then arises as to why that group is observed in BPheo c$^-$ but not in BChl c$^-$. Space-filling models indicate that in BChl c, the δ-methyl is very crowded and cannot rotate freely, whereas in BPheo c, the absence of the Mg atom imparts greater flexibility to the macrocycle thereby allowing conformations in which the δ-methyl group is unhindered. Alternatively, the significant decrease in spin density at the δ-position, predicted by the PPP but not the IEH calculations for the metallo complexes, may account for the missing resonance near 2.6 G, and the peak of the δ-methyl group may be buried under the 1-methyl group or in the peaks with smaller coupling constants centered around ν_H. (Even the IEH calculations lower the spin density at the δ-position if the conformation of BChl c is modified, see Table III.

As expected from the IEH calculations for BPheo$^-$ c and e, the ENDOR results for BPheo e$^-$ enriched in 5-ethyl resemble those for BPheo c$^-$ (Figure 7f). (We have been unable to generate stable radicals of BChl e.)

Low-temperature ENDOR data for BChl a$^-$, Chl$^-$, and Pheo a$^-$ and the results discussed above are compared in Table II. As noted for the optical spectra, the *Chlorobium* Chl anions exhibit properties similar to those of the chlorophylls. Here again, however, their ENDOR parameters differ sufficiently from those of BChl a$^-$ so as to be distinctive and allow their identification even in the presence of BChl a$^-$.

To account for the differences between Chl$^-$ and Pheo$^-$ a in vivo and in vitro, we have previously suggested that the reduced acceptors in PS I and II may be hydrogen bonded at the 9-keto group by protein residues[2f,8] The predicted effects of such interactions on the spin density at various positions in the molecules considered here appear to be small enough so as not to cause major changes in the coupling constants,[44] and the distinction between the *Chlorobium* Chls$^-$ and BChl a$^-$ should still be maintained. The consequence of the BPheo c dimerization suggested by Olson[9b] can also be predicted: if the unpaired electron is equally shared between two molecules on the ESR time scale, then the ENDOR coupling constants would be halved. Again, some of these (the 1- and δ-methyl groups, in particular) would still be clearly distinct from those of BChl a$^-$.

In summary, the in vitro redox data for the *Chlorobium* chlorophylls suggest that they are likely candidates as early electron acceptors in green and brown photosynthetic bacteria. To help identify them in vivo and thereby test the electron transport sequence suggested, we have provided here the optical and paramagnetic spectral signatures of the putative acceptors which would clearly differentiate them from other components in the reaction centers. This "primary" transport chain would include components derived from purple bacteria (P840 and BChl a) and from green plants (Chl derivatives and ferredoxins). Thus, the constituents of the reaction center would mirror those found in the antenna system,[9a,10,13] which also contain BChl a and Chl derivatives and therefore further reinforce the hypothesis that green (and brown) bacteria straddle purple bacteria and green plants on an evolutionary scale.[12,13,45]

Acknowledgment. We thank Dr. J. Olson for valuable discussions and the authors of ref 11, 14, 33, and 46 for communicating their results prior to publication. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy (Contract No. DE-AC02-76CH00016), at Brookhaven National Laboratory and by the National Science Foundation (Grant No. CHE-81-20891) at the University of California.

Registry No. BChl c anion, 85761-74-6; Bchl e anion, 85761-76-8; BPheo c anion, 85761-77-9; BPheo e anion, 85761-79-1; BPheo d anion, 85761-78-0; BChl d anion, 85761-75-7; BChl a anion, 36643-17-1.

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(44) IEH calculations were compared for BChl d$^-$, BChl d$^-$ with the 9-keto group of ring V hydrogen bonded to a hydroxyl function, and BChl d$^-$ with the hydroxy group of ring I bonded to a carbonyl function (structural data taken from the X-ray results for the 4,5-diethyl BPheo d dimer).[23] Bonding at the 9-keto position had minimal effect on all positions of interest (maximum changes $\leq \sim 5\%$, for example C5 increased from 0.092 to 0.097 while C1 remained unchanged). Bonding at the hydroxyl group resulted in maximum changes of $\sim 10\%$ with C1 intact and C5 decreasing from 0.092 to 0.085. Similarly small effects ($\leq \sim 10\%$) were calculated for BChl e$^-$ (formyl group in plane) bonded to hydroxyl functions at the formyl or 9-keto groups.

(45) The reaction center of the green filamentous bacterium *Chloroflexus aurantiacus* appears to be more akin to purple bacteria and contains BPheo a[46] and quinones.[10]

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Spectroscopic Evidence for Proton Transfer within the Bimolecular Complex HI–NH_3 Trapped in Cryogenic Matrices

