## Accurate quantum probabilities and threshold behavior of the $H + O_2$ combustion reaction

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We report accurate 3D quantum reaction probabilities for the  $H+O_2$  combustion reaction and find that they are resonance dominated and rise linearly above threshold. The reaction probability is *not* enhanced by vibrational or rotational excitation of the reactants but does increase above the threshold for vibrationally excited products.

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>1-3</sup> In the combustion of all hydrocarbons it is the rate-limiting, chain-branching step and determines explosion limits and flame propagation rates. It needs to be understood in detail and has been extensively studied, but many questions remain.

Because of its large (0.71 eV or 8200 K) endoergicity, even in a 2500 K flame only the tail of the Boltzmann distribution can produce reaction. That makes the threshold region especially important, and considerable concern has been expressed<sup>1,4</sup> about quantum threshold effects, but, until now, no accurate information has been available about them. There have been no experimental measurements of the threshold behavior, and most theoretical studies to date have been statistical<sup>5</sup> and quasiclassical trajectory (QCT) studies.<sup>1,4</sup> This reaction plagues such theories because it displays a large number of recrossings of transition state dividing surfaces, long-lived snarled trajectories, and many trajectories which form OH product with less than its quantum zero-point energy;<sup>1,4</sup> hence, such theories cannot accurately give the threshold behavior.

In this paper we report the first accurate 3D quantum reaction probabilities for reaction (1), though we understand that another calculation of its cumulative reaction probability is in process.<sup>6</sup> There have been no accurate quantum dynamics studies of this reaction before now because it is significantly more difficult than any that have been treated to date. It has two heavy atoms, and its large endoergicity causes many O2 states to be open at the threshold for product formation. Current ab initio calculations show no barrier along the reaction path;<sup>7,8</sup> instead, there is a deep well, and this causes many asymptotically closed OH states to be locally open. The bound states of this well correspond to the hydroperoxyl radical, OOH, which is nonlinear,<sup>7,8</sup> and this bent intermediate causes more angular momentum coupling than occurs in linearly dominated reactions. 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 has a heavy-light-heavy mass

combination and is allowed at all scattering energies, and there is a dipole-quadrupole  $(R^{-4})$  potential in the product arrangement that is much longer ranged than the usual van der Waals  $(R^{-6})$  potential.

The potential energy surface (PES) used herein is the DBME IV PES of Pastrana *et al.*<sup>7</sup> which appears to be the best global PES available for this reaction; it makes extensive use of both *ab initio* and empirical information. A newer PES<sup>8</sup> is not yet complete.

In common with similar studies<sup>9</sup> of simpler reactions producing OH, the electronic spin and orbital angular momenta are neglected in the present work. Thus, the diatomic angular momenta denoted here by j correspond to the nuclear orbital angular momenta often<sup>10</sup> called N. This gives accurate treatment of the reactants, and  ${}^{16}O_2$  has only odd j=N states as required by its electronic and nuclear spin symmetries,<sup>11</sup> so that its ground vibration-rotation state is  $O_2(v, j) = O_2(0, 1)$ . This neglect of electronic angular momenta also treats the intermediate  $HO_2({}^2A'')$  radical accurately; however, it is not as accurate for  $OH(^{2}\Pi)$ , where the electronic angular momenta and spin-orbit splitting produce a mixture<sup>12</sup> of Hund's cases a and b that shifts its rotational levels by a few meV. We plan to include these effects in future studies. At present, the total nuclear orbital angular momentum, J, is fixed at zero.

We choose the energy zero to be the bottom of the asymptotic  $O_2$  well. With that, 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<sub>2</sub>(0,1) is 0.097 87 eV, and the energy of ground state OH(0,0)+O (the reaction threshold) is 0.811 47 eV. The relative energy at the threshold for reaction is thus 0.713 60 eV.

We use the APH method for reactive scattering.<sup>13</sup> In it, one solves for "surface functions," which are functions of the APH hyperangles, then expands the complete wave function for a given J in terms of the surface functions, Wigner functions of Euler angles, and unknown functions of the hyperradius,  $\rho$ . The functions of  $\rho$  are determined by propagating the coupled channel (CC) equations, keeping all coupling, from small  $\rho$ , where they are regular, to asymptotic  $\rho$ , where a unitary transformation projects them onto functions of the arrangement channel Delves' hyper-



FIG. 1. Total (summed over all final product states) reaction probability from  $O_2(0,1)$  plotted vs total energy E in the threshold region.

spherical coordinates, and then the boundary conditions are applied directly in the Delves' coordinates to obtain the scattering matrix.

The surface functions have the symmetry of the system. The surface functions from  $\rho=3.3 a_0$ , where all their energies are strongly repulsive, to 6.5  $a_0$  were calculated using a discrete variable representation (DVR) method.<sup>14</sup> The surface functions from  $\rho=6.5$  to 30.0  $a_0$  were determined using the analytic basis method (ABM).<sup>15</sup> This large final  $\rho$  is necessary to make the long-range potential less than 0.3 meV for all orientations and allow accurate calculation of resonance positions and thresholds. The parameters and size of the DVR and ABM bases were carefully chosen to give the energies of the asymptotically open channels accurate to better than 0.1 meV and the energies of all locally open channels accurate to about 0.3 meV.

From the surface function energies, one sees that this system always has many open channels. At the reaction threshold, there are 96 asymptotically open channels, and 155 channels are locally open in the well region. At the highest energy considered, 1.42 eV, there are 246 asymptotically open channels and 308 channels locally open in the well.

