Reactive and inelastic collisions of H atoms with vibrationally excited water molecules

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The dynamics of the collisions of H atoms with vibrationally excited H_2O were studied using classical mechanical reactive and quantum mechanical nonreactive scattering calculations. The classical trajectory calculations were performed with the I5 potential surface of Isaacson. These results show the expected behavior for an endoergic reaction with a late barrier, with the cross section exhibiting a high threshold when the water is unexcited, and a much lower threshold if the asymmetric stretch of water is highly excited. Qualitatively this matches experimental results, although the threshold energy for reaction of water in the ground vibrational state is too low to reproduce the measured rate coefficients. The rate coefficient is higher than for ground state water by six orders of magnitude when the asymmetric stretch mode is excited by four quanta. However the rate for reaction from this excited state is still two orders of magnitude smaller than the total reactive+inelastic rate coefficient obtained in recent measurements by Smith and co-workers. Quantum scattering calculations of the vibrational energy transfer rate coefficients show that the pure stretch excited states can have very high deactivation rate coefficients, resulting from transitions to states that are separated by a small energy gap (<50 cm^{-1}) from the initial state. The calculated rate coefficients for reactive+inelastic transitions are therefore dominated by inelastic scattering, and the results we obtain are in good agreement with the Smith data. © *1999 American Institute of Physics.* [S0021-9606(99)00106-3]

I. INTRODUCTION

The reaction of water with H atoms

$$H+H_2O \rightarrow H_2+OH \tag{1}$$

is one of the benchmark systems for both experiment and theory in research on reaction dynamics. Extensive measurements have been performed on the kinetics of the reverse reaction,[1–5] OH+H_2, and a number of dynamics experiments have studied the forward reaction.[6–23] In the dynamics experiments, the stereodynamics of the reaction,[9] as well as the effect of reactant kinetic energy[10–15] and H_2O internal excitation[16–24] have been studied. Particular interest has arisen in studies of the effect of reactant vibrational excitation, as some of the highly excited local modes of water are accessible by overtone absorption,[15–21] thereby making the molecule a good candidate for vibrationally controlled bond selective chemistry. The experiments of Crim *et al.*[15–21] as well as Zare *et al.*[22–24] have demonstrated significant enhancement of the rate of the reaction when the asymmetric stretch mode of water is selectively excited. However, no quantitative data concerning the absolute rate of the reaction have been produced until recently, when experiments by Hawthorne, Sharkey, and Smith[25,26] determined the rate coefficient for the reaction of the $|04\rangle^-$ state of water (four

quanta of OH local mode stretch excitation) with thermal H atoms. In these experiments, highly vibrationally excited water molecules are generated by laser excitation, and the rate of formation of OH radicals resulting from reaction with thermal H atoms is monitored. The rise of the OH concentration is sensitive only to depletion in the concentration of the excited water molecules; it essentially maps this depletion into that of an experimentally measurable signal. As a result, this experiment does not directly determine the rate of the reaction, but rather the rate of loss of excited water due to collisions, reactive *or* inelastic, with H atoms. Resolution of the measured total rate into reactive and inelastic contributions is not possible without additional measurements.

Theory may help to resolve the ambiguity present in the Hawthorne *et al.* experiment. Reaction (1) has been the subject a large number of theoretical studies, being comprehensively reviewed by Bowman and Schatz.[27] The reaction is a testing ground for both classical[28–33] and quantum scattering[34–43] methods. However, there has been surprisingly little work done on the reactivity of excited water with more than two quanta of asymmetric stretch excitation. Most of the results have been based on quasiclassical trajectory calculations, which show significant speedup of the reaction due to vibrational excitation of water,[28–33] but the activation energy is nonzero (>1 kcal/mol) even when the water is excited to states that are well above the barrier to reaction. The only quantum scattering calculations available for states

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above (002) have been based on reduced dimensionality approximations.[37–39] Although none of these studies has considered the state $|04\rangle^-$, a study of the (003) state[39] found a reactive threshold energy that is similar to what has been obtained in the trajectory calculations.

In this article we present the results of theoretical studies designed to model the experiments of Smith *et al.* and to determine the importance of inelastic and reactive processes in $H+H_2O|04\rangle^-$ collisions. In Sec. II we discuss the theoretical methodology and potential surfaces. Section III presents the results of the classical reactive scattering calculations. The results of the quantum inelastic scattering calculations are presented in Sec. IV, and Sec. V is devoted to a discussion of the results.

II. CLASSICAL AND QUANTUM SCATTERING

A. Classical trajectories

Standard technology quasiclassical trajectory calculations were used in this work[44,45] to determine reactive cross sections and rate coefficients. A special feature associated with reactions of polyatomic reactants is the correct modeling of the quantum states of the reagent molecule or molecules. In the present study the water molecule is in an excited state that is best described as an excited O–H stretch local mode. Accordingly, we generated quasiperiodic trajectories with quantized vibrational actions associated with two O–H stretch local modes (one excited and one not) as well as a ground state bend mode (thus approximating the $|04\rangle^-$ state where the bend quantum number is suppressed). By ''quantized'' we mean that the action variable for each mode is equal to $(N+\frac{1}{2})\hbar$ where the quantum number N is determined by the corresponding quantum state.[46] The actions corresponding to the modes were calculated by a Sorbie–Handy-type, fast Fourier transform method.[47] The initial precollision conditions were selected by a Monte Carlo methodology. Reactive trajectories were analyzed by calculating the vibrational and rotational actions of the resulting diatomic molecules. We found, in agreement with earlier work,[48] that physically meaningful threshold energies can be obtained only if the trajectories that lead to H_2 molecules that have a lower action than 0.5 (corresponding to the ground vibrational state of H_2) are discarded. A similar zero-point constraint was not applied to the OH stretch excited state, for reasons that have been discussed previously.[48]

