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# How is the Fluoride Ion Bound to $O_2$, $N_2$, and CO Molecules?

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Fundamental gas-phase clustering reactions for $F^-(Sol)_{n-1} + Sol = F^-(Sol)_n$ for Sol = $O_2$, $N_2$, and CO were studied by using a pulsed electron beam mass spectrometer. While the interaction of $F^-$ with $O_2$ ligands is mainly electrostatic, those with $N_2$ and CO have some contribution from charge transfer (i.e., the formation of incipient covalent bonds in the complexes $F^- \rightarrow N_2$ and $F^- \rightarrow CO$). The cluster ion $F^-(CO)_6$ was found to have an octahedral structure with equivalent $F^-\cdots CO$ bonds. $F^-(O_2)_n$ was found to involve the smallest binding energy among $F^-$ cluster ions ever reported.

## 1. Introduction

Clusters, whether neutral or ionic, are embryonic forms of matter and their physical natures and reactivities provide fundamental information in the fields of gaseous ion chemistry, nuclear physics, radiation chemistry, quantum electronics, phase transitions, crystal growth, surface science, catalysis, solution chemistry, biochemistry, etc. The thermochemical stabilities and reactivities of gas-phase cluster ions are particularly helpful in understanding the mechanisms of the complicated phenomena occurring in the multibody system.

Fluorine reacts with all the elements except $O_2$, He, $N_2$, and Ar at room temperature. $F_2$ is readily decomposed, due to its low bond energy, and yields F atoms which are extremely reactive species. The electronegativity of the F atom is the largest of all atoms. The $F^-$ ion is also a highly reactive nucleophilic reagent and generally forms strong bonds with many Lewis acids in the gas phase.[1] The bond energies of $F^-$ (to a wide variety of Lewis acids including oxides, fluorides, oxofluorides, and alkyl derivatives of boron, carbon, silicon, phosphorus, and sulfur) have already been measured.[2−12] Recently, the interaction of $F^-$ with $CF_4$, $SF_6$, and $NF_3$ is found to be mainly electrostatic.[10−12]

In the present work, the bond strengths of the cluster ions of $F^-$ with diatomic molecules, $O_2$, $N_2$, and CO have been measured by observing these clustering reactions 1−3.

$$F^-(O_2)_{n-1} + O_2 = F^-(O_2)_n \qquad (1)$$

$$F^-(N_2)_{n-1} + N_2 = F^-(N_2)_n \qquad (2)$$

$$F^-(CO)_{n-1} + CO = F^-(CO)_n \qquad (3)$$

It is surprising that these fundamental cluster ions have not been studied yet. It is an intrinsic question whether $F^-$ can be bound to each of three diatomic molecules in the measurable scale under the nominal experimental conditions. Lone-pair electrons of $N_2$ and CO might reject cluster formation with $F^-$. It was found that slight charge transfer takes place in the complexes of $F^-\cdots N_2$ and $F^-\cdots CO$ (i.e., the formation of incipient covalent bonds in these complexes).

## 2. Experiment and Theory

The experiments were made with a pulsed electron-beam high-pressure mass spectrometer.[13,14] Briefly, the major gas, $O_2$, $N_2$, or CO, was purified by passing it through a dry ice−acetone cooled 5 Å molecular sieve trap. Electron capture agent $NF_3$ producing $F^-$ was introduced into ~3 Torr major gas through a flow-controlling stainless steel capillary. The pressures of $NF_3$ were ~0.8, ~45, and ~50 mTorr for $O_2$:$NF_3$, $N_2$:$NF_3$, and CO:$NF_3$ systems, respectively. Because the bond energies of $F^-(O_2)_n$ are weaker than those of $F^-(NF_3)_n$,[11] the pressure of $NF_3$ in $O_2$ major gas must be reduced to lower than 1 mTorr in order to suppress the formation of $F^-(NF_3)_n$. With a decrease of the ion source temperature, charging of the ion source was observed below ~150 K. The charging effect could be moderately reduced by coating the ion source with colloidal graphite (aquadag). The charging problem was most serious for the $N_2$/$NF_3$ system. This made the measurements of the equilibrium constants for reaction 2 below 130 K not possible.

