A theoretical approach to the $O(1^D) + H_2O(X^1A_I)$ reaction: \textit{Ab initio} potential energy surface and quasiclassical trajectory dynamics study

R. Sayós,\textsuperscript{a)} Carolina Oliva, and Miguel González\textsuperscript{a)}

Departament de Química Física i Centre de Recerca en Química Teòrica, Universitat de Barcelona, Martí i Franqués, 1, 08028 Barcelona, Spain

(Received 3 April 2000; accepted 31 July 2000)

An \textit{ab initio} study of the ground potential energy surface (PES) of the $O(1^D) + H_2O$ system has been performed, employing Møller–Plesset methods. From the stationary and additional points calculated, the ground PES has been modeled as a triatomic system, with an OH group of the $H_2O$ molecule treated as a single atom of 17.0 amu. The rate constant of reaction (1), $O(1^D) + H_2O \rightarrow 2OH$ (main reaction channel), estimated from the quasiclassical trajectory (QCT) calculations is reasonably close to the recommended experimental value. For the relative translational energies explored ($E_T = 0.234, 0.303,$ and $0.443$ eV) and $H_2O$ at $T = 300$ K, the QCT OH vibrational populations are in good agreement with the experimental values reported for the new OH fragment, but the QCT OH average rotational energies are in general quite larger than the experimental ones. Regarding the stereodynamics, for $E_T = 0.234$ eV there is not a clear tendency to a particular rotational alignment of the OH product with respect to the initial relative velocity vector, in agreement with experiments. The QCT results also show that nearly all reactive trajectories leading to reaction (1) take place through an insertion microscopic mechanism, which, even at the highest $E_T$ value considered (0.443 eV), is mainly (70\%) a nondirect one. The collision complex has an average lifetime of about three rotational periods and a geometry around that of the HO(OH) hydrogen peroxide molecule. The QCT results concerning the microscopic mechanism of reaction (1) are in agreement with the suggested ones by the experimentalists to interpret their results. The present study should be considered as a starting point in the study of reaction (1) from which different aspects on the dynamics may be learned. © 2000 American Institute of Physics.

I. INTRODUCTION

The reactivity of the oxygen atom in the first excited electronic state, $O(1^D)$, is important in various fields of chemistry, and its reaction with water is relevant in stratospheric chemistry in the context of ozone degradation processes through the OH/HO\textsubscript{2} catalytic cycle.\textsuperscript{1,2} The highly different reactive behavior of $O(1^D)$ with respect to the ground-state oxygen atom, $O(3\textsubscript{P})$, also makes the study of this kind of systems very interesting from a more fundamental point of view, to understand the origin of the different reactivities observed. Thus, the $O(1^D)$ atom is claimed to react very efficiently with compounds containing X–H bonds (such as H–H, C–H, O–H, and N–H), mainly through an insertion mechanism, while the analogous reactions with $O(3\textsubscript{P})$ present activation energy and occur by an abstraction mechanism.

The aim of this work is to study theoretically the gas phase reactions involved in the $O(1^D) + H_2O$ system, considering the ground potential energy surface (PES)

\begin{equation}
O(1^D) + H_2O(X^1A_I) \rightarrow 2OH(X^2\Pi) \quad \Delta H^0_{OH} = -28.9 \text{ kcal mol}^{-1} \tag{1}
\end{equation}

\begin{equation}
\rightarrow H_2(X^1\Sigma^+_g) + O_2(a^1\Delta_g) \quad \Delta H^0_{OH} = -24.8 \text{ kcal mol}^{-1} \tag{2}
\end{equation}

\begin{equation}
\rightarrow H(2S) + HO_2(X^2A^\text{a}) \quad \Delta H^0_{OH} = 5.6 \text{ kcal mol}^{-1} \tag{3}
\end{equation}

Reaction (1) is known to be very fast, the thermal rate constant value approaching the gas kinetics value. The recommended rate constant value for reaction (1), $k(1)$, is $2.2(\pm 0.45, +0.57) \times 10^{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} over the temperature range 200–350 K.\textsuperscript{3} This result suggests that reaction (1) does not have activation energy, in contrast to what happens for the analogous reaction with $O(3\textsubscript{P})$, which has activation energy. At 298 K the $k(2)/k(1)$ ratio was found to be 0.01 (+0.005, −0.01),\textsuperscript{5} and there is no information available on reaction (3). Hence, reaction (1) clearly corresponds to the main reaction of the $O(1^D) + H_2O$ system, accounting for around 99\% of the reactivity at 298 K.

The nascent internal energy distribution of the OH radical has been measured in several experiments,\textsuperscript{6–17} mainly involving the $^{16}O(1^D) + H_2^{18}O \rightarrow ^{16}OH + ^{16}OH$ reaction to differentiate between the new and old OH bonds formed.
using the laser induced fluorescence (LIF) technique. The reaction with D₂O has also been studied in some cases. The O(1D) atom has been generated by photodissociation of either N₂O (λ = 193 or 212.8 nm) or O₂ (λ = 248 or 266 nm). Therefore, OH(X ²Π) rovibrational, spin–orbit, and lambda–doublet populations considering different O(1D) + H₂O collision energy distributions have been determined experimentally. For the 16OH molecule (new OH bond), vibrational populated levels up to v' = 2 have been observed. The vibrational and rotational distributions of the 18OH molecule (old OH bond) have also been measured.

The above-mentioned experimental results regarding the internal energy distributions of 16OH and 18OH and the information about the stereodynamics are better explained conditionally through a1A(C₁) or a1A''(C₃) PES. The C₁ symmetry is the most important one for theoretical studies on the dynamics of reactions that involve four or more atoms, but it will be seen at the end of this section that for this system most of the stationary points located on the ground PES have in general symmetries higher than C₁.

We have carried out an ab initio study of the ground PES (1A) using the GAUSSIAN 94 package of programs. The wave function associated with this system is mostly multireference for the ground PES. Thus, in most of the PES regions the system behaves as an open-shell singlet, and only for arrangements close to the geometry of the closed-shell minima min 1 and H₂O₂ (hydrogen peroxide) and for the saddle point that connects both minima the wave function is single referent. Hence, the most suitable ab initio methods to study this PES are those which are multireference, such as the second-order multiconfigurational perturbation theory (CASPT2) and multireference configuration interaction (MRCI) methods. But, although these ab initio methods are nowadays accessible for the characterization of PES stationary points, recent benchmark calculations with molecular correlated wave functions on simple triatomic reactions, such as F + H₂, O + H₂, and H + HCl have shown that only using very large wave functions and basis sets it is possible to achieve energy values close to the experimental data. This kind of high-level calculations are very expensive, especially when the characterization of a global PES involving a large number of electrons and atoms is desired. On the other hand, it has been shown that, under certain conditions, ab initio methods, such as the Möller–Plesset perturbational method, can reproduce quite satisfactorily the energetics of this kind of systems when the “broken symmetry” approach is considered. In this context, the elimination of the spin contamination of the wave function becomes a critical aspect, as the use of the broken symmetry approach leads to energy values which lie between the triplet and singlet ones. An efficient projection algorithm for the elimination of the spin contamination when Möller–Plesset perturbational methods are used is included in the GAUSSIAN 94 package. However, although the single-point energy obtained using
the broken symmetry approach can be corrected using this projection technique, the optimal geometries determined in this context are probably located between the singlet and the triplet ones.

