Some INDO Calculations of Properties of Molecular Complexes

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Abstract: Properties of several molecular D, A pairs have been calculated as a function of intermolecular distance (R_{DA}) and orientation, using the Pople–Beveridge–Dobosh INDO approximate quantum mechanical technique. The donor molecule (D) is NH_3 for all cases; calculations have been made for the following acceptor (A) molecules: F_2, H_2, N_2, HF, and Cl_2 (using CNDO/2 for the latter). Calculated properties include intermolecular interaction energy (ΔE), extent of charge transfer (F_{IN}), polarization of the acceptor X′X molecule estimated from the charge densities, dipole moment, relative X′X vibration frequency shift, the increase in the dipole moment derivative ($\Delta\mu/\Delta R_{XX'}$), the D–X′ stretching frequency, and the change in X′X equilibrium length. All these properties are shown as a function of intermolecular distance, R_{DA}. Calculations were made for approach of the X′X molecule along the C_3 axis of NH_3; for some systems, calculations were also made for approach along one of the N–H bonds. From the charge-density matrix we examine the changes in the charges when the X′X bond is stretched or compressed as in a vibration, giving a breakdown of different contributions to the infrared intensity change in this vibration expected on complexing. The relationship between calculated relative X′X frequency shifts and calculated extent of charge transfer is examined and found to be similar to the empirical one suggested by Friedrich and Person. An attempt to estimate electrostatic effects is reported. Although they are large, they do not appear to account for all the calculated changes with R_{DA}. Finally, the model emerging from these calculations is compared with the experimental results for pyridine–iodine complexes and found to be in reasonably good agreement.

Electron donor–acceptor (D–A) complexes have been extensively studied for several years.[1] The original interpretation of the experimental spectra from "charge-transfer" complexes was made by Mulliken using an intermolecular charge-transfer resonance theory.[1a] More recently, the importance of charge transfer in these complexes has been questioned,[2] and it has even been suggested that simple electrostatic effects may be of predominant importance, especially for most hydrogen-bonded complexes and for the weaker "charge-transfer" complexes exemplified by the benzene–iodine complex. Theoretical calculations[3,4] on hydrogen-bonded dimers and complexes suggest that the electrostatic effects are indeed important for weak complexes and at long D···H—X distances, whereas charge transfer is of considerable importance for strong hydrogen bonds at short D···H—X distances.

The recent success of CNDO–INDO molecular orbital calculations in a number of applications has led us to apply these methods[5,7] to donor–acceptor complexes. Such calculations are limited to complexes formed from atoms in the first row (or second row for CNDO) of the periodic table. Thus, we have chosen to make INDO calculations for "complexes" of NH_3 with F_2, H_2, N_2, and HF. Less reliable CNDO/2 calculations have been made for NH_3 with Cl_2.

For these complexes, we have calculated a variety of properties as a function of the intermolecular D–A separation, including the energy of interaction, vibrational frequency shifts, intermolecular vibrational frequencies, infrared intensity changes, extent of charge transfer and polarization, and overall dipole moments. Some indication of the expected reliability of these calculated results may be obtained from the comparison given by Kollman and Allen[3,4a] of CNDO-calculated results for hydrogen-bonded systems with *ab initio* calculations. In general, they found the results of the CNDO calculations to be in reasonable agreement with the *ab initio* results.

Although there are no experimental data available for the complexes we have chosen here for study, we do expect that the behavior we calculate for these systems, as a function of intermolecular D–A distance, will provide a *model* for the behavior of real systems. In particular, we believe these calculations provide a useful model for the experimentally known properties of amine·halogen complexes, especially indicating how these properties are expected to change as the two molecules approach each other to form the complex.

Method of Calculation

The physical properties of the complexes of NH_3 with H_2, N_2, F_2, and HF were calculated using the Pople–Beveridge–Dobosh INDO approximate quantum mechanical treatment.[5] The properties of the $NH_3 \cdot Cl_2$ system were calculated using the Pople–Santry–Segal[6] CNDO/2 method[7] for second-row elements. We used the CNDO and INDO molecular orbital program No. 141 from the Quantum Chemistry Program Exchange, University of Indiana. This program was modified as recommended by Santry[8] for second-row

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(1) For a general review, see (a) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969; (b) G. Briegleb, "Elektronen·Donator·Acceptor·Komplexe," Springer·Verlag, Berlin, 1961; (c) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden·Day, San Francisco, Calif.; (d) R. Foster, "Organic Charge Transfer Complexes," Academic Press, London, 1969.

(2) M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968).

(3) See especially P. A. Kollman and L. C. Allen, *ibid.*, **93**, 4991 (1971).

(4) Some of the recent papers on hydrogen·bonded complexes include (a) P. A. Kollman and L. C. Allen, *ibid.*, **92**, 753 (1970); (b) A. S. N. Murthy and C. N. Rao, *Theor. Chim. Acta*, **13**, 81 (1968); *Chem. Phys. Lett.*, **2**, 123 (1968); (c) T. Ocvirk, *Theor. Chim. Acta*, **10**, 197 (1968); (d) A. Pullman and H. Berthod, *ibid.*, **10**, 461 (1968); (e) P. Shuster and T. Funck, *Chem. Phys. Lett.*, **2**, 587 (1968).

(5) (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970; (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(6) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, 120 (1965).

(7) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

(8) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).

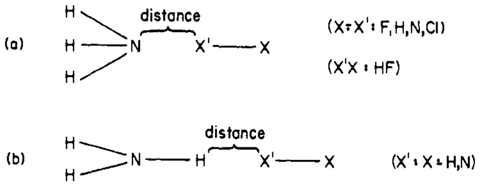

Figure 1. Summary figure defining the D–A distances used to define the complex and plotted in subsequent figures (C_{3v} in a and C_s in b) showing the two different approaches considered.

elements, and the calculations were carried out with an IBM 360-65 computer.

First, calculations were carried out for individual NH_3, N_2, H_2, F_2, HF, and Cl_2 molecules. For the diatomic molecules, calculations were made at different internuclear distances, and for NH_3 the bond angles were fixed at tetrahedral and the NH bond lengths were varied in order to find the distances for which the energy was a minimum. The calculated results reported in Table I are in fair agreement with the experimental bond distances (generally within a few tenths of an ångström), indicating the order of reliability of geometry predictions for the monomers. As Kollman and Allen have previously stated,[4a] however, we expect the *changes* in properties as the complex forms to be predicted with greater reliability.

Table I. INDO-Calculated Equilibrium Distances (R_e) for Isolated Molecules

	R_e, Å	
Molecule	Calcd[a]	Exptl
NH_3	1.067	1.012[b] (α = 106.67°)[b]
F_2	1.128	1.43[c]
Cl_2[d]	2.035	1.988[c]
H_2	0.746	0.742[c]
N_2	1.197	1.094[c]
HF	1.006	0.917[c]

[a] This research. [b] From G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, Table 65. [c] From G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950, Table 39. [d] CNDO calculation.

Next, INDO (CNDO) calculations were carried out on the H_3N–X'X complexes (X' = X = N, H, F, Cl; X'X = HF). In each calculation the geometry of the NH_3 molecule was kept fixed at the value calculated for the monomer (tetrahedral HNH angles, with an NH bond distance of 1.067 Å), and the diatomic molecule was assumed to approach the NH_3 molecule in some specified manner, as shown in Figure 1. Two different approaches were considered: one with the diatomic molecule aligned on the threefold axis of the NH_3, and the other with the diatomic molecule aligned along an N–H bond. At each value of the D–A distance, the X'X distance was varied to find the distance corresponding to the calculated energy minimum for the complex. The D–A distance was measured by specifying the N–X' distance. (See Figure 1.)

We have computed the potential energy for the interaction between D and A molecules by taking the difference between the computed energy of the complex and the sum of the computed energies of the separated molecules. In calculating the intermolecular equilibrium distance, $R^e_{NX'}$, and the intramolecular equilibrium distance, $R^e_{X'X}$, and also in calculating the two corresponding vibrational frequencies associated with stretching the NX' and X'X bonds, we have assumed that the potential energy functions for these two motions are harmonic oscillator functions. We have calculated, for example, the energy of the H_3N–X'X system at a given value of $R_{NX'}$, but for different values of $R_{X'X'}$ with displacements of X' and X atoms varied symmetrically about the estimated minimum-energy value of $R_{X'X}$. These energies are then fitted to a parabola representing the potential energy of a harmonic oscillator with energy given by the minimum of curve and with wave number $\omega_{X'X}$ and equilibrium distance $R^e_{X'X}$ values to fit the curve. These estimated values are expected to be reasonably reliable if the "X'X stretching" vibration and the normal coordinate for the "NX' stretching" vibration are both expected to be the corresponding "pure" stretches, with very little mixing. We believe this approximation is pretty good for weak complexes where $\omega_{X'X}$ is expected to be higher than $\omega_{NX'}$. However, for the $H_3N \cdot Cl_2$ complex the two predicted frequencies on this basis are about the same, suggesting substantial mixing of these two symmetry coordinates to form the actual normal coordinates of this complex.

