J. Phys. Chem. A **2003,** *107,* 2505−2515

Density Functional Study of the Interaction of H_2, N_2, O_2, CO, and NO Diatomic Molecules with H^-, Li^-, and F^- Anions. Prediction of a New Type of Anion Cluster

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Received: May 21, 2002; In Final Form: January 15, 2003

The interaction of the diatomic molecules, H_2, N_2, O_2, CO, and NO, with the anions, H^-, Li^-, and F^- is theoretically examined using a density functional method (B3LYP). It was found that the charge transfer from the anions to diatomic molecules easily occurs and overcomes the electronic repulsion to form the anion clusters. The clustering of the H_2 around H^- is controlled by the novel conjugation through the σ^* orbitals of the H_2 coordinated to the H^- anion center. For the other diatomic molecules, the π^* orbital plays a key role on the clustering process. The charge transfer from the H^- or Li^- to the π^* orbital of the N_2, O_2, CO, and NO induces the attractive interaction between the π^* orbitals and generates the anion cluster with a pentagonal cyclic form consisting of two diatomic molecules and one anion, which is unknown so far according to our knowledge. The geometric structure of the anion cluster significantly depends on the electronic nature of the anions and the diatomic molecules. The interaction in the clustering as well as the geometric structure is discussed in detail.

1. Introduction

The formation of the neutral or ion cluster of diatomic molecules, such as O_2, N_2, and CO, has been an interesting subject in gaseous ion chemistry and has also attracted much attention in the field of solution chemistry, biochemistry, and surface science, because the aggregation of the small molecule is regarded as an origin and an important initial process of the growth of gaseous bubbles in solvent, crystal, and condensed matter.

The existence of the cation cluster of N_2, O_2, and CO with proton, $H^+(B)_n$ (B = N_2, O_2, CO), is experimentally known, and the thermochemical parameter in the clustering reaction has been reported.[1] The structure and the stability of the $H^+(B)_n$ (B = N_2, O_2, CO; $n = 1-6$) cation clusters have also been theoretically examined by the Hartree−Fock (HF)−SCF and CI methods.[2] On the other hand, recently, it was experimentally revealed that the N_2, O_2, and CO molecules form the ion clusters with the F^- anion in the gas phase by Hiraoka et al. using a pulsed electron beam mass spectrometer.[3] They also theoretically examined the bonding nature between the F^- anion and the N_2, O_2, and CO molecules by the Møller−Plesset perturbation method and suggested the slight contribution of the charge transfer to the interaction in the case of the N_2 and CO molecules. However, it is very surprising that the geometric and electronic structure, stability, and the nature of the interaction of the anion cluster little examined[4] despite the fundamental information in the chemistry of the ion cluster, although several investigations have been reported for the proton clusters.[5]

In the present study, therefore, we theoretically examined the anion cluster $X^-(A)_n$ formed by the binding of the diatomic molecules A to the anion X^- by means of density functional method (B3LYP). We adopted the homonuclear (nonpolar) H_2, N_2, and O_2, and the heteronuclear (polar) CO and NO as diatomic molecule, and H^-, Li^-, and F^- as anion. Surprisingly, the homonuclear (nonpolar) H_2, N_2, and O_2 molecules as well as the heteronuclear (polar) CO and NO molecules actually readily bind to the H^-, Li^-, and F^- anions, although we tend to think that the electronic repulsion caused by the extra electron of the anion weakens the binding. The attractive interaction mainly originates from the facile charge transfer from the anion to the σ^* or π^* orbital of the diatomic molecules. Our calculations showed a new type of the anion cluster formed by this charge-transfer interaction. Following the explanation of computational procedures, the anion cluster of the H_2 is first discussed in section 3.1. The anion cluster of the homonuclear (nonploar) N_2 and O_2, and the heteronuclear (polar) CO and NO are discussed in the subsequent sections 3.2 and 3.3, respectively. Conclusions are summarized in the last section.

2. Computational Procedures

All calculations were performed using the Gaussian98 program.[6] The calculations of energetics as well as geometry optimizations were carried out at the B3LYP level of theory, which consists of a hybrid Becke + Hartree−Fock exchange and a Lee−Yang−Parr correlation functional with nonlocal corrections.[7] The basis set used is the 6-311++G** level for all the atoms, i.e., H, Li, C, N, O, and F. All equilibrium structures were optimized without any symmetry restrictions unless otherwise indicated and identified by the number of imaginary frequencies calculated from the analytical Hessian matrix. With respect to the O_2 and NO molecules, the triplet and doublet states were assumed, respectively, even in the cluster system; the unpaired electrons occupy the π^* orbitals. Accordingly, the spin multiplicities of 3, 5, and 13 were assumed in the clusters $(O_2)_n$ ($n = 1, 2, 6$) and of 2, 3, and 5 in the clusters $(NO)_n$ ($n = 1, 2, 4$), respectively. NBO analysis[8] was performed to obtain the atomic orbital (AO) population and the charge. For all the cluster systems, the energies relative to the free molecules, H_2, N_2, O_2, CO, and NO, and the free anions, H^-,

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10.1021/jp021266q CCC: $25.00

TABLE 1: Relative Energies (kcal/mol) of the Anion Clusters at the Various Levels[a]

	B3LYP/ 6-31G	B3LYP/ 6-311G	B3LYP/ 6-311G**	B3LYP/ 6-311++G**	HF/ 6-311++G**	MP2/ 6-311++G**	MP4SDTQ/ 6-311++G**	QCISD(T)/ 6-311++G**	CCSD(T)/ 6-311++G**
1a1	−12.8	−5.4	−5.8	−1.7	−0.3	−1.0	−0.9	−0.7	−0.7
1a2	−22.7	−10.5	−11.3	−3.5	−0.5	−1.8	−1.5	−1.2	−1.2
1a3	−23.0	−10.0	−10.9	−3.7	0.1	−1.9	−1.7	−1.3	−1.3
1b1	−12.6	−4.7	−3.9	−1.0	0.2	−1.0	−0.9	−0.7	−0.7
1b2	−19.0	−8.1	−6.7	−1.9	0.4	−1.8	−1.7	−1.4	−1.4
1b3	−19.0	−8.1	−6.8	−1.9	0.4	−1.8	−1.7	−1.4	−1.4
1b4	−23.8	−9.9	−8.4	−2.2	3.3	−1.9	−1.8	−1.2	−1.2
1d2	−65.2	−39.5	−29.0	−26.1	13.3	−14.9	−14.3	−12.5	−12.3
1d3	−63.5	−38.9	−28.4	−25.4	14.3	−12.6	−12.3	−11.0	−10.7
1e1	−76.8	−53.1	−41.6	−46.3	−31.4	−43.7	−39.9	−38.7	−38.9
1e3	−114.1	−89.2	−74.2	−70.0	−14.1	−66.8	−62.6	−55.5	−55.5
1e4	−111.6	−87.7	−71.8	−67.8	−37.9	−46.5	−42.6	−47.2	−47.3

[a] The optimized geometries at the B3LYP/6-311++G** level were used for all the energy calculations.

Li^-, and F^- are presented. The prefixes, **1**, **2**, and **3**, represent H^-, Li^-, and F^-, and the infixes, **a**, **b**, **c**, **d**, and **e**, represent H_2, N_2, O_2, CO, and NO cluster systems, respectively, in the labels for the structures.

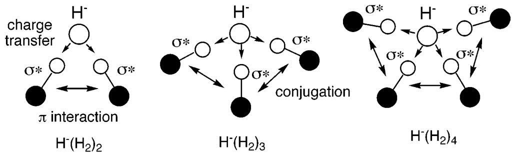
We also calculated the energies for several selected anion clusters at the various levels using the optimized geometries at the B3LYP/6-311++G** level to conform the reliability of our calculation results at the B3LYP/6-311++G** level. The basis set sharply affects the relative energies and it is obvious that the defuse functions are important to especially express the weak interaction for H_2 (**1a1**−**1a3**) and N_2 (**1b1**−**1b4**), as shown in Table 1. On the other hand, the B3LYP level of theory gives a good accordance with the other calculation methods, such as MP4SDTQ, QCISD(T), and CCSD(T), in the relative energies for H_2 (**1a1**−**1a3**) and N_2 (**1b1**−**1b4**), although it tends to overestimate for CO (**1d2**, **1d3**) and NO (**1e1**, **1e3**, **1e4**) compared with the other methods. Here, it should be noted that the order in the stability for the $H^-(H_2)_2$, $H^-(N_2)_2$, $H^-(CO)_2$, and $H^-(NO)_2$ anion clusters, i.e., the linear structure < the bent one, obtained at the B3LYP level is also well-reproduced by the MP4SDTQ, QCISD(T), and CCSD(T) methods except for the $H^-(N_2)_2$ clusters calculated at the QCISD(T), and CCSD(T) levels, where in the bend the energy required for the deformation is estimated to be only slightly larger than the stabilization energy. These results indicate that our findings are not artifacts by the B3LYP level of theory.

