Translated from *Uspekhi Khimii* **59** 229–257 (1990) U.D.C. 541.121;541:571

Present ideas on the influence of the medium on acid–base equilibria. Hydrogen bonds in the gas phase and in solution

L M Epshtein, A V Iogansen
Nesmeyanov Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow
State Scientific Research and Design Institute for the Nitrogen Industry, Moscow

ABSTRACT. Data on acid–base equilibria in different media and in the gas phase have been analysed. Methods for determining the protonation centre in a gas have been discussed. The change in the electronic effects of substituents on going from the gas phase to solution have been examined. The relationships between the strength of ionic hydrogen bonds and the acid–base properties of compounds in the gas phase have been demonstrated, and the results obtained by modelling solvation effects in the gas phase have been examined. New data on the structure and stability of molecular H-complexes in the gas phase and on the increase in the strength of the H-bond on solvation are presented.

The bibliography contains 130 references.

Contents

I. Introduction 134
II. The influence of hydrogen bonds with solvents on acid–base equilibria 134
III. Ionic hydrogen bonds in the gas phase. Relationships between the strength of these bonds and the proton affinity of the partners. Modelling solvation effects 139
IV. The structure of molecular H-complexes in the gas phase 141
V. Solvation of the H-bond 146
VI. Summary 148

I. Introduction

The development of new methods for studying proton transfer reactions in the gas phase (ion cyclotron resonance and high-pressure mass spectrometry) has led to a new attitude to the problem of the influence of the medium on the structure and reactivity of compounds. It has become clear that in the past the part played by these factors has been greatly underestimated. Solvation effects may be comparable with the electronic influence of substituents, and sometimes significantly greater.[1,2] In many cases, the part played by hydrogen bonds is decisive.[3,4]

In recent years, important data have been obtained on the energy of formation of ionic dimers and ionic clusters involving several solvent molecules in the gas phase. The energy of formation of a large number of these clusters has been compared with the energy of solvation of the ions by the solvent. In addition, analogies have been revealed in the solvation of ion–molecule and neutral H-complexes. New methods of high-resolution spectroscopy, which make it possible to establish the structure of intermolecular hydrogen bonds in the gas phase, are being actively developed. This information is direct and reliable, in contrast to that obtained by calculation or by analysing mass-spectrometric data.

Present ideas about the role of the medium in acid–base equilibria are based on a combination of experimental studies in the gas phase and in solvents of different types with quantum-chemical calculations, including in recent years calculations by the methods of molecular dynamics and Monte Carlo methods. The present review does not claim to cover completely all topics and all the published literature, but should provide reference points in this varied and rapidly developing field. Various methodological approaches which help to distinguish the role of hydrogen bonds in the influence of the medium on acid–base equilibria are analysed.

II. The influence of hydrogen bonds with solvents on acid–base equilibria

1. Acid–base properties in water and dipolar aprotic solvents

The basic concepts of the electronic effects of substituents were formulated from the study of acid–base equilibria in aqueous media. Historically, the first acids studied in this connection were benzoic acids and phenols, which ionise in water in an acidity range convenient for study. The subsequent study of acid–base equilibria in dipolar aprotic solvents (DAS) showed that the acidity scale is extended in these solvents, making it possible to distinguish the acidity of compounds having identical pK_a value in water. This characteristic of DAS is referred to as their "differentiating action".[5,6] The pK_a values in DAS and in proton-containing solvents (PS) for organic compounds of the same class are related by linear expressions of the type

$$pK_a(S) = \alpha pK_a + \beta, \quad (1)$$

where the coefficient α characterises the sensitivity to the influence of substituents in DAS. The value of α increases in the order H_2O < ROH < DAS. Deviations from the linear relationship are observed for acids with *ortho*-substituents, which form intramolecular hydrogen bonds or create appreciable steric hindrance.

The differentiating action of DAS increases with increase in the basic strength of the solvent.[7] Thus for benzoic acids the coefficient α increases in the solvent order: H_2O (1) < CH_3OH (1.3) < $(CH_3)_2CO$ (1.72) < CH_3NO_2 (1.81) < DMF (1.98) < CH_3CN (2.5) < DMSO (2.8).[8]

In an analysis of the differences between the pK_a values in N-methylpyrrolidone (NMP) and DMSO, Bordwell and co-workers[7]

examined various acids forming oxo-anions on ionisation (naphthols, phenols, benzoic acids, salicylic acid, etc.). The values of ΔpK_a = pK_a(NMP) – pK_a(DMSO) increase with decrease in the acidity from pK_a = 0.45 to pK_a = 1.95. In more basic anions, the charge localised on the oxygen atom is greater, and the difference in the stabilisation achieved in NMP and in DMSO increases. This is also indicated by data obtained in DMF and DMAA.[9] The pK_a values in NMP and DMSO are related by the linear expression:

$$pK_a(\text{NMP}) = 0.91 pK_a(\text{DMSO}) + b.$$

In the opinion of the authors cited, the acidity values in DMSO (of which more than 600 are known) can be used to predict the pK_a values in any carboxamide solvent, and in other DAS in the absence of strong ion pairing.

In the study of acid–base equilibria in DAS it is necessary to take account of the complicating action of "homoconjugated" hydrogen bonds between the acid and the anion.[3,9] The formation constants of these bonds in NMP[7] and in DMF[9] are ten times those in DMSO. The formation of homoconjugated ions is energetically favourable even in DMSO, however. Thus the equilibrium PhOH...DMSO + PhO^- ⇄ PhO^-...HOPh + DMSO is displaced to the right. The "homoconjugated" hydrogen bond PhO^-...HOPh is 6.1 kcal mol^{-1} more stable than the H-bond between phenol and DMSO.[10]

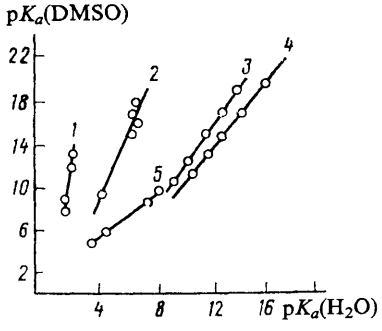


Figure 1. Relationship between pK_a (DMSO) and $pK_a(H_2O)$ for organic acids of different classes: *1*, benzoic acids; *2*, phenols; 3, nitroanilines; *4*, CH-acids; *5*, ammonium acids.[11]

The values of α in Eqn. (1) for XH-acids of different types in DMSO have been compared.[11,12] Fig. 1 shows that the value of α is greatest for benzoic acids, and decreases in the order:

$$XC_6H_4COOH\,(2.43) > XC_6H_4OH\,(2.14) > XCOOH\,(1.94) > X_2NH\,(1.55) > X_3CH\,(1.46) > X_3NH^+\,(1.14).$$

Acids in whose conjugate bases the charge is delocalised have a lesser ability to form H-bonds X^-...HOH with water as proton donor. Decrease in the stability of the H-complex with the anion is accompanied by a decrease in the difference between the acidities in water and in DMSO (OH > NH > CH > NH^+).

For charged (NH^+)-acids, substituents have practically the same influence in DMSO and in water (α = 1.1), since both solvents are good proton acceptors (NH^+...S).[11]

Another widely used method for estimating the sensitivity to the solvent of the effects of substituents is by comparing the coefficients ρ in the Hammett equation:

$$pK_a = pK_0 + \rho\sigma, \qquad (2)$$

where pK_0 is the value of pK_a in water, and σ a substituent constant. The value of ρ increases considerably on going from H_2O to DAS. This is demonstrated for benzoic acids and phenols in Table 1.

The difference in the values of ρ in the solvents CH_3OH and DMF, which belong to different groups (PS and DAS) but which have similar dielectric constants (ε), indicates that non-specific universal interactions have little influence. For benzoic acids, for example, the value of ρ in DMF is approximately 1.5 times that in CH_3OH (Table 1).

Table 1. Values of ρ in Eqn. (2) for phenols and benzoic acids in different media.