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Abstract: The infrared spectra for the 1:1 complexes of HI and either NH_3 or $N(CH_3)_3$ (TMA) isolated in four different matrices (Ar, O_2, N_2, C_2H_4) have been obtained at 10 K. These complexes are mainly characterized by the stretching vibration (ν_s) of the proton along the I–N axis, the frequency of which strongly varies with the nature of the matrix: for HI–NH_3, 1255 (Ar), 1310 (O_2), 1847–1967 (N_2), and 2315 cm^{-1} (C_2H_4); for HI–TMA, 1889 (Ar), 1880–1920 (O_2), 2100–2132 (N_2), and 2315 cm^{-1} (C_2H_4). A comparison with the known spectra of HX–NH_3 (X = F, Cl, Br) and HX–TMA (X = Cl, Br) (1:1) complexes shows that the hydrogen bond is stronger with HI than with other hydro acids, in which the hydrogen atom of HI has tipped toward nitrogen. Thermodynamic arguments about the enthalpy of reaction of proton transfer within a NH_3/HX pair support this conclusion. The matrix frequency shift shows that the rate of proton transfer is strongly matrix dependent and is believed to be complete in an ethylene matrix, for which the ν_s frequencies are the same for both HI–NH_3 and HI–TMA complexes. Such a sensitivity of the proton potential curve to the surroundings had been predicted in recent theories of solvent effects.

The problem of proton transfer within bimolecular hydrogen-bonded complexes has prompted several theoretical (ref 1 and others cited theirein) and experimental studies based on the matrix isolation technique.[2-7] The theoretical approaches deal on the

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one hand with the electronic properties of isolated complexes, such as the HCl–NH_3 system,[8] and on the other hand with the effects of the environment on such complexes via the introduction of a reaction field, derived from both electrostatic and induction interactions between the complex and its surroundings.[9-11] The corresponding experimental work using the matrix isolation technique with Ar and N_2 as diluents has been performed. This allows the vibrational spectra of the complexes to be used to derive probabilities of proton transfer. For practical convenience the bases (B) are either ammonia or volatile organic amines and the acids (AH) are either hydrogen halides or carboxylic species. In no case does complete transfer occur. Only proton sharing between the two proton acceptor sites B and X^- can be identified through the frequency of the stretching mode of the proton along the B···A axis, which is always found below 2000 cm^{-1}. This result corresponds to a remarkably weak force constant for such a mode but is typical of the delocalization of the proton. These results, which are in reasonable agreement with theoretical predictions, have been rationalized by Pimentel,[3] who introduced the vibrational correlation diagram which allows an estimate, according to the proton affinity difference between the two bases B and A^-, of the state of delocalization of the central proton. However, in no case has the second theoretical factor, namely, the effect of the environment on the proton transfer, drawn the attention of experimenters. This is probably because of the limitation in the choice of molecular matrices and their lack of transparency in the infrared.

In the course of extensive hydrogen-bonding studies in matrices, we were led to use as proton donor iodohydric acid, one of the strongest acids, the proton affinity of I^- being 308 kcal mol^{-1} (318, 324, and 366 kcal mol^{-1} for Br^-, Cl^-, and F^-, respectively[1]). It is therefore reasonable to ask whether this acid is not the best candidate for observing the proton-transfer phenomenon. The aim of this paper is to describe the results obtained in HI–NH_3 and HI–$N(CH_3)_3$ (hereafter refered to as TMA) using double-doping experiments of several atomic or molecular matrices, at mole ratios between 600 and 200. This work completes the previous studies by Ault and Pimentel,[2,3] Barnes,[4,6] and Andrews[12] in which HCl, HBr, and HF interacted with the same bases. It allows deeper insight into the acidic properties within the hydroacid series and emphasizes the role of the surroundings on the proton-transfer process.

The presentation of this paper is divided in three parts. The first is devoted to the description of the spectral properties of three acid–basic systems: (i) the spectra of HBr(D)–NH_3–N_2 mixtures are compared in order to check our experimental system to those described by Ault and Pimentel;[3] (ii) spectral studies of HI–NH_3 and HI–TMA trapped in argon, nitrogen, oxygen, and ethylene. The second part involves the analysis of these spectra, the identification of complexes for each system, and discussion of their structure. The third part presents a comparison of the acidic properties of HX molecules with X = F, Cl, Br, and I using both spectral and thermodynamical data.

Experimental Section

The apparatus and techniques were identical with those used earlier. The two reactants were deposited simultaneously from separate jets onto a CsI window maintained at 17 K, at 8 mmol/h for 2 h. The infrared spectra were recorded at 10 K on a Perkin-Elmer Model 225 or a Perkin-Elmer Model 580 infrared spectrometer. The frequency accuracy was ±0.5 cm^{-1} for narrow lines and the spectral slit width was chosen between 1 and 2 cm^{-1}.

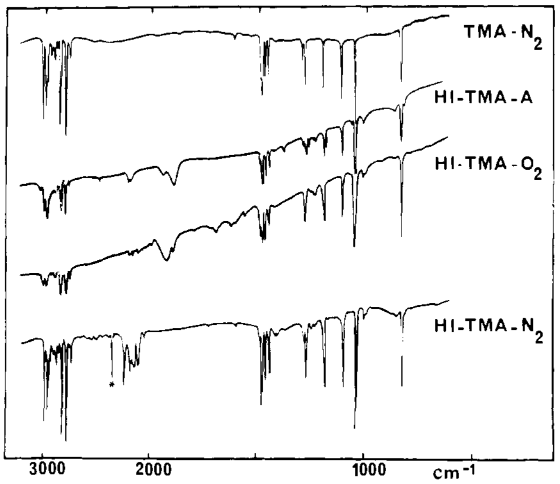

Figure 1. Infrared spectra of HI and TMA isolated in various matrices at 17 K: HI–TMA–matrix = 1:1:200 (the asterisk is the CO_2 line).

