Theoretical Studies of Ammonia–Halogen and Methylamine–Halogen Complexes: Geometries, Harmonic Vibrational Frequencies and Their Infrared Intensities, and Excited States of Ammonia–Chlorine Monofluoride Complex

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The electron correlation effects for the geometry and stability of the ammonia–halogen (NH_3–Cl_2 and NH_3–ClF) and the methylamine–halogen (CH_3NH_2–Cl_2 and CH_3NH_2–ClF) are examined with ab initio molecular orbital calculations. The intermolecular distance, r(N–Cl), with the second order Møller–Presset (MP2) method are substantially shorten from the corresponding values with the self-consistent field (SCF) method. The halogen–halogen distance is slightly lengthened with the MP2 method from those determined with the SCF calculations. With the MP2 method the stabilization energies (ΔE) become large from those of the SCF calculation. Large high-frequency shifts for two intra CH_3–NH_2 coupled motions are found. The frequency shift and intensity change in the complex formation are mode-specific. The potential energy surfaces of the ground and low-lying excited states of NH_3–ClF complex are calculated with the configuration interaction method. The first excited state is directly dissociated to NH_3Cl+F. The charge-transfer excited state lies higher than the $\pi^* \rightarrow \sigma^*$ transition of ClF molecule, and is dissociated into NH_3+Cl+F. The NH_3Cl (C_{3v} symmetry), generated from the lowest excited states, is a stable radical. The reaction $NH_3Cl \rightarrow NH_2$+HCl is also endothermic, though the high barrier prevents the hydrogen shift to chlorine.

There is a long history of experimental studies of the infrared spectra of the molecular complexes. In 1955 Collin and D'Or[1] observed the chlorine–chlorine stretching mode at 526 cm^{-1} in the Cl_2 solution of benzene; its frequency is substantially lower than that of a free Cl_2 molecule at 559 cm^{-1} in the Raman scattering spectra. The I–I stretching of benzene–I_2, pyridine–I_2, and trimethylamine–I_2 were found to be shifted to 207 cm^{-1} from 213 cm^{-1} of a free I_2 molecule in the Raman spectra.[2] It is now a well-established fact that the halogen–halogen stretching mode is shifted to lower frequency and enhanced in the intensity by forming the Charge-Transfer (CT) molecular complexes. The intermolecular vibrational modes in trimethylamine–I_2,[3] pyridine–I_2,[4] pyridine–ICl,[5,6] pyridine–IBr,[5] and 3-picoline–ICl[6] complexes were also examined. The location and infrared intensity of the intermolecular vibrational frequencies have the strong relation to ionization energy of the electron donor and to the electron affinity of the electron acceptor. In addition, the new appearance or enhancement of the infrared absorption bands for the total symmetric mode was also noted in some CT complexes (e.g. C_6H_6–I_2) both experimentally and theoretically.[7—10] More recently, the electron-(intra)-molecular vibration (EMV) interaction model has been presented by solid state physicists.[11,12] The EMV theory is equivalent to the Matsen and Person's theory, which predicts the induced infrared absorption bands by forming the complex. In the previous papers,[13,14] using the ab initio molecular orbital method, we have systematically studied the intramolecular infrared absorption bands induced by the complex formation. The ethylene–chlorine monofluoride complex (C_2H_4–ClF) was first examined, and it was found that the direction of the transition moment for the induced C=C stretching mode is perpendicular to the ethylene plane and that a small change of the amount of the transferred electron induces the observed intensities of the intramolecular total symmetric modes. Then, we have extended the study to elucidate in more details the enhancement in intensity and the shift in frequency of the infrared absorption bands of the π–σ type complexes [C_2H_4–Cl_2 and C_2H_4–ClF], and of the n–σ type CT complexes [NH_3–Cl_2, NH_3–ClF, CH_3NH_2–Cl_2, $(CH_3)_2NH$–Cl_2, and $(CH_3)_3N$–Cl_2]. In methyl-substituted ammonia (mono-, di-, and trimethylamine) complexes, the methyl substitution influences on the N–halogen distance and intermolecular harmonic frequency as well as the halogen–halogen vibrational frequency. The harmonic frequencies of trimethylamine–chlorine were compared with the experimental results of trimethylamine–iodine of the classical paper by Yada, Tanaka, and Nagakura.[3] The induced total symmetrical IR bands of these complexes were also examined. The total symmetrical a_1 modes in ammonia and trimethylamine complexes were substantially enhanced by the complex formation.