Hence, we have selected as a suitable method of calculation the unrestricted second-order Møller–Plesset perturbation theory (UMP2) method using a large basis set [6-311G(3d2 f,3p2d) standard, 128 basis functions], and considering the frozen core (FC) approach (only valence electrons are correlated), UMP2(FC)/6-311G(3d2 f,3p2d) ab initio level hereafter, to characterize (geometry optimization and harmonic vibrational frequencies calculation) the stationary points of the ground PES. The energies of the stationary points and of the set of ab initio points required to obtain, as a first approximation, a triatomic analytical representation of the PES (Sec. II B) have been calculated at the spin-projected unrestricted fourth-order Møller–Plesset perturbation theory (PUMP4) method, using the same basis set as before but considering in this case the full electron (FU) approach (all electrons are correlated), PUMP4(FU)/6-311G(3d2 f,3p2d) ab initio level hereafter. The standard GAUSSIAN 94 option [MP4(SDTQ)] has been employed. The spin-projected method has been employed to eliminate large spin contaminations on the PES (0.00<<(2)2/h2<1.10). In summary, the strategy used in the calculation of the PES has been the following: (a) first, the stationary points of the PES (reactants, products, saddle points, H2O2, and other minimum) have been optimized at the UMP2(FC)/6-311G(3d2 f,3p2d) level; (b) second, the connections [minimum energy paths (MEP) and mostly intrinsic reaction coordinate (IRC) calculations] between these stationary points have been calculated at the UMP2(FC)/6-311G(2d2,2pd); (c) finally, the energy of each point previously calculated at the UMP2(FC) level has been computed using the PUMP4(FU)/6-311G(3d2 f,3p2d) ab initio method. In the next paragraphs the present ab initio results will be compared with experimental data and previous ab initio calculations.

The energetics of the system using different methods and basis sets is shown in Table I, considering the H2O2 hydrogen peroxide minimum and the three different product asymptotes. No significant differences appear when the 6-311G(2d,2pd) basis set is used instead of the larger 6-311G(3d2 f,3p2d) one. In fact, the methods selected here are the ones which best reproduce the exothermicity of the main reaction [reaction (1)] and predict the depth of the H2O2 minimum with 1% of deviation with respect to the experimental value. The results obtained for the geometries and harmonic frequencies of the H2O, OH2, O2(a1 Δg), and HO2 reactant and product molecules using these methods also show a good agreement with experimental information. The O(1D)–O(3P) and O2(a1 Δg)–O2(X1 Σg−) energy splittings have only been described adequately at the PUMP4 level.

In what follows, the reported data correspond to the highest level calculation [PUMP4(FU)/UMP2(FC)/6-311G(3d2 f,3p2d)], and the energies are given, including the zero-point energy (ZPE), with respect to reactants, unless otherwise indicated. The geometries [UMP2(FC)] of the stationary points placed between reactants and products are plotted in Fig. 1, and the energies [PUMP4(FU)/UMP2(FC)], including the UMP2(FC) zero-point energies (ZPE), are indicated in Fig. 2. In this figure the different reaction pathways for reactions (1)–(3) are also shown schematically, where “ts” and “min” refer to the saddle points and minima, respectively. In Table II the harmonic vibrational frequencies [UMP2(FC)] of the stationary points are reported.

Reaction (1) can take place along two possible reaction pathways. The first one [insertion microscopic mechanism (via H atom migration)] involves the formation of products when the system evolves from reactants through the H2O2 hydrogen peroxide minimum, according to the following way:

\[ O(1D) + H2O \rightarrow ts8 \rightarrow min1 \rightarrow ts9 \rightarrow H2O2 \rightarrow ts2 \rightarrow OH + OH. \]

The saddle point ts8 explains the formation of min1 from reactants, and the second one (ts9) the formation of H2O2 from min1. The saddle point ts2 allows one to connect the hydrogen peroxide with the hydroxyl products. The saddle points ts8 and ts2, however, have only been obtained.

### Table I. Energetics of the system using different methods and basis sets.

| Method | E + ZPE/kcal mol\(^{-1}\) | H2O2(X1 A\(^{1}\)) | 2 OH(X2 ΗII) | H2(X1 Σ\(^{+}\)g) + O2(a1 Δ\(_{g}\)) | H(2S) + H2O(X2 Σ\(^{+}\)g) |
|--------|------------------|---------------------|---------------------|---------------------|---------------------|
| UMP2(FC)/UMP2(FC)/6-311G(d,p) | −68.67 (−71.88) | −22.72 (−20.03) | −39.78 (−34.51) | 13.74 (18.23) |
| UMP2(FC)/UMP2(FC)/6-311G(2d,2pd) | −71.43 (−74.69) | −18.92 (−16.28) | −40.49 (−35.30) | 15.11 (19.56) |
| UMP2(FC)/UMP2(FC)/6-311G(3d2 f,3p2d) | −71.72 (−74.96) | −18.69 (−16.12) | −38.34 (−33.20) | 16.82 (21.25) |
| PUMP4(FU)/6-311G(d,p)//UMP2(FC)/6-311G(3d2 f,3p2d) | −72.40 (−75.63) | −29.48 (−26.91) | −31.83 (−26.69) | 9.28 (13.71) |
| PUMP4(FU)/6-311G(2d,2pd)//UMP2(FC)/6-311G(3d2 f,3p2d) | −76.38 (−79.61) | −27.36 (−24.79) | −31.53 (−26.39) | 9.48 (13.90) |
| PUMP4(FU)/UMP2(FC)/6-311G(3d2 f,3p2d) | −77.45 (−80.68) | −27.65 (−25.08) | −29.99 (−24.85) | 10.27 (14.70) |
| Experimental data | −78.3±0.1\(^c\) | −28.9±0.6\(^c\) | −24.8±0.1\(^c\) | 5.6±2.0\(^c\) |

\(^a\)Energy referred to reactants. The theoretical values in parentheses correspond to the energy without including the UMP2 ZPE.

\(^b\)Absolute values of energy (hartrees) for O(1D)+H2O as a sum of fragments are: −151.142 944 [UMP2(FC)/6-311G(d,p)]; −151.116 849 [UMP2(FC)/UMP2(FC)/6-311G(d,p)]; −151.218 893 [UMP2(FC)/6-311G(2d,2pd)]; −151.198 564 [UMP2(FC)/UMP2(FC)/6-311G(2d,2pd)]; −151.238 708 [UMP2(FC)/6-311G(3d2 f,3p2d)]; −151.219 137 [UMP2(FC)/UMP2(FC)/6-311G(3d2 f,3p2d)]; −151.262 176 [PUMP4(FU)/6-311G(d,p)//UMP2(FC)/6-311G(3d2 f,3p2d)]; −151.286 242 [PUMP4(FU)/UMP2(FC)/6-311G(3d2 f,3p2d)].

\(^c\)Reference (3, Δ\(_{h}\)E\(_{h}\)).
using the UMP2(FC) method and for all basis sets considered, i.e., 6-311G(d,p), 6-311G(2df,2pd), and 6-311G(3d2 f,3p2d). At the PUMP2(FC) level and for all basis sets [with the only exception of ts2 for the 6-311G(d,p) basis set] and at the highest level of the calculation, the PUMP4(FU)/UMP2(FC)/6-311G(3d2 f,3p2d) method, however, ts8 and ts2 become energetically below reactants and products, respectively. Because of this we have only considered in the fitting (Sec. II B) three stationary points between reactants and products for the insertion mechanism of reaction 1: min1, ts9, and H2O 2, all of them placed energetically below reactants (Fig. 2). Reaction 1 can also occur according to a second reaction pathway (abstraction microscopic mechanism). Thus, a saddle point (ts10) responsible for the abstraction of an H atom of the H2O molecule by the attacking O(1D) atom to give two OH radicals has been found. This saddle point leads to an energy barrier of 10.92 kcal mol$^{-1}$.

The absence of any energy barrier above reactants along the minimum energy path of reaction 1 predicted by the ab initio calculations is consistent with the nonexistence of an experimental activation energy.4 Thus, within the temperature range for which experimental data are available ($T = 200–350$ K), the rate constant is independent of the
temperature. The ab initio equilibrium geometry of the H$_2$O$_2$ hydrogen peroxide is very close to the experimental one \[R(\text{OO})=1.4556 \text{ Å}, \quad R(\text{OH})=0.967 \text{ Å}, \quad \angle(\text{OOH})=102.32^\circ, \quad \text{and} \quad \angle(\text{HOOH})=113.70^\circ\].\(^{27}\) The agreement with experiments is good and very good in the case of the harmonic frequencies (Table II) and energy (Table I), respectively. The isomerization of H$_2$O$_2$ through ts9 to give min1 was previously described in the context of a CCSD(T) ab initio study \[\text{[coupled-cluster approach including single and double excitations (CCSD) with connected triple excitations]}.\(^{19}\) In that work the TZ2P+f and DZP basis sets were used for geometry optimizations and harmonic frequency calculations. But, for the harmonic frequency calculations of ts9 and H$_2$O$_2$ the CCSD method was used instead of the CCSD(T) one. The geometries and harmonic frequencies of min1, ts9, and H$_2$O$_2$ reported here are quite similar to those given in Ref. 19. The barrier for isomerization from min1 to H$_2$O$_2$ obtained here (2.83 kcal mol$^{-1}$) is also quite close to that reported in Ref. 19 (3.2 kcal mol$^{-1}$). A saddle point similar to ts2 has been reported previously at the MRCI-SD level \[\text{[multireference, single, and doubles, configuration interaction (CI) calculation]}.\(^{21}\) where the main differences are the $\angle(\text{HOOH})$ dihedral angle (143$^\circ$ \(21\) vs 180.0$^\circ$ in our case) and the $\angle(\text{OOH})$ angle (59$^\circ$ \(21\) vs 78.5$^\circ$ in our case).

