

Ab initio study on the (O₂-HCl)⁺ complex

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Abstract

The (O₂-HCl)⁺ complex has been investigated theoretically in the doublet and quartet states. Equilibrium structures have been calculated at the CCSD level of theory with the aug-cc-pVDZ and 6-311++G(2d,2p) basis sets. One non-planar and two planar complexes are found in the doublet and quartet states, respectively. The doublet state complex is predicted to possess the largest interaction energy and be the most stable. Natural bond orbital analysis revealed intermolecular charge transfers occur followed by intramolecular charge rearrangement. The calculated vibrational frequencies are compared with those observed in solid Ne.

1. Introduction

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 [1]. Due to this environmental importance, the measurement of the abundance of HF and HCl was conducted [2]. Furthermore, the reactions of HCl with O_2^+ [3], H_3^+ [4], C^+ [5], Na^+ [6] and $C_3H_2^+$ [7] were investigated to elucidate the contribution of the chlorine compounds to the interstellar and ionosphere chemistry. 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. In solid Ne, the HCl^+ complex with O_2 was observed by Forney et al. [8]. Upon the visible light irradiation of the matrix, the charge transfer reaction occurred followed by the dissociation into HCl and O_2^+ . However, the molecular structures of the $(O_2-HCl)^+$ complexes are not known yet.

In this letter the properties of the $(O_2-HCl)^+$ complexes have been investigated to elucidate the ion-dipole potential. Due to the small difference in their ionization potentials a plus charge may accommodate both on O_2 and HCl. Therefore, we will consider the complex both in the doublet and quartet states.

2. Method of calculation

Geometry optimizations were performed using the coupled cluster theory with single and double substitutions (CCSD). 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 aug-cc-pVDZ. Harmonic vibrational frequency calculation was performed to confirm the predicted structures as local minima and to elucidate zero-point vibrational

energy corrections (ZPE). Analysis of the charge distribution and charge-transfer processes was performed using the natural bond orbital (NBO) partitioning scheme [9]. The basis set superposition error (BSSE) was calculated according to the counterpoise (CP) method proposed by Boys and Bernardi [10]. All calculations were performed using Gaussian 03W [11]. The degree of spin contamination was monitored. For the doublet and quartet systems, the $\langle s^2 \rangle$ values did not exceed 0.7515 and 3.7515, respectively. The wavefunctions were not significantly contaminated by higher order spin states.

3. Results and discussion

3.1. Geometry and charge distribution of the complexes

Bond lengths of monomers, HCl, HCl⁺, O₂ and O₂⁺ are given in Table 1. The calculated values are in good agreement with experimental ones [12-14]. The structures of all stationary points are shown in Figure 1. Table 2 lists the corresponding optimized geometry parameters of complexes. A complex in the doublet state has non-planar structure while complexes in the quartet state have planar structures. A dihedral angle $\phi_{\text{H1Cl2O3O4}}$ of the doublet complex is calculated to be 120.1 degree at the CCSD/6-311++G(2d,2p) level. The planar structure is calculated as a transition state. The H1-Cl2 and O3-O4 bond lengths are lengthened by 0.014 and 0.023 Å as compared with those of HCl and O₂⁺ monomers, respectively. In the parallel quartet complex, the H1-Cl2 bond length is shortened by 0.005 Å from that of HCl⁺ while the O3-O4 bond length is lengthened by 0.012 Å from that of O₂. Contrary to this complex, in the bent quartet complex the H1-Cl2 bond length is lengthened by 0.051 Å as compared with that of HCl⁺. There is almost no change in the O3-O4 bond length. Table 3 gives the natural atomic charges (q) and the changes in natural atomic charges (Δq) for the complexes

calculated with the 6-311++G(2d,2p) basis set. The plus charge is mainly localized in O₂ and HCl moieties in the doublet and quartet states, respectively. Therefore, the changes in atomic charges are compared from those of O₂⁺ and HCl for the doublet complex and O₂ and HCl⁺ for the quartet complexes. In ²(O₂-HCl)⁺, the negativity of the Cl atom and the positivity of the O atoms decrease. In parallel ⁴(O₂-HCl)⁺, the Cl and O4 atoms show the opposite changes in the charges. In bent ⁴(O₂-HCl)⁺, the positivity of the Cl atom decreases while the in-contact O3 and O4 gain the negative and positive charges, respectively. The net charge transfer (CT) from HCl to O₂⁺ was evaluated to be 195.8 me for ²(O₂-HCl)⁺ and from O₂ to HCl⁺ to be 77.4 and 75.6 me for parallel and bent ⁴(O₂-HCl)⁺, respectively.

