

Vibrational frequencies and intensities of H-bonded systems. 1:1 and 1:2 complexes of NH₃ and PH₃ with HF

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Frequencies and intensities are calculated by *ab initio* methods for all vibrational modes of the 1:1 H₃X–HF and 1:2 H₃X–HF–HF complexes (X = N,P). The HF stretching frequencies are subject to red shifts, roughly proportional to the strength of the H bond, and to manifold increases in intensity. Although the intramolecular frequency shifts within the proton acceptors are relatively modest, the intensities of the NH₃ stretches are magnified by several orders of magnitude as a result of H bonding (in contrast to PH₃ which exhibits little sensitivity in this regard). The frequencies and intensities corresponding to bending of the H₃X–HF H-bond rise with increasing H-bond strength while the properties of the other intermolecular modes appear somewhat anomalous at first sight. The intensity patterns are analyzed by means of atomic polar tensors which reveal that intensification of the proton donor stretch is chiefly due to increasing charge flux associated with H-bond formation. The different behavior of the N–H and P–H stretching intensities is attributed to the opposite sign of the hydrogen atomic charges in the two molecules. As a general rule, low intensities can be expected for intermolecular modes with the exception of those which involve motions of hydrogens that appreciably alter the magnitude or direction of a subunit's dipole moment.

I. INTRODUCTION

The potential energy surfaces of H-bonded systems differ markedly from those of common molecules: they are generally rather flat and shallow, containing multiple minima and saddle points.¹ The nuclei consequently undergo motions that are anharmonic to a large degree² and there can be a great deal of coupling amongst the various vibrational modes, leading to IR spectra which puzzle experimentalists and theoreticians alike.^{3,4}

Perhaps most dramatic is the large amount of broadening and intensity enhancement of the XH stretching band of the proton donor molecule and its concomitant shift in frequency resulting from H-bond formation. The freezing of the subsystems' translational and rotational degrees of freedom leads to the appearance of new vibrations characteristic of H bonding. Experimental limitations have hindered measurement of these frequencies as they occur in the very far-IR region. As an example, Thomas's assignment of these frequencies in H₂O–HF was based not on direct measurement but instead on a painstaking and tedious scrutiny of the H–F stretching and bending bands.⁵ It remains unclear whether the low intensities of the intersystem modes, in conjunction with the small concentrations of the relevant dimer species, will allow their direct observation in the future. Additional peculiarities include the fine structure of the H–X stretching region of H bonds of medium⁴ and medium-weak⁶ strength as well as absorption continua in strong H-bond complexes⁷ and the anomalous isotopic effects therein.⁸

Recent advances in *ab initio* techniques have permitted calculation of potential energy and dipole moment surfaces

with reliable accuracy.⁹ When combined with progress in solution of the Schrödinger equation for nuclear motion,¹⁰ one has at one's disposal a powerful means of investigating a wide array of phenomena associated with the spectra of H-bonded systems. Within the subset of weak H bonds, even modest levels of theory, invoking the harmonic approximation, can aid in analysis of the source of the intensity enhancement of the ν_s band as well as identification of modes which resist assignment by purely experimental means.

A substantial body of literature has built up over recent years^{9,11–21} which provides strong indications that qualitative trends are reproduced faithfully by these theoretical approaches which can thus be of great assistance in the interpretation of experimental spectra. For example, in matrix isolation work, the H-bonded dimers of interest commonly coexist with trimers and higher polymers, adding a great deal of complexity to the spectra. Theoretical predictions of the frequencies and intensities of the dimer bands can perhaps be of help in deconvoluting these spectra. From a more fundamental perspective, the frequencies and intensities are both of particular interest because they provide very complementary information: while the frequencies reflect the strength of the bonding and force field, the intensities represent a window into the electronic distribution within the complex.²²

Although the IR spectra of a large number of molecules have been calculated, there is a surprising paucity of work concerning complexes such as H-bonded systems, most of these restricting their attention to the frequencies and ignoring intensities. A recent set of calculations by Zilles and Person¹⁵ led to some potentially very useful insights into the source of the intensification of the OH stretch associated with formation of the OH··O bond in the water dimer. Shortly thereafter, Swanton *et al.*¹⁶ reported the frequencies and intensities of all modes in the same system, calculated

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with a somewhat more extended basis set. In the following year, van Duijneveldt-van de Rijdt *et al.*¹⁷ carried out a systematic study of the effects of molecular geometry upon the vibrational properties of the H-bonded OH group but with an assumption that the O–H stretch represented a true normal mode in all cases. A number of H-bonded complexes including the water dimer were the subjects of recent investigation by Amos and co-workers¹⁸ while Ford *et al.*¹⁹ have extended the range of systems studied somewhat by examining much more weakly bound complexes, e.g., the ammonia dimer. Vibrational intensities have also been calculated for the trimer of HF.²⁰

In an earlier publication,²³ denoted here as paper I, we investigated the structure and energetics of the $\text{H}_3\text{N-HF}$ and $\text{H}_3\text{P-HF}$ complexes. Also considered were the 1:2 complexes of the type $\text{H}_3\text{X-HF-HF}$ which provided some insights into the cooperative nature of a string of H bonds. In the present work, we carry out full normal mode analyses of these complexes and calculate the IR frequencies and intensities of all vibrations. A careful analysis is made of the trends observed in the data, some of which appear at first sight anomalous, in order to identify their origins and to provide a useful qualitative guide for predictions of other systems. In addition, our study of the 1:2 complexes furnishes insights into the cooperative aspects of multiple H bonding upon the IR spectra. Comparison of our calculated data with the previous results determined by matrix-isolation IR spectroscopy²⁴ should be able to point out the possible strengths and weaknesses in using theoretical calculations to assist in the interpretation of experimental spectra.

II. METHODS

Calculations were carried out with the *ab initio* GAUSSIAN-80 package of computer codes^{25(a)} using the polarized split-valence 6-31G** basis set.^{25(b)} This choice is supported by the previous comprehensive examination of various basis sets^{9(b)} which showed that such a set reproduces faithfully the qualitative features of both frequencies and intensities of a large class of (noninteracting) molecules. Of course, more extended basis sets as well as correlation are necessary for quantitative accuracy,^{9(c)} especially in molecular complexes where correlation may play a major role. The fully optimized equilibrium geometries of all species have been described in our earlier work.²³ In summary, both $\text{H}_3\text{N-HF}$ and $\text{H}_3\text{P-HF}$ belong to the C_{3v} point group, containing a linear H bond between HF and the N or P lone pair. The 1:2 $\text{H}_3\text{X-HF-HF}$ complexes are quite bent, as may be seen in Fig. 1, with a $\theta(\text{XFF})$ angle of approximately 70° . Neither H bond is linear; the $\text{X} \cdots \text{HF}$ bond is distorted by 12° – 21° and the $\text{F} \cdots \text{HF}$ bond by about 17° .