B. Quantum scattering

Our studies of $H+H_2O$ inelastic scattering have been done using a quantum scattering method, the details of which are described elsewhere.[49,50] We used quantum rather than classical methods for these calculations for several reasons. First, for inelastic scattering calculations where the average change in quantum number for each mode is small, it is very difficult to calculate this change from the good action variables, as it requires a more precise determination of the action variables than is provided by the Sorbie–Handy method described above. Second, the probabilities of many inelastic processes are so small that they are forbidden classically except at high translational energies. This makes it difficult to determine thermally averaged results. Third, the determination of the maximum impact parameter is numerically ill-behaved for near resonant inelastic scattering processes. By using quantum methods instead, the determination of absolute cross sections for elastic and inelastic scattering, which is a primary goal of this study, is computationally well behaved. The two negative aspects of using quantum calculations are: (1) that it is necessary to make an approximation in the treatment of the rotational motions of the water molecule using the rotational sudden approximation, and (2) that it is not possible to treat the reactive and inelastic nonreactive cross sections in a consistent fashion. Item (2) would be a problem if the reactive and inelastic cross sections were comparable, as then reaction would provide a big perturbation on the inelastic scattering dynamics. However what we find instead is that reaction is a small perturbation on the inelastic collision dynamics, so ignoring reaction in our treatment of the inelastic collision dynamics seems justified.

In the quantum calculations, the three modes of the water molecule are described by the zero angular momentum Watson Hamiltonian. The intramolecular force field of water was described by the spectroscopic potential developed by Polyanski, Jensen, and Tennyson[51] (the PJT2 potential). The intermolecular potential is described in Sec. III. The eigenvalues and eigenfunctions were calculated using a discrete variable representation (DVR) method. States were assigned based on the nodal pattern of the wave function. In the present work we use the traditional normal mode state labels, i.e., $H_2O(\nu_1\nu_2\nu_3)$, to identify states, although for high energy states like (004) it is more meaningful to describe the states using local mode labels, i.e., $|04\rangle^-$. The coupled-channel equations were solved by a sector based numerical method similar to R-matrix propagation. The lowest 80 states were included in all calculations. A few test calculations with smaller numbers of states indicated that the large cross sections for states up to (004) were sufficiently converged with respect to addition or subtracting states from this list. Rotation was treated by the infinite order sudden (IOS) approximation, with cross sections determined by averaging over H_2O orientations using grids in the two Euler angles. The calculations were repeated for each partial wave and over a grid of total energies, and the thermal state-to-state energy transfer rate coefficients were determined by integration of the spline-fitted cross sections over the translational energy grid. Elastic cross sections were calculated by solving the radial equation with vibrational adiabatic potentials from the coupled-channel calculations, including enough partial waves to converge the partial wave sum.

C. Potential energy surfaces

Even though $H+H_2O$ is one of the simplest four-atom reactions, there is no potential surface available in the literature that is completely satisfactory for the study that we want to do. Most of the theoretical work in the literature has been based on the *ab initio* results of Walch and Dunning.[52] The most extensively used fit to these data was developed by Schatz and Elgersma[53] (the WDSE surface), but it is known to have deficiencies. There are various modifications to this surface[33,34] but neither WDSE nor improvements thereon

have been developed to describe reaction or energy transfer with highly excited water. A different approach was taken by Isaacson,[54] who used high quality *ab initio* data of Kraka and Dunning[55] along with a fitting function centered around the minimum energy path to generate a surface called I5. A comparison of the properties at the saddle point of the WDSE and I5 surfaces is given in Ref. 56. The WDSE surface is further compared with a modified surface developed by Alagia *et al.* in Ref. 57. Isaacson's test calculations for the reverse of reaction (1) showed that the experimental thermal rate coefficients can be well reproduced by carefully performed variational transition state theory (TST) calculations. However the ability of the I5 or Alagia *et al.* surfaces to describe reaction or energy transfer involving highly excited H_2O is unknown.

In the classical mechanical *reactive* scattering calculations, we used the I5 potential surface. Only one of the two water hydrogen atoms in the $H+H_2O$ collisions has a properly parametrized potential, so in all of our calculations we have ignored reaction that involves the unphysical hydrogen atom, and then multiplied the cross section associated with the physical hydrogen atom by two. This same procedure has been used in the past with the WDSE potential (where the unphysical hydrogen atom cannot react at all), and it gives absolute cross sections for $H+H_2O(000)$ that are in good agreement with experiment.

