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First-Principles Theory for the H + H_2O, D_2O Reactions

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A full quantum dynamical study of the reactions of a hydrogen atom with water, on an accurate ab initio potential energy surface, is reported. The theoretical results are compared with available experimental data for the exchange and abstraction reactions in H + D_2O and H + H_2O. Clear agreement between theory and experiment is revealed for available thermal rate coefficients and the effects of vibrational excitation of the reactants. The excellent agreement between experiment and theory on integral cross sections for the exchange reaction is unprecedented beyond atom-diatom reactions. However, the experimental cross sections for abstraction are larger than the theoretical values by more than a factor of 10. Further experiments are required to resolve this.

Since molecular beam experiments first examined chemical reactions at the most rigorous elementary level (*1*), there has been intense effort to develop theory for reliable calculations of chemical dynamics. The purpose of this quest for quantitatively accurate theory is to provide a definitive understanding of the mechanisms of chemical reactions—an understanding that will ultimately provide the basis for confident prediction of chemical rates and for control of chemical reactions.

Quantitative theory faces two difficult tasks: the construction of accurate multidimensional potential energy surfaces (PESs) and the performance of reactive scattering calculations on these surfaces. These tasks have been largely achieved for triatomic systems (*2, 3*), in particular for the H + H_2 reaction family (*4, 5*). Accurate theory for tetraatomic reactions should substantially extend our understanding of elementary reaction mechanisms (*3, 6*). Four-atom systems support a much richer variety of phenomena, including competing reaction pathways, steric hindrance, and the influence of different reactant vibrations on the course of the reaction. Over the past several years, advances in accurate reactive scattering calculations (*7–9*) and the construction of PESs (*10–14*) have been combined with the rise in computational power to make accurate ab initio dynamics practicable for four-atom systems. This study reports such calculations for the H + H_2O family

$$H + D_2O \rightarrow D + HOD \quad (1)$$

$$H + D_2O \rightarrow HD + OD \quad (2)$$

$$H + H_2O \rightarrow H_2 + OH \quad (3)$$

These reactions have become the prototype tetraatomic reactions, in which different vibrational modes in the reactants can play an important role in the reaction dynamics (*1*). This role has been extensively studied in the past decade (*15–23*). In addition, the thermal rate coefficient for reaction 3 is known (*24*), and the effect of reactant translational energy on reactions 1 and 3 has been closely examined (*25–29*). Because this system has few electrons and three very light atoms, it is an ideal candidate for the theoretical study of tetraatomic reactions in terms of both practicality and importance. Not surprisingly, these reactions, and the reverse reaction of OH + H_2, have been the focus of the development of quantum reaction dynamics for four-atom systems (*6–9, 30–32*). Once substantial progress had been made with the scattering methodology, attention naturally turned to improving the PES (*33–35*). However, only very recently have PESs been developed that can accurately describe reactions 1 to 3, including the effect of vibrationally excited reactants (*14*). We briefly describe the methods used to obtain "benchmark" descriptions of reactions 1 to 3. The calculations are then compared with the available experimental data to see what stage theory has reached. It will become clear that the substantial amount of computer time expended here was necessary to approach "chemical accuracy," as measured by some types of experimental data. In one case, the theory is sufficiently reliable to suggest that some experimental data ought to be reconsidered.

The PES is constructed as an interpolation of high-level ab initio quantum chemistry data (*36*) evaluated over a large range of molecular geometries. This interpolation scheme for PES (*10–12*) has been demonstrated to be sufficiently accurate for quantum scattering (*13, 14*). The quantum chemistry calculations are discussed in a recent paper (*14*). A data set of 1000 geometries was constructed (which required ~800 days of CPU time on a state-of-the-art workstation). In contrast to earlier work (*14*), no additive or scaling approximations have been employed here. The resulting PES is depicted schematically in Fig. 1. When the total angular momentum $J = 0$, the exact quantum dynamics of the molecule is calculated by using a time-dependent wave packet method (*8*), extended so that the exact total probabilities for reactions 1 to 3 could be evaluated with all six internal degrees of freedom taken into account explicitly. For $J > 0$, the centrifugal sudden (CS) approximation is used (which should only introduce a few-percent error in the total reaction cross sections at medium to high translational energy) (*9*).