The IR spectra were calculated in the framework of the double (mechanical and electrical) harmonic approximation by the standard GF method.²⁶ Cartesian force constant matrices were obtained by numerical differentiation of analytical gradients,²⁷ using finite displacements of $\pm 0.005 \text{ \AA}$. Assignments of modes were verified by the deuterium substitution shifts.

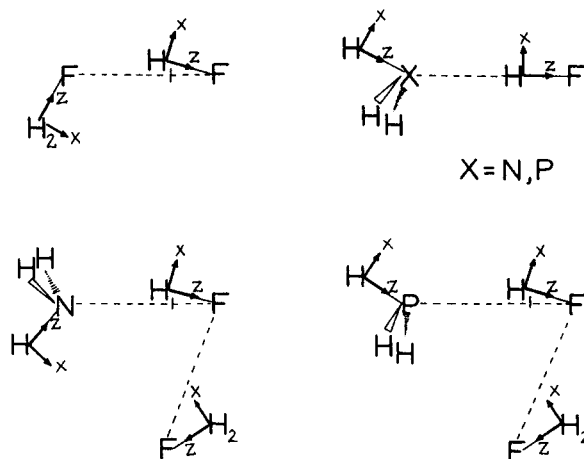
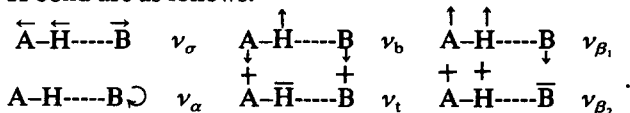


FIG. 1. Structures of 1:1 and 1:2 complexes defining the local coordinate system about each H atom.

III. NOMENCLATURE

In keeping with the prior convention of Bertie and Falk,²⁸ the internal stretch of the H–F bond is denoted ν_s . For the remaining intrasystem modes, we adopt the following terminology: In those systems with C_{3v} symmetry (viz., isolated H_3X and $\text{H}_3\text{X-HF}$), ν_1 and ν_4 correspond to the symmetric (a_1) stretch and bend, respectively, and the doubly degenerate ν_2 , ν_3 and ν_5 , ν_6 (e) sets to asymmetric stretches and bends. The first three vibrations retain their identity as stretches and the second group of three remain bends in the C_s 1:2 complexes.

Intermolecular modes, arising from the formation of the H bond are as follows:



The intermolecular stretch is denoted ν_σ and the torsion about the H-bond axis ν_α . Since it is in general less energetically costly to bend the complex around the proton acceptor atom B than around the central proton, ν_{β_1} and ν_{β_2} typically occur at lower frequency than ν_b and ν_t . (Exceptions to this rule are not uncommon, see e.g., Ref. 29.) Due to the C_{3v} symmetry of the $\text{H}_3\text{X-HF}$ complexes, the in-plane and out-of-plane bends ν_b and ν_t are degenerate, as are ν_{β_1} and ν_{β_2} . ν_α does not occur in $\text{H}_3\text{X-HF}$ since the H–F and X–F axes are collinear. Analogous modes (or combinations thereof) are readily identified in the 1:2 complexes.

Since some of the complexes contain two HF molecules, it will frequently be necessary to indicate which of the two is being referred to. We resolve this ambiguity either by underlining or by appending the number 1 or 2. For example, the ν_s stretch of the central HF subunit in the 1:2 complex can be indicated either by $\text{H}_3\text{X-HF-HF}$ or by $\nu_s(\text{H}_1)$ where the 1 corresponds to the atom numbering in Fig. 1.

It should be stressed that the nomenclature outlined above represents only an idealized and oversimplified version of the true normal modes which generally involve a certain amount of mixing. As discussed below, the F–H stretch ν_s tends to be the purest normal mode with only

minimal participation of other atoms. However, even here, the situation is complicated somewhat in the 1:2 complexes where the ν_s vibrations of the two HF molecules mix with one another. As another example, the 455 cm^{-1} vibration in $(\text{HF})_2$ could be denoted ν_α as well as ν_t . While the assignment is fairly straightforward for the C_{3v} 1:1 complexes, a degree of arbitrariness enters into the 1:2 structures, particularly $\nu_{\beta 1}$, $\nu_{\beta 2}$, and ν_α . Another point which should be borne in mind is that the specific atomic motions involved in each normal mode are altered upon deuteration.

IV. INTRAMOLECULAR VIBRATIONS

A. Proton acceptor

We begin our discussion with the intrasystem vibrations of the XH_3 subunit reported in the "proton acceptor" segment of Table I. The calculated symmetric stretch in NH_3 (3706 cm^{-1}) is lower by 138 cm^{-1} than the asymmetric stretch, in good agreement with the matrix spectrum where the a_1 frequency (3345 cm^{-1}) exceeds $\nu(e)$ by 102 cm^{-1} .^{24(c)} The calculated low intensities of the stretching bands are confirmed by the experimental spectrum. Although the first three frequencies of H_3P are listed as 2570 cm^{-1} in Table I, there is a slight difference between the first and next two (0.5 cm^{-1}) that is lost in the roundoff. The experimental difference observed in Ar matrix^{24(b)} is also quite small, 5 cm^{-1} , also consistent with theory in that the symmetric frequency of 2340 cm^{-1} is the smaller. Formation of either the 1:1 or 1:2 complexes has virtually no effect upon the NH_3 stretches; the failure to observe these lines in the complexes is therefore probably due to their very small separation from the more intense corresponding bands of the monomer. Increases of up to 50 cm^{-1} are observed in the internal stretching frequencies of PH_3 . Focusing on the 1:1 complex for which there is experimental data, addition of HF to PH_3 raises the ν_1 frequency by 26 cm^{-1} and ν_2, ν_3 by 30; the experimental increments^{24(b)} are of the same sign and even quite similar in magnitude, 32 and 20 cm^{-1} , respectively.

Turning now to the bending frequencies, ν_4 of H_3N undergoes a sizable increase of 93 cm^{-1} when H bonded to HF and a further increment of 35 when a second HF is added.