Although the I5 potential is reasonable for describing reactive collisions, it turns out that the long range potential on this surface is unphysical, thereby causing the inelastic scattering cross sections to be useless. The asymmetry of the two hydrogen atoms on this potential is also a source of trouble for inelastic scattering calculations, as it is much more difficult to identify trajectories as physical or unphysical since many trajectories involve significant interaction of the incident hydrogen atom with both hydrogen atoms in the water molecule during a collision. We were therefore unable to do a comparative study of reactive and inelastic $H+H_2O$ cross sections using this surface. To circumvent this, we chose to calculate the inelastic rates with a potential surface that is expected to reflect reality more accurately. To do this, we used the PJT2 potential for the intramolecular potential of the H_2O molecule. For the intermolecular force field, we used (as one choice) standard pairwise atom–atom Lennard-Jones potentials. We shall refer to this combination of force fields as PJT2+LJ. However, this potential is not expected to be realistic, for it is known that on a potential surface that allows reaction to take place, such as $H+H_2O$, the reactant can perturb the intramolecular force field of the molecular partner more strongly than is allowed by the Lennard-Jones potential. As a result, the probability of inelastic events should be larger than is predicted by the PJT2+LJ potential.

In order to understand the importance of this effect, we studied a collision system, H+HF, where the potential is much better known. Inelastic cross sections for the $H+HF(v=4)\rightarrow H+HF(v')$ obtained using classical trajectories on the 6SEC (scaled external correlation) potential surface[58] (a surface that was derived from high quality *ab initio* calculations) are shown in Fig. 1(a). This figure shows that there is a significant cross section (>1 Å^2) for inelastic
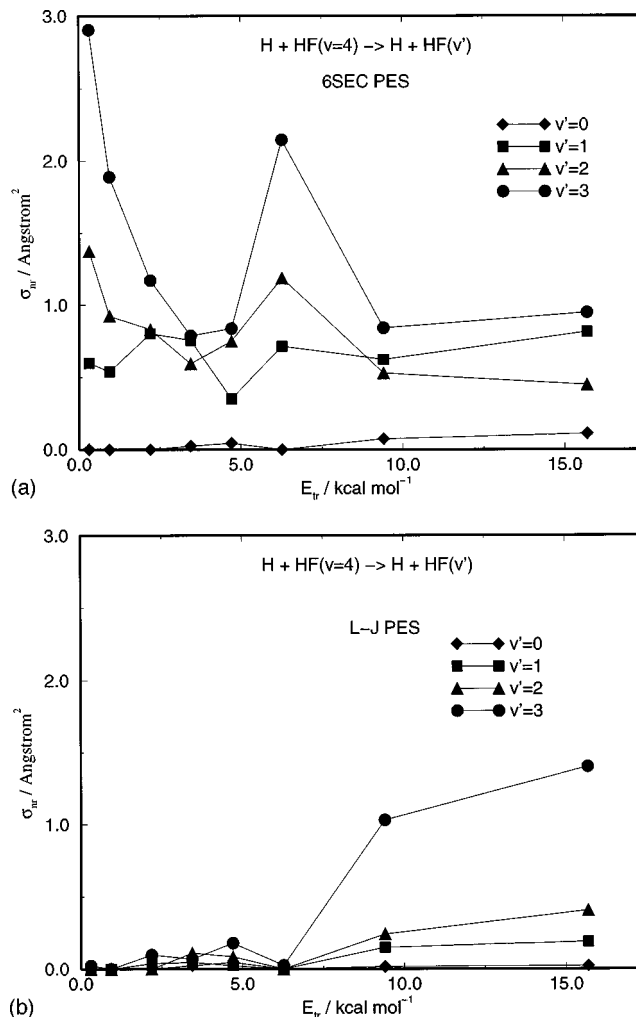

FIG. 1. Inelastic cross sections in the H+HF system obtained in classical trajectory calculations on (a) the 6 SEC potential and (b) using the nonreactive HF interaction from the 6SEC potential and adding pairwise Lennard-Jones potentials between the reactive H atom and the reactant molecule.

collisions, even at low kinetic energies. On the other hand, if the forces acting between HF and H are described by pairwise Lennard-Jones potentials, the inelastic cross sections are much smaller at low kinetic energy, as shown in Fig. 1(b). The reason for the difference is that many inelastic collisions occur through what Hawthorne, Sharkey, and Smith refer to as a frustrated reaction mechanism: The reactant is turned back from deep in the reactant valley near the saddle point for reaction on the 6SEC surface. This suggests that we need to use an intermolecular potential for $H+H_2O$ that contains reactive features. The WDSE and I5 surfaces do this, but they are deficient in other aspects (long-range forces, and inequivalent H atoms) as mentioned above. To circumvent this, we "borrowed" the two- and three-body potential terms from the well-behaved 6SEC potential, using them for the intermolecular force field in the $H+H_2O$ quantum scattering calculations. One justification for this procedure is that the saddle point energies on the H+HF and $H+H_2O$ surfaces are similar, so accessibility of the region of significant intermolecular interaction should be similar for both surfaces at the energies we consider.

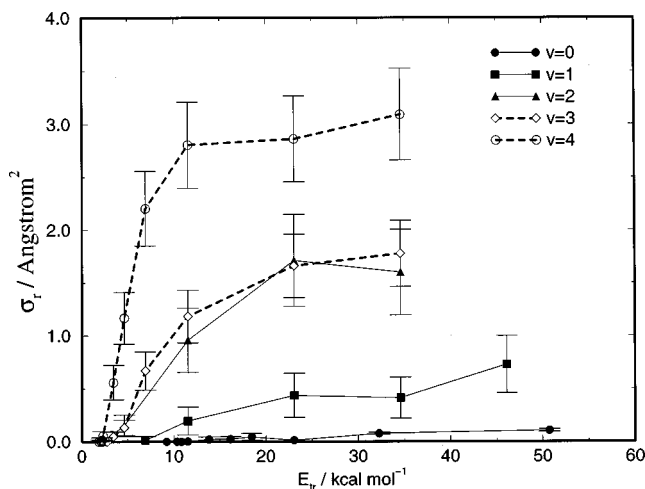We shall refer to this alternative intermolecular potential

FIG. 2. Reactive cross section of reaction (1) as a function of the initial translational energy obtained in classical trajectory calculations on the I5 potential surface for the (00n) states of water.