The dipole moments μ for the molecules and for the complexes are calculated[5] from the calculated charge densities and sp polarization terms, as is the extent of charge transfer. The dipole moment derivatives, $\Delta\mu/\Delta r_i$, are obtained by calculating μ for the complex in a given configuration (specified by values of R_{NX} and $R_{X'X}$) and then again for a different configuration—for example, at R_{NX}, and $R_{X'X} + \Delta R_{X'X}$ to give $\Delta\mu/\Delta R_{X'X}$. The extent of charge transfer is found by summing the charge densities on the atoms in X'X, for example, in the complex at a given configuration, and then subtracting the corresponding values for the free X'X molecule. This definition is expected to correspond to the quantity F_{1N} defined by Mulliken and Person.[1a]

Results

The results of our calculations for the equilibrium values of the properties we investigated here (energy of formation ΔE, extent of charge transfer F_{1N}, the polarization of X'X measured by the difference in electron densities on X' and X atoms in the complex,[9] the calculated dipole moment of the complex, the relative X'X wave-number shift $(\omega_0 - \omega_c)/\omega_0$, the increase in the X'X dipole moment derivative $[(\Delta\mu/\Delta R_{X'X})_c - (\Delta\mu/\Delta R_{X'X})_0]$, the calculated NX' equilibrium distance $R^e_{NX'}$, the calculated X'X equilibrium distance $R^e_{X'X}$, and the calculated NX' stretching vibration frequency $\omega_{NX'}$) are all summarized in Table II. Here a c subscript on a symbol represents the value of that property calculated for the complex; a 0 subscript represents the value of that property cal-

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[9] Polarization is defined as the redistribution of charge in the monomer fragment assuming that charge transfer was symmetric in the dimer and then charge is redistributed. For example, if the charge densities on the H_2 were H' (+0.074 electron) and H (−0.130 electron), the charge transfer would be 0.056 electron and the polarization 0.102 electron. Our polarization differs from Kollman and Allen's "charge shift"[3] in that their term includes charge transfer to X.

Table II. Values of Molecular Properties of Complexes between NH_3 and XX′ Molecules, from INDO Calculations at the Calculated Equilibrium Intermolecular Distance[g]

XX′	$-\Delta E$, kcal/mol	F_{1N} Charge transfer, no. of electrons	Polarization charge, no. of electrons	μ,[a] D	$(\omega_0 - \omega_c)/\omega_0$	$(\Delta\mu/\Delta r)_c - (\Delta\mu/(\Delta r)_f$,[b] D/Å	NX′ (HX′) equilibrium distance, Å	XX′ distance,[c] Å	ω_{NX},[d] cm^{-1}
H–F	31.7	0.149	0.082	5.47	0.097	4.6	1.4	1.05 (0.04)	745
F–F	10.4	0.078	0.064	3.09	0.041	6.2	1.6	1.14 -(0.01)	406
H–H (C_{3v})[f]	7.5	0.056	0.102	2.76	0.036	2.5	1.6	0.78 (0.03)	791
N–N (C_{3v})[f]	6.9	0.018	0.029	2.34	0.012	2.1	1.8	1.15 (0.003)	294
N–N (C_s)[f]	6.9	0.032	0.001	2.06	0.0004	0.08	1.6	1.15 (0.003)	
H–H (C_s)[f]	0.6	0.00008	0.0002	1.89	0.002	0.05	1.8	0.75 (0.00)	
Cl–Cl	21.8	0.185	0.164	6.74	0.037[e]	9.65	1.9	2.07 (0.035)	620[e]

[a] The calculated dipole moment for the isolated NH_3 molecule is μ = 1.89 D. [b] Here $(\Delta\mu/\Delta r)_c$ is the calculated dipole derivative for stretching the XX′ bond in the complex; $(\Delta\mu/\Delta r)_f$ is the corresponding value for the free molecule. [c] Here the value in parentheses is the increase from the free molecule. [d] Calculated value of the intermolecular stretching frequency for the vibration of the NH_3 molecule against the XX′ molecule. This value is expected to be too high approximately by a factor of $\sqrt{2}$; see text. [e] This calculated frequency shift (or frequency) is not expected to be correct, because the X′X stretch is a poor normal coordinator; see text. [f] Here C_{3v} indicates the complex in which XX′ approaches NH_3 along the C_3 axis; C_s indicates the complex in which XX′ approaches along the NH bond; see Figure 1. [g] See footnote 14 for a discussion of the overemphasis on charge transfer that we expect at this $R^e_{NX'}$ distance; also see text.

culated for the free molecule. Our results are probably better pictured by studying in some detail the summary plots of the individual properties for all complexes plotted as a function of the NX′ distance and shown in Figures 2–7. In an attempt to clarify these summary plots, we present in Figures 8 and 9 graphs showing the variation of each single property of a complex as a function of the D–A distance for the $H_3N \cdot HF$ complex (in Figure 8) and for the $H_3N \cdot Cl_2$ complex (in Figure 9). Other individual complexes would have plots similar to Figures 8 or 9, with the data for the single complex selected from the summary Figures 2–7.

We believe that the calculations for the complexes from second-row atoms (for example, in Figure 9) are likely to be less reliable than those for the other complexes, because of the probably less reliable CNDO parameters for second-row atoms.

Now let us examine each of the summary plots in some detail, beginning with the potential energy plots in Figure 2. Three of the complexes have a calculated energy of formation of about −7 kcal/mol, with a calculated $R^e_{NX'}$ about 1.1–1.2 Å shorter than the van der Waals distances estimated from the radii listed by Pauling.[10] Our previous experience with INDO calculations for water dimers[11] suggests that we can expect the calculated energy of formation to be overestimated by about a factor of 2 and the calculated intermolecular equilibrium distance to be underestimated by 0.3–0.5 Å, compared to experimental values. We believe that the results that we calculate at R_{DA} values about 0.3–0.5 Å greater than $R^e_{NX'}$ (in Figures 2–9) are quite reasonable estimates of what might be expected from experimental studies of these systems. Note that we have considered here only one or two orientations of the two molecules. Experimental values of the interaction energy will be weighted averages over all orientations.

Here a slightly stronger interaction is calculated for N_2 and for H_2 than might be expected, with the H_2 interactions strongly dependent on orientation. The interaction between F_2 and NH_3 is predicted to be the strongest of those in Figure 2. Comparison with the results shown in Figure 3 for the extent of charge transfer suggests that the extra stability of the F_2

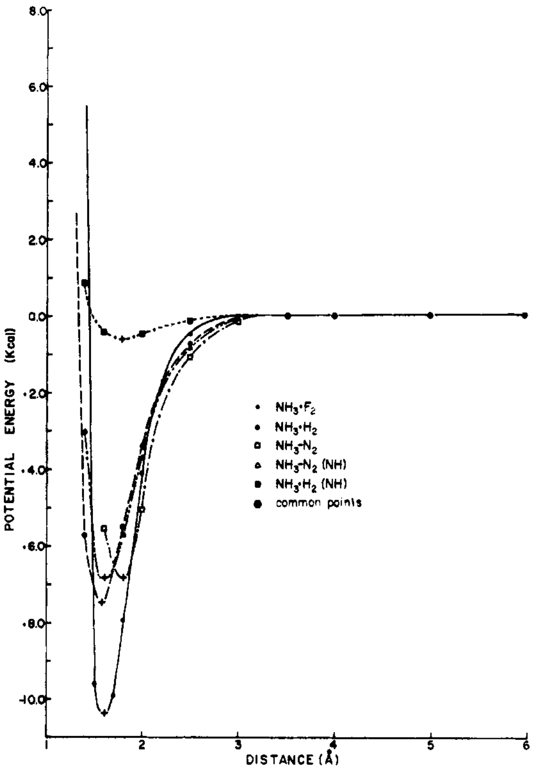

Figure 2. The potential energy calculated from INDO approximate wave functions for complexes of NH_3 with several molecules, plotted as a function of intermolecular distance. (See Figure 1.) Here + marks the calculated equilibrium distance.