Geometries of $F^-(N_2)_n (n = 1, 2)$ and $F^-(CO)_n (n = 1-6)$ clusters were optimized (without symmetry constraint and all electrons included) at the MP2 level of theory using spliced basis sets(6-311+G** on $F^-$;3-21G* on N, C, and O) under the GAUSSIAN 94[15] system of programs. Vibrational frequency calculations, carried out at the same level of theory, were used to characterize the stationary points. The zero-point vibrational energy (ZPE) was scaled down by 0.92 as a component of the enthalpy. Binding energies of $n = 1$ and 2 were computed at MP4(full)/6-311+G* level of theory using the MP2 geometries obtained. The final enthalpies composed

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**TABLE 1: Thermochemical Data, $\Delta H^\circ_{n-1,n}$ in kcal/mol and $\Delta S^\circ_{n-1,n}$ in cal/(mol K), of the Gas-Phase Clustering Reactions $F^-(O_2)_{n-1} + O_2 = F^-(O_2)_n$, $F^-(N_2)_{n-1} + N_2 = F^-(N_2)_n$, and $F^-(CO)_{n-1} + CO = F^-(CO)_n$**[a]

| | $F^-(O_2)_{n-1,n}$ | | $F^-(N_2)_{n-1,n}$ | | $F^-(CO)_{n-1,n}$ | |
|---|---|---|---|---|---|---|
| $n$ | $-\Delta H^\circ_{n-1,n}$ | $-\Delta S^\circ_{n-1,n}$ | $-\Delta H^\circ_{n-1,n}$ | $-\Delta S^\circ_{n-1,n}$ | $-\Delta H^\circ_{n-1,n}$ | $-\Delta S^\circ_{n-1,n}$ |
| 1 | 2.6 $[\underline{2.85}]^c$<br>$[3.37]^c$ | 15 | 4.5 $[\underline{3.41}]^c$<br>$[3.93]^c$ | 19 | 9.8 $[\underline{8.44}]^c$<br>$[8.96]^c$ | 18 |
| 2 | 2.5 $[\underline{2.79}]^c$<br>$[3.83]^c$ | 16 | 2.8 $[\underline{3.46}]^c$<br>$[4.50]^c$ | 16b | 6.3 $[\underline{4.00}]^c$<br>$[5.04]^c$ | 23 |
| 3 | ~1.8 | ~14 | | | 5.5 | 23 |
| 4 | | | | | 5.0 | 25 |
| 5 | | | | | 2.9 | 17 |
| 6 | | | | | 2.5 | 17 |

[a] The experimental errors for $\Delta H^\circ$ and $\Delta S^\circ$ may be within ±0.2 kcal/mol and ±2 cal/(mol K), respectively. [b] Entropy value assumed. [c] In square brackets, present theoretical binding energies at $T = 0$ K (with underlines) and $T = 150$ K (without underlines). Those energies are composed of differences of MP4(full)/6-311+G* electronic energies and MP2/GEN (or ROHF/GEN) zero-point vibrational energies scaled by 0.92 and temperature ($T = 130$ K) corrections (for $n = 0 \rightarrow 1$, $-2RT$, and for $n = 1 \rightarrow 2$, $-(^7/_2)\ RT$, respectively).

of MP4 and scaled ZPEs were corrected to T = 130 K for the clustering reaction.

