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Differential and Integral Cross Sections for the H + O_2 → OH + O Combustion Reaction

Pascal Honvault,† Shi Ying Lin,‡ Daiqian Xie,§ and Hua Guo*,‡

Institut UTINAM, UMR CNRS 6213, University of Franche-Comté, Campus de la Bouloie, UFR Sciences et Techniques, 25030 Besançon cedex, France, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, and Institute of Theoretical and Computational Chemistry, Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

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We present accurate differential and integral cross sections for the H + O_2 → OH + O reaction obtained on a newly developed ab initio potential energy surface using time-independent and time-dependent quantum mechanical methods. The product angular distributions near the reaction threshold show pronounced forward and backward peaks, reflecting the complex-forming mechanism. However, the asymmetry of these peaks suggests certain nonstatistical behaviors, presumably due to some relatively short-lived resonances. The integral cross section increases monotonically with the collision energy above a reaction threshold.

$H(^2S) + O_2(^3\Sigma_g^-) \rightarrow OH(^2\Pi) + O(^3P)$ is a fundamentally important elementary reaction. It is not only considered as the "single most important reaction" in the combustion of hydrogen and hydrocarbons because of its role in the rate-limiting chain branching step,[1] its reverse reaction is also a key process in atmospheres and in interstellar media thanks to the barrierless entrance channel potential dominated by long-range electrostatic attraction between OH and O.[2] It has long been established that the H + O_2 reaction proceeds on the ground-state potential of $HO_2(\tilde{X}^2A'')$ and is endothermic by 0.71 eV. As a result, the reactivity has a quantum threshold corresponding to the opening of the $HO(v_f = 0, j_f = 0)$ + O channel. In addition, the minimal energy path for the reaction has no apparent barrier and is dominated by a deep (2.38 eV from the H + O_2 asymptote) potential well corresponding to the HO_2 species.[3] Consequently, the reaction dynamics is strongly influenced by a long-lived HO_2 intermediate,[4,5] which manifests quantum mechanically as metastable resonances.[6,7] Indeed, the title reaction is considered as a prototype for complex-forming reactions. The large zero-point energy of the HO product and the dominance of resonances render an accurate classical characterization of the reaction near the threshold very difficult, if not impossible.

A key issue concerning the reaction dynamics is whether the title reaction is statistical. In the limiting case where the reaction is completely dominated by long-lived resonances, the products are expected to be statistically populated, and their angular distributions should be forward−backward symmetric. Although no direct measurement of the differential cross section (DCS) has been reported, state-resolved experiments so far have offered some tantalizing evidence supporting the existence of a statistical behavior for this reaction, at least at low collision energies. For example, it was found that both the OH rotational states[8,9] and spin−orbit states of $O(^3P_j)$[10] are near statistically populated. Furthermore, Doppler-resolved laser-induced fluorescence data were consistent with approximately forward−backward symmetric product angular distributions at low collision energies.[11] As energy increases, however, the direct channel gradually gains prominence. On the other hand, the statistical nature of the reaction has been questioned by several theoretical studies,[3,12−14] mostly based on quasi-classical trajectory (QCT) calculations. Due to the ad hoc nature of a QCT in treating quantum features such as zero-point energy and resonances, however, it is unclear if the conclusion remains valid in a quantum treatment. The controversy concerning the statistical nature of this complex-forming reaction can only be resolved by the direct measurement or accurate calculation of the DCS.

Significant uncertainties also exist for the integral cross section (ICS) of the reaction,[15−18] due apparently to experimental difficulties in detecting products with low reactivity. For instance, it has been claimed that a sharp increase of ICS occurs near a collision energy of 1.8 eV.[15,17] However, this feature could not be verified by either the latter experiment[18] or theory.[5,19,20]

An accurate quantum dynamical treatment of the title reaction is truly challenging because of two factors. First, the deep potential well and the heavy oxygen mass necessitate a large quantum basis set. Second, many partial waves have to be included for this barrierless reaction, and the floppy nature of the HO_2 complex entails strong Coriolis coupling.[21] Finally, one needs a global potential energy surface (PES) that is capable of describing the entire configuration space with even accuracy. So far, the most elaborate quantum calculations on the title reaction have been limited to the integral cross section[19,20] on the double many-body expansion (DMBE) IV PES.[3] However, recent studies have shown that the semiempirical DMBE PES may contain significant deficiencies.[22−24]

In this Letter, we report the first accurate quantum DCSs for the title reaction at energies slightly above the reaction threshold using an exact time-independent quantum mechanical (TIQM)

[†] University of Franche-Comté.