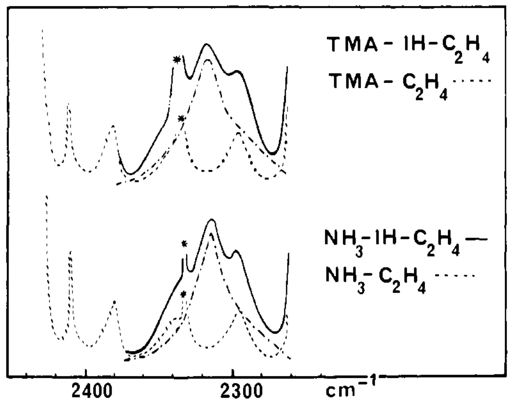

Figure 2. Infrared spectra of codeposited HI and TMA (top) and HI and NH_3 (bottom) with HI–base–ethylene = 1:1:200 in the spectral region 2400–2200 cm^{-1} (the asterisk is the CO_2 line): ···, absorption due to IH–base complex.

HI, HBr, NH_3, and TMA, and C_2H_4 (Matheson) and O_2 (Air Liquide) were purified by condensation with liquid nitrogen to remove volatile impurities followed by one thawing–recondensing cycle.

Results

The spectra of NH_3 and TMA isolated in argon or nitrogen have already been reported.[13-15] Those of HI and DI, which have not been described previously, were carefully recorded at various mole ratios in order to identify the bands of polymeric species.

HBr/DBr–NH_3 System. In a nitrogen matrix the four bands described by Ault et al.[3] at 301, 1220, 1393, and 1752 cm^{-1} are present in our spectra with the same relative intensities. Some other bands, which have not been mentioned by these authors, are also identified: one at 3402 cm^{-1}, with roughly the same optical density as that at 1393 cm^{-1}, but with much narrower bandwidth (8 cm^{-1} fwhm against 70 cm^{-1}); very weak and broad features at 1965, 1840, and 790 cm^{-1}. At last, as shown in Figure 3 of ref 3, the asymmetric and broad band at 1393 cm^{-1} displays a high-frequency narrow satellite at 1430 cm^{-1}. On annealing, intensities of the bands at 790, 1430, and 1752 cm^{-1} grow significantly as compared to the others. In the HBr/DBr experiments

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Table I. Frequency and Relative Integrated Intensity of IR Bands due to HI–TMA Complexes Embedded in Various Matrices

Ar		N_2		O_2	
ν, cm^{-1}	*I*	ν, cm^{-1}	*I*	ν(cm^{-1})	*I*
1983 sh	1	~2165 ep	1	1920 br	1
1889		2132		1882	
1881		2099			
1480	0.04	1482	0.03	1480 sh	
a		1395	0.05	*a*	
		1364.5			
1224	0.04	1240	0.02	1236	0.03
1219		1229.5		1225	
~1004	0.04	999	0.03	1004	0.04
1000		995		1001	
				996 sh	

[a] Masked by absorptions due to $(CH_3)_3NH^+I^-$ crystal.

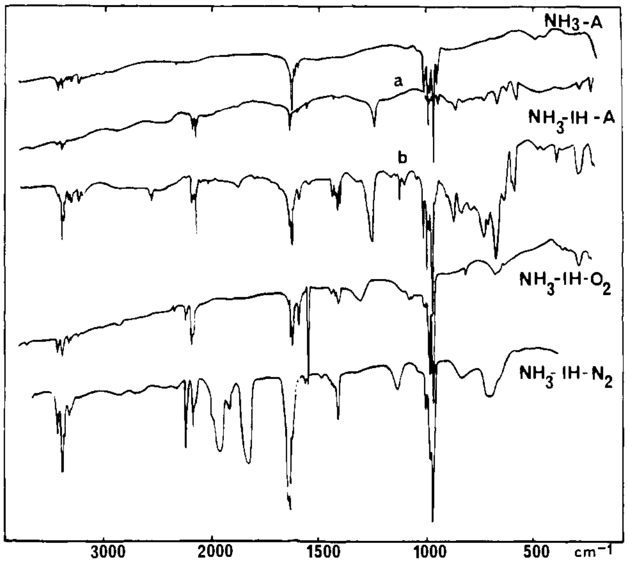

Figure 3. Infrared spectra of HI and NH_3 isolated in various matrices at 17 K: HI–NH_3–matrix = 1:1:200 except case a in which HI–NH_3–A = 1:1:600.

with H/D ratio ca. 0.8, a broad feature at 1125 cm^{-1} is observed in addition to the bands previously described.