FIG. 3. Reactive cross sections for the reaction (a) H+HF→H$_2$+F and (b) H+H'F→HF+H' as a function of the initial translational energy obtained in classical trajectory calculations on the 6SEC potential surface for various vibrationally excited levels of the water molecule.

as PJT2+6SEC. We should note that with the 6SEC potential there are open reactive channels present in the inelastic scattering calculations. These channels are suppressed with the finite basis expansion used in the quantum scattering calculations. However the influence of the barrier region is still included, at least approximately. This treatment is analogous to earlier distorted wave studies of H+H$_2$ and Cl+HCl,[59–61] and should give reasonable results with the right basis set, although it is only a perturbative approach.

III. RESULTS

Reactive rate coefficients. The classical trajectory calculations based on the I5 surface show that the reactivity of the water molecule increases spectacularly when the O–H local mode is excited. Figure 2 shows the reactive cross sections as a function of the translational energy for the (00n) states of the water molecule. The threshold energy for the (000) state is above 10 kcal mol^{-1} and the cross section increases slowly with increasing translational energy above threshold. The threshold energy is lower for reaction from the (001) state, being around 6.3 kcal/mol, and the cross section increases much faster with increasing translational energy than for the (000) state. These tendencies continue as higher excitation is deposited into the water molecule. The lowest threshold energy, as expected, is obtained for the (004) state, but, being around 1.9 kcal/mol, it is still far from zero, even though the total energy is above the barrier. Note that the maximum reactive cross section for (004) (observed in the ''plateau'' region of the σ_r versus E_{tr} curve) is around 3 Å^2.

For comparison, we have calculated the cross sections for the analogous reaction between H atoms and HF(v),

$$H+HF(v)\rightarrow H_2+F, \qquad (2)$$

using the 6SEC potential surface. The results are presented in Fig. 3(a). The threshold energies for reaction of HF(v =0 and 1) are very high and the cross sections are very low, very much like H+H$_2$O(000), so the results are not shown in Fig. 3. Even HF(v=2) gives essentially negligible cross
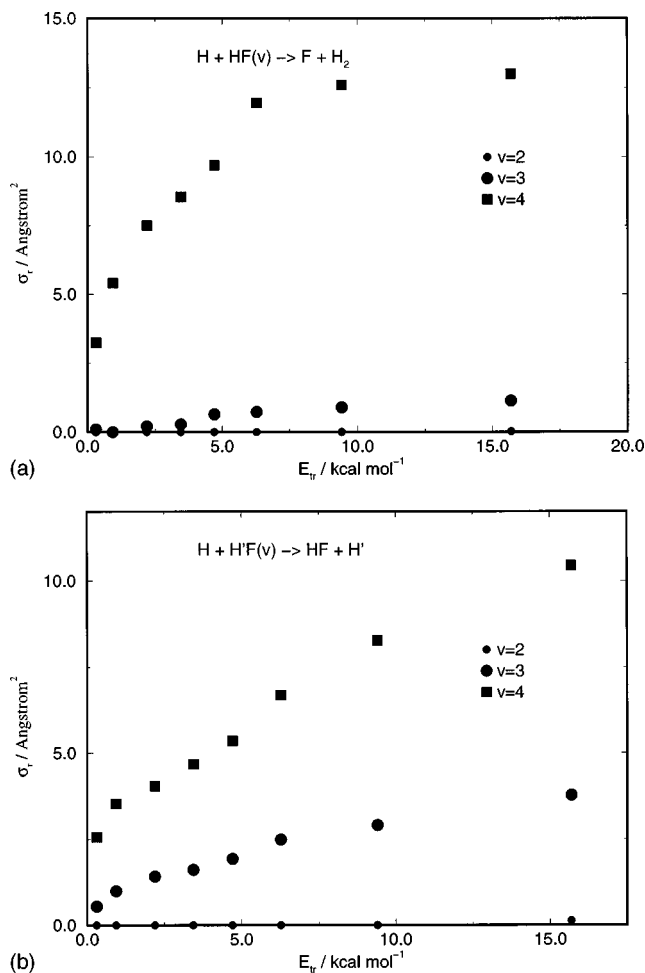
sections, but HF(v=3) has a threshold of about 2 kcal/mol, and HF(v=4) has a threshold of essentially zero, with a cross section of 5 Å^2 at 1 kcal/mol and a plateau cross section of about 13 Å^2. This, of course, is the expected behavior for an endothermic reaction with a late barrier,[62] and it is qualitatively like what we see in Fig. 2. However for H+H$_2$O on the I5 surface, the increase of σ_r for the vibrationally excited reactant is slower and begins at a higher threshold energy, and the absolute values are smaller, than observed for reaction (2). This difference between H+HF and H+H$_2$O could be due to different potential surfaces, but it could also be intrinsic to the dynamics. What we mean by the latter statement is that in a triatomic molecule the spectator modes are not necessarily completely passive so that they can exchange energy with the reactive modes during the course of the reaction. As a result, some of the excess energy could be locked up in those modes, resulting in a nonzero threshold for reaction even when the initial excitation puts the system above the barrier.

