Full-dimensional quantum mechanical calculation of the rate constant for the $H_2+OH \rightarrow H_2O+H$ reaction

Uwe Manthe,[a] Tamar Seideman,[b] and William H. Miller

Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

The cumulative reaction probability (CRP) (the Boltzmann average of which is the thermal rate constant) has been calculated for the reaction $H_2+OH \leftrightarrow H_2O+H$ in its full (six) dimensionality for total angular momentum $J=0$. The calculation, which should be the (numerically) exact result for the assumed potential energy surface, was carried out by a direct procedure that avoids having to solve the complete state-to-state reactive scattering problem. Higher angular momenta ($J>0$) were taken into account approximately to obtain the thermal rate constant $k(T)$ over the range $300 < T < 700$ K; the result is significantly larger than the experimental values (a factor of ~ 4 at 300 K), indicating that a more accurate potential energy surface is needed in order to provide a quantitative description of this reaction.

The $H_2+OH \leftrightarrow H_2O+H$ reaction is emerging as a benchmark for *ab initio* reaction dynamics studies of systems involving more than three atoms (i.e., atom plus diatomic molecule reactions). It is of practical importance for modeling combustion and atmospheric processes, and the fact that three of the four atoms are hydrogen means that there is the possibility of having a high quality potential energy surface from *ab initio* electronic structure calculations and also of being able to carry out accurate quantum dynamical calculations for the reaction.

While much of the recent experimental[1-4] and theoretical[5-8] work on this reaction (and its isotopic variants) has focused on various mode-specific effects and product state distributions, the present paper is concerned solely with the thermal rate constant $k(T)$.[9] Specifically, we report the results of full (six) dimensional quantum calculations of the cumulative reaction probability (CRP) (the Boltzmann average of which gives the thermal rate constant) for total angular momentum $J=0$. These results should be the essentially exact (numerical) results for this quantity for the assumed potential energy surface (that constructed by Schatz and Elgersma[10] from *ab initio* calculations by Walch and Dunning[11]).

We use the theoretical approach of Seideman and Miller[12] and Manthe and Miller.[13] Thus, the CRP $N(E)$ is calculated directly (i.e., without solving the complete state-to-state reactive scattering problem), and the thermal rate constant is given by its Boltzmann average

$$k(T) = [2\pi \hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE \, e^{-E/kT} N(E), \qquad (1)$$

where Q_r is the reactant partition function (per unit volume). In Ref. 13 it was shown that the CRP can be written as

$$N(E) = \text{tr}[\hat{P}(E)] \equiv \sum_k p_k(E), \qquad (2a)$$

where $\hat{P}$ is the reaction probability operator, defined by

$$\hat{P}(E) = 4\hat{\epsilon}_r^{1/2} \hat{G}(E)^\dagger \hat{\epsilon}_p \hat{G}(E) \hat{\epsilon}_r^{1/2}. \qquad (2b)$$

Here, $\hat{G}(E) = (E+i\hat{\epsilon}-\hat{H})^{-1}$ is a modified (in the sense that ϵ is coordinate dependent) Green's function whose nature was discussed in Ref. 12. $\hat{H}$ is the Hamiltonian operator and $\hat{\epsilon} \equiv \hat{\epsilon}_r + \hat{\epsilon}_p$ an absorbing potential which enforces outgoing wave boundary conditions, $\hat{\epsilon}_r(\hat{\epsilon}_p)$ being the part of the absorbing potential in the reactant (product) region.[12] Reference 13 showed that a convenient way of evaluating the trace of $\hat{P}(E)$ in Eq. (2a) is by determining its eigenvalues $\{p_k(E)\}$, the eigenreaction probabilities, whose values all lie between 0 and 1.