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(10) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(11) L. A. Carreira and W. B. Person, unpublished results.

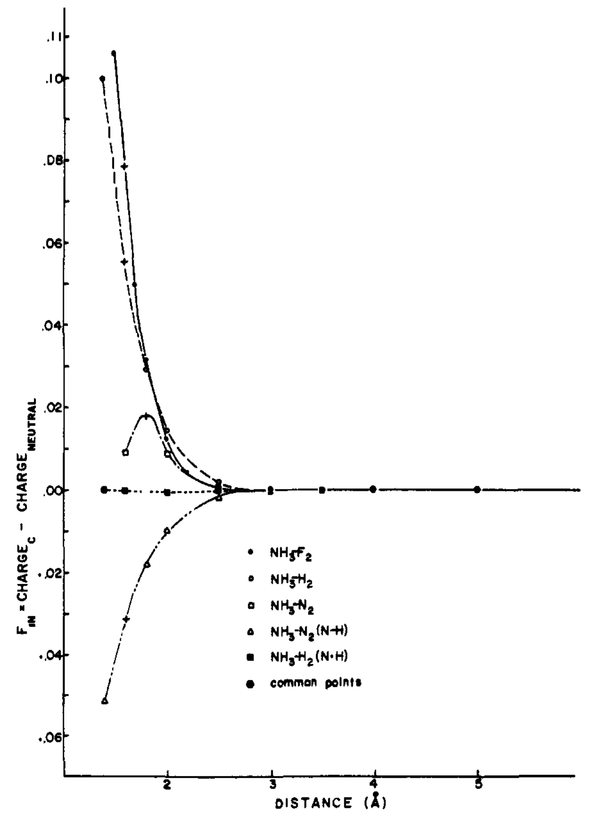

Figure 3. Extent of charge transfer calculated from INDO wave functions as a function of intermolecular distance (see Figure 1) for some complexes with NH_3. Here + on each curve marks the calculated equilibrium distance.

complex is due to the greater extent of charge transfer in that complex. The results for N_2 with NH_3 in Figure 3, we believe, indicate very little charge transfer in that system. It is most interesting, however, to note in Figure 3 that the charge transfer calculated for N_2 approaching NH_3 along the threefold axis is from H_3N to N_2, while that calculated for the approach along the NH bond is from N_2 to H_3N, as expected if there were some charge transfer in this complex. These conclusions are still valid for relative energies calculated at the expected "experimental" distances of $R^e_{NX'}$ + 0.3–0.5 Å.

The most unexpected result in Figure 3 is the extent of charge transfer calculated for the H_2 interaction along the threefold axis. This magnitude of charge transfer is much greater than one might have expected. We think, however, that it may be a significant prediction, since we calculate that no charge transfer occurs when the H_2 molecule approaches along the NH bond.

Because of the tendency for the INDO calculations to underestimate $R^e_{NX'}$, we think the *extent* of charge transfer at the calculated equilibrium distance is probably higher than the actual charge transfer in a real "complex" at its "experimental" equilibrium distance of $R^e_{NX'}$ + 0.3–0.5 Å, but the *relative* calculated magnitudes are probably significant.

Figure 4 shows a plot of the total dipole moment *vs.* N–X′ (H–X′) distance. One would expect the total dipole moment to increase rapidly with increasing charge transfer in the complex, whereas it is not expected to change drastically from the vector sum of dipoles of the isolated molecules for complexes stabilized only by electrostatic bonding. For H_2 and F_2 approaching along the axis, the extent of charge transfer at $R^e_{NX'}$ (Figure 3) is great, and the predicted dipole moments of these complexes do also increase considerably with decreasing distance. For H_2 approaching along the NH bond, the calculated extent of charge transfer was zero, indicating a weak electrostatic interaction, and the calculated dipole moment in Figure 4 does not depend on the intermolecular D–A distance. Only a slight increase in dipole moment is calculated for the "complexes" with N_2, as expected from the calculated small extent of charge transfer shown in Figure 3. Again the expected underestimate of $R^e_{NX'}$ probably means that the calculated dipole moment at $R^e_{NX'}$ of the complex is too large, but we believe that the value from Figure 4 at $R^e_{NX'}$ + 0.3–0.5 Å is a reasonable prediction for the experimental moment. Thus we predict an increase in dipole moment on complexing of about 1.0–1.5 D for F_2 with NH_3.

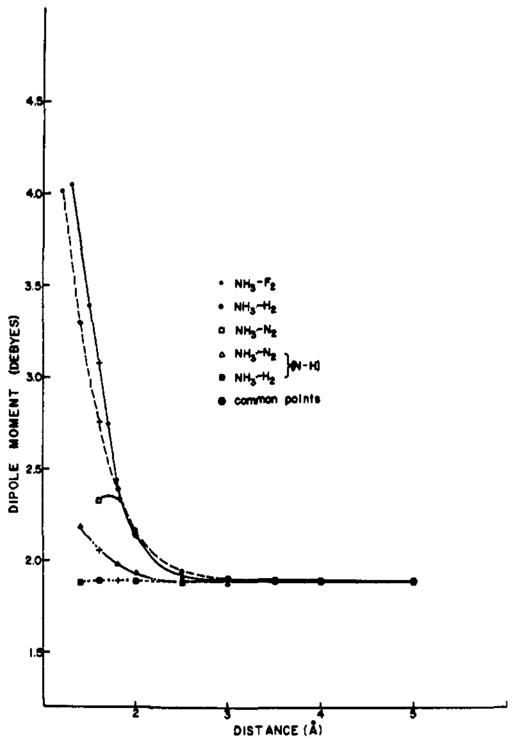

Figure 4. The dipole moments calculated from INDO wave functions, as a function of D–A distance (see Figure 1) for some complexes with NH_3. Here the + on the curve marks the calculated equilibrium distance.

Figure 5 shows the relative frequency shift of the X′–X stretching frequency, $(\omega_0 - \omega_c)/\omega_0$, plotted *vs.* D–A distance. In the complexes with F_2 and H_2 for which the high degree of charge transfer was indicated in Figure 2, the frequency of the X′–X stretch is expected to be lowered considerably. In the complex in which N_2 approaches along the C_3 axis and acts as a weak electron acceptor, we also predict only slight decrease in the frequency, presumably due to weaker charge-transfer effects. Where N_2 approaches along the NH bond and acts as an electron donor (and for H_2 along the NH bond, where there is calculated to be no charge transfer), the X_2 frequency is predicted to be practically unaltered. We have carried out a

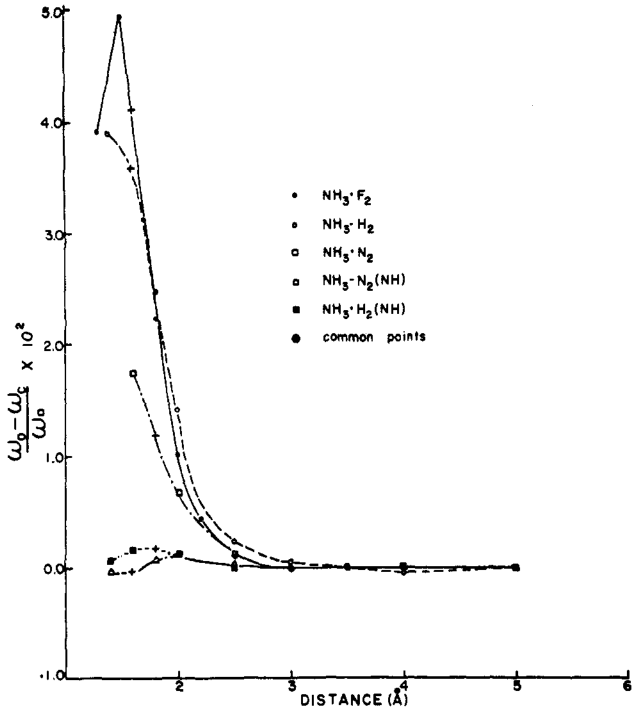

Figure 5. The relative shift of the X′–X stretching frequency, calculated by the INDO procedure, shown as a function of D–A distance (as defined in Figure 1). Here the + signifies the value at the calculated equilibrium distance.

similar calculation for the N–H stretching frequencies of the NH$_3$ in the C_{3v} complexes and find that they are practically unaltered as the intermolecular distance changes, in all cases. For example, the frequency of the NH$_3$ symmetric stretch was calculated to be about 0.1% lower at the equilibrium configuration of the complex than for the free molecule.

