

## LETTERS TO THE EDITOR

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## COMMUNICATIONS

### State-to-state time-dependent quantum calculation for reaction $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$ in six dimensions

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We report benchmark quantum mechanical results of state-to-state reaction probabilities for the title reaction in full dimensions (6D) using the widely used Schatz–Elgersma potential energy surface. The time-dependent wave packet is propagated using the diatom–diatom Jacobi coordinates and the energy-specific state-to-state reaction probabilities are obtained by asymptotic flux calculation. All results reported here are for the reaction resulting from the ground state of  $\text{H}_2 + \text{OH}$  to various product states of  $\text{H} + \text{H}_2\text{O}$  for total angular momentum. © 1996 American Institute of Physics. [S0021-9606(96)02335-5]

The last few years have witnessed significant progress in rigorous quantum mechanical scattering calculations for four-atom reactions in full dimensions using both time-dependent<sup>1–6,9</sup> and time-independent methods.<sup>7,8</sup> Up to date, the rigorous quantum dynamics studies for four-atom reactions in full dimensions have provided reaction probabilities,<sup>1,2,6,9</sup> cumulative reaction probabilities,<sup>7,8</sup> and cross sections and rate constants<sup>1,2</sup> for the benchmark  $\text{H}_2 + \text{OH}$  reaction and for its isotopically substituted reactions,<sup>3,4</sup> and for the resonant  $\text{HO} + \text{CO}$  reaction.<sup>5</sup> Quantum dynamics calculations using coplanar model for  $\text{H}_2 + \text{OH}$  (Ref. 11) and  $\text{HO} + \text{CO}$  (Ref. 10) have also been reported. So far the most detailed calculations have provided dynamics information that are initial state selected but summed over all final product states. This is because the time-dependent wave packet approach, as shown in Refs. 1, 2, and 6 for the benchmark  $\text{H}_2 + \text{OH}$  reaction, is particularly efficient for evaluating total reaction probabilities, i.e., summed over all rovibrational states of the product. As shown in Ref. 2, the total reaction probability for a given initial state can be calculated as reactive flux at a dividing surface which is normally chosen to be near the transition state region for optimal efficiency. In this flux approach, one simply uses an optical potential to absorb the wave function beyond the dividing surface and thus avoid entirely the calculation of numerous product asymptotic states. However, the ultimate goal of quantum reactive scattering theory is to provide complete state-to-state dynamics information, with both initial and final state selections for simple chemical reactions. To achieve this goal, the previous time-dependent approach has to be extended to enable us to calculate explic-

itly final state-specific reaction probabilities or  $S$ -matrix elements for four-atom reactions.

In this communication, we report some preliminary results of state-to-state reaction probabilities for the benchmark  $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$  reaction in full dimensions using previously developed time-dependent wave packet approach but extended to enable state-to-state calculations. The result presented is for zero total angular momentum ( $J=0$ ) of the  $\text{H}_2\text{OH}$  system on the widely used Schatz–Elgersma potential energy surface (PES)<sup>12,13</sup> slightly modified by Clary.<sup>14</sup> We are aware that another state-to-state time-dependent calculation for the reverse reaction  $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$  is being reported by Zhang and Light<sup>15</sup> and both studies are complementary to each other.

The present state-to-state calculation is carried out by the wave packet propagation method using the Jacobi coordinates for the reactant as described in Refs. 1, 2. The final state specific reaction probabilities are obtained by calculating the flux of the wave function in the product asymptotic region.<sup>16</sup> In the flux method, the energy-dependent scattering wave function and its derivation are directly calculated by Fourier transformation of the time-dependent wave function on a dividing surface located in the product asymptotic region. These quantities are subsequently used to calculate the reactive flux after projecting out the product asymptotic states to yield state-to-state reaction probabilities. The method has been discussed in a previous paper two of the authors.<sup>17</sup>

In the following, we use  $j$  to denote the angular momentum quantum number of the triatomic product  $\text{H}_2\text{O}$ . The numerical aspects of the wave packet propagation are essentially similar to those for calculating total reaction probabilities in Refs. 1 and 2, except a much larger basis set and numerical grid are used in the current calculation in or-