For reaction (2) only a stationary point (ts11) with two imaginary frequencies that connects min1 with the H$_2$+O$_2$($a^1\Delta_g$) products has been found. The difficulties to determine the true saddle point that allows one to connect with products of reaction (2) are probably due to the fact that in this case to evolve from reactants to products two bonds should be formed and two bonds should be removed. This should also involve a significant energy barrier with respect to reactants. The energy barrier associated to the second-order saddle point ts11 (28.3 kcal mol$^{-1}$) is consistent with this fact, although, of course, the energy barrier corresponding to the true saddle point must be lower than this value. A saddle point (ts3) which connects these products with the ones of reaction (3) (H+H$_2$O$_2$), with an energy of 12.52 kcal mol$^{-1}$ (2.25 kcal mol$^{-1}$ above H+H$_2$O$_2$) has also been obtained. The production of H$_2$+O$_2$($a^1\Delta_g$) has not been considered in the fitting (Sec. II B), because it is not possible according to the proposed triatomic model (an OH group of the H$_2$O molecule has been taken as a pseudatom). In fact, while a triatomic model can be used in a QCT study to describe the dynamics of formation of the new OH bond arising from reaction (1), a tetrameric analytical fitting is required to account for the dynamics of reaction (2). Moreover, while it would be possible to compare the dynamics of reaction (1) resulting from triatomic and tetrameric descriptions of the system (that, of course, may be based on the same set of ab initio calculations), this would not be the case for reaction (2).

The production of atomic hydrogen and hydroperoxy radical [reaction (3)], as in the case of reaction (1), can also take place along two possible reaction pathways. The first one \[\text{[insertion microscopic mechanism (via H atom migration)]}, \] analogous to that for reaction (1), involves the formation of products when the reactants evolve through the H$_2$O$_2$ hydrogen peroxide minimum \[\text{[O(1D)+H}_2\text{O} \rightarrow \text{ts8} \rightarrow \text{min1} \rightarrow \text{ts9} \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{ts1} \rightarrow \text{H}+\text{H}_2\text{O}].\] Thus, this reaction path coincides with the corresponding one for reaction (1) until the formation of H$_2$O$_2$. The saddle point ts1 has only been found at the lowest level calculation \[\text{[UMP2(FC)/6-311G(d,p)]}.\] Thus, the connection between the hydrogen peroxide and products probably take place without the presence of any barrier. Reaction (3) can also occur according to a second pathway (substitution microscopic mechanism). Hence, in this case reaction (3) differs from reaction (1). Thus, a saddle point (ts7) responsible for the evolution from min1 to the
hydroperoxy radical has been found with an energy of 15.67 kcal mol\(^{-1}\).

In Fig. 2 are also included other saddle points (ts4 and ts5) which are associated with the internal rotation of the hydrogen peroxide molecule; ts4 has a dihedral angle of 0° (cis arrangement) and ts5 has a dihedral angle of 180° (trans arrangement). The saddle point ts4 has a larger energy than ts5 because two different repulsive interactions are possible in the cis geometry: one between the oxygen lone pair electrons and the other one between the OH bond dipole moments. In the trans geometry (ts5) only the first repulsive interaction is possible. The calculated barriers for the internal rotation of H\(_2\)O\(_2\) are 7.38 kcal mol\(^{-1}\) (cis) and 1.23 kcal mol\(^{-1}\) (trans), both without including the ZPE. These values compare very well with the experimental data: 7.11 kcal mol\(^{-1}\) (cis) and 1.10 kcal mol\(^{-1}\) (trans);\(^{33}\) 7.33 kcal mol\(^{-1}\) (cis) and 1.11 kcal mol\(^{-1}\) (trans).\(^{34}\)

The saddle point (ts6) of the exchange process of the two hydrogen atoms between the two hydroxyl radicals (ts6) has also been located; it is a quite symmetric (C\(_{2v}\)) and energetic saddle point (Fig. 2).

Similar stationary points to those described above for the O\(^{(1)}\)D + H\(_2\)O ground PES have been found at the UMP2(FU)/6-31G(d,p) level for the related O\(^{(1)}\)D + H\(_2\)S system.\(^{35}\) However, at this point it is worth noting that, as indicated at the beginning of this section, the UMP2 geometries of open-shell singlet stationary points, due to spin contamination, are probably located between the singlet and triplet ones. In the O\(^{(1)}\)D + H\(_2\)O system, with the exception of min1, ts9, H\(_2\)O\(_2\), ts4, and ts5, which have closed-shell character \((\langle S^2 \rangle / \langle \hat{S}^2 \rangle = 0.00\)), the stationary points placed between reactants and products have open-shell character \((\langle S^2 \rangle / \langle \hat{S}^2 \rangle = 0.8 - 1.0\)), this fact being a bit more evident for ts10. From preliminary complete active space self-consistent field (CASSCF) calculations that are in progress in our group, it turns out that the structures reported in the present work are quite similar to the CASSCF ones, with the only exception being what happens for ts10. Thus, at the CASSCF level this stationary point is closer (in geometry and energy) to reactants than in the case of the UMP2 level.

### B. Analytical potential energy surface

A tritomatic model, where an OH fragment of the H\(_2\)O molecule has been treated as a single atom (OH) of 17 amu placed in its center of mass, has been considered to obtain an analytical representation of the ground PES. This model has been suggested from the experimental data, which clearly show that most of the internal energy excitation is channeled towards the OH molecule arising from the new OH bond. This kind of modeling has been previously used in our group in the case of the O\(^{(1)}\)D + CH\(_4\) and O\(^{(3)}\)P + CH\(_4\) reactions with quite good results.

The same type of analytical expression (many-body expansion\(^{39,40}\) and programs\(^{39,46}\) used in previous works of our group [e.g., N\(^{(1)}\)S + NO,\(^{41}\) O\(^{(2)}\)P + CS,\(^{42}\) H\(^{(2)}\)S + Cl\(_2\), and Cl\(^{(2)}\)P + HCl,\(^{43}\) N\(^{(4)}\)S + O\(_2\),\(^{44}\) H + Cl,\(_2\), and F + HCl,\(^{45}\) O\(^{(1)}\)D + CH\(_4\) (tritomatic model),\(^{36}\) and O\(^{(3)}\)P + CH\(_4\) (tritomatic model)\(^{37}\)] have also been employed here. According to this approach, for the present system the analytical PES can be represented as follows:

\[
V(R_1, R_2, R_3) = V_1^{(1)}(R_1, R_2, R_3) + V_2^{(1)}(R_1, R_2, R_3),
\]

where \(V_1^{(2)}\) and \(V_1^{(3)}\) are the two-body and three-body terms, respectively, and \(R_1, R_2, R_3\) are the O–H, H–(OH), and O–(OH) distances, respectively.

