Theoretical study on the $(O_2\text{-HF})^+$ complex

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Abstract

The potential energy surface of the $(O_2\text{-HF})^+$ complex has been investigated theoretically.   Equilibrium structure has been calculated at the UCCSD/6-311++G(2d,2p) and UCCSD/aug-cc-pVTZ levels of theory.   Two stable complexes, T-shape and collinear, have been found on the surface whose interaction energies are calculated to be -12.36 and -10.19 kcal mol^{-1}, respectively, at the UCCSD(T)/aug-cc-pVTZ level after correcting for the basis set superposition error.   Natural bond orbital analysis revealed intermolecular charge transfers occur followed by intramolecular charge rearrangement.   A large contribution from the n_F to π^*_{OO} is found.

1. Introduction

Many studies on weakly bound hydrogen bonded complex have been conducted experimentally and theoretically [1,2]. Among the hydrogen bonded complexes, an HF complex tends to have large interaction energy due to the large dipole moment of HF. Spectroscopical observation has shown a good correlation between the strength of the hydrogen bond and the vibrational frequency shift from the isolated HF [1]. Chemical substances containing halogen atoms have attracted much attention especially from the environmental point of view strongly linked with the depletion of the ozone layer [3]. Due to this environmental importance, the measurement of the abundance of HF and HCl was conducted [4]. For many ion-molecular reactions the formation of the intermediate complex is the primary step followed by dissociation, rearrangement or charge transfer reaction. The charge transfer reaction is the most distinctive of the secondary reactions with a rate dependent on the reaction exothermicity. The presence of a weakly bound complex will affect the following reactions and product branching ratios. The weakly bound neutral O_2-HF complex was studied experimentally in solid Ne by Hunt [5] and theoretically by Reed et al. [6]. Experimentally the bent structure has been proposed while theoretically the T-shape and collinear structures have been predicted. However, the molecular structures of the $(O_2\text{-HF})^+$ complexes are not known yet. Recent study on the $(O_2\text{-HCl})^+$ complex has revealed the presence of three stationary points in the closely lying doublet and quartet states due to the vicinity of the ionization potentials for O_2 and HCl [7].

In this paper the properties of the $(O_2\text{-HF})^+$ complex have been investigated to elucidate the ion-dipole potential. The HF molecule possesses higher ionization potential (16.06 eV) [8] compared with the O_2 molecule (12.0697 eV) [9]. Therefore, we consider the doublet state complex. The complexation properties will be discussed using the NBO analysis.

2. Results and discussion

2.1. Geometry of the complexes

The initial geometry optimizations were done from several starting points at the UCCSD/6-31++G(d,p) level. Based on the optimized structures, further optimizations at higher level were employed. Fig. 1 shows the optimized structures of the $(O_2\text{-}HF)^+$ complex calculated at the UCCSD/aug-cc-pVTZ level without any constraint. An HF molecule interacts perpendicularly with an O3-O4 bond with C_{2v} symmetry (T-shape) or collinearly approaches the O_2 molecule (collinear). Geometry parameters calculated for the complexes and changes in values from the corresponding monomers are listed in Table 1. The intermolecular distance for the T-shape and collinear complexes are calculated to be 2.456 and 2.416 Å, respectively, at the UCCSD/aug-cc-pVTZ level. The H1-F2 and O3-O4 bond lengths of the T-shape complex are lengthened by 0.006 and contracted by 0.001 Å as compared with those of HF and O_2^+ monomers, respectively while in the collinear complex they are lengthened by 0.005 and 0.001 Å, respectively. The structures of the $(O_2\text{-}HF)^+$ complex form a striking contrast to the non-planar structure of the $^2(O_2\text{-}HCl)^+$ complex [7]. The optimized bond lengths were close to those of the monomers. Therefore, the potential energies were calculated varying the intermolecular distances while the O-O and H-F bond lengths were fixed. Figs. 2 and 3 show the calculated potential energies for T-shape and collinear approaches of HF to O_2^+, respectively, where the hydrogen or fluorine atom of the HF molecule orients toward the O_2^+ molecule. The potentials for F-head approaching are attractive while those for H-head approaching are repulsive.