HI–TMA System. Figure 1 shows the infrared spectra obtained when HI and TMA are codeposited with various atomic (Ar) and molecular (O_2, N_2) matrices at mole ratios of 1:200 in each dopant. In each case there appears a rather broad and intense band in the range 1800–2200 cm^{-1}. This is by far the most important new feature and is not observed in the spectra of the parent molecules isolated at the same concentration. In argon, this band displays a three component pattern around 1900 cm^{-1}, the high-frequency component being weakly temperature dependent. In nitrogen its structure, spread over about 70 cm^{-1} around 2150 cm^{-1}, is difficult to analyze in detail due to the strong overlap with bands due to HI aggregates. In an ethylene matrix, in which the monomeric HI band is shifted to about 2170 cm^{-1},[16] a new absorption due to the complex is observed at 2315 cm^{-1} (Figure 2). The other bands of the complex are badly overlapped by the ethylene absorption bands.

Beside this main absorption, other much weaker features are observed at about 1480, 1370, 1230, and 1000 cm^{-1}. The frequencies of the first and of the last line are seen to be matrix independent within a few wavenumbers while those of the two others, which display a multiple component structure, are lower in argon than in nitrogen (Table I).

HI–NH₃ System. Due to the important spectral changes induced by the nature of the matrix, we shall comment successively the results obtained in Ar, N_2, O_2, and C_2H_4.

Table II. Frequency (cm^{-1}) and Relative Integrated Intensity of IR Bands due to the HI–NH_3 1:1 Complex Embedded in Various Matrices

Ar		N_2		O_2		
ν, cm^{-1}	*I*	ν, cm^{-1}	*I*	ν, cm^{-1}	*I*	assign
		1967	1			
1256	1	1925		1310	1	ν_s
		1847				
3401	0.13	3391	0.20	3397	0.16	$\nu_3(NH_3)$
1623	0.03	1638	0.10[a]			$\nu_4(NH_3)$
1401	0.05	1411	0.08	1421	0.10	$\nu_2(NH_3)$
875	0.22					
590	0.30	~1420 sh	0.05	~1100	*a*	ν_b
301	0.13					

[a] Band overlapping makes measurements inaccurate.

(a) Argon Matrix. Figure 3 shows the spectra of matrix mixtures of HI–NH_3–Ar = 1:1:200 (b) and 1:1:600 (a). At high dilution (spectrum b) several prominent bands are not present in the separate matrix spectra of NH_3 and HI; these bands include a main absorption at 1256 cm^{-1} with full width at half-maximum (fwhm) = 17 cm^{-1} and weaker lines at 3401, 3383, 1623, 1595, 1427, 1416, 1401, 910, 875, 840, 795, 735, 680, 640, 605, 590, and 300 cm^{-1}. At lower dilution (spectrum a), the bands that do not change relative intensity with respect to the 1256-cm^{-1} band are presented in Table II. The other bands show strong relative increases.

(b) Nitrogen Matrix. Extensive experiments were carried out on several isotopic species and will be the object of a separate communication including a force field calculation of the one to one complex. We shall restrict ourselves here to describing the spectra obtained with hydrogenated species which are dominated by the presence of two strong bands in the range 1800–2000 cm^{-1}; the relative intensities of which is constant value independent of the experimental conditions. Weaker peaks also appear that are not present in the spectra of the isolated parent compounds: four of them, at 3391, 1638, 1420, 1411 cm^{-1}, do not change relative intensity with respect to the 1847–1967-cm^{-1} doublet when the concentrations of NH_3 and HI are varied. Others, at 1566, 1435, 1330, 830, and 710 cm^{-1}, are found to increase relative to the invariant bands upon annealing and also in presence of an excess of ammonia with respect to HI. Among the variable bands, those at 830 and 710 cm^{-1} are by far the strongest.

(c) Oxygen Matrix. Preliminary experiments with NH_3–O_2 indicated that there is a dramatic dependence of the NH_3 spectrum on temperature in the range 10–20 K. This is probably related to the possibility of O_2 molecular reorientation (Note: there exists a phase transition for the pure O_2 crystal at 22.8 K). This sensitivity makes an accurate comparison between NH_3–O_2 and HI–NH_3–O_2 spectra in the NH_3 stretching and bending regions difficult. The most easily identifiable differences are the appearance in the spectra of HI–NH_3–O_2 mixtures of two broad bands around 1310 and 675 cm^{-1} and of some narrow features around 1400 cm^{-1}. The band at 675 cm^{-1} is seen to increase, relative to that at 1310 cm^{-1}, on annealing and on increasing the NH_3 concentration in the matrix.

(d) Ethylene Matrix. The lack of transparency of crystalline ethylene does not allow the spectrum of the HI–NH_3 complexes to be observed in detail. However two bands that are not in the parent spectra appear: one at 2315 cm^{-1}, with the same characteristics as the band observed for the HI–TMA complex (Figure 2), and the other at 3385 cm^{-1}, 5 times less intense than the band at 2315 cm^{-1}.

Spectral Analysis

A. Vibrational Properties of the 1:1 Complexes. In the case of HI–TMA mixtures, the strongest absorptions due to the 1:1 complex, which are observed between 1800 and 2300 cm^{-1} depending on the matrix, have to be assigned to the proton motion along the I···N axis (hereafter referred to as ν_s). This assignment, which completely agrees with previous results on HCl– and

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(16) A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, *Trans. Faraday Soc.*, **65**, 3159 (1969).