On the other hand, geometries of $F^-(O_2)_n$ ($n = 1, 2$) were optimized at ROHF level of theory using the spliced basis set. Spin multiplicities are triplet for $n = 1$ and quintet for $n = 2$, respectively. MP2 wave functions suffer heavy spin contaminations (even if after spin annihilation) and give unreasonable geometries. There are some reasons for adopting the above computational method on those three clusters, aside from the limitation imposed by our computing resources. First, the geometry optimization results at MP2(full)/6-311+G** give poor geometries and indicated two or more imaginary frequencies where there should be none. There seems to be an overcompensation effect of the 6-311+G** on the N, C, and O atoms. To address this situation, we opted for the use of the spliced basis set. Second, G2 calculations yielded very poor results because of the presence of some components that do not have diffuse functions on them. We noted that diffuse functions on $F^-$ are very crucial in obtaining plausible structures of the clusters. Third, there is only a small change of structures between 3-21G* and 6-31G* on C, N, and O. For this reason, we employed the mixed(spliced) basis set of 6-311+G** (on F atom) and 3-21G* (on O atom) in the MP2 scheme. All calculations were performed on the CONVEX SPP/1200/XA computer at the Information Processing Center of Nara University of Education.

## 3. Results and Discussion

The results of the experimentally measured equilibrium constants for reactions 1−3 are displayed in the van't Hoff plots in Figure 1. In Table 1, the enthalpy and entropy changes obtained from the van't Hoff plots are summarized.

In Figure 1a for reaction 1, the van't Hoff plots with $n = 1$ and 2 are close to each other and there appears a gap between $n = 2$ and 3. This indicates that the fluoride ion $F^-$ is almost equivalently coordinated by two $O_2$ ligands. This dimer complex, as a core, is further coordinated by $n \geq \sim 3$ solvent molecules. A similar trend is observed in the clustering reactions of $F^-$ with $N_2O$,[9] $CF_4$,[10] and $NF_3$,[11] in which the nature of bonding in the cluster ions is mainly electrostatic. Actually, the bond energies of $F^-(O_2)_n$ ($\leq 2.6$ kcal/mol) are close to the heat of vaporization of liquid $O_2$ (1.63 kcal/mol) and are of the order of the electrostatic interaction. Among the diatomic cluster ions of $F^-(Sol)_n$ (for Sol = $O_2$, $N_2$, and CO), the bond energies of $F^-(O_2)_n$ are the smallest. This may be due to the exchange repulsion between the electron-rich $O_2$ molecule with the closed-shell $F^-$. Apparently, the magnitude of the charge transfer between $F^-$ and the $\pi^*$ SOMO (singly occupied molecular orbital) of $O_2$ with the triplet spin state is very small. The formation of loose bonds in $F^-(O_2)_n$ is reflected on the small values of $-\Delta S^\circ_{n-1,n}$ for $n = 1$ and 2.

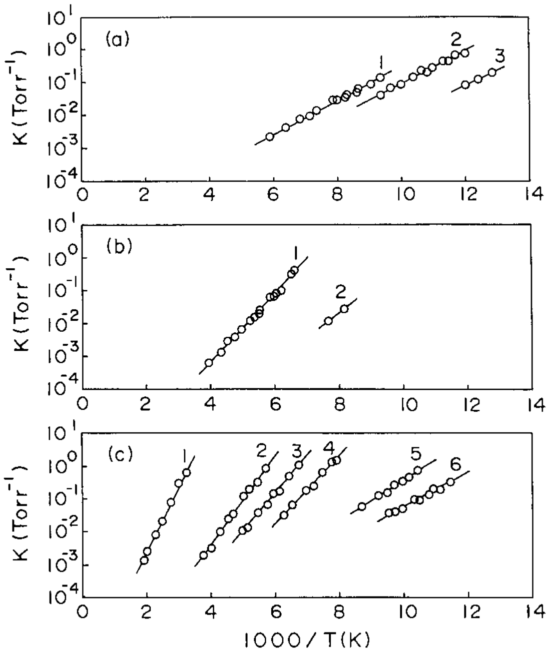


**Figure 1.** Van't Hoff plots for the clustering reactions, (a)$F^-(O_2)_{n-1} + O_2 = F^-(O_2)_n$, (b)$F^-(N_2)_{n-1} + N_2 = F^-(N_2)_n$, and (c)$F^-(CO)_{n-1} + CO = F^-(CO)_n$.

