

UCCSD, UQCISD, and UMP2 studies on O<sub>2</sub>...HF/FH van der Waals complexes: A perspective on the structure, properties and topology

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### Introduction

Molecular O<sub>2</sub> (triplet spin state, X<sup>3</sup>Σ<sup>-</sup><sub>g</sub>) is an interesting open shell system of atmospheric importance. Thus, its interaction with molecular HF (singlet spin state) should presumably add insight for the understanding of weak interaction. The O<sub>2</sub>...HF complex has been studied several times theoretically for its electronic structure, properties and vibrational characteristics using high level *ab initio* techniques<sup>1,2</sup> and eventually, identified and analyzed experimentally using FTMW<sup>3</sup> and IR spectroscopic methods<sup>4,5</sup>. In all these studies, attention has been given to the complexes of O<sub>2</sub>...HF whilst there is almost no study on complexes formed between O<sub>2</sub> and the F end of HF. In this work, we have investigated all the possible types of complexes formed between O<sub>2</sub> and HF/FH. The equilibrium structures, electronic and vibrational properties, and topology of electron charge density at bond critical points of the studied systems are analyzed, compared, and presented.

### Results and Discussion

Figure 1 shows the UCCSD/Aug-CC-pVDZ optimized configurations of the complexes of O<sub>2</sub>...HF and O<sub>2</sub>...FH examined. Figures **a** and **b** are the two close global minima with bent geometry, **c** (T-shape), **d** (linear), and **e** (quasi-linear) are first order saddle point structures of O<sub>2</sub>...HF whilst **f** (T-shape), **g** (linear), **h** (quasi-linear), **i** (bent) and **j** (bent) are all minima on the O<sub>2</sub>...FH hyper-surface. The global minima **a** and **b** are found to be similar to that reported previously at the UCCSD

(T)/aug-cc-pVNZ (N = D, T)<sup>2</sup> although an inconsistency has been found while comparing with the T-shape complex of O<sub>2</sub>...HF, which has been reported as a minimum. The saddle point structures are confirmed by an analysis of the O<sub>2</sub>...HF/FH intermolecular bending frequencies (O<sub>2</sub>...HF/HF bend, see Table 1).

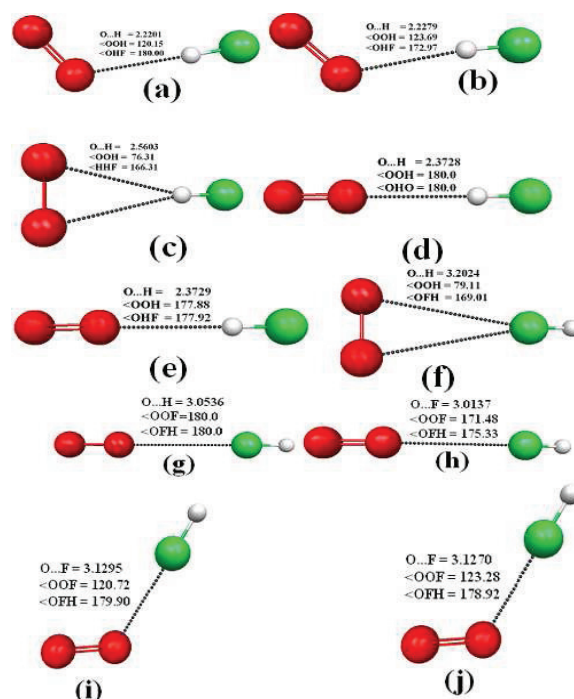


Figure 1: UCCSD/aug-cc-pVDZ optimized geometries of the complexes examined.