These values are quite consistent with the experimentally observed increases of 119 and 61 cm^{-1} . (Experimental values: H_3N , 974; $\text{H}_3\text{N-HF}$, 1093.5; $\text{H}_3\text{N-HF-HF}$, 1154.8.)^{24(a)} The situation reverses in the case of H_3P where ν_4 exhibits a slight red shift of 13 cm^{-1} when HF is added (the experimental decrement is 10 cm^{-1} from 994 in PH_3)^{24(b)} while ν_5 and ν_6 increase by nearly 100 cm^{-1} .

Whereas the internal XH_3 frequencies are relatively insensitive to H-bond formation, there is a great deal of variation seen in the intensities. For example, the intensity of the ν_1 stretch in NH_3 increases by a factor of 35 when H bonded to HF and is magnified by an additional factor of 40 when a second HF subunit is added. Similar increases, albeit of considerably smaller magnitude, are noted in ν_2 and ν_3 . In contrast to this behavior, the stretching intensity of PH_3 is diminished somewhat by the formation of H bonds. The intensities of the bending vibrations of both NH_3 and PH_3 are essentially unaffected by H bonding.

B. Proton donor stretches

It is clear from Table I that the HF stretching frequency decreases from its monomer value of 4495 cm^{-1} as a result of formation of H bonds. Even more striking are the large intensity enhancements. The calculated intensities range from 132 km/mol for the HF monomer to more than seven times that value for the central HF subunit in the $\text{H}_3\text{N-HF-HF}$ complex.

The ν_s vibration was studied in our earlier work²³ where the assumption was made that this mode is a pure HF stretch with no contamination from any other atomic motions, and that the two HF stretches of the 1:2 complex were completely independent of one another. The complete vibrational analysis in the present work allows us to test the validity of this approximation and we find it quite satisfactory. The frequencies computed by the full vibrational analysis and as an independent HF stretch³⁰ are within 0.2%–0.4% of one another, with the exception of $\text{H}_3\text{P-HF-HF}$ where the disagreement amounts to 1.5%. The independent HF stretch approximation also reproduces the relative order of ν_s intensities for the 1:1 and 1:2 complexes, although exaggerating the intensities by a factor between 1 and 2.5. We would con-

TABLE I. Calculated intramolecular frequencies (cm^{-1}) and intensities (km/mol).^a

	H_3P		$\text{H}_3\text{P-HF}$		$\text{H}_3\text{P-HF-HF}$		H_3N		$\text{H}_3\text{N-HF}$		$\text{H}_3\text{N-HF-HF}$		HF-HF	
	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>	ν	<i>A</i>
Proton acceptor														
ν_1	2570	106	2596	40	2604	78	3706	0.2	3706	7	3710	301	4454	182
ν_2	2570	128	2600	91	2615	45	3844	0.8	3842	13	3833	43		
ν_3	2570	128	2600	87	2620	74	3844	0.8	3842	12	3845	16		
ν_4	1125	36	1112	49	1111	33	1141	217	1234	216	1269	174		
ν_5	1156	21	1250	20	1247	13	1812	21	1805	26	1800	24		
ν_6	1156	21	1250	20	1247	26	1812	21	1805	26	1817	31		
Proton donor														
$\nu_s(\text{H}_1)$			4361	529	4218	565			4063	931	3674	946	4406	376
$\nu_s(\text{H}_2)$					4351	442					4251	519		

^a For isolated HF: $\nu = 4495\text{ cm}^{-1}$; *A* = 132 km/mol .

clude that a full vibrational analysis is in general necessary for intensities while certain reasonable assumptions may suffice for calculation of the frequencies.

There are a number of patterns clearly evident in the data in Table I. Formation of the H_3X-HF complex produces a decrease in the HF stretching frequency and an increase in the intensity. These changes are larger for H_3N than for H_3P , consistent with the stronger proton-accepting ability of the former molecule. Attaching a second HF molecule onto the first produces a further increment, illustrating the cooperative aspect of the H bond. The frequency shifts and intensifications are significantly weaker for the terminal HF subunit (H_2) of the 1:2 complexes than for the central subunit.

To be more specific, the frequency shift in the HF stretch of H_3X-HF , relative to the monomer, is 134 and 432 cm^{-1} for PH_3 and NH_3 acceptors, respectively. Adding a second HF molecule nearly doubles these frequency shifts, increasing in the PH_3 case by 143 cm^{-1} and by 389 cm^{-1} for NH_3 . These values are considerably larger than the shift of only 41 cm^{-1} observed when HF is added to another HF monomer. Hence, the presence of the XH_3 subunit makes the HF stretching frequency of H_3X-HF much more sensitive to the addition of the second HF molecule. From the other perspective, addition of PH_3 or NH_3 to a preformed HF dimer lowers the frequency of the inner HF stretch by 236 and 780 cm^{-1} , respectively, as compared to the values of 134 and 432 mentioned above for binding of XH_3 to a HF monomer. From either perspective then, there is a strong cooperative nature to the effect of H bonding upon the HF frequency shifts.

Taking a similar view of the intensities, addition of PH_3 to HF raises the HF stretching intensity by 397 km/mol while the corresponding quantity for NH_3 is 799. Adding HF to the H_3X-HF complex supplies an increment of only 36 and 15 km/mol for the P and N cases, which is smaller than the 50 km/mol increase arising from addition of HF to the HF monomer. Taking as our starting point the HF dimer, addition of PH_3 and NH_3 adds 383 and 764 km/mol, respectively, to the intensity of the HF stretch which is again somewhat smaller than the above values for addition of XH_3 to the HF monomer. The cooperativity in the intensity thus appears to be negative; i.e., the intensity enhancement in the 1:2 complex is smaller than would be expected from addition of the increases observed in the two component dimers.

We turn our attention now to the HF bond of the 1:2 complex which is not directly H bonded to XH_3 but is instead separated from it by the other HF. From the $\nu_s(H_2)$ row of Table I, we see that the frequency of this stretch is 4351 cm^{-1} for $X = P$ and 4251 for $X = N$. These values are respectively 55 and 155 cm^{-1} smaller than the equivalent frequency in the HF dimer, indicating that H bonding to XH_3 is capable of inducing a frequency shift in a H bond further along the chain. Nonetheless, this shift is approximately five times smaller than the effect of the XH_3 upon the HF subunit to which it is directly bonded. A similar reduction by a factor of 5–6 is exhibited by the intensity enhancements when one compares the effect of XH_3 upon its immediate neighbor HF and the more remote HF.

