

PURPOSE OF THE STSM:

Peroxides are present in the Earth's atmosphere as pollutants due to human activities. To monitor these species, it is important to understand their IR and UV spectra. Already the theoretical description of their equilibrium structures can pose a formidable computational problem. Oberhammer [1], in a recent review article titled "Gas Phase Structures of Peroxides: Experiments and Computational Problems", gives an account of our present understanding of the structural properties of a large number of inorganic and organic peroxides, by confronting experimental with theoretical results. He has singled out three molecules, for which theory has failed to describe accurately the experimental results: dimethyl peroxide, difluorine peroxide and the dichlorine peroxide. In our recent publication [2] we solved the problem of the dimethyl peroxide molecule. The objective of my mission was to investigate the structural parameters of the molecules difluorine peroxide and dichlorine peroxide. Both molecules present a disagreement problem in the calculation of the bond lengths O-O, O-F and O-Cl. We notice that the experimental structure is essentially an r_0 structure and not an r_e equilibrium structure. We have studied then its structural parameters using vibrational programs such as VSCF and VMP2. We have also calculated the potential energy as a function of the distance O-O of the FOOF molecule.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The results of calculated equilibrium geometries of ClOOC1 and FOOF in the electronic ground state and their comparison with experimental data are listed, respectively, in Tables 1 and 2. These tables show that with MP2, CCSD(T), CCSD(T)-F12 and MRCI theories the structural parameters do not yield good agreement with the experimental values.

Table 1. Calculated Equilibrium Geometries of ClOOC1 as Obtained with Various Methods and Basis Sets.

Parameters	re(O-Cl) (Å)	re(O-O) (Å)	ClOO (°)	ClOOC1 (°)
MRCI/VTZ	1.705	1.362	109.703	86.80
MRCI/AVTZ	1.703	1.362	109.650	86.03
CCSD(T)-F12/VTZ-F12	1.710	1.405	109.312	82.54
CCSD(T)-F12/AVTZ	1.712	1.403	109.392	82.67
CCSD(T)-F12/AVQZ	1.710	1.403	109.346	82.57
CCSD(T)/AVTZ	1.734	1.403	109.431	83.07
CCSD(T)/AVQZ	1.721	1.400	109.403	82.66
MP2/AVTZ	1.714	1.415	108.856	81.79
Exp[3]	$r_0=1.704$	$r_0=1.426$	110.1	81.0

Table 2. Calculated Equilibrium Geometries of FOOF as Obtained with Various Methods and Basis Sets.

Parameters	re(O-O) (Å)	re(F-O) (Å)	FOO (°)	FOOF (°)
MRCI/AVTZ	1.999	1.567	108.972	87.803
MRCI/AVQZ	1.194	1.563	109.064	87.750
CCSD(T)-F12/VTZ-F12	1.229	1.535	108.506	87.630
CCSD(T)-F12/AVTZ	1.227	1.546	108.638	87.728
CCSD(T)-F12/AVQZ	1.230	1.531	108.479	87.593
CCSD(T)/AVTZ	1.234	1.545	108.533	87.702
CCSD(T)/AVQZ	1.228	1.539	108.585	87.702
MP2/AVTZ	1.166	1.618	110.461	88.650
Exp[4]	$r_0=1.217$	$r_0=1.575$	109.5	87.5

The results of the structural parameter studies for the vibrational ground states (r_0 values) of ClOOC1 and FOOF using vibrational programs such as VSCF and VMP2 and their comparison with experimental data are reported in Table 3. Note that some of the calculations for ClOOC1 are not yet terminated.

Table 3. Calculations of the distance O-O, O-F and O-Cl of the molecule FOOF and ClOOCl at the VSCF and VMP2 program levels.

Methods	FOOF				ClOOCl			
	r_0 (O-O)		r_0 (O-F)		r_0 (O-O)		r_0 (O-Cl)	
	VSCF	VMP2	VSCF	VMP2	VSCF	VMP2	VSCF	VMP2
MP2/VTZ	1.244	1.237	1.514	1.519	1.416	1.402	1.721	1.735
MP2/AVTZ	1.190	1.159	1.593	1.627	1.422		1.718	
MP2/VQZ	1.208	1.195	1.554	1.567	1.417		1.709	
CCSD(T) /VTZ	1.253	1.250	1.535	1.494	1.402	1.390	1.745	1.757
CCSD(T) /AVTZ	1.238	1.233	1.555	1.517	1.409		1.740	
CCSD(T) /VQZ					1.404	1.391	1.729	1.742
CCSD(T)-F12 /VTZ-F12	1.233	1.209	1.546	1.566				
Exp	1.217		1.575		1.704		1.426	

Fig. 1 presents the potential energy curve of FOOF as a function of the O-O distance with the other internal coordinates optimized. These curves are obtained with different methods and the AVTZ basis set. This figure shows that the potential curve obtained with the MRCI and MP2 methods have, respectively, a single minimum at r_e (O-O) = 1.2 Å and r_e (O-O) = 1.17 Å. However, the potential curve is very flat around the minimum, which explains the computational difficulties.

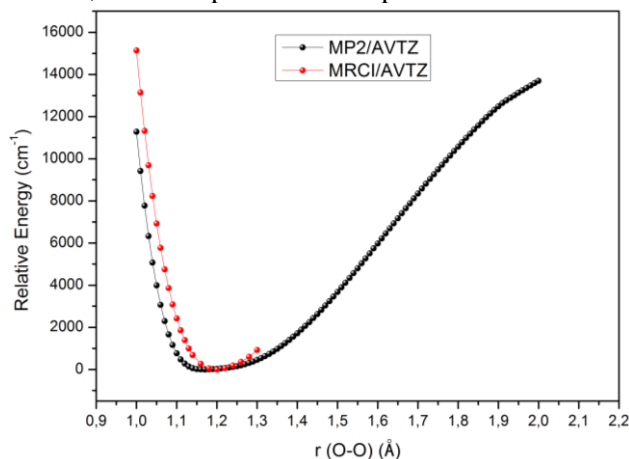


Fig (1): Potential energy curves for FOOF at the MP2 /AVTZ and MRCI /AVTZ levels of theory

Reference

- [1] Oberhammer, H. *ChemPhysChem* **16**, 282–290 (2015).
- [2] Ferchichi, O.; Derbel, N.; Jaidane, N.; Cours, T.; Alijah, A.; *Phys. Chem. Chem. Phys.* **19**, 21500-21506 (2017).
- [3] Jackson, R. H. *J. Chem. Soc.* 4585, (1962).
- [4] Birk, M.; Friedl, RR.; Cohen, EA.; Pickett, HM.; Sander, SP.; *J. Chem. Phys.* **91**, 6588–6597,(1989).

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The r_0 values obtained for FOOF agree with experimental data to 0.01 Å. The r_e values used by other researchers are not sufficient to explain the molecule's structure since the potential curve is very anharmonic.

We further correct the previous assumption, that a MRCI procedure is necessary to reproduce the experimental bond lengths

FUTURE COLLABORATIONS (if applicable)

The next step is to solve the structure parameter problem for ClOOCl and to compute the IR and UV spectra for both molecules.