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CHARGE-TRANSFER COMPLEXES. NH_3-F_2, NH_3-Cl_2, NH_3-ClF, $N(CH_3)_3$-F_2, $N(CH_3)_3$-Cl_2, AND $N(CH_3)_3$-ClF

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Charge-Transfer Complexes. NH_3-F_2, NH_3-Cl_2, NH_3-ClF, $N(CH_3)_3$-F_2, $N(CH_3)_3$-Cl_2, and $N(CH_3)_3$-ClF.

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Abstract

Non-empirical electronic structure theory has been applied to several charge-transfer complexes, which involve ammonia and trimethylamine as electron donors and molecular fluorine, chlorine, and ClF as electron acceptors. The self-consistent-field calculations employed both minimum and double zeta basis sets of contracted gaussian functions. For NH_3-F_2 and NH_3-ClF, the importance of d functions on the N, F, and Cl atoms was investigated. In several cases the minimum basis results do not appear reliable. With the geometries of the donor and acceptor molecules fixed from experiment, the equilibrium geometries of the charge-transfer complexes were predicted. N-X (X = nearest halogen atom) distances are 3.08Å (NH_3-F_2), 2.93Å (NH_3-Cl_2), and 2.65Å (NH_3-ClF), while the predicted binding energies are 0.6 Kcal (NH_3-F_2), 2.4 Kcal (NH Cl_2) and 7.7 Kcal (NH_3-ClF). NH_3-FCl is predicted to be bound by less than 0.1 Kcal/mole. The most intriguing prediction is that the binding energies of the ammonia complexes are greater than those of the corresponding trimethylamine complexes. Although this prediction is in distinct disagreement with accepted chemical intuition, it is consistent with Mulliken populations, which suggest a significantly greater "negative charge" on the ammonia N atom than that for trimethylamine. Further, the dipole moment of NH_3 is significantly larger than that of $N(CH_3)_3$.

Introduction

The term "charge-transfer complex" was introduced by Mulliken[1] in 1950 in his explanation of the observation by Benesi and Hildebrand[2] of a new absorption band in a solution of benzene and iodine dissolved in n-heptane. The observed band did not appear in the spectra of either C_6H_6 or I_2. Mulliken stated that the color of such organic molecular complexes "may be due to an intermolecular charge transfer process during light absorption". These early experimental and theoretical investigations signaled the beginning of a period of intense interest[3-9] in the properties of donor-acceptor complexes, and this interest continues to accelerate. A particularly visible example of current interest is the complex between tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ)[10]. TTF-TCNQ behaves like a one-dimensional metal at room temperature and has rekindled hopes for the eventual discovery of a practical organic superconductor.

A particularly thorny question concerns the relative importance of charge-transfer and classical electrostatic forces in the ground state of complexes such as C_6H_6-I_2. While Mulliken's early work[1,11] successfully exploited the charge-transfer model, more recent work by Hanna[12] and by Stiles[13] has emphasized the electrostatic considerations, e.g., the quadrupole-induced dipole interaction in C_6H_6-I_2. In their most recent paper on the subject, Mulliken and Person[14] conclude that electrostatic forces are likely to dominate the bonding only for the weakest donor-acceptor complexes. In this

regard it should be noted that the quantitative energy decomposition scheme recently proposed by Morokuma[15] might be valuable in resolving the above controversy.

Perhaps surprisingly, there have been very few ab initio theoretical studies reported on charge transfer complexes. An early study, that of Clementi[16] on the $NH_3 \cdot HCl$ complex, suggested a large binding energy (19.5 Kcal/mole relative to the separated molecules) and a considerable similarity with the idealized ionic $NH_4^+Cl^-$ model. Another molecular complex that has been studied ab initio is $BH_3 \cdot NH_3$, which Veillard[17] finds to have a rotational barrier comparable to ethane.

In the present paper we report the first ab initio calculations on charge transfer complexes involving halogen molecules. Halogen molecules are obvious candidates in this regard because of their substantial electron affinities[18]: F_2 (3.08 ± 0.10 eV), Cl_2 (2.38 ± 0.10 eV), Br_2 (2.51 ± 0.10 eV), and I_2 (2.58 ± 0.10 eV). Although known to be substantial, the experimentally determined electron affinities of the interhalogen diatomics are less certain[19]: FCl (∿ 2.7 eV).