In our H+HF(v) calculations, we also obtained nonzero cross sections for the F-atom exchange process

$$H+H'F(v)\rightarrow H'F+H. \qquad (3)$$

TABLE I. The thermal rate coefficients for the reaction $H+H_2O(00v)$ $\rightarrow H_2+OH$ obtained in classical trajectory calculations using the I5 potential surface (in cm^3 molecule^{-1} s^{-1}).

State	300 K	1000 K
(000)	$0.612E-19$	$0.216E-13$
(001)	$0.645E-15$	$0.788E-12$
(002)	$0.375E-12$	$0.953E-11$
(003)	$0.103E-12$	$0.104E-10$
(004)	$0.145E-11$	$0.367E-10$

These results are plotted in Fig. 3(b). Here we see behavior that is a lot like Fig. 3(a), with the cross sections being negligible for $v=0-2$, and the threshold dropping to essentially zero for $v=4$. For $v=4$ the exchange cross section is slightly smaller than the abstraction cross section, but otherwise the energy dependence is very similar.

The importance of exchange in collision processes involving H+HF has been examined previously by Schatz,[63] so we will not discuss this here other than to say that the 6SEC surface that we have used provides a reasonable though not perfect description of the experiments. What we instead consider is whether exchange might play a role in the H+H_2O reaction dynamics. Exchange has only rarely been considered in H+H_2O, for example in the paper by Kudla and Schatz,[31] and in the experiments by Brownsword et al.[64] Although the I5 and WDSE potential energy surfaces have an exchange reaction pathway in them, this pathway was not based on ab initio or empirical input, and thus could be totally erroneous. The only ab initio study of the exchange barrier comes from Talbi and Saxon,[65] who suggest that the exchange barrier is comparable to the abstraction barrier, much as is the case for the H+HF system. We conclude from this that exchange probably does contribute to the H+H_2O system, but it is unlikely to have a cross section for H+H_2O(004) that is much larger than the abstraction cross section.

Now let us return to the results in Fig. 2. The reactive cross sections for the ground state of water in Fig. 2 can be compared with the experimental data obtained on hot-atom systems. According to Jacobs, Volpp, and Wolfrum[13] the cross sections are 0.16 and 0.25 Å^2 at translational energies of 23 and 51 kcal mol^{-1}. Quasiclassical trajectories using the I5 surface yield 0.21 and 1.36 Å^2, respectively, at the same two energies. While the former cross section agrees well with the experiment, the theoretical reactive cross section increases much faster than the experimental.

The thermal rate coefficients show much poorer agreement between theory and experiment. The thermal rate coefficients we obtain from the reactive cross sections shown in Fig. 2 are collected in Table I. The experimental rate coefficient at 295 K is[24] 2.0×10^{-25} cm^3 molecule^{-1} s,$^{-1}$ while our value for the (000) state at 295 K is 6.1×10^{-20} cm^3 molecule^{-1} s,$^{-1}$ a much higher value. The too high theoretical rate coefficient is a consequence of the too low threshold energy on the I5 surface. Note that the threshold energy for reaction from the ground state is higher on the WDSE surface than what we have seen here,[29] and the agreement of thermal rate coefficients is much better.

The thermal rate coefficients calculated for various initial states from the reactive cross sections in Fig. 2 indicate that excitation of the O–H bond in the water molecule causes a significant increase in reactivity. The room temperature rate coefficient is eight orders of magnitude higher for the (004) state than for (000). Although this is a much smaller increase than one obtains if the total reactive+inelastic rate measured by Hawthorne et al. is considered to be fully reactive, the increase is spectacular. As indicated by the quantum scattering calculations described in Sec. IV, the inelastic cross section for deactivation of the (004) state, however, is much larger than the reactive cross section.

IV. QUANTUM INELASTIC SCATTERING CALCULATIONS

The inelastic rate coefficients for the H+H_2O(00n) system obtained with the PJT2+6SEC potential that mimics a reactive interaction are shown in Fig. 4, and in Fig. 5 we
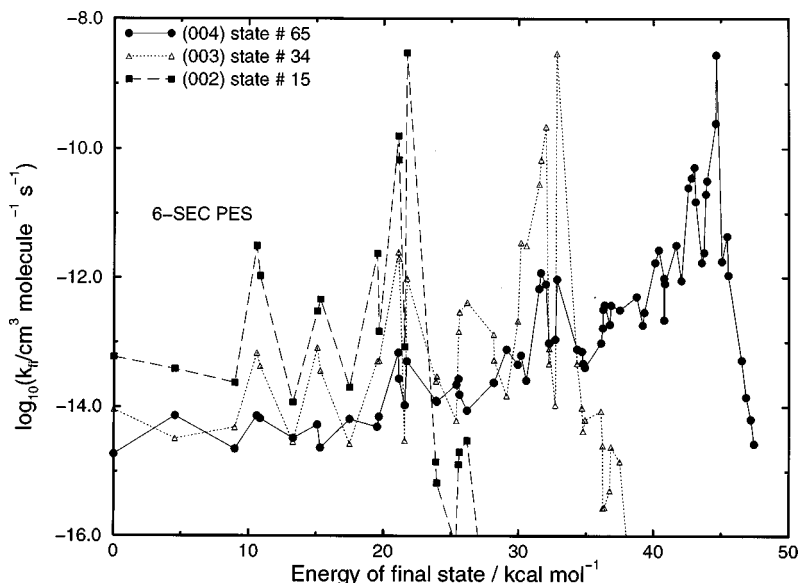

