High Resolution Nuclear Magnetic Resonance Spectra of Hydrogen Fluoride in Solution and in Bihalide Ions. Nuclear Spin Coupling in Strong Hydrogen Bonds

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Abstract: The high resolution ^{1}H and ^{19}F nmr spectra of hydrogen fluoride have been observed in aprotic solvents. In basic solvents the H–F coupling is resolved; in nonbasic solvents it is averaged by exchange. This suggests that HF forms polymers in inert solvents but that it is complexed monomerically to basic solvents. The hydrogen shielding, fluorine shielding, and H–F coupling all are smaller in solution than in gas phase HF. The hydrogen shielding and H–F coupling correlate well with measures of H-bond strength, such as the H–F stretch frequency and the solvent donor number. The fluorine shielding is anomalous and may be controlled by other phenomena, such as overlap effects. The large decrease of the H–F coupling is in contrast to very small increases in C–H and N–H couplings on H-bond formation. Simple molecular orbital arguments suggest that the more polar a bond the more susceptible its coupling to perturbation and that H bonding should decrease the coupling in highly polar bonds. It can also be shown that the coupling in a symmetric complex such as FHF$^-$ should be no greater than half of that in the related molecule. All experimental data so far are in accord with these predictions.

Hydrogen fluoride is the simplest H-bond hydrogen donor molecule. It participates in FHF$^-$, one of the few H-bonded systems for which reasonably accurate *a priori* wave functions may be calculated.[1] Thus precise spectroscopic parameters of HF, if they can be properly interpreted, may provide valuable probes into the electronic rearrangements which accompany H-bond formation. High resolution nuclear magnetic resonance (nmr) provides three such: the hydrogen and fluorine nuclear shieldings, and the internuclear spin–spin coupling. These could make it possible simultaneously to observe three different aspects of local electronic configuration in the H bond.

We have reported the nmr of the bihalide ions FHX$^-$ (X = F, Cl, Br, and I).[2] It has also proven feasible to observe the ^{1}H and ^{19}F high resolution nmr spectra of hydrogen fluoride dissolved in several aprotic solvents of varying basicity. These provide an approximation to a continuous series of complexes of HF of varying H-bond strength. Such a series allows one to evaluate the spectral parameters as gauges of the strength of the interaction and to determine whether H bonding may be described as a simple perturbation of the hydrogen donor or as a superposition of distinct phenomena. It may also be possible to evaluate the degree of charge transfer and to compare complexes of molecular and ionic bases.

We present here the first report of the nmr of solutions of HF in which the coupling has been resolved. Previously,[3,4] in all phases except liquid HF,[5] the H–F coupling was not observable by nmr, since the internuclear spin correlation was averaged out by rapid exchange. We have found that exchange is slow enough to allow observation of the coupling in HF dissolved in basic aprotic solvents which have been carefully purified. In these solvents we cannot only measure the three high resolution nmr parameters, we can set limits on the rates of exchange and speculate on the exchange reaction mechanisms.

A survey of the complete series of complexes of HF to ionic and molecular bases reveals large, parallel variations in the hydrogen shielding and the H–F coupling, which appear to be simply related to the strength of the H bond. The fluorine shielding also changes but in a less regular way. We shall examine the mechanisms of these phenomena and show that a simple model accounts for the first two but not for the last.

Procedures

Most solvents were treated with a drying agent and then fractionally distilled. The middle 50–75% of the final distillate was collected and stored over 4A molecular sieve (ms) in a dry nitrogen glove box. Anhydrous calcium sulfate traps protected solvents from atmospheric water vapor during distillations.

Acetonitrile and *N,N*-dimethylformamide were purified as previously described.[2] Tetramethylsilane (TMS) was stored over ms; no water was detected in the nmr spectrum of the pure liquid. Diethyl ether and perdeuteriocyclohexane were fractionally distilled from lithium aluminum hydride. Propylene carbonate and dimethyl sulfoxide were stirred with calcium hydride and then fractionally distilled at reduced pressure and temperatures under 70°. Trichlorofluoromethane was fractionally distilled at atmospheric pressure.

Hydrogen fluoride was handled in a suitable vacuum system and purified by trap to trap distillation. Solutions of HF were prepared on the vacuum line, concentrations were determined, and samples were sealed into polypropylene tubes as described previously.[2] The inert plastic tubes fit inside standard nmr sample tubes and may be spun in a high resolution nmr probe.

