# Accurate three-dimensional quantum probabilities and collision lifetimes of the $H+O_2$ combustion reaction

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Accurate 3D quantum state-to-state reaction probabilities and collision lifetimes for the  $H+O_2\rightarrow OH+O$  combustion reaction for total angular momentum J=0 are reported. The reaction probabilities are dominated by resonances, many of which overlap. The total reaction probability is *not* enhanced by vibrational or rotational excitation of the reactants. The first accurate final state distributions are presented, and probability is found to spread out into all open product vibrational and rotational channels, with a rather strong tendency to produce highly excited product rotational states. The first calculated collision lifetimes are presented, and resonances with lifetimes of 1–10 ps are found at most energies. Whether the reaction behaves statistically is discussed, and future extensions needed are also discussed. © 1995 American Institute of Physics.

# I. INTRODUCTION

The endoergic reaction,

$$H(^{2}S) + O_{2}(^{3}\Sigma_{g}^{-}) \rightarrow OH(^{2}\Pi) + O(^{3}P),$$
 (1)

is well known to be the single most important reaction in combustion chemistry.<sup>1-4</sup> In the combustion of hydrogen and all hydrocarbons (including natural gas, gasoline, diesel fuel, coal, etc.) it is the rate-limiting, chain-branching step. It determines explosion limits and flame propagation rates and accounts for 80% of the O<sub>2</sub> consumption. As a result of this "overwhelming importance to combustion,"<sup>2</sup> this reaction has been very extensively studied both experimentally and theoretically, and the literature on it is very extensive. We refer the reader to several reviews.<sup>2,5-7</sup> of the subject and give only a limited review here.

The rate of reaction (1) has been measured many times, and the measurements at low temperatures agree well and leave little uncertainty in the rate coefficient. However, until very recently, the results diverged at higher temperatures, with a factor of two difference between the lower<sup>8,9</sup> and higher<sup>10,11</sup> values of the rate coefficient obtained at 2500 K. As a result, there has been considerable controversy<sup>2</sup> over whether or not the rate displays Arrhenius behavior at high temperatures. It appears that this controversy has now been resolved by new measurements<sup>4,12</sup> to much higher temperatures (5300 K). These have been combined with lower temperature measurements<sup>13,14</sup> to give a rate coefficient<sup>4</sup> which appears to be accurate over a wide range of temperature (960–5300 K) and *is* fit by a simple Arrhenius form.

Although the rate of reaction (1) displays Arrhenius behavior, the reverse reaction,

$$OH(^{2}\Pi) + O(^{3}P) \rightarrow H(^{2}S) + O_{2}(^{3}\Sigma_{g}^{-}),$$
 (2)

whose rate coefficient is related to the rate of reaction (1) via the equilibrium constant, displays very non-Arrhenius behavior because it is an exoergic reaction with no barrier. Its rate coefficient decreases as temperature (*T*) increases at low *T* and becomes flat at high T.<sup>4</sup>

Experiments in which fast H atoms are produced by laser photodissociation of a precursor in the presence of  $O_2$  and the products are monitored with laser spectroscopy<sup>3,15–23</sup> are currently yielding more detailed information about reaction (1). While many of these experiments are at high energies, some<sup>16,17,22</sup> include energies low enough to be important to chemical kinetics. Such experiments have yielded the integral reaction cross section as a function of energy,<sup>21,22</sup> the O-atom spin–orbit distributions;<sup>19,20</sup> and the vibrational, rotational, spin–orbit, and  $\Lambda$ -doublet distributions of the OH products.<sup>3,15–18</sup> They are now yielding the differential reaction cross section.<sup>23</sup> Hence, a wealth of experimental information is available.

There have also been many theoretical studies. Several authors<sup>24-30</sup> have performed ab initio calculations, with various levels of sophistication, of points on the relevant potential energy surface (PES); namely, the  $X^{2}A''$  ground electronic state of the HO<sub>2</sub> system. These studies and available experimental information make it clear that reaction (1) is an endoergic one with a well instead of a barrier. Along the minimum energy path<sup>28</sup> the potential falls smoothly with no barrier from the reactant asymptote into a deep well which is due to the bound hydroperoxyl radical, OOH. Then, from there out to products, the potential rises rapidly, contains a very small barrier and well, and then continues out to products. This small barrier and well both lie below the product asymptote and thus do not constitute any real barrier to the reaction. They are due to a transition from a chemically bonding potential to a long range potential due to the interaction of the quadrupole moment of the  $O({}^{3}P)$  atom with the dipole moment of the OH radical; its  $R^{-4}$  behavior is much longer ranged than the usual van der Waals  $(R^{-6})$  potential.

Several global, analytic PES's suitable for reaction dynamics calculations have been reported.<sup>25,26,31–34</sup> The one used herein, which was the best available at the time this

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study began, is the DMBE IV PES of Varandas and co-workers.<sup>34</sup> It incorporates all the experimental information known in 1990 and also many<sup>28,29</sup> of the accurate abinitio results of Walch and co-workers. With the energy zero chosen to be the bottom of the asymptotic  $H+O_2$  well, the HO<sub>2</sub> minimum of the DMBE IV PES is at an energy of -2.378 35 eV, and the bottom of the asymptotic OH channel is at 0.581 51 eV. The energy of ground state  $H+O_2(0,1)$  is 0.097 87 eV, and the energy of ground state OH(0,0)+O (the reaction threshold) is at 0.811 47 eV, so that the relative (collision) energy at the threshold for reaction is 0.713 60 eV. Consistent with experiment, this PES gives a hydroperoxyl radical with an O–O bond length of 2.5413  $a_0$ , an O–H bond length of 1.8345  $a_0$ , and an OOH bond angle of 104.29 deg. Also, its force constants are chosen to given fundamental vibrational frequencies in fairly good agreement with the experimental<sup>35</sup> values of  $\omega_1$ =3436.1951,  $\omega_2$ =1391.7, and  $\omega_3 = 1097.6 \text{ cm}^{-1}$ .

There have also been a number of theoretical studies of the dynamics of reaction (1) and its reverse. Variational transition state theory (VTST) calculations<sup>36</sup> using the Melius–Blint (MB) PES (Ref. 25) did not give a rate coefficient agreeing very well with experiment; it was not clear whether that was due to the theory or the PES used. Troe,<sup>37–39</sup> who avoided the MB PES, has reported statistical adiabatic channel model calculations that do agree quite well with experiment.

Approximate quantum dynamics calculations have been reported<sup>27,40,41</sup> for the rate of the reverse reaction, reaction (2). However, the fact that reasonable agreement with experiment was obtained<sup>27,40</sup> is not very reassuring because the simple capture model<sup>41</sup> used only includes the long range and centrifugal interactions of O+OH and assumes that all systems that enter the OOH well region exit into the H+O<sub>2</sub> arrangement.

In addition, quasiclassical trajectory (QCT) studies of reactions (1) and/or (2) have been reported by many authors.<sup>1,16,17,26,31,34,42-48</sup> These studies have contributed much to the understanding of the reaction and have given many properties in agreement with experiment. However, they have also caused some confusion. They show the existence of many long-lived, snarled trajectories that often tend to recross most transition state dividing surfaces that might be chosen, and this has led to a controversy. Statistical arguments lead one to expect that the rates of decay of such long-lived complexes into the various arrangement channels will be determined by the phase space volumes of the channels. Instead, Miller<sup>1</sup> and Varandas and co-workers<sup>34,44</sup> observed important nonstatistical recrossing effects, with many more trajectories started out in the O+OH arrangement returning there than expected, which also contradicts the simple quantum capture model<sup>27,40,41</sup> discussed in the preceding paragraph. On the other hand, Troe<sup>37,38</sup> argued that those effects are due to the PES used and do not require invoking nonstatistical effects. Also, Nyman and Davidsson<sup>43</sup> have noted that the amount of recrossing obtained depends on the details of how different QCT methods handle quantum zero-point energies. We discuss these next.