(Fig. 1, Tables 1-3)

Dipole moments of HCl and HCl⁺ are calculated to be 1.15 and 1.52 D with the 6-311++G(2d,2p) basis set. Complexation gave dipole moments of 2.94, 4.74 and 3.65 D for ²(O₂-HCl)⁺, parallel ⁴(O₂-HCl)⁺ and bent ⁴(O₂-HCl)⁺ complexes, respectively.

3.2. Interaction energy of the complexes

Table 4 shows the total energies, zero-point energies and relative energies calculated at the CCSD(T) level including BSSE correction for complexes. The O₂ + HCl⁺ lies higher in energy than the O₂⁺ + HCl. The interaction energy to form the doublet complex is calculated to be -13.2 and -14.2 kcal mol⁻¹ at the CCSD(T)/6-311++G(2d,2p) and CCSD(T)/aug-cc-pVDZ levels, respectively. The interaction energy of the ²(O₂-HCl)⁺ complex is much greater than those of the ⁴(O₂-HCl)⁺ complexes. For the quartet complexes, bent ⁴(O₂-HCl)⁺ is predicted to be more stable than parallel ⁴(O₂-HCl)⁺.

(Table 4)

3.3. Vibrational spectra

Table 5 shows the calculated vibrational frequencies, infrared intensities and assignment. For ${}^2(\text{O}_2\text{-HCl})^+$, the highest vibrational frequency corresponds to the H-Cl stretching. The frequency is red-shifted from that of the isolated monomer by 118.4 and 112.7 cm^{-1} with the 6-311++G(2d,2p) and aug-cc-pVDZ basis sets, respectively. This is in agreement with the fact that the H-Cl bond length is lengthened. The O-O stretching vibrational frequency undergoes large red-shift of 275.2 cm^{-1} at the CCSD/6-311++G(2d,2p) level and gains in intensity. For parallel ${}^4(\text{O}_2\text{-HCl})^+$, the H-Cl stretching vibrational frequency is slightly blue-shifted while the O-O stretching vibrational frequency is red-shifted with respect to that of monomers. These changes correspond to the changes in the bond lengths. The vibrational frequencies and intensities of bent ${}^4(\text{O}_2\text{-HCl})^+$, show the typical properties for the proton bound complex [15]. The H-Cl stretching vibration is largely red-shifted in frequency and gains in intensity.

(Table 5)

It is interesting to compare the calculated frequencies with observed ones. For comparison, the scale factors for monomer HCl and O_2 vibrations were determined to be 0.978 and 0.949, respectively using the observed values $\nu_{\text{HCl}}^{\text{exp}} = 2899.6 \text{ cm}^{-1}$ and $\nu_{\text{O}_2}^{\text{exp}} = 1554 \text{ cm}^{-1}$ in solid Ne [8,16]. Based on the scale factors, the calculated H-Cl and O-O stretching vibrational frequencies for the complexes were scaled. The scaled frequencies for the H-Cl and O-O vibrations are 2784 and 1624 cm^{-1} , 2610 and 1479 cm^{-1} , and 1927 and 1534 cm^{-1} for ${}^2(\text{O}_2\text{-HCl})^+$, parallel ${}^4(\text{O}_2\text{-HCl})^+$ and bent ${}^4(\text{O}_2\text{-HCl})^+$, respectively. In solid Ne, the $\text{O}_2\text{-HCl}^+$ complex showed the peaks at 2720 and 1574.9 cm^{-1} in the infrared spectrum. Compared with the results of the present calculation, ${}^2(\text{O}_2\text{-HCl})^+$ complex would be formed in solid Ne.