The Hamiltonian is expressed in terms of the normal coordinates of the transition state of the H_2OH complex; i.e., the Watson Hamiltonian is used, as described for a general reaction in Ref. 12(b). (Vibrational angular momentum terms have been neglected since they were seen in earlier work[12(b)] to have negligible effect, which should also be the case here.) A discrete variable representation[14] (DVR)—i.e., a basis set of grid points—is used to represent the operators in Eq. (2). For the two most strongly coupled modes, which predominantly describe the bond being broken and the one being formed (i.e., the $H \cdots H$ stretch and the $H_2 \cdots O$ stretch), a sinc-function DVR[15] is used which allows a maximum kinetic energy of ~ 2.2 eV. It consists of ~ 200 grid points for this two-dimensional space. The other four less strongly coupled modes are described by a Gauss–Hermite DVR[16] of four to seven grid points each. The composite grid is then truncated by a potential energy cut off ($V_{max}=2.2$ eV) and the resulting six-dimensional grid consists of $\sim 1 \times 10^5$ to 2×10^5 grid points (the more grid points the higher the energy). Convergence tests were carried out to insure that this basis (and the absorbing potentials that were used) is sufficient to achieve convergence over the energy range reported.

The eigenvalues of the $\hat{P}(E)$ matrix of Eq. (2) were determined by the Lanczos scheme described in Ref. 13, requiring 3 to 44 iterations (the more iterations, the higher the energy since one typically needs a few more iterations than the number of nonzero eigenvalues). The evaluation of the Green's function was carried out via the generalized minimum residual (GMRES) algorithm[17] using the diag-
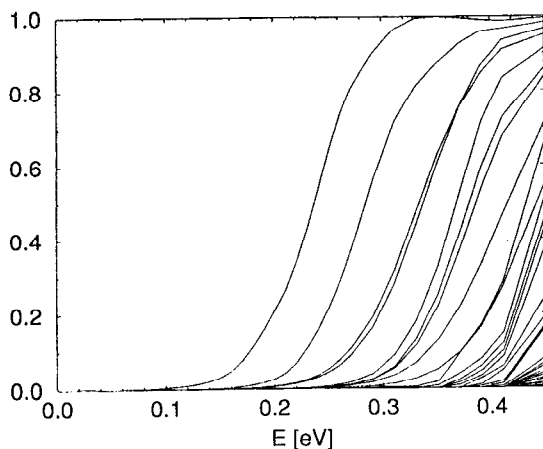
FIG. 1. Eigen reaction probabilities [the eigenvalues of the operator $\hat{P}(E)$ of Eq. (2b)] for the $H_2+OH\leftrightarrow H_2O+H$ reaction, as a function of total energy E for total angular momentum $J=0$. The zero of energy is the ground state of reactants H_2+OH at infinite separation

onal part of the Hamiltonian as preconditioner; this required 50 to 600 iterations (the more iterations, the higher the energy). More details of the computational procedures will be presented with the full report of this work.

Figure 1 shows the individual eigenreaction probabilities $\{p_k(E)\}$ as a function of energy. They all rise essentially monotonically from 0 to 1 in transition state-like fashion, just as one would expect at low energy for a reaction like this which has a single saddle point (i.e., transition state). Figure 2 shows the CRP [the sum of the $p_k(E)$'s], and here the primary qualitative observation is that no vestige of the staircase structure[18] of classical transition state theory (TST) survives in the quantum result. The reason for this is apparent from Fig. 1: The density of states of the activated complex is sufficiently large that their individual transmission probabilities [the $p_k(E)$] overlap.

Also shown in Fig. 2 is the approximate $N(E)$ (dashed line) obtained from Wang and Bowman's[19] reduced dimensionality calculation. In their approach the three bending modes (in Jacobi coordinates) are treated adiabatically within a harmonic approximation, while the three stretching modes are dealt with exactly (i.e., via a coupled channel scattering calculation). One sees that this approximation works quite well at low energies and is only 15%–20% too low at the highest energies.