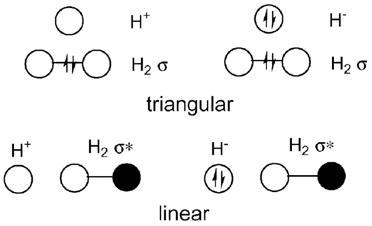
3. Results and Discussion

3.1. $X^-(H_2)_n$ Cluster. We first discuss the H_2 anion cluster, $X^-(H_2)_n$. The clustering of the H_2 molecules easily takes place with the H^- and F^- anions, whereas it takes place not at all with the Li^- anion due to the strong repulsive interaction between the H_2 molecule and the Li^- anion.

H^- Anion. The H_2 molecule readily clusters around the H^- anion. As displayed in Figure 1, one H_2 molecule interacts with the H^- anion by the end-on fashion to form **1a1**, which has the linear structure with the $H^-{-}H^1$ distance of 2.501 Å. The H_2 molecule is stretched by 0.016 Å by the charge transfer from the doubly occupied s orbital of the H^- to the σ^* orbital of the H_2 (the σ^* orbital of the H_2 molecule is occupied by 0.039 e in **1a1**). The charge of the H^- is reduced to −0.952 e, and as a result, the H_2 has a negative charge of −0.048 e, as shown in Table 2. The coordinated H_2 is highly polarized, and the electrons are accumulated at the H^2 atom, which is on the far side from H^-, to avoid the electronic repulsion with the electron rich H^-. The fact that linear arrangement is more favorable than the triangular one has been well understood by the orbital interaction.[9] The 2e interaction of the s orbital of the H^- with the σ^* orbital of the H_2 illustrated as follows, which is attractive, is dominant in the linear arrangement.

SCHEME 1: HOMO Orbitals





However, this attractive interaction disappears, and the 4e interaction between the s orbital of the H^- and the σ orbital of the H_2, which is repulsive, becomes large in the triangular arrangement. In contrast, the $H^+(H_2)$ cluster prefers the triangular arrangement, as is well-known.[9] Because the unoccupied s orbital of the proton more strongly interacts with the σ orbital of the H_2 in the triangular arrangement with the larger orbital overlap between them. In both structures, there is no interaction between the unoccupied s orbital of the proton and the σ^* orbital of the H_2.

Two H_2-coordinated cluster, $H^-(H_2)_2$, has two structures; one is a linear structure (**1a2**), and the other is a bent one (**1a3**) with bending angle 68.9°. Here, it should be noted that the $H^-{-}H^1$ distance of 2.467 Å in **1a2** is shortened by 0.034 Å compared with that in **1a1**, although the charge transfer from the H^- anion to the H_2 molecule does not change at all, as shown in Table 2. This indicates that the 4e repulsion between the H^- s and the H_2 σ orbitals is reduced by the decrease in the population of the H^- s orbital, because the electrons of the H^- s orbital are released to the σ^* orbitals of the H_2 molecules on both the right- and left-hand sides by the charge transfer. In the bent structure **1a3**, the $H^-{-}H^1$ distance is further shortened to 2.288 Å. This phenomenon originates from the charge transfer, which becomes stronger in **1a3** than in **1a2**. As shown in Table 2, the negative charge (as well as population) of the H^- is smaller in **1a3** than in **1a2**, whereas the negative charge of the H_2 is larger in **1a3** than in **1a2**. The HOMO displayed in Scheme 1 reveals the reason of the preference of the bent structure **1a3** over the linear structure **1a2**. The σ^* orbitals of two H_2 molecules, which are occupied by the electrons transferred from the s orbital of the H^-, form a π-type bonding, because the

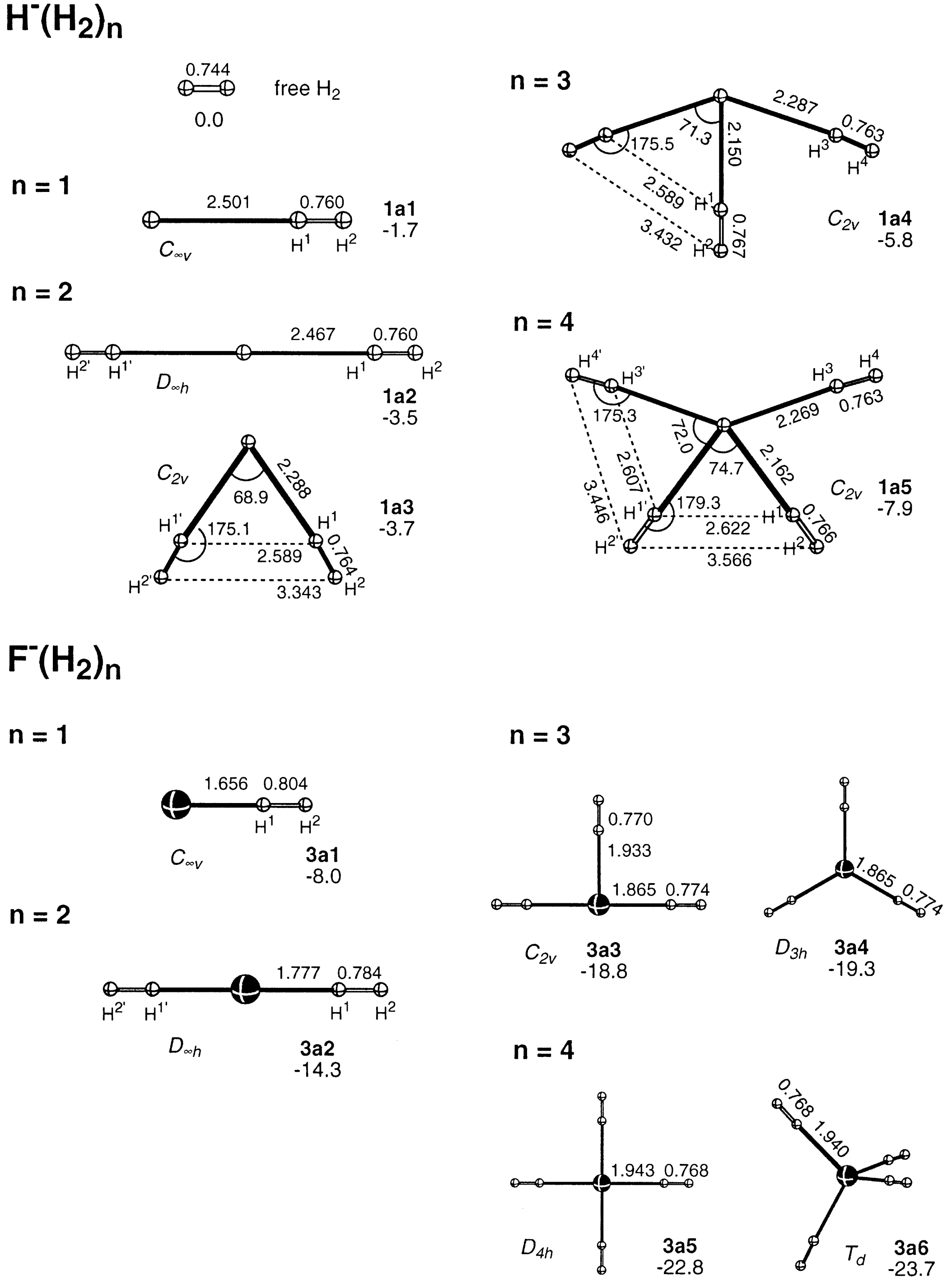
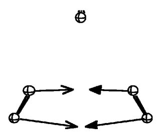