Our natural inclination was study the classic benzene-halogen systems. And, in fact, nonempirical studies employing a minimum basis set were completed for C_6H_6-F_2 and C_6H_6-Cl_2. For axial (C_{6v}) approaches the predicted equilibrium distances from the center of the benzene ring to the nearest halogen atom were 3.63Å (C_6H_6-F_2) and 4.18Å (C_6H_6-Cl_2). However the binding energies relative to the infinitely separated molecules were calculated to be only 0.03 and 0.06 Kcal/mole.

Since the uncertainty in the theoretical method used is at least 1 Kcal/mole, the value of the calculations is severely limited, except to establish that the attractions are indeed rather weak. For C_6H_6-F_2, several other orientations of approach were also considered, but most proved to be repulsive.

Given this unsatisfactory initial experience, a decision was made to pursue a series of more strongly bound charge-transfer complexes. A review of the literature[3-9] suggested the amine·halogen complexes as an important series of model compounds with the desired property. Particularly important in this regard is the work of Nagakura and co-workers[20,21] on amine·iodine complexes in solution (usually n-heptane). Their experimental ΔH values are summarized in Table I, which also gives the ionization potentials of the electron-donor amines. There we see that the binding energies vary from 4.8 Kcal/mole for ammonia to 12.1 Kcal/mole for trimethylamine. This is of course consistent with the chemical intuition that the methyl group is a much better electron donating group than hydrogen. Nagakura's ΔH values also reflect the expected (in terms of Mulliken's charge transfer model) inverse relationship with the amine ionization potentials.

The molecules investigated in our theoretical study were derived from all possible combinations of NH_3 and $N(CH_3)_3$ with F_2, Cl_2, and FCl. From Nagakura's experiments one expects these charge-transfer complexes to have dissociation energies of the order of 5 Kcal/mole. This conclusion is supported by the semi-empirical calculations of Carreira and Person[22], who predict NH_3-F_2 and NH_3-Cl_2 to be bound by 10 and 22 Kcal/mole, respectively. Hence these molecules should

lend themselves to meaningful study by *a priori* quantum mechanical methods. The goal of the present research, then, is to begin to understand, in a systematic way, the electronic structure of model charge transfer complexes. As will be seen, at least one of the trends predicted here theoretically is quite contrary to accepted chemical intuition and the experimental data presented in Table I.

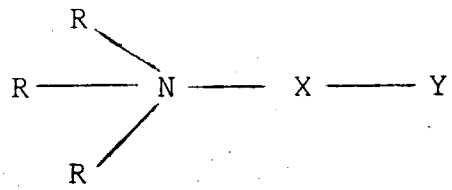
Theoretical Details

All results were obtained at the single configuration self-consistent-field (SCF) level of theory. The interactions under study are of strength comparable to hydrogen bonds, and hence one expects SCF theory to be adequate in this regard.[23] Two types of basis sets were generally used. The first of these was a three-gaussian expansion of a minimum basis set of Slater functions.[24] Secondly, Dunning's double zeta basis sets[25,26] for H, C, N, F, and Cl were used. Our general philosophy was to compare the results obtained using the two basis sets on the smaller complexes, and then use the differences to estimate uncertainties likely for the larger complexes, where only the minimum basis set was used.

All calculations were carried out on the Berkeley Datacraft 6024/4 minicomputer. Two computer programs were used, GAUSSIAN 70[27] and the Cal Tech-Ohio State-Berkeley version of POLYATOM.[28] For the largest complex considered, C_6H_6-Cl_2, one hour of minicomputer time was required for a complete calculation at a single geometry, using GAUSSIAN 70.