[‡] University of New Mexico.

[§] Nanjing University.

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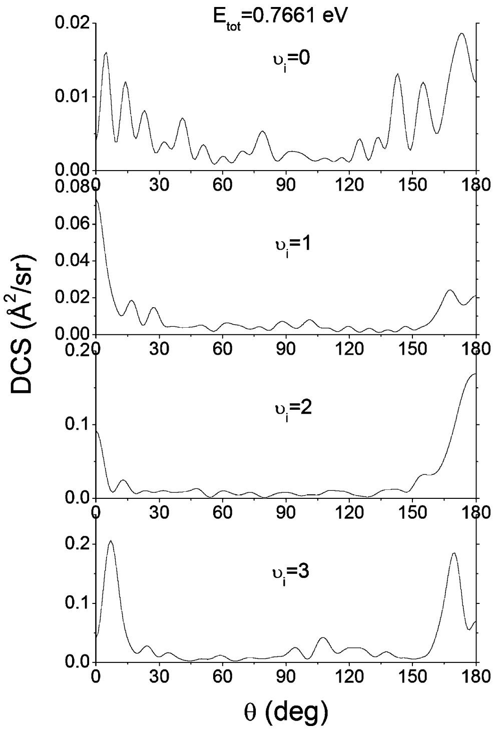

Figure 1. Differential cross sections for the H + $O_2(\upsilon_i, j_i = 1) \rightarrow$ OH + O reaction at $E_{tot} = 0.7661$ eV.

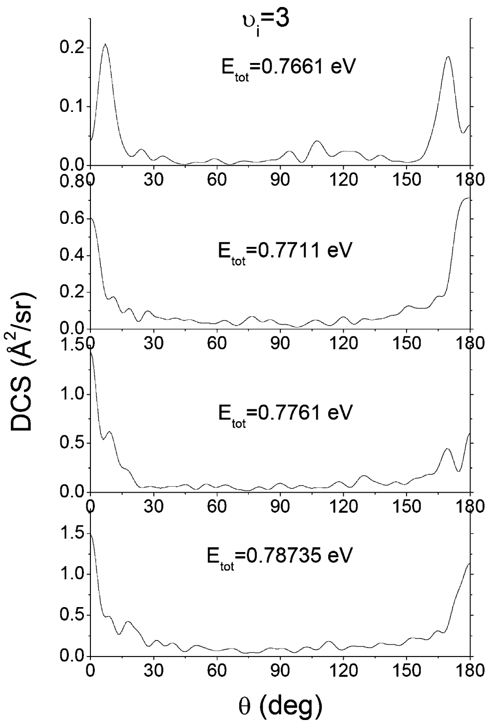

Figure 2. Differential cross sections for the H + $O_2(\upsilon_i = 3, j_i = 1) \rightarrow$ OH + O reaction at four energies.

TABLE 1: Initial State-Specified Integral Cross Sections (Å^2) at $E_{tot} = 0.7661$ eV

j_i	1	3	5	7
$\upsilon_i = 0$	0.002425	0.002204	0.001744	0.001625
$\upsilon_i = 1$	0.003418	0.002552	0.002502	0.001827
$\upsilon_i = 2$	0.006931	0.006718	0.005481	0.003976
$\upsilon_i = 3$	0.012083	0.009503	0.006909	0.005951

method. The fully quantum state-resolved DCSs provide the most detailed information on the reaction dynamics, which can be directly compared with experiment. In addition, integral cross sections have been computed up to 1.0 eV of collision energy with an exact time-dependent quantum mechanical (TDQM) method. These calculations were performed on a new ab initio PES of the HO_2 system (denoted as XXZLG),[25,26] which has been demonstrated to drastically improve the agreement with experimental vibrational frequencies.