In Fig. 2, we compare theoretical integral cross sections for the exchange reaction with the experimental results (*28, 29*): the absolute cross sections at a relative translational energy of 1.5 and 2.2 eV and the excitation function of the reaction in the line-of-center functional model (*29*). The first-principles theoretical results agree excellently with the experiments in all respects. We note that the experimental result is thermally averaged over the initial rotation of D_2O, whereas the theoretical result is for initial nonrotating D_2O (preliminary calculations showed that rotational excitation of the triatomic reactant has no substantial effect on the integral cross section).

The agreement between theory and experiment for the abstraction reactions is both positive and negative. A comparison of the experimental data (*24*) with the theoretical

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rate coefficient (and the contributions to this coefficient from individual vibrational states of the reactants) shows that the theoretical rate coefficient is ~25 to 40% smaller than the corresponding experimental values (Fig. 3). Why? First, a further expansion of the basis set and a more complete treatment of electron correlation may reduce the barrier to reaction by ~1 to 3 kJ mol^{-1}, sufficient to bring theory and experiment into better agreement. Second, our scattering calculation has been performed for nonrotating H_2O rather than a thermal distribution of rotational energy levels. This is a good approximation for low excited rotational states, but if the reaction cross section increases with high rotational excitation of the reactant H_2O, our theoretical estimate of the thermal rate will be too low. In addition, the CS approximation used in $J > 0$ calculations may also introduce a small error in the rate constant (*9*). Nevertheless, the agreement between experiment and theory is good for the rate coefficient of reaction 3 (Fig. 3). Figure 3 also shows that, in the low-temperature region, the thermal rate coefficient is dominated by the contributions from the excited OH stretching states $(02)^{\pm}$ and $(01)^{\pm}$, in particular from the $(02)^{\pm}$ states [in the local mode notation (*16*)]. In the high-temperature region, the contributions from $(03)^{\pm}$ also become important. This observation is in agreement with the recent quasi-classical trajectory results of Schatz *et al.* (*35*). The low-temperature rate of reaction 3 has not been observed directly but can be inferred from the reverse reaction rate and the equilibrium constant. The rate coefficient at 298 K was estimated (*37*) to be $(2.1 \pm 1.3) \times 10^{-25}$ cm^3 s^{-1}, which is in agreement with our calculated value of 0.9×10^{-25} cm^3 s^{-1}.

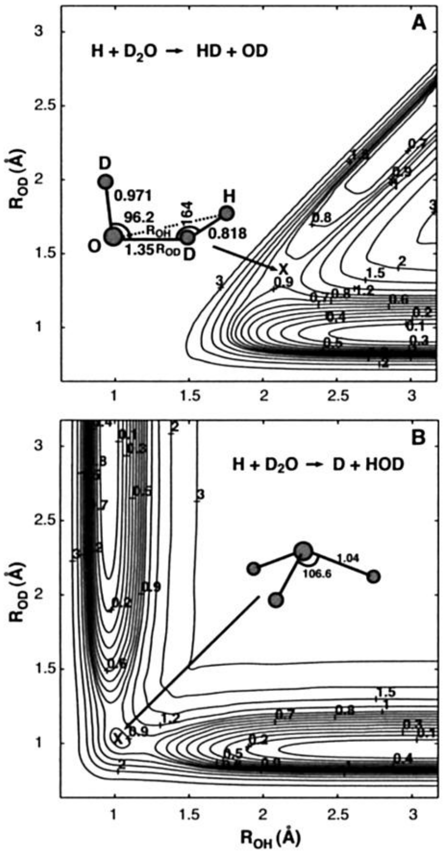

Fig. 1. Potential energy contours for the H + D_2O system as a function of the OH and one OD bond length (R_{OH} and R_{OD}, respectively). In each panel, the energy has been minimized with respect to the remaining degrees of freedom in the vicinity of minimum energy paths. (**A**) The saddle point for the abstraction reaction and (**B**) the C_{3v} symmetry minimum for the exchange reaction are marked with x.

In contrast, there is no agreement between the calculations and the reported integral cross sections (*25–27*) for reactions 2 and 3 involving ground state reactants. The theoretical cross sections are smaller than the experimental results by a factor of 10 to 20 (Fig. 4). Given the agreement between theory and experiment for the thermal rate coefficient for reaction 3, we are unable to rationalize this discrepancy, assuming that the H_2O molecule has a vibrational temperature of ~300 K (our calculations employ ground state H_2O).