3.4. NBO analysis

To clarify the nature of the complexation, NBO analysis was carried out. Due to the close values of the ionization potential of O₂ (12.0697 eV [17]) and HCl (12.79 eV [18]), large interactions between the electron donor and acceptor orbitals will be expected for the (O₂-HCl)⁺ complex. Table 6 gives the second-order perturbation energies ($E^{(2)}$) calculated using the 6-311++G(2d,2p) basis set. The distinctive intermolecular CT interactions are $n_{3\text{ Cl}} \rightarrow \pi_{1\text{ O}_3\text{O}_4}^*$ and $n_{2\text{ Cl}} \rightarrow \pi_{1\text{ O}_3\text{O}_4}^*$ for ²(O₂-HCl)⁺. The $\pi_{1\text{ O}_3\text{O}_4}^*$ and $\pi_{2\text{ O}_3\text{O}_4}^*$ orbitals correspond to the π_{g2p} molecular orbitals of monomer O₂ molecule. Mainly due to these CTs, $\pi_{\text{O}_3\text{O}_4}^*$ orbitals gain the population leading to the bond elongation. For parallel ⁴(O₂-HCl)⁺, the $\pi_{2\text{ O}_3\text{O}_4}$ and $n_{3\text{ Cl}}$ orbitals are effectively overlapped to result in a large contribution to the CT interaction. For bent ⁴(O₂-HCl)⁺, the large CT interactions of σ_{HCl}^* with $n_{3\text{ O}_3}$, $n_{1\text{ O}_3}$ and $\pi_{2\text{ O}_3\text{O}_4}$ orbitals are predicted where $n_{3\text{ O}_3}$, $n_{1\text{ O}_3}$ and $\pi_{2\text{ O}_3\text{O}_4}$ correspond to the σ_{g2p} , σ_{u2s} and A'' π_{u2p} orbitals of the O₂ monomer, respectively. Corresponding to the above interactions, the population in the σ_{HCl}^* orbital increases by 74.3 me. The increase in electron density of the antibonding orbital leads to weakening of the H1-Cl2 bond accompanied by its elongation by 0.05 Å and large red-shift in frequency by 660 cm⁻¹.

(Table 6)

4. Summary

Weakly bound (O₂-HCl)⁺ complexes have been studied by ab initio calculations. One non-planar and two planar complexes are found in the doublet and quartet states, respectively. NBO analysis reveals that the intermolecular CTs from HCl to O₂⁺ and from O₂ to HCl⁺ take place for the doublet and quartet state complexes, respectively. Large contributions from the n_{Cl} to the $\pi_{\text{O}_3\text{O}_4}^*$ in the ²(O₂-HCl)⁺ complex, from the $\pi_{\text{O}_3\text{O}_4}$ to

the n_{Cl} in the parallel ${}^4(O_2-HCl)^+$ complex are found. For the proton bound bent ${}^4(O_2-HCl)^+$ complex, the σ orbitals as well as the π orbital of O3-O4 have contributions to CTs to the σ^*_{HCl} orbital.

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Figure Caption

Fig. 1. Optimized structures of $(\text{O}_2\text{-HCl})^+$ complexes (a) doublet, (b) parallel quartet and (c) bent quartet calculated at the CCSD level of theory. Intermolecular distances are denoted in Å for 6-311++G(2d,2p) (upper) and aug-cc-pVDZ (lower) calculations.

Table 1

Monomer bond lengths in Å calculated at the CCSD level.

Species	6-311++G(2d,2p)	aug-cc-pVDZ	exp
HCl	1.272	1.291	1.27460 ^a
HCl ⁺	1.313	1.330	1.3152 ^b
O ₂	1.207	1.211	1.20739 ^a
O ₂ ⁺	1.114	1.120	1.1164 ^c

^a Ref. [12]^b Ref. [13]^c Ref. [14]

Table 2

Geometry parameters of the $(\text{O}_2\text{-HCl})^+$ complexes calculated at the CCSD level.