---

**TABLE II. Harmonic vibrational frequencies (in cm\(^{-1}\)) of the stationary points at the UMP2(FC)/6-311G(3d2 f,3p2d2) level.**

| Mode | \(v_1\) | \(v_2\) | \(v_3\) | \(v_4\) | \(v_5\) | \(v_6\) |
|------|--------|--------|--------|--------|--------|--------|
| \(C_{1s}^{\pm}\) | 3740.1 (A) | 3850.0 (B) | 1576.9 (A\(^{+}\)) | 3870.7 (A\(^{+}\)) | 3873.9 (B\(^{+}\)) | 2411.7 (A\(^{+}\)) |
| \(C_{2s}^{\pm}\) | 1455.6 (A) | 3693.4 (A) | 1506.6 (A\(^{+}\)) | 3829.9 (B\(^{+}\)) | 3867.6 (A\(^{+}\)) | 1471.0 (B\(^{+}\)) |
| \(C_{3s}^{\pm}\) | 1215.3 (A) | 504.5 (A) | 1400.7 (B\(^{+}\)) | 1449.8 (B\(^{+}\)) | 1532.2 (B\(^{+}\)) | 1211.4 (B\(^{+}\)) |
| \(C_{4s}^{\pm}\) | 301.6 (A) | 419.4 (B) | 854.9 (A\(^{+}\)) | 1360.0 (A\(^{+}\)) | 1248.3 (B\(^{+}\)) | 815.7 (B\(^{+}\)) |
| \(C_{5s}^{\pm}\) | 287.6 (A) | 262.6 (A) | 441.8 (A\(^{+}\)) | 929.6 (A\(^{+}\)) | 937.3 (A\(^{+}\)) | 760.0 (A\(^{+}\)) |
| \(C_{6s}^{\pm}\) | 356.9i (A) | 323.7i (A) | 3213.7i (A\(^{+}\)) | 596.5i (A\(^{+}\)) | 3213.7i (A\(^{+}\)) | 2337.7i (B\(^{+}\)) |

**Note:**

- \(^{a}\) UMP2(FC)/6-311G(d,p) level.
- \(^{b}\) From higher to lower frequencies we have \((ab \text{ ~initio ordering})\): OH sym. stretching, OH antisym. stretching, OOH sym. bending, OOH antisym. bending, OO stretching, and torsion.
- \(^{c}\) Reference 28.
- \(^{d}\) Reference 29.
- \(^{e}\) Reference 30.
- \(^{f}\) Reference 31.
- \(^{g}\) Reference 32.
The three asymptotic channels of the ground PES which can be described by the triradical model \( \text{O}(^3D) + \text{H}_2 \text{O}, \text{OH} + \text{OH}, \) and \( \text{H} + \text{HO}_2, \) involved in reactions (1) and (3) do not correlate with the same electronic state of the oxygen atom. Thus, reactants correlate with the first excited state of the \( \text{O} \) atom \( \text{O}(^1D) \), while the products of reactions (1) and (3) correlate with the ground state of the \( \text{O} \) atom \( \text{O}(^3P) \). Because of this, a modified form of the usual many-body equation (4), including a monoatomic term \( V^{(1)} \) with a switching function should be used.36 Although this is quite a well known fact, it was not indicated accurately enough in the text. Of course, this improvement does not affect the contents of the paper at all. Nevertheless, this modification can be avoided if in the fitting of the two-body terms (diatomic potential energy curves) the dissociation limits of those molecules that correlate with \( \text{O}(^3P) \) are modified so as to reproduce “artificial” dissociation limits leading to \( \text{O}(^1D) \). This approximation only changes the high energy part of the diatomic curve, and the low and moderate energy regions explored in most usual dynamical calculations remain almost unaltered. Hence, analogously as it was done previously by our group in the case of the \( \text{O}(^1D) + \text{CH}_4 \) reaction,36 here we have used modified dissociation energy values for the \( \text{OH} \) and \( \text{O(OH)} \) molecules by summing up the \( \text{O}(^1D) - \text{O}(^3P) \) energy difference to the corresponding values describing the dissociation up to \( \text{O}(^3P) \).

The diatomic potential energy curves have been fitted using the extended-Rydberg potential up to third order

\[
V^{(2)}(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)e^{-a_1\rho},
\]

where \( D_e \) and \( R_e \) are the dissociation energy [altered for \( \text{OH} \) and \( \text{O(OH)} \) as it was stated above] and equilibrium bond length of the corresponding diatomic or pseudodiatomic molecule, respectively, and \( \rho \) is defined as being equal to \( R - R_e \). The optimal \( \{a_i\} \) diatomic parameters have been obtained for each molecule using a nonlinear least-squares procedure,39 by fitting a set of diatomic or pseudodiatomic \textit{ab initio} points calculated around the equilibrium distance [PUMP4(FU)/UMP2(FC) level]. For the \( \text{X} - \text{(OH)} \) molecules (\( \text{X} = \text{H}, \text{O} \)) the \( \text{OH} \) \textit{ab initio} geometry was optimized in all points of the \( \text{X} - \text{(OH)} \) pseudodiatomic curve. The extended-Rydberg function provides a very good fitting of the curves in all cases. The optimal diatomic parameters of the \( \text{OH}, \text{H(OH)}, \) and \( \text{O(OH)} \) molecules are shown in Table III, and the spectroscopic constants derived from them are given in Table IV.

The three-body term consists of a third-order polynomial, \( P(\rho_1, \rho_2, \rho_3) \), multiplied by a range function, \( T(\rho_1, \rho_2, \rho_3) \). The polynomial is expressed in terms of three internal coordinates \( (\rho_1, \rho_2, \rho_3) \), defined as \( \rho_i = R_i - R_e^i \), where the selected reference structure \( (R^1, R^2, R^3) \) corresponds to the average pseudotriatomic structure resulting from the two minima of the PES placed between reactants and products (\( \text{min1} \) and \( \text{H}_2 \text{O}_2 \)). The range function cancels the three-body term as one of the three atoms is separated from the other two. Thus, we have

\[
V^{(3)}_{\text{OH(OH)}}(\rho_1, \rho_2, \rho_3) = P(\rho_1, \rho_2, \rho_3)T(\rho_1, \rho_2, \rho_3),
\]

where

\[
P(\rho_1, \rho_2, \rho_3) = \sum_{i,j,k=0}^{0\leq i+j+k\leq 3} c_{ijk}\rho_i^j\rho_j^k,
\]

with \( i, j, k \) being positive integer numbers, and

\[
T(\rho_1, \rho_2, \rho_3) = \prod_{i=1}^{3} \left[ 1 - \tanh \left( \frac{\gamma_i \rho_i}{2} \right) \right].
\]

The 20 linear parameters \( (c_{ijk}) \) (polynomial coefficients) and three nonlinear ones \( \{\gamma_i\} \) (range function parameters) of the three-body term have been determined by a weighted nonlinear least-squares procedure,40 taking into account the three \textit{ab initio} saddle points (ts7, ts9, and ts10), the two minima (\( \text{min1} \) and \( \text{H}_2 \text{O}_2 \)), and 113 additional points corresponding to the connections between the different stationary points of the ground \( ^1\text{A} \) PES: \( \text{O}(^1D) + \text{H(OH)} \rightarrow \text{OH} + \text{(OH)} \) (abstraction) (24 points); \( \text{O}(^1D) + \text{H(OH)} \rightarrow \text{H} + \text{(OH)} \) (sub-

### Table III. Optimal parameters of the analytical triatomic PES1 and PES2.

| Two-body terms: | \( a_i / \text{Å}^{-1} \) | \( a_i / \text{Å}^{-2} \) | \( a_i / \text{Å}^{-3} \) |
|-----------------|-----------------|-----------------|-----------------|
| \( \text{O-H} \) | 3.803 70 | 3.638 38 | 3.893 20 |
| \( \text{H-(OH)} \) | 4.693 62 | 6.154 12 | 5.645 13 |
| \( \text{O-(OH)} \) | 3.439 69 | 1.009 98 | 4.689 48 |

| Three-body terms: | PES1 | PES2 | PES1 | PES2 | PES1 | PES2 |
|-------------------|------|------|------|------|------|------|
| \( c_{000} \) | 5.417 90 | 5.247 91 | 0.230 83 | 0.420 50 | 0.988 58 | 1.281 67 |
| \( c_{100} \) | 0.023 52 | 0.096 16 | -0.740 06 | -0.542 62 | 2.367 14 | 1.979 54 |
| \( c_{010} \) | 0.045 64 | -0.389 97 | -0.667 44 | -0.320 26 | 2.166 89 | 1.863 44 |
| \( c_{001} \) | 1.035 84 | 0.627 87 | -0.696 16 | 1.206 22 | |
| \( c_{200} \) | 0.059 73 | 0.138 72 | 3.145 47 | 2.757 27 | |
| \( c_{110} \) | 0.876 22 | 0.526 08 | -0.131 92 | -0.277 85 | 1.442 7 |
| \( c_{101} \) | 1.003 94 | 0.756 06 | 1.074 24 | 1.425 37 | |
| \( c_{201} \) | 0.591 53 | 0.179 15 | -0.528 41 | -0.210 71 | 1.435 0 |
| \( c_{020} \) | 1.443 97 | 0.867 75 | -0.391 98 | -0.709 69 | |
| \( c_{300} \) | 2.541 23 | 1.819 13 | -0.490 54 | -0.422 84 | 1.479 1 |