In Figure 6 we show the variation predicted for $\Delta\mu/\Delta R_{XX'}$ as a function of D–A distance. We calculate a large increase in the value of $\Delta\mu/\Delta R_{X'X}$ at $R^e_{NX'}$ (or at $R^e_{NX'}$ + 0.3−0.5 Å) from that for the free molecule, especially for the complexes with large charge transfer. The resulting increase in the intensity of the X′X stretching vibration is an empirically observed characteristic behavior of halogen complexes.[1a] We shall discuss this behavior in more detail below. Note here just that the ordering of the calculated values of $\Delta\mu/\Delta R_{X'X}$ (and thus the intensification) is the same as the ordering of the complexes according to the calculated total charge transfer, in agreement with expectations based on experimental results from I$_2$ complexes and from the more qualitative resonance structure arguments.[1a]

Finally, in Figure 7 we see the predicted relative increase in the length of the X′X bond as the complexes form. Again this behavior is expected qualitatively because the charge transfer on complex formation is thought[1a] to be into an antibonding orbital on X′X. However, the calculated change in bond length here is quite small except, surprisingly, for the C_{3v} complex with H$_2$. Because the effect *is* so small, in general, we shall not try to attach much significance to this result.

The results in Figure 8 for the H$_3$N·HF system are of considerable importance in that they can be compared,

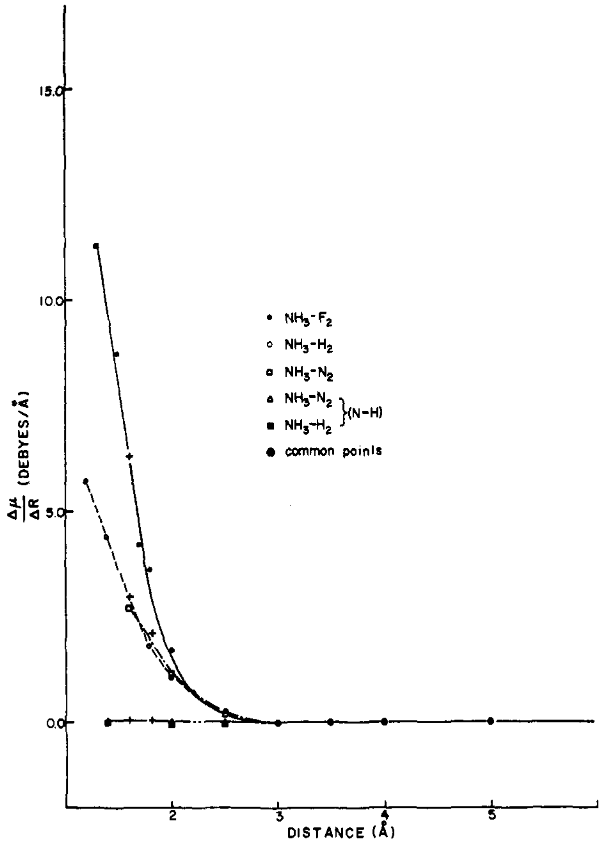

Figure 6. The values of the dipole derivative $\Delta\mu/\Delta R_{X'X}$ for the X′X stretching vibration, calculated from INDO wave functions, for various X′X complexes with NH$_3$, shown as a function of D–A distance. The + signifies the value at the calculated equilibrium distance.

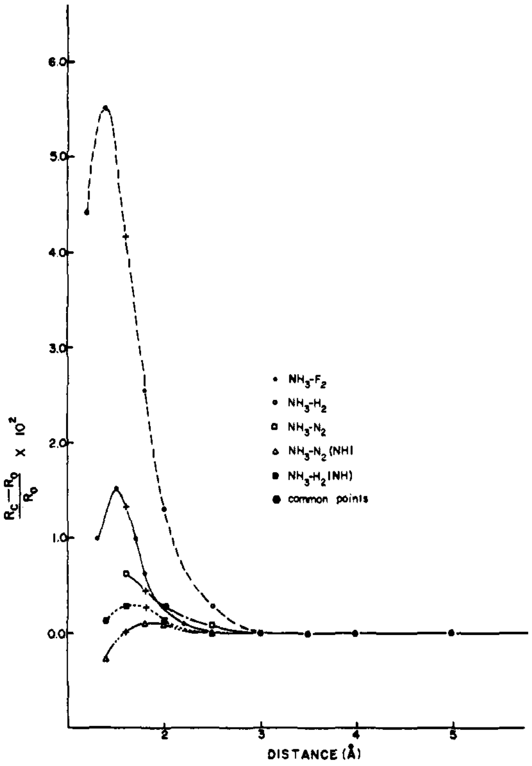

Figure 7. The relative change in the calculated X′X bond lengths (from the INDO procedure) shown as a function of D–A distance (defined in Figure 1) for some X′X complexes with NH$_3$. Here the + signifies the calculated equilibrium position.

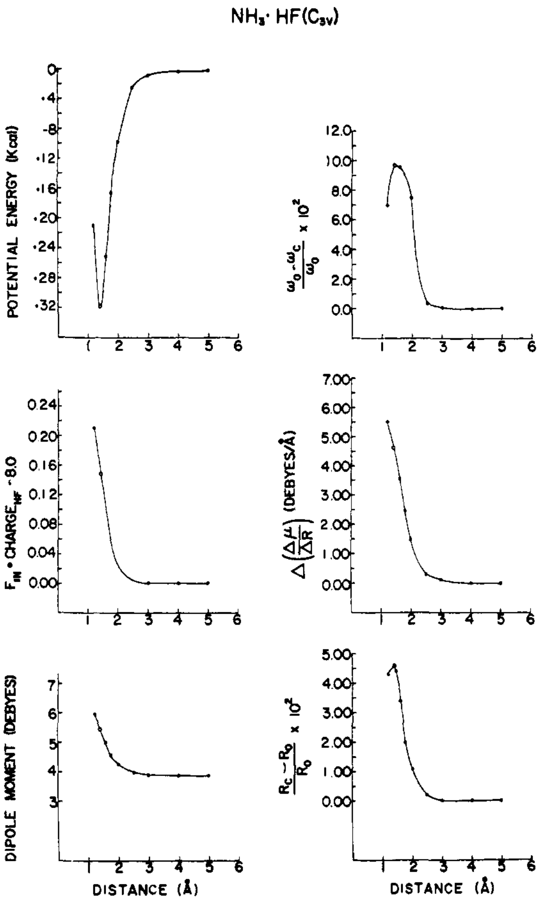

Figure 8. Summary of properties calculated from INDO wave functions for the $H_3N \cdot HF$ complex, shown as a function of D–A distance (see Figure 1). ○ marks the calculated equilibrium distance.

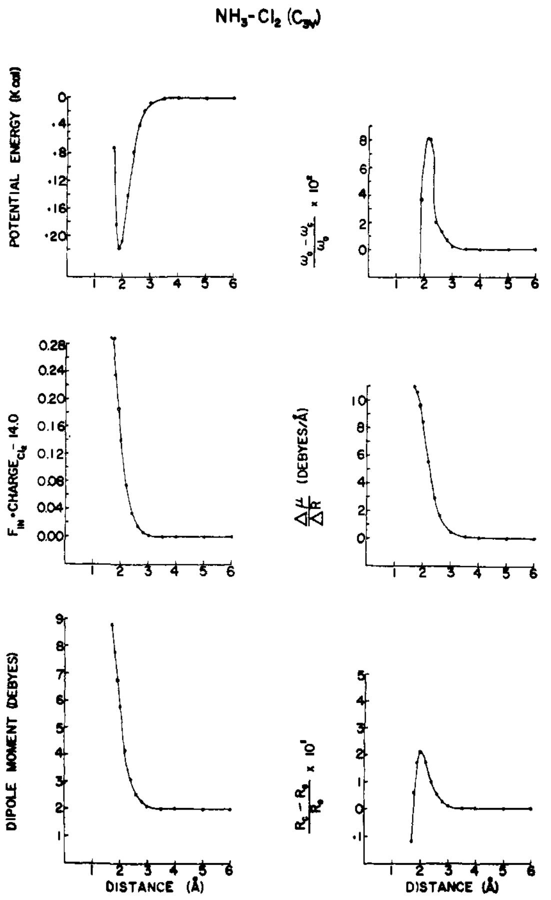

Figure 9. Summary of properties calculated from CNDO/2 wave functions for the $H_3N \cdot Cl_2$ complex, shown as a function of D–A distance (see Figure 1). Here ○ marks the calculated equilibrium distance.

