Vibrational frequencies and intensities of H-bonded and Li-bonded complexes. H₃N··HCl and H₃N··LiCl

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The geometries, energetics, and vibrational spectra are calculated for the two complexes at the SCF and correlated MP2 levels using the 6-31G** basis set, augmented by a second set of d functions on Cl. While correlation represents an important factor in the binding of $H_3N \cdot \cdot HCl$, it contributes little to the stronger Li bond. Unlike the HCl stretch ν_s which decreases substantially in frequency and is greatly intensified in $H_3N \cdot \cdot HCl$, the frequency of the LiCl stretch undergoes an increase and little change is noted in its intensity, conforming to prior spectral measurements. The intensities of the intramolecular stretching modes of NH_3 are greatly strengthened by formation of a H bond and even more so for a Li bond. These intensity patterns are analyzed via atomic polar tensors which reveal that formation of a H bond dramatically lessens the ability of the electron density to shift along with the proton. A stretch of H–Cl hence leads to a large increase in molecular dipole moment. This "freezing" of the electron cloud is much smaller in the Li bond and its effect on the ν_s intensity is counteracted by a much reduced Li atomic charge in the complex. Another distinction between the H and Li bonds relates to the destination of charge transferred from the NH_3 subunit which accumulates on Cl in the former case but on Li in the latter.

INTRODUCTION

Infrared intensities represent a valuable window into electron density distributions[1] and a sensitive means of detecting molecular interactions. Unfortunately, complete analysis of experimental intensities in terms of dipole moment derivatives is commonly hindered by ambiguity in the signs of these quantities, in addition to difficulties in unraveling and identifying overlapping bands. *Ab initio* calculations can help alleviate some of these problems since the dipole moment and its various derivatives can be computed in a straightforward fashion. The recent flurry of activity in this area, spurred on by progress in evaluating analytical derivatives,[2-7] has provided strong indications that such *ab initio* calculations are indeed useful.[7-13] A good deal of data has accumulated by which one can assess the likely accuracy of a given theoretical approach and adjust for intrinsic errors. Sosa and Schlegel[8] have recently published a comprehensive examination of the basis set dependence of the dipole moment derivatives of CH_3F. The earlier work on a series of simple molecules by Yamaguchi *et al.*[9] has also provided useful hints in selection of theoretical method. The body of work by Bacskay *et al.*[10-12] confirms that fairly high levels of theory which include electron correlation are fully capable of treating IR intensities quantitatively.

The usefulness of atomic polar tensors (APTs) for analyzing and understanding IR intensities has been reviewed by Person.[14] With specific connection to H bonds, early papers by Zilles and Person[15] and by Swanton *et al.*[16] dealing with the water dimer served to break important ground. Examples of other H-bonded systems examined in this framework are $(NH_3)_2$,[17] $(H_2S)_2$,[18] and $NH_3(HF)_n$, $n = 1,2$.[19]

In the current communication we focus our attention upon two specific problems. Although a good deal of theoretical calculations have recently been carried out on IR intensities of H-bonded complexes,[16-20] none of these have included the effects of electron correlation. The MP2 method will be applied here to examine the magnitude and character of changes in intensities due to correlation, thereby assessing the validity of the SCF approach. Second, it has been established that the vibrational spectra of H-bonded systems differ in several fundamentally important respects from analogous Li-bonded complexes,[21] most important of which being the lack of intensification of the ν_s stretching mode in Li bonds. While this discrepancy has been the subject of previous *ab initio* study, there is little reliable information concerning the underlying reasons[21-24] since understanding of these differences requires a full vibrational analysis accompanied by intensity evaluations.

Our strategy here is to perform calculations at an identical level of accuracy upon a pair of systems, H_3N–HCl and H_3N–LiCl. The calculated spectra may be checked for reliability against the experimental data which are available for both of these systems. Analysis of the intensity changes for all the modes, interpreted in terms of electron density redistributions in the two complexes, with and without correlation, should identify the sources of the difference between H and Li bonds on the most fundamental level.

METHODS

Following the conclusions of earlier studies that a polarized double-ζ basis set yields the intensity ratios correctly,[8] the 6-31G** basis set has been employed throughout the present study. This set was augmented by a second set of d functions on Cl, the exponent of which was optimized to 0.28 by maximization of the perpendicular induced moment of isolated HCl. The *ab initio* calculations made use of the

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GAUSSIAN-82 system of computer codes.[25] Geometry opti-
mization was performed at both the SCF and MP2 levels.
The final interaction energies at either level are corrected for
basis set superposition effects by the counterpoise procedure
of Boys and Bernardi.[26]

Atomic polar tensors (APTs) at the MP2 level were
calculated as numerical derivatives (for Cartesian displace-
ments of $\pm$ 0.005 Å) of the dipole moments which were, in
turn, evaluated via analytical differentiation of the MP2 en-
ergy with respect to electric field. Cartesian force constants
at the MP2 level were also obtained by numerical differenti-
ation of analytical first derivatives. Although SCF APTs can
be computed analytically, the numerical route was followed
so as to ensure consistency with the MP2 data.