In this paper, to examine the electron correlation effects, the geometry and the formation energies of the ammonia–halogen and methylamine–halogen complexes (NH_3–Cl_2, NH_3–ClF, CH_3NH_2–Cl_2, and CH_3NH_2–ClF) with the MP2 calculation are studied. The potential energy surfaces (PES) of low-lying states in the NH_3–ClF complex are also examined with the configuration interaction (CI) method. Since Mulliken[15] proposed the CT theory in 1952, many experimental studies of the

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electronic states for the CT complexes were reported, but only the schematic potential surfaces for the excited states of several CT complexes were often drawn qualitatively. Only a few ab initio studies of the excited states, particularly for the CT excited states, have been reported previously. We discuss the PESs of several electronic states and the photodissociation on the excited surfaces of the NH_3–ClF. Finally we study the photodissociation product, NH_3Cl radical, and its stability.

Method of Calculation

MP2 calculation. The geometrical structure, harmonic vibrational frequencies and their infrared absorption intensities for ammonia–chlorine (NH_3–Cl_2) (**I**), ammonia–chlorine monofluoride (NH_3–ClF) (**II**), methylamine–chlorine (CH_3NH_2–Cl_2) (**III**), and methylamine–chlorine monofluoride (CH_3NH_2–ClF) (**IV**) complexes were studied with the ab initio SCF molecular orbital method. The geometries of all the complexes and isolated molecules were optimized by using the analytical energy gradient method with the second-order Møllar–Plesset perturbation (MP2) theory including both inner-core and valence orbitals. For the ammonia complexes, the basis sets used were Huzinaga–Dunning double-zeta plus polarization (DZP) augmented with the diffuse sp type GTF's on chlorine (ζ=0.0483), fluorine (ζ=0.1076) and nitrogen (ζ=0.0639) atoms. The 6-31+G** basis set were used for the methylamine complexes. The harmonic frequency analysis of the amine complexes at the MP2 level were performed with the analytical second-order gradient method. The basis set superposition error (BSSE) for the optimized geometry were estimated with the counterpoise method which is based on the following equations;

$$\begin{aligned}\Delta E\ (\text{corrected}) &= E_{DA}{}^{C}(c_D \otimes c_A) \\ &- E_D{}^{m}(c_D) - E_A{}^{m}(c_A) \\ &+ [E_D{}^{C}(c_D) - E_D{}^{C}(c_D \otimes c_A) \\ &+ E_A{}^{C}(c_A) - E_A{}^{C}(c_D \otimes c_A)]\end{aligned}$$

where c_D and c_A are the basis functions on donor and acceptor molecules, respectively. The E^C and E^m are the energies calculated at the geometries of the complex and each isolated molecule.[16]

All the calculations were carried out with GAUSSIAN 88[17] and GAUSSIAN 92[18] on the HITAC S-820 at Institute for Molecular Science and on the HP 9000/735 at our laboratory.

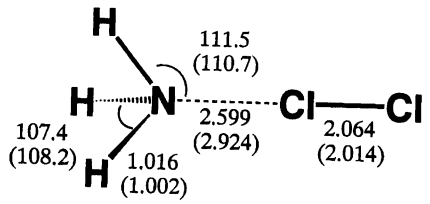
Potential Energy Surfaces for NH_3–ClF Complex. To carry out the configuration interaction (CI) calculations for complex **II**, the occupied orbitals were first determined with the closed shell self-consistent-field (SCF) method. Then, the valence-type antibonding orbitals were determined with Iwata's VALVAC method.[19] Six molecular orbitals mostly consisting of 2p of F and 3p of Cl and the nonbonding orbital of N were defined as the active orbitals. The inner-valence orbitals, 2s of F, 2s of N, 3s of Cl, and σ_{NH} were defined as core orbitals. The inner shell orbitals, 1s of F and N, and 1s, 2s, and 2p of Cl were frozen. The other vacant orbitals were defined as external orbitals. In the CI calculations, the reference configuration state functions (CSF) were all electronic configurations generated from

