Structures and Electronic States of the Electron Donor−Acceptor Complexes NH_3-X_2 ($X = F$ and Cl): An *ab-Initio* MO Study

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The geometrical structures and the electronic states of the electron donor−acceptor (EDA) complexes for both ground and excited states have been studied by means of the *ab-initio* MO method. As models of the EDA complex, σ-type EDA complexes composed of ammonia and halogen molecules NH_3-X_2 ($X = F$ and Cl) were chosen. For comparison, the NH_3-X_2 complexes ($X = Br$ and I) were also studied with only a small basis set. Geometry optimization of the complexes gave the van der Waals (vdW) structure whose the ammonia molecule is weakly interacting to the halogen molecule for the ground state and the distorted structure whose ammonia molecule is largely deformed for the excited charge-transfer (CT) state. This large distortion at the CT state is due to the fact that a dipole induced by bending deformation of the ammonia cation coordinates the halogen anion. Potential energy curves (PECs) for the formation of the EDA complexes were calculated by singly excited CI and MP2 methods for both the ground and CT states. The first excitation band of the intramolecular transition in X_2 of the CT complex showed a considerably large blue shift relative to that of the monomer molecule. This result was in qualitative agreement with the experimental feature. For the CT state, the transition energy is largely red-shifted due to the complex formation if the geometrical distortion is permitted. The structural model for the CT state was proposed on the basis of the theoretical results.

1. Introduction

An electron donor−acceptor (EDA) complex plays an extensive role in a charge-transfer process at exited state[1] and in an ion-pair formation process.[2] A large number volume of experimental data on the EDA complex has been accumulated and have indicated that the absorption spectrum of the EDA complex is characterized by a broader spectrum, a large spectral shift relative to the monomer spectrum, and increased intensity. To understand these phenomena, a theory for the EDA complex was proposed by Mulliken in 1952.[3] According to the Mulliken theory, the ground-state wave function is expressed by

$$\psi_g = a\psi(D\cdot A) + b\psi(D^+\cdot A^-) \qquad (1)$$

where a and b are MO coefficients, $\psi(D\cdot A)$ is a wave function of the van der Waals (vdW) state, and $\psi(D^+\cdot A^-)$ is one of the ionic states. The excited wave function is given by

$$\psi_e = a^*\psi(D\cdot A) + b^*\psi(D^+\cdot A^-) \qquad (2)$$

At the ground state, coefficient a is larger than b, while $a^* \approx b$ and $b^* \approx a$ at the excited state. Thus, the calculation of the wave functions for ground and excited states would provide detailed information on the electronic states of the EDA complexes.

Nagakura and co-workers calculated the wave function of the π-type charge-transfer complex composed of tetracyanoethylene and 1,3,5-trimethylbenzene by means of the configuration interaction (CI) method at semiempirical level.[4] The ground-state wave function thus calculated showed that the interactions between the donor and acceptor molecules at the ground and first excited states are composed of vdW and ionic states, respectively.

For the σ-type EDA complex, systematic studies have been carried out by several groups as well as for the π-type complexes. Especially, the EDA complexes formed between amine and halogen molecules were well-studied experimentally.[5] These experiments suggested that the absorption spectrum of the halogen molecule is largely blue-shifted as a result of complex formation and that the charge-transfer absorption band appears at somewhat shorter wavelength.[5c,d] This is an interesting point in the σ-type EDA complex.

Recently, the σ-type EDA complexes of NH_3 with hydrogen molecules were studied theoretically by Roeggen and Dahl.[6] They suggested that the Coulomb interaction between distorted monomers was the main origin of the intermolecular interaction at the ground state. More recently, Jonas and Frenking studied an EDA complex H_3N-BF_3 by means of the *ab-initio* MO method and predicted that the structure of the H_3N-BF_3 complex possesses a B−N bond of 1.6 Å.[7] By using the

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(1) (a) Prout, C. K.; Kamenar, B. *Molecular Complexes*; Foster, R., Ed.; Elek: London, 1973; Vol. 1, Chapter 3. (b) Hanna, M. W.; Lippert, J. L. *Molecular Complexes*, Foster, R., Ed.; Elek: London, 1973; Vol. 1, Chapter 3.