GEOMETRIES AND ENERGETICS

Monomers

The calculated properties of the isolated monomers are
displayed in Table I where they are compared with the ex-
perimental quantities in the last column. The geometries are
fairly accurately predicted by the calculations, particularly
at the MP2 level. Correlation has only a minor influence
upon the dipole moments of the molecules. The moment of
LiCl is affected the most, diminishing by 3%. Correlation
lowers the dipole of HCl by a smaller amount while that of
NH_3 undergoes a 2% increase. [The latter increase is due in
part to the smaller $\theta(HNH)$ angle in the MP2 geometry;
correlation *lowers* μ for fixed geometry.] In comparison to
experiment, all the correlated dipole moments remain too
high with the overestimates varying between 3% for LiCl to
26% for NH_3.

Complexes

The optimized geometries of the C_{3v} complexes are re-
ported in the upper portion of Table II. The first row illus-
trates the 0.2 Å contraction of the intermolecular distance
caused by including electron correlation in the H-bonded
system. In contrast, the SCF and MP2 values of $R(N\cdots Cl)$
are nearly identical for $H_3N\cdots LiCl$. The Z–Cl bond length
(Z = H,Li) is listed in the next row of Table II, followed by
the stretching induced in this bond by complexation. Specifi-
cally, Δr is defined as the difference between $r(Z–Cl)$ in the
complex and in the isolated ZCl monomer, both optimized
at the same level of theory. This stretching is equal to 0.0287

TABLE I. Geometries and dipole moments of monomers.

	SCF	MP2	Expt.[a]
NH_3			
r (Å)	1.0009	1.0118	1.012
θ (HNH) (deg)	107.58	106.27	106.7
μ (D)	1.8384	1.8674	1.48
HCl			
r (Å)	1.2680	1.2742	1.274
μ (D)	1.2821	1.2758	1.11
LiCl			
r (Å)	2.0637	2.0661	2.021
μ (D)	7.4346	7.2373	7.13

[a]Reference 27.

TABLE II. Calculated geometries, energetics, and dipole moments of com-
plexes.

	$H_3N\cdots HCl$		$H_3N\cdots LiCl$	
	SCF	MP2	SCF	MP2
$R(N\cdots Cl)$ (Å)	3.2346	3.0315[a]	4.1430	4.1395
$r(Z–Cl)$ (Å)	1.2967	1.3379	2.0941	2.0891
$\Delta r(Z–Cl)$[b] (Å)	0.0287	0.0637	0.0304	0.0230
$r(NH)$ (Å)	1.0014	1.0129	1.0036	1.0144
$\theta(HNH)$ (deg)	107.84	107.45	107.09	106.56
$-\Delta E^c$ (kcal/mol)	7.12	9.62	24.26	24.49
μ (D)	4.436	5.194	10.418	10.282
$\Delta\mu^d$ (D)	1.316	2.051	1.145	1.177

[a]Experimental value from gas-phase microwave spectrum is 3.1367 Å from
E. J. Goodwin, N. W. Howard, and A. C. Legon, Chem. Phys. Lett. 131,
319 (1986).
[b]$r(Z–Cl)_{complex}-r(Z–Cl)_{monomer}$; Z = H,Li.
[c]Corrected for basis set superposition error.
[d]Difference between μ of complex and sum of dipoles of isolated monomers.

Å in $H_3N\cdots HCl$ at the SCF level but is more than doubled
when correlation is included. In the Li-bonded analog, on
the other hand, correlation reduces the magnitude of the Li-
Cl stretch. The opposite effects of electron correlation upon
the two types of systems are reflected also in the energetics of
these complexes. The binding energy of $H_3N\cdots HCl$, evaluat-
ed using the counterpoise correction, is increased from 7.12
to 9.62 kcal/mol by correlation. In contrast, the MP2 bind-
ing energy of the Li-bonded analog is nearly identical to the
SCF value.