FIG. 4. Inelastic thermal rate coefficients for the H+H_2O(00n)$\rightarrow$H+H_2O (ijk) obtained in quantum scattering calculations on the PJT2+6SEC surface for $n=2$, 3, and 4.
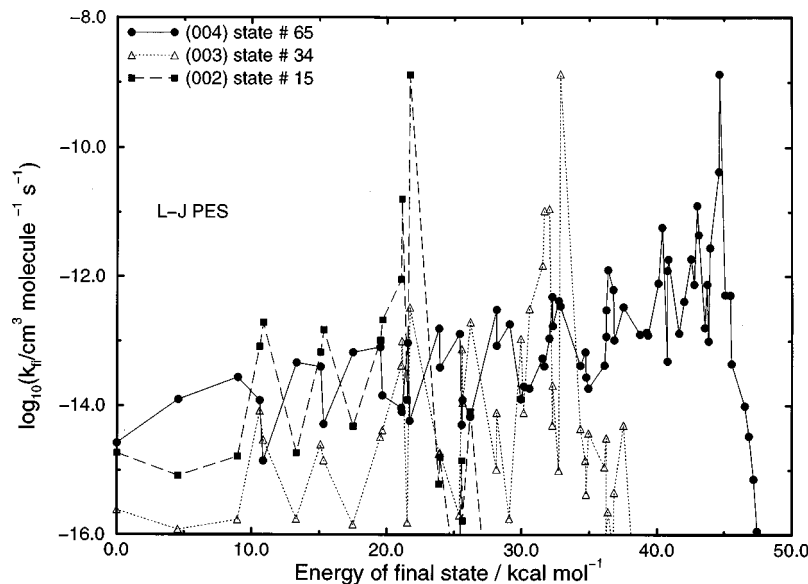
FIG. 5. Inelastic thermal rate coefficients for the $H+H_2O(00n) \rightarrow H+H_2O$ (*ijk*) obtained in quantum scattering calculations on the PJT2+LJ surface for $n = 2$, 3, and 4.

present the analogous data obtained when the two partners interact through nonreactive Lennard-Jones pair potentials (PJT2+LJ). The plots show, on a semilogarithmic scale, the inelastic rate coefficients at 300 K from the (002), (003), and (004) states, respectively, as a function of the energy of the final state. The high elastic peak shows the location of the initial state. The ''spectrum'' of inelastic rate coefficients associated with each of the three initial states does not show any strong propensity for transitions within the same mode. In other words, if we consider transitions starting from (004), the $(004) \rightarrow (003)$ transition is—although it has a higher rate than the transitions to the other neighboring states near (003)—not the most probable process. What seems to be more important is the energy gap between the initial state and the final state. For the (004) state, the largest inelastic rate coefficient is associated with a state that is closest in energy. This state is a mixed state, mostly corresponding to the configuration (*nm*0) with *n* and *m* both large, and it is separated by only 13.1 cm^{-1} from (004). Other large cross sections are associated with small energy gaps, and there is an overall envelope to the probability distribution that drops off rapidly for energy gaps larger than 50 cm^{-1}. This dominant influence of energy gap on determining the propensities for inelastic transition probabilities is similar to what was observed by Bowman and Padmavathi[66] in their quantum scattering studies of the Ar+HCN system.

The role of the energy gap is apparently stronger for high initial excitation where there is a considerable mixing of states. At lower excitation, say from the (002) and (003) states, the preferred inelastic transition is associated with the third and fourth closest state, which is (200) and (300), respectively. What is important with respect to the comparison of the reactive and inelastic cross sections is that the magnitude of the largest inelastic rate coefficient is greater than $10^{-10} cm^3 molecule^{-1} s,^{-1}$ in particular, it is found to be $2.45 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ for the fastest transition deactivating the $H_2O(004)$ molecule. The sum of inelastic rate coefficients out of (004) is 4.47×10^{-10}. The largest inelastic transition probabilities from (003) and (002) are also above

$10^{-10} cm^3 s^{-1}$. Note in Fig. 5 that these rate coefficients are down by a factor of 10 for the LJ interaction potentials compared to 6SEC.

V. DISCUSSION

The inelastic rate coefficient we obtained for the deactivation of the (004) state of water is very close to what Hawthorne *et al.* obtained in their measurements[25,26] ($4.3 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$) for the sum of the reactive and inelastic rates initiated from this state. The calculations indicate that the reactive rate coefficient, being around $1.45 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$, is less than 1% of the inelastic rate coefficient. The contribution of the reactive rate coefficient to the loss of $H_2O(004)$ concentration is therefore minor. Even if the threshold for reaction were zero, the rate coefficient (obtained the plateau value of the cross section in Fig. 2) would be $7.7 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ which is still less than 20% of the total inelastic rate coefficient.