Figure 1. Optimized structures (in ångstroms and degrees) of the H_2 anion clusters, $X^-(H_2)_n$ ($X^- = H^-, F^-$; $n = 1-4$), together with that of the free H_2. The energies (kcal/mol) relative to the free H_2 and anions are presented.

phase of their orbitals matches each other. The electron flow from the s orbital of the H^- to the σ^* orbital of the H_2 is further promoted by this bonding to strengthen the interaction between the H^- and the H_2 molecule. The H^1-H^2 distance of the H_2 molecule is also longer in **1a3** than in **1a2**, consistently. Thus, the $H^--H^1-H^2$ axis is not linear but is slightly bent with the $\angle H^-H^1H^2$ angle of 175.1° by the π-type bonding between the σ^* orbitals of the H_2. The electron population was larger in the $H^2-H^{2'}$ (0.060 e) than in the $H^1-H^{1'}$ (0.020 e), although the $H^2-H^{2'}$ distance is much longer than the $H^1-H^{1'}$ distance. Because the electrons transferred from the H^- are localized at the terminal H^2 of the H_2, as mentioned earlier. The normal-mode analysis also showed the vibrational coupling between two H_2 presented here:



$\nu = 134.5$ cm^{-1}

Thus, the bent structure **1a3** is stabilized in energy by the π interaction between the σ^* orbitals, although the structure is largely deformed, which was never suggested in the previous study.[2b,10]

TABLE 2: Charges and Atomic Orbital (AO) Populations for the H_2 Anion Clusters, $X^-(H_2)_n$ ($X^- = H^-, F^-$; $n = 1-4$)

structure	atomic charge X^-	H^1	H^2	total charge H_2	AO population[a] X^-	H^1	H^2
			$H^-(H_2)_n$				
1a1	−0.952	0.075	−0.123	−0.048	1.952	0.923	1.113
1a2	−0.903	0.074	−0.122	−0.048	1.903	0.925	1.113
1a3	−0.875	0.071	−0.133	−0.062	1.874	0.927	1.118
			$F^-(H_2)_n$				
3a1	−0.909	0.160	−0.251	−0.091	1.923	0.837	1.241
3a2	−0.881	0.143	−0.203	−0.060	1.898	0.855	1.195
3a4	−0.864	0.130	−0.176	−0.046		0.869	1.170
3a6	−0.858	0.120	−0.155	−0.035		0.879	1.151

[a] For F^- in **3a1** and **3a2**, the population for the p orbital on the cluster axis is presented.

TABLE 3: Charges for the N_2 and O_2 Anion Clusters, $X^-(N_2)_n$ and $X^-(O_2)_n$ ($X^- = H^-, Li^-, F^-$; $n = 1, 2$)

structure	atomic charge X^-	N^1 or O^1	N^2 or O^2	total charge N_2 or O_2
		$H^-(N_2)_n$		
1b1	−0.966	0.028	−0.062	−0.034
1b2	−0.938	0.028	−0.060	−0.032
1b3	−0.937	0.028	−0.060	−0.032
1b4	−0.872	0.020	−0.084	−0.064
		$F^-(N_2)_n$		
3b1	−0.942	0.050	−0.109	−0.059
3b2	−0.918	0.050	−0.091	−0.041
3b3	−0.917	0.050	−0.092	−0.042
		$H^-(O_2)_n$		
1c1	−0.478	−0.195	−0.327	−0.522
1c2	−0.309	−0.155	−0.191	−0.346
		$Li^-(O_2)_n$		
2c1	0.005	−0.682	−0.323	−1.005
2c2	−0.007	−0.496	−0.496	−0.992
2c3	0.019	−0.380	−0.129	−0.509
2c4	−0.030	−0.242	−0.242	−0.484
		$F^-(O_2)_n$		
3c1	−0.827	0.017	−0.190	−0.173
3c2	−0.764	0.031	−0.149	−0.118
3c3	−0.763	0.031	−0.149	−0.118

When three H_2 molecules cluster around the H^- anion, an "umbrella" structure with the C_{2v} symmetry, **1a4**, is most stable in energy. The T-shape and the trigonal structures were slightly higher in energy, and both of them were not the true equilibrium structure. In **1a4**, the $H^-{-}H^1$ distance is 0.137 Å shorter than the $H^-{-}H^3$ distance, indicating that the charge transfer from the H^- to the H^1H^2 is stronger than that from the H^- to the H^3H.[4] The $\angle H^3H^-H^1$ angle of 71.3° is much smaller than 90°, which largely deforms the structure from the T-shape, and the $H^-{-}H^3{-}H^4$ axes are slightly bent toward the H^1H^2 by the π bondings between the H^1H^2 and the H^3H^4 mentioned earlier (see Scheme 1). The electrons transferred to the H_2 σ^* orbitals are delocalized through their orbitals. In the case of the $H^-(H_2)_4$ cluster, the structure has C_{2v} symmetry with the C_2 axis bisecting the $H^1{-}H^-{-}H^{1'}$ triangle through H^- (**1a5**). The calculated imaginary frequencies show that both tetrahedral and the square-planar structures are not the equilibrium structure. The $H^-{-}H^3{-}H^4$ axes are bent toward the H^1H^2, although the $H^-{-}H^1{-}H^2$ axes are nearly linear in **1a5**. The angles $\angle H^3H^-H^1$ and $\angle H^1H^-H^{1'}$ are 72.0° and 74.7°, respectively, and both of them are much smaller than 90° due to the conjugation among the σ^* orbitals of the clustered H_2, as illustrated in Scheme 1. The charge transfer from the H^- s orbital to the H_2 σ^* orbital would more strongly take place in the inner part than in the outer part, as sensitively reflected on the $H^-{-}H_2$ distances; the $H^-{-}H^1$ distances are shorter by 0.107 Å than the $H^-{-}H^3$ distances. The conjugation energy that enlarges with the increase in the number of the coordinated H_2 is also reflected on the stability of the anion clusters, as displayed in Figure 2; the increase in the stabilization energy from **1a1** to **1a5** is not proportional, and the increment is amplified with the slow curvature deviating form the linear. We did not further investigate the $H^-(H_2)_n$ cluster, which has n more than 5, because the fifth H_2 molecule was crowded out of the plane of the cluster **1a5**. The H_2 molecule does not cluster around the Li^- anion and goes away from the Li^- anion by the strong repulsive interaction between the H_2 molecule and the Li^- anion. This would be ascribed to the high aptitude of Li to donate the electron, which comes from its quite small electronegativity (see below for the detailed discussion).

F^- Anion. The F^- anion more strongly attracts the H_2 molecule. It is evident when we compare their energies. In one H_2-bound cluster, **3a1**, for the F^- anion is 6.3 kcal/mol more stable in energy than **1a1** for H^-, both structures being similarly linear. The charge transfer, which is the origin of the attractive interaction, occurs from the p orbital of the F^- anion directed toward the H_2 to the H_2 σ^*. This is stronger compared with the case of H^-, as shown by the total charge of −0.091 for the coordinated H_2 (Table 2), so that the $F^-{-}H^1$ distance is shortened to 1.656 Å and the $H^1{-}H^2$ distance is stretched to 0.804 Å, which is longer by 0.044 Å than that in **1a1** for H^-. The coordinated H_2 is highly polarized and the positive charge at the nearside H^1 is enhanced to 0.160 e to reduce the electronic repulsion with the valence electrons of the F atom.

Although the structure is also linear in the $F^-(H_2)_2$ cluster **3a2**, the $F^-{-}H^1$ distance becomes longer, whereas the $H^1{-}H^2$ distance becomes shorter, in contrast to the case for H^-. Because the charge transfer to two H_2 on the left- and right-hand sides weakens to each other, the bent structure corresponding to **1a3** found for H^- did not exist in the case of F^-. The occupied p orbital perpendicular to the molecular axis prevents the π interaction between the σ^* orbitals of two H_2 generated by the bend of the $H^1{-}F^-{-}H^{1'}$ axis. In addition, the orbital overlap between the p orbital of the F^- and the s orbital of the H^- becomes maximum in the linear arrangement.