The last two rows of Table II contain the calculated
dipole moments of the complexes, followed by a comparison
of this result with the sum of the dipoles of the isolated mo-
nomers. $\Delta\mu$ thus represents a measure of the moment en-
hancement caused by the interaction of the two subunits. As
is the case for the geometries and energetics, correlation
causes a marked increase in $\Delta\mu$ for the H-bonded system
while it is apparently unimportant for $H_3N\cdots LiCl$. At the
MP2 level, the dipole moment enhancement is nearly twice
as large for the former system than for the latter.

VIBRATIONAL FREQUENCIES

Intramolecular modes

The calculated vibrational spectra of the two complexes,
as well as the isolated subunits from which they arise, are
presented in Table III along with experimental data for the
H bond and Li bond, respectively, measured in Ar matrix.
The frequency of the symmetric a_1 stretching mode of isolat-
ed NH_3 is computed to be 3706 cm^{-1} at the SCF level. Com-
plexation with HCl produces no change in this frequency nor
in the e stretching mode of NH_3. (The effects of HCl upon
the NH_3 internal vibrations appear to be rather characteris-
tic of H bonding since the frequencies and intensities calcu-
lated for $H_3N\cdots HCl$ here are quite similar to our previous
results for $H_3N\cdots HF$.[19]) On the other hand, both of these
stretching frequencies are lowered slightly by formation of a
Li bond. Although the MP2 frequencies are uniformly lower
than their SCF counterparts, we see the same trends: H

TABLE III. Frequencies (cm^{-1}) and intensities (km/mol) of the complexes and isolated subunits.

		$H_3N + ZCl$		$H_3N \cdot \cdot HCl$		$H_3N \cdot \cdot LiCl$	
		ν	A	ν	A	ν	A
				NH_3			
$\nu_{st}(a_1)$	SCF	3706	0.15	3706	4	3693	26
	MP2	3568	0.3	3565	6	3558	11
	Expt.	3337,[a] 3345[c]					
$\nu_{st}(e)$[e]	SCF	3843	1.5	3843	22	3817	166
	MP2	3726	1.0	3723	36	3700	60
	Expt.	3444[a]		3420[b]			
		3435,[b] 3447[c]					
$\nu_b(a_1)$	SCF	1143	217	1217	200	1319	574
	MP2	1116	170	1187	119	1247	191
	Expt.	950,[a] 974[b,c]		1072[b]			
$\nu_b(e)$[e]	SCF	1812	42	1805	56	1800	156
	MP2	1727	32	1713	52	1712	50
	Expt.	1627,[a] 1639[b,c]					
				ZCl			
ν_s Z = H	SCF	3164	120	2740	1087		
	MP2	3084	46	2186	2283		
	Expt.	2888[b]		1371[b]			
Z = Li	SCF	637	135			710	331
	MP2	623	123			716	111
	Expt.	611[d]				538[d]	
				intermolecular			
ν_σ	SCF			173	10	248	24
	MP2			200	43	238	10
	Expt.			166[b]			
ν_β [e]	SCF			239	46	525	550
	MP2			276	44	499	208
	Expt.			733[b]			
$\nu_{b,t}$ [e]	SCF			700	150	56	80
	MP2			912	114	70	22
	Expt.			1289[b]			

[a] Gas phase; Ref. 28.
[b] Ar matrix; Ref. 29.
[c] Ar matrix; Ref. 30.
[d] Ar matrix; Ref. 21.
[e] The intensities of doubly degenerate modes have been multiplied by 2.

bonding has little influence upon the NH_3 internal stretches while Li bonding causes a small reduction in these frequencies. The low sensitivity of the e stretching frequency to H bonding is confirmed by the experimental observations in Ar matrix.

Of the NH_3 normal modes, the a_1 bending vibration is most affected by complexation. At the MP2 level, H bonding increases this frequency by 71 cm^{-1} and Li bonding produces a larger increment of 131 cm^{-1}. The former value agrees rather well with the experimental increase of 98 cm^{-1} in Ar matrix. The NH_3 bending mode of e symmetry is less sensitive to complexation. It is therefore not surprising that this band has not been observed in the experimental spectrum since it would probably be hidden by the e stretch of the NH_3 monomer.

More dramatic changes are observed in the stretching mode of HCl or LiCl, generally denoted ν_s. The HCl stretching frequency drops by 424 cm^{-1} at the SCF level when interacting with NH_3, more than twice this amount (898 cm^{-1}) at the MP2 level. Recent DZP/CI calculations of $H_3N \cdot \cdot HCl$ by Bouteiller et al.[31] have shown that $\Delta\nu_s$ is equal to 445 cm^{-1} in the harmonic approximation and increases to 700 cm^{-1} when anharmonicity is accounted for. The much smaller harmonic value suggests our MP2 result may represent an overestimate. In any case, the frequency of LiCl follows opposite behavior, increasing as a result of complexation. The increments are 73 and 93 cm^{-1} at the SCF and MP2 levels, respectively.