Because of the large endoergicity of reaction (1), it re-

quires an incident relative energy of 0.71 eV or (8200 K) to reach the threshold for reaction. Because of the large vibrational zero-point energy of the OH product, the quantum threshold for OH formation lies 0.23 eV above the classical threshold. As a result, even at energies well above the quantum threshold, most reactive classical trajectories form the OH product with less than its quantum zero-point energy. This has caused much concern<sup>1,43-48</sup> about the validity of classical mechanics for reaction (1) and continuing attempts<sup>43,45-48</sup> to develop ways to incorporate zero-point effects into the classical mechanics. These have not yet been very successful, and QCT methods are still unable to specify the threshold behavior. There have been no experimental measurements of the threshold behavior, and the first reliable information about that behavior appeared in a preliminary report<sup>49</sup> of the present work.

In this paper we report accurate 3D quantum coupled channel (CC) calculations of reaction probabilities and collision lifetimes for reaction (1) for total angular momentum J=0; a preliminary account of this work has already been published.<sup>49</sup> In similar work, Leforestier and Miller<sup>50</sup> have recently published a calculation of the cumulative reaction probability, and Zhang and Zhang<sup>51</sup> have just published calculations of the total reaction probability out of several initial states. The present work is the first able to calculate detailed state-to-state reaction probabilities for this reaction.

There have been no accurate quantum dynamics studies of this reaction earlier than those noted<sup>49-51</sup> because it is significantly more difficult than most reactions treated to date. It has two heavy (nonhydrogenic) atoms, and the large endoergicity of the reaction causes many of the closely spaced O<sub>2</sub> vibration-rotation states to be open before the energy reaches the threshold for product formation. In addition, the deep OOH well causes many states that diabatically connect to OH product vibration-rotation states to dip down to become locally open in the well region and thus contribute additional coupled channels. The hydroperoxyl radical is nonlinear, and, at reactive collision energies, it can access all configurations from the linear prolate symmetric top through all asymmetric tops to the triangular oblate symmetric top.<sup>52</sup> This floppiness causes much more angular momentum coupling than occurs in linearly dominated reactions and assures<sup>53</sup> that there exists no optimum body-frame axis system for this reaction. In addition, two other effects conspire to require integration to large distances before applying the boundary conditions. The exchange of the H atom between the two O atoms, which is allowed at all scattering energies, has a heavy-light--heavy (HLH) mass combination with its attendant small skew angle, and the aforementioned dipolequadrupole  $(R^{-4})$  potential in the product arrangement is much longer ranged than the usual van der Waals  $(R^{-6})$  potentials. This large number of coupled channels and large integration distance would make this an especially difficult reaction to treat in detail with those methods which use radial basis functions and arrangement channels internal basis functions. The hyperspherical method used herein makes this reaction feasible because it uses locally adiabatic internal basis functions, and the cost of the radial propagation is simply linear in the distance propagated.

In the next section we describe the calculations performed. Section III contains our results and a discussion of them, and Sec. IV contains our conclusions and a discussion of future work needed on this system.

### **II. CALCULATIONS**

# A. APH method: Potential energy surface

We use the APH method which we have detailed elsewhere.54-56 In brief summary, it uses the adiabatically adjusting principal axes hyperspherical (APH) coordinates and expands the wave function for a given total angular momentum (J) in terms of Wigner D functions of the Euler angles, "surface functions"  $\Phi$  of the APH hyperangles  $\theta$  and  $\chi$ , and unknown functions  $\psi$  of the hyperradius  $\rho$ . The set of  $\Phi$  form a compact basis of internal states determined by solving, at a series of  $\rho$  values, a two-dimensional Schrödinger equation that depends parametrically on  $\rho$ . The set of  $\Phi$  for a given value of  $\rho$  are used in a sector centered at that  $\rho$  value and are independent of  $\rho$  on that sector. The  $\psi(\rho)$  are determined by propagating the coupled channel (CC) equations, keeping all coupling, from small  $\rho$ , where they are regular, to asymptotic  $\rho$ , where a similarity transformation takes the R matrix from APH coordinates to arrangement channel Delves' hyperspherical coordinates, and then the boundary conditions, which have been transformed from Jacobi to Delves' coordinates, are applied directly to obtain the **K** matrix and the scattering (**S**) matrix.

As noted in the Introduction, we use the DBME IV PES,<sup>34</sup> and consistent with the use of this single-valued ground state potential and in common with similar studies<sup>57</sup> of simpler reactions involving OH, we neglect all coupling of the nuclear motions to the electronic orbital and spin angular momenta. This amounts to treating both O<sub>2</sub> and OH as Hund's case (b) molecules.<sup>58</sup> For the  $H(^2S) + O_2(^3\Sigma_g^-)$  reactants this is an accurate approximation; for the  $O(^{3}P)+OH(^{2}\Pi)$  products it is much more approximate as discussed in Sec. IV. Thus, the diatomic angular momenta denoted here by j correspond to the nuclear orbital angular momenta usually<sup>59</sup> called R by spectroscopists.  $^{16}O_2$  has only odd integer *j* states as required by its electronic and nuclear spin symmetries,<sup>60</sup> so that its ground vibration-rotation state is  $O_2(v, j) = O_2(0,1)$ . OH has all integer j. In the present calculations, the total nuclear orbital angular momentum, denoted here by J, is fixed at zero.

Plots of the behavior of the DMBE IV PES in other coordinates have been given elsewhere.<sup>34</sup> To give some idea of its behavior in APH coordinates, plots of it vs  $\theta$  and  $\chi$  at fixed  $\rho$  are shown in Fig. 1. All energies are measured relative to the bottom of the asymptotic H+O<sub>2</sub> well. The hyperradius  $\rho$  is large (10  $a_0$ ) in Fig. 1(a), so that the arrangement channels are separated from each other. The larger channels are those of the H+O<sub>2</sub> arrangement; the smaller ones are those of the two O+OH arrangements. Six channels show because each arrangement appears together with its mirror image as discussed elsewhere.<sup>54</sup> Rotation of each of the diatomic fragments corresponds to movement in the potential wells parallel to the contours; vibration corresponds to movement perpendicular to the contours. The two OH+O



FIG. 1. Contour plots of the DMBE IV PES at fixed values of  $\rho$ . These are stereographic projections of the surface of an upper half sphere. The APH angle  $\theta$  runs from 0 at the north pole (center of plots) to ( $\pi/2$ ) at the equator (heavy circle). (Points outside the equator are not physical.) The APH angle  $\chi$  is measured from the positive *x* axis on these plots and grows as one goes counterclockwise. The repulsive regions with energy above the solid contour at 2.0 eV are shaded. The dashed contours are at energies of -2.0, -0.4, 0.2, 0.83, and 10.0 eV. (a)  $\rho = 10 a_0$ ; (b)  $\rho = 4.7 a_0$ .

channels appear close together because H atom exchange has a HLH mass combination as noted in the Introduction. In Fig. 1(b),  $\rho$ =4.7  $a_0$  is in the potential well region near the OOH minimum which occurs at 4.5  $a_0$ . Here the arrangement channels are overlapping. Looking at the upper half of the figure, the "eyes" in the "mask" are the potential wells corresponding to bound OOH; the "nose" and "ears" are potential hills. Motion in  $\theta$  near the minima corresponds mostly to the highest frequency ( $\omega_1$ ) OH stretching vibration of OOH; motion in  $\chi$  is mostly the intermediate frequency ( $\omega_2$ ) bending vibration; and motion in  $\rho$  (not shown) is mostly the lowest frequency ( $\omega_3$ ) OO stretching vibration of OOH. This order is consistent physically with the order in which the APH theory treats the variables.