In the system of $n = 3$, the T-shape (**3a3**) and the trigonal (**3a4**) structures, and in the system of $n = 4$, the square-planar (**3a5**) and the tetrahedral (**3a6**) structures exist as an equilibrium structure. In both systems, the latter, in which steric contact is minimum, is more stable in energy than the former. The $F^-{-}H^1$ distance becomes longer with the increase in n, indicating that the charge transfer from the F^- to the H_2 is gradually weakened. In fact, the negative charge of the coordinated H_2 decreases in the order, **3a1** > **3a2** > **3a4** > **3a6**, as shown in Table 2. Therefore, the stability of the anion clusters does not increase in proportion to the number of n, as displayed in Figure 2. The plots of the stabilization energy versus n describe the curvature decreasing the slope, its shape being opposite to the case of H^- involving the conjugation energy.

3.2. $X^-(N_2)_n$ and $X^-(O_2)_n$ Clusters.

In this section, we discuss the anion clusters of N_2 and O_2. The electronic state of O_2 is assumed to be triplet, where two electrons separately occupy the degenerate two π^* orbitals.

H^- Anion. The H^- anion approaches the N_2 molecule to donate the electrons of the s orbital to the π^* orbital of the N_2. Therefore, the N_2 is negatively charged (−0.034 e; see Table 3), and the π^* orbital is occupied by 0.031 e in the formed $H^-(N_2)$ cluster **1b1**. The energy of **1b1** is lowered by 1.0 kcal/mol by this charge transfer interaction. However, the repulsive 4e interaction between the doubly occupied s orbital of the H^- and the π orbital of the N_2 enlarges the $\angle H^-N^1N^2$ angle to

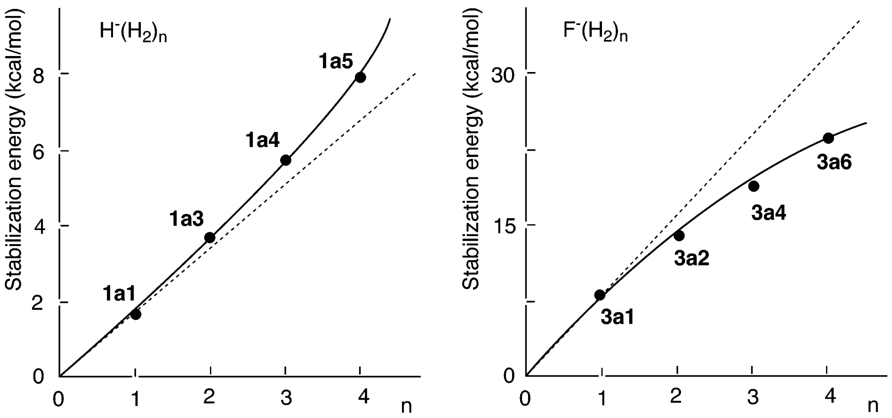


Figure 2. Plots of the stabilization energy versus n in the $H^-(H_2)_n$ and $F^-(H_2)_n$ ($n = 1-4$) clusters.

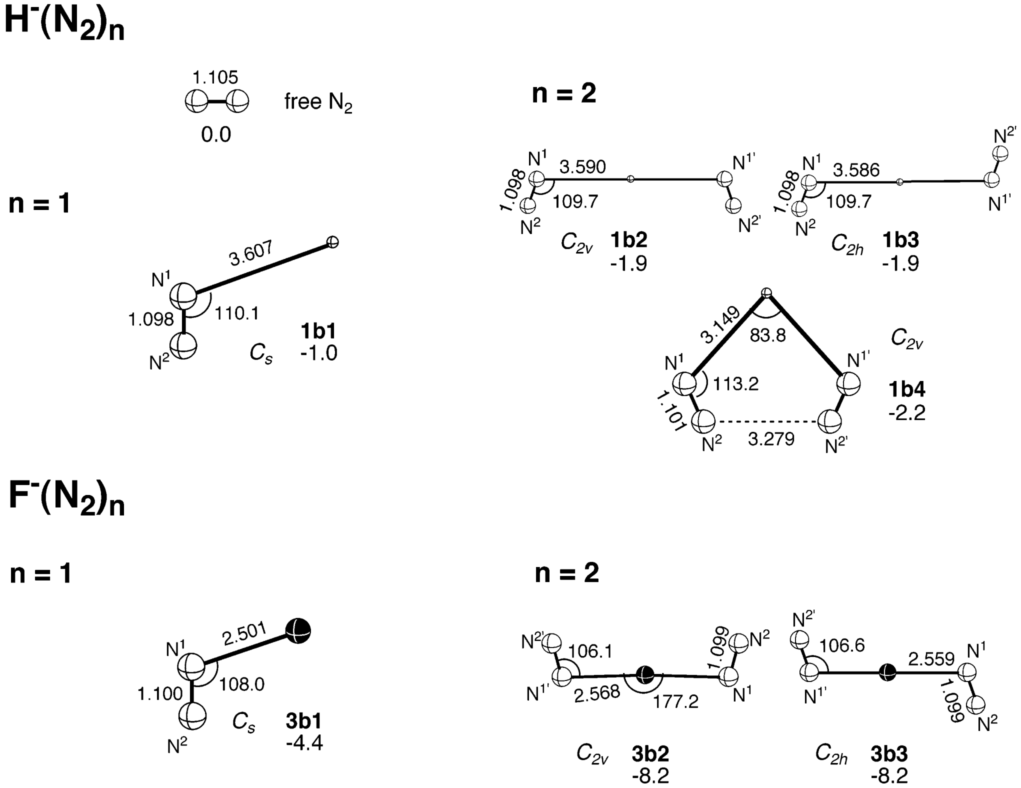
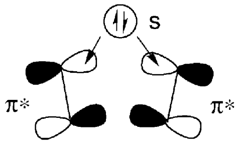


Figure 3. Optimized structures (in ångstroms and degrees) of the N_2 anion clusters, $X^-(N_2)_n$ ($X^- = H^-, F^-$; $n = 1, 2$), together with that of the free N_2. The energies (kcal/mol) relative to the free N_2 and anions are presented.

110.1° and lengthens the $H-N^1$ distance to 3.607 Å, as presented in Figure 3. The negative charge of the H^- anion induces the polarization of the N_2 and generates the positive and the negative charges at the N_1 and the N_2, respectively, as shown in Table 3. The Coulomb interaction between the N^1 and the N^2 shortens the N^1-N^2 distance to 1.098 Å, which is a little shorter than that of the free N_2 (1.105 Å).

The $H^-(N_2)_2$ anion cluster has the linear and bent structures. The linear structure furthermore has two arrangement with respect to the N_2, i.e., **1b2** and **1b3**, which have the same energy. The H^--N^1 distance is only slightly shorter in **1b2** and **1b3** than in **1b1**, because the repulsive 4e interaction between the s orbital of the H^- and the π orbital of the N_2 is reduced by the decrease in the negative charge of the H^- (see Table 3). On the other hand, the H^--N^1 distance of 3.149 Å in the bent structure **1b4** is 0.458 Å shorter than that in **1b1**, because the charge transfer from the s orbital of the H^- to the π^* orbital of the N_2 is promoted to provide the electrons required for the bonding between two N^2 atoms through the π^* orbitals illustrated as follows (see section 3.1 for the similar discussion).



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The bent structure **1b4** is, therefore, lower in energy than that of the linear structures **1b2** and **1b3**, despite the large structural deformation with the $\angle N^1-H^--N^1$ angle of 83.8°. The anion clusters with $n = 3$, 4 similar to **1a4** and **1a5** for H_2 were not found in the case for N_2.