Due to its intensity, the HF stretching vibration is generally the most amenable to experimental measurement and all the ν_s frequencies of the complexes examined here have hence been measured within an Ar matrix.²⁴ Since vibrational frequencies calculated at the Hartree–Fock level are as a rule substantially higher (by $\sim 10\%$ – 15%) than the experimental quantities, we focus not on the frequencies themselves but rather on the *shifts* in the frequencies accompanying the formation of various H bonds. A very good linear correlation was found between the experimental and theoretical frequency shifts $\Delta\nu_s$, suggesting the calculations reproduce the essential features of the interactions. On the other hand, the theoretical values of $\Delta\nu_s$ are uniformly only 40% as large as the experimental shifts.

We attribute a part of this discrepancy to the omission of electron correlation from the calculations. Correlation has been demonstrated in the past to be responsible for a significant stretch of the A–H bond in A–H \cdots B interactions, over and above the lengthening observed at the SCF level.³¹ For example, the elongation of $r(HF)$ caused by H bonding to PH_3 is twice as large at the MP2 level as compared to the SCF stretch.³² The correlation-induced increase in the HF stretch can be expected to lead to a further weakening in the H–F bond and consequently to an additional diminution in the appropriate vibrational frequency, improving the agreement with experiment.

A second factor is associated with our use of the harmonic approximation. It is well known that the H-bonding X–H \cdots Y interaction increases the anharmonicity of the X–H bond,² allowing it to dissociate more readily, and thereby lowering ν_s by up to several hundred cm^{-1} .³³

A third factor in the discrepancy between calculated and experimental frequency shifts probably arises from the measurement of the spectra within the context of an Ar matrix whereas the theoretical results apply to an isolated gas-phase situation. As the HF bond elongates, a neutral-pair complex of the type F–H \cdots B resembles more and more an ion-pair structure $^-F \cdots H-B^+$. The dielectric effect of the surrounding medium will preferentially stabilize the latter complex, thereby allowing a greater stretch and accompanying increased frequency shift than would be present in the gas phase which the calculations are designed to mimic. This notion is supported by a number of experimental studies which have demonstrated a surprising degree of sensitivity of the frequency shift and band structure to the precise nature of the matrix medium.³⁴ For example, even slight changes in the characteristics of this medium can result in considerable shifts and drastic changes of absorption bands.³⁵

V. INTERMOLECULAR VIBRATIONS

A. Bending at proton: ν_b and ν_t

It is clear from the first row of Table II that the bending frequency in H_3N-HF (876 cm^{-1}) is much higher than in the H_3P-HF analog (467 cm^{-1}) which may be attributed to the stronger interaction between the subunits in the former case. These values agree quite well with the experimental frequencies which are 916 and 477 cm^{-1} , respectively. For

TABLE II. Intermolecular frequencies (cm^{-1}) and intensities (km/mol).

	HF-HF		$\text{H}_3\text{P-HF}$		$\text{H}_3\text{N-HF}$		$\text{H}_3\text{P-HF-HF}$		$\text{H}_3\text{N-HF-HF}$	
	ν	A	ν	A	ν	A	ν	A	ν	A
ν_b	601	167	467	134	876	208	(H_1)800 (H_2)504	247 292	1162 711	264 343
ν_t	455	279	464	134	877	208	(H_1)603 (H_2)454	275 6	1024 606	245 110
$\nu_{\beta 1}$	127	111	108	6	236	10	247	10	417	49
$\nu_{\beta 2}$			117	6	238	10	175	0.1	307	13
ν_α							114 68	0.01 8	131 119	0.06 20
$\nu_\sigma(\text{FF})$	230	154					204	0.3	231	6
$\nu_\sigma(\text{XF})$			113	1	240	3	140	5	290	13

$(\text{HF})_2$, the experimentally observed value of 401 cm^{-1} is closer to the calculated ν_t (455) than to ν_b (601). It must be considered, however, that $(\text{HF})_2$ is notoriously difficult to calculate, as witnessed by a previous SCF value of 491 cm^{-1} for ν_b with a large basis set³⁶ while CISD raises the frequency to 607 cm^{-1} ,¹² quite close to our value; the best agreement with experiment occurs for the CC result¹¹ of 420 cm^{-1} .

Addition of a second HF subunit to form the 1:2 complex raises the frequency by a considerable amount in either case. Due to the C_{3v} symmetry of the 1:1 complexes, the in-plane ν_b and out-of-plane ν_t bends are equivalent. This symmetry is broken in the 1:2 complexes where the ν_t frequencies are somewhat smaller than ν_b , as would normally be expected. Very similar behavior is exhibited by the intensities which also indicate enhancement of the H bonding in $\text{H}_3\text{X-HF}$ by addition of a second HF molecule.

We turn now to the other H-bonding proton of the 1:2 complexes; i.e., that belonging to the terminal HF subunit. As may be seen by the (H_2) entries for ν_b and ν_t in Table II, the frequencies associated with in-plane and out-of-plane bends of $\text{H}_3\text{X-HF-HF}$ are considerably smaller than those of the $\text{H}_3\text{X-HF-HF}$ (H_1) proton. Again, this decrease is consistent with the weaker nature of this interaction. In contrast to the lower frequency of the $\text{H}_3\text{X-HF-HF}$ ν_b vibration, the intensity of this bend is increased compared to $\text{H}_3\text{X-HF-HF}$. The ν_t intensity, on the other hand, follows an opposite trend, with $\text{H}_3\text{X-HF-HF}$ smaller than $\text{H}_3\text{X-HF-HF}$. These patterns are quite interesting and in some cases rather unexpected. We have probed the source of these intensities and a detailed analysis is provided below.

B. Bending at proton acceptor ν_β and torsion ν_α

From Table II, it is immediately obvious that the ν_β frequencies are several times smaller than those corresponding to bending at the H-bonding proton. Also of particular note are the much lower intensities of $\nu_{\beta 1}$ and $\nu_{\beta 2}$ as compared to ν_b and ν_t . The stronger character of the $\text{H}_3\text{N-HF}$ complex in comparison to $\text{H}_3\text{P-HF}$ is reflected in the ν_β frequencies which are twice as large for the former system. A large further increase is associated with addition of a second HF molecule to either 1:1 complex which does not appear to alter the intensities in any systematic fashion. The torsional

frequencies ν_α in the 1:2 complexes are rather small and of low intensity.