There is an important assumption which underlies the present conclusions as well as those of Hawthorne *et al.*, namely, that the evolution of the $H_2O(004)$ state is governed by kinetic rate theory with energy transfer from $H_2O(004)$ producing a much smaller reactive state. Obviously, a more complete treatment will involve solution of the master equation, with the energy transfer and reaction steps included.

VI. CONCLUSION

The relative importance of the reactive and inelastic collisions in reaction (1) was studied in a composite theoretical investigation that includes classical reactive and quantum inelastic scattering calculations.

The classical trajectory studies indicate that the rate of the reaction increases significantly with increasing vibrational excitation of the O–H local mode of water. The threshold energy decreases significantly and the absolute magnitude of the reactive cross section increases. The 300 K thermal rate coefficient increases by eight orders of magnitude in going from the (000) state to the (004) state. The

thermal rate coefficient for reaction from the (004) state is found to be around $1.45 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$.

The quantum scattering calculations show that the inelastic rate coefficients are very large for the highly excited pure stretch states. The thermal rate coefficient for deexcitation of the (004) state at 300 K is found to be $4.47 \times 10^{-10} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$, about two orders of magnitude larger than the corresponding reactive rate coefficient. The corresponding average thermal cross section (obtained as $\langle \sigma \rangle = k / \langle v \rangle_{\text{thermal}}$) is around $17 \, \text{Å}^2$.

The inelastic rate coefficient, and so the sum of the inelastic and reactive rate coefficients is close to what Hawthorne *et al.* reported. The measured rate coefficient is dominated by the inelastic contributions according to our calculations.

The very large role of the inelastic collisions can be understood based on the potential energy surfaces. If there is the possibility of reaction, the reactant atom penetrates near to the barrier region of the potential surface. There is, however, not necessarily enough energy to surmount the barrier, and even if there is, the strong interactions invoke an extensive energy exchange between the modes. As a consequence, there is an increased possibility for inelastic collisions to occur. This frustrated reaction mechanism for vibrational energy transfer is apparently more important for $H + H_2O$ than for $H + HF$ (comparing the inelastic cross sections in Figs. 1 and 4). One feature which promotes this is the small energy gap ($< 50 \, \text{cm}^{-1}$) between (004) and the closest state in energy. The importance of the reactive scattering in producing large inelastic rates is supported by the observation that on the purely nonreactive PJT2+LJ surface the inelastic rates are an order of magnitude smaller than on the ''reactive'' PJT2+6SEC surface. We should emphasize, however, that accuracy of our calculations depends on the quality of the potential surfaces. It seems to us, that currently there is no potential surface for $H + H_2O$ with sufficient accuracy to provide chemically accurate reactive or inelastic rate coefficients. In order that the new, highly sophisticated and computationally demanding four-atom quantum scattering calculations could provide results that can be compared with experiments, a new, high-quality potential surface is badly needed.