As well as N_2, O_2 is a nonpolar molecule having a double bond. However, different from N_2, O_2 takes a triplet state where two electrons occupy the degenerate two π^* orbitals. This

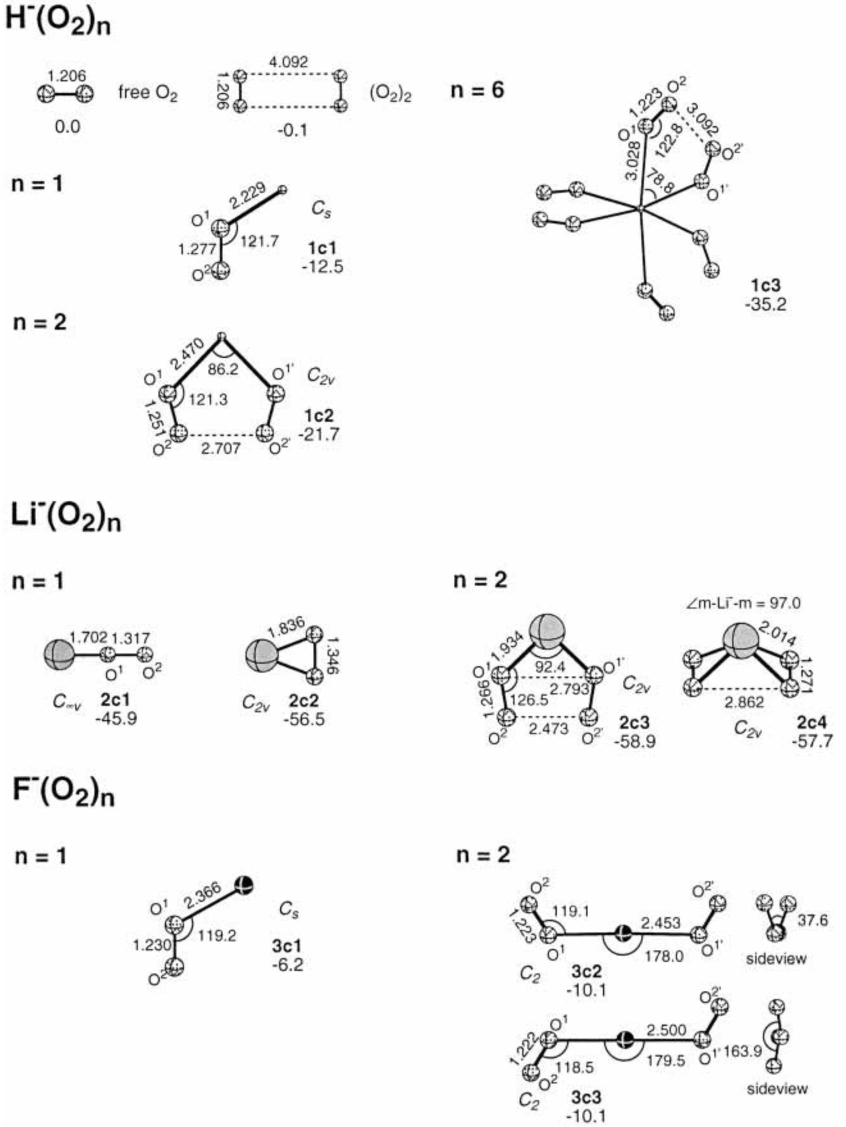
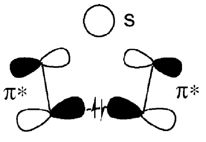


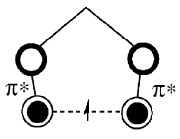
Figure 4. Optimized structures (in ångstroms and degrees) of the O_2 anion clusters, $X^-(O_2)_n$ ($X^- = H^-, Li^-, F^-$; $n = 1, 2, 6$), together with those of the free O_2 and the O_2 dimer. The energies (kcal/mol) relative to the free O_2 and anions are presented. The notation m in 2c4 represents the midpoints of the coordinated O_2 molecules.

electronic nature significantly affects the geometry of the cluster. Without anion, two free O_2 molecules can very weakly interact with each other, as presented in Figure 4. The energy level of the π^* orbital is significantly lowered by the electron occupation.[11] As a result, the mutual charge transfer between the π and π^* orbitals between two O_2 molecules becomes possible. In the case of $n = 1$, the $\angle H^-O^1O^2$ angle of 121.7° in **1c1** is larger by 11.6° than the corresponding angle of **1b1**, due to the repulsive interaction of the H^- s orbital with the O_2 π^* orbital occupied by one electron in addition to that of the H^- s orbital with the O_2 π orbital. Nevertheless, the $H^-{-}O^1$ distance is shorter by more than 1 Å compared with the corresponding distance of **1b1** for N_2. This is attributed to the π^* orbital of O_2, which lies much lower in energy compared to that of N_2. The negative charge of the O_2 is enlarged to −0.522 e (see Table 3) by the facile electron donation from the s orbital of the H^- to the π^* orbital of the O_2, and **1c1** is stabilized by 12.5 kcal/mol. The transferred electrons are accumulated at the O^2 rather than at the O^1.

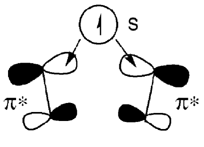
In the case of $n = 2$, there was no linear arrangement like **1b2** and **1b3** found for N_2. The $O^1{-}H^-{-}O^2$ axis is bent with the $\angle O^1{-}H^-{-}O^2$ angle of 86.2° in **1c2**, which largely deforms its structural features from the linear arrangement. The π^* orbitals of two O_2 molecules are placed face to face and interact with each other (see orbital illustration I displayed above), so that the $O^2{-}O^{2'}$ distance is shortened to 2.707 Å. This $O^2{-}O^{2'}$ interaction is strong compared with the corresponding interaction in the case for N_2, because the electron donation from the s orbital of the H^- to the π^* orbital of the O_2 readily occurs and, moreover, the π^* orbital originally has one electron. The electrons in the π^* orbitals of two O_2 molecules are rather localized in the $O^2{-}O^{2'}$ region, as described here:



II



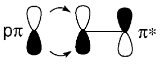
III



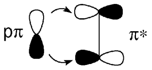
IV

The normal-mode analysis also showed the vibrational coupling between two O_2, which has the frequency of 90.3 cm^{-1}. The $H^-(O_2)_4$ anion cluster consisting of two units of the structure **1c2** was not found, although the $H^-(O_2)_6$ anion cluster **1c3** consisting of three units of structure **1c2** was found.

Li^- Anion. The N_2 molecule does not form any anion cluster with the Li^- anion. In contrast, the O_2 molecule readily forms Li^- anion clusters, due to the low-lying π^* orbital of O_2 which is an electron acceptor, as mentioned earlier. In one O_2-coordinated cluster, there exist two coordination modes, i.e., end-on and side-on, by the mixing of the $p\pi$ orbital of Li, as presented here:



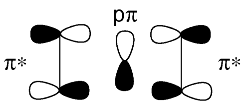
V



VI

The charge transfer from the $p\pi$ orbital of the Li^- to the π^* orbital of the O_2 is stronger for the side-on mode than for the end-on mode by the larger orbital overlap, so that the energy is lower by 10.6 kcal/mol for **2c2** than for **2c1** (Figure 3). The negative charge of the Li^- is nearly transferred to the O_2 as shown in Table 3, due to the small electronegativity of Li.[12] The stability of the anion clusters are 4−5 times larger for Li^- than for H^- by the strong charge-transfer interaction.

In the case of $n = 2$, two structures, **2c3** and **2c4**, were found. The linear structure by the end-on coordination of O_2 and the square-planar type structure by the side-on coordination of O_2 expected on the basis of the structures **2c1** and **2c2**, did not exist as an equilibrium structure. As a matter of fact, the structural features of **2c3** are similar to those of **1c2** for H^-. Both $\angle O^1Li^-O^{1'}$ and $\angle Li^-O^1O^2$ angles are reduced to 92.4° and 126.5°, respectively, to form a pentagonal structure. However, the $Li^-{-}O^1$ (1.934 Å) and the $O^2{-}O^{2'}$ (2.473 Å) distances are shorter whereas the $O^1{-}O^2$ distance (1.266 Å) is longer than the corresponding distances in **1c2**, because the electron donation to the π^* orbital of the O_2 is stronger for Li^- than for H^-. In **2c4**, two O_2 molecules coordinated to Li^- by the side-on mode come closer to each other to interact through the π^* orbitals, as illustrated here:

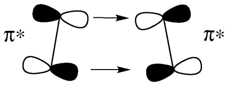


VII

Therefore, the structure is not square-planar-like but square-pyramid-like. Here, the p orbital of the Li^- contributes to the charge transfer to the π^* orbital of the O_2. The energy was slightly lower for **2c3** than for **2c4**.