C. Intersystem stretching mode ν_σ

Inspection of Table II illustrates a correlation between the strength of the H bond and the frequency of the ν_σ stretch, pertaining to the distance between subunits. ν_σ is larger for $\text{H}_3\text{N-HF}$ than for $\text{H}_3\text{P-HF}$; both of these frequencies are increased by addition of the second HF molecule, again suggesting the cooperative nature of the H-bonding interaction. On the other hand, the F-F stretching frequency appears rather insensitive to the presence of the H_3X subunit. Any increments in the F-F stretching force constant arising from cooperativity are countered by an increased reduced mass for this vibration due to the additional XH_3 subunit. By careful examination of combination bands, Andrews was able to assign ν_σ for $(\text{HF})_2$ as 127 cm^{-1} ,^{24(d)} in reasonable agreement with our value of 230. Similarly, our two ν_σ for $\text{H}_3\text{N-HF-HF}$, 290 and 231 cm^{-1} , are consistent with his frequencies in the somewhat stronger $(\text{CH}_3)_3\text{N-HF-HF}$ complex (412 and 174).^{24(e)} The overall level of agreement is encouraging in the sense that not only intrasystem but also intersystem frequencies (which are more anharmonic) can be treated with some confidence.

Turning now to the intensities, that of the X-F stretch is quite small in $\text{H}_3\text{X-HF}$ but is significantly enhanced by the addition of the second HF molecule. The F-F stretching intensity, on the other hand, while reasonably large in $(\text{HF})_2$, is very much reduced by the XH_3 subunit in the 1:2 complexes.

D. Comparison between calculated and experimental intensities

The most intense band of the calculated spectrum of NH_3 is the symmetric bend ν_4 (217 km/mol), followed by the degenerate asymmetric bend (ν_5, ν_6) with a combined intensity of 42 km/mol . This ratio of 5 precisely matches the experimental spectrum.^{24(c)} The calculations indicate that the stretches are much less intense, with the asymmetric stretch slightly stronger than ν_1 , again duplicating experimental findings. Comparison is also possible in the case of $\text{H}_3\text{N-HF}$ where the calculations indicate the proton donor

stretch to be most intense (931 km/mol), followed by the degenerate (ν_b, ν_t) pair (416), and then by the symmetric bend ν_4 within H_3N (216). The same pattern is observed in the experimental spectrum: ν_s is quite strong and relatively broad, making its integrated intensity clearly the largest. In addition, rather strong sharp bands are evident for (ν_b, ν_t) and ν_4 , with the former somewhat more intense.^{24(a)}

VI. ANALYSIS OF INTENSITY CHANGES

A. Intrasystem modes

1. HF stretches

Perhaps the most striking feature of the spectra of H-bonded systems is the very substantial enhancement of the intensity of the stretching vibration of the proton donor molecule. The calculations reported above have suggested a substantial intensification occurs in these 1:1 and 1:2 complexes as well, with the largest magnification seen in the $\text{H}_3\text{N}-\text{HF}-\text{HF}$ stretch which is seven times more intense than in the isolated HF monomer. It would be particularly useful to identify the mechanism by which this intensification occurs. One means of analyzing the spectra which has proven itself quite helpful in the past is to partition the total intensity into contributions from each individual atom within the complex.²²

More specifically, one begins with the "double harmonic" approximation wherein the intensity of a given band is proportional to the square of the derivative of the molecular dipole moment vector with respect to a displacement along the normal coordinate of that vibration. Since the normal coordinate is composed of motions of individual atoms, it is possible to partition the change in dipole into contributions from each atom. The atomic polar tensor (APT) of a given atom α is defined as $P_{ij}^\alpha = \partial\mu_i / \partial q_j^\alpha$ where μ_i is the i th component of the molecular dipole moment vector and q_j^α represents the $x, y,$ or z coordinate defined for atom α .²² For example, P_{xz}^α represents the change in the x component of the dipole moment when a given atom α is translated along its z axis.

Usage of the same molecule-fixed coordinate system for all atoms hinders a comparison of the APTs of atoms in the same or different molecules. Hence, a transformation of coordinates is performed to a local framework for each atom.²² The local coordinate axes for each H atom are specified in Fig. 1 as bond coordinate systems since in all cases the z axis is collinear with the H-F bond. The x axis is perpendicular to z and within the plane of the complex; y is perpendicular to both x and z in a right-handed system and represents an out-of-plane coordinate.

The P matrix for each H atom is listed in Table III, along with some of their characteristics^{22,37} invariant to choice of coordinate system: χ is termed the "effective charge" and is defined as the square root of 1/3 the sum of squares of all nine elements of P . Although the sign of χ is ambiguous in its definition, we will make the reasonable assumption that the H atoms are positive since they are bonded to the much more electronegative F. The "mean dipole derivative" \bar{p} is equal to 1/3 the sum of diagonal elements of P . The anisotropy is defined in terms of the two previous invariant quantities

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

and provides a measure of the deviation of P from a constant diagonal tensor. We also report the ratio \bar{p}/β which is inversely related to the deformability of the electron cloud.

Inspection of the APTs in Table III reveals that the elements of largest magnitude fall along the diagonal. Indeed, all off-diagonal terms of the APT of any atom must be zero when it lies along a C_n symmetry axis with $n > 2$. The only off-diagonal terms of any appreciable magnitude are associated with the 1:2 complexes wherein displacement of a H atom directly away from its covalently attached F (the z direction) is likely to perturb the x component of the molecular dipole moment due to the highly bent, pseudocyclic geometry of these complexes. Nevertheless, it is the diagonal elements which are largest and to which we turn our attention.

The out-of-plane component P_{yy} of the HF monomer suffers a small loss of up to 0.10 as a result of H-bond formation. This decrease is not directly related to the strength of the bond since the smallest value of 0.35 is associated with $\text{H}_3\text{P}-\text{HF}$, the weakest of those bonds considered here. The changes in P_{xx} brought about by H-bond formation are not consistent, increasing in some cases and decreasing in others. This element covers a range of 0.19 between its minimum and maximum values. The component which is by far the most sensitive to the environment is P_{zz} which increases by up to 0.78 in $\text{H}_3\text{N}-\text{HF}-\text{HF}$, more than three times its value in the HF monomer. In fact, P_{zz} is very nearly proportional to the band intensities, listed in the last column of Table III (correlation coefficient = 0.97) and hence serves as an excellent indicator of this quantity.