$$[(3e)\ (9a_1)\ (4e)\ (10a_1)\ (11a_1)]^{12}$$

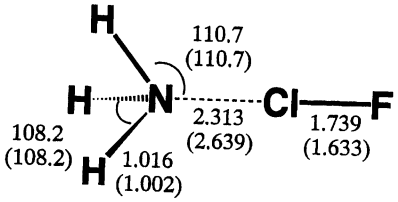
where the sum of occupation number of 3e—11a_1 was twelve. Then, from these complete active space configuration space (CAS), the polarization CI (POLCI) calculations were carried out. In POLCI calculations, the [active to external], [core to external] and [core to active] excited configurations were generated from the reference CAS. The basis sets were chosen MIDI4 of Tatewaki and Huzinaga augmented with the polarization function on nitrogen and the diffuse functions on chlorine and fluorine (MIDI4+d) and nitrogen (MIDI4*+d). The symmetry of the complex were kept C_{3v}. The bond length of nitrogen and hydrogen and the N–H–Cl angle were fixed at 1.003 Å and 111.0°, respectively. Those were the optimal parameters at the SCF/6-31+G* method.[14]

Results and Discussion

Geometries of NH_3–Cl_2 and NH_3–ClF Complex. In the previous paper[14] we have already examined the geometry of both **I** and **II** with the closed shell SCF method. In the present paper the effect of the electron correlation on the geometrical parameters of the complexes are mainly examined. The geometrical parameters are compared in Fig. 1. The intermolecular distances (**I**: 2.599 Å, **II**: 2.313 Å) with the MP2 method are substantially shortened from the corresponding values (**I**: 2.924 Å, **II**: 2.639 Å) with the SCF method. The minimum of the N–Cl distance for **II** on the potential energy surfaces calculated with the CI method is 2.304 Å, which is very close to the



(I)



(II)

Fig. 1. The optimized geometrical parameters for ammonia–chlorine (NH_3–Cl_2) (**I**) and ammonia–chlorine monofluoride (NH_3–ClF) (**II**) complexes with the MP2/DZP+diffuse calculation. Those in the parenthesis are with the SCF/DZP+diffuse calculation.

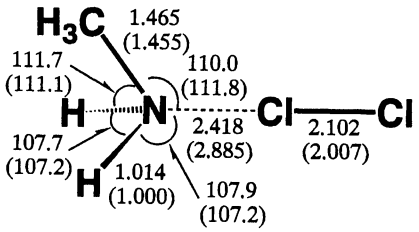
one obtained with the MP2 method, though the basis sets used are different. We have found in the previous paper that the intermolecular distance determined with the SCF method becomes longer with the quality of the basis sets. The electron correlation has a substantial effect on the intermolecular distance. On the other hand, the halogen–halogen distances are only slightly lengthened with the MP2 method (Cl_2 : 2.064 Å, ClF : 1.739 Å) from those determined with the SCF method (Cl_2 : 2.014 Å, ClF : 1.633 Å). The Cl–F bond with the CI calculation is further lengthen as longer as 1.916 Å. Almost no geometrical changes within an ammonia molecule in the complex are found with the MP2 method.

