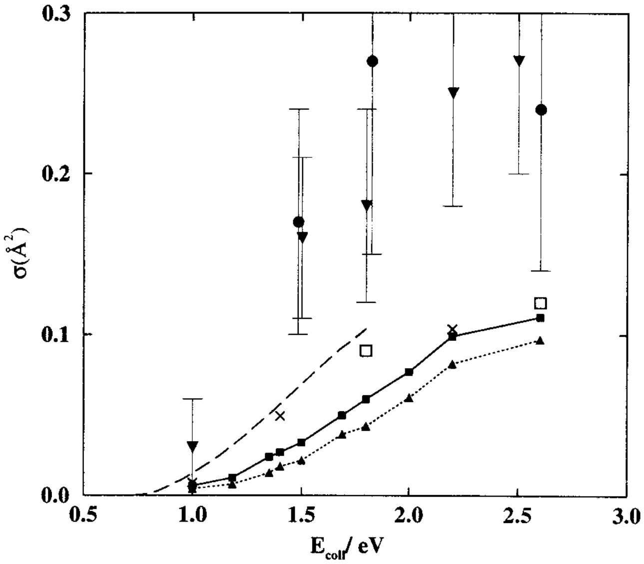

Figure 1. Absolute integral cross sections for the reaction H + H_2O → OH + H_2. Filled squares: QCT results on the OC PES without ZPE constrains. Filled triangles: results with ZPE contrains. Crosses: QCT results on the WDSE PES.[13] Squares: QCT results on the WDSE PES. Dashed line: QM results on the WDSE PES trajectory.[18] Filled triangles down: experimental results from ref 7. Filled circles: experimental results from ref 5.

calculations on the WDSE PES,[13] QM results on the WDSE PES,[18] and the available experimental measurements.[5,7] Also we have done QCT calculations on the WDSE PES under the same conditions described in ref 13 and plotted in Figure 1 as squares. One can note that all the theoretical results clearly underestimate the experimental values in the energy range considered. In previous QCT and QM studies on the WDSE PES, it was realized that in that PES one of the H atoms of the H_2O molecule was not reactive and thus the cross sections were multiplied by a factor of 2 in order to somehow correct this defect. This was done as well for the QCT calculations on the I5 PES although for this PES both H atoms of the H_2O molecule are reactive but not in an equivalent way as discussed in ref 13. As mentioned before, this defect is not present in the OC PES and we have checked that both H atoms are equally reactive.

Given the fair agreement between the QCT and QM excitation functions from the WDSE PES, it seems that QM dynamical effects may not be sufficient as an explanation for the disagreement with the experiment. Of course, the QM results of ref 18 are exact 6D for total angular momentum $J = 0$ and use the centrifugal sudden (CS) approximation for $J > 0$ but this approximation has been proved to be accurate for total integral cross sections. One caveat of all the QCT and QM calculations shown is that they were carried out for non-rotating H_2O while in the experiments the H_2O molecules have a rotational distribution at room temperature. However, as pointed out in ref 11, averaging on the initial rotational angular momentum states populated at room temperature would not be very important for calculating absolute reaction cross sections. With regard to the present QCT calculations on the OC PES, we point out that the cross sections for $E_{coll} < 2.2$ eV are lower than the previous results on the WDSE and I5 PESs.[13]

As can be seen, our ZPE constrained results, that reject trajectories that lead to H_2 molecules with less energy that its ZPE, are as expected smaller. The considerations may lead to the conclusion that the barrier in the all PES considered so far is too high. Nevertheless, the QCT calculations reproduce the behavior showed by the experimental points in Figure 1, i.e., the reaction cross sections increase monotonically with collision energy and then level off at energies above 2.2 eV.

TABLE 2: Reaction Cross-Sections, σ (in Å^2), and Energy Partitioning, for the H + $H_2O(000)$ → OH + H_2 Reaction Calculated on OC PES. (The statistical uncertainty for all the Cross-Sections is 0.003 Å^2.)