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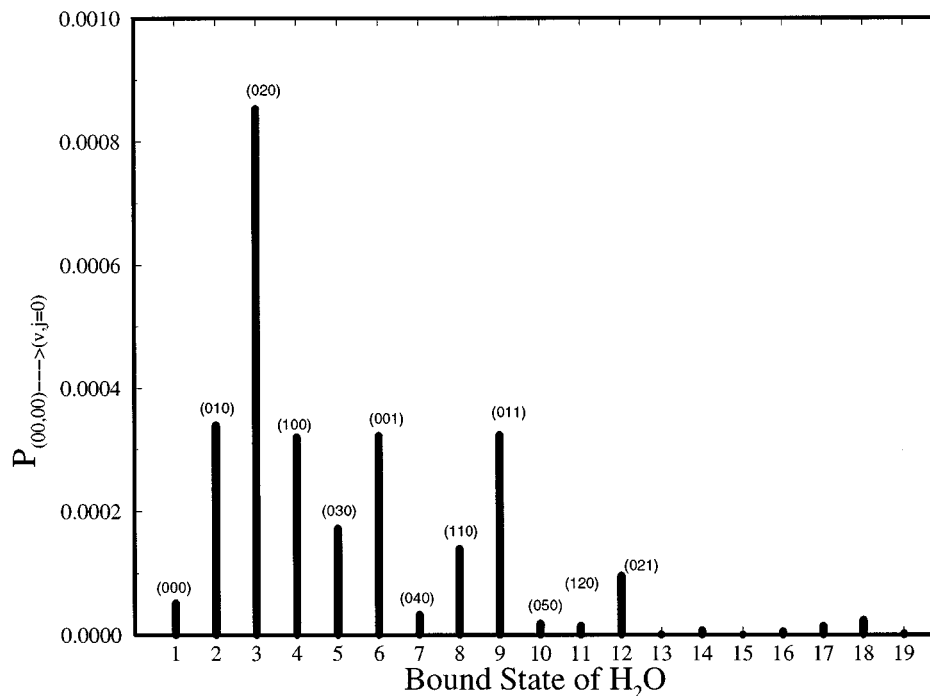


FIG. 1. Product vibrational state distribution of H<sub>2</sub>O from the reaction H<sub>2</sub>(00)+OH(00)→H+H<sub>2</sub>O ( $v,j=0$ ) for zero total angular momentum of H<sub>2</sub>OH at a reactant kinetic energy of 0.4 eV. The vibrational state label of H<sub>2</sub>O( $\nu_1,\nu_2,\nu_3$ ) follows the standard convention.

der to extract state-to-state dynamics information. A time increment of 15 au. in each step of the wave function propagation is found to be sufficient for current applications and a total propagation time of 12 000 au. ( $\approx 300$  fs) is used to complete the propagation for all the energies of current interest.

Figure 1 shows reaction probabilities from the ground state of H<sub>2</sub>+OH to various vibrational states of H+H<sub>2</sub>O ( $j$

$=0$ ). We can see from Fig. 1 that the reaction probabilities to various vibrational states of water at  $j=0$  are very small (on the order  $10^{-5}$  to  $10^{-4}$ ). Therefore, absolute convergence of these small probabilities is difficult as they are generally quite sensitive to changes of numerical parameters. We advise the reader to take this into perspective when comparing these small state-to-state probabilities to their own calculations. The result in Fig. 1 is from the best calculation in