Figure 1b displays the van't Hoff plots for clustering reaction 2. A rather large gap appears between the plots with $n = 1$ and 2. In Table 1, the rapid decrease in both $-\Delta H^\circ_{n-1,n}$ and $-\Delta S^\circ_{n-1,n}$ is observed between $n = 1$ and 2. This suggests that the slight charge transfer (CT) takes place in the complex $F^- \rightarrow N_2$ and the nature of bonding becomes largely electrostatic in $F^-(N_2)_2$. Actually the bond energy of $F^-(N_2)_1$ (4.5 kcal/mol) is much larger than that of $F^-(O_2)_1$ (2.6 kcal/mol) although the polarizability of $O_2$ (1.6 Å$^3$) and $N_2$ (1.7 Å$^3$) are of the same order.

The van't Hoff plots for reaction 3 are shown in Figure 1c. Compared with Figures 1a and b, those plots are quite peculiar. The plot with $n = 1$ is isolated in the high-temperature region which is followed by the rather close three plots with $n = 2-4$. Again the gap appears between $n = 4$ and 5. The observed isolation of $n = 1$ plot at higher temperature strongly suggests the semicovalent bond formation in the $n = 1$ complex, $F^-\cdots CO$. The gap between the van't Hoff plots corresponds to the difference in the free energy changes for the formation of neighboring cluster ions. From the relationship, log $K$ =

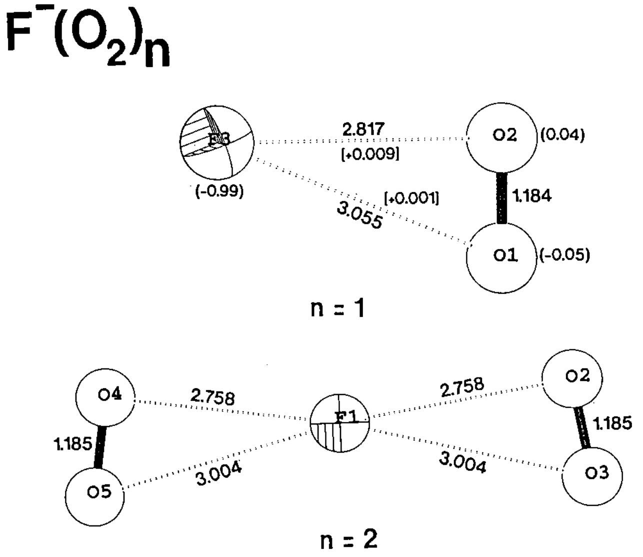


**Figure 2.** Geometries of $F^-(O_2)_n$ ($n = 1$ and 2) with the MP2/spliced basis set. Distances are in angstroms. Values in parentheses of $n = 1$ denote net atom electronic charges (positive, cationic), and those in square brackets stand for atom−atom bond populations (negative, antibonding).

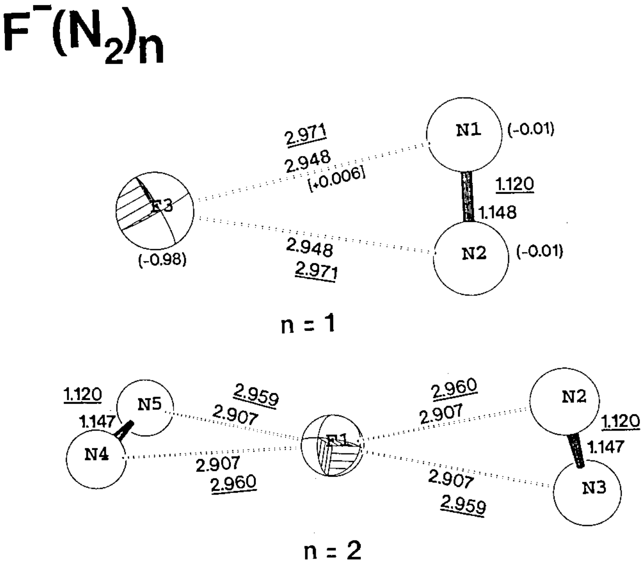


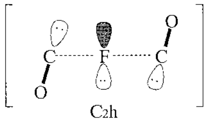
**Figure 3.** Geometries of $F^-(N_2)_n$ ($n = 1$ and 2) with the MP2/spliced basis set. Distances with underlines were obtained with MP2(full)/6-311+G**.