Spectra were obtained using Varian HA-60 and HA-100 spectrometers, retuned as needed for ^{19}F resonance. Internal tetramethylsilane (TMS) was used as a hydrogen reference and lock. The fluorine reference was internal CF$_4$. A 50% v:v solution of trifluoroacetic acid in acetonitrile placed between the polypropylene and glass tubes served as the fluorine lock.

Observations

Line Widths. Solvent purification was carried out with the intent of resolving the H–F coupling. We consider that water is the impurity most likely to catalyze the internuclear exchange of hydrogen fluoride in dilute solution in aprotic solvents. Our solvents ultimately contained water at concentrations below the limit of detection by standard methods, such as Karl Fischer titration, nor was water detectable by nmr. Our ultimate criterion of purity was, of necessity, the width of the components of the spin coupling multiplet. Purification was carried out until the lines were as narrow as possible and their positions reproducible.

The sharpest lines we obtained were still significantly more broad than those characteristic of normal field inhomogeneity and relaxation in these solvents. Thus even the minimum line widths are almost certainly determined by spin exchange. There is no reason to believe that the minimum exchange rate we found in any solvent is characteristic of anything other than the lowest level of impurities happened to achieve in that solvent. Nevertheless it is possible to perceive certain gross differences in exchange behavior between classes of solvent, which we believe to be significant.

In basic solvents, the minimum line widths were fairly consistent: about 10 Hz at −40° and about 50 Hz at +34°, observed in acetonitrile, dimethyl sulfoxide (+34° only), and N,N-dimethylformamide (−40° only). Coupling was resolved in the other two basic solvents only at −40°. The line widths were about 30 Hz in propylene carbonate and about 40 Hz in diethyl ether.

On the other hand, in all the nonbasic aprotic solvents we observed only spectra which were single, exchange averaged lines at all temperatures. We do not believe that this reflects a higher level of impurities in the inert solvents TMS, C_6D_{12}, and $CFCl_3$. They do not complex acidic or basic impurities and are known to be relatively easy to purify. In TMS and C_6D_{12} the nmr signals were less intense than in the other solvents. It appears that a considerable fraction of the hydrogen fluoride remained in the gas phase above these solutions.

Shieldings and couplings of HF at 0.22 M in various solvents are presented in Table I. No significant variation of the coupling was observed as the temperature was changed from −40 to +34°. There were small changes of shieldings in this range. Shieldings and coupling appear to be independent of concentration. In acetonitrile in the range 0.05 to 0.22 M neither shielding changed by as much as 0.05 ppm; the coupling was unchanged to within experimental error. The shieldings presented in Table I may be taken to be reliable to ±3 in the last figure given.

For purposes of comparison, the table also presents the shieldings[3] and coupling[6] in gaseous HF and corresponding data for HF in the bihalide ions[2] and dilute in liquid sulfur dioxide.[4] We also give the Gutmann donor numbers[7] of the basic solvents and the observed infrared stretch frequencies of a number of HF complexes.

Discussion

Exchange Processes. We believe that the more rapid exchange of HF in nonbasic solvents is significant. HF also exchanges rapidly in the gas, by a process which is supposed to involve cyclic polymers as intermediates.[5] Presumably TMS, cyclohexane, and $CFCl_3$ are such weak bases that an acidic solute such as HF is extremely weakly solvated in them. The high vapor pressure of HF over these solvents suggests that this is so. In such a case, HF will associate with the strongest base available, which is HF. Thus one would expect a reasonable concentration of polymeric species in nonbasic solvents and enhanced exchange.

There is evidence that in basic solvents hydrogen fluoride is complexed to the solvent and monomeric.[8] An interaction which stabilizes the monomer will decrease the polymer concentration and inhibit exchange, consistent with the observation of coupling in the basic solvents.

Shielding Correlations. It has been noted[2] that there is a parallel between the strength of a H bond and the associated decrease in the hydrogen shielding. Since there are no measurements of the energies of solvation of hydrogen fluoride, other measures of the H-bond strength must be used. The relationship between the energy of the H bond and the

decrease of the hydrogen stretching vibration frequency is well established.[9] It has recently been shown[10] that in one system at least the enthalpy change, the infrared frequency shift, and the hydrogen shielding change on H-bond formation are all linearly related. Thus there is good reason to look for some degree of correlation of our nmr data with the infrared stretching frequencies.