TABLE I. Input parameters for the H+O2 ABM calculations.

Arrangement	1	2 and 3
atomic mass (amu)	1.007 825 03	15.994 914 61
scale factor d	0.591 208 29	1.717 087 40
$\omega_{e}$ (a.u.)	$7.199\ 889(-3)^{a}$	$1.703\ 049(-2)$
$\omega_e x_e$ (a.u.)	5.4589(-5)	3.86748(-4)
$r_e(a_0)$	2.281 88	1.832 39
$\nu_{ m max}$	10	7
$j_{\rm max}$	73	32
nhermt	13	24
nglegn	74	61

<sup>a</sup>This notation implies 7.199  $889 \times 10^{-3}$ .

## **B. Surface functions**

The APH coordinates make the symmetry of the system very clear as is apparent from Fig. 1, and this symmetry was utilized in the calculations of the surface functions  $\Phi$  to reduce the size of the calculations and only generate functions of the symmetry desired. The surface functions from  $\rho=3.3$  $a_0$ , where all the surface function energies are strongly repulsive, to 6.5  $a_0$  were calculated using a discrete variable representation (DVR) method which we have detailed elsewhere.<sup>55</sup> The calculations used 55 intervals in  $\theta$  and 90 intervals in  $\chi$ . The  $E_{cut}$  parameter varied from 23.0 to 2.8 eV across the range, and the  $V_{\rm max}$  parameter was kept equal to 1.5 times  $E_{\rm cut}$ . All these parameters were carefully chosen to give the eigenvalues of all states lying below 1.3 eV converged to within about 0.3 meV at all  $\rho$  on this range. With the sequential truncation-diagonalization method this required solving eigenvalue equations of dimensions ranging from 415 to 1665, and the lowest 350 eigenfunctions and eigenvalues were kept.

The surface functions from  $\rho = 6.5$  to 30.0  $a_0$  were determined using the analytic basis method (ABM) which we have recently described in detail.<sup>56</sup> This large final  $\rho$  value is necessary to make the magnitude of the long-range  $(R^{-4})$ potential in the product arrangement less than 0.5 meV for all OH orientations and its average<sup>33</sup> magnitude less than 0.3 meV and thus allow calculation of resonance positions to that accuracy. Attempting to stop at much shorter distances will give inaccurate threshold and resonance positions. The parameters and size of the basis were optimized to give the asymptotic diatomic eigenenergies accurate to better than 0.1 meV, to give the eigenvalues of all states lying below 1.3 eV accurate to about 0.3 meV at all  $\rho$ , to keep the quadratures an order of magnitude more accurate than the energies, and to join onto the DVR results smoothly with good completeness of the overlap matrix. The parameters of the primitive basis are given in Table I and II. With symmetry, this basis gives an eigenvalue problem of dimension 671, and the lowest 350 eigenfunctions and eigenvalues were again kept.

The centers of the sectors at which the surface functions were determined were spaced logarithmically, with each  $\rho$  being 1.01 times the previous value. (This is a conservative spacing which assures good overlaps between sectors.) The DVR functions were thus calculated for 68 sectors and the ABM functions for 155 sectors for a total of 223 sectors. The

TABLE II. Variational parameters for the H+O<sub>2</sub> ABM calculations.

Arrangement	1	2 and 3
$r_x$ $c_\alpha$ $a_n$ $\zeta$	1.035 0.94 0.95 1.0	1.15 0.82 0.88 1.0
δ	0.01	0.01

overlap matrix between the last set of DVR functions and the first set of ABM functions were calculated. Then, the results were combined, so that the propagation, which only requires the coupling and overlap matrices, could be done as if the surface functions had all been calculated by one method.

The surface function eigenvalues  $\mathscr{E}(\rho)$  show many crossings and avoided crossings as a function of  $\rho$ . If the eigenvalues are connected from one  $\rho$  to the next in simple energy (adiabatic) order, they often look rather like "spaghetti",<sup>61</sup> and it becomes very difficult for the eye to follow them, as demonstrated by Fig. 2(a), which shows the eigenvalues that lie between 0.5 and 1.0 eV for  $\rho$  between 6 and 9  $a_0$ . If, however, one connects the eigenvalues at one  $\rho$  with those at the next using algorithms<sup>62</sup> which maximize the eigenfunc-



FIG. 2. Surface function eigenvalues (eV) plotted vs  $\rho$  over a small range of energy and distance. (a) Adiabatic connection of the points. (b) Diabatic connection of the points. See the text for a definition of the diabatic method.



FIG. 3. Diabatic surface function eigenvalues plotted over a wider range of energy and distance. See text for discussion.

tion overlaps, one gets "diabatic" curves, such as those shown in Fig. 2(b), which appear much smoother and more continuous. One sees gently rising and falling curves which asymptotically approach reactant  $H+O_2$  states and steeply rising curves, some of which have barriers, which asymptotically approach product OH+O states.

All the "diabatic" curves obtained from the 350 adiabatic curves are plotted over a wider range of energy and distance in Fig. 3. In the interest of space, the curves for  $\rho$ from 11.5 to 30  $a_0$ , which change slowly with distance, are not plotted. In Fig. 3 one can clearly see where each of the vibrational states of O<sub>2</sub> lie at large distances, and one also sees clearly that the strongly bound surface functions connect diabatically solely with O+OH products rather than with the H+O<sub>2</sub> reactants. This should perhaps not be surprising; the bond length and OH stretching frequency in OOH are very little changed from those of isolated OH. However, it does explain why so many coupled channels are required in this problem; for any energy *E*, the number of open channels at any  $\rho$  is the number of curves lying below that *E*. At threshold (0.811 47 eV), at asymptotic distances there are 95 open O<sub>2</sub> vibration-rotation states and one open symmetrized OH state for a total of 96 open channels. At this same energy there are a maximum of 155 locally open channels at  $\rho$ =5.0  $a_0$ . At the highest energy considered (1.42 eV), 246 channels are open asymptotically—220 O<sub>2</sub> reactant states and 26 sym-

TABLE III. Convergence of reaction probabilities with respect to distance at which boundary conditions are applied.  $N_{\text{chanl}}$ =350. See text for discussion.