The formation energies (ΔE) after the BSSE correction with the MP2 method are -17.2 kJ mol^{-1} (**I**) and -38.9 kJ mol^{-1} (**II**), and the BSSE of **I** and **II** are estimated 10.9 kJ mol^{-1} and 9.2 kJ mol^{-1}, respectively. With the SCF calculation the ΔE with BSSE correction are -8.8 kJ mol^{-1} (**I**) and -22.8 kJ mol^{-1} (**II**) and the BSSEs of 1.7 kJ mol^{-1} (**I**) and 2.5 kJ mol^{-1} (**II**). It has been known that the MP2 energy has a larger BSSE than the SCF energy.[20]

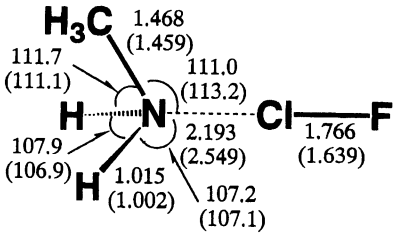
Geometries of Methylamine Complexes. In the previous paper[14] we reported the geometry and stability of three methyl-substituted ammonia (mono-, di-, and trimethylamine)–chlorine complexes, CH_3NH_2–Cl_2, $(CH_3)_2NH$–Cl_2, and $(CH_3)_3N$–Cl_2, with the SCF/6-31G method. In this section we examine the electron correlation effects in **III** and **IV**. The optimized parameters of **III** and **IV** with the MP2/6-31+G** and SCF/6-31+G** basis set are given in Fig. 2. It is found, as in the ammonia complexes, that the intermolecular distances of r(N–Cl) with the MP2 method [2.418 Å (**III**) and 2.193 Å (**IV**)] are shorter than with the SCF method [2.885 Å (**III**) and 2.570 Å (**IV**)], and that the halogen–halogen distance becomes slightly longer; from 2.007 Å to 2.102 Å (**III**) and from 1.638 Å to 1.766 Å (**IV**). A larger change in the intermolecular distance of the ClF complex than that of the Cl_2 complex is consistent with the larger electron affinity of ClF than that of Cl_2.

The formation energies (ΔE) of the methylamine complexes after the BSSE correction with the MP2 method are -19.5 kJ mol^{-1} (**III**) and -49.6 kJ mol^{-1} (**IV**). With the SCF method the ΔEs after the BSSE correction are -11.8 kJ mol^{-1} (**III**) and -29.8 kJ mol^{-1} (**IV**), which are smaller than those of the MP2 method. Again the BSSEs with the MP2 calculation [13.3 kJ mol^{-1} (**III**) and 14.3 kJ mol^{-1} (**IV**)] are larger than the BSSEs with the SCF calculation [1.7 kJ mol^{-1} (**III**) and 2.1 kJ mol^{-1} (**IV**)].

Harmonic Frequencies and Their Intensities of Methylamine Complexes. The harmonic vibrational frequencies, infrared intensities of **III**, **IV**, and CH_3NH_2 (**V**) with the MP2/6-31+G** method are listed in Table 1. The corresponding experiments



(III)



(IV)

Fig. 2. The optimized geometrical parameters for methylamine–chlorine (CH_3NH_2–Cl_2) (**III**) and methylamine–chlorine monofluoride (CH_3NH_2–ClF) (**IV**) complexes with the MP2/6-31+G** calculation. Those in the parenthesis are with SCF/6-31+G** calculation.

for two methylamine complexes are not reported in our knowledge. The halogen–halogen stretching modes are shifted towards lower frequency from those of free molecules; from 540 to 397 cm^{-1} in Cl_2 and from 781 to 576 cm^{-1} in ClF complexes. The larger shift of the ClF complexes than that of Cl_2 is consistent with the bond distance lengthening by the complex formation. The infrared intensity of the Cl–Cl stretching, which is infrared forbidden in free Cl_2, is as large as 105.2 km mol^{-1} in the complex. The intensity of the Cl–F stretching is significantly enhanced in the complex; from 23.8 to 286.8 km mol^{-1}. The intermolecular stretching modes, at 150.9 cm^{-1} in the Cl_2 complex and at 243.3 cm^{-1} in the ClF complex, have a substantially large infrared intensity. Two intermolecular bending modes of 69.6 and 221.6 cm^{-1} (**III**) and 115.2 and 339.4 cm^{-1} (**IV**) are also found.