E_{coll}	1.4 eV	2.2 eV
N	100000	100000
N_r	372	1406
σ	0.026	0.099
F_{trans}	0.51	0.45
H_2 F_{rot}	0.15	0.12
H_2 F_{vib}	0.16	0.17
OH F_{rot}	0.08	0.10
OH F_{vib}	0.10	0.15

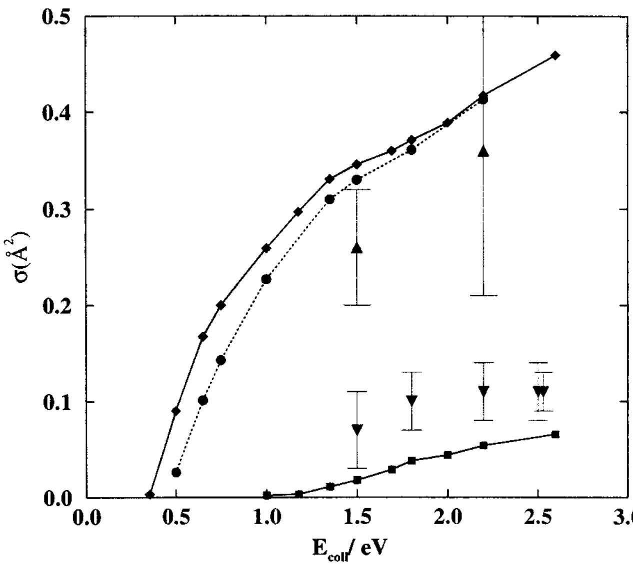

Figure 2. Absolute integral cross sections for the reaction H + D_2O → OD + H_2. Filled squares: present QCT results on the OC PES. Filled triangles down: experimental results from ref 23. Filled diamonds: QCT results on the OC PES for H + D_2O → D + HOD exchange reaction. Filled triangles up: experimental results from ref 25.

Table 2 shows cross sections and energy partitioning information for the H + H_2O reaction on the OC PES at two selected energies from our calculation without ZPE constrains. Note that we have not rounded off the vibrational and rotational actions before calculating the fractions for vibration, F_{vib}, and rotation, F_{rot}, of the diatomic products. As in previous QCT studies by Bradley and Schatz,[13] we find that the OH product is barely excited rotationally and vibrationally as opposed to the H_2 product which is relatively more excited.

In Figure 2 the QCT, without ZPE constrains, absolute cross sections for reactions

$$\begin{aligned} H + D_2O(000) &\rightarrow OD + HD \\ &\rightarrow HOD + D \end{aligned} \quad (4)$$

are displayed together with the experimental determinations.[22−25] Again for the H + $D_2O(000)$ → OD + HD abstraction channel the theoretical cross sections fall quite below the experiment. However, for the exchange channel, H + $D_2O(000)$ → HOD + D, the agreement is noticeably better. It may be argued that imposing ZPE constrains on the OH/OD stretch and HOD bending vibrational modes would reduce the reaction cross sections for the exchange channel. We have imposed ZPE