E(eV)	$ ho_{ m end}$	$N^0(E)$	$P_{0,1}(\text{tot})$	$P_{0,29}(tot)$	$P_{3,1}(tot)$	$P_{0,1}(0,0)$
0.8170	14.248	1.151	2.425e - 2	0.911 <i>e</i> -2	6.623 <i>e</i> -3	1.937e - 2
	21.213	1.286	3.049e - 2	1.135e - 2	2.292e - 3	2.938e - 2
	30.051	1.304	2.699e - 2	1.046e - 2	4.159e - 3	2.524e - 2
0.8440	14.248	1.210	2.260e - 2	8.460 <i>e</i> -3	0.907 <i>e</i> -2	3.510 <i>e</i> -3
	21.213	1.261	1.946e - 2	8.991 <i>e</i> -3	1.314e - 2	7.583e - 3
	30.051	1.262	2.169e - 2	9.020 <i>e</i> -3	1.059e - 2	7.430e - 3
0.8755	14.248	2.256	4.954e - 2	6.582 <i>e</i> -3	4.439 <i>e</i> -2	7.381 <i>e</i> -3
	21.213	2.379	8.230e - 2	5.673e - 3	3.290e - 2	9.417e - 3
	30.051	2.375	8.860e - 2	5.344e - 3	3.412e - 2	8.178e - 3
1.0200	14.248	3.608	7.469e - 2	4.271 <i>e</i> -2	7.625e - 2	8.074 <i>e</i> -3
	21.213	3.601	8.529e - 2	4.486e - 2	6.738e - 2	9.155e - 3
	30.051	3.592	7.779e - 2	4.194e - 2	8.900e - 2	9.304e - 3
1.2200	14.248	5.594	1.567e - 1	4.529e - 2	1.088e - 1	1.968e - 2
	21.213	5.612	1.566e - 1	4.982e - 2	1.183e - 1	2.315e - 2
	30.051	5.605	1.586e - 1	4.758e - 2	1.190e - 1	2.246e - 2
1.4200	14.248	9.820	3.534 <i>e</i> -1	4.619e-2	1.849e - 1	1.365e - 2
	21.213	9.897	3.417e - 1	4.599e - 2	1.438e - 1	1.767e - 2
	30.051	10.012	3.348 <i>e</i> -1	4.630 <i>e</i> -2	1.556 <i>e</i> -1	1.675e-2

metrized OH product states. This number rises to a maximum of 308 locally open channels at 5.7  $a_0$ . From Fig. 3 it is seen that these extra channels that are locally open in the well region connect diabatically to asymptotically closed OH vibration-rotation states.

## C. Propagation: Final state analysis

The coupled channel (CC) equations, including all coupling, were propagated using the log derivative method.<sup>63</sup> All propagations were started at  $\rho = 3.3a_0$  where all the  $\mathscr{C}(\rho)$  are so repulsive that the amplitudes of all the  $\psi(\rho)$  are negligible. Calculations were performed at a few random energies across the full energy range to test convergence with respect to the  $\rho_{end}$  at which the propagation was stopped, and the production calculations were then ended at 30.0  $a_0$ . Calculations were also performed to test convergence with respect to the number of steps taken per shortest asymptotic wavelength, and  $N_{steps}=24$  was then used. Calculations were also performed to test convergence with respect to the number of CC equations propagated, and  $N_{chanl}=350$  was then used.

These propagations are the most time consuming part of the calculations. (To calculate all the surface functions at all distances took less cpu time than to do the propagations at eight energies.) The propagations were performed on networks of SUN and HP workstations at Los Alamos and the University of Oklahoma. For example, a typical propagation at one energy required 7339 symmetric matrix inversions to propagate across the 223 sectors and 444 matrix multiplications to transform at the sector boundaries and required 9.4 h on a HP 735 or 49 h on a SUN Sparc 2 workstation. The main group of calculations for the present work includes 170 energies. To speed the process a simple but effective distributed processing algorithm was implemented as follows: A grid of 1241 energies spanning total energies from 0.80

 $\rho_{end}$ =30.051. See text for discussion. N<sub>steps</sub>  $P_{0,1}(0,0)$ E(eV) $N^0(E)$  $P_{0,1}(tot)$  $P_{0,29}(tot)$  $P_{3,1}(tot)$ 0.8170 2.699e - 21.046e - 24.159e - 32.524e - 224 1.304 30 1.308 2.709e - 21.035e - 24.328e - 32.558e - 21.4200 24 10.012 3.348e - 14.630e - 21.556e - 11.675e - 230 10.012 3.341e - 14.640*e*-2 1.548*e*-1 1.678e - 2

ber of propagation steps per asymptotic wavelength.  $N_{\text{chanl}}$ =350 and

through 1.42 eV in steps of 0.0005 eV was defined, and a blank *R* matrix was created for each. Then, those for the energies wanted were deleted. As each computer finished a given energy, it would look to find the first missing *R* matrix, recreate a blank copy, and then do the calculation at that energy. In this way, several workstations could simultaneously work steadily without interfering with each other. The present work includes every point from point 23 (0.8110 eV) though point 121 (0.8600 eV) with 0.0005 eV spacing, every other point from 123 (0.8610 eV) through 221 (0.9100 eV), i.e., with 0.001 eV spacing, and every 50th point from 241 (0.9200 eV) through 1241 (1.4200 eV), i.e., with 0.025 eV spacing, for a total of 170 energies.

In addition to the above calculations, runs at 11 selected energies were made in which the energy derivative of the log derivative matrix was propagated along with the log derivative matrix to allow the direct calculation<sup>64</sup> of the energy derivative of the **R**, **K**, and **S** matrices and thus of Smith's<sup>65</sup> collision lifetime matrix (**Q**). The energies of these calculations were chosen to span the full energy range of the main set of calculations, and those at the lower energies were chosen to be where there appeared to be peaks or valleys in the probabilities. Then, because very narrow peaks were found

TABLE V. Convergence of reaction probabilities with respect to the number of coupled channels propagated.  $\rho_{end}$ =30.051. See text for discussion.

E(eV)	$N_{\rm chanl}$	$N^0(E)$	$P_{0,1}(\text{tot})$	$P_{0,29}(tot)$	$P_{3,1}(tot)$	$P_{0,1}(0,0)$
0.8170	300	1.326	2.786e - 2	1.077e - 2	4.269 <i>e</i> -3	2.619e-2
	330	1.303	2.714e - 2	1.045e - 2	4.230e - 3	2.541e - 2
	350	1.304	2.699e - 2	1.046e - 2	4.159e - 3	2.524e - 2
0.8440	300	1.263	2.169e - 2	9.130 <i>e</i> -3	1.014e - 2	7.538 <i>e</i> -3
	330	1.263	2.180e - 2	9.048e - 3	1.046e - 2	7.513e-3
	350	1.262	2.169e - 2	9.020e - 3	1.059e - 2	7.430 <i>e</i> -3
0.8755	300	2.368	8.646 <i>e</i> -2	5.255e - 3	3.512e - 2	7.848 <i>e</i> -3
	330	2.370	8.696e - 2	5.278e - 3	3.398e - 2	7.949e - 3
	350	2.375	8.860e - 2	5.344e - 3	3.412e - 2	8.178 <i>e</i> -3
1.0200	300	3.571	7.938 <i>e</i> -2	4.380e-2	8.584e - 2	9.964 <i>e</i> -3
	330	3.593	7.763e - 2	4.216e - 2	9.040e - 2	9.265e - 3
	350	3.592	7.779e - 2	4.194e - 2	8.900e - 2	9.304 <i>e</i> -3
1.2200	300	5.595	1.912e - 1	3.889e - 2	1.201e - 1	1.345e - 2
	330	5.601	1.595e - 1	4.683e - 2	1.161e - 1	2.085e - 2
	350	5.605	1.586e - 1	4.758e - 2	1.190e - 1	2.246e - 2
1.4200	300	10.495	4.146 <i>e</i> -1	5.869e - 2	1.331 <i>e</i> -1	2.247e - 2
	330	10.017	3.475e - 1	5.197e - 2	1.521e - 1	2.216e - 2
	350	10.012	3.348e - 1	4.630e - 2	1.556e - 1	1.657e - 2

in the probabilities, additional calculations, including the energy derivative, were performed for 26 more energies near 0.817 eV with a grid that could be made as fine as 0.000 02 eV to see just how narrow the peaks there are and how large the collision lifetime becomes in their vicinity. We discuss the results in the next section.