In Ar matrix, H bonding drops the ν_s frequency of HCl by 1517 cm^{-1},[29] a considerably larger shift than even our MP2 value. A major source of this discrepancy is no doubt the ability of the matrix to stabilize a charge-separated species such as $H_3NH^+ \cdot \cdot Cl^-$. The proton is thus free to move further away from the Cl atom in the matrix than in the gas phase, thereby lowering ν_s. Indeed, the H–Cl stretching frequency shift in $Me_2O \cdot \cdot HCl$ has been measured as being 1.8 times greater in an inert matrix as in the gas phase[32] so the ratio of 1.7 found here between the experimental Ar-matrix frequency shift for $H_3N \cdot \cdot HCl$ and our calculated value of $\Delta\nu_s$ is consistent with the experimental data.

Intermolecular modes

As in earlier work,[19] v_σ refers to the oscillation of the intermolecular separation, $R(\text{N}\cdot\cdot\text{Cl})$. At either the SCF or MP2 level, this frequency is higher for the Li bond than for $\text{H}_3\text{N}\cdot\cdot\text{HCl}$, consistent with the stronger interaction in the former system discussed earlier. With regard to the effects of correlation, the MP2 value of v_σ in the H-bonded system is significantly higher than the SCF frequency while the SCF and MP2 results are much closer together for $\text{H}_3\text{N}\cdot\cdot\text{LiCl}$. This observation conforms to the earlier finding that correlation makes a substantial contribution to the binding energy of $\text{H}_3\text{N}\cdot\cdot\text{HCl}$ but not to the Li-bonded analog.[24] The calculated MP2 frequency of 200 cm^{-1} in the H-bonded system is in surprisingly good coincidence with the experimental measurement of 166 cm^{-1}.

The frequencies $v_{\beta 1}$ and $v_{\beta 2}$ are degenerate and are hereafter denoted simply as v_β; they represent a rocking of the H/Li acceptor molecule NH_3. This frequency is about twice as large in $\text{H}_3\text{N}\cdot\cdot\text{LiCl}$ as in the H-bonded system, again reflecting the stronger binding in the former. Also repeated is the opposite influence of electron correlation upon the two vibrations. A large part of the discrepancy between the calculated and experimental v_β frequencies of the H-bonded system is probably related to the aforementioned perturbing influence of the matrix which produces an equilibrium structure with considerably greater $\text{H}_3\text{NH}^+\cdot\cdot\text{Cl}^-$ character. The closer approach of the proton to the N atom makes it energetically more costly to rock the NH_3 subunit.

A bending motion about the bridging H or Li atom is denoted by v_b. (v_t, the out-of-plane vibration is equivalent to v_b in these C_{3v} geometries.) This frequency is many times larger in $\text{H}_3\text{N}\cdot\cdot\text{HCl}$ than in the Li counterpart due in part to the much smaller mass of the proton. In either case, $v_{b,t}$ increases by some 25%–30% when correlation is included. Even after correction by MP2, the calculated v_b frequency of $\text{H}_3\text{N}\cdot\cdot\text{HCl}$ remains about 30% below the experimental value. This underestimate may again be connected with the greater degree of proton transfer in the matrix.

INTENSITIES

Inspection of the calculated intensities reported in Table III immediately reveals an important distinction between H and Li bonding. Whereas the SCF and MP2 intensities are generally fairly similar for $\text{H}_3\text{N}\cdot\cdot\text{HCl}$, correlation leads to very substantial decreases (by factors between 2 and 4) in the intensities of the Li analog.

The first row of Table III illustrates the strong increase in the intensity of the a_1 stretch of NH_3 when it is involved in a H bond (20-fold at the MP2 level). The intensity of this vibration is even stronger when the interaction is of Li-bond type. Similar progressive intensifications are observed in the e stretch as well. A clear distinction between H and Li bonding appears also in the a_1 bend of NH_3. Whereas the intensity of this mode is diminished by H bonding, it is strengthened by interaction with LiCl. Although the SCF intensities of the e bends are quite different in the H and Li-bonded complexes, this discrepancy disappears at the MP2 level.