Figure 1 demonstrates that the hydrogen shielding and the infrared stretching frequency of HF are related in complexes to anionic and molecular bases. Since infrared lines in these systems are broad and there is considerable disagreement among reports in the literature,[8,11-15] as indicated by the error bars about the points, we may claim that the graph shows a linear correlation which is about as good as the data. Except in the cases of HF gas and FHF^-, a small frequency range on the graph usually means that there is only one literature value of the frequency available, rather than that the value is particularly accurate. We have compared the ir frequency of HF in hexane to the nmr shielding in cyclohexane and the frequency in CCl_4 to the shielding in $CFCl_3$, since it appears that the values for similar inert solvents do not differ perceptibly.[15]

It is evident that H bonding lowers the stretch frequency and the hydrogen shielding of HF in proportion. There appears to be a marginally significant tendency for anionic and molecular complexes to define separate sequences in Figure 1.

There is evidence that the strength of H bonding to a common hydrogen donor is determined primarily by the base strength of the hydrogen acceptor.[1] We have found that the deshielding of hydrogen on forming an anion complex is linearly related to the proton affinity of the anion.[2] Table I suggests that the greater the Gutmann donor number, a measure of solvent basicity, the greater the changes in shielding and coupling. Figure 2 relates the hydrogen and fluorine shieldings to the solvent donor numbers. The points at zero donor number are those of gas phase HF. The horizontal lines at the left of each diagram give the shieldings in solvents such as TMS, C_6D_{12}, $CFCl_3$, and SO_2, whose donor numbers are undetermined but certainly small. It is clear that the hydrogen shieldings are more closely related to the solvent basicities than are the fluorine shieldings.

Hydrogen Shieldings. We have established[16] that the hydrogen shielding in a hydrogen halide or a bihalide ion is controlled by the electron charge density on the hydrogen, via the local diamagnetic term and the halogen paramagnetic term. Both are positive, and both are proportional to the hydrogen 1s electron population. It is reasonable that H-bond formation, which results in charge polarization[1] in the sense H^+F^-, should result in a decrease of the hydrogen shielding and that the decrease is proportional to the strength of the H bond.

Deviations from correlations of the sort seen in Figure 1 are usually considered to arise from the long range shielding effect of magnetically anisotropic groups in the hydrogen acceptor.[17] There is a clear tendency for the anion complexes FHX^- to have greater shielding than the molecular complexes. We have shown[2,16] that in these cylindrically symmetric bihalides there will be significant positive contribution to the hydrogen shielding arising from the complexing halide ion which may not occur in complexes of lower symmetry.

Fluorine shieldings correlate poorly with all measures of H-bond strength; Figure 2b is typical. It does appear that H-bonded hydrogen fluoride characteristically has a lower fluorine shielding than the free molecule. Fluorine shieldings and spin-rotation constants[18,19] are dominated by the inherently negative local paramagnetic term, which

Table I. Hydrogen Fluoride in Various Media (Nmr spectra at 0.22 M)

Medium	T, °C	Hydrogen shielding, ppm vs. int TMS	Fluorine shielding, ppm vs. int CF	Coupling constant $^1J_{HF}$, Hz	Gutmann donor no.[a]	Infrared H-F stretch frequency, cm^{-1}
Gas	+30	-2.2[b]	151[f]	+529 ± 23[c]		3960
Tetramethylsilane[d]	+34	-3.93	132.1			
Perdeuteriocyclohexane[d]	+34	-3.97				
Hexane						3858[g]
Trichlorofluoromethane	+34	-4.07	133.0			
Carbon tetrachloride						3856[g]
Sulfur dioxide	+34	-4.4[e]	128[e]			3700[h]
Acetonitrile	+34	-7.20	121.4	479 ± 4	14.1	3475,[g] 3310[i]
	-40	-7.64	118.7	476 ± 1		
Propylene carbonate	-40	-8.43	120.6	453 ± 5	15.1	
Diethyl ether	-40	-9.05	124.5	464 ± 5	19.2	3221[g]
Dimethyl sulfoxide	+34	-10.44	104.9	410 ± 10	29.8	2700[i]
N,N-Dimethylformamide	-40	-11.80	117.5	412 ± 1	26.6	3148,[g] 2850[i]
IHF$^-$ [f]	-40	-7.4	82 ± 4	437 ± 5		3145,[i] 3200[i]
BrHF$^-$ [f]	-40	-8.88	83.2	427.1 ± 0.2		2900,[i] 3050[i]
ClHF$^-$ [j]	-40	-10.43	83.3	403.4 ± 0.2		2710,[i] 2850[i]
FHF$^-$ [j]	-30	-16.37	83.35	120.5 = 0.1		1450,[k] 1473[l]