F^- Anion. As well as the H^- anion, the F^- anion forms the "boomerang" structure regardless of the coordinated molecule, N_2 and O_2, in the case of $n = 1$, which is neither an end-on nor side-on structure. In the case of $n = 2$, the bent structure as in **1b4** and **1c2** does not exist for both N_2 and O_2, as mentioned in section 3.1 for H_2. The $N^1{-}F^-{-}N^{1'}$ axis deviates by 2.8° from linear in **3b2**, which has N^2 and $N^{2'}$ atoms in the same side, whereas it is linear in **3b3**, which has N^2 and $N^{2'}$ atoms in the opposite side. On the other hand, the $O^1{-}F^-{-}O^{1'}$ axes deviate from linear in both **3c2** and **3c3**, and also two O_2 molecules mutually twist out from the plane of the clusters, which is displayed by their side view. The length of the coordination bond is shorter for O_2 than for N_2, and the energy of the anion cluster is about 2 kcal/mol lower for O_2 than for N_2.

3.3. $X^-(CO)_n$ and $X^-(NO)_n$ Clusters. We finally discuss the polar molecules, CO and NO. Here, the electronic state of the NO molecule is a doublet with one electron in the π^* orbital. The π^* orbital of NO is lowered by the electron occupation.[11] Consequently, the clustering of two NO molecules by the charge transfer interaction presented as follows becomes possible even without anion, although the stabilization energy is only 0.2 kcal/mol (Figure 6).



VIII

The structure of the formed NO dimer is asymmetric, because the charge transfer from the π^* orbital occupied by one electron to the unoccupied π^* orbital takes place from one NO to the other NO. Accordingly, the N−O distance is shorter for one NO (1.146 Å) and is longer for the other NO (1.150 Å) compared with that of the free NO (1.148 Å).

H^- Anion. The CO molecule coordinates to the H^- anion by receiving the electrons from the H^- by the π^* orbital. As presented in Figure 5, not the O atom but the C atom is attached to the H^- in **1d1** because the C atom is electron deficient due to the strong polarization of CO. The angle $\angle H^-CO$ becomes more than 90° by the electronic repulsion between the orbitals of the H^- and the O atoms as mentioned earlier.

The structural features of **1d1** are retained in the system of $n = 2$, aside from the values of the geometric parameters. The $H^-{-}C$ distance becomes longer whereas the C−O distance becomes shorter, because the charge transfer from the s orbital of the H^- to the π^* orbital of the CO is weakened by being divided into two directions. In **1d3**, in which two CO are oriented toward the opposite direction, the $C{-}H^-{-}C$ axis is only slightly distorted from the linear. However, it is largely distorted, when two CO are oriented toward the same direction, as shown by the $\angle C{-}H^-{-}C$ angle of 156.4° in **1d2**. Nevertheless, **1d2** is more stable in energy than **1d3**, due to the attractive interaction between two O atoms through the π^* orbitals as mentioned earlier (see illustration I).

On the other hand, the H^- anion can attach to not only the N atom but also the O atom of NO by donating the electrons of the s orbital to the unoccupied π^* orbital of NO. The charge-transfer interaction between the occupied H^- s and the unoccupied NO π^* orbitals can overcome the repulsive 4e interaction between the occupied H^- s and the occupied NO π orbitals even at the O side due to the low polarization of NO (see Table 4). However, the energy is 5 times higher for **1e2** than for **1e1** according to the contribution of the 4e repulsion, although both of them have similar structural features (Figure 6). It should be noted here that the H atom is positively charged whereas both N and O atoms are highly negatively charged, as shown in Table 4. The Coulomb interaction between the N and the O atoms would promote the stretch of the N−O bond and simultaneously the formation of the N−H and the O−H bonds, as reflected on their distances; the N−O distance is considerably long, whereas the N−H and the O−H distances are quite short. Thus, the electron flow into the π^* orbital is larger for NO than for CO, which is ascribed to the high electronegativity of the N atom[12] and the low lying π^* orbital of the NO molecule.[11]

In the $H^-(NO)_2$ system, when the N atom is attached to the H^-, two kinds of structure, **1e3** and **1e4**, exist according to the orientation of the NO molecules, which is similar to the case for CO. The charge transfer to generate the cluster occurs from the s orbital of the H^- to the unoccupied π^* orbital of the NO.

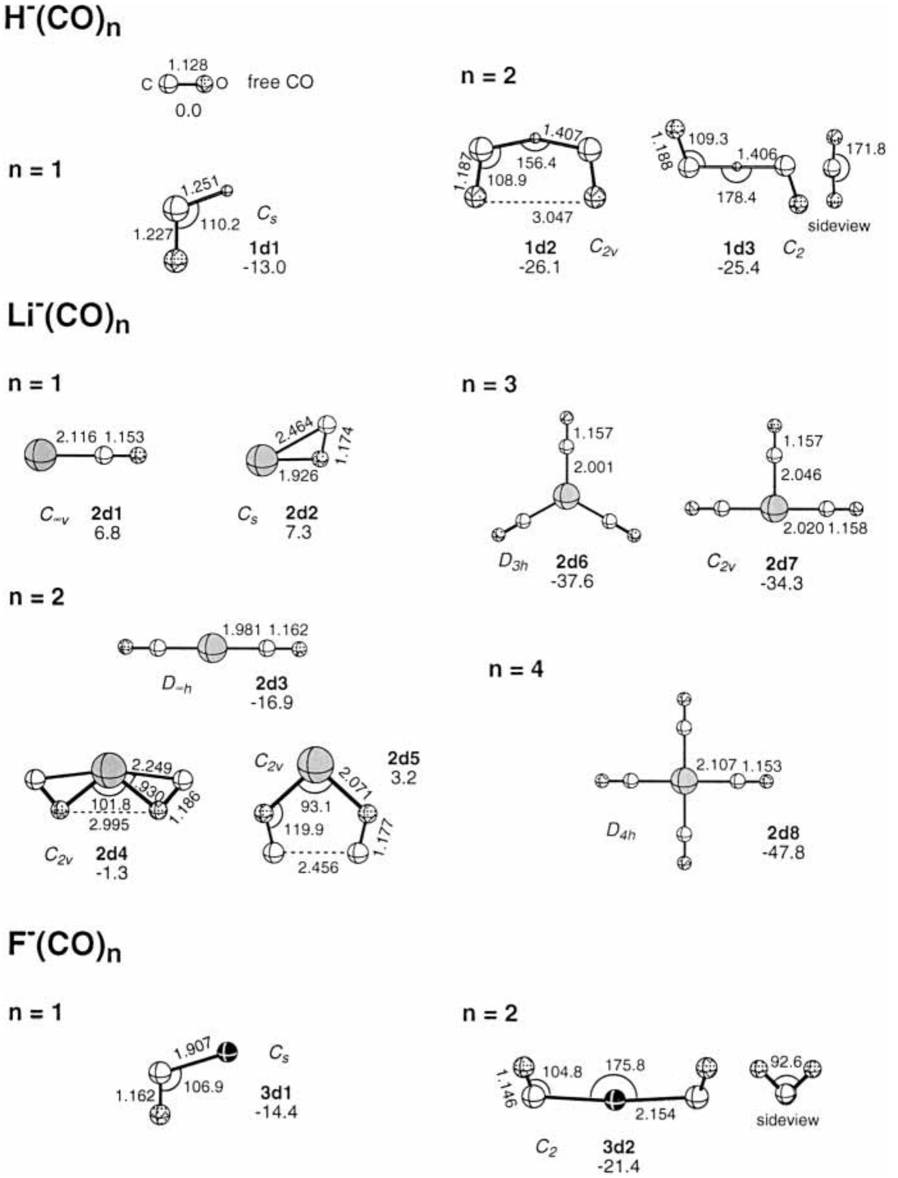
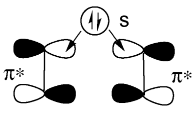
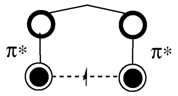


Figure 5. Optimized structures (in ångstroms and degrees) of the CO anion clusters, $X^-(CO)_n$ ($X^- = H^-, Li^-, F^-$; $n = 1-4$), together with that of the free CO. The energies (kcal/mol) relative to the free CO and anions are presented.