The intensification of v_s upon H bonding is a well known phenomenon which is reproduced here. The intensity of the HCl stretch is magnified by a factor of 9 at the SCF level and by 50 when correlation is included. The situation for LiCl is quite different. Although a moderate intensification (less than threefold) is observed upon complexation with NH_3 at the SCF level, the intensity of this mode in $\text{H}_3\text{N}\cdot\cdot\text{LiCl}$ is lowered by correlation to the point where Li bonding produces a very slight *decrease* in intensity. This finding conforms to the experimental observation of no appreciable intensification in Li bonds.[21]

Correlation plays an exceedingly important role in a comparison of the intensities of the H- and Li-bonded systems. For example, whereas the v_σ stretch is more than twice as intense in $\text{H}_3\text{N}\cdot\cdot\text{LiCl}$ as in $\text{H}_3\text{N}\cdot\cdot\text{HCl}$ at the SCF level, the order is reversed when correlation is included and the latter is more intense by a factor greater than 4. At the MP2 level, the intensity of v_β is considerably stronger in the Li-bonded complex while the reverse is true for the $v_{b,t}$ mode.

ANALYSIS OF INTENSITY DATA

Earlier work has demonstrated that a detailed understanding of the vibrational intensities can be achieved by the use of atomic polar tensors (APTs) which partition the total intensity into contributions from each individual atom.[14–19] After first defining a local coordinate framework for each atom α, the APT is defined as $P_{ij}^\alpha = \partial\mu_i/\partial q_j^\alpha$ where μ_i refers to the i component of the molecular dipole moment and q_j^α is the j coordinate of atom α.

Within the "equilibrium charge–charge flux" (ECCF) interpretation (see, e.g., Ref. 33) which incorporates a modified form of the bond moment hypothesis, the components of the APT have two sources. Defining the z axis as the bond direction in an (axially symmetric) diatomic molecule, a small motion ∂x of one of the atoms with charge q parallel to the x axis merely rotates the bond without distorting it. Such a motion therefore yields a change in the x component of the molecular dipole moment equal to $q\partial x$. Thus, $\partial\mu_x/\partial x = P_{xx} = q$ and similarly, $P_{yy} = q$. When the atomic motion involves a bond stretch, however, the ensuing distortion alters the polarity of the bond. This additional factor is represented as a "charge flux," i.e., flow of electron density towards or away from the atom. Hence, infinitesimal displacement of the atom along the bond or z direction by ∂z adds a second term to the change in μ_z: $\partial\mu_z = q\partial z + z\partial q$. The diagonal component P_{zz} thus becomes $\partial\mu_z/\partial z = q + z(\partial q/\partial z)$. When the atom in question lies along a symmetry axis of order 3 or higher (the z direction), P_{xx} must equal P_{yy} and we may take this value as the atomic charge q. Subtracting this quantity from P_{zz} leaves the charge flux $z(\partial q/\partial z)$, abbreviated herein as CF.

In addition to the atomic polar tensor $\mathbf{P}$ itself, it is also useful to define a number of derived quantities which are invariant to the choice of coordinate system. The effective charge χ is equal to the square root of 1/3 the sum of squares of all nine elements of $\mathbf{P}$. The mean dipole derivative $\bar{p}$ is evaluated as the arithmetic mean of the three diagonal ele-

TABLE IV. Data derived from APTs of bridging H and Li atoms (all quantities in a.u. except A in km/mol).

	q	CF	χ	$\bar{p}$	β^2	A_s
			SCF			
HCl	0.210	0.008	0.213	0.213	0.000	120
$H_3N\cdots HCl$	0.190	0.859	0.625	0.477	0.738	1087
LiCl	0.750	0.149	0.803	0.800	0.022	135
$H_3N\cdots LiCl$	0.628	0.288	0.737	0.724	0.083	331
			MP2			
HCl	0.208	0.006	0.210	0.210	0.000	46
$H_3N\cdots HCl$	0.163	1.356	0.887	0.615	1.839	2186
LiCl	0.729	0.129	0.775	0.772	0.017	123
$H_3N\cdots LiCl$	0.593	0.262	0.692	0.681	0.068	111

ments. The anisotropy is defined in terms of the above two invariants

$$\beta^2 = 9/2(\chi^2 - \bar{p}^2).$$

Z–Cl stretch

In order to analyze the ν_s vibration, we define the Z–Cl bond, coincident with the N$\cdots$Cl axis, as the local z coordinate for the bridging H and Li atoms. Since this axis represents a C_3 rotation axis of the complex (C_∞ in Z–Cl), the APT of the H and Li atoms must be diagonal. As discussed above, then, the charge of each atom is defined as the $P_{xx} = P_{yy}$ element of the APT. Subtracting this value from P_{zz} leaves the charge flux CF.