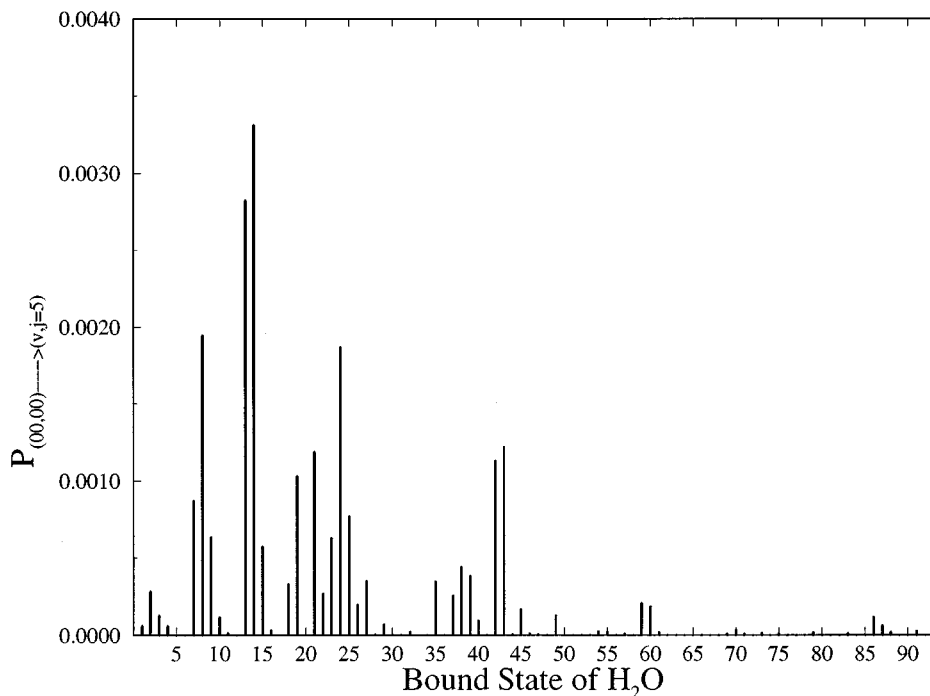


FIG. 2. Same as in Fig. 1 but for OH<sub>2</sub> at  $j=5$ .

TABLE I. Vibrational energies of OH<sub>2</sub> at rotational states of  $j=0$  and  $j=5$  for even total parity [defined as  $(-)^{p+j}$  where  $p$  is the standard inversion symmetry] on the Schatz–Elgersma PES. The zero energy is defined as the minimum of the asymptotic H<sub>2</sub>+OH potential. All energies are in units of eV.

$j=0$		$j=5$									
$n$	$E$	$n$	$E$	$n$	$E$	$n$	$E$	$n$	$E$	$n$	$E$
1	-0.088	1	-0.048	13	0.276	25	0.413	37	0.537	49	0.621
2	0.088	2	-0.048	14	0.281	26	0.415	38	0.556	50	0.628
3	0.238	3	-0.033	15	0.303	27	0.424	39	0.562	51	0.637
4	0.348	4	-0.025	16	0.328	28	0.429	40	0.571	52	0.651
5	0.358	5	-0.010	17	0.358	29	0.432	41	0.576	53	0.651
6	0.371	6	0.008	18	0.386	30	0.445	42	0.578	54	0.680
7	0.454	7	0.128	19	0.390	31	0.448	43	0.579	55	0.695
8	0.519	8	0.129	20	0.393	32	0.449	44	0.588	56	0.706
9	0.539	9	0.145	21	0.395	33	0.462	45	0.595	57	0.707
10	0.582	10	0.160	22	0.406	34	0.488	46	0.599	58	0.719
11	0.657	11	0.181	23	0.409	35	0.491	47	0.608	59	0.719
12	0.681	12	0.206	24	0.410	36	0.530	48	0.610	60	0.723

terms of basis set and numerical grid in the present study and the average error bar is estimated to be around 30%. Similar vibrational state distributions can be shown for different rotational states  $j$  and the convergence property is better for relatively larger state-to-state probabilities such as those for H<sub>2</sub>O at  $j=5$  in Fig. 2. However, the spectroscopic assignment of these vibrational states for H<sub>2</sub>O using the Schatz–Elgersma PES poses a serious challenge because most states are quite mixed. In addition, the proliferation of the number of open states with the increase of water angular momentum  $j$  makes the task of assignment very difficult. As shown in Fig. 2, the number of open vibrational states of H<sub>2</sub>O for  $j=5$  is significantly larger than that for  $j=0$  in Fig. 1. In fact, the total number of open rovibrational states of H<sub>2</sub>O (including all  $j$ 's) is close to 1000 at the highest energy of the present

calculation. We therefore postpone the task of spectroscopic assignment to a subsequent study. For easy reference, the corresponding eigenenergies of H<sub>2</sub>O for  $j=0$  and  $j=5$  on the Schatz–Elgersma PES are listed in Table I. We note that the eigenvalues of H<sub>2</sub>O in Table I are not in good agreement with experimental results, which is one of the deficiencies of the Schatz–Elgersma PES. Although this deficiency is not expected to be very important for the calculation of total reaction probabilities, it certainly will affect the product state distribution in a significant way. We should keep this point in mind.