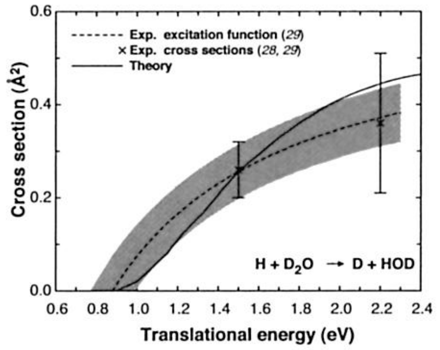

Fig. 2. Comparison between the experimental and theoretical integral cross sections for the H + $D_2O \rightarrow D$ + HOD reaction. The dashed line is the experimental excitation function. The shaded area reflects the statistical uncertainty (1σ) of the global least squares fit procedure used to determine the optimum excitation function [see (*29*) for details].

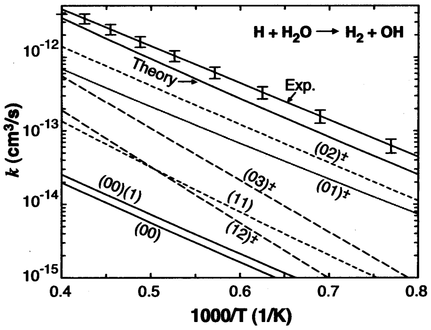

Fig. 3. Theoretical thermal rate constant for the H + $H_2O \rightarrow H_2$ + OH reaction and the contributions to this coefficient from individual vibrational states of the reactants, compared with the experimental results of Michael and Sutherland (*24*). $(AB)^{\pm}$ denotes the contribution to the thermal rate constant from $(AB)^{+}$ and $(AB)^{-}$ states. Error bars indicate statistical uncertainty (1σ).

The effect of vibrational excitation of the H_2O and D_2O reactants on the abstraction reactions with hydrogen atoms has been studied previously. Bronikowski *et al.* (*20*) measured the effect of relatively low levels of excitation. They found that one-quantum excitation of the asymmetric stretch in D_2O (or the combination of one quantum each of bend and asymmetric stretch) increased the cross section for reaction 2 by at least (and probably much more than) a factor of 5. Using a relative collision energy of the reactants of 1.5 eV, we calculate enhancement factors of 23 for the stretch excitation and 34 for the combination band. The effect of two, three, or four quanta of OH stretch excitation [the $(02)^-$, $(03)^-$, and $(04)^-$ states] on reaction 3 was measured by Sinha *et al.* (*16*). With a thermal (T = 300 K) distribution of relative velocities for the H and H_2O reactants, our calculations give rate coefficients of 2.15×10^{-12}, 2.896×10^{-11}, and 6.01×10^{-11} cm^3 s^{-1} for these three states, respectively. Hence, the product yields for the $(02)^-$ and $(03)^-$ states are 0.036 and 0.48, respectively, relative to that for the $(04)^-$ state. The corresponding observed relative yields are 0.06 (with an error range of 0 to 0.2) and 0.49 ± 0.13, respectively. The agreement between theory and experiment is excellent. In addition, our calculation also gives a rate coefficient of 3.14×10^{-12} cm^3 s^{-1} for

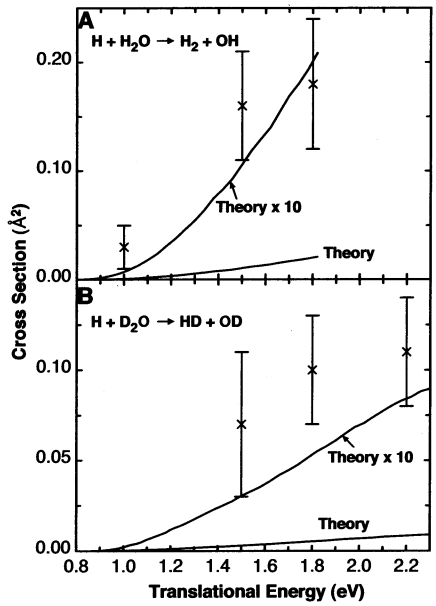

Fig. 4. Comparison between experimental (in crosses) and theoretical integral cross sections for (**A**) the H + $H_2O \rightarrow H_2$ + OH and (**B**) H + $D_2O \rightarrow$ HD + OD reactions. The theoretical cross sections are also shown enlarged by a factor of 10. However, the experimental data are not multiplied by this factor. Error bars indicate statistical uncertainty (1σ).

the $(12)^-$ state, which is only 50% larger than that for the $(02)^-$ state and a factor of 9 smaller than that for the $(03)^-$ state [in good agreement with the work of Sinha *et al.* (*16*)]. It is encouraging that, albeit several years after the experiments were performed, direct reliable comparison of theory with these experiment is possible.