The harmonic frequency of the internal rotation (329.1 cm^{-1}) of the methyl group in free methylamine (**V**) increases by complex formation to 480.5 cm^{-1} for **III** and 616.9 cm^{-1} for **IV**. This large shift results from the interaction with two intermolecular a″ modes, the rotation around N–Cl–Cl (F) at 106.9 cm^{-1} (**III**) and 162.4 cm^{-1} (**IV**) and the out-of-plane vibration at 209 cm^{-1} (**III**) and 260.9 cm^{-1} (**IV**). The latter two vibrations are very weak in the infrared absorption. The internal rotation of the methyl group is more hindered by the complex formation.

Table 1. Harmonic Frequencies and Their Infrared Intensities of CH_3NH_2–Cl_2, CH_3NH_2–ClF, and CH_3NH_2.

	Methylamine–Cl_2 (**III**)[a]				Methylamine–ClF (**IV**)[b]				Methylamine (**V**)[c]	
	Frequency	(shift)	Intensity		Frequency	(shift)	Intensity		Frequency	Intensity
	cm^{-1}		km mol^{-1}	Ratio	cm^{-1}		km mol^{-1}	Ratio	cm^{-1}	km mol^{-1}
a′(intermolecular bending)	69.6		1.7		115.2		0.6			
a″(CH_3 rotation around N–Cl–X)	106.9		3.5		162.4		0.2			
a′(intermolecular stretching)	150.9		89.5		243.3		82.3			
a″(CH_3 out-of- Cl–N–C plane)	208.7		0.5		260.9		1.2			
a′(intermolecular bending)	221.6		73.1		339.4		74.5			
a′(halogen stretching)	396.5	(−144)	105.2		576.1	(−205)	286.8	12.1		
a″(CH_3 internal rotation)	480.5	(+151)	30	0.7	616.9	(+288)	28.5	0.7	329.1	43.2
a′(CH_3 rocking+NH_2 wagging)	930.5	(+64)	106.6	0.6	1003	(+137)	78.6	0.4	866.2	188.7
a″(CH_3 bending+NH_2 twisting)	985.3	(−5.1)	0.2	47.4	995.6	(+5.2)	0.1	17.5	990.4	0
a′(CH_3 rocking+NH_2 wagging)	1212	(+6)	1.2	0.1	1230	(+24)	5.63	0.6	1206	9.7
a″(CH_3 bending+NH_2 twisting)	1362	(−15)	0.1	2.9	1361	(−16)	0.1	2.3	1377	0
a′(C–N stretching)	1087	(−10)	27.1	2.2	1083	(−14)	37.6	3	1097	12.4
a′(CH_3 deformation)	1502	(−3)	18.1	5.7	1502	(−2)	10.8	3.4	1505	3.2
a′(CH_3 deformation)	1547	(−4)	3.9	0.5	1546	(−5)	5.45	0.7	1551	7.3
a″(CH_3 deformation)	1563	(−8)	7.2	2.0	1557	(−14)	8.67	2.3	1571	3.7
a′(C–H stretching)	3113	(+26)	68.5	0.9	3131	(+44)	42.3	0.5	3087	81
a′(C–H stretching)	3211	(+24)	13.3	0.4	3231	(+44)	9.68	0.3	3187	33.1
a″(C–H stretching)	3249	(+16)	13.3	0.5	3264	(+31)	7.24	0.3	3233	27
a′(NH_2 deformation)	1677	(−28)	29.1	0.8	1675	(−30)	32.4	0.9	1705	37.1
a′(N–H stretching)	3580	(−15)	15.9	159.0	3572	(−23)	22.7	227	3595	0.1
a″(N–H stretching)	3688	(−14)	16.7	4.0	3678	(−24)	29.3	7	3702	4.2

a) Calculated harmonic frequency and intensity of the Cl–Cl stretching mode with MP2/6-31+G** are 540.5 cm^{-1} and 0.00 km mol^{-1}, respectively. The experimental Raman scattering frequency of this mode is 559 cm^{-1}.[21] b) Calculated harmonic frequency and intensity of the Cl–F stretching mode with MP2/6-31+G** are 781.1 cm^{-1} and 23.8 km mol^{-1}, respectively. The experimental frequency of this mode is 786 cm^{-1}.[21] c) Experimental frequencies of Raman spectra of CH_3NH_2 in water were reported as following. ν=1034, 1110, 1174, 1428, 1474, 1614, 2822, 2904, 2964, 3322, and 3382 cm^{-1}.[22]