Other properties of the APTs which are rather well correlated with the intensity are the effective charge χ of the H atom and the mean dipole derivative \bar{p} . However, due to the small magnitude of the off-diagonal elements and the relatively small variations in P_{xx} and P_{yy} , the sensitivity of both χ and \bar{p} to environment may be attributed chiefly to P_{zz} . From the foregoing analysis, we conclude that the intensity enhancement observed in the HF stretching bands as a result of H-bond formation arises from a sharp increase in the sensitivity of the molecular dipole moment to the HF bond length. Combining this result with the direct relationship noted between the intensity and the H-bond energy, it appears that one result of a stronger bond is a more deformable charge distribution, easily distorted by displacement of the proton along the H-bond axis, which is in turn responsible for the more intense band.

2. NH stretches

While the intensity increases in the HF stretches caused by H-bond formation are indeed large, perhaps even more dramatic are the analogous enhancements in the symmetric and asymmetric N-H stretches within the NH_3 subunit. For example, as shown in Table I, the intensity of the symmetric ν_1 stretch in NH_3 is quite weak, only 0.2 km/mol, a result which agrees with prior quantum mechanical calculations.^{9(b)} Complexation with HF raises this intensity to 7, a magnification by a factor of some 35. A further increase to

TABLE III. Atomic polar tensors and associated invariants of H atoms bonded to F. Local coordinate systems defined in Fig. 1, entries in atomic units except A (km/mol).

		\mathbf{P}	χ	\bar{p}	β^2	\bar{p}/β	A
HF		$\begin{pmatrix} 0.45 & 0.0 & 0.0 \\ 0.0 & 0.45 & 0.0 \\ 0.0 & 0.0 & 0.36 \end{pmatrix}$	0.422	0.420	0.008	4.69	132
HF-HF	H ₁	$\begin{pmatrix} 0.42 & 0.0 & 0.02 \\ 0.0 & 0.42 & 0.0 \\ 0.02 & 0.0 & 0.63 \end{pmatrix}$	0.502	0.492	0.046	2.30	376
	H ₂	$\begin{pmatrix} 0.46 & 0.0 & 0.03 \\ 0.0 & 0.46 & 0.00 \\ 0.01 & 0.0 & 0.43 \end{pmatrix}$	0.452	0.451	0.002	9.62	182
H ₃ N-NF		$\begin{pmatrix} 0.38 & 0.0 & 0.0 \\ 0.0 & 0.38 & 0.0 \\ 0.0 & 0.0 & 0.96 \end{pmatrix}$	0.637	0.574	0.342	0.98	931
H ₃ N-HF-HF	H ₁	$\begin{pmatrix} 0.42 & 0.0 & -0.09 \\ 0.0 & 0.37 & 0.0 \\ -0.14 & 0.0 & 1.14 \end{pmatrix}$	0.741	0.644	0.602	0.83	946
	H ₂	$\begin{pmatrix} 0.51 & 0.0 & -0.12 \\ 0.0 & 0.40 & 0.0 \\ -0.10 & 0.0 & 0.67 \end{pmatrix}$	0.546	0.527	0.091	1.74	519
H ₃ P-HF		$\begin{pmatrix} 0.35 & 0.0 & 0.0 \\ 0.0 & 0.35 & 0.0 \\ 0.0 & 0.0 & 0.73 \end{pmatrix}$	0.509	0.478	0.139	1.28	529
H ₃ P-HF-HF	H ₁	$\begin{pmatrix} 0.44 & 0.0 & -0.15 \\ 0.0 & 0.35 & 0.0 \\ -0.17 & 0.0 & 0.80 \end{pmatrix}$	0.579	0.528	0.255	1.05	565
	H ₂	$\begin{pmatrix} 0.54 & 0.0 & -0.09 \\ 0.0 & 0.40 & 0.0 \\ -0.06 & 0.0 & 0.58 \end{pmatrix}$	0.515	0.505	0.046	2.36	442

301 km/mol arises from addition of a second HF subunit; however, the identity of this symmetric stretch is obscured by the loss of C_{3v} symmetry in the 1:2 complex (see below).

In order to understand the source of the intensity enhancements, we turn to the atomic polar tensors of the N-H hydrogens which are displayed along with their related invariants in Table IV. (In keeping with our prior convention, local z axes point toward the N atom, as illustrated in Fig. 1.) As in the earlier case of HF hydrogens, the off-diagonal ele-

ments are rather small. Although P_{xx} and P_{yy} are fairly large, they exhibit little variation from one complex to the next. It is again P_{zz} which is most sensitive to the molecular environment of the N-H bond, increasing by a factor of 8 from NH_3 to $\text{H}_3\text{N-HF}$ and doubling again in $\text{H}_3\text{N-HF-HF}$.

Earlier workers have partitioned terms like $\partial\mu_z/\partial z$ into various separable contributions.^{15,22,37} First of all, since the H atom has some fractional charge q within the molecule, its displacement by a distance d along any axis would cause a

TABLE IV. Atomic polar tensors and associated invariants of H atom of NH_3 , z axis is along N-H bond, y perpendicular to plane containing H, N, and F. Entries in atomic units except A (km/mol).

		\mathbf{P}	χ	\bar{p}	β^2	\bar{p}/β	A_s
NH_3		$\begin{pmatrix} 0.30 & 0.0 & 0.01 \\ 0.0 & 0.18 & 0.0 \\ -0.09 & 0.0 & 0.01 \end{pmatrix}$	0.209	0.162	0.078	0.582	0.2
$\text{H}_3\text{N-HF}$		$\begin{pmatrix} 0.29 & 0.0 & 0.00 \\ 0.0 & 0.20 & 0.0 \\ -0.07 & 0.0 & 0.08 \end{pmatrix}$	0.211	0.189	0.040	0.949	7
$\text{H}_3\text{N-HF-HF}$		$\begin{pmatrix} 0.35 & 0.0 & -0.02 \\ 0.0 & 0.20 & 0.0 \\ -0.11 & 0.0 & 0.18 \end{pmatrix}$	0.263	0.244	0.043	1.170	301

change in the component of μ along that axis by an amount qd . Hence, the change in moment per unit displacement $\partial\mu_\alpha/\partial\alpha$ ($\alpha = x, y, z$) is equal to q . The matrix representation of the contribution to the P tensor of the charge on H is therefore q times the unit matrix $\mathbf{1}$. Taking the partial charge q as the Mulliken charge q_H ,^{15,22} and subtracting this quantity along the diagonal of the APT tensors, leaves the matrices reported in Table V.