In our calculations, the energy zero was chosen at the potential minimum of the H + O_2 asymptote. As a result, the threshold for the H + $O_2(\upsilon_i = 0, j_i = 1) \rightarrow OH(\upsilon_f = 0, j_f = 0)$ + O reaction is 0.66 eV on the XXZLG PES, which is slightly smaller than that in the DMBE PES (0.71 eV). The DCSs were computed with a fully Coriolis-coupled TIQM method based on the body-frame hyperspherical democratic coordinates approach. Details of this method can be found in ref 27. This method is robust and accurate and has already been used for insertion reactions[28,29] and ultracold collisions.[30,31] An important advantage of this method is that it yields the entire S matrix at a given energy. However, it is computationally demanding. Specifically, we were able to converge the results for $\upsilon_i = 0$, 1, 2, and 3 at $E_{tot} = 0.7661$ eV and $\upsilon_i = 3$ at $E_{tot} = 0.7661$, 0.7711, 0.7761, and 0.78735 eV with $J_{max} = 32$.

Figure 1 displays the DCSs for the $j_i = 1$, $\upsilon_i = 0$, 1, 2, and 3 states of the O_2 reactant at $E_{tot} = 0.7661$ eV, which corresponds to collision energies (E_c) of 0.668742, 0.475772, 0.286551, and 0.102697 eV for the four initial states, respectively. (The cross sections reported in this work have included the electronic degeneracy factor (1/3) for the H + O_2 asymptote). At $E_{tot} = 0.7661$ eV, only the ($\upsilon_f = 0$, $j_f = 0$, 1) states of the OH product are populated; therefore, the DCS is nearly state-to-state. Several observations are immediately in order. First, the DCSs are highly oscillatory. Such oscillations stem apparently from quantum interferences inherent in the partial wave summation. Second, all DCSs are dominated by forward and backward peaks, indicative of the existence of a reaction intermediate. However, the angular distributions are not completely symmetrical. For instance, the $\upsilon_i = 1$ distribution is more forward biased, while that for $\upsilon_i = 2$ is more backward biased. The asymmetry suggests that although an intermediate is involved, its lifetime might not be sufficiently long to render the reaction completely statistical. Finally, the reactivity is greatly enhanced by vibrational excitation in the reactant, as evidenced by the ICSs for the four υ_i values (0.002425, 0.003418, 0.006931, and 0.012083 Å^2) at this energy. This important feature will be further discussed below. Interestingly, the excitation of the initial O_2 rotation also has a high impact on the reactivity. For each initial vibrational state, the cross section decreases at all considered energies as the rotational quantum number j_i increases. This trend, as shown by the corresponding ICSs for $j_i = 1$, 3, 5, and 7 at $E_{tot} = 0.7661$ eV given in Table 1, is not consistent with the prediction of a statistical model.

To examine the energy dependence, we plot in Figure 2 the DCSs for the H + $O_2(j_i = 1, \upsilon_i = 3)$ reaction at several energies. It can be seen that although the forward−backward bias in the DCS is maintained in all four energies, the precise shape of the angular distribution is a sensitive function of the energy. The ICSs, which are 0.012083, 0.037555, 0.056655, and 0.084680 Å^2, increase monotonically with energy.

The TIQM method used in calculating the DCSs becomes prohibitively expensive at higher energies because of its steep scaling laws with respect to the dimensionality. To calculate the ICS over a large energy range, we took advantage of a wave packet approach based on Chebyshev propagation, which is equivalent to time propagation[32] and has been applied previously