(2) (a) Tachikawa, H.; Murai, H.; Yoshida, H. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2369. (b) Tachikawa, H.; Takatori, Y.; Ohtake, A.; Kumagai, J.; Yoshida, H. *J. Mol. Struct. (THEOCHEM)*, in press. (c) Reed, A. E.; Weinhold, F., Weiss, R.; Macheleid, J. *J. Phys. Chem.* **1985**, *89*, 2688. (d) Ha, T.; Bühler, R. *Radiat Phys. Chem.* **1988**, *32*, 117.

(3) (a) Mulliken, S. R. *J. Am . Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, S. R. *J. Am. Chem. Soc.* **1950**, *72*, 600.

(4) (a) Iwata, S.; Tanaka, J.; Nagakura., S. *J. Am. Chem. Soc.* **1966**, *88*, 894. (b) Kobayashi, T.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2603.

(5) (a) Bloemisk, H. I.; Legon, A. C. *J. Chem. Phys.* **1995**, *103*, 876. (b) Bloemisk, H. I.; Legon, A. C.; Thorn, J. C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 4157. (c) Nagakura, S. *J. Am. Chem. Soc.* **1958**, *80*, 520. (d) Yada, H.; Tanaka, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1660.

(6) Roeggen, I.; Dahl, T. *J. Am. Chem. Soc.* **1992**, *114*, 511.

(7) Jonas, V.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1489.

(8) Fujiang, , D.; Fowier, P. W.; Legon, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 113.

(9) Legon, A. C.; Warner, H. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1397.

0020-1669/95/1334-6546$09.00/0

Table 1. Optimized Parameters for NH_3-X_2 Complexes (X = F and Cl) for the Ground and Excited CT States[a]

	NH_3-F_2		NH_3-Cl_2	
	vdW	CT	vdW	CT
r_1	3.1574 (2.5755)	3.1435	2.8528 (2.5180)	3.4473
r_2	1.3335 (1.4300)	2.4552	2.0156 (2.0793)	2.5594
r_3	1.0011 (1.0138)	0.9966	1.0001 (1.0138)	0.9990
θ	111.44 (112.49)	79.82	111.05 (111.30)	84.64

[a] Values for vdW and CT states are calculated at the HF/6-311G(d,p) and SE-CI/6−311G(d,p) levels, respectively. The MP2/6-311G(d,p) values are given in parentheses. Bond length and angles are in angstroms and in degrees.

Table 2. Optimized Parameters for NH_3-X_2 Complexes (X = Br and I) for the Ground and Excited CT States[a]

	NH_3-Br_2		NH_3-I_2	
	vdW	CT	vdW	CT
r_1	2.5951 (2.4186)	3.1031	2.7549	3.3608
r_2	2.1593 (2.1743)	2.5183	2.6041	3.0186
r_3	1.0317 (1.0553)	1.0369	1.0317	1.0356
θ	113.62 (115.01)	81.04	113.60	81.68

[a] Values for vdW and CT states are calculated at the HF/STO-3G* and SE-CI/STO-3G* levels, respectively. The MP2/STO-3G* values are given in parenthesis. Bond length and angles are in angstroms and in degrees.

Table 3. Excitation Energies (E_{ex}, eV), Charges on Each Atom, and Oscillator Strength (*f*, au) for the $F_2-F_1\cdots NH_3$ EDA Complex Calculated at the SE-CI+MP2 Level with 6-311G(d,p) Basis Sets

		charge[b]				
state	E_{ex}[a]	N	H	F_1	F_2	f[c]
$^1A_1$	0.0	−0.560	0.192	0.020	−0.036	
^1E	6.30(4.88)	−0.561	0.187	0.072	−0.073	0.00
2^1A_1	8.07(8.24)	0.166	−0.034	−0.036	−0.029	0.156
2^1E	9.62(8.78)	−0.552	0.182	0.006	0.00	0.00

[a] SE-CI values are given in parentheses. [b] Numbers on atoms indicate $F_2-F_1\cdots H_3$. [c] Oscillator strengths are calculated at the SE-CI/6-311G(d,p) level.