HBr–TMA complexes, must be complemented by two remarks: (i) in a nitrogen matrix the band is split into three components spread over a quite large frequency range (70 cm^{-1}), suggesting multiple-site trappings for the complex; (ii) in an ethylene matrix the frequency is higher than that of the isolated proton donor, a unique situation which had not been encountered previously in matrix studies and which demonstrated that under favorable conditions the proton is no longer tied to the iodine atom.

The assignment of the proton motion perpendicular to the N–I axis (ν_b mode) to one of the weak peaks listed in Table I is difficult because there does not appear to be a clear correlation for this mode within the hydroacid series. The trend toward higher frequencies observed by Ault et al.[2,3] from HCl–TMA to HBr–TMA (1370 and 1600 cm^{-1}, respectively) is no longer valid for HI–TMA since the band of highest frequency due to the complex is located at 1480 cm^{-1}, excluding the ν_s band. Among the features listed in Table I are those at about 1230 and 1000 cm^{-1} which are close to absorptions assigned by Ault to perturbed vibrations of the parent amine. Thus the ν_b mode has probably to be assigned to one of the two peaks around 1480 or 1380 cm^{-1}.

For the HI–NH$_3$ system dilution and annealing experiments allow the axial vibration of the proton to be assigned in the 1:1 complex at 1256, 1310, 1847–1967, and 2315 cm^{-1}, in argon, oxygen, nitrogen, and ethylene, respectively. Two important conclusions can be drawn: (i) there is a large matrix dependence of the proton delocalization, (ii) in the case of the nitrogen matrix there is an important band splitting, larger than that observed for the HI–TMA system trapped in nitrogen. These observations might throw a new light on the controversy surrounding the ν_s frequency of the HCl–NH$_3$ system: it was located at 700 cm^{-1} in a nitrogen matrix by Ault[2] and assigned by Barnes[6] to an absorption at 1290 cm^{-1} in argon. This difference is compatible with item i, in spite of the inversion in the relative frequencies (lower frequency for HCl and higher frequency for HI in nitrogen matrices) that will be discussed later. Item ii weakens Barnes' argument according to which the splitting observed by Ault for the mode at 700 cm^{-1} is due to degeneracy lifting of an E mode.

The other vibrations of the 1:1 HI–NH$_3$ complex have been identified. The ν_3 (degenerate) and ν_1 (symmetrical) NH$_3$ stretching vibrations are respectively measured at about 3400 and 3300 cm^{-1}, the position of the second one being dubious because of its very weak intensity. Such an intensity decrease of ν_1 relative to ν_3 has already been observed in experiments on pure NH$_3$ at liquid-like densities in the hyper critical region[17] and interpreted in terms of variation molecular geometry, i.e., as a decrease of the pyramidal height of ammonia (tendency towards planarity). This explanation is the only one which we can propose for the quasi-disappearance of ν_1, the bandwidth of which is expected to be narrow enough to prevent strong overlap with the bands of NH$_3$ aggregates. On the other hand, the overall intensity of the ν_1 and ν_3 modes does not exceed 20% of that of the ν_s band, leading us to conclude that there is a very large dipole moment derivative for the shared proton (about four times that of one N–H oscillator of ammonia). The NH$_3$ bending modes are located around 1620 (E mode) and 1400 cm^{-1} (A$_1$); these frequencies agree with previous results according to which the A$_1$ mode is the only one to strongly depend on molecular interactions.[18] The ν_b mode, characterizing the motion of the central proton perpendicular to the N–I axis, is seen to be strongly matrix dependent. It is assigned in argon to one of the two bands at 875–590 cm^{-1}; the large splitting between them excludes a degeneracy lifting of this mode, and we therefore suggest assigning the band at 590 cm^{-1} to this mode and that at 875 cm^{-1}, in spite of its quite strong intensity, to the combination 590 + 300 cm^{-1}. In nitrogen there is no absorption below 1300 cm^{-1} which can be assigned to the 1:1 complex; consequently we suggest ν_b is located around 1400 cm^{-1}, in the neighborhood of the symmetric NH$_3$ bending mode; and finally, in oxygen a broad band around 1100 cm^{-1} could be assigned partly to ν_b and partly to ν_2 bending modes of ammonia aggregates.

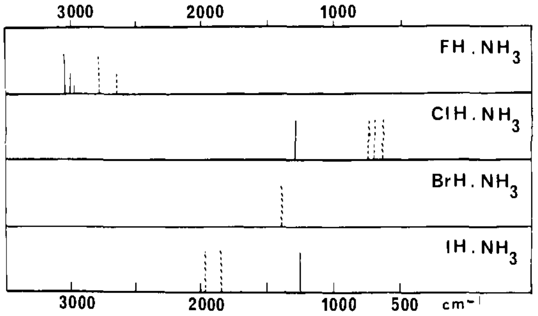

Figure 4. Halogen dependence of the ν_s frequency for XH–NH$_3$ (1:1) complexes trapped in argon (full line) and nitrogen (dotted line).