The symmetry of the resulting **K** matrices (and hence the unitarity of the **S** matrices) is excellent. However, the energy derivatives obtained are not so stable, and it was found necessary to symmetrize the calculated  $d\mathbf{K}/dE$  to obtain collision lifetimes that are always stable, smooth functions of the energy.

## **III. RESULTS AND DISCUSSION**

#### A. Convergence tests

The results of the convergence test calculations are given in Tables III–V. One sees in all of them that the most highly averaged quantity, the cumulative reaction probability  $^{66-69}$  or number of reacting states,  $N^0(E)$ , quickly converges, the larger partially averaged total reaction probabilities out of given initial vibration-rotation (v, j) states show intermediate convergence, and the smaller total probabilities and the state to state reaction probability to go from ground state (v, j) = (0,1) reactants to ground state (0,0) products are the most sensitive. The results of the tests of convergence with respect to the  $\rho_{end}$  at which the propagation was ended are given in Table III. One sees that, except at the lowest energy shown,  $N^0(E)$  seems converged to within about 5% by  $\rho_{\rm end} = 14 \ a_0$  and, at all the energies, to within about 1% by  $\rho_{\text{end}}$ =21  $a_0$ . For the total and individual probabilities shown, many are fairly close at  $\rho_{end} = 14 a_0$ , but others are inaccurate by as much as a factor of 2. Even at  $\rho_{end}=21 a_0$ , where most of the entries agree with those obtained with  $\rho_{end}=30$  $a_0$ , there are several that differ by 15%–25%, and one that differs by almost a factor of 2. Part of this sensitivity is caused by the fact that any approximation can shift narrow resonances onto or off a given energy. However, since we wanted these calculations to be benchmarks with accurate probabilities and locations of resonances, we chose to use  $\rho_{\rm end}$ =30  $a_0$  in all the production calculations. We note that this is feasible here because the cpu time required by the CC method, while cubic in the number of internal states  $(N_{chanl})$ used, is strictly linear in the distance propagated, and it could be made even less than that if we were to propagate separately in each arrangement channel outside the exchange region. On the other hand, the cpu time required by all of the current time-dependent or time-independent methods which use grids or basis functions in all variables, while often touted to be less than cubic, grows significantly faster than linear with the distance covered.

The results of calculations testing convergence with the number of propagation steps per shortest wavelength are given in Table IV. There one sees that, at both the highest and lowest energies, most of the probabilities are converged to well within 1%, with the smallest one at its most sensitive energy (see Table III) within 4%, for the two values of  $N_{\text{steps}}$  shown. Accordingly,  $N_{\text{steps}}$ =24 was used in all the production calculations.



FIG. 4. Cumulative reaction probability or number of reacting states plotted vs total energy. The points give the raw data; the line is only to guide the eye. (a) Plot over the full energy range of the calculations. (b) Blow up of the low energy region to show the structure. (c) Further blow up of a very narrow energy region showing smoothness of the structures with a very fine grid.

The convergence with the number of coupled channels  $(N_{\text{chanl}})$  propagated is shown in Table V. One sees that most of the probabilities show convergence to within 1%-3% with 300-330 internal channels. However, from the results at the highest two energies, it is clear that calculations with



FIG. 5. Total (summed over all final product states) reaction probability starting from  $O_2(0,1)$  plotted vs total energy *E* and compared with the results of Zhang and Zhang (Ref. 51) (ZZ). (a) Plot over the full energy range of the calculations. The points are the present results; the line gives the results of ZZ. (b) Blow up of the low energy region to show the structure. The points are the present results; the line gives the results of ZZ. (c) Blow up of the low energy region; both the points and the line are the present results. (d) Further blow up of a very narrow energy region showing smoothness of the structures with a very fine grid; both the points and the line are the present results.

these smaller numbers of channels are becoming inadequate there. To get results accurate within a few percent at the highest energies and assure accurate description of narrow resonances at low energies, we elected to use  $N_{\text{chanl}}=350$  in all the production calculations.

We believe that all the other numerical parameters in all steps of the calculation are consistent with accuracy at least as great as given by the parameters tested in these three tables, and that the convergence in these tables is representative of the real accuracy with which the present calculations treat reactive scattering on the DMBE IV PES. We note that the present results are slightly different from and better converged than the results in our preliminary report<sup>49</sup> of this work.

#### B. Reaction probabilities

#### 1. Cumulative reaction probability

Figure 4 shows the cumulative reaction probability or number of reacting states  $N^0(E)$ . This quantity was defined by Miller<sup>66</sup> who showed that the thermal rate coefficient is essentially  $N^J(E)$  summed over all J and averaged over a Boltzmann distribution. Figure 4(a) shows  $N^0(E)$  over the whole energy range at which calculations were done. We note that it shows much fine structure as a function of energy at the low energies at which a fine energy grid was used. We hasten to point out that we expect this structure to continue to all energies shown; the only reason that less structure appears at higher energies is because a coarse energy grid was used, and for that reason the actual points at which the calculations were done are shown. A blowup of the low energy portion of Fig. 4(a) is shown in Fig. 4(b). There one sees that there is much sharp resonance structure which is still not fully resolved at the 0.5 meV grid spacing at which these calculations were performed. Accordingly, Fig. 4(c) shows calculations on a much finer grid yet in a narrow region about the peaks near 0.817 eV; this plot shows that the results in this vicinity are smooth and fully resolved on this scale.

Much of the current interest in the cumulative reaction probability stems from the recognition<sup>67–69</sup> that steplike structures in  $N^0(E)$  are a signal of quantized transition states. As we showed in Ref. 49, smoothing<sup>68</sup> of Fig. 4(b)

produces a plot which shows some faint steplike structures at about 0.83, 0.855, and 0.885 eV, and these are approximately the energies of the barriers in three effective potentials in the 8  $a_0$  region of Fig. 2(b) that correlate with rotationally excited states of the OH product. However, the correlation is not perfect, and we do not wish to claim too much for it. Because this reaction has no real potential barrier and has so many open coupled channels, one should perhaps not expect quantized transition states to be very obvious.

We note at this point that a calculation of  $N^0(E)$  which should be comparable with Fig. 4 has recently been published by Leforestier and Miller.<sup>50</sup> Their results agree qualitatively with the present results; however, on the average their  $N^0(E)$  is smaller than the present results by about 20%. We believe that the results of Ref. 50 are not converged for two reasons (1) The convergence tests discussed above indicate that the present  $N^0(E)$  is converged to well within 1%, and (2) the magnitudes of the results of Zhang and Zhang<sup>51</sup> for some of the probabilities that contribute significantly to  $N^0(E)$  agree very well with our results as discussed below.