In **1e3**, the N−H⁻−N axis is significantly distorted from the linear by the attractive interaction between two NO that have the same orientation through the π* orbitals:



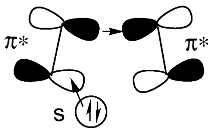
IX



X

On the other hand, **1e4** with two NO oriented to the opposite direction to each other has the N−H⁻−N axis, which is linear. As presented in Figure 7, when the interaction between two O atoms in **1e3** is broken by the rotation of the NO around the N−H⁻ axis, the ∠NH⁻N angle α as well as the energy remarkably increases. Both clusters, **1e3** and **1e4**, are much more stable in energy compared with the corresponding clusters for CO.

When the O atom is attached to the H⁻ anion, only **1e5** was found. In **1e5**, the H⁻ anion is strongly attracted to one of the NO molecules, and the charge transfer occurs from one NO highly negatively charged by the attachment of the H⁻ to the other NO through the π* orbitals of the N atoms:



XI

Here, the π* orbitals of two NO is the unoccupied π* orbitals. This charge transfer between two NO through the N atoms is very strong, as evidenced by the short N^1-N^2 distance of 1.734 Å. Therefore, **1e5** is considerably stabilized compared with **1e2**. The positively charged H atom also has a electrostatic interaction with another negatively charged O atom with the H−O distance of 1.502 Å.

Li⁻ Anion. The Li⁻ anion forms the regular end-on structure **2d1** interacting with the CO carbon. The contribution of the pπ orbital of the Li makes the formation of the linear structure possible, where the charge transfer takes place from the pπ orbital of the Li to the π* orbital of the CO (see illustration V presented earlier). However, **2d1** is unstable in energy because

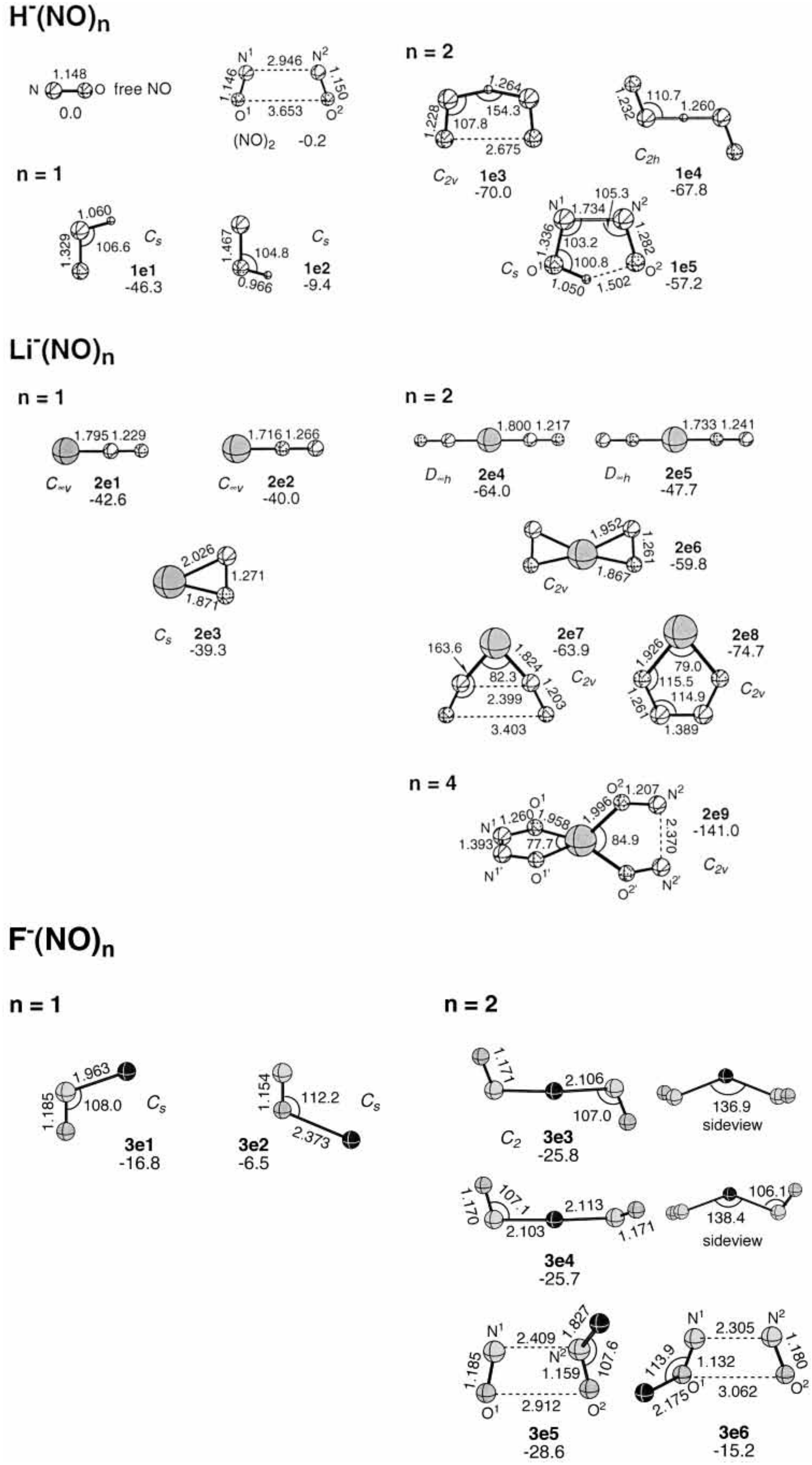


Figure 6. Optimized structures (in ångstroms and degrees) of the NO anion clusters, $X^-(NO)_n$ ($X^- = H^-, Li^-, F^-$; $n = 1, 2, 4$), together with those of the free NO and the NO dimer. The energies (kcal/mol) relative to the free NO and anions are presented.

this charge-transfer interaction is weak due to the high-lying π^* orbital of CO. Half of the negative charge remains on the Li, although the electronegativity of Li is considerably low, which causes the repulsion with the occupied orbital of the CO.

TABLE 4: Charges for the CO and NO Anion Clusters, $X^-(CO)_n$ and $X^-(NO)_n$ ($X^- = H^-, Li^-, F^-$; $n = 1-4$)[a]

structure	atomic charge X^-	atomic charge C or N	atomic charge O	total charge CO or NO
free CO		0.483	−0.483	
$H^-(CO)_n$				
1d1	−0.133	−0.133	−0.735	−0.868
1d2	−0.040	0.137	−0.616	−0.479
1d3	−0.052	0.152	−0.626	−0.474
$Li^-(CO)_n$				
2d1	−0.548	0.066	−0.518	−0.452
2d2	−0.490	0.232	−0.742	−0.510
2d3	0.201	−0.042	−0.558	−0.600
2d6	0.401	0.100	−0.567	−0.467
2d8	0.535	0.192	−0.576	−0.384
$F^-(CO)_n$				
3d1	−0.759	0.400	−0.642	−0.242
3d2	−0.761	0.468	−0.587	−0.119
free NO		0.190	−0.190	
NO dimer		0.201/0.178	−0.179/−0.199	0.022/−0.021
$H^-(NO)_n$				
1e1	0.176	−0.507	−0.669	−1.176
1e2	0.398	−0.692	−0.707	−1.399
1e3	0.225	−0.208	−0.405	−0.613
1e4	0.214	−0.176	−0.431	−0.607
1e5	0.430	−0.124/−0.141	−0.579/−0.586	−0.703/−0.727
$Li^-(NO)_n$				
2e1	−0.016	−0.555	−0.428	−0.983
2e2	0.014	−0.190	−0.824	−1.014
2e3	0.007	−0.350	−0.657	−1.007
2e4	0.701	−0.425	−0.425	−0.850
2e5	0.677	−0.180	−0.659	−0.839
2e6	0.816	−0.335	−0.573	−0.908
2e7	0.279	−0.271	−0.368	−0.639
2e8	0.022	0.046	−0.556	−0.510
2e9	0.871	0.039/0.006	−0.505/−0.476	−0.466/−0.470
$F^-(NO)_n$				
3e1	−0.725	0.117	−0.392	−0.275
3e2	−0.884	0.031	−0.147	−0.116
3e3	−0.664	0.163	−0.331	−0.168
3e5	−0.627	0.018/0.256	−0.354/−0.294	−0.336/−0.038
3e6	−0.809	0.175/0.014	−0.063/−0.318	0.112/−0.304

[a] The values on the left- and right-hand sides of the slash are for N^1 and N^2 or O^1 and O^2 or N^1O^1 and N^2O^2, respectively.