Table 4. Excitation Energies (E_{ex}, eV), Charges on Each Atom, and Oscillator Strength (*f*, au) for the $Cl_2-Cl_1\cdots NH_3$ Complex Calculated at the SE-CI+MP2 Level with 6-311G(d,p) Basis Sets

		charge[b]				
state	E_{ex}[a]	N	H	Cl_1	Cl_2	f[c]
$^1A_1$	0.0	−0.546	0.186	0.025	−0.036	
^1E	6.30(4.44)	−0.566	0.206	0.073	−0.125	0.00
2^1A_1	7.61(7.14)	−0.074	0.141	−0.157	−0.191	1.191
2^1E	7.73(7.98)	−0.557	0.203	0.025	−0.078	0.00

[a] SE-CI values are given in parentheses. [b] Numbers on atoms indicate $Cl_2-Cl_1\cdots H_3$. [c] Oscillator strengths are calculated at the SE-CI/6-311G(d,p) level.

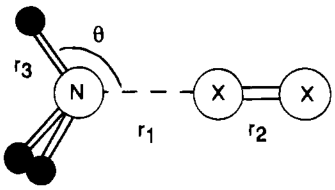
geometry obtained, Fujiang *et al.* have calculated the nuclear quadruple coupling constants for ^{10}B, ^{11}B, and ^{14}N atoms.[8] Their results were in good agreement with experiment.[9]

Almost all calculations on the σ-type EDA complexes have been thus performed for only the ground state, but the excited-state properties (especially structure at the excited state) are scarcely known. The potential energy surface for the excited state would provide important information on the charge-transfer process via the excited state and on the ion-pair formation process.[2]

In the present study, the electronic states and structures of the σ-type EDA complexes at both ground and excited states are investigated by means of *ab-initio* MO methods. The main purposes of this study are (1) to determine theoretically the structure of the σ-type EDA complex for the excited state and (2) to discuss the electronic states at both ground and excited states.

2. Method of Calculations

Since the state energies of the stable and unstable molecules have been known to be strongly affected by electron correlation and the choice of basis sets,[10] we carefully checked the effects of the basis sets and electron correlation on the calculated results. A valence triple-ζ plus polarization type basis sets 6−311G(d,p) are used for calculating NH_3-F_2 and NH_3-Cl_2 complexes.[11] For comparison, NH_3-Br_2 and NH_3-I_2 complexes are also studied with only the STO-3G* basis set. In order to include the effect of the electron correlation, we employed the second order Møller−Plesset perturbation (MP2) calculation. The single excited configuration interaction (SE-CI) method was also used to obtain the excited wave functions. The potential energy curves (PECs) were obtained by means of the MP2 calculations with SE-CI wave functions (SE-CI+MP2 level). The geometrical parameters used are given as follows:



The symmetry of the complex was assumed to be C_{3v} throughout, as treated by Roeggen and Dahl and as suggested by the X-ray experiment.[6,12]