B. Spectra and Structure of Larger Aggregates. The presence of larger complexes than the one to one previously described has been shown by very typical bands below 1000 cm^{-1}: 680–737 cm^{-1} in Ar, 675 in O$_2$, and 670 and 830 cm^{-1} in N$_2$. They are by far the strongest absorptions associated with these new complexes and consequently have to be assigned to axial motion of a delocalized proton equally shared between two acceptor sites. Such frequencies, only weakly matrix dependent, suggest the formation of centrosymmetric ions within trimolecular aggregates with two possible ionic structures; either a centrosymmetric cation (H$_3$N–H–NH$_3$)$^+$I$^-$ or a centrosymmetric anion (IHI)$^-$NH$_4^+$. This last complex, which has already been studied by Ault[20] in an argon matrix with alkali metal as counterion, is characterized by a ν_3 frequency varying from 603 (Na$^+$) to 673 cm^{-1} (Cs$^+$), i.e., lying in the same spectral range as the bands under study. Two observations are in favor of the existence of the cationic species: (i) in a nitrogen matrix, a relative increase of these bands is found proportional to NH$_3$ concentration; (ii) the anionic species IHI$^-$ is probably asymmetrical in presence of the ammonium ion, as the FHF$^-$ anion observed by Andrews[12] from experiments with ammonium bifluoride.

Discussion

A. Spectroscopic Approach. Coming after several studies of the interaction between hydroacids HF, HCl, and HBr and ammonia or TMA, this work provides a new contribution to the study of proton transfer within an acid–base bimolecular system surrounded by a more or less inert medium, which, in the case of molecular matrices, submits this pair to strong anisotropic constraints.

Consider first the role of the nature of the acid HX interacting with a given base in the proton-transfer process, the pair being trapped in a given crystal. The state of transfer is characterized by the frequency of ν_s which has been shown to be the mode the most sensitive to the proton delocalization and which is generally assigned without ambiguity on account of its strong intensity. Figure 4 gathers the position and structure of ν_s for the various HX–NH$_3$ pairs trapped in Ar and N$_2$. The parallel evolution of the frequencies in both cases is easily understood in terms of increasing acidity from HF to HI. In the HF case the molecule is not broken but undergoes a medium strength perturbation. With HCl the molecule looses its individuality, as theoretically predicted by Clementi;[8] the frequency decrease from Ar to N$_2$ may be understood as arising from a more delocalized proton on the nitrogen, i.e., accidental perfect sharing between the two proton acceptors Cl$^-$ and NH$_3$, as observed for instance in dihalide ions.[19,20] With HBr, and to a larger extent with HI, the proton has been tipped toward the nitrogen atom of the base, which means that the minimum of the potential energy function is moved nearer to this atom. The replacement of NH$_3$ by a stronger base such

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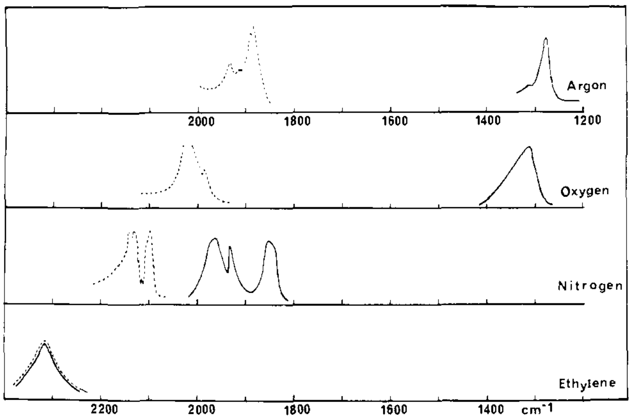

Figure 5. Behavior of the ν_s band of HI-NH$_3$ (full line) and HI-TMA (dotted line) (1:1) complexes as a function of the matrix.

as TMA increases the proton-transfer rate, as previously shown by Pimentel's group, and the outstanding question is whether complete proton transfer may occur within a bimolecular complex, giving rise to an ion pair, $X^{-+}HB$. A positive answer seems to be suggested by the matrix effects on the ν_s frequency shown in Figure 5. This probably constitutes the most important result of the experiments described in this paper. It should be noted that in this figure, as expected from theoretical predictions relating to the effect of a reaction field on a proton-transfer process,[9-11] the more perturbing the matrix[21] is, the more important is the transfer. It appears then that a common limit (2315 cm^{-1}) is reached in the most perturbing material, ethylene, by both HI–NH$_3$ and HI–TMA systems. This limit, we believe, is characteristic of the stretching vibration ν(NH) within an ion pair $R_3NH^+\cdots I^-$ in spite of a much lower value than in the crystal phase (2740 cm^{-1} for (CH$_3$)$_3$NH I). This is probably because of a shorter interionic distance linked to a more specific interaction between the two ions. A quantitative discussion on the role of the matrix in the proton-transfer process seems to be impossible without a high degree of sophistication in the calculations which have to take into account the anisotropic part of the matrix-complex interaction potential. An estimation of this contribution involves a knowledge of the equilibrium configuration of the complex with respect to the host lattice—a huge problem for molecular matrices, which has been approached in one case only, that of HCl trapped in nitrogen.[22,23] A very crude discussion on the nature of the matrix effects may however be founded on an estimate of the preponderant contributions to the potential. The complex is known to have a large dipole moment, of the order of 4 D, so that anisotropic interactions are of electrostatic (dipole–quadrupole) + induction types in molecular matrices and only of induction type in argon. Since the mean polarizabilities are nearly the same for Ar, O$_2$, and N$_2$, it seems reasonable to suggest that the electrostatic contribution is responsible of the ν_s frequency increase from Ar to O$_2$ (small quadrupole) and especially to N$_2$ (large quadrupole). In the same way the ν_s frequency increase from N$_2$ to C$_2$H$_4$, both of which have same absolute value of quadrupole, may be understood as arising from the larger value of the mean polarizability of ethylene. In other words, the g factor introduced by Tapia to simulate the reaction field acting on the complex—but which has not been explicitely formulated–cannot be taken as a simple numerical coefficient but as a tensor of rank two. The vibrational response of the complex appears to be an extraordinary sensitive probe to the crystalline environment as proved by large site effects (of the order of 100 cm^{-1}) observed in some cases of molecular matrices.