[a] Reference 7. [h] Reference 3. [c] Reference 6. [d] Concentration of HF is less than 0.22 M. [e] Reference 4. The equation on p 2680, giving the temperature dependence of the hydrogen shielding of liquid HF, is inconsistent with the graph on the same page. We assumed that the last term in the equation is negative, in order to estimate the shielding of hydrogen in HF dilute in liquid SO_2. [f] Reference 2. The solvent is acetonitrile. [g] Reference 15. [h] Reference 14. [i] Reference 8. [j] Reference 13. [k] Reference 11. [l] Reference 12.
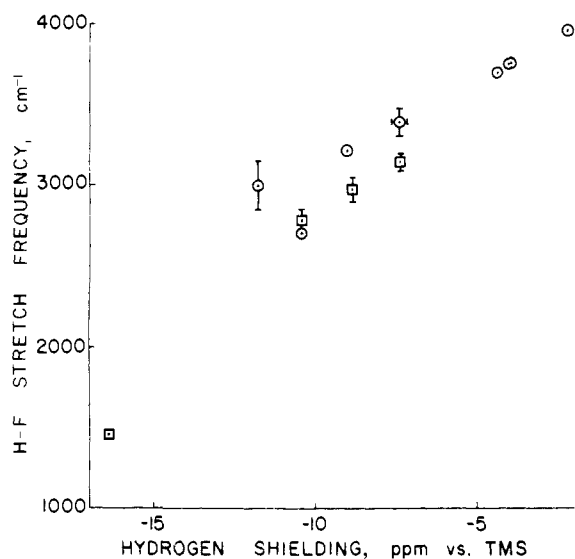

Figure 1. Correlation of the stretch vibration frequency with hydrogen shielding of hydrogen fluoride in solution (circles) and in bihalide ions (squares).

is zero in fluoride ion. Thus the charge shift on H-bond formation, which makes the fluorine more negative, should increase the shielding. The opposite is observed. This anomaly is not without parallel. Oxygen in water[20] and nitrogen in ammonia,[21] amines,[22,23] and amides[24] all become deshielded when the molecule acts as a H-bond donor. Since their shieldings are also controlled by the local paramagnetic term, the same argument should apply.

Fluorine shieldings are very sensitive to solvent effects,[25] and nonspecific interactions appear to have an effect comparable to that of H bonding. It is likely that factors other than the local effect of H bonding control the variation of the fluorine shielding in associated HF.

Coupling Correlations. The H-F couplings in complexes of hydrogen fluoride are striking in two respects. They are much smaller than in the isolated molecule, and they show a decrease with increasing H-bond strength which parallels that of the hydrogen shielding. The correlation with hydrogen shielding is shown in Figure 3. It is not linear, but it is quite regular. There is a tendency for the anion complexes
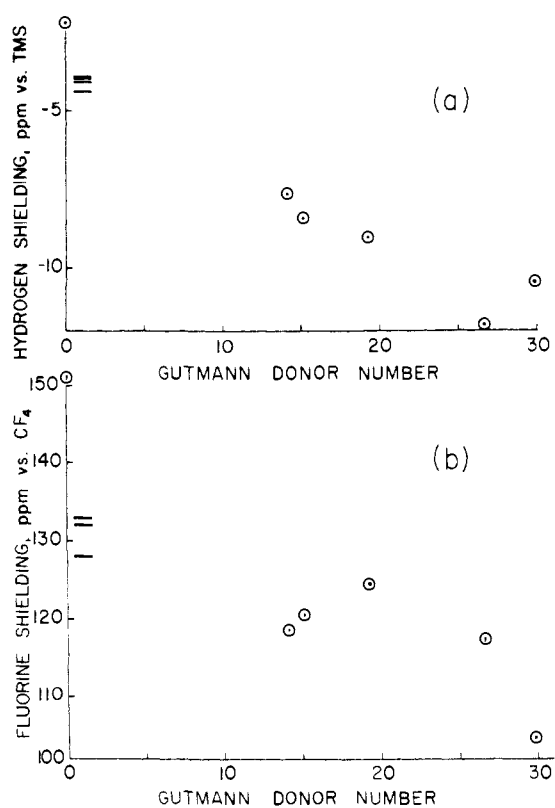

Figure 2. Correlation of hydrogen and fluorine shieldings of hydrogen fluoride in solution with the solvent Gutmann donor number. The gas phase shieldings are placed at zero donor number. The horizontal bars give the shieldings in nonbasic solvents.

to define a separate sequence, of somewhat higher shielding than the solvates, as observed before.