Compounds	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH	DMF	CH_3CN	DMSO	Refs.
Benzoic acids	1.0	1.38	1.66	—	2.03	2.37	2.57	[8]
					2.3	2.4	2.4	[9, 10]
Phenols	2.1	—	—	2.25	4.5	4.7	4.88	[11]
							4.29	[9]
							5.3	[10]

To lower the influence of solvation factors, it is necessary to use the most inert solvents. The study of proton transfer reactions in these media is associated with a number of difficulties, including the low solubility of salts in these solvents, the formation of hydrogen bonds between the reagents, dimerisation of the acids, etc. The main complication, however, is that in media with a low polarity and low dielectric constants (ε = 2–6), ion pairs are not dissociated ($K_d \leqslant 10^{-8}$), so that the observed relative strengths of acids depend on the nature of the base chosen for comparison.[13]

The influence of the acidic and basic properties of the partners and the medium on proton transfer and the formation of ion pairs by an acid with a neutral base has been studied intensively in recent years by molecular spectroscopy and low-temperature NMR spectroscopy. This work has been reviewed in detail.[14,15] The extensive studies of the formation of strong hydrogen bonds and ion pairs with charged acids have also been reviewed.[16] †

2. Acid–base equilibria in relatively inert media

Acid–base equilibria in dimethoxyethane (DME), cyclohexylamine (CHA), and tetrahydrofuran (THF) have been studied for CH-acids which form highly delocalised carbanions and which do not tend to undergo ionic aggregation, and also for acids whose carbanions contain substituents with charges localised on them.[17,18] Data have recently been obtained on the acidity of polyarylmethanes and fluorenes in tetrahydrofuran,[19,20] and the pK values of sulphur-containing compounds in CHA and DMSO have been compared.[21]

† See also I S Perelygin *Ionnaya Sol'vatatsiya* (Ion Solvation), Izd. Nauka, Moscow, 1987, p. 164

Expressions relating the ion-air acidity in comparatively inert media with the "ionic" acidity in DMSO, in which the salts are completely dissociated, have been proposed.[22-24] Two types of equilibria were compared:

$$R_iH + R_0^- \ldots M^+ \rightleftarrows R_i^- \ldots M^+ + R_0H, \quad \text{in ethers and cyclohexylamine} \qquad (3)$$

$$R_iH + R_0^- \rightleftarrows R_i + R_0H. \quad \text{in DMSO} \qquad (4)$$

The ion-pair (pK_{ip}) and free-ion (pK_i) acidities are found from the usual relationship

$$pK = pK_0 + \lg K_d$$

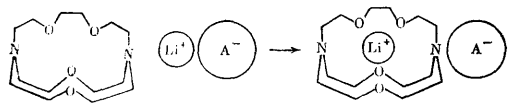
applied to equilibria (3) and (4). If the dissociation constants (K_d) of the ion pairs, which can be determined spectrophotometrically or conductometrically, are known, the pK_{ip} values can be used to obtain the free-ion acidity in media with a low polarity (pK'):

$$pK' = pK_{ip} + \lg(K_{d_0}/K_d), \qquad (5)$$

where K_{d_0} is the dissociation constant of the ion pair formed by a standard carbanion with the cation. The pK' values practically coincide with the pK_i values in DMSO. The differences between pK_{ip} and $pK_i \simeq pK'$ depend on the structure of the carbanion, and also on the ability of the cation to form ion pairs. They are greatest for anions in which the charge is localised on a substituent. The differences are greatest for the Li^+ cation, and decrease with increase in the cation size.

Data published in 1988 on ion-pair and ionic acidities in THF [20] show excellent agreement with these conclusions.[23,24] The difference in the values of the ion-pair and ionic acidities in DME and THF is less than 0.2 pK unit. The values of pK_a in THF, CHA, and DME are related by linear expressions, and the coefficient α is close to 1 (0.999–1.02).[21]

In a new approach to the study of acid–base properties in media with a low polarity and the analysis of the influence of solvation,[25,26] the use of the cryptates of organolithium compounds has been proposed for the construction of an acidity scale. The systematic spectral and conductometric study of the lithium salts of aliphatic and aliphatic–aromatic hydrocarbons in the presence of cryptands has established reliably that, irrespective of the polarity of the medium, they form ion pairs separated by the cryptand.



Thus 4,7,13,18-tetraoxa-1,10-diazabicyclo[8,5,5]eicosane forms a stable inclusion complex with the lithium cation, shielding it from the solvent and the anion. As a result, the ion-pair acidity in media with a low polarity is linearly related to the ionic acidity in DMSO with a coefficient α practically equal to 1. Thus for THF:

$$pK_a(\text{DMSO}) = 1.01pK_a(\text{THF}) + 17.2. \qquad (6)$$

The ionic acidity in the solvent in the absence of specific solvation was related to the acidity in the gas phase

$$\delta\Delta G^S(HA/HA_0)_i = \delta\Delta G_A^{gas}(HA/HA_0)_i + b/\varepsilon_S. \qquad (7)$$

Thus the ionic acidity under these conditions is a linear function of the quantity $1/\varepsilon$. The values of ΔG_A^{gas} obtained using Eqn. (7) coincided with the results of direct determinations (only four such determinations have as yet been carried out, however).

Thus it has now been reliably established that dipolar aprotic solvents have a differentiating action, which is due chiefly to the decrease in the strength of the solvation of the anions as a result of the formation of H-bonds. Approaches to the establishment of acidity scales for CH-acids in media with a low polarity have been found. The use of cryptands should make it possible to study the acid–base properties of acids of other types in these media.

3. Acid–base properties in the gas phase and in solution

Studies of acid–base equilibria, which are being carried out on an increasing scale, have accumulated a large amount of data on organic compounds of different classes (see the published reviews[2,3,27] and monographs[18,28]). These results have made it necessary to re-examine existing ideas about the electronic effects of substituents. The present theory of intramolecular interactions between a substituent and a reaction centre is based on non-empirical molecular orbital calculations, and the fairly approximate model of point charges is used for a qualitative examination (see the papers by Taft[2] and Koppel' [29] and references therein).

For most classes of organic compound, the sensitivity to the influence of substituents in the gas phase is greater than that in DAS, and much greater than that in water; in other words, using the terminology adopted to describe acid–base equilibria in solutions, the gas phase has the greatest "differentiating action". Since however the acidity in the gas is a characteristic "internal" acidity, it is more correct to speak of the action of the medium levelling the electronic influence of the substituents.

The chief factor for the levelling of the acidic properties in PS and in water is the formation of hydrogen bonds with the anions. Thus the sensitivity of benzoic acid derivatives to the influence of substituents is greatest in the gas phase; it is 1.6 times smaller in water, and almost 4 times smaller in DMSO.[2] An interesting feature is that the levelling action of an aqueous medium decreases with decrease in the ability of the anions formed to act as electron donors in H-complexes A^-...HOH, and is not observed for carbanions with a highly delocalised charge.[2,18] The order of change in the coefficient α in the series XC_6H_4COOH (10.6) > XC_6H_5OH (6.6) > XCOOH (3.5) > X_3CH (1) agrees with the order obtained for XH-acids of the same types in DMSO(see above).