(Figs. 1-3 and Table 1)

In solid Ne, the neutral O_2-HF complex was found to possess the bent structure [5]. The H-F stretching vibrational frequency of the complex showed a small red shift of 16 cm^{-1} from that of an isolated monomer, indicative of small interaction energy. Reed et al. reported the T-shape and collinear neutral complexes [6]. The intermolecular distance was calculated to be 2.88 Å for the T-shape complex at the MP2/6-31G(d) level. The intermolecular distance of the cation T-shape is much shorter than that of the neutral complex. There is considerable difference in the structures between collinear neutral and cation complexes. In neutral complex the H atom points to the O_2 molecule while in cation complex the F atom points to the O_2^+ molecule due to its high electronegativity of the F atom.

2.2. Interaction energy of the complexes

The interaction energies were calculated as O_2^+ and HF molecules approach to form the $(O_2$-HF$)^+$ complexes. Calculated BSSE and interaction energies including BSSE correction for complexes are listed in Table 2. The T-shape complex is more stable in energy than the collinear complex. The smaller basis set aug-cc-pVDZ underestimates the interaction energies compared with the aug-cc-pVTZ basis set. However, the basis set and electron correlation method dependences of the interaction energies are not significant. BSSE is reduced as the basis set becomes larger and more flexible. At the highest level, UCCSD(T)/aug-cc-pVTZ, the interaction energies for T-shape and collinear complexes are calculated to be −12.36 and −10.19 kcal mol^{-1}. Electron correlation correction for the interaction energies is calculated to be 3.4 and 1.5 % for T-shape and collinear complexes, respectively, at the UCCSD(T)/aug-cc-pVTZ level. Slight increase in interaction energies indicates that not the dispersion but the electrostatic interaction is important for the attraction. For the $^2(O_2$-HCl$)^+$ complex, the correlation

energy has been calculated to be 6.31 kcal mol^{-1} at the UCCSD/6-311++G(2d,2p) level which occupies 44.8% of the interaction energy.   Significant changes in the correlation energy are also found in other complexes including a halogen compound [1,10].   Large difference in dispersion energy may affect the complex conformation.   For neutral T-shape and collinear complexes, the interaction energies were calculated to be –0.71 and –0.79 kcal mol^{-1}, respectively, at the MP2/6-31G(d) level [6].   The interaction energy of the $(O_2\text{-HF})^+$ complex is much greater than that of the O_2-HF complex indicative of a deep ion-dipole potential.

<center>(Table 2)</center>

2.3. Vibrational analysis

Table 3 shows unscaled vibrational frequencies and infrared intensities of the complexes and changes in values from the corresponding monomers calculated using the 6-311++G(2d,2p) basis set.   For the T-shape complex, there are 5 in-plane modes and 1 out-of-plane mode.   The H-F stretching vibrational frequency is found to decrease by 86.2 cm^{-1} from the monomer frequency, corresponding to bond weakening and gains infrared intensity, while the O-O stretching vibrational frequency is shifted to higher frequency by 8.6 cm^{-1}.   In- and out-of-plane F-H bending vibrations have nearly equal frequencies and intensities.   Intermolecular stretching vibration is calculated to be 187.1 cm^{-1}.   For the collinear complex, there are 7 vibrational modes.   H-F and O-O vibrational frequencies are red-shifted by 71.6 and 4.6 cm^{-1}, respectively.   The O-O vibaration gains infrared intensity due to the asymmetric structure.   Corresponding to the weaker interaction energy of the collinear complex compared with that of the T-shape complex, intermolecular stretching mode of the collinear complex shows 13.9 cm^{-1} smaller value than that of the T-shape complex.