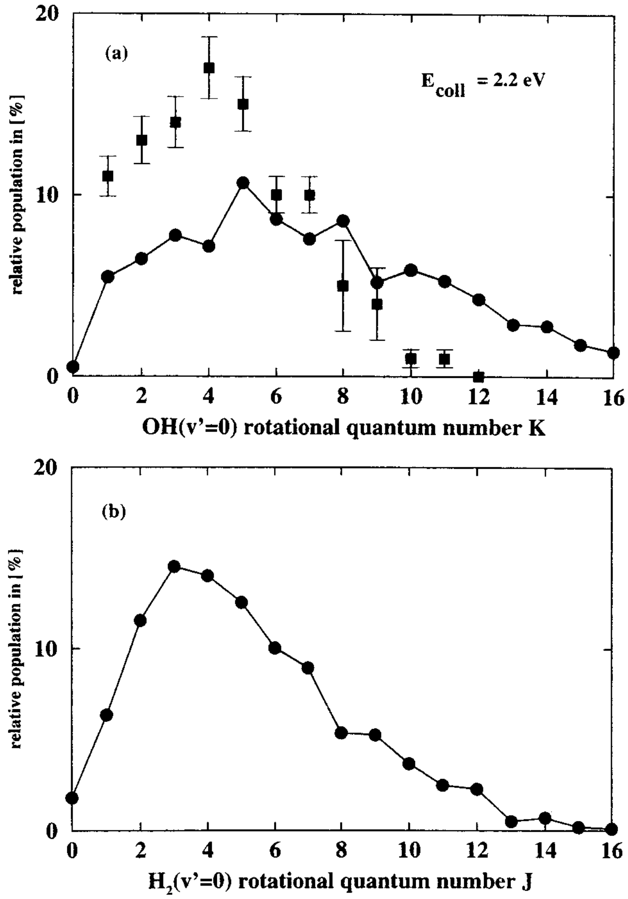

Figure 3. Rotational distributions for the H + $H_2O \rightarrow OH(v' = 0)$ + $H_2(v' = 0)$ reaction at E_{coll} = 2.2 eV. (a) $OH(v' = 0)$ rotational distribution. Filled circles: QCT results on the OC PES. Filled squares: experimental results from ref 7. (b) QCT $H_2(v' = 0)$ rotational distribution on the OC PES.

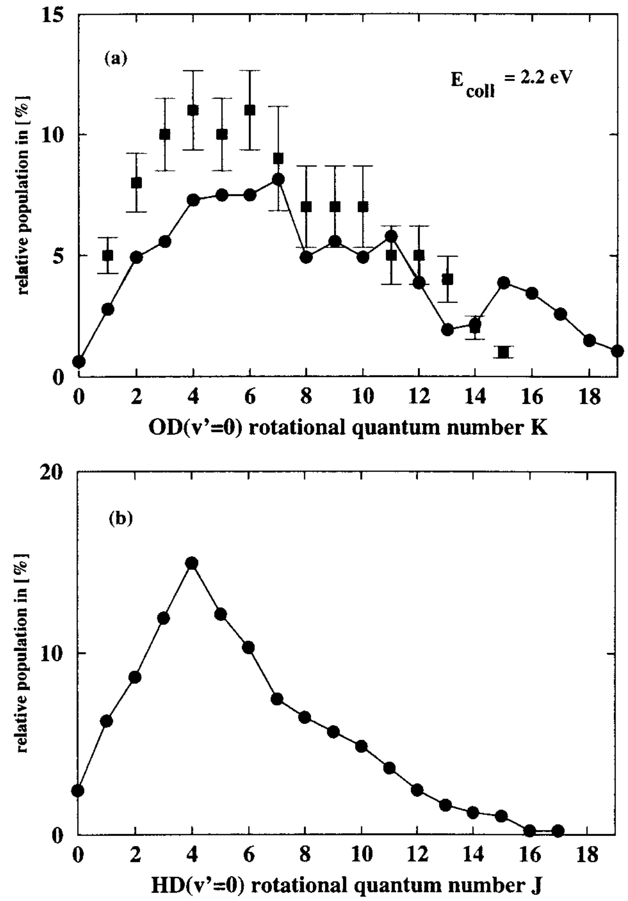

Figure 4. Rotational distributions for the H + $D_2O \rightarrow OD(v' = 0)$ + $HD(v' = 0)$ reaction at E_{coll} = 2.2 eV. (a) $OD(v' = 0)$ rotational distribution. Filled circles: QCT results on the OC PES. Filled squares: experimental results from ref 23. (b) QCT $HD(v' = 0)$ rotational distribution on the OC PES.

constrains in this case by rejecting trajectories leading to HOD products with less than its zero-point energy. As can be seen on Figure 2, this correction has the effect of raising slightly the threshold energy from 0.4 to 0.5 eV which is in better agreement with the experimental estimation of 0.88 ± 0.11 eV reported in ref 25.