In the methylamine complexes, the large high-frequency shifts for two intramolecular CH_3–NH_2 modes are found; the one from 329.1 to 480.5 (**III**) and 616.9 cm^{-1} (**IV**), and the other from 866.2 to 930.5 (**III**) and 1003 cm^{-1} (**IV**). The former mode is the coupled motion of the internal rotation (bending) of CH_3 and NH_2 rotation, and the latter is the coupled motion of the CH_3 rocking and NH_2 wagging. The latter infrared intensity is reduced by the complex formation, while the former's is enhanced. Three C–H stretching modes are shifted towards the higher frequency from those of free molecule, and their intensities is reduced. The N–H stretching and C–N stretching shift to lower frequencies, and their intensities is slightly enhanced. The CH_3 deformation modes are not changed or slightly shifted to lower. In the NH_2 deformation frequency is shifted to lower and its intensity is not changed. In the previous papers,[13,14] we found a kind of symmetry rule for the infrared intensity enhancement. In the CH_3NH_2 complexes, however, because of its low symmetry (C_s), such symmetry rule cannot be noticed, but the frequency shift and intensity change in the complex formation are mode-specific.

Excited States of NH_3–ClF Complex. Figure 3 shows the potential energy curves (PEC) of the low-lying states of **II** for the Cl–F bond length. The intermolecular distance is fixed at the equilibrium length (2.304 Å). The potential energy surfaces (PES) of the bond lengths N–Cl and Cl–F are shown in Fig. 4(a) for the ground state 1 $^1A_1$, in Fig. 4(b) for 1 ^1E state and in Fig. 4(c) for 2 $^1A_1$ state. By assuming the quasi-colinear triatomic model, the skewed angle coordinate system

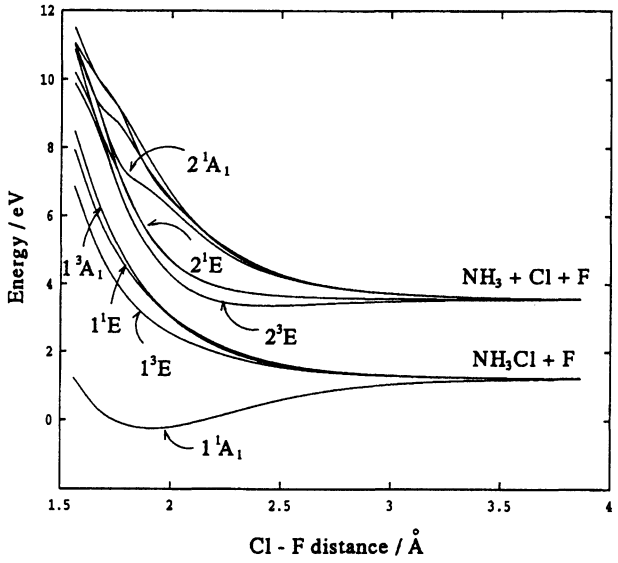


Fig. 3. Potential energy curves of NH_3–ClF complex (**II**) as the functions of R_{ClF} for a fixed R_{NCl}=2.304 Å

which diagonalyzes the kinetic part of the Hamiltonian is used in the figures. The characteristics of the PESs of the 1 ^3E and 1 $^3A_1$ states are also similar to those in Fig. 4(c). In these PECs and PESs, the geometrical structure of the NH_3 moiety is assumed unchanged.