<center>(Table 3)</center>

2.4. NBO analysis

To clarify the nature of the complexation, NBO analysis was carried out.   Table 4 gives the natural atomic charges (q) and the changes in natural atomic charges (Δq) for the complexes.   In the T-shape complex, the in-contact F2, O3 and O4 atoms gain charges while the H1 atom loses the charge.   In the collinear complex, in-contact bonds become more polarized.   The net charge transfers (CT) from HF to O_2^+ were evaluated to be 1.4 and 3.2 me for the T-shape and collinear complexes, respectively, using the aug-cc-pVTZ basis set.   Table 5 gives the second-order perturbation energies ($E^{(2)}$) calculated with the aug-cc-pVTZ basis set.   The distinctive intermolecular CT interaction, $n_F \rightarrow \pi^*_{O3O4}$ is found for the complexes.   In addition, the $\pi_{O3O4} \rightarrow \sigma^*_{H1F2}$ and $n_{1\ O3} \rightarrow \sigma^*_{H1F2}$ interactions have contributions for the T-shape and collinear complexes, respectively.

(Tables 4 and 5)

3. Conclusions

The $(O_2\text{-HF})^+$ complex has been studied by ab initio calculations at the UCCSD level.   Two stable complexes have been found on the potential energy surface, namely T-shape and collinear complexes, where the fluorine atom of the HF molecule orients toward the O_2^+ molecule.   The T-shape complex has larger interaction energy than the collinear complex.   Compared with the neutral O_2-HF complex, the electrostatic interaction is predicted to be larger.   NBO analysis reveals that the intermolecular CT from HF to O_2^+ takes place followed by the intramolecular charge rearrangement.   A large contribution from the n_{F2} to the π^*_{O3O4} in the O_2^+-HF complex is found.

4. Method of calculation

Geometry optimizations and frequency calculations were performed at the coupled cluster (CCSD) level of theory.   For weak bonding, both diffuse and polarization functions must be included in the basis set, so we used the 6-311++G(2d,2p) and Dunning's correlation consistent triple zeta basis set augmented with diffuse functions, aug-cc-pVTZ.   Single point energies were calculated up to the UCCSD(T)/aug-cc-pVTZ level.   Analysis of the charge distribution and charge-transfer processes was performed using the natural bond orbital (NBO) partitioning scheme [11].   The basis set superposition error (BSSE) was calculated according to the counterpoise (CP) method proposed by Boys and Bernardi [12]. All calculations were performed using Gaussian 03W [13].   The degree of spin contamination was monitored.   The $<s^2>$ values did not exceed 0.7501 indicating the wavefunctions were not significantly contaminated by higher order spin states.

References

[1] S. Scheiner, Hydrogen Bonding, Oxford University Press, New York, 1997.

[2] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond, Oxford University Press, Oxford, 1999.

[3] For example. E.A. Parson, Protecting the Ozone Layer, Oxford University Press, New York, 2003.

[4] C.P. Rinsland, J.S. Levine, A. Goldman, N.D. Sze, M.K.W. Ko, D.W. Johnson, J. Geophys. Res. A. 96 (1991) 15523-15540.

[5] R.D. Hunt, L. Andrews, J. Chem. Phys. 86 (1987) 3781-3786.

[6] A.E. Reed, F. Weinhold, L.A. Curtiss, D.J. Pochatko, J. Chem. Phys. 84 (1986) 5687-5705.

[7] N. Tanaka, H. Nishikiori, T. Fujii, W.N. Sisk, Chem. Phys. Lett. 397 (2004) 62-66.

[8] G. Bieri, A. Schmelzer, L. Asbrink, M. Jonsson, Chem. Phys. 49 (1980) 213-224.

[9] R.G. Tonkyn, J.W. Winniczek, M.G. Michael, Chem. Phys. Lett. 164 (1989) 137-142.

[10] N. Tanaka, T. Tamezane, H. Nishikiori, T. Fujii, W.N. Sisk, Chem. Phys. 306 (2004) 25-34.

[11] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899-926.

[12] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553-566.

[13] Gaussian 03, Revision B.03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

Figure Captions

Fig. 1. Optimized structures of the $(O_2\text{-HF})^+$ complex.

Fig. 2. Potential energies for the intermolecular distance of F-head and H-head of T-shape approaches calculated at the UCCSD(T)/6-311++G(2d,2p) level.

Fig. 3. Potential energies for the intermolecular distance of F-head and H-head of collinear approaches calculated at the UCCSD(T)/6-311++G(2d,2p) level.