Comparison of the heats of hydration and the thermodynamic characteristics of deprotonation in the gas phase and in water has shown that most of the gain in ionisation energy observed with increase in the electron-acceptor properties of the substituents is compensated by the decrease in the energy of hydration of the anion formed. The marked decrease in the ability of these anions to form hydrogen bonds is due to the delocalisation of the negative charge, and leads to destabilisation of the anions. The equilibrium is displaced towards the undissociated acid. As a result, the range of change in the acidity in water becomes narrower.[2,3] A generalised scheme for the influence of the solvent has been proposed;[30] it examines the specific interaction of the solvent with the acid and the conjugate anion, including the formation of H-complexes with substituents such as COR, NO_2, SO_2Ph, etc. For example, for *p*- and *m*-substituted phenols a rigorously linear relationship is observed between ΔG(gas) and $\Delta G(H_2O)$ (the coefficient α = 6.6), deviations from which are related to the specific solvation of the substituents.[30]

A detailed analysis of the influence of different solvation effects on the protonation of substituted pyridines[31-33] has established that the principal role in the decrease in the strength of the effect of

substituents in water is played by hydrogen bonds with the pyridinium ions (XPy...HOH). The energy of formation of ionic H-complexes is five times the energy of the neutral H-bonds of substituted pyridines $XPyH^+...O_2H$. The decrease in the range of change in the basic strength in water is determined by the opposed influences of the substituent on the formation of ionic H-bonds and on protonation. The solvation model of the hydrogen bond has provided a quantitative description of the levelling in water (a three-fold decrease in the strength of the effect of substituents) which shows good agreement with experiment.[31] The anomalously low basic strength of 2,6-di-t-butylpyridine in water is attributed to steric hindrance to hydration. This compound is a very strong base in the gas phase.[32] A similar effect was recently detected in the study of other sterically hindered pyridines.[33]

A comparison of the changes in the basic strengths of two groups of secondary amines in the gas phase and in water[34] showed that alkyl substituents have a marked levelling influence in H_2O ($\alpha = 4.3$). The introduction into the alkyl substituent of functional groups which contain heteroatoms and which delocalise the charge decreases this effect by a factor of 1.6 (Fig. 2). In aqueous medium there is not only a decrease in the electronic influence of the substituents but also a change in the relative contribution of the components of this influence. The effect of polarisability in the gas phase is predominant, but in water its role decreases sharply, compared with the inductive field effect. The same change in the contributions of the components of the electronic effect was also noted for other classes of organic compound.[2,29] For primary amines, the influence of solvation as a result of the formation of additional H-bonds is greater than the electronic influence of the substituent[34] (the point for R = H does not lie on the straight line in Fig. 2). The influence of hydrogen bonds on the ionic hydration of primary amines was previously examined[35] using data on monitored solvation in the gas (this approach is examined in more detail in the next section). The role of H-bonds has been confirmed by a theoretical analysis at the level of non-empirical quantum-chemical calculations.[36]

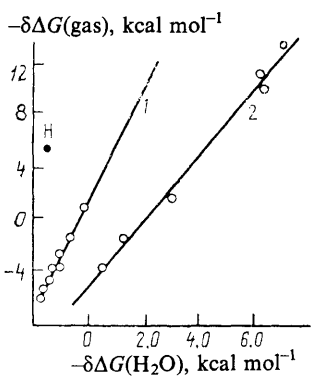


Figure 2. Relationship between the values of the basic strength $\delta\Delta G$ of secondary amines in the gas phase and in water: *1*, RNH_2 (slope 4.3); *2*, XCH_2NH_2 (slope 2.7).[34]

The study of acid–base equilibria in the gas phase has shown that solvation interactions can not only decrease the differences in the strengths of acids and bases but can also change the sequential order of compounds with similar structures.

A number of examples of opposite sequences of the change in the thermodynamic characteristics of the dissociation of substituted halogenoacetic acids, aliphatic alcohols, thiols, and amines in the gas phase and in water have been discussed.[1,2] The order of change in the acidity of aliphatic XH-acids in the gas phase is the opposite of that previously established for aqueous and aqueous-alcoholic media: in the gas phase, MeXH < EtXH < PrXH < t-BuXH, and in water t-BuXH < PrXH < EtXH < MeXH. Thus the strengths of these acids in water and alcohols are determined not by the electronic influence of the substituents but by solvation interactions with the corresponding anions.[2,37] According to quantum-chemical calculations, polarised alkyl groups may show either donor or acceptor properties, depending on the magnitude and sign of the charge on the X atom. A scale of polarisability parameters based on non-empirical calculations was recently published.[38]

The order of the acidity of alcohols in DMSO is the same as that in water,[39] that is although it is usually assumed that DAS solvate ions weakly, the energy of deprotonation in DMSO is not determined by "internal" factors. The role of ion–dipole interaction with DMSO requires further study.

The opposite order of change in the basic strength in the gas phase relative to solution was observed for methyl- and phenylphosphines.[40] The "internal" basic strength of Ph_3P (the proton affinity PA) is greater than that of Me_3P. At the same time, the basic strength of alkylphosphines in water is greater than that of phenylphosphines by several powers of ten. The same applies to the basic strength relationships for the phosphines in nitromethane.[11] Thus contrary to the published opinion,[12] nitromethane cannot be regarded as a medium in which specific solvation interactions are weak.

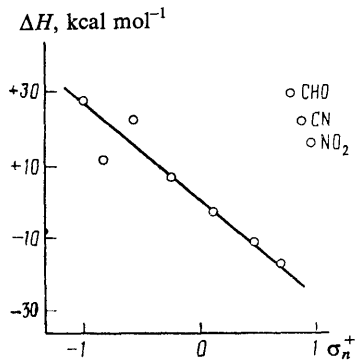


Figure 3. Correlation between the basic strength of PhX and the constants σ_n^+ of the substituents.[41]

The next step in the study of acid–base equilibria is the study of compounds in which transfer of the reaction centre is possible, and the identification of protonation centres in the gas phase.[41–47] For anilines, the coordination centre in solution is the lone pair of electrons of the nitrogen atom. The published conclusion[41] that the protonation of aniline in the gas phase involves the π-system of the ring was therefore surprising. The authors cited analysed the linear relationship between the basic strength of monosubstituted benzenes

in the gas phase and the σ^+ constants of the substituents. Fig. 3 shows that the points corresponding to compounds with strong electron-acceptor substituents do not lie on the straight line. The observed deviations towards higher basic strengths indicate that the ring is not the protonation centre in these cases. According to quantum-chemical calculations, protonation at nitrogen is energetically slightly more favourable than protonation at the ring,[42] but the differences are very small (1–3 kcal mol^{-1}). Finally, the basic strengths of fifteen substituted anilines in the gas phase have been compared[43] with the experimentally measured ionisation energies of the 1*s* electron of the nitrogen atom ($E_B N_{1s}$). A linear relationship between these quantities is observed for all the compounds except *m*-MeO-, *m*-MeS-, *m*-OH-, and *m*-NH_2-anilines, which are assumed to be protonated at the ring. Fig. 4 shows that the points corresponding to the "hydration" of these compounds in the gas phase, measured for the monitored addition of water ($BH^+ + OH_2 \rightleftarrows BH^+...OH_2$) also do not lie on a straight line. From this it was concluded that aniline in the gas phase is protonated at nitrogen, but that in various *meta*-substituted compounds with donor substituents the coordination centre is the benzene ring.

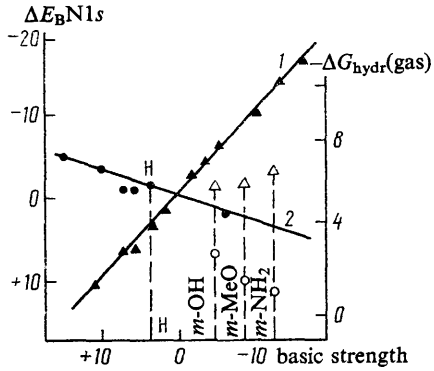


Figure 4. Dependence of the gas-phase basic strength of anilines on the ionisation energy of the N1*s* electrons (*1*) and on the energy of "hydration" in the gas phase ($BH^+ + OH_2 \rightleftarrows BH^+...OH_2$) (*2*).[43]

Single-parameter linear correlations between the PA values and the energies of the core electrons were previously observed for alcohols, ethers, carbonyl compounds, amines, and phosphines.[44] The existence of these correlations for compounds having two centres, for example amides (in which oxygen is the protonation centre), pyridines, and aminonaphthalenes,[45] made it possible to establish the protonation centres, and also to determine the conditions under which the correlation breaks down. In a number of studies, a similar analysis was based on empirical relationships between PA and the first ionisation potential (found by photoelectron spectroscopy). For example, a linear relationship was established between the proton affinity and the first ionisation potential of various compounds of phosphorus(III).[46] The points for cyclic and acyclic phosphites also lie on this straight line, indicating that the protonation centre in these compounds is the phosphorus atom, and not oxygen. The existing two-parameter expressions relating the PA to the energy of the electrons of the core and the first ionisation potentials[47] can be used to predict the protonation centre in the gas phase, since the correlation coefficients are different for O-, N-, and C-bases.