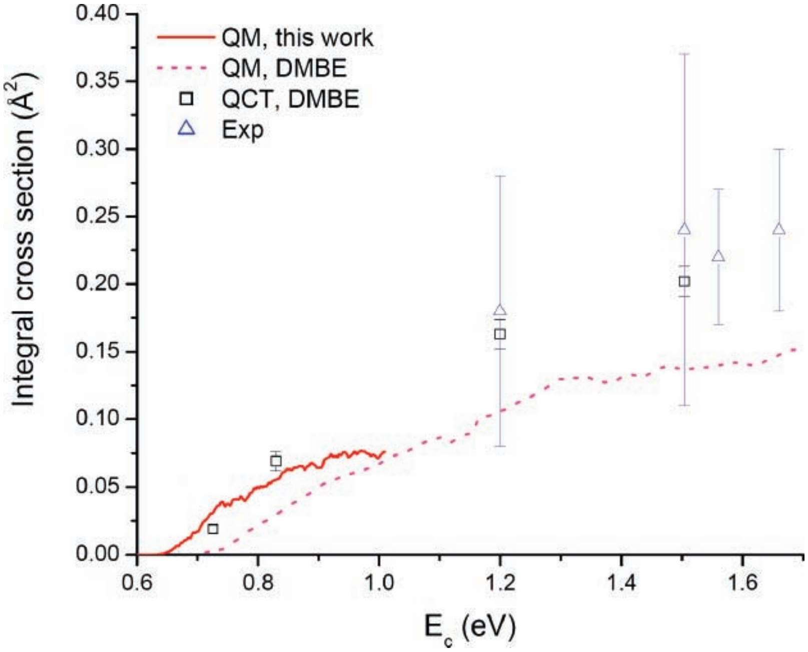

Figure 3. Comparison of integral cross sections for the H + $O_2(v_i = 0, j_i = 1) \rightarrow$ OH + O reaction obtained from various theoretical calculations and from experiment.

in insertion reactions.[33,34] In this TDQM method, an initial state-specified wave packet was propagated with a three-term recursion formula. The total reaction probability was computed near the exit of the product channel using a flux method[35] The Coriolis-coupled Hamiltonian was discretized with a mixed pointwise and functional basis in the reactant Jacobi coordinates, which allows the adaptation of the O−O exchange symmetry. Since the major arithmetic operations involve matrix−vector multiplications, the scaling laws of the TDQM method are much more favorable. In addition, a single propagation yielded the reaction probability in the entire energy range.

The energy dependence of the initial state ($v_i = 0$, $j_i = 1$)-specified ICS is shown in Figure 3 up to 1.0 eV of collision energy. This was achieved by including all partial waves with $J_{max} = 50$. The ICS shows a threshold near 0.65 eV and increases nearly monotonically with the collision energy, reaching approximately 0.072 Å^2 at $E_c = 1.0$ eV. Due to the absence of a barrier, the ICS has contributions from nearly all partial waves. In the same figure, the ICS is compared with those obtained on the DMBE PES using both TDQM[19] and QCT methods[5] and with those from the experimental data.[17,18] It is apparent that the XXZLG PES has a smaller reaction threshold than the DMBE PES, but the energy dependence is quite similar. Although the newly calculated ICS does not yet reach the experimental energies, the level of its agreement with the experimental data can be expected from extrapolation to be similar to that on the DMBE PES. Calculations with larger J values are ongoing in our group. On the other hand, the ICS on the DMBE PES obtained from the QCT model is significantly higher than the corresponding QM values, despite an ad hoc correction of the zero-point energy of the OH product.[5] Hence, its agreement with the experimental data, which are also displayed in the same figure, is probably superficial.

The initial state ($v_i = 0$, $j_i = 1$)-specific rate constant (not shown here) computed from the corresponding ICS is roughly 1 order of magnitude smaller than the recommended experimental values. The discrepancy might be due to the absence of the contributions from the vibrationally excited O_2 reactant. This assertion is supported by the cross sections shown in Figure 1, which indicate that the vibrational enhancement of the reactivity is very substantial. It might also stem from other factors, including the nonadiabatic couplings between low-lying electronic states.

In summary, we report here an elaborate quantum mechanical investigation of the dynamics of a key combustion reaction on an accurate ab initio PES. The DCSs just above the reaction threshold confirm the dominance of a complex-forming mechanism but suggest significant nonstatistical behaviors. The ICS was found to be small, but it increases monotonically with the collision energy above the threshold. In addition, the reactivity is substantially enhanced by vibrational excitation of the O_2 reactant and also effected by rotational excitation. Again, that suggests deviation from the pure statistical limit. Although much more work needs to be done, the results reported here represent an important step toward full state-resolved characterization of the dynamics of this important elementary reaction.

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