Throughout, the NH_3, $N(CH_3)_3$, F_2, Cl_2, and FCl molecules were fixed at their experimentally determined equilibrium geometries. For ammonia, an N-H bond distance of 1.0124Å and H-N-H bond angle of 106.67° were used.[29] For trimethylamine the geometry of Wollrab and Laurie[30] was used and we note that the nuclear repulsion energy at this geometry is +138.98685 hartrees. For F_2, Cl_2, and ClF, bond distances of 1.417, 1.988, and 1.628Å were assumed.[31]

For all of the complexes except NH_3-F_2, a C_{3v} geometry was assumed, of the general type



(1)

For NH_3-F_2, excursions about the C_{3v} potential minimum were considered but shown to be higher in total energy than the assumed orientation. Thus it seems likely that the equilibrium geometry of NR_3-XY charge transfer complexes is the one generally postulated.

Binding Energies and Geometrical Structures

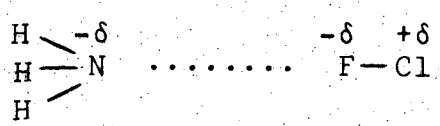
Our principal results are summarized in Table II. Let us first turn to the binding energies, in particular those of NH_3-F_2 and NH_3-Cl_2. For these two complexes the minimum basis and double zeta results are in qualitative agreement. Both basis sets predict NH_3-Cl_2 to be the more strongly bound, a result consistent with the greater polarizability of Cl_2. In both cases the more flexible DZ basis yields a deeper potential well. For the F_2 complex, the MBS and DZ binding energies differ by only 0.17 Kcal/mole, while the analogous difference is much greater, 1.29 Kcal/mole, for NH_3-Cl_2.

Since it is quite important to establish whether significant differences occur when the basis set is extended beyond the DZ level, two larger basis sets were used for the NH_3-F_2 complex. The first, labeled "extended" in Table II, employs a more flexible set of p functions on the N and F atoms. Instead of the (9s 5p/4s 2p)

contraction used in the DZ studies, a (9s 5p/4s 3p) set was adopted, again following Dunning's suggestions.[25] As seen in Table II, this extended basis increases the binding energy by only 0.02 Kcal/mole relative to the DZ result.

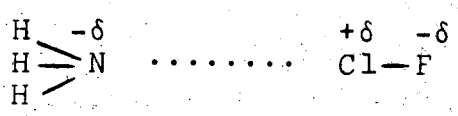
The entry labeled "polarized" in Table II uses a (9s 5p 1d/ 4s 2p 1d) basis on the N and F atoms. That is, d functions have been added to the heavy atom DZ basis sets. The d functions have a more profound effect on the binding energy, increasing it by 0.19 Kcal/mole relative to the DZ results. However, this difference is of a quantitative rather than qualitative nature, and tends to support our use of the DZ basis in general. Further support of this conclusion is given by the NH_3-ClF results obtained with a comparable polarized basis.

The first serious clash between the MBS and DZ results occurs for the N_3H-FCl complex. There the smaller basis yields a substantial binding energy (0.93 Kcal/mole), while the larger suggests no attraction at all in the expected region, r(N-F) varying from 2 to 5Å. Simple chemical reasoning suggests that the NH_3-ClF attraction should be stronger than that for NH_3-FCl, since the "repulsive"



(2)

interaction is clearly less favorable than the "attractive"



(3)

interaction. However, the use of the word "repulsive" to describe the NH_3-FCl interaction does not preclude the possibility that this complex might be bound, for example, by one Kcal/mole. Nevertheless, considering the tests on NH_3-F_2 using larger basis sets, we conclude that the double zeta results for NH_3-FCl are reliable.

The MBS and DZ results again disagree for NH_3-ClF, with the small basis yielding only a small attraction (0.17 Kcal/mole) and the larger basis predicting a strongly bound (7.66 Kcal/mole) charge transfer complex. At this point, chemical intuition clearly favors the double zeta results, in that they predict (3) to be significantly lower in energy than (2). Further, the DZ ordering of binding energies

$$NH_3\text{-ClF} > NH_3\text{-}Cl_2 > NH_3\text{-}F_2 \qquad (4)$$

is reasonable, although the fact that the ClF complex is more than three times more strongly bound than the Cl_2 complex would have been quite difficult to guess. However, in light of the additional NH_3-ClF calculations carried out with the polarized basis, this conclusion seems quite reliably established.