Another interesting comparison between theory and experiment is provided in Figures 3a and 4a where rotational distributions of $OH(v' = 0)$ and $OD(v' = 0)$ products for reactions 4 and 5, respectively, are depicted at E_{coll} = 2.2 eV. As can be seen, the agreement is good for the OD rotational distribution and somewhat worse for OH. For both cases the agreement could be improved, in principle, by running more trajectories to have a smaller statistic uncertainty. However, for a very detailed comparison it would be necessary to include the splitting of levels of OH(OD) due to spin−orbit interaction and electronic−rotational angular momentum interaction which is rather difficult to implement. Nevertheless, the lack of vibrational excitation and the low rotational excitation of the OH(OD) product radicals has led to the conclusion that reactions 4 and 5 hardly involve the formation of a H_3O long-lived intermediate and thus a direct abstraction mechanism must be invoked.

Figures 3b and 4b show the $H_2(v' = 0)$ and $HD(v' = 0)$ rotational distributions for reactions 4 and 5 at E_{coll} = 2.2 eV. The $HD(v' = 0)$ rotational distributions are in qualitative agreement with those reported by Adelman et al.[20] who investigated reaction 2 at $E_{coll} \approx$ 2.5−2.8 eV and the QCT distributions obtained by Kudla et al.[12] on the WDSE PES at E_{coll} = 2.7 eV. Further comparison can be made with the HD vibrational distributions P_v. At E_{coll} = 2.6 eV the present results are P_0 = 0.56, P_1 = 0.27, and P_2 = 0.10, while Adelman et al.[20] obtained P_0 = 0.47 ± 0.1, P_1 = 0.45 ± 0.08, and P_2 = 0.08 ± 0.02 at $E_{coll} \approx$ 2.7 eV.

Additionally, we have calculated the cross sections for the reaction

$$H + D_2O(000) \rightarrow OH + D_2 \tag{5}$$

Koppe et al.[23] detected very weak $OH(v' = 0)$ signals in their experiments for the H + D_2O reaction and gave upper limits, R^*, for the branching ratio $R = \sigma(OH + D_2)/\sigma(OD + HD)$. They reported a value of $R^* = (4.9 \pm 0.4) \times 10^{-3}$ at E_{coll} = 2.2 eV that is in qualitative agreement with our determined value of $R = (74 \pm 3) \times 10^{-3}$. This small branching ratio R^* seems to reinforce the above conclusion that very few reactive collisions proceed via complex formation.

V. Conclusions

QCT calculations have been presented for the reactions H + H_2O and H + D_2O on a new ab initio potential energy surface due to Ochoa and Clary and termed OC PES. It has been found that QCT predictions on the new OC PES reproduces qualitatively the experimental excitation functions determined by Jacobs et al. for the abstraction channels for both reactions although theoretical cross sections are significantly smaller that the corresponding experimental values. We have argued that QM effects may be compensated in the QCT calculations and therefore are not important for these reactions on the basis of the comparison of QM and QCT calculations on the WDSE PES. However, this assertion has to be taken with caution and only accurate QM calculations on the OC PES can settle this matter. On the other hand, the calculated QCT cross sections for the $H + D_2O \rightarrow HOD + H$ exchange reaction agree very well with the experimental values. Other comparisons have been made concerning the rotational distributions of OH, OD, and HD products. It has been found in very reasonable agreement with the experiments indicating that the dynamical properties of the transition state are well described by the OC PES. However, for a more accurate assessment of the quality of this PES for the reactions studied it will be necessary to obtain more detailed magnitudes such as differential cross sections and polarization-dependent differential cross sections. Work along this line is currently in progress.

Acknowledgment. We gratefully acknowledge G. Ochoa and D. C. Clary for providing us with a copy of the FORTRAN code of their OC PES. We thank D. H. Zhang and co-workers for sending us their QM results from ref 18 and H.-R. Volpp for the rotational distributions of OH and OD from refs 7 and 23. Also we thank F. J. Aoiz and L. Banares for fruitful discussions. This work has been partially supported by the DGCYT of Spain under contract PB98-0843. The calculations were performed on the SG Origin 2000 of the “Centro de Supercomputación Complutense”. J.F.C. acknowledges financial support through the program “Acciones para la reincorporación de doctores y tecnólogos” from the Ministry of Education and Culture of Spain.

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