Table III. Variations of Ionic Dissociation of Alkali Halides, $\Delta D_i(X \rightarrow X')$, and of Enthalpy of Reaction 1, $\Delta(\Delta H_{PT})$, in the Halide Series ($\Delta D_i(X \rightarrow X') = D_i(X^-M^+) - D_i(X'^-M^+)$)[a]

	$F^- \rightarrow Cl^-$	$\rightarrow Br^-$	$\rightarrow I^-$ (1)
Na⁺	21.2	4.2	7.0
K⁺	21.0	3.8	7.1
Rb⁺	20.1	3.7	6.7
Cs⁺	18.1	3.1	7.1
mean value	20.1	3.7	7.0
$\Delta(\Delta H_{PT})$	−22.0	−2.3	−3.0

[a] All data in kcal mol^{-1}.

Table IV. Variation of the Enthalpy of Reaction 1 in the Hydro Acid Series When $D_i(XNH_4)$ Is Identified to $D_i(XRb)$[a]

X	PA(X⁻)	D_i(XRb)	ΔH_{PT}
F	−366	129	+24
Cl	−324	109	+2
Br	−318	105	0
I	−308	98	−3

[a] PA(NH$_3$) = −213. All data in kcal mol^{-1}.

B. Thermodynamic Considerations. The enthalpy variation for the reaction of proton transfer within an AH/B pair can be expressed as a function of the proton affinities (PA) of the bases A$^-$ and B and of the dissociation energy D_i of the (A^{-+}HB) ion pair according to

$$AH \rightarrow A^- + H^+ - PA(A^-)$$

$$B + H^+ \rightarrow BH^+ + PA(B)$$

$$\underline{A^- + BH^+ \rightarrow A^{-+}HB - D_i(A^{-+}HB)}$$

$$AH + B \rightarrow A^{-+}HB + \Delta H_{PT}$$

with $\Delta H_{PT} = PA(B) - PA(A^-) - D_i(A^{-+}HB)$. While PA's of many organic and inorganic bases are accurately known from ion cyclotron resonance spectrometry data, D_i's are generally unknown. Ault and Pimentel therefore suggested to empirically correlate the spectral data characterizing the state of proton delocalization between the two acceptor sites to the normalized proton affinity difference between the two bases, $\Delta = PA(A^-) - PA(B)/PA(B) + PA(A^-)$. For the case we are concerned with namely the ΔH_{PT} values within the hydroacid/ammonia series, the D_i's of the ion pair $X^-NH_4^+$ may be approximated by considering the ammonium cation as a pseudo alkali ion, the ionic dissociation of which is known from spectroscopic data.[24] Two approaches are then possible. (i) The change in D_i with the halogen is nearly independent of the choice of alkali cation. An evaluation of the change in ΔH_{PT} from one halide to the other is possible, vis., Table III. (ii) If it is assumed that NH$_4^+$ and Rb$^+$ are identical because the closeness between the crystal properties of materials involving these two cations, the knowledge of D_i for RbX molecules gives access to the values of ΔH_{PT} in Table IV.

The first approach is less restrictive and clearly shows the trend toward proton transfer from HF to HI, with a large energetic gap between F and Cl, as evidenced by the analysis of the spectroscopic data. The second approach tends to support the possibility of proton transfer within the HI/NH$_3$ pair since the ΔH_{PT} of reaction is negative (the entropy contribution being disregarded at the low temperature employed).

These thermodynamic considerations, which do not take into account the matrix effects, are comparable to Ault and Pimentel's analysis.[3] They correlated the proton delocalization directly with ΔH_{PT} rather than with the parameter Δ, which has a rather peculiar value in case of proton sharing (−0.23). On the other

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(21) The perturbing power of a given matrix may be defined on vibrational grounds by the frequency shift experienced by an isolated dopent embedded in this matrix. For hydroacids this red shift increases in the order Ar < O$_2$ < N$_2$ < C$_2$H$_4$.

(22) G. Girardet, D. Maillard, A. Schriver, and J. P. Perchard, *J. Chem. Phys.*, **70**, 1511 (1979).