A successful solution to the problem of the protonation centre in the gas phase was recently achieved by comparing experimental data with the results of non-empirical quantum-chemical calculations.[48,49] A study of the protonation of phosphine oxide and the amides of acids of phosphorus(V) established that protonation takes place preferentially at the oxygen atom; the difference between the protonation energies of the oxygen and nitrogen atoms, according to quantum-chemical calculations, was 100 kcal mol^{-1}.[48] The basic strength of nitrogen-containing heterocyclic compounds in the gas phase has been examined.[49] A comparison of the PA values, the energies of the N_{1s} electrons, and the results of non-empirical calculations established that the protonation centre in a series of azaindoles is the nitrogen atom of the pyridine ring, and not the indole ring.

Without adding to the number of examples, mention may be made of various regular features of the change in the intramolecular interactions on going from the gas phase to solution. In this case it is possible to observe a levelling of the strengths of acids and bases, reversal of the sequence for compounds with similar structures, and a change in the protonation centre. The levelling action of the solvent indicates that solvation effects play a less important role than intramolecular effects. The reversal of the sequence indicates that the effect of the medium is stronger than the influence of the substituent.

In all cases, the influence of the solvent competes with that of the substituent. Among solvation effects, the most important role is played by the solvation of charged species (the anion A^- or the protonated base BH^+). The strength of the ion–dipole interactions and the energy of formation of hydrogen bonds are greater, the smaller the ion and the more localised the charge in it. Thus solvation effects bring about the greatest stabilisation of small ions. These ions, however, are less stable in the gas phase. Increase in the size of the anion and increase in the polarisability of the substituent increase the ability of the ions to delocalise their charge, leading to their stabilisation in the gas phase, and hence to an increase in the "internal" acid strength (basic strength). This effect is called "internal solvation".[1] At the same time, these ions are stabilised to a smaller extent under the influence of the solvation effects of solvents.

These ideas make it possible to understand the cases in which levelling of the eletronic effects should take place, and those ion which reversal of the sequences of the acid–base properties in solution or a change in the protonation centre should take place.

In those classes of organic compound including large molecules of similar size, such as aromatic and heterocyclic compounds (the benzoic acids, phenols, pyridines, etc. already examined), solvation effects decrease the difference in the acid–base properties. In *ortho*-substituted compounds with intramolecular hydrogen bonds or substituents with a large volume creating steric hindrance to solvation, however, the sequence of changes in the internal acid strength (basic strength) in solution may break down.[32,33] Deviations from the linear relationships between PA(gas) and $pK_a(H_2O)$ are also possible for substituents forming strong hydrogen bonds with water.[30]

Reversal of the order of change in the acid–base properties on going from the gas phase to solution can be expected in those

homologous series where the first members are compounds giving small ions and where the size and shape of the molecules change considerably with increase in the number of carbon atoms. This applies to aliphatic compounds such as alcohols, thiols, etc., and also to aliphatic compounds with substituents differing considerably in their polarisability and their ability to delocalise the charge on the ion. A change in the protonation position may take place if the potential protonation centres of the molecule have similar proton affinities and differ considerably in their ability to undergo solvation.[41,43]

The relative contributions of the components of the electronic effect change on going from the gas phase to solution (the polarisability effect is weakened to a greater extent than the inductive and resonance effects). The radical differences in the mechanisms of the stabilisation of ions in the gas phase and in solution require the special selection of materials for analysing intramolecular effects in compounds of different classes; it is necessary to compare compounds with similar dimensions and containing similar numbers of carbon atoms, that is compounds whose heats of solvation differ little.

III. Ionic hydrogen bonds in the gas phase. Relationships between the strength of these bonds and the proton affinity of the partners. Modelling solvation effects

Considerable progress in the understanding of the role of solvation has been made as a result of a range of studies of ionic hydrogen bonds in the gas phase. These studies are being carried out in two related directions: 1) the determination of the energy of formation of H-bonded cationic and anionic dimers, and the analysis of the relationships between the strength of the H-bond and the acid–base properties of the partners in the gas phase; and 2) the determination of the energy of H-bonds formed on the successive addition to the protonated ion of from one (in the dimer) to 4–6 solvent molecules, that is modelling the effects of solvation in the gas phase and comparing with solvation in solution.

1. Relationship between the strength of H-bonds in ionic dimers and the acid–base properties of the partners in the gas phase

On the basis of insufficiently accurate thermochemical data it was at first concluded that an overall linear relationship exists between the energy of the hydrogen bond AH...Cl^- and the acidity in the gas phase of acids of different classes.[50] It was later established[51,52] that this conclusion is erroneous. The examination of H-bonds of the type A^-...HOH and BH^+...OH_2 showed that these relationships are more complex. Fig. 5 shows the relationship between the energy of the H-bonds formed by different acids BH^+ with H_2O (NH_3) and the quantities $\Delta PA = PA(B) - PA(B_0)$, where $B_0 = H_2O$ and NH_3. For acids BH^+ of different types, a linear relationship between ΔH_{compl} and ΔPA is not observed. The slope of the curve increases from −0.12 for weak acids BH^+ (pyridinium ions) to −0.75 for the strongest acid (H_3O^+). An approximately linear relationship ws obtained for representative series of substituted pyridinium ions.

The energy of the strong hydrogen bonds AH...F^- and AH...Cl^- has been compared with the energy of proton transfer in the gas.[53,54] Linear relationships between these quantities were established for aliphatic alcohols. The points corresponding to acids of other types do not lie on the straight line. The magnitude of the deviations from linearity for the bonds XH...F^- depends on the electronegativity of the atoms. For similar gas-phase acidity, the energies of the H-bonds decrease in an order similar to that in solution: OH > NH > SH > CH.[53] The energy of the H-bond with Cl^- is less sensitive to the heteroatom joined to the acidic proton.[54] Similar conclusions were reached[55] in an analysis of the hydrogen bonds ROH...B^- with different anions. The stability of the H-complexes MeOH...^-RO in the gas phase depends linearly on the proton affinity of the anions OR^-. The hydrogen bonds formed by anions of other types (F^-, $C{\equiv}CR^-$, etc.) with similar proton affinities have different strengths, however. Table 2 shows that the enthalpies increase with increase in the electronegativity of the anion (χ). An expression relating the X^-...HY bond energy to the values of $\chi(X)$ and $\chi(Y)$ has been published.[56]

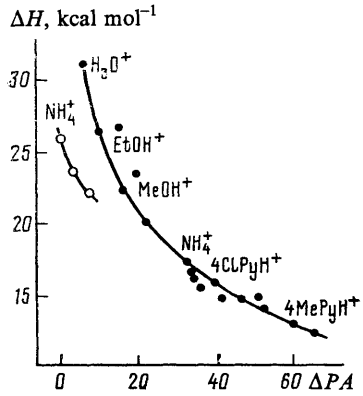
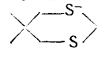


Figure 5. Relationship between the strength of the hydrogen bond BH^+...B and ΔPA (dark circles: $B_0 = H_2O$, light circles: $B_0 = NH_3$).[51]

Table 2. Stability of various bound dimers ($\Delta H_{0,1}$) and the group electronegativity of the anions (χ) in the complexes MeOH...B^-.[55]

B^-	$\Delta H_{0,1}$, kcal mol^{-1}	PA, kcal mol^{-1}	χ
F^-	29.6	371.5	4.0
$^-OCH_2$-t-Bu	18.6	371.8	3.5
$^-C{\equiv}CPh$	14.3	370.3	3.3
	14.8	372.9	2.5

The relationships between the stability of ionic dimers and the ΔPA values have been the subject of a large number of systematic studies.[57–60] Organic compounds of different classes, with a wide range of H-complex energies (ΔH_d^0) of 10–50 kcal mol^{-1} and ΔPA values 0–70 kcal mol^{-1}, were examined. The existence of the linear relationships

$$\Delta H_d^0 = \Delta H_d^0(0) - b\Delta PA, \qquad (8)$$

where $\Delta H_d^0(0)$ is the dissociation energy of the dimer with $\Delta PA = 0$, was reliably established.