One would expect a correlation of coupling with infrared stretch frequency; this is shown in Figure 4. The correlation is linear in the region shown, but the least-squares line passes above the FHF$^-$ point by about 100 Hz in both figures. There is no tendency for the points in Figure 4 to define separate sequences for the anionic and molecular bases. This suggests that the coupling and stretch frequency reflect the same aspects of the H-bond perturbation and that
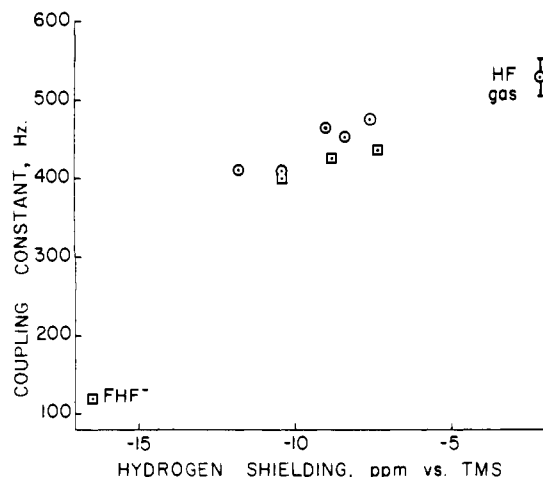
Figure 3. Correlation of the H–F coupling constant and the hydrogen shielding of hydrogen fluoride in solution (circles) and in bihalide ions (squares).

Figure 5. Correlation of the H–F coupling constant of hydrogen fluoride in solution with the solvent Gutmann donor number. The gas phase coupling is placed at zero donor number.
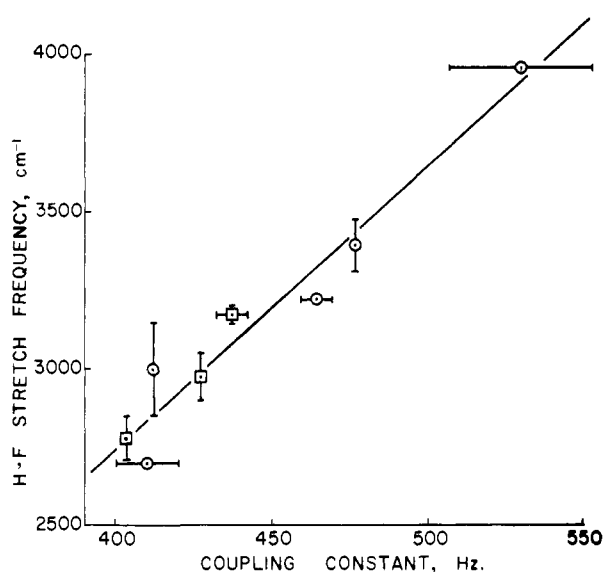

Figure 4. Correlation of the stretch vibration frequency with the H–F coupling constant of hydrogen fluoride in solution (circles) and in bihalide ions (squares). The point for bifluoride ion is omitted; it lies far outside the range of this graph.

there is no additional mechanism corresponding to the base anisotropy which affects only the hydrogen shielding.

Figure 5 demonstrates a correlation of nuclear coupling constant with the solvent donor number. The line determined by a least-squares fit to our data passes through the axis of zero donor number at $^1J_{HF}$ = 528 Hz. This is close to the observed gas phase coupling, 529 ± 23 Hz.[6] This is gratifying and enhances the concept of the donor number as a measure of solvent base strength: zero donor number corresponds to zero interaction with HF.

Nuclear Coupling in H Bonds.

Nearly a decade ago, Watts and Goldstein suggested that the internuclear coupling to hydrogen should be an excellent probe of the H bond, since it is transmitted by the electrons directly involved and should be insensitive to long range anisotropy effects.[26] The coupling constant changes observed on H bonding of $^{13}C-H$[26–28] and $^{15}N-H$[22,29] have therefore been rather disappointing. On formation of the H bond, the coupling in the hydrogen donor characteristically increases by a small amount, of the order of 1%.