Table 1

Geometry parameters of the $(O_2\text{-HF})^+$ complexes computed at the UCCSD level of theory.

Parameter[a]	T-shape				Collinear			
	6-311++G(2d,2p)		aug-cc-pVTZ		6-311++G(2d,2p)		aug-cc-pVTZ	
r_{H1F2}	0.921	(+0.006)	0.924	(+0.006)	0.920	(+0.005)	0.923	(+0.005)
r_{O3O4}	1.113	(−0.001)	1.108	(−0.001)	1.115	(+0.001)	1.110	(+0.001)
r_{F2O3}	2.538		2.518		2.420		2.416	
r_{F2O4}	2.538		2.518					
r[b]	2.476		2.456					
$\phi_{H1F2O3O4}$	180.0		180.0					

Changes in values from the corresponding monomers are given in parentheses.

[a] Bond lengths r and angle ϕ are in Å and degrees, respectively.

[b] Distance between the F atom and the center of the contacting O-O bond.

Table 2

BSSE and BSSE corrected interaction energies ΔE (kcal mol^{-1}) of the (O$_2$-HF)$^+$ complexes.

	T-shape		Collinear	
	BSSE	ΔE	BSSE	ΔE
UCCSD(T)/6-311++G(2d,2p)	−0.72	−12.01	−0.76	−10.05
UCCSD(T)/aug-cc-pVDZ	−1.01	−11.88	−0.73	−9.94
UHF/aug-cc-pVTZ	−0.23	−11.94	−0.13	−10.04
UMP2/aug-cc-pVTZ	−0.49	−12.44	−0.32	−10.26
UMP4(SDTQ) /aug-cc-pVTZ	−0.50	−12.31	−0.33	−10.22
UCCSD/aug-cc-pVTZ	−0.49	−12.28	−0.32	−10.14
UCCSD(T)/aug-cc-pVTZ	−0.50	−12.36	−0.33	−10.19

Table 3

Unscaled harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) of the O_2^+-HF complex calculated at the UCCSD/6-311++G(2d,2p) level of theory.

Assignment	ν	$\Delta\nu$	I	ΔI
T-shape				
H-F stretch	4119.0	−86.2	240.8	+127.3
O-O stretch	1995.6	+8.6	0.0	0
H-F out-of-plane bend	288.3		219.1	
H-F in-plane bend	287.3		220.1	
Intermolecular stretch	187.1		17.8	
Deform	128.3		1.4	
Collinear				
H-F stretch	4133.6	−71.6	232.9	+119.4
O-O stretch	1982.4	−4.6	1.8	+1.8
H-F bend	302.0		211.2	
H-F bend	286.5		212.8	
Intermolecular stretch	173.2		17.9	
Deform	89.1		1.1	
Deform	18.0		2.4	

Table 4

Natural atomic charges of the $(O_2\text{-HF})^+$ complexes and changes in values from isolated monomers

Atom	T-shape				Collinear			
	6-311++G(2d,2p)		aug-cc-pVTZ		6-311++G(2d,2p)		aug-cc-pVTZ	
	q / e	Δq / me	q / e	Δq / me	q / e	Δq / me	q / e	Δq / me
H1	+0.6031	+45.0	+0.6032	+44.9	+0.5969	+38.8	+0.5965	+38.3
F2	−0.6023	−44.2	−0.6018	−43.6	−0.5941	−36.0	−0.5932	−35.0
O3	+0.4996	−0.4	+0.4993	−0.7	+0.5217	+21.7	+0.5208	+20.8
O4	+0.4996	−0.4	+0.4993	−0.7	+0.4755	−24.5	+0.4760	−24.0

Table 5

Charge transfer interaction in the $(O_2\text{-HF})^+$ complexes.