in part, with calculations on this system by Kollman and Allen.[3,4a] When we do so, we find again that the INDO calculations tend to overemphasize the bonding effects in this interaction, in agreement with the findings for the water dimer mentioned earlier. For example, we calculate that the equilibrium N–H distance in the complex is 1.4 Å, corresponding to an N–F distance of 2.45 Å, about 0.3 Å shorter than found from the *ab initio* calculation of Kollman and Allen.[3] At the calculated equilibrium distance, we predict an energy of formation greater by a factor of about 2.5 than that predicted in the *ab initio* calculation.[3] At that distance (2.45 Å) we estimate the extent of charge transfer to be 0.15 electron compared to 0.03 electron calculated at the equilibrium found from the *ab initio* calculation.[3] At $R^e_{NX'}$ + 0.3–0.5 Å, however, we calculate F_{IN} to be about 0.05–0.08, in reasonable agreement with the *ab initio* calculation. On the other hand, we estimate that the HF bond length increases only by about 5% in the complex, compared to an estimated increase by Kollman and Allen[3] of 10%.

In spite of the lack of *quantitative* agreement between our results and those of Kollman and Allen,[3] we do find the *general* agreement to be acceptable. As expected, our INDO results agree fairly well with the CNDO calculation by Kollman and Allen,[4a] with almost exact agreement between the calculated equilibrium distances and with our INDO calculated energy of formation 50% greater than that from the CNDO calculation. It is perhaps worth noting here that we, also, do *not* predict ion-pair formation to $NH_4^+F^-$ for this system, in contrast to the $H_3N \cdot HCl$ system.[12]

This comparison suggests that we can expect the INDO results to exaggerate the bonding effects, so that the magnitudes of the calculated changes for properties that vary with D–A distance may be overestimated, but qualitatively correct.

Finally, it is interesting to examine the $H_3N \cdot Cl_2$ system, shown in Figure 9. We see there (and in Table II) that our calculations predict a very high energy of formation for this complex, with quite short R^e_{NCl}, and with quite high charge transfer (0.18 electron). These values can be compared with *ab initio* results by van Duijneveldt and Mulliken,[13] whereupon we find that our calculated R^e_{NCl} is too short by about 0.5 Å. Our calculated energy and F_{IN} values at the equilibrium value calculated by van Duijneveldt and Mulliken[13] are comparable to theirs. Again, we must conclude that the repulsion energy is underestimated in our CNDO calculation, but that the properties calculated at R^e_{NCl} + 0.3–0.5 Å can be expected to be in fair agreement with the *ab initio* calculation and probably with experiment. Furthermore, we believe the trends (such as increasing F_{IN} with decreasing D–A distance) predicted by this simple CNDO calculation are in good

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(12) E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967).

(13) F. B. van Duijneveldt and R. S. Mulliken, to be published.

Table III. Atomic Charges from the Charge-Density Matrix from the INDO Wave Functions for Complexes of XX′ Molecules with NH_3[a]

Atom		Free NH_3	XX′					
			F_2 (C_{3v})[b]	H_2 (C_{3v})[b]	N_2 (C_{3v})[b]	N_2 (C_s)[b]	H_2 (C_s)[b]	Cl_2 (C_{3v})[b]
				At the XX′ Distance R				
NH_3	N	5.2456	5.2094[e]	5.2225	5.2149[e]	5.2839[e]	5.2476[e]	5.1597
	H_{axial}	c				0.8946[e]	0.9159[e]	
	H	0.9181	0.9141[e]	0.9085	0.9223[e]	0.9266[e]	0.9184[e]	0.8875
XX′	X′[d]		6.9819[e]	0.9278	4.9802[e]	4.9845[e]	0.9997[e]	6.9306
	X		7.0664[e]	1.1241	5.0381[e]	4.9838[e]	1.0000[e]	7.2472
				At an XX′ Distance R + 0.02				
NH_3	N		5.2053	5.2206[e]	5.2126	5.2846	5.2476	5.1570[e]
	H_{axial}					0.8938	0.9159	
	H		0.9130	0.9077[e]	0.9221	0.9267	0.9183	0.8859[e]
XX′	X′[d]		6.9817	0.9258[e]	4.9810	4.9841	0.9997	6.9286[e]
	X		7.0741	1.1304[e]	5.0402	4.9839	1.0001	7.2567[e]

[a] The numbers in the table are the numbers of valence-shell electrons on the atom. The neutral H, N, F and Cl atoms, of course, have 1.0, 5.0, 2.0 and 7.0 electrons, respectively. [b] C_{3v} designates a complex with XX′ along the C_3 axis; C_s designates a complex with XX′ along an NH bond (see Figure 1). [c] A blank space means that the complex has C_{3v} symmetry, so that the populations of all three H atoms in NH_3 are the same. [d] Here the X′ atom is closest to the N atom in the complex (see Figure 1). [e] Equilibrium values.

agreement with the *ab initio* results and with the experiment.[14]

Charge Distribution in the Complex

It is of considerable interest to examine more closely the results from the charge-density matrix of the INDO calculation. We have listed these results in Table III for the complexes studied here, given for the calculated equilibrium configuration and again for a configuration in which the X′X bond is stretched or compressed from the equilibrium value. The results are perhaps most readily visualized in Figure 10a, where the charge distribution calculated near the equilibrium configuration is given for $H_3N \cdot F_2$.

We see there that the extent of charge transfer to F_2 (in this configuration) is calculated to be 0.0426 electron, but the negative charge (0.066 electron) is concentrated on the F atom away from the electron donor. It is interesting, also, to note that the F′ atom nearest the donor acquires a slight positive charge (+0.02 electron). The charge is transferred primarily from the N atom in the donor, with smaller contributions from the H atoms.

Thus, the calculations indicate not only an appreciable charge transfer but also considerable polarization of the F_2 molecule in the complex. This calculated polarization (or "charge shift," as Kollman and Allen referred to a similar phenomenon indicated in their calculations for hydrogen-bonded systems)[9] is an important result. One of the questions that was never clearly resolved in the Mulliken resonance structure description of complexing was the extent to be expected for such polarization.[1a] Recently, experimental results from nuclear quadrupole resonance measurements of halogen complexes[15] have shown that the charge on X′ is not equal to that on X, but is in semiquantitative agreement with the charge distribution indicated in Figure 10a.

Now consider the change in this equilibrium charge distribution occurring as the F′–F bond is stretched by 0.02 Å. The resulting charge distribution is shown in Figure 10b. We see that stretching this bond results in an increase in the charge transferred to the F_2 molecule.

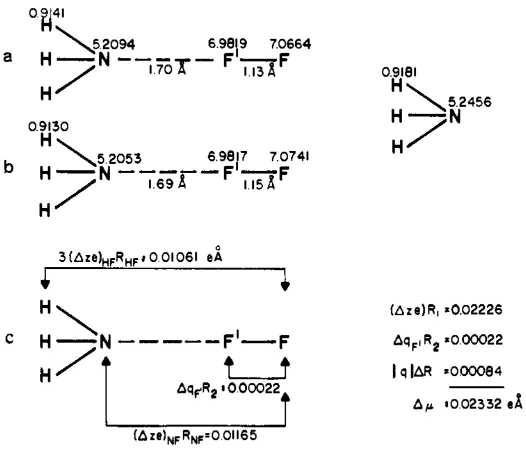

Figure 10. Charge distribution calculated from INDO wave functions for $H_3N \cdot F_2$ in two different nuclear configurations: (a) near equilibrium; (b) same as a, except that the F′F bond is stretched by 0.02 Å; (c) definition of terms contribution to $\Delta\mu$.

Surprisingly enough, *all* of the increased charge is transferred to the far F atom; the charge on F′ remains constant. The largest contribution of charge from the donor comes from the N atom, but the three H atoms contribute almost an equal amount of charge, in total, to the F atom.