$-\Delta H°/2.3RT + \Delta S°/2.3R$, the large gap may be attributed to the decrease in the inclination of the van't Hoff plots (i.e., decrease in bond energies) and/or to the large negative shift of the van't Hoff plots in the log $K$ axis (i.e., large entropy loss). From Table 1, one can see that the large free energy gap between $n = 1$ and 2 can be factored into the sharp decrease in $-\Delta H°_{n-1,n}$ (9.8 → 6.3 kcal/mol) and also into the increase in $-\Delta S°_{n-1,n}$ (18 → 23 eu) with $n = 1 \rightarrow 2$. That is, the cluster growth of $F^-(CO)_1 \rightarrow F^-(CO)_2$ accompanies the considerable entropy loss despite the decrease in bond energies. This is due to the equally strong bond formation in OC···F⁻···CO (see the latter section). As the entropy changes ($-\Delta S°_{n-1,n}$), continuing to increase with $n$ up to 4 and decrease between $n = 4$ and 5, it seems likely that the number of ligand CO molecules up to 4 belong to the first shell, while the second shell starts with $n = 5$. Interestingly, however, theoretical calculations predicted that the ligands up to $n = 6$ belong to the first shell as described later. With $n = 4 \rightarrow 5$, the structure of the whole cluster becomes loosened and the entropy-favored structure comes into play (see Table 1).

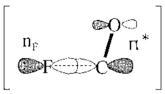
Geometries of the present cluster ions are examined theoretically. Figure 2 shows geometries of $F^-(O_2)_n$. In accord with the small binding energies, distances between $F^-$ and $O_2$ are quite large in $n = 1$ and 2. In $F^-(O_2)_1$, the oxygen molecule is polarized ($O^{\delta+} = O^{\delta-}$). A very small atom−atom electron population [+0.009] is accumulated in the $F^3 \cdots O^2$ region. $F^-(O_2)_1$ is of a slightly asymmetric geometry, while $F^-(O_2)_2$ is of $C_2$ symmetry. Figure 3 exhibits geometries of $F^-(N_2)_n$ which have high-symmetry point groups $C_{2v}$ for $n = 1$ and $D_{2d}$ for $n = 2$. They also correspond to long-range interactions. The extent of charge transfer of $F^- \rightarrow N_2$, $F^-(-0.98)$, is slightly larger than that of $F^- \rightarrow O_2$, $F^-(-0.99)$. For both $F^-(O_2)_n$ and $F^-(N_2)_n$, the distances between $F^-$ and diatomic molecules of $n = 2$ are smaller than those of $n = 1$. Exchange repulsions are relaxed in $n = 2$ owing to the dual charge transfer.

The geometries of $F^-(CO)_n$ are displayed in Figure 4. The $F^- \cdots C$ distances are 2.1 − 2.3 Å, while the $F^- \cdots O$ ones are 2.6−2.7 Å in $n = 1-6$. Although the experimental energy gap between $n = 1$ and 2 is large, as shown in Table 1, the geometry of $F^-(CO)_1$ is not so much affected by addition of the second CO molecule. The apparent gap between the falloff of $n = 1 \rightarrow 2$ binding energies and the symmetric geometry of $F^-(CO)_2$ may be explicable as follows. While the charge transfer, $F^- \rightarrow CO$, occurs equally in $n = 1$ and 2, the second CO molecule cannot undergo the electrostatic attraction so much as the first one. This is because $F^-$ is not a complete monoanion in $F^-(CO)_1$ anymore. From $n = 4$ to $n = 5$, the steric crowd by CO ligands increases. The increase corresponds to the large falloff in $n = 4 \rightarrow 5$. The $n = 6$ geometry is almost perfectly hexagonal. The $n = 7$ cluster would be improbable, because there are no more directions available to the seventh CO ligand.