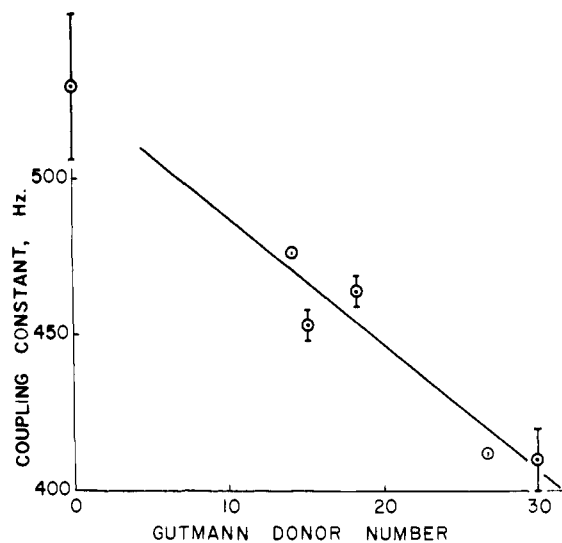In contrast, H bonding causes a very large decrease of

the H–F coupling: of the order of 20%, if we regard FHF⁻ as a special case. The coupling appears to be a reliable and sensitive indicator of the H-bond strength. We believe that we can demonstrate good reasons why this should be so for HF and not for NH and CH,

Calculations of coupling in HF appear frequently in the literature, since this is one of the few heteronuclear systems whose coupling has been measured and which is accessible to accurate *a priori* calculation. Estimates of the coupling using limited basis sets appear to give the wrong sign by analytic perturbation theory[30] or by the method of finite perturbations.[31] The sum over excited states in analytic perturbation calculations involves large terms of alternating sign and converges slowly if at all.[32] Only one large basis analytic perturbation calculation[33] and one by finite perturbations[34] have correctly reproduced the positive sign.

It is not yet clear whether computations may be relied on to converge to stable values of coupling of the correct sign. We shall not attempt to predict numerical values of the coupling. Instead, we shall examine the effect of H bonding on the molecular wavefunction with a view to picking out terms which should control the coupling. They may be expected to cause the coupling change on H bonding in a way which is independent of the nature of a particular computation. Thus we may be able to predict the sensitivity of the coupling to H-bond induced change, even though we cannot yet accurately predict the values of the coupling.

All methods of computing the coupling lead to similar mathematical forms.[31] The independent electron LCAO-MO theory of Fermi contact coupling[30] gives the formula

$$^1J_{HX} = (\text{constant}) \sum_{o,u} \frac{C_{oh}C_{uh}C_{ox}C_{ux}}{E_u - E_0} \qquad (1)$$

The sum is over all pairs of occupied (o) and unoccupied (u) orbitals. The c's are the expansion coefficients of s functions on the hydrogen (h) and the other (x) nuclei which are coupled.

Symmetric complexes, *i.e.*, FHF⁻ [35] and NHN,[36] are the only systems found so far in which nuclear spin coupling has been observed across a H bond. In both cases the observed coupling is much less than that in the reference compound, *i.e.*, HF or the amine. One can readily demonstrate

that this is to be expected.

The LCAO molecular orbitals of a reference compound HX are based on the hydrogen functions ϕ_h and the X (F or N) functions ϕ_x. Resolution of the secular determinant of the appropriate molecular Hamiltonian yields orbital expansion coefficients c_{ih} and c_{ix}, which are used in eq 1 to compute the coupling. In the symmetric complex XHX, the correct basis is the set of symmetric functions ϕ_h and $(1/\sqrt{2})(\phi_{x1} + \phi_{x2})$ and the antisymmetric functions $(1/\sqrt{2})(\phi_{x1} - \phi_{x2})$. The antisymmetric functions do not mix with the symmetric ones and thus cannot contribute to the coupling, since they lead to orbitals in which the coefficients c_{ih} are zero.

There are as many symmetric basis functions in XHX as there are functions in HX. The symmetric secular determinant of XHX will be closely related to the secular determinant of HX. To a first approximation the two matrices will have identical diagonal elements and off-diagonal elements which are related by a constant (equal to $\sqrt{2}$ if the resonance integrals in XHX are the same as those in HX). There are circumstances under which such determinants will have identical eigenvectors. One such would be the case where all basis functions connected by significant off-diagonal elements had substantially identical diagonal elements, i.e., Coulomb integrals. This is the condition which leads to a nonpolar bond and weak H-bond interaction.