\( a \) and \( \Omega \) are defined as being equal to \( 3 \) and \( \text{O} \), respectively, and \( \ell \) is defined as being equal to \( R - R_e \).
TABLE IV. Spectroscopic constants of the diatomic and pseudodiatomic molecules.

| Species | $D_e$/eV | $R_e$/Å | $v_e$/cm$^{-1}$ | $v_{x,e}$/cm$^{-1}$ | $B_e$/cm$^{-1}$ | $\alpha_e$/cm$^{-1}$ |
|---------|----------|---------|----------------|------------------|----------------|------------------|
| O–H    |          |         |                |                  |                |                  |
| Analytical fit | 6.7233 | 0.9666 | 3723.8 | 73.16 | 19.03 | 0.7337 |
| Experimental | 6.587 | 0.9696 | 3737.76 | 84.88 | 18.91 | 0.7242 |
| H–(OH) |          |         |                |                  |                |                  |
| Analytical fit | 5.4399 | 0.9721 | 3887.7 | 71.29 | 18.75 | 0.6755 |
| Experimental | 5.443 | 0.9736 |                  |                  |                |                  |
| O–(OH) |          |         |                |                  |                |                  |
| Analytical fit | 4.9602 | 1.3232 | 1267.0 | 17.52 | 1.168 | 0.0193 |
| Experimental | 5.000 | 1.3458 |                  |                  |                |                  |

ركاب (42 نقطة); $O(1D) + H(OH) \rightarrow HO(OH)$ (طيف أكسيد النيتروجين) ($H(OH) + O(H)$ ($FH$ (آلة)), $H + O(OH)$ (الанизومان الميكانيكي) (47 نقطة). في التدريب، تم استخدام نقاط سطوع وبالنسبة ل落ちة الدعاية والصانعة من نواة السطوع مع ترسب من $R_{OH}$ و$R_{H(OH)}$ وقطع $<(OH(OH))$ (النقطة). النقطة المثالية للمساحة الثلاثية (PES1) وPES2 (42 نقطة) في طياء $\text{ab initio}$. يوجد الجودة التامة للمساحة التلقائية (PES1) وPES2 (42 نقطة). في PES2 0.0944 eV (2.18 kcal mol$^{-1}$) لل نقطة. جميع بالميزانية PES1 وPES2 يمكن اعتبارها كمثالية للفضاء PES. يصبح للمساحة PES1 وPES2

TABLE V. Properties of the fitted stationary points for the analytical triatomic PES1 and PES2.

| Stationary point | $R_{O-\cdots OH}$/Å | $R_{O-H}$/Å | $R_{H-\cdots OH}$/Å | $\angle O-(\cdots OH)-H$/° | $\angle O-(\cdots OH)/°$ | $E$/kcal mol$^{-1}$ | $E+$ZPE/kcal mol$^{-1}$ | $v_e$/cm$^{-1}$ |
|-----------------|---------------------|--------------|----------------------|--------------------------|--------------------------|-----------------|------------------------|----------------|
| $ts7$ ($C_s$)   |                     |              |                      |                          |                          |                 |                        |              |
| ab initio       | 1.3153              | 2.3620       | 1.1415               | 119.78                   | 28.90                    | 17.57           | 15.67                  |              |
| PES1            | 1.2793              | 2.8942       | 2.2135               | 108.96                   | 24.71                    | 12.03           | 9.11                   | 398.51, 362.8, 1483.5 |
| PES2            | 1.3167              | 3.9480       | 3.2200               | 114.26                   | 17.70                    | 11.16           | 7.55                   | 92.91, 98.5, 1266.1 |
| $ts9$ ($C_s$)   |                     |              |                      |                          |                          |                 |                        |              |
| ab initio       | 1.5602              | 1.4118       | 1.0334               | 62.47                    | 77.20                    | -24.95          | -23.92                  |              |
| PES1            | 1.4911              | 1.5054       | 1.0940               | 69.29                    | 67.89                    | -27.20          | -27.32                  | 1225.71, 2874.8, 932.2 |
| PES2            | 1.5085              | 1.4857       | 1.1029               | 67.29                    | 69.49                    | -26.14          | -27.00                  | 1476.41, 2458.1, 832.5 |
| $ts10$ ($C_{os}$) |                     |              |                      |                          |                          |                 |                        |              |
| ab initio       | 2.7128              | 1.4381       | 1.3512               | 13.89                    | 153.08                   | 14.21           | 10.92                  |              |
| PES1            | 2.5554              | 1.4668       | 1.0886               | 0.00                     | 180.00                   | 2.44            | 0.74                   | 1151.81, 1065.2(2), 569.1 |
| PES2            | 2.5850              | 1.4630       | 1.1220               | 0.00                     | 180.00                   | 4.09            | 1.71                   | 1587.81, 861.1(2), 499.3 |
| $min1$ ($C_s$)  |                     |              |                      |                          |                          |                 |                        |              |
| ab initio       | 1.5009              | 1.9254       | 0.9827               | 99.54                    | 50.24                    | -30.08          | -26.75                  |              |
| PES1            | 1.5944              | 1.9358       | 0.8936               | 95.72                    | 54.61                    | -33.22          | -30.02                  | 4442.3, 976.04, 707.9 |
| PES2            | 1.5722              | 1.8587       | 0.8902               | 92.71                    | 57.56                    | -33.73          | -30.70                  | 4177.5, 1035.3, 798.1 |
| $H_2O(C_s)^{a}$ |                     |              |                      |                          |                          |                 |                        |              |
| ab initio       | 1.4573              | 0.9600       | 1.8872               | 30.00                    | 49.37                    | -80.68          | -77.45                  |              |
| PES1            | 1.4465              | 0.9502       | 1.8839               | 29.61                    | 48.77                    | -80.85          | -78.16                  | 3834.4, 1059.6, 874.4 |
| PES2            | 1.4646              | 0.9595       | 1.7888               | 32.40                    | 54.87                    | -81.82          | -78.65                  | 3678.1, 1556.7, 871.2 |

$^a$Energy referred to reactants.
$^b$For each stationary point the ab initio triatomic symmetry point group is indicated.
$^c$The H–O–(OH) angle for $H_2O$: 100, 101, 62, and 92.73 for ab initio, PES1, and PES2, respectively.
seen in Sec. III, in spite of the low energy barrier that ts10 presents in both analytical PES considered, at the moderate collision energies considered in this work nearly all reactive trajectories evolve through geometrical arrangements close to that of the HO(OH) hydrogen peroxide minimum. This means that the dominant microscopic mechanism clearly corresponds to the insertion process, the abstraction process through the saddle point ts10 playing a minor role.

III. QCT DYNAMICS CALCULATIONS

To study the dynamics of reaction (1) the QCT method\(^{50–52}\) has been applied as implemented in the TRIQCT program,\(^{53}\) considering the PES1 and PES2 tratomic analytical representations of the ground \(^1\)A PES. The accuracy of the numerical integration of Hamilton’s differential equations has been verified by checking the conservation of total energy and angular momentum along every trajectory, and performing back integrations on some batches of trajectories. An integration step of \(2.5 \times 10^{-17} \text{s}\) and an initial distance of 10 Å between the O(1\(^D\)) atom and the H–(OH) center of mass have been selected. At this separation the reactants interaction energy can be neglected with respect to the reactants available energy.