Isomeric structures other than those in Figure 4 are examined. First, in view of the large falloff between $\Delta H°_{0,1}$ and $\Delta H°_{1,2}$ $F^- \cdots CO \cdots CO$ structures have been explored, but there are no stable isomers of the CO−CO interaction.[16] Second, a $C_{2h}$ symmetry structure has been examined and was also found to be absent.



Coplanarity of lone-pair orbitals gives rise to instability. Thus the twisted geometry of $n = 2$, in Figure 4, is more favorable than the one with $C_{2h}$ symmetry. Third, a tetrahedral-type geometry of $F^-(CO)_4$ has been checked, but the $T_d$ type geometry cannot be obtained. According to the orbital mixing of a 2p atomic orbital of $F^-$, $\Pi_{CO}$, and $\Pi^*_{CO}$, the charge-donating FMO (frontier molecular orbital) is $n_F$.



The $\pi^*$ MO of the second CO molecule interacts also with $n_F$ effectively. This is the reason C···F···C should be linear. The linearity is retained even in the $n = 5$ geometry. Therefore, the fifth CO ligand stays at a top ("odd") position of the $F^-(CO)_4$ square. Fourth, a trigonal bipyramidal ($D_{3h}$ symmetry like) structure of $F^-(CO)_5$ has been scrutinized, but it is isomerized spontaneouly to that in Figure 4 during geometry optimization calculation.

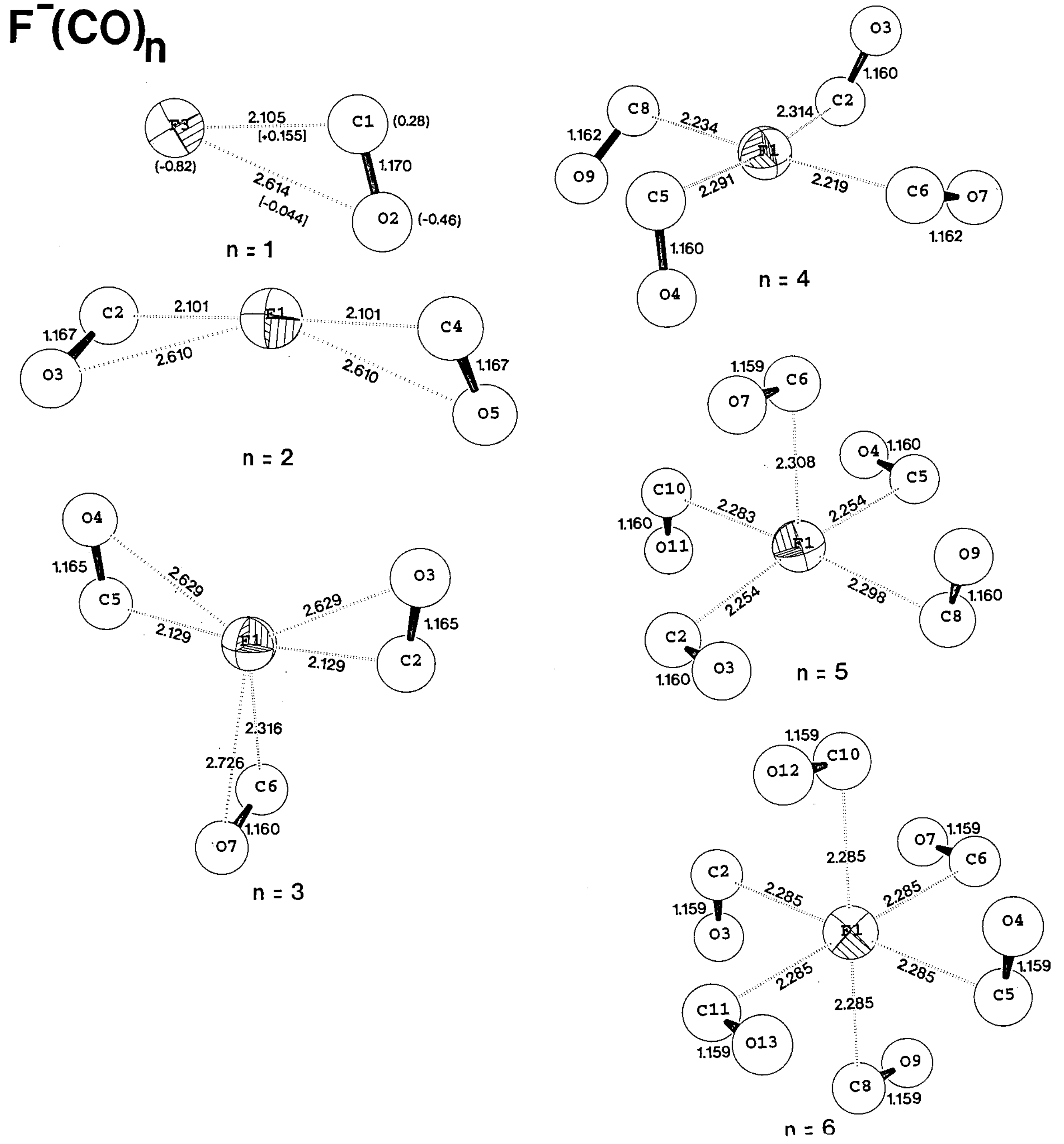
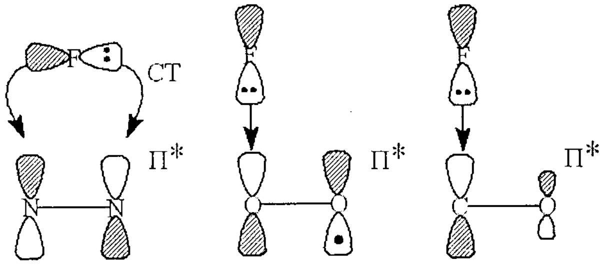