3. Results

3.1. Structures of NH_3-X_2 Complexes. The structures of halogen molecules (X_2, where X = F and Cl) and negatively charged halogen molecules (X_2^-) were optimized by means of the energy gradient method. The geometrical parameters are calculated to be 1.4119 Å for F_2, 2.0284 Å for Cl_2, 1.9151 Å for F_2^-, and 2.6666 Å for Cl_2^- at the MP2/6-311G(d,p) level. For both cases, the bond distance between atoms is largely elongated by accepting an excess electron to form X_2^-. Increments of the distance (Δr) are calculated to be 0.5032 Å for F_2 and 0.6382 Å for Cl_2. This elongation is due to the fact that the excess electron is occupied in the π* orbital of the X_2 molecule. Fully optimized geometries of the NH_3-X_2 complexes are listed in Tables 1 and 2. It is should be noted that at the ground state the X−X distance of the NH_3-X_2 complexes is slightly elongated from that of the X_2 monomer. This feature is in good agreement with both an experimental one obtained by Bloemisk and Legon[5a] and a theoretical one obtained by Roeggen and Dahl,[6] suggesting that the level of theory employed

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(10) (a) Tachikawa, H. *J. Phys. Chem.* **1995**, *99*, 255. (b) Tachikawa, H.; Ohta, N. *Chem. Phys. Lett.* **1994**, *224*, 465. (c) Tachikawa, H.; Takamura, H.; Yoshida, H. *J. Phys. Chem.* **1994**, *98*, 5298. (d) Tachikawa, H.; Tomoda, S. *Chem. Phys.*, **1994**, *182*, 185. (e) Tachikawa, H.; Ohtake, A.; Yoshida, H. *J. Phys. Chem.* **1993**, *97*, 11944. (f) Tachikawa, H.; N. Hokari, N.; Yoshida, H. *J. Phys. Chem.* **1993**, *97*, 10035. (g) Tachikawa, H. *Chem. Phys. Lett.* **1993**, *212*, 27. (h) Tachikawa, H.; Lunnel, S.; Tornkvist, C.; Lund, A. *Int. J. Quantum. Chem.* **1992**, *43*, 449; *J. Mol. Struct. (THEOCHEM)* **1994**, *304*, 25.

(11) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *82*, 213. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (c) Frish, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Topiol, S.; Pople, J. A. *Ab-initio molecular orbital calculation program GAUSSIAN86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1986.

(12) Stromme, O. *Acta Chem. Scand.* **1959**, *13*, 268.

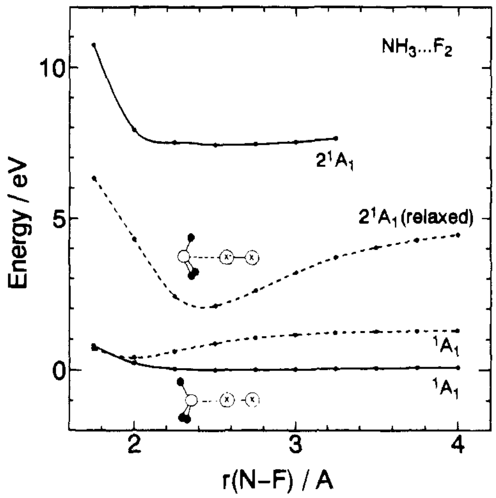

Figure 1. Potential energy curves for the NH_3-F_2 complex formation calculated at the SECI+MP2 level with the 6-311G(d,p) basis set. Solid and dotted lines indicate the PECs calculated as a function of the N−F distance, while the other geometrical parameters are fixed to those of the vdW state (solid line) and those of the CT state (dotted lines), respectively.

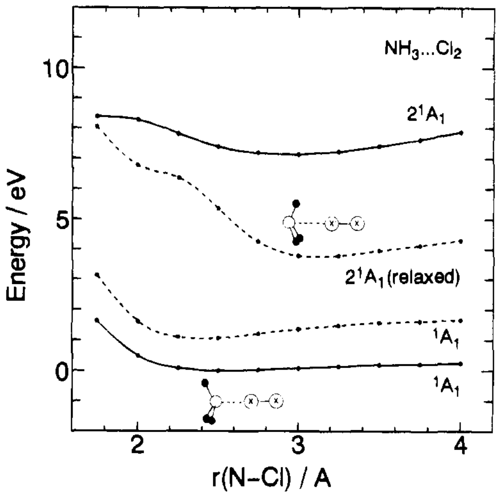

Figure 2. Potential energy curves for the NH_3-Cl_2 complex formation calculated at the SECI+MP2 level with the 6-311G(d,p) basis set. Solid and dotted lines indicate the PECs calculated as a function of the N−Cl distance, while the other geometrical parameters are fixed to those of the vdW state (solid line) and those of the CT state (dotted lines), respectively.

here would permit us to further discuss the excited property of the complex.