There is a simple explanation of the apparently spurious MBS results for the interaction between ammonia and chlorine monofluoride. It is, as seen in Table III, that the MBS predicts the wrong sign for the dipole moment of ClF. This error makes the reasoning in (2) and (3) incorrect and yields the otherwise confusing prediction that NH_3-FCl is more strongly bound than NH_3-ClF. To test if

this dipole moment prediction were due to the approximation of each Slater function by a linear combination of three gaussians, addition computations were performed. However, using 4- and 5-gaussian expansions[24], dipole moments of 0.44 and 0.43 debye (Cl^-F^+) were obtained. We conclude that a minimum basis is inadequate for the theoretical study of the interaction of ClF with amines.

Since the trimethylamine complexes have been studied using only the MBS, only qualitative conclusions may be made. Note as expected, that the erroneous dipole moment of ClF results in the spurious prediction that $(CH_3)_3N$-FCl is more strongly bound than $(CH_3)_3N$-ClF. However, the F_2 and Cl_2 complexes should exhibit no such problems, although a DZ or larger basis would be expected to yield larger binding energies.

The key result concerning the trimethylamine complexes is that <u>all four have smaller binding energies than the corresponding ammonia complexes</u>. This result is certainly in conflict with chemical reasoning, which holds that methyl is superior to hydrogen as an electron donating group. This in turn should result in the nitrogen atom being more negatively "charged" in $(CH_3)_3N$ than in H_3N and hence in a more effective charge transfer interaction. Even more important, the theoretical predictions clash with the experimental binding energies of Nagakura and co-workers[20,21], illustrated in Table I. It should be noted, however, that the theoretical differences between the NH_3 and $N(CH_3)_3$ complexes are of a much smaller magnitude than those obtained from experiment.

The validity of simple chemical reasoning may be challenged in light of Table III. There it is seen that both MBS and DZ calculations predict nitrogen to have a more negative charge in NH_3 than in $N(CH_3)_3$. Further, this ab initio conclusion is supported by experiment in that the dipole moment of ammonia is 1.47 debye, while that of trimethylamine is much less, 0.61 debye.

If the present ab initio binding energies do predict the correct ordering of the ammonia complexes relative to the trimethylamine complexes, there is perhaps only one plausible explanation of the experimental results summarized in Table I. This is that the theoretical results are appropriate only to the gas phase, and that gas phase charge transfer complex binding energies are inherently different from solution ΔH values of the type reported by Nagakura. This in turn would mean that solvent effects dominate the binding energies of such molecular complexes in solution. This conclusion is quite reminiscent to some of those arrived at by ion-cyclotron resonance (ICR) experimentaists concerning acidities and basicities of species in solution and the gas phase.[32] To take the example closest to the systems studied here, it has long been known[33] that the proton-acceptor abilities of amines in solution are in the order

$$NH_3 < RNH_2 = R_2NH > R_3N$$

In the gas phase, however, the order of basicity is now known to be[34]

$$NH_3 < RNH_2 < R_2NH < R_3N$$

The predicted intermolecular separations R(N-X) are easily correlated with the binding energies ΔE. That is, the stronger the charge transfer complex, the shorter is the N-X equilibrium separation. For NH_3-ClF, the N-Cl distance is quite short, 2.65Å, while for NH_3-F_2, a N-F distance of 3.08Å was predicted with the larger DZ basis. Incidentally, both the "extended" and "polarized" basis sets yield similar structures for NH_3-F_2, allowing us to put a reasonable degree of trust in the DZ geometry predictions. As with the binding energy, the very poor MBS result for the structure of NH_3-ClF may be attributed to the failure of the MBS to correctly predict the sign of the dipole moment of ClF.

Dipole Moments and Electronic Structure Considerations

For charge transfer complexes, a particularly significant observable is the dipole moment. More specifically the difference $\Delta\mu$ between the dipole moment of the complex and that of the separated donor and acceptor molecules is of considerable importance. The binding energy of a charge-transfer complex may be thought of as arising from the superposition of a number of interactions[35], including permanent multipole-permanent multipole, permanent multipole-induced multipole, dispersion, charge transfer, and short range repulsion interactions. Of these, only the second and fourth will lead, in a qualitative picture, to a dipole moment in excess of the vector sum of the donor and acceptor dipoles. Thus, when both

the binding energy and dipole moment of a molecular complex are known, it may be possible to make qualitative conclusions concerning the nature of the interaction.