**Figure 4.** Geometries of $F^-(CO)_n$ ($n = 1-6$) with the MP2/spliced basis set.

The charge transfer of $F^- \rightarrow CO$ is of much larger magnitude than that of $F^- \rightarrow O_2$ and $F^- \rightarrow N_2$, and a semicovalent bond is formed in $F^3\cdots C^1$ as is shown both by the short distance (2.105 Å) and by the large atom−atom bond population [+0.155]. Noteworthy is the antibonding character between $F^3$ and $O^2$ atoms. In contrast with the binary attraction mode in $F^-\cdots O_2$ and $F^-\cdots N_2$, the $F^-\cdots CO$ bond is composed of an entire one-center attraction.

While $F^-(N_2)_1$ is of $C_{2v}$ symmetry, $F^-(O_2)_1$ and $F^-(CO)_1$ are of $C_s$ symmetry. The geometry of $F^-(O_2)_1$ lies midway between the symmetric one of $F^-(N_2)_1$ and the asymmetric one of $F^-(CO)_1$. In $F^-(N_2)_1$, the antisymmetric CT interaction leads to the $C_{2v}$ geometry. In $F^-(O_2)_1$, the $\pi^*$ MO (SOMO) has an electron and the antisymmetric interaction suffers the exchange repulsion between the $F^-$ lone-pair electrons and the $\pi^*$ electron. Through the one-site type CT interaction, the $\pi^*$ electrons escapes from the CT interaction region. In $F^-(CO)_1$, $F^-$ is linked to the carbon atom to form an effective CT.