The main electron configuration of the ground state ($^1A_1$) of **II** is

$$(6a_1)^2\ (7a_1)^2\ (8a_1)^2\ (2e)^4\ (3e)^4\ (9a_1)^2\ (4e)^4\ (10a_1)^2.$$

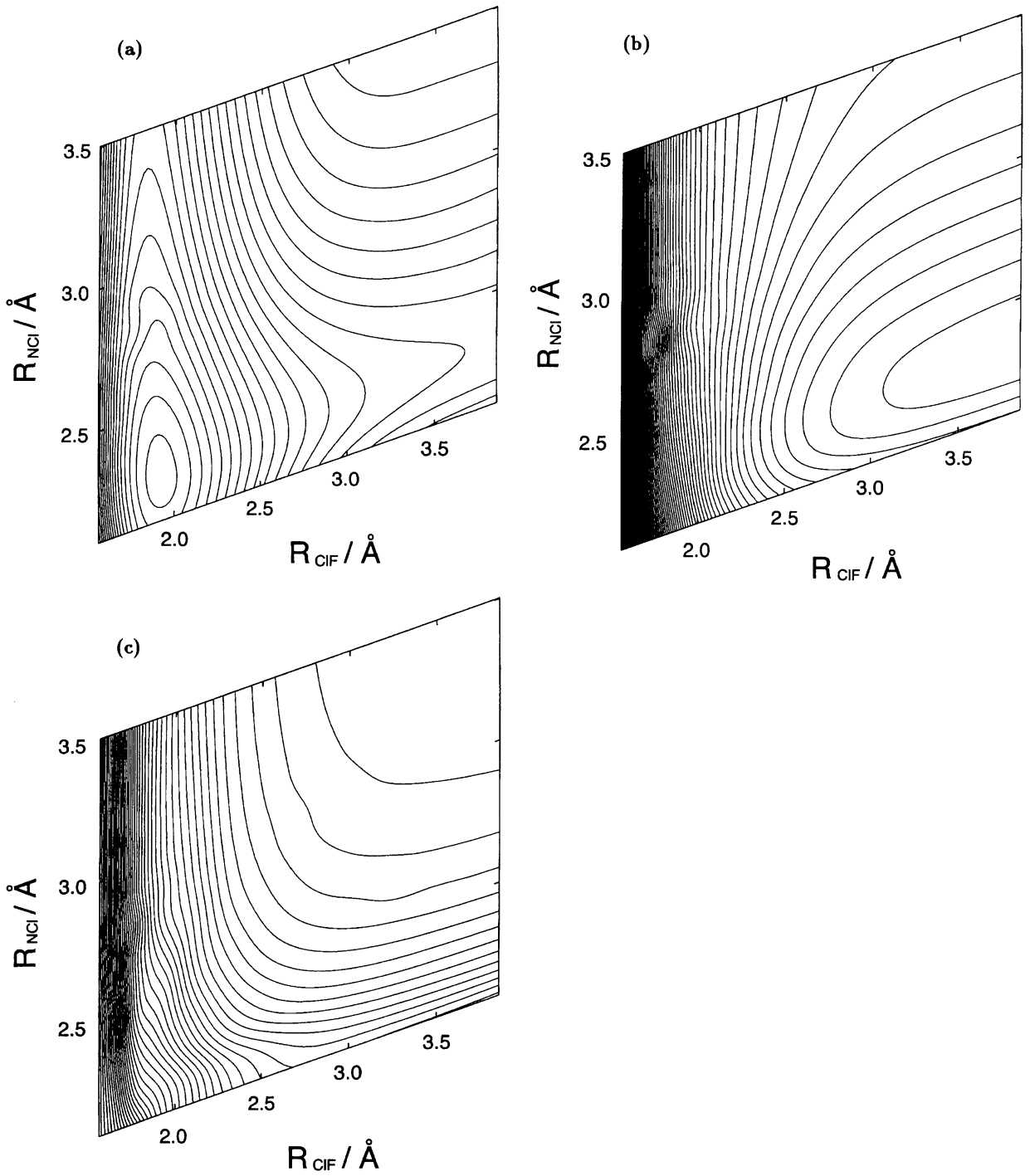


Fig. 4. Potential energy surface of NH_3–ClF complex (**II**) as the function of R_{ClF} and R_{NCl}. (a) the ground state 1 $^1A_1$. (b) the 1 ^1E state. (c) the 2 $^1A_1$ state.

The highest occupied molecular orbital (HOMO) of $10a_1$ is the nonbonding orbital of nitrogen, and the lowest unoccupied molecular orbital (LUMO), $11a_1$, is the σ^*_{ClF} orbital.