For partially summed reaction probabilities, however, we have more confidence in convergence. Figure 3 shows the reaction probability of the ground vibrational state but summed over all rotational states of water at several ener-

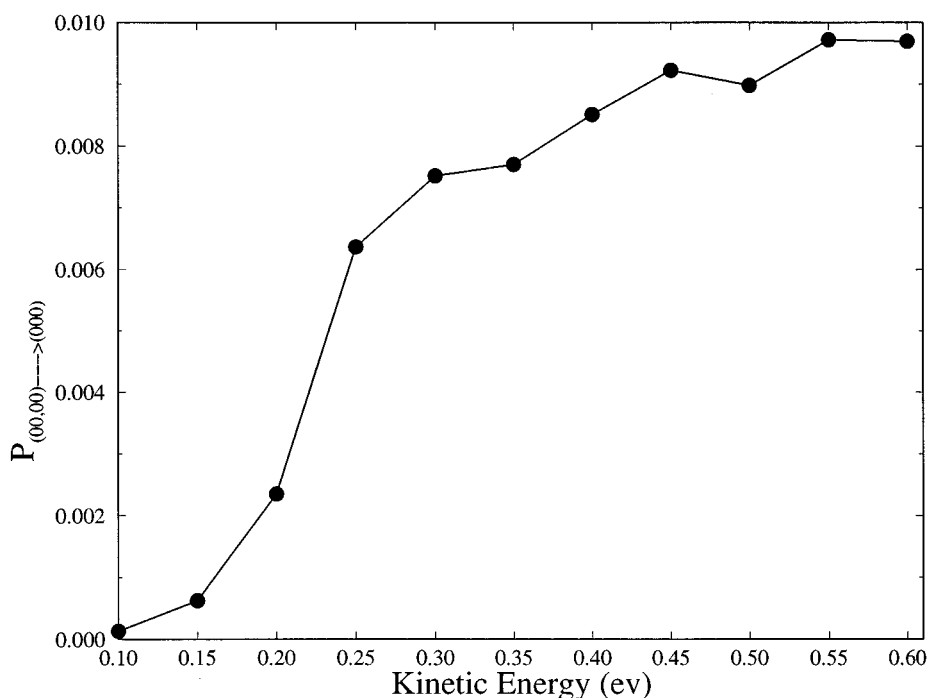


FIG. 3. The probability of H<sub>2</sub>(00)+OH(00) reaction to produce ground vibrational state of H<sub>2</sub>O( $v=000$ ) summed of all rotational states of H<sub>2</sub>O as a function of kinetic energy.

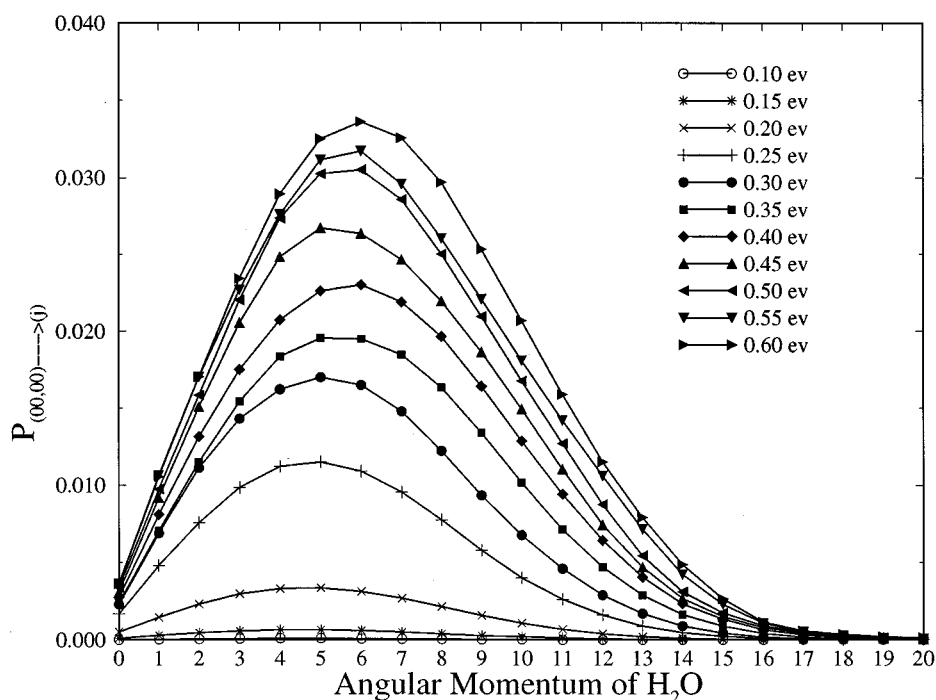


FIG. 4. Product rotational state distribution of  $\text{H}_2\text{O}$  from the reaction  $\text{H}_2(00)+\text{OH}(00)\rightarrow\text{H}+\text{H}_2\text{O}(j)$  summed over all vibrational states for kinetic energies of 0.10–0.6 eV.