Parameter	$E^{(2)}$ / kcal mol^{-1}
T-shape	
$n_{3\ F2} \rightarrow \pi^*_{\ O3O4}$	0.36
$\pi_{\ O3O4} \rightarrow \sigma^*_{\ H1F2}$	0.14
Collinear	
$n_{2\ F2} \rightarrow \pi^*_{2\ O3O4}$	0.35
$n_{1\ F2} \rightarrow \pi^*_{2\ O3O4}$	0.33
$n_{1\ O3} \rightarrow \sigma^*_{\ H1F2}$	0.41

Fig. 1. N. Tanaka et al. "Theoretical study on the $(O_2\text{-HF})^+$ complex".

−249.90

−249.92

−249.94

−249.96

Energy / hartrees

F
|
H
⋮ r
O—O

H
|
F
⋮ r
O—O

2   3   4   5   6   7

r / Å
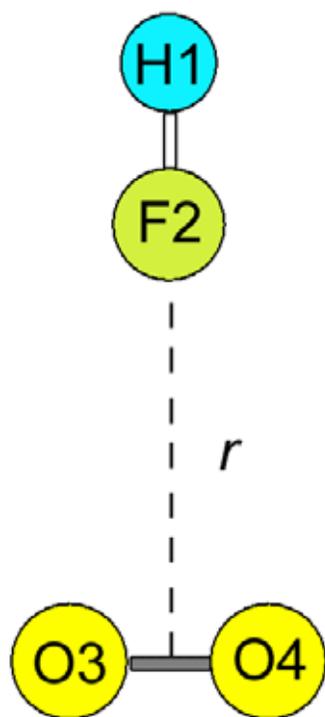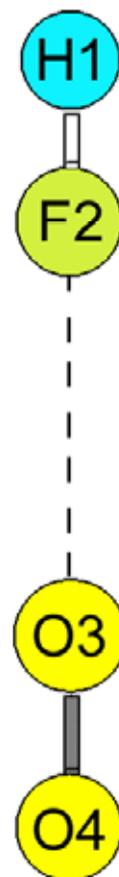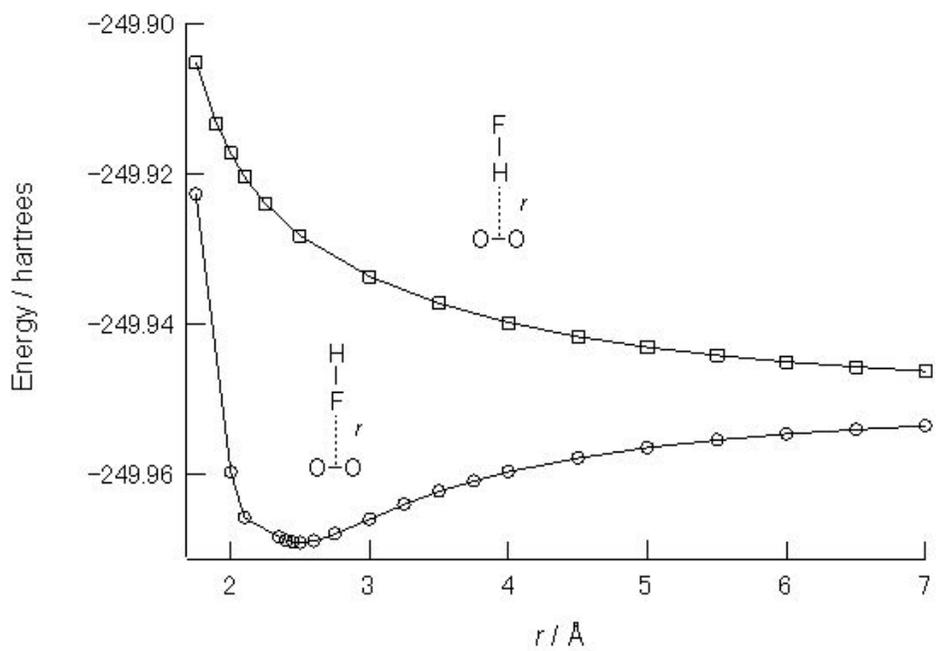
Fig. 2. N. Tanaka et al. "Theoretical study on the (O$_2$-HF)$^+$ complex".

Fig. 3 N. Tanaka et al. "Theoretical study on the $(O_2\text{-HF})^+$ complex".