In comparing all of the above theoretical and experimental results, it is worthwhile to keep in mind the very different sources of error in each case. The thermal rate coefficient for reaction 3 is, in one sense, both the most difficult to calculate theoretically and the simplest to measure experimentally. The theory is difficult because only with very large basis sets and very high level treatments of electron correlation can ab initio quantum chemistry provide a barrier height for these reactions that is accurate to within ~1 to 2 kJ mol^{-1}. The quantum dynamics calculation is also made more difficult by the fact that the thermal rate coefficient is dominated by contributions from vibrationally excited states of the reactants, requiring a large vibrational basis and separate calculations for many initial states. Achieving agreement for this seemingly mundane quantity to within ~35% is a substantial achievement for theory.

On the other hand, the theoretical calculation of the integral cross sections for reactions 1 and 2 (for near–ground state reactants at translational energies well above the barrier height) is relatively much easier. Given the accuracy of theory for the thermal rate coefficient, these integral cross sections may be seen to represent a more stringent test of experiment than of theory. The excellent agreement between the present results and experiments for reaction 1 illustrates the accuracy of our calculation in regard to the exchange region of the PES and the accuracy of the experimental measurement of absolute intensities. Unfortunately, the experimental cross sections for reactions 2 and 3 are completely inconsistent with our calculation and are seemingly inconsistent with the observed thermal rate coefficient. This is a case where the error anticipated for the theoretical result is relatively small. Reexamination of this experiment is therefore important, either to correct the presently accepted experimental results or to reveal the existence of some hitherto unsuspected problem with the theoretical calculations. Finally, it is particularly interesting to observe the huge difference in theoretical cross sections for the exchange and abstraction reactions shown in Figs. 2 and 3, although the barrier heights for these two reactions are coincidentally very close. This is the very effect of dynamics.

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A Light-Emitting Field-Effect Transistor

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We report here on the structure and operating characteristics of an ambipolar light-emitting field-effect transistor based on single crystals of the organic semiconductor α-sexithiophene. Electrons and holes are injected from the source and drain electrodes, respectively. Their concentrations are controlled by the applied gate and drain-source voltages. Excitons are generated, leading to radiative recombination. Moreover, above a remarkably low threshold current, coherent light is emitted through amplified spontaneous emission. Hence, this three-terminal device is the basis of a very promising architecture for electrically driven laser action in organic semiconductors.

Field-effect transistors (FETs) are generally unipolar devices and minority carrier effects are negligible. However, ambipolar FETs, which operate as either n- or p-channel devices, depending on the polarity of the gate bias, can operate in a mixed or bipolar mode, in which both electron and hole currents are injected into the device at separate electrodes. Ambipolar FETs have been realized with amorphous silicon (*1*, *2*), organic semiconductor heterostructures (*3*), and organic single crystals (*4*, *5*). The formation of ohmic source and drain contacts and the use of a high-quality gate insulator are essential for the fabrication of such devices in order to ensure good charge transport for electrons and holes. Equal injection of electron and hole currents can be achieved in such devices by adjusting gate-source voltages (V_g) and drain-source voltages (V_d) (*6*). This leads to the formation of a pn-junction within the device, and consequently the generation of excitons might be expected. Although the use of such devices as light emitters has been proposed (*7*), no light emission has been reported from any kind of single FET device. We recently demonstrated ambipolar transistor action in the organic semiconductor α-sexithiophene (α-6T) (*5*), a material known to exhibit a reasonably high electroluminescence yield (*8*). Electron and hole mobilities as high as 0.7 and 1.1 cm^2 V^{-1} s^{-1} at room temperature have been observed in the high-temperature (HT) polymorph of this organic semiconductor. In addition, there have been reports of optically pumped lasing in sexithiophene (*9*) or related oligothiophene single

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