The 1 ^3E and 1 ^1E states correspond to the local excitation ($\pi^* \rightarrow \sigma^*$) in halogen molecule, and the main electron configuration is

$$(4e)^3\ (10a_1)^2\ (11a_1)^1.$$

These states are repulsive, and the complex dissociates to NH_3Cl radical (**VI**) and fluorine atom. The N–Cl distance in the product, **VI**, is slightly longer than in the ground state of **II**. The vertical excitation energy is blue-shifted from 2.1 eV in the isolated molecule ClF to 3.8 eV in **II**.

At the equilibrium geometry of the ground state, the main electron configuration of 2 $^1A_1$ state is

$$(4e)^4\ (10a_1)^1\ (11a_1)^1,$$

and the coefficients of the configuration state functions (CSF) in the CI wavefunction are 0.849 for $(n_N)\rightarrow(\sigma^*_{ClF})$, 0.205 for $(n_N)^2\rightarrow(\sigma^*_{ClF})^2$ and 0.199 for $(\pi_{ClF})\rightarrow(\sigma^*_{ClF})$. It has the charge-transfer character at the shorter N–Cl distances, and as is seen in Fig. 4-(c), this state directly dissociates to a fluorine atom, a chlorine atom and an ammonia molecule.

All the low-lying excited states in Fig. 3 are repulsive. The lower excited states ($1\ ^3E$, $1\ ^1E$, and $1\ ^3A_1$) dissociate into **VI**+F, and the higher excited states ($2\ ^3E$, $2\ ^1E$, $2\ ^1A_1$, and the doubly excitations) dissociate into NH_3+Cl+F.

Stability of Photodissociation Product. As is shown above, the product of the photodissociation with the UV excitation is NH_3Cl radical (**VI**). The optimized geometry of the radical with the unrestricted MP2 calculations is shown in Fig. 5. All the harmonic frequencies are real at this geometry. This product is a complex of an ammonia molecule and a chlorine atom. The nitrogen–chlorine distance is 2.403 Å which is longer than of **II**. The Mulliken charge population is −0.159 on chlorine atom. The BSSE-corrected binding energy of **VI** is $-28.5\ kJ\,mol^{-1}$, in which the counterpoise correction term is $9.2\ kJ\,mol^{-1}$. Because the binding energy of N–Cl is so small, this bond might be also broken during the dissociation process.

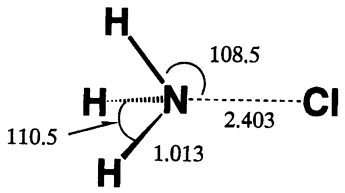
In addition to this decomposition, there are other possible reactions of **VI**. One is the hydrogen shift and dissociation reaction:

$$NH_3Cl \rightarrow NH_2 + HCl.$$

This reaction is endothermic and the reaction energy is $+84.5\ kJ\,mol^{-1}$ with the MP2 method. Besides, the high reaction barrier in the hydrogen shift is found. Another possibility is the hydrogen elimination reaction:

$$NH_3Cl \rightarrow NH_2Cl + H,$$

where NH_2Cl is a substituted ammonia. The reaction energy is as large as $+250.2\ kJ\,mol^{-1}$ with the MP2 method. Therefore, there is a possibility that **VI** may survive after the photodissociation of **II**, in particular,



(VI)

Fig. 5. The optimized geometrical parameters of NH_3Cl radical (**VI**) with the MP2/6-31+G* calculation.

in clusters and in matrix and that it could be observed with the laser spectroscopy.

Conclusion

1. From the MP2 calculations, we have found the importance of the electron correlation on the ground state properties of ammonia–halogen and methylamine–halogen complexes.
2. In methylamine complexes the vibrational mode dependence of the harmonic frequency shift is found, and the weaker modes in infrared absorption transition are in most cases enhanced by complex formation.
3. The first excited state ($1\ ^3E$) of NH_3–ClF complex is directry disociated to NH_3Cl+F. The CT excited state ($2\ ^1A_1$) is dissociated to NH_3+Cl+F.

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