Table III indicates that the DZ dipole moments of both NH_3 and FCl are predicted to be significantly larger than experiment. However, the difference in the dipole moment brought about by the formation of the charge transfer complex should be predicted in a qualitatively reasonable way. Comparison of Tables II and III shows that for NH_3-F_2 and NH_3-Cl_2 these $\Delta\mu$ values are 0.34 and 1.07 debye from double zeta calculations. The minimum basis set predicts the dipole moment enhancements to be less, 0.14 and 0.54 debye. In both calculations, however, the $\Delta\mu$ value is roughly three times greater for NH_3-Cl_2 than for NH_3-F_2. When d functions on N are added to the basis set, the SCF dipole moment for NH_3 is reduced by 0.37 debye to 1.97 debye. Table II in turn shows that the NH_3-F_2 dipole is reduced by 0.41 debye, a nearly comparable amount. Thus, the dipole moment enhancement remains 0.3 debye to one significant figure.

The basis set including d functions yielded an SCF dipole moment of 1.35 debyes for ClF. However the $\Delta\mu$ value obtained with the polarized basis set is 1.17 debye, quite close to the 1.12 debye obtained with the double zeta set. Thus we find the interesting result that the $\Delta\mu$ values for NH_3-Cl_2 and NH_3-ClF are quite comparable.

For the $N(CH_3)_3$ complexes, $\Delta\mu$'s have been obtained from the minimum basis calculations. Although the ClF complex results are

not meaningful, those for $N(CH_3)_3$-F_2 (0.11 debye) and $N(CH_3)_3$-Cl_2 (0.45 debye) should be. Comparison with the minimum basis results for NH_3-F_2 and NH_3-Cl_2 shows that the trimethylamine complex $\Delta\mu$'s are smaller, consistent with the prediction that the $N(CH_3)_3$ complexes have smaller binding energies. Thus our unconventional ordering of the NH_3 and $N(CH_3)_3$ complexes is supported by the $\Delta\mu$ results.

Another measure of the electronic structure changes upon complex formation is the Mulliken population analysis.[36] Table IV summarizes the Mulliken analyses for the systems studied here. Comparison with Table III would seem to imply that permanent multipole-induced multipole effects are larger than actual charge transfer from amine to halogen. Considering the DZ results for NH_3-F_2 , it is seen that to within our round-off criterion of 0.01 electrons, there is <u>no</u> transfer of charge from NH_3 to F_2. A small shift within the ammonia molecule occurs, with 0.01 being transferred from the hydrogens to the N atom. However, there is a sizeable separation of charge (0.08 "electrons") induced in the F_2 molecule, presumably by the dipole moment of NH_3. The same effect is seen to a greater degree in the NH_3-Cl_2 system. There 0.01 is transferred to the Cl_2 molecule, in which a charge separation of 0.17 is induced. The effect within the NH_3 molecule is also much larger, and the enhancement of the ammonia dipole moment may be credited to the quadrupole moment of Cl_2.

The Mulliken populations for NH_3-ClF cannot be analyzed in quite as transparent a manner, as Table III shows ClF to have

considerable charge separation (0.74 "electrons") by itself. In the complex, this separation becomes 0.86 electrons, implying that a charge separation of 0.12 electrons is induced by the ammonia molecule. Also in NH_3-ClF, 0.02 electrons are actually "transferred" from NH_3 to ClF. Quotation marks are used here and elsewhere to emphasize that such statements are based on the Mulliken analysis, which is necessarily arbitrary and of primary value for comparative rather than absolute purposes. For NH_3-ClF, the electronic rearrangement (transfer of 0.06 electrons from the hydrogens to N) in ammonia is twice as large as was the case for NH_3-Cl_2. This is an expected result in light of the sizeable dipole moment of ClF.