ACKNOWLEDGMENTS

[1] A. A. Westenberg and N. DeHaas, J. Chem. Phys. **58**, 4061 (1973).
[2] A. R. Ravishankara, J. M. Nicovich, R. L. Thompson, and F. P. Tully, J. Phys. Chem. **85**, 2498 (1981).
[3] V. Schmidt, G. Y. Zhu, K. H. Becker, and E. H. Fink, Ber. Bunsenges. Phys. Chem. **89**, 321 (1985).
[4] P. Frank and Th. Just, Ber. Bunsenges. Phys. Chem. **89**, 181 (1985).
[5] J. V. Michael and J. W. Sutherland, J. Phys. Chem. **92**, 3853 (1988).
[6] C. P. Fenimore and G. W. Jones, J. Phys. Chem. **62**, 693 (1958).
[7] G. Dixon-Lewis, M. M. Sutton, and A. Williams, Trans. Faraday Soc. **61**, 255 (1965).
[8] S. Madronich and W. Felder, J. Phys. Chem. **88**, 1857 (1984).
[9] M. Brouard, H. M. Lambert, S. P. Rayner, and J. P. Simons, Mol. Phys. **89**, 403 (1996).
[10] A. Jacobs, H.-R. Volpp, and J. Wolfrum, *24th International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1992).
[11] A. Jacobs, H.-R. Volpp, and J. Wolfrum, Chem. Phys. Lett. **196**, 249 (1992).
[12] A. Jacobs, H.-R. Volpp, and J. Wolfrum, Chem. Phys. Lett. **218**, 51 (1994).
[13] A. Jacobs, H.-R. Volpp, and J. Wolfrum, J. Chem. Phys. **100**, 1936 (1994).
[14] K. Kessler and K. Kleinermanns, Chem. Phys. Lett. **190**, 145 (1992).
[15] K. Honda, M. Takayanagi, T. Nishiya, H. Ohoyama, and I. Hanazaki, Chem. Phys. Lett. **180**, 321 (1991).
[16] A. Sinha, M. C. Hsiao, and F. F. Crim, J. Chem. Phys. **92**, 6333 (1990).
[17] A. Sinha, J. Phys. Chem. **94**, 4391 (1990).
[18] F. F. Crim, M. C. Hsiao, J. L. Scott, A. Sinha, and R. L. van der Wal, Philos. Trans. R. Soc. London Ser. A **332**, 259 (1990).
[19] A. Sinha, M. C. Hsiao, and F. F. Crim, J. Chem. Phys. **94**, 4928 (1991).
[20] M. C. Hsiao, A. Sinha, and F. F. Crim, J. Phys. Chem. **95**, 8263 (1991).
[21] F. F. Crim, J. Phys. Chem. **100**, 12725 (1996).
[22] M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, J. Chem. Phys. **95**, 8647 (1991).
[23] M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, J. Phys. Chem. **97**, 2194 (1993).
[24] M. J. Bronikowski, W. R. Simpson, B. Girard, and R. N. Zare, J. Phys. Chem. **97**, 2204 (1993).
[25] G. Hawthorne, P. Sharkey, and I. W. M. Smith, J. Chem. Phys. **108**, 4693 (1998).
[26] I. W. M. Smith, XXIII. Informal Conference on Photochemistry, Pasadena, CA, 10–15 May 1998.
[27] J. M. Bowman and G. C. Schatz, Annu. Rev. Phys. Chem. **46**, 169 (1995).
[28] H. Elgersma and G. C. Schatz, Int. J. Quantum Chem., Symp. **15**, 611 (1981).
[29] G. C. Schatz, M. C. Colton, and J. L. Grant, J. Phys. Chem. **88**, 2971 (1984).
[30] K. Kudla and G. C. Schatz, Chem. Phys. Lett. **193**, 507 (1992).
[31] K. Kudla and G. C. Schatz, J. Chem. Phys. **98**, 4644 (1993).
[32] K. Kudla and G. C. Schatz, Chem. Phys. **175**, 71 (1993).
[33] O. Rashed and N. J. Brown, J. Chem. Phys. **82**, 5506 (1985); J. Chem. Phys. **85**, 4348 (1986).
[34] D. C. Clary, J. Chem. Phys. **95**, 7298 (1991).
[35] D. C. Clary, Chem. Phys. Lett. **192**, 34 (1992).
[36] G. Nyman and D. C. Clary, J. Chem. Phys. **99**, 7774 (1993).
[37] D. Wang and J. M. Bowman, Chem. Phys. Lett. **207**, 227 (1993).
[38] J. M. Bowman and D. Wang, J. Chem. Phys. **96**, 7852 (1992).
[39] D. Wang and J. M. Bowman, J. Chem. Phys. **98**, 6235 (1993).
[40] H. Szichman, I. Last, A. Baram, and M. Baer, J. Phys. Chem. **98**, 828 (1994).
[41] H. Szichman and M. Baer, J. Chem. Phys. **101**, 8620 (1994).
[42] H. Szichman and M. Baer, Chem. Phys. Lett. **242**, 285 (1995).
[43] D. H. Zhang and J. C. Light, J. Chem. Phys. **104**, 4544 (1996).
[44] J. T. Muckermann and D. G. Truhlar, in *Atomic and Molecular Collisions, a Guide to the Experimentalist*, edited by R. B. Bernshtein (Plenum, New York, 1979), p. 505.
[45] R. N. Porter and L. Raff, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976).
[46] H. Elgersma and G. C. Schatz, Int. J. Quantum Chem., Symp. **15**, 611 (1981).
[47] G. C. Schatz, Comput. Phys. Commun. **51**, 135 (1988).
[48] G. C. Schatz, J. Phys. Chem. **99**, 516 (1995).
[49] G. C. Schatz and G. Lendvay, J. Chem. Phys. **106**, 3548 (1997).
[50] G. Lendvay and G. C. Schatz, Ber. Bunsenges Phys. Chem. **101**, 587 (1997).
[51] O. L. Polyansky, P. Jensen, and J. Tennyson, J. Chem. Phys. **105**, 6490 (1996).
[52] S. P. Walch and T. H. Dunning, J. Chem. Phys. **72**, 1303 (1980).
[53] G. C. Schatz and H. Elgersma, Chem. Phys. Lett. **73**, 21 (1980).
[54] A. D. Isaacson, J. Chem. Phys. **107**, 3832 (1997).
[55] E. Kraka and T. H. Dunning, Jr. (to be published).

[56] K. S. Bradley, G. C. Schatz, J. Chem. Phys. **108**, 7994 (1998).

[57] M. Alagia, N. Balucani, P. Casavecchia, D. Stranges, G. G. Volpi, D. C. Clary, A. Kliesch, and H.-J. Werner, Chem. Phys. **207**, 389 (1996).

[58] S. L. Mielke, G. C. Lynch, D. G. Truhlar, and D. W. Schwenke, Chem. Phys. Lett. **213**, 11 (1993); **E217**, 173 (1994).

[59] G. C. Schatz, Chem. Phys. Lett. **150**, 92 (1988).

[60] G. C. Schatz, B. Amaee, and J. N. L. Connor, Chem. Phys. Lett. **132**, 1 (1986).

[61] G. C. Schatz, L. M. Hubbard, P. S. Dardi, and W. H. Miller, J. Chem. Phys. **81**, 231 (1984).

[62] M. H. Mok and J. C. Polanyi, J. Chem. Phys. **51**, 1451 (1969).

[63] G. C. Schatz, J. Chem. Phys. **106**, 2277 (1997).

[64] R. A. Brownsword, M. Hillenkamp, T. Laurent, H.-R. Volpp, J. Wolfrum, R. K. Vatsa, and H. S. Yoo, J. Phys. Chem. A **101**, 6448 (1997).

[65] D. Talbi and R. P. Saxon, J. Chem. Phys. **91**, 2376 (1989).

[66] J. M. Bowman and A. Padmavathi, Mol. Phys. **88**, 21 (1996).