From  $N^0(E)$ , one could calculate the J=0 contribution to the rate coefficient exactly; however, J=0 contributes a small fraction of the total rate coefficient. Also, with a Jshifting approximation,<sup>70</sup> one could estimate the experimental rate coefficient. Leforestier and Miller<sup>50</sup> have done that and found that, because the present reaction lacks a welldefined transition state at which to calculate the rotational energies, the uncertainties in the procedure allow one to get a rate coefficient either larger or smaller than experiment. We do not report J shifting approximate results here; similar approximations and their results for the present reaction are being studied by Yang and Klippenstein.<sup>71</sup>

#### 2. Total reaction probabilities

Now let us consider a less-but partly-averaged quantity, namely, the probability for reaction from a given initial vibration-rotation state of the O2 reactant summed over all possible final product states, denoted  $P_{v, j}^{R}$  (total). We first consider  $P_{0,1}^{R}$  (total), the total reaction probability out of ground state reactants; it has very recently also been calculated by Zhang and Zhang<sup>51</sup> (ZZ) using a time-dependent method, and their results are compared directly with the present results in Fig. 5. In Fig. 5(a) the solid line gives the results of ZZ, and the points are the present results. We note that their results<sup>51</sup> confirm what had been expected;<sup>49</sup> namely, that the narrow structures continue to all energies. Also, we note that the agreement is generally very good; their line passes through or near most of our points, so that they agree to within mutual uncertainties (a few percent in each). This confirms both calculations because completely different methods are used.

A blowup of the low-energy fine-grid region is shown in Fig. 5(b). It is clear from it that not only do our results and those of ZZ (Ref. 51) have the same magnitude, but they are also describing the same resonance structures. The differences seen are due to the fact that ZZ can only propagate over a finite time, and that gives their results a finite energy resolution which tends to smear the results a little, so that their peaks are a little lower and their valleys a little higher



FIG. 6. Total (summed over all final product states) reaction probability starting from  $O_2(0, j)$  plotted vs total energy *E* over the full energy range. The panels are for small initial *j* (3, 5, 7, and 9) as labeled.

than ours. It also causes their method to miss a few of the very narrowest peaks. This can be seen by comparing Fig. 5(c), in which the line simply connects the present points, with Fig. 5(b). Our time-independent CC calculations have essentially infinite energy resolution, and, if they are done on a fine enough grid, as shown in Fig. 5(d), where  $P_{0,1}^R$  (total) is



FIG. 7. Total (summed over all final product states) reaction probability starting from  $O_2(0, j)$  plotted vs total energy *E* over the full energy range. The panels are for large initial *j* (11, 21, 31, and 41) as labeled.



FIG. 8. State-to-state reaction probabilities  $P_{0,1}^R(0, j)$  vs total energy *E* for going from ground (0,1) state reactants to product states (v, j) with v=0 and *j* equal to (a) 0–7 and (b) 8–15, as the panels are labeled.

plotted over a very narrow energy range with a very fine grid, they show that the peaks are smooth and have finite widths. However, to carry out CC calculations on a very fine grid over a very wide energy range gets expensive. Thus, *in practice*, our energy resolution is better than that of ZZ in our fine grid region, and theirs is *much* better in our coarse grid region shown in Fig. 5(a).

At this point we compare the costs of the calculations of ZZ (Ref. 51) and ourselves. About 20 cpu hours of CRAY-YMP time were required<sup>72</sup> to produce the ZZ results shown



FIG. 9. State-to-state reaction probabilities  $P_{0,1}^R(1, j)$  vs total energy *E* for going from ground (0,1) state reactants to vibrationally excited product states (v, j) with v = 1 and *j* equal to 0–7 as the panels are labeled.

in Fig. 5. From our experience, the CRAY-YMP is roughly 10 times faster than the HP 735 for our programs, so that, with the times noted in Sec. II, that effort was about the same as that required for 20 energies via our CC calculations. To get a resolution equalling that of ZZ across the whole energy range shown in Fig. 5(a) would require CC calculations at roughly 600 energies. That means that, to generate Fig. 5, the time-dependent method of ZZ is faster than our CC method by a factor of about 30. However, their method, which gives the total reaction probability out of a given initial state, cannot presently give final state distributions, and it must be repeated for every initial state wanted. The present CC method, on the other hand, gives the complete S matrix with all its detailed information at each energy at which it is run. That means that, if one wants  $P_{v, i}^{R}$  (total) for relatively few v and j at a large number of energies, the method of ZZ is much faster; however, if one wants many initial states or detailed final state distributions at relatively few energies, the present CC method is much faster. ZZ give results for four initial states, and we present results for a total of about 200 energies, so the results of this paper actually cost about 2 to 3 times the cpu time as those of ZZ's paper.<sup>51</sup>

In our earlier report<sup>49</sup> we noted that this reaction, in contrast to the similar He+H<sub>2</sub><sup>+</sup> reaction,<sup>69,73</sup> shows *no* enhancement due to initial vibrational or rotational excitation of the O<sub>2</sub> reactant, and we presented plots of  $P_{v,j}^{R}$  (total) for (v, j)=(3,1) and (0,29) there. Zhang and Zhang<sup>51</sup> have shown results for (1,1), (2,1), and (3,1) which agree with present results. The present  $P_{v,j}^{R}$  (total) for (4,1), (5,1), and (6,1) (not shown) grow slowly smaller as the initial vibrational excitation v grows larger but show no interesting new structure or behavior.

To give the reader a better idea of the dependence of the



FIG. 10. State-to-state nonreactive (elastic and rotationally inelastic) probabilities  $P_{0,1}^N(0, j)$  vs total energy *E* for going from O<sub>2</sub> ground (0,1) state to O<sub>2</sub> states (0, *j*) with small final *j* equal to 1, 3, 5, and 7 as labeled.

 $P_{0, j}^{R}$  (total) on *j*, Fig. 5(a) shows it for j=1, and Fig. 6 shows it for j=3, 5, 7, and 9. One sees that the magnitudes of these total probabilities are similar, but that, even though these rotational states of O<sub>2</sub> are closely spaced in energy, the narrow resonance structures vary strongly with *j*. The same quantities for the larger values of j=11, 21, 31, and 41 are shown in Fig. 7. One sees that, due to rotational and centrifu-



FIG. 11. State-to-state nonreactive (rotationally inelastic) probabilities  $P_{0,1}^N(0, j)$  vs total energy *E* for going from O<sub>2</sub> ground (0,1) state to O<sub>2</sub> states (0, *j*) with large final *j* equal to 11, 21, 31, and 41 as labeled.



FIG. 12. State-to-state nonreactive (vibrationally inelastic) probabilities  $P_{0,1}^N(v,1)$  vs total energy *E* for going from O<sub>2</sub> ground (0,1) state to O<sub>2</sub> states (v,1) with final *v* equal to 1–5 as labeled.

gal effects (j=l for J=0), colliding reactants with large initial j are kept out of the region of strong interaction with product states and have small total reaction probability. The  $P_{0, j}^{R}$ (total) for  $j \ge 45$  (not shown) are never larger than 0.01 on this range even though O<sub>2</sub>(0, j) states with much larger jare open asymptotically.

At this point we note that the  $P_{v,j}^{R}$  (total) for both v and j excited (not shown) are similar in appearance to those already shown. Also, we were curious to see whether there would be any enhancement of reaction probability out of those H+O<sub>2</sub> states, such as (v, j) = (0,63), (1,53), (2,43), (3,29), (3,27), and (4,1), which are at nearly the same energy as the ground O+OH(0,0) state, so that the incident and final translational energies are nearly equal. There is none; hence, plots of those results are not shown here.

TABLE VI. Properties of the collision lifetime matrix at several energies. Energies are in eV, and times are in femtoseconds. See the text for discussion.