Our overall conclusion is that "charge-transfer" per se appears to be less important in these molecular complexes than are classical electrostatic considerations. The fact that the NH_3-ClF binding is three times stronger than that for NH_3-Cl_2 seems best understood in terms of the dipole-dipole attraction. We come to this conclusion since both the $\Delta\mu$ values and the induced charge separations (from Mulliken populations) for NH_3-ClF and NH_3-Cl_2 are comparable. Further, a simple classical calculation shows the dipole-dipole attraction between NH_3 and ClF to be of the order of 2 Kcal/mole. However, we should point out that, although the magnitudes are small, twice as much Mulliken population is transferred from NH_3 to ClF than from NH_3 to Cl_2. Also it may be worth noting that this "charge transfer" occurs over a somewhat longer distance than does the charge separation induced in the halogen molecules.

Finally, in Table V we report orbital energies for the complexes studied with the double zeta basis. Perhaps the most interesting point to be made concerning these data is that the orbital energies differ from those of the separated molecules to a degree roughly proportional to the binding energies. Consider as an example the orbitals corresponding to the ammonia le orbital. For NH_3-F_2 the complex orbital energy, -0.632 hartrees, is 0.003 hartrees lower than that of isolated NH_3. For NH_3-Cl_2 and NH_3-ClF the analogous differences are progressively larger, 0.013 and 0.031 hartrees. Similar trends can be seen for the other orbitals.

As each molecular complex is formed, the donor (NH_3) orbital energies are lowered, while those of the acceptor halogen are raised. As seen in Table V, this general rule is followed for every orbital of the three complexes. This trend is perhaps most apparent for the NH_3-Cl_2 complex. For the separated molecules the $3a_1$ orbital of NH_3 lies 0.37 hartrees above the $2\pi_g$ orbital of Cl_2. However, for the molecular complex these two orbitals become nearly degenerate, their energies lying within 0.001 hartrees of each other. Thus the donor and acceptor one-electron energy levels tend to become equalized upon formation of the molecular complex.

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Table I. Experimental binding energies[20] of several amine·iodine charge transfer complexes.

Electron Donor	Ionization Potential(ev)	ΔH(Kcal/mole)
NH_3	10.15	-4.8
$NH_2(CH_3)$	8.97	-7.1
$NH_2(C_2H_5)$	8.86	-7.4
$NH(CH_3)_2$	8.24	-9.8
$NH(C_2H_5)_2$	8.01	-9.7
$N(CH_3)_3$	7.82	-12.1
$N(C_2H_5)_3$	7.50	-12.0

Table II. Theoretical predictions of the structures, dissociation energies ΔE, and dipole moments μ of several amine·halogen molecular complexes. Here X signifies the halogen atom closest to the nitrogen nucleus. Several types of basis sets were used in these self-consistent-field calculations, including minimum basis set (MBS) and double zeta (DZ) set.

Complex	R(N-X), Å	ΔE(Kcal/mole)	μ(debye)
H_3N-F_2			
MBS	2.81	0.43	1.93
DZ	3.08	0.60	2.68
Extended	3.08	0.62	2.68
Polarized	3.04	0.79	2.27
H_3N-Cl_2			
MBS	2.95	1.09	2.33
DZ	2.93	2.38	3.41
H_3N-FCl			
MBS	2.71	0.93	2.52
DZ	Repulsive Potential Curve		
H_3N-ClF			
MBS	3.32	0.17	1.45
DZ	2.65	7.66	5.06
Polarized	2.62	7.42	4.49

Table II. Cont.

Complex	R(N-X), Å	ΔE(Kcal/mole)	μ(debye)
$(CH_3)_3N-F_2$			
MBS	2.84	0.32	1.12
$(CH_3)_3N-Cl_2$			
MBS	3.01	0.83	1.46
$(CH_3)_3N-FCl$			
MBS	2.76	0.70	1.71
$(CH_3)_3N-ClF$			
MBS	3.39	0.12	0.63

Table III. Mulliken populations and dipole moments for the polar molecules employed as electron donors and electron acceptors. The minimum basis results are presented first, with the double zeta results in prarentheses.