The distorted side-on structure **2d2** is also unstable in energy by the same reason.

In contrast, NO forms the stable anion clusters regardless of its coordination mode because the low-lying π^* orbital of NO makes the charge-transfer interaction with the Li facile. In fact, all the negative charge of the Li^- is transferred to the NO and the Li is finally positively charged after the clustering (see Table 4). In the end-on structure, two kinds of arrangement, i.e., Li−N−O (**2e1**) and Li−O−N (**2e2**), are possible, the former being more stable by 2.6 kcal/mol than the latter. The side-on structure **2e3** is less stable than these end-on structures. This trend is opposite to the case for O_2, because the electronic repulsion between the Li and the highly negatively charged NO oxygen reduces the stability in the side-on structure.

The clustering of the CO molecules more than two remarkably stabilizes the anion cluster when the linearity of the Li^-−C−O axis is maintained, because the repulsive interaction between the Li and the CO mentioned earlier is decreased by the change in the charge of the Li from negative to positive. The positive charge of the Li increases with the increase in the number of the coordinated CO by the electron donation (see Table 4). The negative charge is extremely localized at the terminal oxygen in any case due to the high polarization of CO.

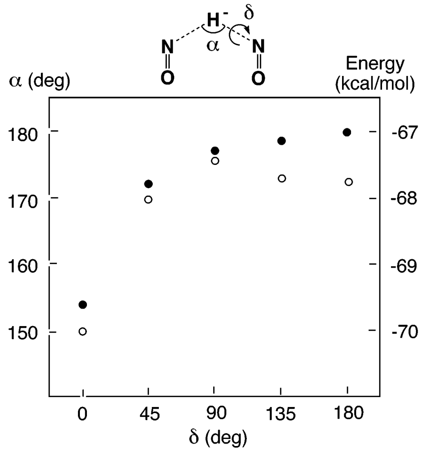


Figure 7. Plots of the angle α (●) and the energy (○) of the $H^-(NO)_2$ anion cluster **1e3** versus the angle δ (∠ONH⁻N). The energies relative to the free NO and H^- anion are presented.

In the case of $n = 2$, **2d3**, which has linear structure, is stabilized by 16.9 kcal/mol compared with the free CO and Li^- anions. On the other hand, **2d4** and **2d5**, which has the Li−O interaction, remain unstable. However, it should be noted that these clusters form a cyclic structure by the attractive interaction between two O atoms in **2d4** and between two C atoms in **2d5** through the π^* orbitals (see above for the detailed discussion about this interaction).

For $n = 3$ and 4, we optimized restricting to the structure that has the linear Li^-−C−O axis because the side-on and the bent structures in the case of $n = 2$ were unstable. As a result, it was found that the anion clusters exist as the trigonal (**2d6**) and the T-shape (**2d7**) structures for the case of $n = 3$, and as the square-planar structure (**2d8**) for the case of $n = 4$. The tetrahedral structure does not exist as an equilibrium structure.

For the less polarized NO, the bent structure as well as the linear structure was stable in energy. One can find a tendency when three clusters in the case of $n = 2$, **2e4**, **2e5**, and **2e6**, are compared. The stability of these anion clusters increases, as the O atoms go away from the Li and instead the N atoms come closer to Li, as shown by the order **2e4** > **2e6** > **2e5**. However, this tendency is reversed in the bent structure; **2e8** is more stable in energy than **2e7**. Both **2e7** and **2e8** have a cyclic form to get stabilization by the attractive interaction between the terminal atoms as mentioned earlier (see illustration I). This interaction is stronger for **2e8** than for **2e7** as revealed by their distances, which yields the stability sequence **2e8** > **2e7**. It would be worth noting that **2e8** is most stable in energy though the oxygen is attached to the Li. The cyclic form of **2e8** was also retained in the $Li^-(NO)_4$ cluster **2e9**. However, the electrons provided from the Li to the π^* orbital of NO (see illustration I) are localized on the left half part. Therefore, the N^1−$N^{1'}$ distance is shorter than the N^2−$N^{2'}$ distance whereas the O^1−N^1 and the $O^{1'}$−$N^{1'}$ distances are longer than the O^2−N^2 and the $O^{2'}$−$N^{2'}$ distances. The planar structure for **2e9** in which both O^1−Li^-−$O^{1'}$ and O^2−Li^-−$O^{2'}$ planes are on the same plane did not exist.

F^- Anion. The F^- anion attaches to only the C atom in the case for CO by the electron donation to the π^* orbital of CO. The angle ∠F^-CO in **3d1** is larger than 90°, as presented in Figure 5, which is similar to case for H^-. The $F^-(CO)_2$ cluster, **3d2**, is not the bent structure, although the C−Li−C axis slightly deviates from the linear.

In the case for NO, the F^- anion attaches to not only the N atom (**3e1**) but also the O atom (**3e2**), forming the cluster similar to **3d1** for CO (Figure 6). The electron donation from the F^- to the π^* orbital of the NO is larger in **3e1** than in **3e2**, as reflected in the stability sequence **3e1** > **3e2**. In the $F^-(NO)_2$ system, two NO cannot have the same orientation, although two N atoms come closer to each other by reducing the ∠NLi$^-$N angle to 137−138° (**3e3** and **3e4**). When two NO have the same orientation, the F^- anion migrates to one of two NO (**3e5** and **3e6**). The distance between two NO in **3e5** and **3e6** is much shorter than that in the NO dimer without the F^- anion, because the charge-transfer interaction between two NO (see illustration VIII) is strengthened by the attachment of the F^- anion; the electron donation from the F^- to the NO enhances the electron donation from the NO to the other NO.

4. Concluding Remarks

We focused on the clustering of the diatomic molecules H_2, N_2, O_2, NO, and CO with the anions H^-, Li^-, and F^- and examined their geometric structures and the nature of the interaction on the clustering process using the density functional method (B3LYP). Our calculations showed a new type of anion cluster formed by the novel interaction between the σ^* or π^* orbitals of the diatomic molecules. Both H^- and F^- anions form the cluster with each diatomic molecule, whereas the Li^- anion does not with H_2 and N_2. The interaction between the diatomic molecules and the anions is mainly determined by the balance of the charge transfer interaction and the electronic repulsion. The electron donation from the anions to the diatomic molecules readily occurs, so that the anions can approach and attach, even if the diatomic molecule is nonpolar. In the clustering of H_2 around the H^- center, the electrons transferred to the σ^* orbital of the H_2 play a key role. The conjugation through the σ^* orbitals (Scheme 1), which is unknown before, controls the clustering process and determines the structure. The conjugation energy, which is amplified by the increase in the number of the coordinated H_2, more stabilizes the $H^-(H_2)_n$ cluster. With the other diatomic molecules, N_2, O_2, CO, and NO, the H^- anion generates not only the linear structure but also the bent one in the case of $n = 2$, although the F^- anion generates only the linear structure. Here, the π^* orbital of the diatomic molecule plays an important role. The bent structure stabilizes by taking a pentagonal cyclic form, because the charge transfer from the anion to the π^* orbitals of the clustered diatomic molecules induces the attractive interaction between the π^* orbitals (illustration I). The Li^- anion also similarly generates the pentagonal cyclic form by the clustering with O_2, CO, and NO. The geometric structure and the interaction in the clustering strongly depend on the combination of the anion and the diatomic molecule.

Acknowledgment. The calculations were in part carried out at the Computer Center of the Institute for Molecular Science, Japan. T.M. was partly supported by the Grants-in-Aid from the Ministry of Education, Science, Sports, and Culture, Japan.

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(11) The order in the energy level of the σ^* orbital of H_2 and the π^* orbitals of N_2, O_2, CO, and NO is as follows: $H_2(0.02019) > N_2(-0.03782) > CO(-0.04245) > NO(-0.11887$(unoccupied), -0.22734(singly occupied)$) > O_2(-0.32307)$.

(12) The sequence of the electronegativity in the Pauling's value is as follows; F(3.98) > H(2.20) > Li(0.98); N(3.04) > C(2.55). For example, see: *The Elements*, 3rd ed.; Emsley, J., Ed.; Oxford University Press: New York, 1998.