The quantity we have calculated (and shown in Fig. 2) is $N(E,J)$ for $J=0$. The complete $N(E)$, which gives the rate constant via Eq. (1), is
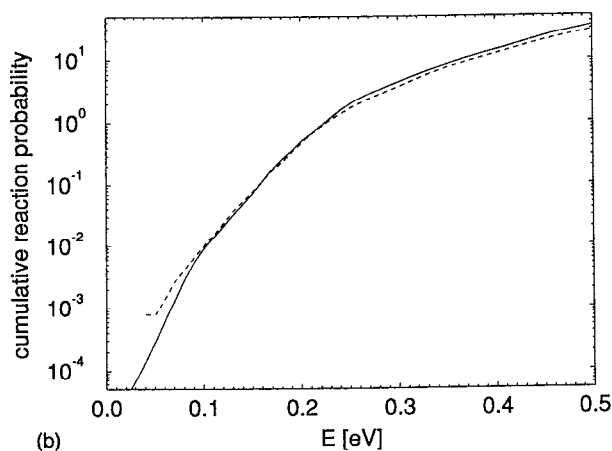
$$N(E)= \sum_{J=0} (2J+1)N(E,J). \tag{3}$$

In lieu of having carried out calculations for $J>0$, we invoke the "J-shifting" approximation[20] (essentially a molecular version of the modified wave number approximation[21] of atomic physics),

$$N(E,J)\cong \sum_{K=-J}^{J} N(E-\epsilon_{rot}^{JK},0), \tag{4}$$
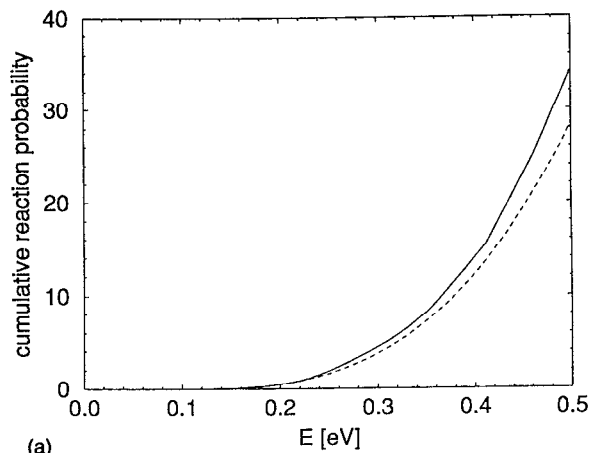
FIG. 2. Cumulative reaction probability $N(E)$ as function of total energy (for $J=0$); solid curves are the present results and the dashed curves the approximate results of Bowman and Wang (Ref. 19). (a) Linear scale, (b) logarithmic scale.

where ϵ_{rot}^{JK} is the rotational energy of the H_2OH complex. It is then easy to show that Eq. (1) becomes

$$k(T) \cong [2\pi\hbar Q_r(T)]^{-1}Q_{rot}^{\ddagger} \int_{-\infty}^{\infty} dE\, e^{-E/kT}N(E,J=0), \tag{5}$$

where $Q_{rot}^{\ddagger}$ is the rotational partition function for the H_2OH complex,

$$Q_{rot}^{\ddagger}(T)= \sum_{J=0}^{\infty} (2J+1) \sum_{K=-J}^{J} e^{-\epsilon_{rot}^{JK}/kT}, \tag{6a}$$

which is well approximated by the classical expression,

$$Q_{rot}^{\ddagger} \cong \left(\frac{\pi(kT)^3}{A^{\ddagger}B^{\ddagger}C^{\ddagger}}\right)^{1/2}, \tag{6b}$$

$A^{\ddagger},B^{\ddagger},C^{\ddagger}$ being the three principal rotation constants (defined in terms of the three principal moments of inertia as $A^{\ddagger}=\hbar^2/2I_A^{\ddagger}$, etc.) at the transition state geometry. [The ratio of transition state to reactant electronic partition functions[22] also adds the factor $(1+e^{-\Delta\epsilon_{el}/kT})^{-1}$ to the right-hand side of Eq. (5), with $\Delta\epsilon_{el}=140$ cm^{-1}.]