We have tried to break down the dipole change on stretching the X′X bond ($\Delta\mu/\Delta R_{X'X}$) into contributions as follows

$$\Delta\mu = e(\Delta z)_1 + (\Delta q)R_{X'X} + q(\Delta R_{X'X})$$

Here q is the charge on X′ at equilibrium (here +0.0181 electron); Δq is the change (only +0.0002 electron here for $\Delta R_{X'X}$ of 0.02 Å) as the X_2 bond is stretched, so that $(\Delta q)R_{X'X}$ is the contribution of this charge shift to $\Delta\mu/\Delta R_{X'X}$. After the charge shift, the charge on the X′ atom is at its "stretched" value, so that we consider all of the charge transferred ($e\Delta z$) during the

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(14) It is important to emphasize that the comparison of our results to the *ab initio* calculation for $H_3N \cdot Cl_2$[13] shows that the properties we calculate *at the calculated equilibrium* distance exaggerate badly the effect of charge transfer. It seems likely that better *ab initio* calculations will show that the charge-transfer effects are much smaller. On the other hand, the *trends* we find here are probably correct.

(15) (a) G. A. Bowmaker and S. Hacobian, *Aust. J. Chem.*, **22**, 2047 (1969); (b) H. C. Fleming and M. W. Hanna, *J. Amer. Chem. Soc.*, **93**, 5030 (1971).

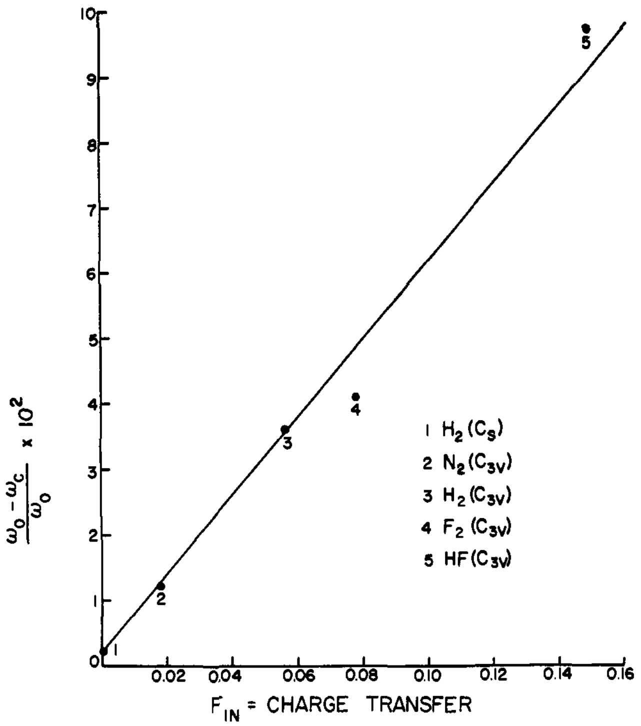

Figure 11. Plot verifying the postulated relationship between the relative frequency shift and the extent of charge transfer. Here we show the calculated values of each property (from Table II) at the calculated equilibrium distance.

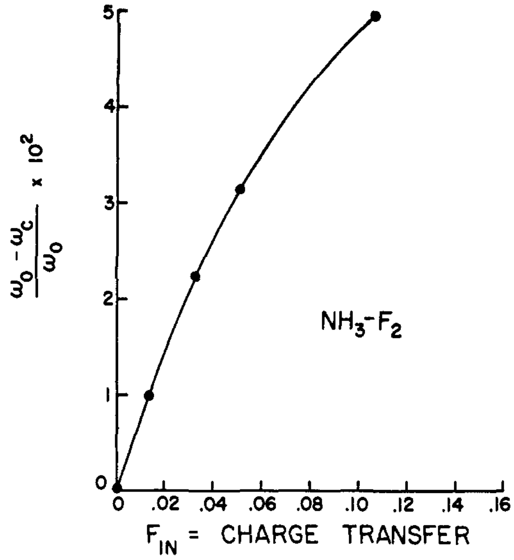

Figure 12. The calculated relative frequency of the F′F stretching vibration, plotted *vs.* the calculated extent of charge transfer in $H_3N \cdot F_2$ at different R_{DA} distances (large when the charge transfer is zero and small when the charge transfer is large).

vibration from H_3N to X′X to go to the X atom. We break down $e\Delta z$ into two components, one which describes the flow of charge from the hydrogen atom of NH_3 (H_N) to the X atom, and one describing the charge flowing from the nitrogen atom (N_H) to the X atom. Each of these charges moves a different distance; the composite is designated R_1. (See Figure 10c for a better definition of these terms.) Table IV shows the contribution from each of these terms to the resultant value of the change in dipole moment. By inspection, the charge transfer ($e\Delta zR_1$) is by far the largest term contributing to $\Delta\mu/\Delta R_{X'X}$ and the intensification of the infrared absorption due to the X′X stretching vibration.

Table IV. A Breakdown into Components of the Change in Dipole Moment ($\Delta\mu$) Occurring as the X′X Bond is Stretched in C_{3v} $NH_3 \cdot X'X$ Complexes[a]

	NH$_3$ complex with			
	F_2	H_2	N_2	Cl_2
$3(e\Delta z)_{HX}$	0.0033	0.0024	0.0006	0.0048
$(e\Delta z)_{NX}$	0.0041	0.0018	0.0023	0.0027
$e\Delta z_T$	0.0074	0.0042	0.0030	0.0075
R_{HX}	3.187	2.717	3.307	4.307
R_{NX}	2.830	2.360	2.950	3.950
$3(e\Delta z)_{HX}R_{HX}$	0.0106	0.0065	0.0021	0.0207
$(e\Delta z)_{NX}R_{NX}$	0.0116	0.0043	0.0069	0.0107
$(e\Delta z)R_1$	0.0222	0.0109	0.0091	0.0314
$\Delta q_{X'}$	0.0002	0.0201	−0.0008	0.0020
$R_{X'X}$	1.130	0.760	1.15	2.05
$\Delta q_{X'}R_{X'X}$	0.0002	0.0015	−0.0010	0.0041
$\lvert q\rvert$	0.0422	0.0981	0.0290	0.1583
ΔR_2	0.020	0.02	0.02	0.02
$\lvert q\rvert\Delta R_2$	0.0008	0.0019	0.0006	0.0032
$\Delta\mu$, eÅ	0.0233	0.0143	0.0087	0.0387
$\Delta\mu$, D	0.112	0.069	0.042	0.186
$\Delta\mu_{full}$,[b] D	0.109	0.061	0.044	0.195

[a] All charges (($e\Delta z$), $|q|$, etc.) are given as numbers of electrons; all distances are given in ångströms. Charges are from Table III. Calculations and symbols are described in the text. [b] Here $\Delta\mu_{full}$ is the calculated difference in dipole moments ($\mu_2 - \mu_1$) calculated for configurations 1 and 2 from the full INDO program for each configuration separately.

Relative Frequency Shift and Extent of Charge Transfer

It is of some interest also to investigate the relationship between the relative frequency shift of the X′X stretching vibration [($\omega_0 - \omega_c$] and the extent of charge transfer. Freidrich and Person[16] had argued that the relative frequency shift (or actually the relative shift in force constant $(k_0 - k_c)/k_0$, which is approximately twice the relative frequency shift for weak complexes) is expected to measure F_{IN} (or $b^2 + abS_{01}$) (see also ref 1a, Chapter 6). While the reasoning in the original paper was not entirely correct, later examination[1a] led essentially to the same postulate. We have tested this assumption for our INDO calculations by plotting the calculated relative frequency shift *vs.* the calculated extent of charge transfer, as obtained at the calculated equilibrium configuration for these several different complexes. The results are given in Figure 11. We see there that the points fit approximately to a straight line with slope about 0.6, as might be expected for the plot of $\Delta\nu/\nu$ (instead of $\Delta k/k$) if the postulate is correct. The fit is quite similar to that for the corresponding experimental results for other complexes[1a] which led Friedrich and Person to this postulate.

The calculated results can be used to test this postulate for a *single* complex by plotting calculated relative frequencies *vs.* calculated extent of charge transfer at different configurations (measured by R_{DA}) as the molecules come together from infinite separation. The results are shown for $H_3N \cdot F_2$ in Figure 12. As the molecules come together to form the complex, the extent of charge transfer increases as does the relative frequency shift. (See Figures 3 and 5.) In Figure

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(16) H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

12 we see an initial, approximately linear, relation with approximately the expected slope, until the extent of charge transfer reaches its largest value at the smallest N–F′ distance in our calculations. There we believe that the N–F′ repulsion force has a marked effect on the frequency computed for the F′F stretching motion, causing the computed relative frequency to be smaller than expected naively for this extent of charge transfer.