Table 3 shows that these relationships are observed for many cationic complexes containing the heteroatoms of periods II and III (N, O, S). Anionic complexes have been less extensively studied; linear relationships between ΔH^0 and ΔPA were found for $O^-...HO$ systems.[60]

Table 3. Linear relationships between the energy of H-complexes ΔH_d^0 and the difference between the proton affinities of the partners ΔPA, Eqn. (8).

Type of complex	$-\Delta H_d^0(0)$, kcal mol^{-1}	b	n[a]	r[b]	Refs.
$NH^+...OH_2$	30.0	0.26	19	0.923	[57]
$NH^+...O$	28.3	0.23	48	0.979	[57]
$NH^+...N$	23.2	0.25	8	0.897	[57]
$OH^+...OH_2$	30.4	0.30	20	0.979	[57]
$SH^+...O$	18.6	0.164	6	—	[59]
$NH^+...S$	22.3	0.26	5	0.970	[57]
$NH^+...N\equiv C$	35.3	0.34	7	0.997	[58]
$H_3NH^+...N\equiv C$	32.7	0.38	4	0.984	[58]
$C\equiv NH^+...N\equiv C$	28.1	0.37	7	0.947	[58]
$OH^+...N\equiv C$	30.9	0.43	18	0.975	[58]
$C\equiv NH^+...O$	28.3	0.31	5	0.977	[58]
$RO^-...HO$	27.5	0.29	8	0.987	[60]
$RCOO^-...HO$	29.6	0.31	7	0.997	[60]
$O^-...HO$	28.1	0.29	13	0.981	[60]

[a] Number of systems studied. [b] Correlation coefficient.

An interesting feature is that the differences in the values of the slopes (b) of the linear relationships for complexes of different classes are small ($b = 0.2-0.3$). Increase in the polarity of the partners leads to an increase in the sensitivity of the energy of formation of the dimers to the ΔPA values. Thus for the H-complexes with nitriles, $b = 0.38$ for the $NH^+...N\equiv C$ system, and $b = 0.43$ for the $OH^+...N\equiv C$ system.[58] A low value of the coefficient b, 0.16, was also observed for the complexes $SH^+...O$.[59] For dimers of a different type, containing a less electronegative atom (sulphur) as the base ($NH^+...S$), however, the coefficient b has the usual value (0.26). In all the compounds studied, the highest dissociation energy is shown by the dimers whose partners have equal proton affinities ($\Delta PA = 0$). The inverse relationship between the stability of the H-complexes and the ΔPA values can readily be understood if the formation of the ionic H-bonds $HX^+...B$ is regarded as partial charge transfer.[56] Increase in the proton affinity of X makes the charged acid a less effective proton donor, and decrease in the value of PA for B leads to a decrease in the proton-acceptor properties. As a result, the energy of the H-complexes decreases with increase in ΔPA.

Analysis of the deviations from the linear relationship (8) helps to identify such structural features as the presence of intramolecular hydrogen bonds, the formation of multiple H-bonds in polyfunctional ions, and the existence of steric hindrance to solvation. Thus the bonds formed by polyethers, crown ethers, and polyamides with RNH_3^+ are stronger than might have been assumed from the dependence of ΔH_d^0 on ΔPA. The energy of the H-bonds increases by 8 ± 1 kcal mol^{-1} when a second bond is formed, and by 4 ± 1 kcal mol^{-1} when a third bond is formed. An interesting feature is that the enthalpy of formation of H-bonds for compounds with bulky substituents does not decrease if the optimum geometry of the H-complexes can be achieved in even one conformation. At the same time, steric hindrance leads to marked entropy effects, as shown by substituted pyridines with bulky substituents in the *ortho*-position.[33]

Various general trends in the change in the stability of H-complexes of the ionic type were recently analysed[61] for the case of hydride dimers. It was established that the strength of the H-bond in the symmetrical dimers generally increases from left to right along a period and upwards within a group, that is the order of change in stability with change in the position of the heteroatom in the periodic system shows a similarity between ionic and neutral dimers: (F, O > N > S > P) for $(AH_n)_2H^+$ and (F > O > Cl > Br > I > S > N > P) for $(AH_{n-1}^-...AH_n)$.

Comparison showed that cationic dimers are usually more stable than the corresponding anionic dimers. This was established for dimers containing oxygen, nitrogen, and sulphur atoms. The situation was different, however, for the most stable dimers, containing fluorine atoms. The enthalpy of formation of the $(FHF)^-$ ion is 39 ± 1 kcal mol^{-1}, which is greater than the corresponding value for $(HF)_2H^+$ and $(CH_3F)_2H^+$, 32 ± 2 kcal mol^{-1}.[61]

The authors cited consider that important characteristics of symmetrically bonded hydrides are the greater stability of the systems containing more electronegative atoms (F, O > N) and the absence of a correlation between ΔH and the basic strength. An interesting feature is that the strength of the H-bonds in symmetrical dimers, for example $OH^+...O$ and , remains unchanged when the hydrogen atoms of the hydrides are replaced by the most varied substituents. With wide variation in the substituents, the energy of formation $[-\Delta H_d^0(0)]$ of oxygen-containing symmetrical dimers is 31 ± 2 kcal mol^{-1}, and that of nitrogen-containing dimers is 23 ± 2 kcal mol^{-1}.[57] Like the coefficient b mentioned above, $\Delta H_d^0(0)$ increases with increase in the polarity of the partners. Thus the stability of the ionic H-complexes with nitriles is greater than that of the corresponding complexes with amines, although nitriles are weaker bases than amines.[58] Even smaller values of $\Delta H_d^0(0)$ are observed for complexes containing a sulphur atom (an element of period II).[59]

A non-empirical quantum-chemical calculation for cationic complexes[62] showed that for distances A–B shorter than 2.55 Å, a significant contribution to the energy is made by covalent bonding. This component increases with increase in the electronegativity of the atoms. The same conclusions were reached from non-empirical calculations at the highest level for unsymmetrical anion–water dimers.[63] On going from elements of the first period to the less electronegative elements of the second period (halogens, oxo- and thio-anions), the stability of the complexes decreases by 10–12 kcal mol^{-1}. Decrease in the covalent component is revealed by a decrease in the deviation from linearity of the optimum geometry of the complex. These deviations are less than 12° for localised ions of period I, and reach approximately 20° for ions of period II; for delocalised ions of period I (carboxylates, cyanides), the bending is intermediate. An examination of the relationships between the energy of ionic complexes and the ΔPA values,[62] and later studies,[64] confirmed the existence of linear relationships of type (8). The values of the slope obtained by calculation were close to the experimental values, and differed little for compounds of

different classes ($b \simeq 0.2$); a decrease in the energy of H-complexes containing elements of period II was predicted.

The same linear relationships of type (8) as for ionic H-complexes have been given for neutral hydrogen bonds.[65]

A general expression for the non-linear relationship between ΔH and ΔPA, covering ionic and molecular complexes, was proposed. The energy $\Delta H^0(0)$ for symmetrical dimers $(AH)_2$ obtained from these relationships, however, was 10–20 times the experimental value. The differences in the energies of dimerisation of $(AH)_2H^+$ (40–20 kcal mol^{-1}) and $(AH)_2$ ($\leqslant$4 kcal mol^{-1}) are so large that it appears impossible to find a general correlation equation applying to both ionic and neutral H-bonds.

2. Modelling solvation in the gas phase

High-pressure mass spectrometry has given useful results in the study of this problem.[57,66–68] Studies of ion–molecule equilibria of the type: $X^{\pm}(S)_{n-1} + (S) \rightleftarrows X^{\pm}(S)_n$ make it possible to determine the enthalpy ($\Delta H^0_{n-1,n}$) and free energy ($\Delta G^0_{n-1,n}$) of the addition of the nth molecule of the solvent (S) on the monitored addition of the latter ($n = 1-5$). Particular attention was paid to the study of hydration.