If the secular determinant of HX and the symmetric one of XHX were to yield identical expansion coefficients c_{ix}, the couplings in HX and XHX will be in the ratio 2:1. This is readily demonstrated. In eq 1, one uses c_{ix} in the calculation of the HX coupling; however, in the XHX case the coefficient of ϕ_x will appear, that is, $(1/\sqrt{2})c_{ix}$. This will produce a numerator which is one-half that of the corresponding term in the free molecule. If the expansion coefficients and orbital energies are the same, the calculated coupling in XHX will thus be one-half that in HX.

Intuitively one might expect that equal expansion coefficients would appear where the H-bond interaction was relatively weak. The symmetric system involving nitrogen is one of a series of formazans[36] where the NHN interaction is imposed by the large scale geometry, rather than by an exceptionally strong H bond.

(2)
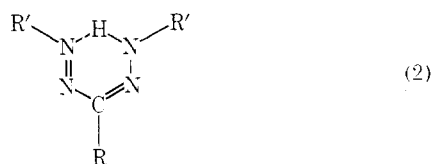
In the event, the observed coupling is 46.5 Hz, just half of the value 90 to 95 Hz typical of such N-H bonds. Our MO treatment is formally equivalent to the postulate of Mester, et al.,[36] that the N-H bond is shared equally by the two nitrogens.

The coupling in bifluoride ion is about one quarter of that in free hydrogen fluoride. It is reasonable to expect that the very strong H bond will affect the coupling. We shall now consider the effect of H bonding on the coupling in a hydrogen donor molecule or fragment XH.

Perturbed Hydrogen Donors. The coupling in a bond X-H, computed by eq 1, is determined by products of the form $c_{oh}c_{uh}c_{ox}c_{ux}$. Atomic orbitals occur in small sets of similar energy, and only the valence orbitals overlap significantly. The significant products will involve valence shell atomic orbitals from a relatively small set, particularly on hydrogen. If the orbitals are orthonormal, the squares of coefficients will be constrained to sum to a constant value. On perturbation, the coefficients will vary in a complementary

way. The variation of products of numbers whose sum is constant will be dominated by the variation of the smallest number in the product. In the case of the polar molecule HF, this will be the coefficient of the hydrogen orbital in the occupied MO.

This can be illustrated by a minimum basis calculation of the coupling in the fragment XH. We shall use the hydrogen 1s function $|h\rangle$, the X atom valence shell s function and its valence shell p function of σ symmetry. If we simplify the basis by combining the X atom orbitals to give a hybrid

$$|\sigma\rangle = (n + 1)^{-1/2}(|s\rangle + n|p\rangle)\qquad(3)$$

the two significant molecular orbitals will be the occupied bonding orbital

$$\psi_o = c_{oh}|h\rangle + c_{ox}|\sigma\rangle\qquad(4)$$

and the unoccupied antibonding orbital

$$\psi_u = c_{uh}|h\rangle + c_{ux}|\sigma\rangle\qquad(5)$$

Since these are the only MO's in which $|h\rangle$ appears, the coupling formula will have only the one term

$$^1J_{HX} = (\text{constant})\frac{c_{oh}c_{ox}c_{uh}c_{ux}}{(n + 1)(E_u - E_0)}\qquad(6)$$

Orthonormality imposes the constraints

$$c_{oh}^2 = c_{ux}^2 = (1 - c_{uh}^2) = (1 - c_{ox}^2)\qquad(7)$$

In this approximation the coupling is controlled by the ground state hydrogen 1s electron density c_{oh}^2, through the function

$$^1J_{HX} = (\text{constant})\frac{c_{oh}^2(1 - c_{oh}^2)}{(n + 1)(E_u - E_0)}\qquad(8)$$

The hydrogen coefficient c_{oh}^2 determines the polarity of the H-X bond. The bond is nonpolar if $c_{oh}^2 = 0.5$; it is pure ionic in the sense H^+X^- if $c_{oh}^2 = 0$. Figure 6 shows the way in which the coupling function $c_{oh}^2(1 - c_{oh}^2)$ varies with c_{oh}^2. It is evident that the coupling is zero in the ionic form and reaches a maximum in the nonpolar form. The slope of the graph, which represents the sensitivity of the coupling to perturbation, is zero for a nonpolar bond and increases as the bond becomes more polar.

If we accept that the primary effect of H bonding is a decrease of the hydrogen 1s density c_{oh}^2, we can make two predictions based on our simple model.