Thus, we believe these calculations summarized in Figures 11 and 12 are quite consistent with the postulated[16] relationship between the X′X frequency shift and the extent of charge transfer.

Electrostatic Effects

It is of some considerable interest for us to examine the magnitude of the electrostatic effects contributing to the properties of the complexes we have studied here. We have estimated the magnitude of the electrostatic energy of attraction, and of the increase in dipole moment due to electrostatic effects alone, for the $H_3N \cdot N_2$ system in both C_{3v} and C_s orientations.

We have assumed a point dipole for NH_3 located at the electrical center of the molecule (about 0.1 Å from N toward the H-atom plane along the C_3 axis). The X′X molecule is considered to be a polarizable point located at the center of the X′X bond. The magnitude of the NH_3 dipole was taken to be the INDO-calculated value of 1.89 D. Corresponding to the distance $R_{NX'}$ (defined for C_{3v} geometry in Figure 1), we used a point-dipole-to-polarizability distance of $0.1 + R_{NX'} + {}^1/_2\, R_{X'X}$. A similar calculation was made for the C_s configuration.

The polarizability of X_2 was taken to be

$$\alpha_{X_2} = (\cos^2\theta)\alpha_{\parallel} + (\sin^2\theta)\alpha_{\perp}$$

Here θ is the angle made by the point dipole of NH_3 on the C_3 axis with the X_2 axis, $\alpha_{\parallel}$ is the polarizability of X_2 along the internuclear axis, and $\alpha_{\perp}$ is the polarizability perpendicular to the internuclear axis. The polarizabilities are listed in Table V. The dipole moment induced by NH_3 in X′X is [17]

$$\mu_{X_2}{}^{\text{ind}} = \frac{\mu_{NH_3}\alpha_{X_2}(3\cos^2\theta + 1)}{2r^3(\cos^2\theta + 1)}$$

The energy of interaction is then[17]

$$E = [\mu^2{}_{NH_3}\alpha_{X_2} + (\mu_{X_2}{}^{\text{ind}})^2\alpha_{NH_3}](3\cos^2\theta + 1)/2r^6$$

The charge shifted in the X_2 molecule due to the polarization by the NH_3 dipole is $q' = \mu_{X_2}{}^{\text{ind}}/R_{X'X}$. The dipole moment and charge shift along the X_2 internuclear axis are calculated by multiplying the total values calculated for these properties by cos θ. The magnitude of the total dipole moment of the complex is

$$\mu_T = [(\sin^2\theta)(\mu_{NH_3} + \mu_{X_2}{}^{\text{ind}})^2 + (\cos^2\theta)(\mu_{NH_3} + \mu_{X_2}{}^{\text{ind}})^2]^{1/2}$$

Table V. The Polarizabilities of Molecules Used for the Electrostatic Calculation[a]

	NH_3 (C_{3v})	NH_3 (C_s)	N_2 (C_{3v})	N_2 (C_s)	H_2 (C_{3v})	H_2 (C_s)
θ, deg	0	109	0	109	0	109
$\alpha_{\parallel}$	24.2[b]	24.2[b]	23.8	23.8	9.3	9.3
$\alpha_{\perp}$	21.8[c]	21.8[c]	14.5	14.5	7.1	7.1
α	24.2	22.1	23.8	15.5	9.3	7.3

[a] Values from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, ref 17. Here θ refers to the angle made by the direction of approach of the X′X molecule with the C_3 axis. [b] Value parallel to the X′X axis. [c] Value perpendicular to the X′X axis.

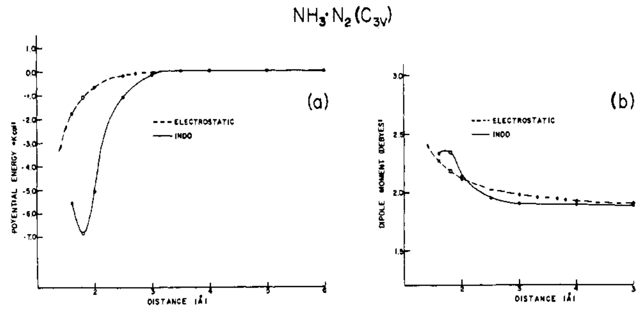

Figure 13. Comparison of the results from the classical electrostatic calculation with those from the INDO calculation for the $H_3N \cdot N_2$ complex: (a) calculated potential energy, (b) calculated dipole moments.

Table VI gives a comparison of the physical properties of the complexes calculated using this simple electrostatic model with those calculated using the INDO method. The electrostatic energy of interaction is much greater for the complex in the C_{3v} configuration than for the C_s configuration. The lower electrostatic energy of interaction for the latter configuration is due to longer distance between the point dipole and the point of polarizability, to the smaller X_2 polarizabilities along that direction, and to the smaller effective NH_3 dipole in that orientation.

Table VI. Comparison of Properties of Some Complexes with NH_3 Calculated from INDO Wave Functions with Those from an Electrostatic (ES) Model

	NH_3 with—			
	N_2 (C_{3v})	N_2 (C_s)	H_2 (C_{3v})	H_2 (C_s)
$-\Delta E^a$ (ES)	1.08	0.05	1.21	0.02
$-\Delta E^a$ (INDO)	6.9	6.9	7.5	0.60
$\mu_{\text{ind}}(X_2)^b$ (ES)	0.29	0.05	0.20	0.02
$\mu_T{}^c$ (ES)	2.18	1.93	2.09	1.91
$\mu_T{}^d$ (INDO)	2.34	2.06	2.76	1.89
Polarization charge[e] (ES)	0.053	0.010	0.054	0.007
Polarization charge[e] along axis (ES)	0.053	0.003	0.054	0.002
Polarization charge[f] along axis (INDO)	0.029	0.001	0.102	0.0002

[a] In units of kilocalories per mole. [b] $\mu_{\text{ind}}(X_2)$ is the dipole moment induced by the permanent dipole of NH_3 in the X′X molecule as the latter approaches the NH_3 molecule. The units are debyes. The value here is calculated at the calculated equilibrium distance, $R^e{}_{NX'}$. [c] The vector sum of $\mu_{\text{ind}}(X_2)$ and μ_{NH_3}, in debyes, at $R^e{}_{NX'}$. [d] Calculated dipole moment from INDO wave functions at $R^e{}_{NH'}$, in debyes. [e] Here the polarization charge (the number of electrons) is calculated from: polarization charge $= \mu_{\text{ind}}(X_2)/R_{X'X}$, where $R_{X'X}$ is the X′X distance in ångströms and $\mu_{\text{ind}}(X_2)$ is the dipole moment in electrons Å. The polarization charge along the axis is obtained from the component of μ_{ind} along the X′X axis. [f] Number of electrons; from Table II.

Because of this difference in electrostatic energies for the two orientations of the complexes, and because the energies calculated from the INDO method for the two

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(17) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954.

orientations in $H_3N \cdot N_2$ are the same, we conclude that the charge-transfer effects must be considerably more important in the C_s configuration of N_2 with NH_3 than in the C_{3v} configuration.

The calculated variation of electrostatic energy with R_{DA} for the $H_3N \cdot N_2$ complex is compared with the corresponding potential energy calculated by the INDO method in Figure 13a. We see there that if our estimate of each effect is indeed correct, then the electrostatic energy forms only a relatively small contribution to the total energy for this system. On the other hand, the dipole moment change with decreasing R_{DA} clearly seems to be due almost entirely to the electrostatic effect.

Our calculation is expected to give only the lower limit for the electrostatic effects expected. Another estimate of the electrostatic energy can be obtained by choosing the point dipole of NH_3 to be located in the lone pair of electrons, or about 1.0 Å closer to the acceptor. If so, the electrostatic curves in Figure 13 would both be shifted about 1 Å to the right, bringing the energy curve approximately into coincidence with the potential curve from the INDO calculation, still with fair agreement between the dipole moment curve and the curve predicted from the INDO calculation. We believe that the true electrostatic effects are somewhere in between these two extremes, but that most of the effect calculated by the INDO method for $H_3N \cdot N_2$ is probably due only to the electrostatic attraction.

At the same time, we note that the electrostatic effects will be quite similar for all the molecules we are considering here. For H_2 the polarizability (Table V) is about one-half that for the others, but it is somewhat smaller in size so that it can approach the NH_3 molecule closer before repulsion sets in. Thus the net potential energy from electrostatic attraction balanced by repulsion is expected to be similar to that for N_2.