The first column of Table IV indicates that the atomic charge q of the proton in isolated HCl is 0.21 at the SCF level; this value is virtually unchanged by correlation. At either level, the charge flux is practically zero, suggesting this charge will be little affected by a bond stretch. Formation of a H bond with NH_3 lowers the charge q somewhat. Much more dramatic, however, is the very large charge flux in the complex as compared to its value near zero in the monomer.

The first two diagonal elements of the APT are little affected by H-bond formation while P_{zz} undergoes a sharp increase. Since χ and $\bar{p}$ each contain contributions from P_{zz} as well as from the other two diagonal elements of the APT, both of these quantities reflect the large increase in charge flux. Note that the effective charge χ is quite similar in magnitude to q in the isolated HCl but is much larger in the complex due to the contribution from charge flux. At either the SCF or MP2 levels, the anisotropy β^2 of the hydrogen APT is zero in HCl. The interaction with NH_3 provides displacement of the proton along the H-bond axis with a very strong influence upon the moment, causing the large increase in the anisotropy parameter.

In isolated HCl, then, the hydrogen has only a small positive charge and stretching of the bond leads to little change, since the electron cloud follows the proton in its motion. Upon formation of the H bond, the ability of the electronic density to keep up with the proton is impaired, perhaps even shifting in the opposite direction.[34] Hence, q_H rapidly becomes more positive as the proton moves away from chlorine. This pattern makes sense if one considers that

a finite motion of the proton towards the nitrogen would take the system towards the ion pair $H_3NH^+\cdots Cl^-$. The ensuing rapid rise of molecular dipole moment is responsible for the large intensification of the H–Cl stretch caused by H-bond formation, reproduced in the last column of Table IV. The above effects are magnified somewhat by correlation, leading to the stronger intensity at the MP2 level.

The patterns in the Li analogs are quite different in some respects. First, comparing the isolated LiCl and HCl monomers, the charge q on the Li atom is much more positive than is the hydrogen. Also considerably higher is the charge flux of the Li. As a result, the effective charge χ of Li is nearly four times larger than χ_H as is the case for the mean dipole derivative $\bar{p}$. All things being equal, the Li–Cl stretch would therefore be of considerably stronger intensity than H–Cl. However, the heavier mass of Li leads to a greatly reduced amplitude for ν_s which compensates for its larger charge and the result is a vibration of intensity comparable to that in HCl.

Complexation with NH_3 lowers the charge q on Li quite a bit, by more than 0.1 at either the SCF or MP2 level. This drop in positive charge is significantly larger than occurs in H bonding. As in $H_3N\cdots HCl$, the charge flux of the Li atom rises when the Li bond is formed but to only a fraction of the charge flux in the H bond. Due to this much smaller increase in CF, both the effective charge χ and $\bar{p}$ of the Li atom suffer a decrease upon complexation, in contrast to the very sizable increases observed in H bonding.

In physical terms, the Li–Cl bond is highly polar in the isolated monomer. The low electron density about the Li finds difficulty in moving along with this nucleus, leading to a higher positive charge on the atom when it is stretched away from Cl and therefore to a substantial value of CF. Interaction with NH_3 adds electron density to the Li atom (lower q) and leads to an increase in the charge flux (although less dramatic than in the H bond). These two effects are approximately equal in magnitude in $H_3N\cdots LiCl$ and hence cancel one another to a great extent, leading to no substantial increase in $\partial\mu/\partial z$ upon complexation. The intensity of ν_s is thus not very sensitive to formation of a Li bond.

One final application of these APTs relates to the effect of electron correlation upon the atomic charges. It may be noted in Table IV that in either complex the MP2 value of q is somewhat lower than the SCF result. Hence, a motion of these atoms perpendicular to the bond axis will produce a smaller change in the molecular dipole moment at the MP2 level. Since the $\nu_{b,t}$ vibrations consist primarily of just such a perpendicular displacement of the bridging atoms, it is gratifying to note in Table III the weaker intensities of these vibrations after correlation has been included. The weaker intensity of this vibration in $H_3N\cdots LiCl$ as compared to the H-bonded analog is due in large measure to the greater mass of Li and the resulting smaller amplitude of the pertinent vibration (despite the larger effective charge of Li).

NH₃ internal modes

Our assignment of the local coordinate system for each NH_3 hydrogen places the z axis along the N–H bond and defines the xz plane as containing this bond as well as the Cl

TABLE V. Atomic polar tensor elements of H atom of NH_3 (all quantities in a.u. except A in km/mol).