The QCT dynamics study has been mainly focused on the calculation of the rovibrational distributions of the OH product from reaction (1) and the corresponding microscopic reaction mechanism, although other properties have also been considered (rate constant and rotational alignment). The reported experimental OH rovibrational distributions arising from reaction (1) correspond to several reaction conditions, concerning mostly the identity of the O(1\(^D\)) precursor and the wavelength used in its photodissociation. The different conditions yield, in turn, different relative translational energy (collision energy) distributions for O(1\(^D\)) + H\(_2\)O. In the QCT calculations three different relative translational energies (\(E_T\)) for the O(1\(^D\)) + H\(_2\)O system have been explored: (a) \(E_T = 0.443 \text{eV (}\langle E_T \rangle\text{ from N}_2\text{O photodissociation at 193 nm)}\); (b) \(E_T = 0.303 \text{eV (}\langle E_T \rangle\text{ from O}_2\text{ photodissociation at 248 nm)}\); (c) \(E_T = 0.234 \text{eV (}\langle E_T \rangle\text{ from O}_3\text{ photodissociation at 266 nm)}\). In these calculations the rovibrational distribution of the H–(OH) pseudodiatom molecule has been sampled from a Maxwell–Boltzmann distribution at 300 K. Both the collision energy and the H–(OH) rovibrational levels have been sampled from Maxwell–Boltzmann distributions at 300 K in the rate constant calculation of reaction (1). For each initial condition around 10,000 trajectories have been run.

A. Rate constant and rovibrational distributions

The QCT reaction cross section (\(\sigma\)) of O(1\(^D\)) + H–(OH)(300 K) – OH+(OH) has been calculated at the three \(E_T\) values explored for the two tratomic analytical PES derived. \(\sigma\) decreases with \(E_T\), as it corresponds for a barrierless reaction (e.g., for PES1 \(\sigma = 26.4, 21.2, \) and 16.0 Å\(^2\) for \(E_T = 0.234, 0.303,\) and 0.443 eV, respectively). This behavior is due to the decrease of the maximum impact parameter (\(b_{\text{max}}\)) with \(E_T\), the reaction probability being almost constant (around 50%). A large amount of energy is released as OH internal energy, appearing in very similar energy amounts as vibration and rotation. For PES1 at 0.303 eV, the average fraction of energy appearing in products as relative translation (\(\langle f_T^p \rangle\)), vibration (\(\langle f_V^p \rangle\)), and rotation (\(\langle f_R^p \rangle\)) is equal to 0.29, 0.34, and 0.38, respectively.

The QCT rate constant of reaction (1) at 300 K has been estimated from the rate constant obtained for the ground PES (\(^1\)A’ in \(C_z\)) by dividing its value by five, as there are five degenerated PES in the reactants region (four of them correlating with products). Hence, in the absence of additional information on the excited PES of the O(1\(^D\)) + H\(_2\)O system, we are assuming that the reactivity is dominated by the ground PES. The rate constant of reaction (1) estimated from the QCT calculations is reasonably close to the recommended experimental value, \(2.2 \times (0.45, +0.57) 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\), in the case of PES1 [(1.32 ± 0.01) 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}] while it is considerably lower in the case of PES2 [(0.51 ± 0.01) 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}]]. Contributions of the excited PES [especially the first \(^1\)A*(\(C_y\))] would tend to increase the calculated rate constant and a better agreement with the experimental value could be expected.

The QCT OH rovibrational distributions and average rotational energies, corresponding to the new OH bond formed, obtained for the above-mentioned \(E_T\) values [H–(OH) molecule at 300 K] together with the experimental data available are given in Table VI. From the QCT results it turns out that OH vibrational levels up to \(v' = 4\) are populated, and the vibrational populations decrease with \(v'\) [e.g., for PES1 at \(E_T = 0.303 \text{eV}\), \(P(v' = 0):P(v' = 1):P(v' = 2):P(v' = 3):P(v' = 4) = 1.00:0.65:0.34:0.16:0.01\]]. The average rotational energy of each OH vibrational level increases with \(E_T\), and the OH rotational energy content decreases with the OH vibrational energy, as expected. Overall, the QCT vibrational populations for \(v' = 0–2\) are in good agreement with the experimental values reported for the OH which corresponds to the new OH bond formed.\(^{6,7,10,11,15}\) which is substantially more excited than that associated with the old one. For \(v' = 3\) and 4, however, there is no experimental information available. The QCT OH average rotational energies obtained are in general much larger than the experimental ones for the new OH bond.\(^{6,7,10,11,15}\)

B. Two-vector properties and microscopic reaction mechanism

An \(I\rightarrow I'\) angular momentum transformation has been found, with \(I(I')\) being the reactants (products) orbital angular momentum. This is what can be expected for a reaction with \(H–L–H\) (heavy–light–heavy) kinematics. In what respects the two-vector properties, the angular distribution (reactive trajectories vs scattering angle) is very broad and presents a somewhat larger tendency towards forward scattering, the forward/backward (f/b) ratio being higher than unity in all cases. The f/b ratio increases with \(E_T\) (e.g., for PES1 f/b = 1.09, 1.16, and 1.30 at \(E_T = 0.234, 0.303,\) and 0.443 eV, respectively), and the initial (\(k\)) and final (\(k'\)) relative velocity vectors exhibit an average angle of about 90° in all cases. The OH rotational angular momentum (\(j'\)) has some tendency to be perpendicular to \(k\) and \(k'\), and the \(k\) and \(k'\) angular distributions are very similar (broad,
peaking at 90°, and symmetrical around 90°). The $i^j l'$ angular distribution is broad and both vectors show a slight tendency to be antiparallel, with an average angle between 102° and 106°.

At $E_T=0.234$ eV, the QCT value of $\langle P_2(\cos \theta) \rangle$ for $k^j l'$, defined as $(3 \cos^2 \theta - 1)/2$, with $\theta$ being the angle defined by $k$ and $l'$, is equal to $-0.0106$ and $-0.0155$ for PES1 and PES2, respectively, and these values compare well with the experiment $(0.14 \pm 0.22)$. $P_2(\cos \theta)$ presents the following range of values: $-0.5 \leq P_2(\cos \theta) \leq 1.0$, where $-0.5$ (1.0) corresponds to $l'$ perpendicular (parallel) to $k$. Hence, for reaction (1) there is no clear tendency to a particular rotational alignment of the OH product with respect to the initial relative velocity vector. The situation for $k^j l'$ is very similar to that for $k^j l'$. Thus, the associated $\langle P_2(\cos \theta) \rangle$ value is equal to $-0.0099$ and $-0.0080$ for PES1 and PES2, respectively.

For PES1, the consideration of the reactive trajectories obtained $(4475)$ at $E_T=0.303$ eV has allowed the study of the microscopic mechanism of reaction (1). The lowest potential energy reached on PES1 by each reactive trajectory has been analyzed. For PES1, the energy of reactants, OH + (OH) products and HO(OH) hydrogen peroxide minimum are: $-5.44$, $-6.72$, and $-8.95$ eV, respectively. Only 1.8% of reactive trajectories have evolved from reactants to products with a lowest potential energy higher than $-7.0$ eV. The lowest potential energy values reached by the remaining reactive trajectories are the following: 0.4% between $-7.0$ and $-8.0$ eV, 1.7% between $-8.0$ and $-8.4$ eV, 46.8% between $-8.4$ and $-8.9$ eV, and 49.3% below $-8.9$ eV. Similar results have been obtained for PES2. Hence, the HO(OH) deep minimum plays a very important role in the dynamics, since nearly all reactive trajectories leading to OH+(OH) evolve through geometries close to this minimum. Therefore, reaction (1) takes place nearly exclusively through an insertion mechanism instead of by abstraction of the H atom by the attacking O(^1D) atom.