ClF	Cl	F	μ(theory)	μ(expt)
s	5.95 (5.96)	3.98 (4.00)		
p	11.03 (10.67)	5.05 (5.37)		
Total	16.98 (16.63)	9.02 (9.37)	-0.50 (+1.60)	+0.88[a]

NH_3	N	H(3)	μ(theory)	μ(expt)
s	3.59(3.68)	0.84 (0.71)		
p	3.88(4.20)	- (-)		
Total	7.47(7.88)	0.84 (0.71)	1.79 (2.34)	1.47[b]

$N(CH_3)_3$	N	C	$H_a(6)$	$H_s(3)$	μ (theory)	μ (expt)
s	3.52 (3.58)	3.16 (3.42)	0.93 (0.81)	0.96 (0.85)		
p	3.75 (3.69)	2.92 (3.02)	- (-)	- (-)		
Total	7.27 (7.27)	6.08 (6.44)	0.93 (0.81)	0.96 (0.85)	1.01 (1.15)	0.61[c]

[a] D. A. Gilbert, A. Roberts, and P. A. Griswold, Phys. Rev. **76**, 1723 (1949)

[b] D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, Phys. Rev. **82**, 877 (1951).

[c] D. R. Lide and D. E. Mann, J. Chem. Phys. **28**, 572 (1958).

Table IV. Mulliken populations for several amine·halogen molecular complexes. The subscript a refers to the halogen atom closest to the nitrogen atom.

	Basis Set	Amine H	Amine C	Amine N	Halogen F_a	Halogen F_b	Halogen Cl_a	Halogen Cl_b
H_3N-F_2	MBS	0.84	-	7.47	8.98	9.02	-	-
	DZ	0.70	-	7.89	8.96	9.04	-	-
H_3N-Cl_2	MBS	0.84	-	7.47	-	-	16.97	17.04
	DZ	0.69	-	7.91	-	-	16.92	17.09
H_3N-FCl	MBS	0.84	-	7.47	9.00	-	-	17.00
	DZ	Repulsive Potential Curve						
H_3N-ClF	MBS	0.84	-	7.47	-	9.04	16.96	-
	DZ	0.68	-	7.94	-	9.44	16.58	-
$(CH_3)_3N-F_2$	MBS	0.96, 0.93	6.08	7.27	8.99	9.01	-	-
$(CH_3)_3N-Cl_2$	MBS	0.96, 0.93	6.08	7.27	-	-	16.98	17.03
$(CH_3)_3N-FCl$	MBS	0.96, 0.93	6.08	7.27	9.01	-	-	16.99
$(CH_3)_3N-ClF$	MBS	0.96, 0.93	6.08	7.27	-	9.04	16.97	-

Table V. Valence orbital energies for amine·halogen molecular complexes. Results presented here were obtained using the double zeta basis. In parentheses are the orbital energies of the isolated NH_3, F_2, Cl_2, and ClF molecules.

Symmetry Type	NH_3-F_2	NH_3-ClF	NH_3Cl_2
a_1	-1.752 ($2\sigma_g$ -1.777)	-1.603 (5σ -1.649)	-1.219 ($4\sigma_g$ -1.244)
a_1	-1.478 ($2\sigma_u$ -1.504)	-1.184 ($2a_1$ -1.151)	-1.164 ($2a_1$ -1.151)
a_1	-1.154 ($2a_1$ -1.151)	-1.076 (6σ -1.115)	-0.996 ($4\sigma_u$ -1.024)
e	-0.791 ($1\pi_u$ -0.817)	-0.682 (2π -0.728)	-0.642 (1e -0.629)
a_1	-0.714 ($3\sigma_g$ -0.741)	-0.646 (7σ -0.679)	-0.558 ($5\sigma_g$ -0.584)
e	-0.651 ($1\pi_g$ -0.677)	-0.660 (1e -0.629)	-0.552 ($2\pi_u$ -0.578)
e	-0.632 (1e -0.629)	-0.465 (3π -0.504)	-0.430 ($2\pi_g$ -0.456)
a_1	-0.422 ($3a_1$ -0.419)	-0.453 ($3a_1$ -0.419)	-0.430 ($3a_1$ -0.419)

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