The total energy of the addition of n solvent molecules to the ions changes in the same order as the energy of formation of dimers by these ions. Thus the energy of formation of clusters (containing two and three water molecules) is greater for the 4-CNPyH$^+$ cation than for PyH$^+$, and the same is true of the energies of the dimers: 4-CNPyH$^+$...OH$_2$ > PyH$^+$...OH$_2$.[66] Similar trends were observed in the series $RNH_3^+...nH_2O$.[35] The total energy of formation of a cluster containing several water molecules approaches the energy of solvation by water as solvent. Analysis of the results of the study of varied onium ions,[57,66–68] supplemented by a comparison of the enthalpy of addition of four water molecules in the gas phase ($\Delta H^0_{0,4}$) with the values of the differences ($\delta\Delta H_{gas\rightarrow H_2O}$),[2] leads to a number of important generalisations.

It has been reliably established that the energy of the hydrogen bonds $\Delta H^0_{n-1,n}$ decreases with increase in n. This can readily be understood by taking account of the fact that the ionic charge is delocalised with increase in the size of the cluster. For singly protonated ions, the energy of addition of a second molecule ($-\Delta H_{1,2}$) is 0.7 $\pm$ 0.05 times the energy of the dimer ($-\Delta H_{0,1}$). The enthalpy of addition of a third molecule ($\Delta H^0_{2,3}$) is even smaller, and is equal to 0.85 $\pm$ 0.05 times ($-\Delta H_{1,2}$) As a result, the ratio of the total enthalpy of solvation of the ion with the addition of four H_2O molecules to the energy of the H-bond with one molecule ($\Delta H_{0,4}/\Delta H_{0,1}$) is constant for a wide range of onium ions; for singly protonated ions the value is 2.8.

A slight increase in this ratio ($\Delta H_{0,4}/\Delta H_{0,1} = 3.1$) is observed for ions of the type ROH_2^+, RNH_3^+, etc.

For most ions, the variation in the values of the enthalpies of solvation by water as solvent is determined completely by the variation in the strength of the hydrogen bonds. The energy of the specific hydration of BH$^+$ ions by four water molecules is close to the enthalpy of transfer $\Delta H^0_{gas\rightarrow H_2O}$ ($\pm$2 kcal mol^{-1}). Deviations have been observed only for ions containing phenyl substituents. The values of $\Delta H_{0,4}/\Delta H_{0,1}$ and the linear relationship (8) between the energy of the dimers ($\Delta H_{0,1}$) and the ΔPA values can be used to predict the energies of hydration of most onium ions. Modelling the effects of solvation for DAS gave similar results. The total energy of the addition of three DMSO molecules is 92% of the energy of solvation of the proton by this solvent.[69] The results of a non-empirical quantum-chemical analysis of this process have been published.[70] The energies of solvation was a result of the formation of H-bonds ($\Delta H_{n-1,n}$) by solvents of different types (ethers, ketones, amides, nitriles, etc.) have been compared.[57] In spite of the differences in the polarisability and dipole moments, in all cases the enthalpy decreases with increase in n, and the ratios $\Delta H^0_{0,n}/\Delta H^0_{0,1}$ are comparable with those given above for hydrated clusters. An interesting feature is that a similar relationship was found for hydrated metal ions (Li^+, Na^+, K^+).[71] Comparison of the "solvation" of a series of oxonium ions by acetonitrile in the gas phase with their hydration in the gas phase and in water[72] showed that the effect of hydration is similar to the effect of the formation of an H-bond with one CH_3CN molecule. According to the data obtained,[72] the relative free energy of solvation of the oxonium ions in water is twice the energy of formation of the hydrogen bond $OH^+...N{\equiv}CMe$ and three times the energy of the addition of one H_2O molecule in the gas phase.

A theoretical analysis of the addition of several solvent molecules, carried out successfully by model quantum-chemical calculations (STO-3G basis set), covers a large number (61) or oxo-anions.[29] The influence of mono-, di-, and tri-hydration on the geometry and extent of charge transfer was examined in relation to the size of the anion and the delocalisation of its charge. An example of the successful use of quantum-chemical calculations at this level for cations is provided by the calculation of the energy of solvation of primary amines in a cluster containing three water molecules.[36] Quantum-chemical calculations for ionic bonds have been reviewed in a recent book.‡

In recent years, considerable progress in the solution of problems related to the solvation of ions has been achieved by the methods of molecular dynamics (MMD) and Monte Carlo methods (MCM) using intermolecular potentials based on the results of non-empirical quantum-chemical calculations for the dimers. An example is provided by MCM calculations for carboxylate anions and ammonium cations,§ which gave important information on the structure of the solvation layers and the number and geometry of ionic hydrogen bonds.

Thus experimental studies of ion–molecule interactions in the gas phase, supplemented by determinations of the enthalpies of transfer of an ion from the gas phase to solution and quantum-chemical calculations, have demonstrated convincingly the relationship between the strength of the ionic hydrogen bonds in the dimers and the acid–base properties of the partners (in the gas phase). They have also established that the differences in the heats of solvation of ions in solution are determined by the formation of hydrogen bonds by the ions with several solvent molecules.

IV. The structure of molecular H-complexes in the gas phase

Mass spectrometry determines the energy examined above, but gives no information on the internal structure of free ionic H-complexes, for example the position of the proton in them. At the same time, the structure of many uncharged H-complexes in the

‡C A Deakyne *Structure and Energetics*, Vol. 4, VCH Publ. Inc., 1987, p. 105

§W L Jorgensen, J Gao *J. Phys. Chem.*, 1986, **90** 2174; G Alagona, P J Kollman *J. Am. Chem. Soc.*, 1986, **108** 185; see also the references given in these papers.

free state is now well known, but their energies have as yet been little studied. This complementarity of the data, on the one hand, sets the present section apart, but at the same time it may stimulate the theoretical generalisation of the two types of hydrogen bond.

In the last ten years, remarkable progress in the study of molecular H-complexes has been achieved by the use of high-resolution spectroscopy, primarily rotational microwave (MW) and vibrational (infrared) spectroscopy. Of key importance in this work has been the preparation of the specimen, involving deep adiabatic cooling (to ~ 10 K) of a supersonic gas stream or pulse expanding in a vacuum. The "freezing" of the thermal excitations in this molecular beam greatly simplifies the spectrum, which otherwise cannot be interpreted, and the elimination of particle collisions and the usual Doppler effect decreases considerably the lines due to the remaining transitions. The corresponding spectral apparatus makes it possible to resolve effectively the fine (rotational) and hyperfine (nuclear) structure of the spectrum, and its interpretation gives the detailed structure of the H-complex. Thus it is possible to determine the accurate equilibrium geometry of the complex, its deformation (zeroth amplitudes of the mutual orientation of the partners), the elasticity of the stretching and bending of the H-bond, and the increase in the length of the A–H bond on H-bond formation (to within $10^{-3}-10^{-4}$ Å). The fine structure of the infrared band can be used to determine the contraction of A–H...B on excitation of the proton vibration ν_S, and the displacements of the ν_S frequency can be measured with an accuracy which is 10^2-10^4 times greater than that when a broad band is used. After the "cold" rotational spectrum has been interpreted, it is possible to interpret the spectrum of the gas in thermal equilibrium, to determine low frequencies which cannot be measured directly, to estimate the elasticity and dissociation energy of the H-bond, etc. All these topics have been reviewed in detail.[73,74]

The number of complexes in a molecular beam is sufficient to make it possible to record the MW spectrum by sensitive MBERS (molecular beam electrical resonance spectroscopy) methods[73,74] and Flygare Fourier spectroscopy,[74] but is often insufficient to allow direct recording of the infrared spectra of the same complexes (the proportion of radiation absorbed is too small). It is possible, however, to detect changes in the actual beam (an increase or decrease in the number of particles in a given state) as a result of vibrational excitation or photo-dissociation of the complexes by the sufficiently powerful infrared radiation of a tunable laser. This method makes it possible to obtain good high-resolution infrared spectra (and also to estimate the lifetime of the excited complexes, opening up new possibilities for the study of the kinetics of the elementary acts); the results have been reviewed.¶ Thus the new spectroscopy has successfully brought "non-rigid" molecular complexes with their unavoidably large zero-point vibrations into the general sphere of the traditional spectroscopy of simple molecules.