**SCHEME 1: The charge Transfer (CT) from the Lone-Pair Orbital of Fluoride Ion to Π* MO of $N_2$, $O_2$, and CO**



Theoretical binding energies of $F^-(O_2)_n$, $F^-(N_2)_n$, and $F^-(CO)_n$ ($n = 1$ and 2) are in good agreement with the experimental data in Table 1. Since electronic energies are small, temperature corrections contribute rather largely to binding energies. The apparent problem, $-\Delta H°_{0,1}$ (3.37 kcal/mol) < $-\Delta H°_{1,2}$ (3.83

kcal/mol), arises from those corrections in the $F^-(O_2)_{n-1,n}$ cluster. The stabilizing component, the CT, is in delicate balance against the destabilizing effect of exchange repulsion. In particular, $F^-(O_2)_n$ and $F^-(N_2)_n$ have such critical counterbalance. Although very slight, the present computational method would overestimate the exchange repulsion in particular for the $F^-(N_2)_{n-1,n}$ cluster. As a result, the intermolecular distances are smaller and binding energies are larger in $F^-(O_2)_2$ and $F^-(N_2)_2$ than those of $F^-(O_2)_1$ and $F^-(N_2)_1$, respectively.

Clustering entropies are difficult to obtain theoretically. This is because the present weakly interacting systems have very shallow energy potentials (small binding energies) and the anharmonicity of vibrations is significant for obtaining the vibration entropies. Therefore, experimental entropy changes are discussed. In the $F^-(O_2)_{n-1,n}$ cluster, the $\Delta H°_{0,1}$ value is almost equal to the $\Delta H°_{1,2}$ one, which corresponds to the result that the value of $\Delta S°_{0,1}$ is to that of $\Delta S°_{1,2}$. In the $F^-(CO)_n$ cluster, the $-\Delta S°_{0,1}$ value (=18 eu) is too small in view of $-\Delta H°_{0,1} = 9.8$ kcal/mol. The reason is not clear. There is a fall off of binding energies between $n = 4$ and 5. This fall off is also shown by entropy changes ($-25 \rightarrow -17$ eu) and the geometry of the axial coordination of the fifth CO molecules (Figure 4).

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## References and Notes

(1) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(2) McMahon, T. B.; Northcott, C. J. *Can. J. Chem.* **1978**, *56*, 1069.

(3) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944.

(4) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

(5) Hiraoka, K.; Mizuse, S. *J. Chem. Phys.* **1987**, *87*, 3647.

(6) Hiraoka, K.; Mizuse, S.; Yamabe, S. *J. Phys. Chem.* **1988**, *92*, 3943.

(7) Hiraoka, K.; Yamabe, S. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 133.

(8) Hiraoka, K.; Fujimaki, S.; Aruga, K,; Yamabe, S. *Chem. Phys. Lett.* **1993**, *208*, 491.

(9) Hiraoka, K.; Aruga, K.; Fujimaki, S.; Yamabe, S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 58.

(10) Hiraoka, K.; Nasu, M.; Fujimaki, S.; Ignacio, E. W.; Yamabe, S. *Chem. Phys. Lett.* **1995**, *245*, 14.

(11) Hiraoka, K.; Nasu, M.; Fujimaki, S.; Yamabe, S. *J. Phys. Chem.* **1995**, *99*, 15822.

(12) Hiraoka, K.; Shimizu, A.; Minamitsu, A.; Nasu, M.; Fujimaki, S.; Yamabe, S. *Chem. Phys. Lett.* **1995**, *241*, 623.

(13) Kebarle, P. In *Techniques for the Study of Ion-Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley: New York, 1971; p 221.

(14) Hiraoka, K.; Yamabe, S. In *Dynamics of Excited molecules*; Kuchitsu, K., Ed.; Elsevier: Amsterdam, 1994; p 399.

(15) *Gaussian 94*, Revision B.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Ciosiowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision B.1; Gaussian, Inc.; Pittsburgh, PA, 1995.

(16) In our previous work (Hiraoka, K.; Mizuse, S.; Yamabe, S. *J. Phys. Chem.* **1988**, *92*, 3943), the stability and structure of the $F^-(H_2O)_n$ cluster were examined. Binding energies, $-\Delta H°_{0,1} = 23.3$ kcal/mol and $-\Delta H°_{1,2} = 19.2$ kcal/mol, were obtained. In spite of this large fall off(∼4 kcal/mol), the $F^-(H_2O)_2$ cluster had a $C_2$ symmetric structure.