Parameter ^a	$^2(\text{O}_2\text{-HCl})^+$		Parallel $^4(\text{O}_2\text{-HCl})^+$		Bent $^4(\text{O}_2\text{-HCl})^+$	
	6-311++G(2d,2p)	aug-cc-pVDZ	6-311++G(2d,2p)	aug-cc-pVDZ	6-311++G(2d,2p)	aug-cc-pVDZ
r_{H1Cl2}	1.286	1.304	1.308	1.325	1.364	1.386
r_{O3O4}	1.138	1.143	1.219	1.223	1.207	1.212
r_{Cl2O3}	2.434	2.433	2.674	2.652	2.975	2.969
r_{Cl2O4}	3.106	3.097	2.754	2.703	3.836	3.765
r_{H1O3}	2.886	2.919	2.670	2.655	1.616	1.588
θ_{Cl2H1O3}					174.1	174.0
θ_{H1O3O4}					125.2	119.9
θ_{H1Cl2O3}	96.9	98.2	75.7	75.7		
θ_{Cl2O3O4}	116.0	115.2	80.7	79.1		
$\phi_{\text{H1Cl2O3O4}}$	120.1	116.7	180.0	180.0	0.0	0.0
<i>A</i>	63.94521	62.31159	37.51779	37.04930	97.58470	78.66015
<i>B</i>	3.81936	3.83316	4.26489	4.39214	2.57870	2.64194
<i>C</i>	3.66329	3.67638	3.82956	3.92664	2.51231	2.55609

^a Bond lengths, angles and rotational constants are in Å, degrees and GHz, respectively.

Table 3

Natural atomic charges (e) of the $(\text{O}_2\text{-HCl})^+$ complexes and changes (me) in values from isolated monomers.^a

Atom	$^2(\text{O}_2\text{-HCl})^+$		Parallel $^4(\text{O}_2\text{-HCl})^+$		Bent $^4(\text{O}_2\text{-HCl})^+$	
H1	+0.2955	(+47.2)	+0.3229	(+2.8)	+0.3280	(+7.9)
Cl2	-0.0997	(+148.6)	+0.5997	(-80.2)	+0.5964	(-83.5)
O3	+0.4096	(-90.4)	-0.0089	(-8.9)	-0.1744	(-174.4)
O4	+0.3946	(-105.4)	+0.0863	(+86.3)	+0.2500	(+250.0)

^a Changes in natural atomic charges from those of O_2^+ and HCl , and O_2 and HCl^+ for doublet and quartet complexes are given in parentheses, respectively.

Table 4

Total energies (hartrees), zero-point energy (ZPE) corrections (hartrees) and relative energies (kcal mol^{-1}) calculated at the CCSD(T) level.

	6-311++G(2d,2p)			aug-cc-pVDZ		
	Total energy	ZPE ^a	Relative energy	Total energy	ZPE ^b	Relative energy
$\text{O}_2^+ + \text{HCl}$	-609.9289495	0.011282	0	-609.8544829	0.011397	0
$\text{O}_2 + \text{HCl}^+$	-609.9095124	0.009726	11.2	-609.8340807	0.009855	11.8
${}^2(\text{O}_2\text{-HCl})^+$	-609.9513647	0.012715	-13.2	-609.8785146	0.012832	-14.2
Parallel ${}^4(\text{O}_2\text{-HCl})^+$	-609.9154140	0.011612	8.7	-609.8415408	0.011635	8.3
Bent ${}^4(\text{O}_2\text{-HCl})^+$	-609.9194965	0.011150	5.8	-609.8454379	0.011302	5.6
${}^3\text{HO}_2^+ + \text{Cl}$	-609.8762743	0.013395	34.4	-609.8025264	0.013181	33.7
${}^1\text{HO}_2^+ + \text{Cl}$	-609.8661830	0.014325	41.3	-609.7922446	0.014140	40.8

^a Calculated at the CCSD/6-311++G(2d,2p) level.

^b Calculated at the CCSD/aug-cc-pVDZ level.

Table 5

Unscaled harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) calculated at the CCSD level.