gies. Similar plots can be shown for probabilities to other vibrational states of  $\text{H}_2\text{O}$  but the spectroscopic assignment of these vibrational states has not yet been completed due to difficulties mentioned above. The complete rotational state distribution of water (summed over all vibrational states of  $\text{OH}_2$ ) at various energies is given in Fig. 4. As seen clearly in Fig. 4, the rotational state distribution of  $\text{H}_2\text{O}$  is generally Boltzmann-type and the maximum distribution is generally between  $j=5-7$  for energies shown. These partially summed reaction probabilities are generally converged to around 5–10%. We hope to be able to converge the complete state-to-state reaction probabilities to a more accurate level in the near future, and the work in this direction is currently in progress.

At this point, we should mention previous state-resolved quantum dynamics studies for  $\text{H}_2\text{OH}$  system using reduced dimensionality approaches. The 3D reduced dimensionality calculation of Wang and Bowman<sup>18</sup> generated vibrational state resolved reaction probabilities that are more than an order of magnitude larger than the present result in Fig. 3. However, the calculation of Ref. 18 should be interpreted as summed over all rotational states in the  $\text{H}_2+\text{OH}$  channel and is thus not directly comparable to the present calculation from a single rovibrational state of  $\text{H}_2+\text{OH}$ . The planar 4D calculation for the  $\text{H}_2\text{OH}$  system by Echave and Clary<sup>19</sup> has also provided some state resolved dynamics information but the results are not given in a way to allow a direct comparison with the present result. We need to have a more precise interpretation of the reduced dimensionality results before being able to make a meaningful comparison with them at the state-to-state level. The most recent state-to-state calculation of Zhang and Light has provided reaction probabilities

from the ground state for the reverse reaction  $\text{H}+\text{H}_2\text{O}\rightarrow\text{OH}+\text{H}_2$ .<sup>15</sup> Thus the only quantity that can be directly compared with the present calculation is the transition probability from ground reactant state to ground product state, and both numbers agree to about 10% of each other.

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- <sup>1</sup>D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* **99**, 5615 (1993); **100**, 2697 (1994).
- <sup>2</sup>D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* **101**, 5615 (1994).
- <sup>3</sup>(a) D. H. Zhang and J. Z. H. Zhang, *Chem. Phys. Lett.* **232**, 370 (1995); (b) D. H. Zhang, J. Z. H. Zhang, Y. Zhang, D. Wang, and Q. Zhang, *J. Chem. Phys.* **102**, 7400 (1995).
- <sup>4</sup>Y. Zhang *et al.*, *J. Phys. Chem.* **99**, 16824 (1995).
- <sup>5</sup>D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* **103**, 6512 (1995).
- <sup>6</sup>D. Neuhauser, *J. Chem. Phys.* **100**, 9272 (1994).
- <sup>7</sup>U. Manthe, T. Seideman, and W. H. Miller, *J. Chem. Phys.* **99**, 10078 (1993).
- <sup>8</sup>U. Manthe, T. Seideman, and W. H. Miller, *J. Chem. Phys.* **101**, 4759 (1994).
- <sup>9</sup>D. H. Zhang and J. C. Light, *J. Chem. Phys.* **104**, 4544 (1996).
- <sup>10</sup>E. M. Goldfield, S. K. Gray, and G. C. Schatz, *J. Chem. Phys.* **102**, 8807 (1995).
- <sup>11</sup>W. H. Thompson and W. H. Miller, *J. Chem. Phys.* **101**, 8620 (1994).
- <sup>12</sup>S. P. Walch and T. H. Dunning, Jr., *J. Chem. Phys.* **72**, 1303 (1980).
- <sup>13</sup>G. C. Schatz and H. Elgersma, *Chem. Phys. Lett.* **73**, 21 (1980).
- <sup>14</sup>D. C. Clary, *J. Chem. Phys.* **95**, 7298 (1991).
- <sup>15</sup>D. H. Zhang and J. C. Light, *J. Chem. Phys.* (in press).
- <sup>16</sup>D. J. Tannor and D. E. Weeks, *J. Chem. Phys.* **98**, 3884 (1993).
- <sup>17</sup>J. Dai and J. Z. H. Zhang, *J. Phys. Chem.* **100**, 6898 (1996).
- <sup>18</sup>D. Wang and J. M. Bowman, *J. Chem. Phys.* **96**, 8906 (1992).
- <sup>19</sup>J. Echave and D. C. Clary, *J. Chem. Phys.* **100**, 402 (1994).