In a few years, intensive spectral studies have examined a wide range of systems, mainly heterodimers of the type AH.B. A published list[74] gives 68 complexes of different AH from hydrogen fluoride to fluoroform and acetylene with various partners B from ammonia to nitrogen. In addition, the simplest triatomic complexes of AH with noble gases (9 systems) and cyclic heterodimers of carboxylic acids and amides (14 systems) have been studied.[73] A large amount of information leading to important conclusions has been accumulated, and is increasing rapidly (becoming broader, deeper, and more accurate), and includes associates with a high multiplicity, new dimers, the isomerism of H-complexes, their stability and dynamics, etc. (see the Summary).

The structures of a representative series of H-complexes from the simplest to the more traditional, established from the rotational spectra, are shown in Fig. 6, and Table 4 gives as an example the parameters of selected complexes from the most widely studied series FH.B. Some of the results and conclusions may be noted.

Table 4. Parameters of various H-complexes B...HF;[73,75] R = interatomic distances; μ_a and $\Delta\mu$ are the longitudinal component of the dipole moment and its increase in the complex; k_σ is the H-bond stretching force constant.

B	R_{FB}, Å[a]	R_{HB}, Å	μ_a, D	$\Delta\mu$, D	k_σ, N m^{-1}
Ar	3.5095	2.58	1.3353	—	1.4
N_2	3.082	2.16	—	—	5.5
CO	3.047	2.12	2.352	0.55[b]	8.5
CO_2	2.93	2.00	2.2465	0.60	2.2
NCCN	2.862	1.94	—	—	14.2
HCN	2.796	1.87	5.612	0.80	18.2
CH_3CN	2.759	1.83	—	—	20.1
$(CH_3)_3CCN$	2.725	1.80	—	—	—
NH_3		1.78[b]	—	1.3[b]	—
C_2H_2	3.075[c]	2.15	2.3681[b]	0.65[b]	—
C_2H_4	3.141[c]	2.21	2.384[b]	0.67[b]	—
C_3H_6[d]	3.021[c]	2.09	—	—	11.5
HF	2.79	1.86	2.9885	0.60	13.6
H_2S	3.25	2.32	2.6239	0.78	12.0
H_2O	2.69	1.80[b]	4.07	0.96	24.9
$(CH_2)_2O$	2.627	1.70	3.85	0.99	—
$(CH_2)_3O$	2.586	1.66	—	—	—

[a] A recent recalculation of some of the R_{FB} values with improved averaging with respect to the zero-point amplitudes gave differences of 0.005–0.017 Å (A C Legon, D J Millen *Chem. Phys. Lett.*, 1988, **147** 484); this probably provides a measure of the accuracy of the values; [b] data of Peterson and co-workers[76]; [c] from the C–C line; [d] cyclopropane.

Linearity of the H-bond. It has been established by direct experiment that an isolated single H-bond is in fact linear, that is the three atoms A–H...B lie on the same straight line;[73] previously, this was only postulated, on the basis of crystallographic data. The slight deviations from linearity obtained in non-empirical calculations for the simplest H-complexes[77] are comparable with the uncertainty in the measurements (5–10° [73]), and it is not clear how real these are.

Non-rigidity of the H-bond. It has been shown that the H-bond has a low rigidity and is easily deformed, particularly round the electron-donor atom B; this also agrees with crystallographic data. Thus in $CH_3C{\equiv}N...H-F$, the force constant of the bending of the H...N≡C angle is 3–4 times lower than that for the F–H...N angle[74] (and, like the chemical bonds in molecules, is 10 times lower than the force constant of the stretching of the H-bond). This "flexibility" of the H-bond corresponds to the high zeroth amplitudes of the angles of orientation of the partners. For example, the average values of the angles of rotation (libration) of HF in its complexes with H_2O, CO_2, and Ar are 18 3, 25.17, and

¶ R E Miller *Science*, 1988, **240** 447

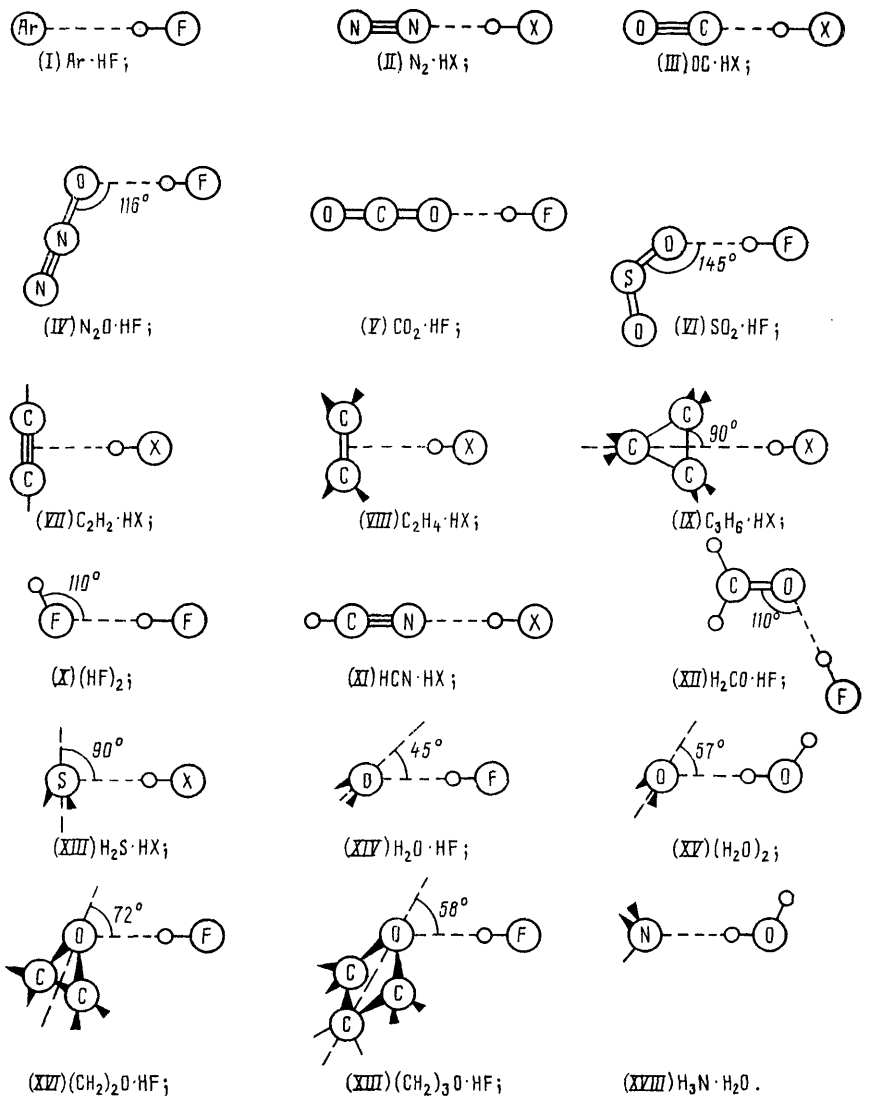


Figure 6. Configurations of various gaseous H-complexes AH.B, established from the rotational spectra;[73–75] for the interatomic distances A...B and other parameters see Table 4.

41.27° respectively.[73,76] At ordinary temperatures, when the librations are highly excited, the configuration of the H-complex should differ to an even greater extent from that shown in Figure 5 (the equilibrium configuration). It is the non-rigidity (difficulty of averaging) that limits the accuracy of the determination of the equilibrium geometric parameters of the H-complex from the extremely accurately measured rotational spectrum; the same applies to the dipole moments.