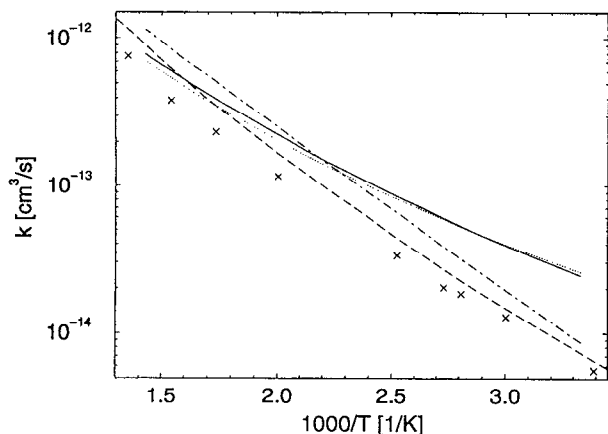The Boltzmann average in Eq. (5) can be obtained reliably for the temperature range 300 K $< T <$ 700 K from

FIG. 3. Rate constant of $H_2+OH \rightarrow H_2O+H$. Solid curve (present results), dotted curve (Ref. 23), long dashed curve [Ref. 6(a)], long–short dashed curve (present three-mode approximation), and crosses (experimental values, Ref. 9).

the energy range (~ 0.05–0.50 eV) over which we have converged results for $N(E)$ (cf. Fig. 2). Figure 3 shows the rate constant given by Eq. (5) (solid line) over this temperature range, compared to several other results. First, the rate obtained by Wang and Bowman[23] (dotted line) is in close agreement with our result, as it should be, of course, since the CRP's are very similar. Clary[6(a)] has used a simpler (but cruder) reduced dimensionality approximately—the OH stretch and the two H_2 rotational degrees of freedom are frozen and the energy shifted by their transition state ground state values—and this result (long dashed line) is seen to be significantly below ours (a factor of ~ 4 at 300 K). We can mimic Clary's approximation by treating the three normal modes that are predominantly the ones he has frozen as uncoupled harmonic oscillators (with their transition state frequencies), and this result (long–short dashed line in Fig. 3) is seen to be quite similar to his. [Our approximation is not identical to that in Ref. 6(a) because the transition state normal modes are not identical to the Jacobi coordinates used there.] Not shown in Fig. 3 is a transition state theory calculation by Schatz and Walch[5(a)] that uses a simple one-dimensional Wigner tunneling correction factor, and one by Isaacson[24] using a multidimensional semiclassical tunneling correction; the former is smaller than our result, by a factor of ~ 4 at $T=300$ K, and the latter larger, by a factor of ~ 1.2 at this temperature. Also shown in Fig. 3 is the experimental rate constant (the crosses) of Tully and Ravishankara and Ravishankara et al.[9]

One thus has the awkward (but not uncommon) situation that the more rigorous theoretical treatments (the present work, and that of Refs. 23 and 24) agree less well with experiment (the crosses in Fig. 3) than more approximate calculations![5(a),6(a)] We feel that one must regard this latter good agreement with experiment as fortuitous, the conclusion being that a more accurate potential energy surface is needed to describe the rate of this reaction quantitatively. It is hoped that the present work, which shows that the reaction dynamics for this reaction can now be

treated accurately in its full dimensionality, will serve as a motivation for producing a more accurate potential surface.

Note added to proof. We have received a private communication from D. Clary noting that he obtains good agreement with our present results for $N(E)$ if he treats H_2 mode vibrationally adiabatically rather than freezing it and shifting the energy [as was done in Ref. 6(a)].

[a] Present address: Fakultät für Physik, University of Freiburg, 7800 Freiburg, Germany.

[b] Present address: Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

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