The remaining quantities along the diagonal of $\mathbf{P} - q_H \mathbf{1}$ have been identified with a "charge flux."²² Specifically, as an atom moves along a given axis, its charge will not remain constant since the electron density is being redistributed. An increase in positive charge accompanying the motion would supply an additional contribution to the dipole moment along that axis. In fact, the negative entries for the $(\mathbf{P} - q_H \mathbf{1})_{zz}$ elements in Table V indicate that the NH hydrogens undergo a loss of positive charge as they move away from the nitrogen, i.e., they pick up additional electron density.

Within the framework of this analysis, the very low intensities of the NH stretches in NH_3 are due to a cancellation between two opposing effects: the motion of a H atom away from N causes an increase in $|\mu_z|$ due to its positive charge q_H but at the same time, this displacement causes a buildup of electron density on H, lowering its charge. The net result is that motion of the hydrogen produces little change in the dipole moment. Participation of NH_3 as electron donor in a H bond produces two effects: It first raises the positive charge of each H atom while at the same time reducing the ability of the remaining NH_3 electron density to follow the proton as it is moved away from N. Both of these effects contribute to the increase in dipole moment caused by an N-H stretch in $\text{H}_3\text{N-HF}$, i.e., the larger value of $\partial\mu_z/\partial z$ for this complex.

This pattern is continued when a second HF molecule is added to $\text{H}_3\text{N-HF}$. The charge on each NH hydrogen increases by 0.03 and the ability of the electron cloud to follow the proton, as reflected in the zz element of $\mathbf{P} - q_H \mathbf{1}$, diminishes by 0.07. As a result, $\partial\mu_z/\partial z$ in the P matrix of $\text{H}_3\text{N-HF-HF}$ in Table IV is more than twice as large as for $\text{H}_3\text{N-HF}$ and the N-H stretch is accordingly much more intense in the 1:2 complex.

The hydrogen atom of $\text{H}_3\text{N-HF-HF}$ whose APT is list-

ed in Tables IV and V is the one which forms a pseudo-H-bond to the terminal F atom. Despite the weakness of this interaction, as evidenced by the absence of a red shift in its stretching frequency (see ν_1 in Table I), the intensity increases by nearly two orders of magnitude. We may conclude that the intensity enhancement of the N-H stretch offers a much more sensitive gauge of any additional bonding than does the frequency shift.

3. PH stretches

It was mentioned earlier that whereas the intensities of the NH stretches increase quite dramatically as a result of H-bond formation, the situation is rather different for the analogous PH bonds. As may be seen in Table I, the PH stretching intensities are not particularly sensitive to complexation with HF. This contrast with NH_3 is quite interesting and we again turn to the APTs for an explanation. The relevant tensors and their invariants are contained in Table VI in a format identical to that of Table IV.

Considering first the off-diagonal elements, we note that P_{xz} is quite small whereas P_{zx} is rather large, reaching a maximum value of -0.20 . Nevertheless, these terms as well as all of the diagonal elements remain fairly constant from one system to the next. This behavior is in contrast to the NH stretches where P_{zz} increases substantially as H bonds are formed; indeed the magnitude of P_{zz} undergoes a significant decrease for PH_3 . A second major difference is that in the case of PH_3 , P_{zz} , and indeed all of the diagonal terms, are negative.

In order to understand these trends, we again partition the diagonal elements into contributions from the fractional charge q_H and the charge flux. We note first from Table VII that the H atoms in PH_3 are negatively charged, in contrast to their positive charges in NH_3 , due presumably to the lesser electronegativity of P. It is hence not surprising that the diagonal elements are negative since motions of the PH proton in any direction would naturally cause the component of the dipole moment along that axis to become more negative. Subtraction of q_H from the diagonal of the APT leaves the matrices reported in Table VII. The zz entries in these tables are surprisingly similar to those for the NH bonds reported in Table V. In either case, the negative values indicate the atomic charge of the hydrogen atom becomes more negative as it moves away from N or P.

We are now in a position to analyze the source of the intensities of the stretches. Unlike NH_3 where the positive fractional charge and negative charge flux work at cross purposes, leaving an extremely weak band, the negative charge of the PH_3 hydrogens combined with their charge flux of like sign produce a fairly strong stretching band. Addition of an HF molecule withdraws electron density from PH_3 , leaving the hydrogens of the latter subunit less negatively charged. Their motion therefore leads to a smaller decrement in the dipole moment and a weaker stretch ensues. The charge on the PH_3 hydrogens is intermediate between these two extremes in $\text{H}_3\text{P-HF-HF}$, as is the intensity. In summary, the very different patterns in the stretching intensities of the complexes containing NH_3 as opposed to PH_3 may be direct-

TABLE V. Atomic polar tensors of NH hydrogens after subtraction of Mulliken charge q_H along the diagonal.

	q_H	$\mathbf{P} - q_H \mathbf{1}$
NH_3	0.264	$\begin{pmatrix} 0.04 & 0.0 & 0.01 \\ 0.0 & -0.09 & 0.0 \\ -0.09 & 0.0 & -0.26 \end{pmatrix}$
$\text{H}_3\text{N-HF}$	0.293	$\begin{pmatrix} -0.01 & 0.0 & 0.00 \\ 0.0 & -0.09 & 0.0 \\ -0.07 & 0.0 & -0.21 \end{pmatrix}$
$\text{H}_3\text{N-HF-HF}$	0.321	$\begin{pmatrix} 0.03 & 0.0 & -0.02 \\ 0.0 & -0.12 & 0.0 \\ -0.11 & 0.0 & -0.14 \end{pmatrix}$

TABLE VI. Atomic polar tensors and associated invariants of H atom of PH₃, z axis is along P-H bond, y perpendicular to plane containing H, P, and F. Entries in atomic units except A_s (km/mol).

	P	χ	\bar{p}	β^2	\bar{p}/β	A_s
PH ₃	$\begin{pmatrix} -0.03 & 0.0 & 0.04 \\ 0.0 & -0.07 & 0.0 \\ -0.16 & 0.0 & -0.32 \end{pmatrix}$	0.211	-0.137	0.115	-0.403	106
H ₃ P-HF	$\begin{pmatrix} -0.05 & 0.0 & 0.03 \\ 0.0 & -0.07 & 0.0 \\ -0.16 & 0.0 & -0.27 \end{pmatrix}$	0.184	-0.127	0.080	-0.448	40
H ₃ P-HF-HF	$\begin{pmatrix} -0.09 & 0.0 & -0.01 \\ 0.0 & -0.07 & 0.0 \\ -0.20 & 0.0 & -0.26 \end{pmatrix}$	0.199	-0.141	0.089	-0.471	78

ly attributed to the opposite charges of the H atoms in these two molecules.