E(eV)	$t_{\rm max}$	$t_{\min}$	trace Q	Largest components
0.812 00 0.816 30 0.817 44	1 688 1 164 4 078	$-16\ 607$ $-24\ 564$ $-10\ 288$	-25 994 -48 831 -16 668	Reactants Reactants Products and reactants
0.818 00 0.833 50 0.844 00 0.854 00 0.875 50 1.020 00 1.220 00 1.420 00	2 638 2 101 477 2 397 3 430 379 9 542 6 719	$\begin{array}{r} -8\ 680\\ -4\ 206\\ -5\ 394\\ -3\ 120\\ -2\ 833\\ -6\ 097\\ -1\ 613\\ -4\ 891 \end{array}$	$-15\ 188\\-8\ 284\\-15\ 887\\-7\ 422\\-7\ 695\\-19\ 163\\-2\ 268\\-26\ 523$	Products and reactants Products and reactants Reactants Products Products Reactants Reactants Products



FIG. 13. Maximum eigenvalue  $t_{max}$  in femtoseconds of the collision lifetime matrix plotted vs the total energy in eV with a very fine grid over a very narrow energy range to trace out a resonance.

#### 3. Final state distributions

Now, let us consider detailed state-to-state reaction probabilities. Because there is so much resonance structure in all the plots, the final state distribution varies much with energy, and we do not attempt to simply give a few final state distribution plots or perspective plots but instead give in Figs. 8 and 9 the reaction probabilities for going from the ground (0,1) state reactants to each of the open product (v', j')states. Figure 8 gives the probabilities to form (0, j') product states. There one sees that the resonance peaking depends strongly on j'. Also, it is seen that, averaged over energy enough to smear the resonance peaking, the reaction probability tends to grow with i' and to peak at high energies at the high product rotational states with i' = 13 and 14. This peaking of the product rotational distribution at large i' for high energies is consistent with both experimental<sup>3,15-18,22</sup> and classical trajectory studies<sup>47</sup> of this reaction. Figure 9 gives the probabilities to form the vibrationally excited product (1, j') states. Even the lowest of these is only open for energies greater than 1.2559 eV. From the figure one sees that their probabilities tend to peak at smaller j', depend more weakly on j', and to be half as large as the probabilities to form the ground v'=0 product states.

In the early report<sup>49</sup> of the present work, we noted that there is an increase in the slope of  $P_{01}^{R}$  (total) above 1.256 eV [see Fig. 5(a)], attributed it to the opening up of the v'=1OH channel, and suggested that, if a similar increase occurs at the opening of the v'=2 OH channel at 1.680 eV, it could provide an interpretation of the steep rise seen in the experimental cross section<sup>21,22</sup> beginning at that energy. On closer examination of Figs. 8 and 9, it appears that the situation is more complicated. The highly excited rotational states of OH with v'=0 that are becoming open at these energies appear to be contributing as much to the increased growth of  $P_{01}^{R}$  (total) as the product states with v'=1. Hence, what might cause the steep rise at the higher energy is not yet clear.

The final state distribution of the nonreactively scattered  $H+O_2$  is also of interest. Selected state to state probabilities

for elastic and rotationally inelastic scattering are shown in Figs. 10 and 11, and some for vibrationally inelastic scattering are shown in Fig. 12. One sees from them that the elastic scattering probability, while larger on average than any of the other state to state inelastic or reactive probabilities, is not very large, and represents a small fraction of the total scattering. Significant rotationally inelastic scattering starting from the ground  $O_2(0,1)$  state extends up to  $O_2(0,41)$  but is very small past (0,45). Significant vibrationally inelastic scattering vibrational quantum numbers greater than 5. We note that vibrationally inelastic scattering is about as probable as rotationally inelastic scattering for this system because the strong potential well mixes both the motions strongly.

### **C.** Collision lifetimes

In Table VI are shown results of the collision lifetimes calculations performed at the 11 selected energies spanning the full energy range of the present work. One sees from it that, at all of the energies, the maximum eigenvalue  $t_{max}$  of Smith's<sup>65</sup> collision lifetime matrix  $\mathbf{Q}$  is always greater than 379 fs, corresponding to a significant delay due to the interaction. At many of the energies,  $t_{max}$  is of the order of several picoseconds; this shows that the reaction is, in fact, dominated by long-lived resonances. We note that the minimum eigenvalue of Q is always negative and of the order of several picoseconds. The reason for this is that the eigenvalues of **Q** represent the *difference*<sup>65,74</sup> between the actual lifetime of the collision and the time required if the reactants went past each other with no interaction. Looking at Fig. 3, one can see that particles that sense the deep attractive well are accelerated by it and also hit the repulsive wall, shortening the distance traveled relative to no interaction. Both these effects can make the collision lifetime significantly negative, especially for those channels that are very near threshold and thus for which the lifetime of passage with no interaction gets very long.

We have also tabulated the trace of Q because this quantity is important in recombination kinetics;<sup>74,75</sup> it is seen that this trace is negative at all but one of the energies in Table VI. We discuss this more in a future paper.<sup>76</sup> Also, we note that **Q** is labeled by the asymptotic channels, so that those channels which are the largest components of its eigenvector with the largest eigenvalue  $t_{max}$  are those asymptotic states which interact most strongly with the longest-lived resonant state at that energy. In the last column of Table VI we have noted that those states are sometimes dominated by states in the reactant arrangement, sometimes the product arrangement, and sometimes both. It is these latter resonances that connect reactants and products efficiently and enhance the reaction probability. For example, the largest components of the 4 ps lifetime resonance at 0.817 44 eV are (in order) the (v, j) states (0,0) of the OH product and the states (2,17), (0,17), and (2,1) of the O<sub>2</sub> reactant, and the reaction probabilities between them have peaks near this energy.

To show the behavior of  $t_{\text{max}}$  with energy it is plotted in Fig. 13 on a very fine grid for energies near 0.817 eV. One sees that it smoothly rises from about 1 ps to 4 ps and then declines again as it traces out the resonance. We note that

 $t_{\text{max}}$  peaks near 0.817 44 eV, but the probabilities plotted in Figs. 4(c) and 5(d) peak near 0.817 24 eV, and so does  $P_{2,17}^R(0,0)$  (not shown), the reaction probability connecting the largest components of the resonance. This difference of 0.2 meV occurs here because the probabilities depend only on the **S** matrix while the lifetimes also depend on its energy derivative; it can occur because the energies of resonances are only defined to within the width of the resonance, and the value obtained depends on the method of calculation.

### D. Origin of resonances

A resonance is a nonstationary state with a prolonged lifetime. In the present system they correspond to fragments colliding, getting trapped and oscillating for a time, and then separating into products or reactants. To analyze in detail all the overlapping resonances evidenced in the results of this work would take considerable effort and has not been done yet. However, the basic mechanism for their formation is qualitatively visible from Fig. 3; the system comes in on some curve that is asymptotically open, transitions or tunnels to one of the curves that is asymptotically closed (Feshbach) or has a barrier higher than E (quasibound), and oscillates in that curve until it transitions or tunnels to and exits on the original or another asymptotically open curve.

## E. Is this reaction statistical?

For reactions that form long-lived complexes (resonances) the standard argument is that the complex forgets from which arrangement channel it was formed and decays statistically into the different arrangements according to their available phase space volumes. However, as we noted in Sec. I, there has been considerable controversy<sup>1,34,37,38,43,44</sup> about whether the present reaction displays statistical behavior. The present results have some bearing on this question. If we look at a specific resonance at a specific energy, its decay is clearly not statistical. From Table VI it is clear that some resonances connect mostly to reactant states, some mostly to product states, and some connect to both reactants and products. Furthermore, it is clear from Figs. 5(c) and 5(d) for example, that the peak reaction probability at specific resonances is not determined by the product and reactant phase space available. On the other hand, if we look at the state to state probabilities of Figs. 8–12, we see that on the average, there is a great tendency for the probability to be spread out into many final states and to be of the same order of magnitude for a large number of final product and reactant states. Similarly, if we look at the cumulative reaction probability shown in Fig. 4, which is the important quantity for chemical kinetics, it is clear that on a fine energy scale it does not behave statistically. Whether it behaves statistically when averaged over energy or summed over J is not yet clear. Yang and Klippenstein<sup>71</sup> are currently doing calculations on this reaction using several statistical methods, and their results may help to answer this question.