	P_{xx}	P_{yy}	P_{zz}	q	CF	$A_{st}(a_1)$
			SCF			
NH_3	0.302	0.178	0.005	0.351	−0.346	0.15
$H_3N\cdot\cdot HCl$	0.267	0.194	0.080	0.312	−0.232	4
$H_3N\cdot\cdot LiCl$	0.296	0.208	0.142	0.324	−0.183	26
			MP2			
NH_3	0.279	0.169	−0.004	0.335	−0.339	0.3
$H_3N\cdot\cdot HCl$	0.225	0.193	0.111	0.288	−0.177	6
$H_3N\cdot\cdot LiCl$	0.276	0.195	0.140	0.313	−0.172	11
NH_3 (calc.)[a]	0.271	0.161	0.036			
NH_3 (expt.)[b]	0.238	0.141	0.035	0.270	−0.235	

[a] SCF level with $[8s6p4d\ 1f/6s3p1d]$ basis set (Ref. 4).
[b] From Ref. 36.

TABLE VI. Atomic charge and charge flux (in e) calculated from atomic polar tensor of H atom of HCl and HF.

	HCl		HF	
	q	CF	q	CF
SCF	0.210	0.008	0.450	−0.090
MP2	0.208	0.006	0.427	−0.140
SCEP/CEPA[a]	0.180	0.00	0.404	−0.100
Expt.[b]	0.179	−0.01	0.408	−0.092
Expt.[c]			0.415	−0.098

[a] Theoretical values from Ref. 37; basis set $[11s9p3d\ 1f/9s7p3d\ 1f/5s2p1d]$ for [Cl/F/H].
[b] Experimental value quoted in Ref. 37.
[c] From Ref. 36.

and bridging atoms. The diagonal elements[35] of the APTs are reported in Table V. It is clear that both P_{xx} and P_{yy} are fairly insensitive to complexation with HCl or LiCl. On the other hand, P_{zz} undergoes a sharp increase upon H bonding and is further enlarged in the Li-bonded complex. These increases parallel quite closely the pattern of intensities of the a_1 stretch of the NH_3 subunit listed in the last column of Table V. [$A_{st}(e)$ follows a very similar pattern.]

The atomic charge and charge flux are reported in Table V. Note the negative values of CF which indicate that a stretch of each H away from N adds electron density to the hydrogen. Comparison of the first two rows illustrates the drop in positive charge experienced by the NH_3 hydrogens as a result of H-bond formation. Li bonding also leads to a decrease, albeit a smaller one. But most important, the changes in q are much smaller than those observed in CF. The latter quantity becomes much less negative when NH_3 interacts with HCl; the change is even greater in the case of LiCl. These more positive quantities parallel the increases noted in P_{zz} and the vibrational intensity in the final column.

The intensification of the NH_3 internal stretching modes (e as well as a_1) can therefore be traced to the less negative charge flux term in the complexes. As pointed out earlier,[19] this intensity is extremely weak in isolated NH_3 due to the cancellation between the positive charge and the negative charge flux term. This cancellation is less complete in the complex with HCl and even less so with LiCl. Consequently, the intensity of the NH stretch increases upon complex formation.

Accuracy of atomic polar tensors

It is possible to compare our APT data with a recent calculation of NH_3 which made use of a very extended basis set containing f functions on N and d functions on H.[4] The APT obtained in that calculation, restricted to the SCF level, is displayed in the penultimate row of Table V. The APT has also been extracted from experimental data[36] and is reported in the last row.

As may be noted by comparison of the first and last rows of Table V, both P_{xx} and P_{yy} of NH_3 are substantially overes-

timated at the SCF level with the 6-31G** basis set, consistent with the aforementioned exaggeration of the dipole moment of this molecule. Either inclusion of electron correlation or expansion of the basis set leads to significant reductions. It is reasonable to suppose that combination of these two factors, e.g., MP2 calculations with a large basis set, would quite nearly reproduce the experimental values.

A comparison of theoretical and experimental APTs of HCl and the very similar HF are presented in Table VI. As for NH_3, the charge on hydrogen is overestimated in HCl and HF as well, although by a smaller margin, again consistent with the exaggeration of the monomer's dipole moment. Note from the third row of the table that the theoretical approach closely mimics experiment when sufficient account is taken of electron correlation with a large flexible basis set. The molecular dipole moment seems to be a critical parameter in evaluating the suitability of a particular theoretical approach for calculations of this type. Since previous work[38] has demonstrated that MP2 calculations are capable of yielding quite accurate reproductions of dipole moments when combined with basis sets of sufficient quality, we suggest such a direction as most cost effective when demands for quantitative accuracy are more stringent.

