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The reactivity of the oxygen atom in the first excited electronic state, $O(^1D)$, is important in various fields of chemistry, and its reaction with water plays an important role in the HO_x chemistry, which in turn participates in the stratospheric ozone depletion.¹

Several years ago a full dimensional potential energy surface (PES) for the ground state hydrogen peroxide molecule, H_2O_2 , was developed by our group.² Recently, this PES was improved to accurately reproduce all the reaction channels and the minimum energy pathways for the different chemical reactions involved in the $O(^1D) + H_2O(X^1A_1)$ reaction system (see Figure 1). The aim of this work is to study theoretically the gas phase reactions involved in the $O(^1D) + H_2O(X^1A_1)$ system, considering this new full dimensional ground state PES.

Potential energy surface:

The PES applied in this work is a full dimensional potential energy surface for the ground singlet state of hydrogen peroxide, H_2O_2 . This potential is based on a 3×3 matrix to accurately reproduce all the dissociation channels in accordance with the Wigner–Witmer rules. The figures 1 display the most relevant features of this PES.

QCT Dynamics Calculations:

The quasiclassical trajectory (QCT) method has been applied to study the dynamics and kinetics of this system. To run the classical trajectories we have used an extensively adapted version of the Venus computer code³ which accommodates the H_2O_2 PES and makes the appropriate assignment of all reactive channels. Specifically, we have run QCT calculations for the $O(^1D) + H_2O(X^1A_1)$ and $O(^1D) + D_2O(X^1A_1)$ reactive collisions. The figures 2, Table 1 and Table 2 display some results of our preliminary calculations.

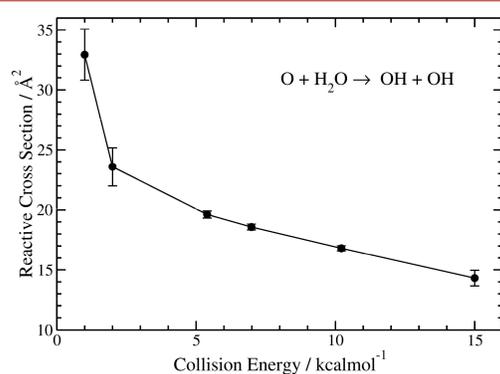


Figure 2. Reactive cross-section as function of the initial translational energy for the reactions $O + H_2O \rightarrow 2OH$.

Table 2. Vibrational populations and average rotational energy (kcal mol⁻¹) of the OH molecules.

E_{rot}/eV	results	$P_1/P_0(\langle E_R \rangle_{v=0})$	$P_2/P_1(\langle E_R \rangle_{v=1})$	$P_3/P_2(\langle E_R \rangle_{v=2})$	$P_4/P_3(\langle E_R \rangle_{v=3})$
0.234	This work	0.42 (9.1)	0.33 (6.9)	0.16 (4.6)	0.01 (2.6)
	ref. 4	0.58 (23.5)	0.55 (14.9)	0.37 (9.5)	0.03 (3.3)
	ref. 5.a)	0.78 (5.2)	0.50 (3.2)		
0.303	This work	0.44 (9.6)	0.33 (7.2)	0.16 (5.3)	0.06 (3.6)
	ref. 4	0.65 (22.6)	0.53 (16.7)	0.46 (10.7)	0.07 (4.1)
	ref. 5.b)	1.08 (38.8)	0.50 (9.1)		
0.443	This work	0.45 (10.0)	0.36 (8.3)	0.21 (6.0)	0.10 (4.2)
	ref. 4	0.69 (23.8)	0.60 (17.6)	0.57 (12.3)	0.16 (5.9)
	ref. 5.c)	0.68 (11.9)	...	(4.4)	

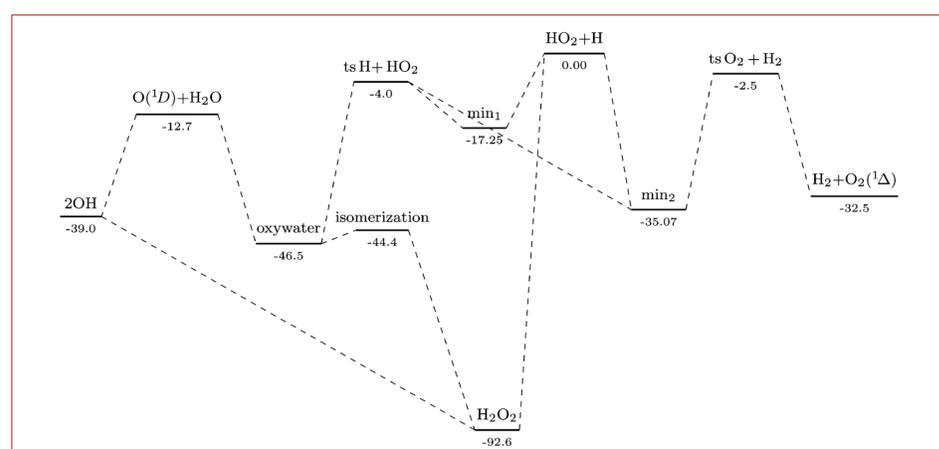


Figure 1. Energy diagram (kcalmol⁻¹), connecting the stationary points and dissociation channels for the ground state potential of the H_2O_2 . The energies are given in relation to the $H + HO_2$ dissociation energy.

Table 1. Rate constants for the $O(^1D)+H_2O(X^1A_1)$ and $O(^1D) + D_2O(X^1A_1)$ reactions.

	T/K	N total	N react	cross section/Å ²	$k/10^{-10} \text{cm}^3 \text{s}^{-1}$	k_H/k_D
$O+H_2O$	50	3515	1004	175.9 ± 4.7	1.243 ± 0.033	1.013 ± 0.038
$O+D_2O$	50	3420	987	177.7 ± 4.8	1.226 ± 0.033	
$O+H_2O$	75	4497	1244	146.9 ± 3.5	1.271 ± 0.031	1.083 ± 0.042
$O+D_2O$	75	3428	832	138.9 ± 4.2	1.174 ± 0.035	
$O+H_2O$	127	6317	1651	118.2 ± 2.5	1.332 ± 0.028	1.064 ± 0.034
$O+D_2O$	127	5261	1324	113.9 ± 2.7	1.252 ± 0.030	
$O+H_2O$	296	10631	2462	80.2 ± 1.4	1.380 ± 0.024	1.048 ± 0.025
$O+D_2O$	296	12243	3054	78.4 ± 1.2	1.316 ± 0.021	

References

- B. Lewis and G. von Elbe, *Combustion, Flames and Explosion of Gases*, Academic Press Inc., New York, 2nd ed, **1961**; P. Berhman, B. Parise, R. Liseau, B. Larsson, H. Olofsson, K. M. Menten and R. Güsten, *Astron. Astrophys.*, **2011**, *531*, L8;
- D.V. Coelho and J. Brandão, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 1378.
- W. L. Hase, R.J. Duchovic, et al., *QCPE Bull.*, **1996**, *16*, 43.
- R. Sayós, C. Oliva, and M. González, *J. Chem. Phys.*, **2000**, *113*, 6736.
- a) K.-H. Gericke, F. J. Comes, and R. D. Levine, *J. Chem. Phys.*, **1981**, *74*, 6106; b) D. G. Sauder, J. C. Stephenson, D. S. King, and M. P. Casassa, *J. Chem. Phys.*, **1992**, *97*, 952; c) N. Tanaka, M. Takayanagi, and I. Hanazaki, *Chem. Phys. Lett.*, **1996**, *254*, 40.

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