## **IV. CONCLUSIONS AND FUTURE WORK**

In this paper we have presented accurate 3D coupled channel (CC) calculations of reactive scattering for the title reaction using the DMBE IV (Ref. 34) potential energy surface. The convergence tests presented herein show that the results are accurate to within a few percent. All the results show many narrow and overlapping resonances. The resulting cumulative reaction probabilities appear to be better converged than those of Leforestier and Miller.<sup>50</sup> The total reaction probabilities agree very well with those of Zhang and Zhang,<sup>51</sup> and, as we have discussed in more detail in an early report of this work,<sup>49</sup> they show that the reaction probability is not enhanced by the initial excitation of either vibration or rotation of the reactants. We have also presented the first detailed state to state probabilities and final state distributions. We find that the probabilities are very highly structured due to resonances, that these structures vary strongly from one transition to another, and that the probability spreads out into very many final vibrational and rotational channels in both the product and reactant arrangements. In particular, there is a rather strong tendency to produce very highly rotationally excited products. Significant differences between this reaction and the similar  $He+H_2^+$  reaction were discussed in Ref. 49.

We have also presented herein the first accurate calculations of the collision lifetimes for this system. Resonances with lifetimes of one to ten picoseconds are found at most energies. Some of these resonances connect mainly to product, some mainly to reactants, and some "reactive" resonances connect reactants to products and enhance reactivity. All these resonances result from the system getting trapped in states behind barriers or that are locally open but asymptotically closed.

Whether this reaction behaves statistically has also been discussed. We conclude that on a detailed level the reaction is certainly not statistical, but that, at the resolution involved in chemical kinetics, it not yet clear whether it behaves statistically.

The present results represent an accurate solution of the problem attacked in this paper. However, much still remains to be done on this system before one can say that the real physical problem has been solved. For example, the present results are all for total angular momentum J=0. We estimate that to calculate integral or differential cross sections or rate constants at the energies at which most experiments have been done would require calculations with J up to about 100. In addition, the intermediate in the reaction,  $HO_2$ , is very floppy; Fig. 1(b) shows that configurations varying all the way from linear through all asymmetric tops to the oblate symmetric top geometry are accessible. That means that all components  $\Lambda$  of the total angular momentum,  $0 \leq \Lambda \leq J$ , will be accessible and coupled. To do full CC calculations including this coupling would be computationally very expensive, and we currently do not have enough support for this work to attempt them. Using angular momentum decoupling approximations would make calculations at all J feasible; however, this floppy system is far from optimum for use of currently available decoupling approximations, so that the accuracy of the results would not be clear. Work along this line is continuing.

In addition, although the DMBE IV PES (Ref. 34) used herein describes much about reactions (1) and (2) well, it has serious limitations. Its most obvious deficiency, in our opinion, is that it is a smooth, single-valued function which represents only the ground  $(X^2A'')$  state of the HO<sub>2</sub> system and contains no information about any excited electronic states. In fact, it is known from the recent accurate ab initio calculations of Walch and co-workers<sup>28-30</sup> that the true ground state surface has two conical intersections with higher surfaces. One of these has  $C_{2v}$  symmetry, and the other has collinear  $(C_{\infty v})$  symmetry. Paths completely encircling both are accessible at energies far below the reaction threshold. Hence, geometric phase effects due to both conical intersections need to be included at all reactive scattering energies. In addition, from the collinear conical intersection on inward, there is a collinear saddle point,<sup>30</sup> occurring at energies as low as 0.4 eV and thus accessible at all reactive energies, at which the X  ${}^{2}A''$  state and the lowest  ${}^{2}A'$  state become the two degenerate components of a  $\Pi$  electronic state, and there will thus be Renner-Teller coupling between them.

In addition to the intersections and degeneracy just listed, Graff and Wagner<sup>27</sup> have pointed out that, due to the nonzero electronic angular momentum of the OH radical and the O atom, there are several PES's which all become nearly degenerate in the O+OH region of the reaction where they display<sup>27</sup> many narrowly-avoided crossings and are split apart only by spin–orbit coupling. Several of these can get involved in the real process. One of these is again the lowest <sup>2</sup>A' state, and this is the electronic state involved in the reaction

$$\mathbf{H}(^{2}S) + O_{2}(^{1}\Delta_{g}) \rightleftharpoons \mathbf{OH}(^{2}\Pi) + \mathbf{O}(^{3}P).$$
(3)

Several authors<sup>4,22,39,77</sup> have noted that the accessibility of this excited-state PES may mean that, particularly under some experimental conditions, reaction (3) may contribute to, compete with (via its reverse reaction), or crossover (via the collinear degeneracy) to reaction (1). Hence, all these intersection and degeneracy effects need to be included.

In other work we<sup>78</sup> have used the diatomics in molecules (DIM) method as a framework to fit the best available *ab initio* calculations<sup>28–30</sup> on this system and have thus obtained global fits to all the low-lying <sup>2</sup>A" and <sup>2</sup>A' PES's of this system that explicitly contain the conical intersections and degeneracies. We<sup>79</sup> are currently studying their geometric phase and coupling effects; that work, which will also include fully the indistinguishability of the two O atoms, will be reported later.

Also, as noted in Sec. II, the present work, consistent with the use of a single-valued ground state potential, has neglected all coupling of the nuclear motions to the electronic spin and orbital angular momenta. In the reactant arrangement channel, where the only electronic degeneracies are due to the spin degeneracies of the  $H(^2S)$  and the  $O_2(^3\Sigma_g^-)$ , and the  $O_2$  is well described as a Hund's case (b) molecule,<sup>80</sup> the spin splitting is very small (~1 cm<sup>-1</sup> or 0.1 meV), and neglecting coupling to the electronic angular momenta is an excellent approximation.<sup>80</sup> As the reactants come together to form the OOH ( $X^2A''$ ) intermediate, in most configurations the only degeneracy is again just spin degeneracy, the splitting of the two components of the doublet is negligible, and the approximation is again justified. The places

where it fails are the vicinities of the conical intersections and collinear degeneracies discussed in the preceding paragraphs and being considered in other work.<sup>79</sup> However, as the system exits into the product arrangement channel, both the  $O({}^{3}P)$  and the  $OH({}^{2}\Pi)$  have nonzero electronic orbital and spin angular momenta. The spin-orbit splitting (~100  $cm^{-1}$  or 10 meV) is not negligible, and several<sup>27,28</sup> nearly degenerate electronic states and their couplings should be included and allowed to affect the motion of the nuclei. As part of such an extension, the coupling of the electronic spin, electronic orbital, and nuclear orbital angular momenta in the  $OH(^{2}\Pi)$  product need to be included to reproduce the experimental observation<sup>81</sup> that it is neither Hund's case (a) nor (b) but a nearly equal mixture of the two cases. These extensions, which we hope to include in some future work, will complicate the calculations considerably and will significantly affect the probabilities and cross sections at the reaction threshold.

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