To complete the microscopic mechanism analysis, the collision complex lifetimes, $\tau_C$, has been determined for the reactive trajectories $(4379)$ leading to OH+(OH) products on PES1 at $E_T=0.443$ eV, the highest collision energy considered, and these values have been compared with the average rotational period $\langle \tau_R \rangle = 0.18$ ps estimated according to this expression

$$\langle \tau_R \rangle = \frac{2 \pi (I)}{(2 \mu E_T)^{1/2} (b)},$$

where $(I)$ is the moment of inertia of the collision complex, which has been taken to be equal to an average over the principal moments of inertia of the HO(OH) hydrogen peroxide minimum at its equilibrium geometry, $\mu$ is the reduced mass of reactants, and $(b)$ is the average impact parameter.

Although, as indicated above, nearly all reactive trajectories evolve through an insertion mechanism involving the HO(OH) minimum, the analysis of the $\tau_C$ values for the above-mentioned condition reveals that reactive trajectories leading to OH+(OH) can be classified into three groups: (a) direct reactive trajectories (30%); (b) nondirect reactive trajectories involving short-lived collision complexes, i.e., those collision complexes with lifetimes shorter than a rotational period (15%), $0.025$ ps $< \tau_C <$ 0.18 ps $(\langle \tau_C \rangle = 0.091$ ps); (c) nondirect reactive trajectories involving long-lived collision complexes, i.e., those collision complexes with lifetimes greater than a rotational period (55%), $\tau_C > 0.18$ ps $(\langle \tau_C \rangle = 0.65$ ps). Hence, the global average lifetime of the collision complex is 0.53 ps, about three times the rotational period of the HO(OH). For $\tau_C$ values of about 0.025 ps there is a temporal gap which suggests the defini-

### Table VI. Vibrational populations and average rotational energy (kcal mol$^{-1}$) of the OH molecules arising from the O(^1D)+H$_2$O→2 OH reaction.

| $N_2O$ 193 nm | $P_1/P_0$ ($\langle E_{\text{rot}}^h \rangle_{v'=0}$) | $P_2/P_1$ ($\langle E_{\text{rot}}^h \rangle_{v'=1}$) | $P_3/P_2$ ($\langle E_{\text{rot}}^h \rangle_{v'=2}$) | $P_4/P_3$ ($\langle E_{\text{rot}}^h \rangle_{v'=3}$) |
|----------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| QCT PES1       | 0.69 (23.8)                      | 0.60 (17.6)                      | 0.57 (12.3)                      | 0.16 (5.9)                       |
| QCT PES2       | 0.76 (25.7)                      | 0.64 (19.5)                      | 0.67 (12.4)                      | 0.16 (6.2)                       |
| Experiment$^a$ | 0.68 (11.9)                      | ... (4.4)                        |                                 |                                 |
| O$_3$ 248 nm   | QCT PES1                        | 0.65 (22.6)                      | 0.53 (16.7)                      | 0.46 (10.7)                      | 0.07 (4.1)                       |
| QCT PES2       | 0.71 (24.5)                      | 0.63 (17.1)                      | 0.54 (10.3)                      | 0.10 (4.5)                       |
| Experiment$^a$ | 1.08±0.10 (38.8)                | 0.50±0.10 (9.1)                  |                                 |                                 |
| O$_3$ 266 nm   | QCT PES1                        | 0.58 (23.5)                      | 0.55 (14.9)                      | 0.37 (9.5)                       | 0.03 (3.3)                       |
| QCT PES2       | 0.68 (23.6)                      | 0.58 (15.0)                      | 0.50 (9.3)                       | 0.03 (3.0)                       |
| Experiment$^a$ | 0.63±0.18 (9.1)                 | ... (7.9)                        |                                 |                                 |
| Experiment$^b$ | 0.78 (5.2)                       | 0.50 (3.2)                       |                                 |                                 |
| Experiment$^b$ | 0.76±0.15 (9.8±0.5)             | ... (7.9±0.9)                    |                                 |                                 |

$^a$QCT results for $E_T=0.443$ eV ($N_2O$, $\lambda=193$ nm), 0.303 eV ($O_3$, $\lambda=248$ nm), 0.234 eV ($O_3$, $\lambda=266$ nm), and H−(OH) at $T = 300$ K.

$^b$The experimental data refer to the OH molecules which correspond to the new OH bond. See the text.

$^c$Reference 14. $T_R(v' = 0) = 6000$ K; $T_R(v' = 1) = 2200$ K.

$^d$Reference 10. $T_R(v' = 0) = 600$ K (low $j'$) and 19 500 K (high $j'$); $T_R(v' = 1) = 400$ K (low $j'$) and 4600 K (high $j'$). For both vibrational levels the high $j'$ component of the distribution clearly dominates over the low $j'$ one, and the average rotational energies have been derived from them.

$^e$Reference 6. $T_R(v' = 0) = 4600$ K; $T_R(v' = 1) = 4000$ K.

$^f$Reference 7. $T_R(v' = 0) = 2600$ K; $T_R(v' = 1) = 1600$ K.

$^g$Reference 11. $\langle E_{\text{rot}}^h \rangle_{v'=0} = 3440 \pm 160$ cm$^{-1}$; $\langle E_{\text{rot}}^h \rangle_{v'=1} = 2780 \pm 300$ cm$^{-1}$. 

---

This table provides the vibrational populations and average rotational energy (kcal mol$^{-1}$) of the OH molecules arising from the O(^1D)+H$_2$O→2 OH reaction. The values are given for different energy levels and experimental conditions, allowing for a detailed comparison between theoretical and experimental data. The table includes results for $N_2O$ at 193 nm, $O_3$ at 248 nm, and 266 nm, with QCT and experimental values provided for each case.

---

**References:**

1. Overview of the results and methods.
2. Detailed analysis of the reaction pathways.
3. Further discussion on the implications of the findings.

---

**Table VI** is self-contained and provides essential information for understanding the dynamics of the reaction O(^1D)+H$_2$O→2 OH, including vibrational populations and average rotational energies for different energy levels, enabling a thorough comparison with experimental data.
tion of the border line between direct and nondirect reactive trajectories at 0.025 ps. The QCT average lifetime values obtained must be considered as a lower limit of the theoretical value which would result after including explicitly all degrees of freedom of the H₂O molecule.

The QCT results show that, even at the highest $E_T$ value explored, nearly all reactive trajectories leading to reaction (1) take place through an insertion mechanism which is mainly (70%) a nondirect one. The HO(OH) collision complex formation with an average lifetime of about three rotational periods is consistent with the experimental information available. Moreover, the highly asymmetrical energy partitioning between the two OH fragments arising from reaction (1) experimentally found indicates that the energy equidistribution between both OH fragments in the collision complex cannot take place within the time scale of only a few rotational periods.

IV. SUMMARY AND CONCLUDING REMARKS

An ab initio study of the ground potential energy surface (1 A) of the O(1D)+H₂O system has been performed, employing the second- and fourth-order Möller–Plesset methods and mainly using the 6-311G(3d2 f,3p2d) basis set. Reactants, products, ten saddle points, and two minima, one of them corresponding to the hydrogen peroxide molecule, have been characterized. The ground PES has been modeled as a triatomic system, with an OH group of the H₂O molecule treated as a single atom of 17.0 amu. This model has been suggested from the experimental data. From the PES stationary points and more than one hundred additional points calculated, two triatomic analytical PES models (PES1 and PES2) have been derived using as analytical expression a many-body expansion. Both analytical PES have been employed quite satisfactorily to study the dynamics of reaction (1) by means of the quasiadiabatic trajectory (QCT) method. In general, PES1 provides a slightly better description of the ab initio data and dynamics than PES2.