Returning now to the F-H stretches, similar partitioning of P_{zz} provides useful insights into the source of the very strong intensity enhancements observed. While the positive charge of these hydrogens does experience a small increase as the H bond is strengthened, a much more sizable increase is associated with the charge flux term. The dominating influence of the charge flux in enhancing the F-H stretching intensity is entirely consistent with the findings of Zilles and Person for the water dimer.¹⁵ This pattern also fits nicely into a picture derived from quantum mechanical calculations wherein motion of a proton along the H-bond axis induces a flow of electron density in the opposite direction.³⁸ The large intensity enhancements of the N-H stretches caused by H-bond formation are likewise due to reinforcement of changes in the effective charge and the charge flux, with the latter again playing a larger role than the former. The P-H hydrogen charges remain rather stable and are unable to contribute to changes in the P-H stretching intensities.

B. Intersystem modes

Prior work has shown that the intersystem stretching mode of (H₂O)₂ is of rather high intensity.^{15,16,18(a)} The intensity of the stretch in (HF)₂ is likewise quite strong, as

TABLE VII. Atomic polar tensors of PH hydrogens after subtraction of Mulliken charge q_H along the diagonal.

	q_H	P - q_H 1
PH ₃	-0.059	$\begin{pmatrix} 0.04 & 0.0 & 0.04 \\ 0.0 & -0.01 & 0.0 \\ -0.16 & 0.0 & -0.26 \end{pmatrix}$
H ₃ P-HF	-0.041	$\begin{pmatrix} -0.05 & 0.0 & 0.03 \\ 0.0 & -0.03 & 0.0 \\ -0.16 & 0.0 & -0.22 \end{pmatrix}$
H ₃ P-HF-HF	-0.053	$\begin{pmatrix} -0.04 & 0.0 & -0.01 \\ 0.0 & -0.02 & 0.0 \\ -0.20 & 0.0 & -0.21 \end{pmatrix}$

may be seen in Table II. In contrast, however, all other intersubunit stretching vibrations in the complexes investigated here are surprisingly weak, a phenomenon which we would very much like to understand. Our above analyses of the intrasystem stretching intensities have made profitable use of an approach whereby we first consider the properties of the isolated monomer and then include the influence of the other subunits as a perturbation. We adopt a similar strategy for treatment of the intersubunit stretches as follows.

On combining the amplitudes of the motions of each individual atom in the pertinent vibrational mode, as determined by the respective eigenvector for the entire complex, with the APTs of the atoms, calculated within the context of the isolated monomer, one obtains the change in the dipole moment vector of the complex that would result from the correct motions of all atoms, but with all direct interactions between the subunits turned off.

If the electronic structures of the monomers are unaffected by one another, any intersubunit stretch which involves changes in neither the orientations of the subunits relative to one another nor their internal geometries would lead to no alteration of the dipole moment of the complex and hence to very low intensity. This is very nearly the case for H₃N-HF where ν_σ is composed almost entirely of the rigid motion of the H₃N and HF subunits away from one another. A very small intensity (for the noninteracting subunits) of 0.4 km/mol arises due to the mixing into the normal mode of a certain amount of internal H-F stretch and some rocking and internal bending of the NH₃. An additional 2.3 km/mol is added when the two subunits are allowed to interact with one another, making up the total of 2.7 km/mol reported in Table II. The ν_σ normal mode in H₃P-HF is very much akin to that in H₃N-HF, explaining its similarly low intensity.

The situation is quite different in (HF)₂ where the ν_σ mode contains large contributions from rotation of the two HF molecules relative to one another as well as some stretching of the HF bonds. Consequently, even in the absence of an interaction, the calculated intensity would be quite high: 111 km/mol. Permitting the interaction to take place adds 43 km/mol for a total of 154. A similar conclusion was reached by Swanton *et al.* in their analysis of the strong intensity of

the ν_o mode of water dimer, 70% of which is recovered from the noninteracting monomers.¹⁶

Thus, the strong intensity of the intersystem stretch in $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$ is due to incorporation of other types of motion, e.g., wagging of one molecule or intramolecular stretches. Despite the strong nature of the interaction in $\text{H}_3\text{N}-\text{HF}$ which is potentially capable of inducing an increment in the dipole moment of the complex, the relatively pure character of the intersystem stretching mode leads to a rather weak band.

Turning now to the 1:2 complexes, each contains two different ν_o modes, one for the X-F stretch and one for F-F. Considering first the former, the addition of the second HF molecule does not substantially alter the character of the ν_o normal mode. It is hence not unexpected that the intensities of these stretching vibrations remain rather low. Increases by a factor of 4 or 5 do occur and are due primarily to the additional HF molecule which undergoes a small amount of rotation and internal stretching as part of the normal mode.

With respect to the F-F stretch, it is clear from Table II that the intensity of this vibration in $(\text{HF})_2$ is drastically decreased upon addition of PH_3 or NH_3 . To understand the source of this decrease, recall from our earlier discussion that the high intensity in $(\text{HF})_2$ is due in large part to the wagging of the hydrogen not participating in the H bond. When XH_3 is added, it forms a H bond to this hydrogen, preventing it from undergoing such a wag. The ensuing ν_o mode thus becomes much closer to a pure intersubunit stretch with its associated low intensity. In summary, ν_o stretches can be expected to be of low intensity unless the hydrogen(s) of at least one subunit are free to wag about as occurs for $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$.

This conclusion is reinforced by the behavior of the intensities of the remaining intersystem bending deformations. The ν_b and ν_t bends involve principally substantial motions of the H-bonded proton which will reorient the dipole moment vector of the proton-donating subunit. It is therefore not surprising that these vibrations are very intense, as is indeed observed in the experimental spectrum. Moreover, the APT of the H-bonding proton undergoes the largest change upon H-bond formation, leading to the observed correlation between the strength of the bond, the change in the APT, and the intensity of the band. On the other hand, the other intersystem deformations are of low intensity. ν_β involves only motions of the proton acceptor hydrogen atoms, whose APTs include much smaller elements. The torsions occurring in ν_α (which only occur in the 1:2 complexes) do not affect the dipole moment to any large extent as they involve principally the motion of the terminal HF or XH_3 subunit as a whole.

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