CHARGE REARRANGEMENTS

Pictoral representations of the total density and electron density difference maps have provided useful insights into the nature of H and Li bonding. Alternatively, numerous attempts have been made to partition the density in various regions of space to one nucleus or another so as to assign a "charge" to each atom. A problem with procedures of this type, of which the Mulliken algorithm is a prime example, is that any such partitioning is more or less arbitrary and the atomic charges thus possess little physical meaning since there is no quantum mechanical operator for atomic charge. On the other hand, since the vibrational intensities are measurable quantities, the APTs derived from them have a real physical meaning. A set of charges can be assigned to atoms which will reproduce vibrational intensities, i.e., the molecular dipole moment and its derivatives. Such "spectroscopic" charges model real observable physical properties. To avoid any confusion in comparison with atomic charges derived directly from the electronic structure, we stress the spectro-

TABLE VII. Changes in atomic charges (in e) as a result of complexation.[a]

	H_N	N	Z	Cl	CT[b]
		SCF			
$H_3N\cdots HCl$	-0.039	$+0.223$	-0.020	-0.085	0.105
$H_3N\cdots LiCl$	-0.027	$+0.199$	-0.122	$+0.003$	0.119
		MP2			
$H_3N\cdots HCl$	-0.047	$+0.320$	-0.046	-0.134	0.180
$H_3N\cdots LiCl$	-0.022	$+0.197$	-0.136	$+0.005$	0.131

[a] Charges of H (or Li) atoms in isolated monomers are as follows: SCF: NH_3, 0.351; HCl, 0.211; LiCl, 0.750. MP2: NH_3, 0.335; HCl, 0.209; LiCl, 0.729.
[b] Charge transferred from NH_3 to ZCl.

scopic charges correspond only to that part of the total electron density which is visible through the window of IR spectroscopy; higher moments and their derivatives are completely neglected.

Table VII describes the difference in atomic charge between the complexes in the first column and the isolated monomers. For example, the first entry in the table indicates that at the SCF level, the charge of each hydrogen of NH_3 becomes more negative (i.e., picks up additional electron density) by 0.039 when it forms a complex with HCl. At the same time, the nitrogen atom loses 0.223 electron, accounting for a total loss of 0.105 from the NH_3 subunit, as indicated by the charge transfer (CT) entry in the table. Most of this density transferred to HCl (81%) finds its way to Cl, with the bridging hydrogen picking up only 0.020. Although the redistributions within the NH_3 subunit of $H_3N\cdots LiCl$ are fairly similar, the Li-bonded complex differs qualitatively in that essentially all of the charge lost by NH_3 is acquired by Li, with Cl being virtually unaffected. A similar picture emerges from analysis of Mulliken populations. [22,23]

Adding electron correlation produces only very minor perturbations in the case of Li bonding. $H_3N\cdots HCl$ is affected to a somewhat higher degree; correlation removes additional electron density from N, again most of it going to Cl. In summary, H and Li bonding differ fundamentally in both the quantity and the ultimate destination of the density withdrawn from the nitrogen. This charge is drawn primarily to Cl in the H-bonded system while the Li bond removes somewhat less density and places it exclusively on the Li atom. The combination of a smaller quantity of transferred charge and its motion to a less distant atom leads to the smaller value of $\Delta\mu$ noted earlier in Table II for the Li-bonded complex.

The v_σ vibration is related to the approach of the two subunits toward one another as the H or Li bond is formed. The accompanying transfer of electron density from the base to ZCl is a prime factor in lending intensity to the v_σ band, suggesting a connection between this intensity and the charge transfer parameter in Table VII. A correlation is in fact evident in that v_σ is predicted to be more intense in $H_3N\cdots LiCl$ than in the H-bonded analog at the SCF level, just as CT is larger for the former system than for the latter. Inclusion of correlation sees a reversal of this relationship in both the intensity and in CT.

As a final note concerning the charges, a hypothesis has

been advanced of a correlation between these quantities and the ability of the monomer to form a H bond. [36] Based on this and our earlier work, we calculate the charges q on the H atoms of HCl and HF to be 0.21 and 0.45, respectively, at the SCF level. This order is consistent with our calculated NH_3 binding energies of 7.1 and 11.7[39] kcal/mol, respectively. In comparison, both the charge on Li (0.75) and the binding energy (-24.3 kcal/mol) are substantially larger than the data for the two H bonds.

ACKNOWLEDGMENTS

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