Assignment	6-311++G(2d,2p)		aug-cc-pVDZ	
	ν	I	ν	I
$^2(\text{O}_2\text{-HCl})^+$				
H-Cl stretch	2846.7	222.0	2876.5	215.9
O-O stretch	1711.8	1222.1	1737.0	1134.5
H-Cl bend	445.1	47.7	442.0	46.0
H-Cl bend	307.8	29.9	306.0	31.7
Intermolecular stretch	181.7	71.2	182.3	63.0
Torsion	88.1	38.7	88.7	39.9
Parallel $^4(\text{O}_2\text{-HCl})^+$				
H-Cl stretch	2668.3	229.3	2721.1	216.8
O-O stretch	1558.9	65.0	1551.2	74.3
H-Cl in-phase in-plane bend	327.9	64.5	335.7	68.5
H-Cl out-of-phase in-plane bend	153.2	18.4	166.1	23.1
Intermolecular stretch	121.4	19.0	146.0	13.6
H-Cl out-of-plane bend	64.3	57.2	40.9	58.6
Bent $^4(\text{O}_2\text{-HCl})^+$				
H-Cl stretch	1970.8	2438.6	1964.6	2607.4
O-O stretch	1616.1	55.8	1606.6	61.9
H-Cl in-phase in-plane bend	643.1	52.1	657.1	53.7
H-Cl out-of-plane bend	558.6	52.7	545.2	51.8
Intermolecular stretch	211.9	84.3	223.0	96.4
Out-of-phase in-plane bend	96.6	16.0	110.5	12.3
Monomer				
HCl	2965.1	36.4	2989.3	29.0
HCl ⁺	2631.5	252.0	2684.8	240.6
O ₂	1637.9	0.0	1641.4	0.0
O ₂ ⁺	1987.0	0.0	2013.4	0.0

Table 6

Charge transfer interaction in the $(\text{O}_2\text{-HCl})^+$ complexes.

Parameter	$E^{(2)} / \text{kcal mol}^{-1}$
Doublet	
$n_{3 \text{ Cl}} \rightarrow \pi^*_{1 \text{ O}_3\text{O}_4}$	22.66
$n_{2 \text{ Cl}} \rightarrow \pi^*_{1 \text{ O}_3\text{O}_4}$	10.99
$n_{2 \text{ Cl}} \rightarrow \pi^*_{2 \text{ O}_3\text{O}_4}$	5.42
Parallel $^4(\text{O}_2\text{-HCl})^+$	
$\pi_{2 \text{ O}_3\text{O}_4} \rightarrow n_{3 \text{ Cl}}$	21.92
Bent $^4(\text{O}_2\text{-HCl})^+$	
$n_{3 \text{ O}_3} \rightarrow \sigma^*_{\text{HCl}}$	23.22
$n_{1 \text{ O}_3} \rightarrow \sigma^*_{\text{HCl}}$	14.25
$\pi_{2 \text{ O}_3\text{O}_4} \rightarrow \sigma^*_{\text{HCl}}$	6.19

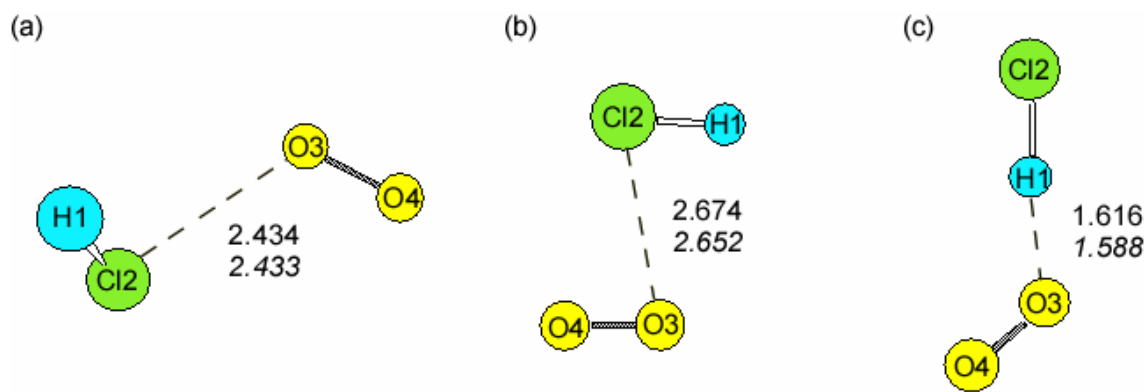


Fig. 1. N. Tanaka et al. "Ab initio study on the $(\text{O}_2\text{-HCl})^+$ complexes".