3.2. Electronic State and Excitation Energy. In order to elucidate the bonding nature for both ground and excited states, charges on each atom of the NH_3-X_2 complexes were calculated with the natural orbitals obtained from the SECI+MP2 calculations. The charges for the NH_3-F_2 complex are given in Table 3 together with the excitation energies (E_{ex}) and oscillator strengths (f). At the ground state, the charge on the NH_3 moiety of the complex is close to that of the neutral NH_3 molecule and the charge on F_2 molecule is close to the neutral one, suggesting that the interaction between NH_3 and X_2 is composed of the vdW force.

Since the electronic transitions from the ground to the first excited states (denoted by the $^1A_1 \rightarrow {}^1E$ transition) corresponds to the local excitation within the F_2 molecule, the charge is not changed by the excitation. However, the first excitation energy of free F_2 calculated to be 5.59 eV indicates a remarkably large blue shift as a result of the complex formation, although the calculated excitation energy is slightly different from the corresponding experimental one.[5]

By analyzing the natural orbitals, the second excitation, the $^1A_1 \rightarrow 2^1A_1$ transition, can be attributed to a charge-transfer (CT) transition from NH_3 to F_2 molecules, so that at the second excited state 2^1A_1 the charge on the F_2 molecule becomes slightly negative (−0.07). For the NH_3-Cl_2 complex, the results obtained were similar to those shown in Table 4. Charges of the complex are separated at the CT state as −0.35 for Cl_2 and +0.35 for NH_3. As will be shown in the next section, the charge separation on NH_3 and X_2 becomes much larger as a results of the structural deformation at the excited state. The oscillator strength of the $^1A_1 \rightarrow 2^1A_1$ transition in the NH_3-Cl_2 complex ($f = 1.191$ au) is much larger than in NH_3-F_2 ($f = 0.156$ au).

3.3. Structures of the EDA Complexes at the Excited State. At the excited state, it can be expected that the structure is largely deformed from the vdW structure because the electronic state of the CT state is much different from that of the ground vdW state. In order to obtain the structure of the excited CT state, the energy gradient calculations in which the vdW structure is chosen as an initial geometry are performed at the SE-CI level. The optimized parameters for the excited CT state are given in Tables 1 and 2. It is found that the structure for the CT state is considerably distorted from that of the vdW state for all cases: the angle of X−N−H is calculated to be ca. 110° for the ground-state complex, whereas the one for the CT state is ca. 80°, which is much smaller than that of the planer structure $\theta = 90°$. The umbrella structure constituted of the NH_3 moiety in the complex is inverted by the electronic excitation. It should be emphasized here that the structural distortion spontaneously occurred without the activation barrier at the CT state. The excited-state wave functions show that the charges on NH_3 and X_2 for X = F and Cl after structural deformation are $(NH_3)^{+0.61}\cdots(F_2)^{-0.61}$ and $(NH_3)^{+0.87}\cdots(Cl_2)^{-0.87}$, respectively. This implies that the charges on NH_3 and X_2 are fully separated by the structural deformation at the excited state.

The reason why structure is largely distorted at the CT state can be explained in terms of the bonding nature between NH_3 and X_2 at each state. The nonbonding orbital of the NH_3 molecule interacts weakly with the nonbonding σ (nσ) orbital of X_2 molecule at the ground state, whereas at the CT state the interaction is composed of the Coulomb force between NH_3^+ and X_2^- anion. In order to form a more strong interaction, a larger dipole moment may be induced by the bending deformation of NH_3^+, and then the dipole coordinates X_2^-. This charge−dipole interaction is the main origin of the large deformation at the CT state.