To include enough closed channels to prevent loss of flux, 350 CC equations were propagated from 3.3 to  $30.0 a_0$  as described above.<sup>13</sup> Convergence tests, to be published later, indicate that the resulting reaction probabilities are accurate to within a few percent. Calculations were done at a total of 186 scattering energies: 164 of these cover the total energies from 0.8115 to 0.8930 eV with a grid spacing of 0.0005 eV, and the other 22 run from there to 1.42 eV with a spacing of 0.025 eV.

A few key results are shown in the figures. Figures 1 through 3 show plots over the fine energy grid region of the total reaction probability out of three representative initial states of  $O_2$ , namely, the ground (0,1) state, a vibrationally excited (3,1) state, and a rotationally excited (0,29) state. One notes that all three probabilities are about the same



FIG. 2. Total reaction probability from  $O_2(3,1)$  plotted vs total energy E in the threshold region.

magnitude and are totally dominated by resonance structures. In future work we will report the lifetimes of some of these resonances. At present, we note that the full widths at half maximum (FWHM) of some are narrower than 1 meV; from the uncertainty principle, their lifetimes must be at least half a picosecond.

Figure 4 shows these same three probabilities over the full energy range, and we note that the points show the actual energies of the calculations; the lines are to help the eye of the reader. From all the structure in these plots, we expect a fine energy grid to find that the narrow resonances continue over the full energy range; the current structures appear broad only because the energy grid is coarse. Also, we note from these figures that the reaction probability is largest out of the ground initial state; it is *not* enhanced by initial excitation of either vibrational or rotational motion.

We mention that the reaction probabilities to specific final states of OH spread out into all available product



FIG. 3. Total reaction probability from  $O_2(0,29)$  plotted vs total energy E in the threshold region.

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FIG. 4. Total reaction probabilities for  $O_2(v,j)$  plotted vs total energy E over a wide energy range. The energy grid is 0.0005 eV in the threshold region and 0.025 eV at higher energies. The upper points (solid line) give the total probability out of (0,1); the middle points (dashed line) give the total probability out of (3,1); and the lower points (solid line) give the total probability out of (0,29).

states and appear quite similar to Figs. 1 through 4.

Figures 5 and 6 show the cumulative reaction probability or number of reacting states  $N^0(E)$ . Both the raw  $N^0(E)$  and one smoothed<sup>16,17</sup> (over a Gaussian with a FWHM of 0.05 eV in the coarse grid region and 0.01 eV in the fine grid region) are plotted.  $N^0(E)$  is of interest because it is directly related to the thermal rate constant.<sup>17,18</sup> From it, with a J shifting approximation,<sup>19</sup> one could estimate the experimental rate constant; however, we restrict the present Communication to accurate results. Figure 6 is a blowup of the fine grid portion of Fig. 5. One sees that the smoothed  $N^0(E)$  has a steplike structure which may represent quantized transition states,<sup>17,18</sup> and we mention that the positions and spacing of the steps correspond well with some exit channel centrifugal barriers.



FIG. 5. Cumulative reaction probability or number of reacting states plotted vs total energy over a wide energy range. The points give the raw data; the dashed line is the result after smoothing.



FIG. 6. Cumulative reaction probability or number of reacting states plotted vs total energy in the threshold region. The points give the raw data; the dashed line is the result after smoothing.

In discussing this reaction, it is convenient to compare and contrast it with a similar reaction for which accurate calculations have been performed,<sup>16,20</sup> namely, He  $+H_2^+ \rightarrow$ HeH<sup>+</sup>+H. Like the title reaction, it is endoergic with a well and no barrier. Its endoergicity is similar; however, its well is much shallower, and its intermediate is linear. The reaction probabilities in both reactions are resonance dominated; however, in the HeH<sub>2</sub><sup>+</sup> reaction, most resonances are broad enough to be smoothly resolved by a 0.0005 eV energy spacing; here, they are narrower than that.

In  $\text{HeH}_2^+$  there is strong vibrational enhancement with the reaction probability out of excited initial vibrational states being more than an order of magnitude larger than that out of the ground state. Here, there is no vibrational or rotational enhancement at all despite the endoergicity. We believe that the bent intermediate in the present reaction causes the motions in the reactants to couple poorly to the motions producing the product.

One reason the  $H+O_2$  reaction is slow is because it is so endoergic; another reason is shown by the present results: In the  $HeH_2^+$  reaction, the reaction probabilities rise very rapidly (within 0.1 meV) from zero at threshold to values as large as they ever get. However, one sees from the figures shown (and others not shown) that, in the present reaction, they tend to rise essentially linearly from zero at the threshold at 0.811 47 eV. This is also manifest in Fig. 6, where the cumulative reaction probability rises quickly from zero at threshold to a value of only about 0.2 at the first calculated point at 0.8115 eV and then (on average) rises more slowly and approximately linearly from there; in  $HeH_2^+$  it rises very quickly to about 1.0 before flattening into a similar linear rise.<sup>16</sup>

Also, we note a change in slope at E=1.256 eV in the upper curve in Fig. 4, with  $P_{0,1}(total)$  rising more steeply at higher energies. This phenomenon, which occurs in the reaction probabilities out of many of the low-lying, thermally populated states of O<sub>2</sub>, and also occurs<sup>16</sup> in HeH<sub>2</sub><sup>+</sup>, is due to the opening of the v'=1 product vibrational chan-

nel. If a similar increase occurs at the opening of the v'=2 OH channel at 1.680 eV, it could provide an interpretation of a steep rise in the experimental cross section<sup>21</sup> starting at that energy.

More details of the present calculations will be published later. Also, much remains to be done on this reaction, and we are working on several extensions and improvements.

In summary, we have presented accurate quantum results for the important  $H+O_2$  combustion reaction that show for the first time that the reaction probabilities are resonance dominated, rise linearly above threshold, are not enhanced by internal excitation of the reactants, and are enhanced by accessible vibrationally excited product states.

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