1. The nuclear spin coupling in a highly polar bond such as F-H will be relatively sensitive to H-bond perturbation, while that in a nonpolar bond such as C-H and perhaps N-H will be insensitive. The coupling change in F-H should be simply related to measures of the H-bond strength. No such prediction can be made about the coupling changes in nonpolar bonds.

2. The coupling in a polar bond such as F-H will decrease in magnitude as the strength of the H bond increases. The much smaller changes in a nonpolar bond, which may not be controlled by this mechanism, cannot be predicted; they could be of either sign.

It is clear that the large decreases in coupling on H bonding to hydrogen fluoride reported here, and the small irregular increases in coupling in C-H and N-H bonds,[22,26-29] are in accord with the predictions we have made. Although they are based only on a minimum basis computation, which we admit predicts incorrectly the sign of the coupling in the unperturbed molecule,[30] we believe that they are true in general. All terms of significance in a general expansion of the form of eq 1 should be controlled by c_{oh}^2, since c_{oh}
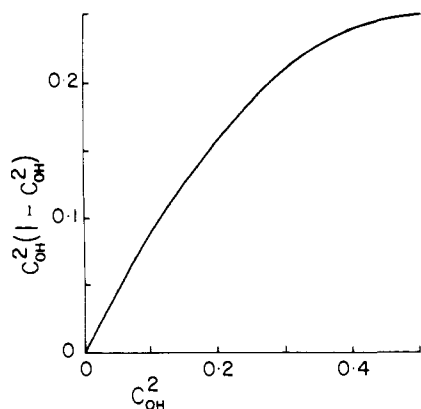
Figure 6. The coupling function vs. the hydrogen ground state population number.

must appear in all nonzero terms. Since it is small in a polar bond, its variation will dominate the change of all these terms when the bond is perturbed. As H bonding causes c_{oh}^2 to decrease, all terms in the coupling expression will become smaller in magnitude, whatever their sign. Unless there is a drastic reordering of the various states when the H bond forms, the coupling must become smaller in magnitude.

We believe that calculations which give unsatisfactory numerical predictions may nevertheless account for the effect of perturbations on the couplings. For example, an INDO calculation[37] which got wrong the sign and magnitudes of the couplings still predicted with remarkable accuracy that the couplings in HF and FHF$^-$ would be in the ratio 4.0; the observed ratio is 4.4.[6,35]

It is interesting that Figure 6 shows negative curvature; inclusion of the FHF$^-$ point suggests negative curvature in Figures 3 and 4. The hydrogen shielding and stretch frequency are both linearly related to c_{oh}^2; thus the coupling function of eq 8 correctly predicts the direction in which the FHF$^-$ point deviates from linearity.

Conclusions

Exchange of the hydrogen fluoride nuclear spins is much slower in basic aprotic solvents than it is in inert solvents or in the gas phase. It is also slow in the bihalide ions.[2] Evidently the one to one complexes of HF to basic solvent molecules or to anions are more stable than the exchange intermediates, either polymers or fluoride ions; thus formation of such strong complexes inhibits exchange processes.

There are reasonable correlations of both the hydrogen shielding and the H–F coupling with other measures of the H-bond strength, in both bihalides and solvates of hydrogen fluoride. As the base strength of the hydrogen donor increases, the H bond becomes stronger. This is accompanied by a decrease in the H–F stretch vibration frequency, a decrease in the hydrogen shielding, and a decrease in the H–F coupling.

The hydrogen deshielding appears to reflect directly the decrease in hydrogen 1s electron population on H-bond formation, though the effect of base anisotropy is perceptible. The fluorine shielding decreases when HF is taken from the gas phase into a solvent or a bihalide. This decrease is in the sense opposite to that predicted by simple MO theory for a first row atom in a hydrogen donor. It appears likely that other phenomena, such as direct overlap interaction, influence the fluorine shielding as much as or more than does H

bonding.

Hydrogen fluoride is the only hydrogen donor molecule in which H bonding produces a significant coupling change which is directly related to the H-bond strength. Simple molecular orbital arguments suggest several relationships which may be compared with experiment. The H–X coupling in a symmetric complex XHX with four bonding electrons should be no greater than one-half the coupling in the related molecule or fragment HX with two bonding electrons. Increasing polarity of a bond XH should lead to greater sensitivity of the H–X coupling to perturbation. A polar bond acting as a hydrogen donor will become more polarized in the sense H^+X^-; in such a H bond the coupling should be controlled by the hydrogen 1s population and should decrease in magnitude. All known couplings in FH, NH, and CH bonds behave in accord with these predictions.

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