3.4. Potential Energy Curves. PECs for the formation of the NH_3-F_2 complex are plotted in Figure 1 as a function of the N−F distance r(N−F). An energy minimum with a binding energy of 1.74 kcal/mol, corresponding to the vdW complex (r(N−F) = 2.5 Å), is found on the ground-state PEC ($^1A_1$). The PECs for the excited CT state are also plotted in Figure 1 (upper solid curve). Vertical excitation energy to the 2^1A_1 state for the NH_3-F_2 complex (i.e., the geometry at the excited state is fixed to that of the vdW state) is calculated to be 8.07 eV. Adiabatic PEC (i.e., the geometries are fixed to those of the optimized structure at CT state except r(N−F)) is given in Figure 1 (upper dotted curve). It is obviously seen that the adiabatic PEC is largely shifted to the low-energy region and that the complex at the excited state is strongly bound with respect to the dissociation limit $NH_3^+ + X_2^-$. This result suggests that the structural relaxation at the excited CT state plays an important role in determining the excited-state properties. An avoided crossing between the vdW (lower dotted curve) and the CT states (upper dotted curve) is clearly seen at r(N−F) =

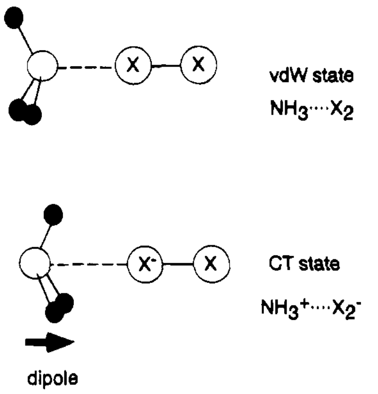

Figure 3. Schematic illustration of a structural model for the CT state of the NH_3-X_2 complex. At the CT state, the dipole induced by the bending deformation of NH_3^+ coordinates X_2^- by dipole–charge interaction.

2.4 Å. The PECs for the NH_3-Cl_2 complex were calculated with the same manner as the NH_3-F_2 system and plotted in Figure 2. The adiabatic PEC is much lower than the vertical excited-state PEC as well as in the NH_3-F_2 system.

4. Discussion

4.1. Excited-State Structures of NH_3-X_2 Complexes.

First, we discuss the structures for both ground and CT states and propose a structural model for the excited CT state of the σ-type complex on the basis of theoretical results. At the ground state, the NH_3 moiety of the complex resembles the structure of the neutral ammonia molecule, suggesting that the interaction between NH_3 and X_2 is composed of the vdW force. In contrast, the corresponding structure of the excited CT state was largely distorted from that of the ground state. These features are schematically illustrated in Figure 3. At the excited CT states, the dipole, caused by the deformation of NH_3^+, interacts with X_2^-. It can be concluded that the bonding natures between the NH_3 and X_2 molecules for the ground and excited CT states are composed of the vdW and the dipole–charge interactions, respectively.

4.2. Absorption Spectra.

Second, the absorption spectra of the NH_3-X_2 complexes are discussed on the basis of the electronic states and transition energies. The previous experiments for the σ-type NH_3-X_2 complexes indicated that the first absorption band was attributed to an intramolecular transition of the X_2 molecule and was characterized by a large blue shift relative to that of the free X_2 molecule. This blue shift is qualitatively represented by the present calculation, as described in section 3.3. The natural orbital analysis shows that the blue shift is caused by both stabilization of the ground state and instability of the excited state as a result of the complex formation.

We used medium class basis sets for calculation of the excitation energies in the present study. More elaborate calculation with a larger basis set and more accurate wave function, such as MC-SCF-CI calculations, would provide more reliable values for the excitation energy and spectral shift. Despite the approximation employed here, it was shown that a theoretical characterization of the σ-type EDA complex enables us to obtain valuable information on the electronic states and structures of the EDA complexes.

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