Some physical properties of the complexes are summarized in Table 1. First of all, the intermolecular bond distances range from 2.220 (O<sub>2</sub>..HF bent) to 3.202 Å (O<sub>2</sub>..FH T-shape) which are less than or close to the sum of the van der Waals radii of atoms involved in bond

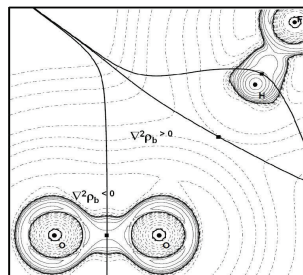
formation ( $H = 1.20 \text{ \AA}$ ,  $O = 1.55 \text{ \AA}$ , and  $F = 1.47 \text{ \AA}$ ). The dipole moment enhancement (results from an inductive effect) is an important measure of an interaction and is reflected upon complex formation. As shown in Table 1, there is no regular ordering among the values of  $\Delta\mu$  (compared with  $\Delta E$ ) in the set of complexes examined, however, the most

Complex type	$\Delta r(\text{HF})$	$\mu$	$\Delta\mu$	$\Delta E$	O...H/F	$\Delta v$	O2..FH/HF bend
O2...HF bent (120)	0.0009	2.134	0.324	-4.46	2.2201	-15	36.4
O2...HF bent (123)	0.0011	2.147	0.337	-4.38	2.2279	-23	38.7
O2...HF T-shape	0.0003	2.008	0.198	-2.38	2.5603	-4.7	-142.6
O2...HF linear	0.0003	2.103	0.293	-2.81	2.3715	-3.7	-53
O2...HF quasi-linear	0.0004	2.104	0.294	-2.81	2.3729	-3.3	-50
O2...FH Tshape	-0.0003	1.88	0.07	-2.21	3.2024	1.8	30.4
O2...FH linear	-0.0004	1.912	0.108	-2.32	3.048	4	40.6
O2...FH quasi-linear	-0.0005	1.912	0.108	-2.25	3.0137	3.4	34.3
O2...FH bent (120)	-0.0003	1.884	0.080	-1.85	3.1288	1.1	5.8
O2...FH bent (123)	-0.0003	1.885	0.081	-1.84	3.1264	1.2	7.2

stable complex is accompanied by a largest value of  $\Delta\mu$ .

Table 1: Physical parameters of O<sub>2</sub>...HF and O<sub>2</sub>...FH complexes obtained from the UCCSD/ aug -cc-pVDZ level.

Figure 2: The  $\nabla^2\rho$  contour map of O<sub>2</sub>...HF (bent,  $\angle\text{OOH} \approx 120^\circ$ ) complex.



Furthermore, the H-bonded complexes were examined to be red-shifted ( $\Delta v$ ) with a concomitant elongation of the HF bond ( $\Delta r(\text{HF})$ ) whilst the complexes with O<sub>2</sub> weakly bonded to the F end of HF are blue-shifted with a concomitant HF bond contraction. A red-shift of  $15 \text{ cm}^{-1}$  is predicted for the HF stretch of O<sub>2</sub>...HF bent complex ( $\angle\text{OOH} \approx 120^\circ$ ), which is in agreement with a shift of  $12.9 \text{ cm}^{-1}$  observed experimentally<sup>4</sup>. The UQCISD and UMP2 results are in consistent with those obtained from the UCCSD level, and analyzed.

Analysis of the bonding features using the quantum theory of atoms in molecules (QTAIM) reveals that the existence of bond

critical points (see Figure 2) (electron density at bcp:  $\sim 0.0097 \text{ au}$  for *a* and *b*;  $\sim 0.0052 \text{ au}$  for T-shape, and  $\sim 0.0056 \text{ au}$  for linear), positive values of Laplacian of charge density ( $\nabla^2\rho$ ) at bcp ( $0.038 \text{ au}$  for *a* and *b*,  $0.021 \text{ au}$  for T-shape;  $0.024 \text{ au}$  for linear), mutual penetration for all, loss of charge on H ( $0.0034e$  for *a* and *b*;  $0.0008e$  for T-shape;  $0.0023e$  for linear),

energetic destabilization of H atom, dipolar polarization, and H atom volume decreased for all the complexes satisfying the eight necessary criteria of Popelier & Koch's criteria for hydrogen bonds<sup>6</sup>. Thus as expected, the bonding effect is greater for the *a* and *b* complexes compared to the other geometries. It is also evident from this analysis that the O<sub>2</sub>...HF bent configuration ( $\angle\text{OOH} \approx 120/123^\circ$ ) satisfies the necessary and sufficient conditions of a hydrogen bonded interaction whilst the O<sub>2</sub>...FH improper complexes are at the extreme end of weak interactions.

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