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hand, the vibrational correlation diagram proposed by these authors, which is significant for weak to medium strength hydrogen bonding, becomes meaningless at the proton sharing point beyond which the system has to be described rather as an BH^+ oscillator perturbed by an anion A^- than as a AH vibrator. This statement is clearly proved in the $HI-NH_3-C_2H_4$ and $HI-N(CH_3)_3-C_2H_4$ cases.

Registry No. HI, 10034-85-2; NH_3, 7664-41-7; $N(CH_3)_3$, 75-50-3; Ar, 7440-37-1; O_2, 7782-44-7; N_2, 7727-37-9; C_2H_4, 74-85-1.

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^{13}C NMR of Arylgermanes and Arylgermyl Anions. Main-Group Elements as Anionic π-Donor Substituents. 2[1]

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Abstract: ^{13}C NMR spectra of the compounds $(C_6H_5)_nGeH_{4-n}$ and $(C_6H_5)_nGeH_{3-n}Na$ ($n = 1, 2, 3$) as well as $(p\text{-}CH_3C_6H_4)_3GeM$ ($M = H, Na$) have been recorded and assigned. Comparison of the chemical shifts with those of analogous group 5B compounds demonstrates that the extent of delocalization of the negative charge of the germyl anions into the aromatic rings is significantly less than that found in the anions of phenyl-substituted phosphines and arsines. The distribution of π electrons in monosubstituted benzenes whose substituents are anionic centers appears to be the result of the balance between mesomeric effects and a polarization dependent upon the degree to which the negative charge is localized on the substituent atom. The magnitudes of these effects depend somewhat on the extent and nature of solute–solvent interaction, ion pairing, and association in the solutions of these salts which in turn are a function of the polarity of the solvent.

It has been demonstrated[2] that, in the absence of significant neighbour anisotropy effects, carbon-13 chemical shifts of sp^2-hybridized carbon atoms in planar conjugated systems are proportional to the π-electron densities. The theoretical rational for such observations has been presented by Karplus and Pople.[3] In the case of monosubstituted benzenes it is apparent that only the para and perhaps the meta carbon atoms are sufficiently distant from the substituent so that such a proportionality may be generally valid.[4] Data and arguments have been presented[5] which indicate that the ^{13}C chemical shift of the para carbon atom in monosubstituted benzenes is linearly related to the total π-electron density at that position. It was also suggested that the difference between para carbon chemical shift and that of the meta carbon is linearly related to the π-electron density at the para carbon atom due to resonance with the substituent on the ring. The validity of this latter conclusion may be somewhat difficult to establish unambiguously. However we note that monosubstituted benzenes, with positively charged substituents, appear to give rise to the largest shifts to low-field strength for a meta carbon resonance.[4] Consistent with this it is also observed that monosubstituted benzenes possessing negatively charged substituents, such as those considered in this paper, are among the very few compounds which display a significant shift of the meta carbon resonance to higher field strength from that of benzene. This suggests that the chemical shift of the meta carbon resonance is predominantly influenced by electrostatic field effects which undoubtedly affect the para carbon in an analogous way. Calculations[6] show that energetically the inductive effects of meta and para substituents are of comparable magnitude. It seems, therefore, that the simple difference $(\delta_p - \delta_m)_{^{13}C}$ may well be the best indicator of the degree of resonance delocalization of charge from the substituent into the ring of a monosubstituted benzene.

Using these arguments, it has been show[1] that phenyl-substituted phosphines and arsines display little, if any, resonance between the nonbonded pair of electrons on the group 5B atom and the benzene ring, whereas the corresponding anions (e.g., $C_6H_5PH^-$) exhibit considerable resonance. This resonance in the anions is undoubtedly the main reason that phenyl substitution of phosphine or arsine increases the acidity of the remaining protons.[7] It has been observed, however, that phenyl substitution of germane decreases the acidity of the remaining protons.[8] This difference in the behavior of germanes, compared to that of arsines, has been rationalized by Jolly.[9] His argument is that the single nonbonding pair of electrons in, for example, $C_6H_5GeH_2^-$ would have predominantly s-orbital character and thus could undergo little delocalization into the benzene ring. On the other hand, $C_6H_5AsH^-$ has two nonbonded electron pairs which would have appreciable p-orbital character and therefore some delocalization could occur.

It would be expected that if indeed the monoanions of phenyl-substituted germanes exhibit little or no conjugation between the nonbonded electron pair on germanium and the phenyl rings, then, in the ^{13}C NMR spectra of these anions, the para carbon resonances would not be greatly shifted to higher field strength than the meta carbon resonances. We now present ^{13}C NMR data for a series of aryl-substituted germanes and their monosodium salts which demonstrate that mesomeric effects in these anions are considerably less than in the analogous arsine and phosphine anions.[1]

Olah and Hunadi[10] have reported the ^{13}C NMR parameters for several tertiary phenyl-substituted silyl anions and have concluded, on the basis of the smaller shifts to higher field strength of the para carbon resonances in these anions compared to those of analogous carbanions, that conjugation between the phenyl ring and substituent is much reduced in the silyl anions. Their results indicate to us that primary and secondary phenysilyl anions would display much less conjugation between phenyl ring and substituent

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