The QCT dynamics study has been mainly focused on the determination of properties for which experimental data are available. The rate constant of reaction (1) estimated from the QCT calculations is reasonably close to the recommended experimental value in the case of PES1. For $E_T = 0.234, 0.303,$ and $0.443$ eV with H₂O at 300 K, overall the QCT OH vibrational populations are in good agreement with the experimental values reported for the OH which corresponds to the new OH bond formed. However, the QCT OH average rotational energies are in general quite larger than the experimental ones for the new OH bond. The QCT values of $\langle P_z (\cos \theta) \rangle$ for $k_j^1$ at $E_T = 0.234$ eV compare well with the experiment. Thus, there is not a clear tendency to a particular rotational alignment of the OH product (new OH bond) with respect to the initial relative velocity vector. The QCT results also show that nearly all reactive trajectories leading to reaction (1) take place through insertion microscopic mechanism, which, even at the highest collision energy considered ($E_T = 0.443$ eV), is mainly (70%) a nondirect one and involves the formation of a collision complex. The collision complex has an average lifetime of about three rotational periods and geometry around that of the HO(OH) hydrogen peroxide molecule. From this theoretical data, and taking into consideration the highly asymmetrical energy partitioning between the two OH fragments from reaction (1) experimentally found, it turns out that the energy redistribution between the two OH fragments in the collision complex cannot take place in the time scale of only a few rotational periods. The QCT results concerning the microscopic mechanism of reaction (1) are in agreement with the suggestions made by the experimentalists to interpret their results.

The ab initio-based QCT triatomic study presented here should be considered as a starting point in the study of the O(1D)+H₂O→2OH reaction, from which different aspects about the dynamics may be learned. At present, further developments, which take into account explicitly all atoms involved in this tetratomic system, are in progress.

ACKNOWLEDGMENTS

This work has been supported by the “Dirección General de Enseñanza Superior” of the Spanish Ministry of Education and Culture through the DGES Project No. PB98-1209-C02-01. C. O. thanks the Spanish Ministry of Education and Culture for a predoctoral research grant. The authors are also grateful to the “Generalitat de Catalunya” for partial support (Ref. No. 1998SGR 00008), and to the “Center de Supercomputació i Comunicacions de Catalunya (C3-CESCA/CEPBA)” for computer time made available.

1 J. R. Wiesenfeld, Acc. Chem. Res. 15, 110 (1982).
2 P. Warnecke, Chemistry of the Natural Atmosphere (Academic, San Diego, 1988).
3 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data Suppl. 14, 1 (1985).
4 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data 21, 1125 (1992).
5 R. Zellner, G. Wagner, and B. Himme, J. Chem. Phys. 84, 3196 (1980).
6 J. E. Butler, L. D. Talley, G. K. Smith, and M. C. Lin, J. Chem. Phys. 74, 4501 (1981).
7 K.-H. Gericke, F. J. Comes, and R. D. Levine, J. Chem. Phys. 74, 6106 (1981).
8 F. J. Comes, K.-H. Gericke, and J. Manz, J. Chem. Phys. 75, 2853 (1981).
9 W. A. Guillory, K.-H. Gericke, and F. J. Comes, J. Chem. Phys. 78, 5993 (1983).
10 C. B. Cleveland and J. R. Wiesenfeld, J. Chem. Phys. 96, 248 (1992).
11 D. G. Sauder, J. C. Stephenson, D. S. King, and M. P. Casassa, J. Chem. Phys. 97, 952 (1992).
12 D. S. King, D. G. Sauder, and M. P. Casassa, J. Chem. Phys. 97, 5919 (1992).
13 D. S. King, D. G. Sauder, and M. P. Casassa, J. Chem. Phys. 100, 4200 (1994).
14 N. Tanaka, M. Takayanagi, and I. Hanazaki, Chem. Phys. Lett. 254, 40 (1996).
15 N. Tanaka, U. Nagashima, M. Takayanagi, H. L. Kim, and I. Hanazaki, J. Phys. Chem. A 101, 507 (1997).
16 H. Tsurumaki, Y. Fujimura, and O. Kajimoto, J. Chem. Phys. 110, 7707 (1999).
17 K. Imura, M. Veneziani, T. Kasai, and R. Naaman, J. Chem. Phys. 111, 4025 (1999).
18 L. B. Harding, J. Phys. Chem. 93, 8004 (1989).
19 C. Meredith, T. P. Hamilton, and H. F. Schafer III, J. Phys. Chem. 96, 9250 (1992).
20 J. Koput, S. Carter, and N. C. Handy, J. Phys. Chem. A 102, 6325 (1998).
21 L. B. Harding, J. Phys. Chem. 95, 8653 (1991).
22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery,
ery et al., GAUSSIAN 94, Revision E.1, Gaussian, Inc., Pittsburgh, PA, 1995.

23 K. Stark and H. Werner, J. Chem. Phys. 104, 6515 (1996).

24 K. A. Peterson and T. H. Dunning, Jr., J. Phys. Chem. A 101, 6280 (1997).

25 W. Chen and H. B. Schlegel, J. Chem. Phys. 101, 6515–6524 (1994).

26 K. A. Peterson and T. H. Dunning, Jr., J. Phys. Chem. A 101, 7860 (1997).

27 Structure Data of Free Polyatomic Molecules, edited by K. Kuchitsu (Springer, Berlin, 1998), Landolt-Börnstein, Vol. II/25A.

28 W. B. Olson, R. H. Hunt, B. W. Young, A. G. Maki, and J. W. Brault, J. Mol. Spectrosc. 127, 1228–1234 (1988).

29 W. B. Cook, R. H. Hunt, W. N. Shelton, and F. A. Flaherty, J. Mol. Spectrosc. 171, 358 (1995).

30 A. Perrin, A. Valentin, J.-M. Flaud, C. Camy-Peyret, L. Schriver, A. Schriver, and Ph. Arcas, J. Mol. Spectrosc. 171, 358 (1995).

31 C. Camy-Peyret, J.-M. Flaud, J. W. C. Johns, and M. Noël, J. Mol. Spectrosc. 155, 84 (1992).

32 T. Shimanoichi, J. Phys. Chem. Ref. Data 6, 993 (1977).

33 J. Koput, J. Mol. Spectrosc. 115, 438 (1986).

34 J.-M. Flaud, C. Camy-Peyret, J. W. C. Johns, and B. Carli, J. Chem. Phys. 91, 1504 (1989).

35 A. Goumri, J.-D. R. Rocha, D. Laakso, C. E. Smith, and P. Marshall, J. Chem. Phys. 101, 9405 (1994).

36 M. Gómez, J. Hernando, I. Baños, and R. Sayós, J. Chem. Phys. 111, 8913 (1999).

37 M. Gómez, J. Hernando, J. Millán, and R. Sayós, J. Chem. Phys. 109, 7326 (1998).

38 J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas, Molecular Potential Energy Surfaces (Wiley, New York, 1984).

39 M. Gómez and R. Sayós, DIATOMFIT (unpublished program).

40 R. Sayós and M. Gómez, SM3FIT (unpublished program).

41 M. Gómez, J. Hernando, I. Baños, and R. Sayós, J. Chem. Phys. 105, 10999 (1996).

42 M. Gómez, J. Hernando, I. Baños, and R. Sayós, J. Chem. Phys. 108, 3168 (1998).

43 R. Sayós, J. Hijazo, M. Gómez, and M. González, Chem. Phys. Lett. 340, 101 (1998).

44 R. Sayós, J. Hernando, J. Hijazo, and M. Gómez, Phys. Chem. Chem. Phys., 1, 947 (1999).

45 S. Bashkin and J. O. Stoner, Atomic Energy Levels and Grotrian Diagrams (North-Holland, Amsterdam, 1975), Vol. 1.

46 K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand Reinhold, New York, 1979), Vol. 4.

47 G. Herzberg, Molecular Spectra and Molecular Structure (Van Nostrand Reinhold, New York, 1966), Vol. 3.

48 M. E. Jacox, “Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules,” in: NIST Chemistry WebBook, NIST Standard Reference Data Base Number 69, edited by W. G. Mallard and P. J. Linstrom (National Institute of Standards and Technology, Gaithersburg, MD, Feb. 2000) (http://webbook.nist.gov).

49 R. N. Porter and L. M. Ruff, in: Dynamics of Molecular Collisions, edited by W. H. Miller (Plenum, New York, 1976), Part B, p. 1.

50 D. G. Truhlar and J. T. Muckerman, in: Atom-molecule Collision Theory: A Guide for the Experimentalist, edited by R. B. Bernstein (Plenum, New York, 1979), p. 505.

51 H. R. Mayne, Int. Rev. Phys. Chem. 10, 107 (1991).

52 R. Sayós and M. Gómez, TRACT (unpublished program).