Thus, we conclude also that the *extra* effects (larger than those for $H_3N \cdot N_2$) predicted for the complexes from INDO calculations at $R^e_{NX'} + 0.3\text{–}0.5$ Å are true charge-transfer effects. Basically, these extra effects include extra stability, extra increases in the dipole moment, extra frequency shifts in the X′X stretching frequency, the intensification of this vibration, and extra changes in the X′X bond length. All these effects are correlated with the calculated extent of charge transfer, F_{1N}. Some changes in these properties are predicted for $H_3N \cdot N_2$, either because of a small amount of charge transfer in that system or because the electrostatic effects are similar to charge transfer effects. However, the larger magnitudes predicted for those effects are characteristically larger for the cases where F_{1N} calculated to be larger than it is for the cases where only electrostatic effects are expected.

Finally, we note in Table VI that the quantity we have called "polarization charge" in Table II is a good measure of the electrostatic induced dipole on the X′X molecule. Thus, the value from the INDO calculation in Table II agrees semiquantitatively with that calculated from the classical electrostatic induced dipole $[\mu_{ind}(X_2)/R_{X'X}]$. When this value is small (in Table II) and when the calculated value of F_{1N} is large, then we may expect a true "charge-transfer complex." Conversely, when the polarization charge is large and the charge transfer is small, we have only an ordinary electrostatic interaction. Obviously from Table II, both effects are expected to be important for these complexes. (However, see footnote 14.)

Comparison with Experimental Values

Finally let us consider the comparison of these calculated results with experiment. Obviously, we do not expect to find experimental data for these particular complexes. Our results for $H_3N \cdot H_2$, if valid, suggest that a careful examination of the mixed second virial coefficients for a mixture of these gases might be worthwhile. A comparison between mixed virial coefficients from $H_3N \cdot H_2$ and $H_3N \cdot N_2$, for example, might show some interesting differences.

For $H_3N \cdot F_2$ and $H_3N \cdot Cl_2$, these results are most useful as a *model* for $R_3N \cdot I_2$ interactions. We see from Table II (and elsewhere) that our calculations predict an increase in F_{1N} at $R^e_{NX'}$ as we go from $H_3N \cdot F_2$ to $H_3N \cdot Cl_2$. Although the predicted increase in F_{1N} may not be so large at the expected true R_{DA} distance, it seems reasonable to extrapolate as the X atom is changed from one halogen to another down the periodic table. Thus, we expect that the calculated F_{1N}, stability, and other properties, although exaggerated for $H_3N \cdot F_2$ at $R^e_{NX'}$, are just about right for the stronger $R_3N \cdot I_2$ complexes.

In order to examine this argument, we have compared some of the experimental properties of I_2 complexes with the INDO calculations on $H_3N \cdot F_2$ in Table VII. A general agreement does exist between the calculated properties and the experimental ones. Remembering that the experimental results are from experiments in solution, we expect, possibly, quite large corrections to the experimental value of ΔE, which is certainly overestimated in the calculation. Both corrections are expected to bring the experimental values of ΔE into closer agreement with the calculated values. Making this allowance for ΔE, we see that μ calculated for $H_3N \cdot Cl_2$ is in pretty good agreement with the experimental value for $(CH_3)_3N \cdot I_2$; however, F_{1N} calculated for the Cl_2 complex is quite a bit less than that estimated for the I_2 complex from the experimental results. We recall[1a] that the "experimental" value of F_{1N} comes from the dipole moment, assuming that the charge transferred is distributed equally between the X′ and X atoms. If this polarization is taken into account, we would estimate that the extent of

Table VII. Comparison between the INDO-Calculated Properties of $H_3N \cdot X'X$ Complexes and the Experimentally Known Properties of Amine $\cdot I_2$ Complexes

	Property				
Complex	$-\Delta E$, kcal/mol	F_{1N}	μ, D	$(R_c - R_0)/R_0$	X′X $(\omega_0 - \omega_c)/\omega_0$
$H_3N \cdot F_2$[a]	10.4	0.08	3.1	0.01	0.04
$H_3N \cdot Cl_2$[a]	21.8	0.18	6.7	0.02	0.04[c]
$(CH_3)_3N \cdot I_2$[b]	12.1	0.3–0.4	6.5	0.06	0.11[c]
py $\cdot I_2$[b]	7.8	0.25–0.29	4.5		0.12[c]
py $\cdot$ ICl[b]		0.30		0.08	0.22[c]

[a] Calculated values at $R^e_{NX'}$ from Table II. [b] "Experimental" values from Mulliken and Person, ref 1a; py is pyridine. [c] The X′X stretching motion is not a good normal coordinate for these strong complexes, so the observed frequency shift probably should not be compared directly with a calculated value.

Table VIII. Comparison between INDO-Calculated Vibrational Properties of $H_3N \cdot F_2$ and Those Observed Experimentally for Pyridine–Halogen Complexes

	Property				
		X′X stretch		NX′ stretch	
Complex	F_{IN}[a]	$(k_0 - k_c)/k_0$	$\partial\mu/\partial R_{X'X}$, D/Å	k_c/k_0[b]	$\partial\mu/\partial R_{NX'}$, D/Å
$H_3N \cdot F_2$[c]	0.08	0.08	+6.2	0.10	−3.4
		k_{12} = 0.4 mdyn/Å			
py·I_2[d]	0.25–0.3	0.07	+5.8	0.15	−4.8
py·ICl[e]	0.25–0.3[f]	0.27	+8.6 (+6.1)[g]	0.27	

[a] From Table VIII. [b] Here k_0 is assumed to be 5.0 mdyn/A for a full N–F bond and 2.5 for the N–I bond. See ref 18 and 19 for further definitions. [c] Calculated values from Table II. Here k_c for the N–F′ stretching vibration is estimated from our calculations to be 0.48 mdyn/Å. [d] Values taken from Yarwood and Person, ref 18. [e] Values taken from Yarwood and Person, ref 19. [f] A value of F_{IN} = 0.25 is estimated for this complex by Fleming and Hanna from nqr measurements (ref 15b). [g] This value of +6.1 D/Å represents the *increase* in $\partial\mu/\partial R_{ICl}$ from the value for *free* ICl, and is the value to be compared with the calculated $\partial\mu/\partial R_{X'X}$.

charge transfer for $(CH_3)_3N \cdot I_2$ is lower—perhaps about 0.25 instead of 0.4. Similar (but smaller) corrections should be made to the experimental estimates of extent of charge transfer for the other complexes. Thus, the experimental properties (with these corrections) of the py·I_2 complex, for example, appear to fall about halfway between the INDO calculated properties for $H_3N \cdot F_2$ and those for $H_3N \cdot Cl_2$.

The other experimental indication of the extent of charge transfer, F_{IN}, came from the infrared spectrum (see ref 1a, Chapter 6). The comparison between calculated and experimental vibrational properties is presented in a separate Table VIII. We recall[1a] that the estimates for F_{IN} from the relative change in force constant depended rather severely, for these strong complexes, on the particular assumption made for the value of the interaction force constant, k_{12}.[18,19] Earlier workers were not able to evaluate this constant; the value believed to be most reliable (k_{12} = 0.4 mdyn/Å) gave estimates for F_{IN} that were thought to be too small (*i.e.*, smaller than estimates from μ). Thus, the present conclusion that F_{IN} perhaps *is* actually smaller than previously realized suggests that k_{12} is indeed about 0.4 mdyn/Å, and only that value is considered in Table VIII (see ref 18 and 19 for more detail).

We see in Table VIII that the experimental vibrational properties of the X′X and NX′ stretching vibrations [as measured by intensity changes (or $\partial\mu/\partial R_{X'X}$ and $\partial\mu/\partial R_{NX'}$) and frequency shifts (as measured by $\Delta k/k_{X'X}$ and $\Delta k/k_{NX'}$)] are in reasonably good agreement with those predicted by the INDO calculation for the $H_3N \cdot F_2$ complex. Until it is possible to make the better quantum mechanical calculations needed to predict properties of I_2 complexes, we believe that these INDO calculations for $H_3N \cdot F_2$ provide a reasonable semiquantitative model for their behavior.

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(18) J. Yarwood and W. B. Person, *J. Amer. Chem. Soc.*, **90**, 594 (1968).

(19) J. Yarwood and W. B. Person, *ibid.*, **90**, 3930 (1968).