The flexibility of the complexes corresponds to the low wavenumbers of the librations of the sub-molecules (ν_β). They have not yet been observed directly in the spectrum, but are calculated indirectly from the changes in the spectra with change in temperature, or from the amplitudes of the angles. For the lightest hydrides, the values of ν_β reach 40–70 cm^{-1},[74,78–80] but in ordinary H-complexes they do not usually exceed 10–30 cm^{-1}. The excitation of these librations of the partner molecules is the main reason for the unique broadening of the vibrational bands by the H-bond at ordinary temperatures[78,79,81] (see, however, the papers by Millen[80] and Sokolov and Sakun[82]). The broadened band corresponds to a whole set of vibrational transitions, and not to one normal vibration. In this respect, the vibrational spectra of a complex AH.B and a simple molecule XYZ differ considerably. To make them comparable, it is necessary either to heat XYZ above 3000 K or to cool AH.B below 30 K, as is done in molecular beam spectroscopy.

Configuration of H-complexes. The orientation of the partners of the H-complex (in particular diatomic complexes; see the HF dimer in Fig. 6) is completely different from the favourable orientation of the dipoles. This is consistent with the known fact that there is no correlation between the dipole moment and the strength of the H-bond.[83]

The direction of the H-bond to some extent corresponds to the directions (valence angles) of the chemical bonds of the molecules (Fig. 6). Protonophiles of the first period tend to adopt the tetrahedral orientation, but hydrogen sulphide adopts the orthogonal orientation; a characteristic feature is the difference in the angles of the H-bonds with different cyclic ethers.[73]

In their systematisation of experimental data, Legon and Millen formulated the following rules. "The gas-phase geometry of a dimer B...HX can be obtained in terms of the non-bonding and π-bonding electron pairs on B as follows: (i) the axis of the HX molecule coincides with the supposed axis of a non-bonding pair as conventionally envisaged, or, if B has no non-bonding electron pairs but has π-bonding pairs, (ii) the axis of the HX molecule intersects the internuclear axis of the atoms forming the π-bond and is perpendicular to the plane of symmetry of the π-orbital. Rule (i) is definitive when B has both non-bonding and π-bonding pairs".[74]

These rules are not absolute. The pyramidal structure of $FH.OH_2$ [(XIV) in Fig. 6] has only been calculated for the equilibrium configuration, but in fact is not realised; the barrier to inversion is so low (0.36 kcal mol^{-1}) that the complex is effectively planar. Other complexes $XH.OH_2$ are even more likely to be planar, and the equilibrium pyramidal structure is only assumed.[74] Finally, the weak H-complex $HCCH.OH_2$ is recognised as definitely planar.[76] The hydrogen bond formed by AH with benzene is directed towards the centre of the ring at right angles to its plane,[74] and the (stronger!) bond with cyclopropane lies in the plane of the ring and is directed towards the centre of a C–C bond [(IX) in Fig. 6]. The dimer $CO_2.HF$, which is isoelectronic with $N_2O.HF$, is not bent like this compound, but is linear, contrary to the "rules" [(IV) and (V) in Fig. 6]. With weaker electrophiles, in particular HCN, the same CO_2 now forms a *T*-shaped complex $O_2C.NCH$ with an intermolecular C...N bond,[74] and not the isomeric linear complex OCO...HCN with an H-bond (energetically less favourable, but also observed later). A similar structure is shown by the symmetrical complex with water, $O_2C.OH_2$; this intermolecular C...O bond shows some similarity to a double bond (the internal rotation of H_2O is strongly hindered).[76] On the other hand, the "rules" are apparently applicable to stronger ("ordinary") H-bonds.

Structure of the dimers $(AH)_2$. The actual existence of the rotational absorption spectrum excludes non-dipole cyclic homodimers, and in fact all $(AH)_2$ studied are open and have a single H-bond AH...AH [(X) and (XV) in Fig. 6]. It has been shown, in particular, that the $(HF)_2$ ring is an unstable state corresponding to a saddle point of the potential.[76,77] The initial assumption that the dimer of methanol (and water) in a matrix is cyclic[83] was found to be due to the insufficient resolution of the infrared spectrum; improvement of the resolution showed clearly that the dimer is open[84] (as in the case of water also[85]). The free dimer of water [(XV) in Fig. 6] is now one of the most fully studied H-complexes.[73,74,76]

Thus prolonged argument has concluded that the dimers are open; four-membered $(AH)_2$ rings with the corresponding non-linear (90°) hydrogen bonds apparently do not exist. Other gaseous dimers, formed by CH_3OH, C_2H_5OH, H_2S, CH_3SH, CH_3NH_2, and $(CH_3)_2NH$, also have a dipole moment and therefore cannot be symmetrical rings, and are probably also open. The polymeric associates of these molecules, on the other hand, are non-polar and probably have a cyclic structure.[73]

Nature of the hydrogen bond. The data on the geometry of H-complexes have been interpreted from different viewpoints. In Dyke's opinion, the configuration of H-complexes indicates that "...the hydrogen bond is essentially covalent",[73] and the experimental results show excellent agreement with the HOMO/LUMO donor–acceptor model.[86] In the latter, the H-complex is regarded as an electron donor–acceptor complex, in which the electron pair is transferred from the highest occupied molecular orbital (HOMO) of the Lewis base to the lowest unoccupied molecular orbital (LUMO) of the Lewis acid, and the maximum overlap of the HOMO and LUMO is achieved in the dimer.[73]

In the opinion of Legon and Millen,[75] however, the orientation of the molecules is determined only by the favourable orientation of their dipole and quadrupole moments, and the experimental results are successfully described by a recent electrostatic model.[87]

It should be remembered, however, that simple electrostatics, that is the attraction of charges which remain unchanged in the interaction, cannot explain the distinctive spectroscopic and chemical properties of the hydrogen bond, namely the unique increase in the intensity and decrease in the frequency of the longitudinal vibration of the proton, the non-additivity of the dipole moments of the partners, and, finally, the cooperative effect—the significant increase in the strength of alternating H-bonds. Thus simple electrostatics apparently represents an unjustified resurrection of long abandoned ideas. Naturally, simple electrostatics cannot be identified with the so-called electrostatic (more accurately, Coulombic) contribution, distinguished in the non-empirical calculation of the energy of the H-bond. It hardly appears possible, however, to isolate the corresponding contribution from the experimental values to confirm the theory directly.

Interatomic distances. The lengths of H-bonds, which until recently were known only for crystals, have now been determined for various single H-bonds in isolated gaseous dimers, including the simplest and most important. In the complexes FH.NC the length of the hydrogen bond changes in accordance with the protophilic character of the nitrile group, but this regularity is not observed in the lengths of more varied H-bonds F–H...B (Table 4). The weak bond with CO_2 is shorter than the stronger H-bonds with π-electron donors and with cyclopropane; the H...B distances change less regularly than the classical spectral characteristics of the H-bond.

Comparison of the interatomic distances provides new and convincing confirmation of the cooperative character of H-bonds; the H-bonds of the polymer chains in HF and H_2O crystals are appreciably shorter than the bonds in the dimers; the difference is 0.30 Å and 0.14 Å respectively.[73] The O–O distances in the chain crystals of formic and acetic acids (2.58 Å and 2.61 Å respectively) are also appreciably shorter than those in the heterodimers of carboxylic acids (2.67 Å); according to Dyke,[73] this decrease in the length of the H-bond in the crystal may be due to the stronger cooperative effect in the chain of H-bonds, compared with the ring. Other factors may also be responsible, however: the higher temperature of the gas and the freedom of deformation of the dimer. A cooperative effect is also observed in gaseous trimers, that is when two H-bonds are conjugated. Thus the H-bonds in the linear trimers HCN.HCN.HA are 0.107–0.030 Å shorter than those in the dimers HCN.HA, where A = F, Cl, CN, CF_3.

The increase in the A–H distance on H-bond formation has been measured accurately in a number of dimers, and it has been shown that this increase in length rises approximately linearly with increase in the strength of the H-bond.[74] Direct confirmation has been

obtained for the long-predicted Stepanov–Sheppard effect,[88,89] that is the decrease in the length of A–H...B when the stretching vibration of the proton is excited; in HCN.HF it is 0.034 Å.[74] The existence of the opposite effect, that is a decrease in the strength of the H-bond as a result of the transverse vibration of the proton (ν_B), is indicated by the opposite "shading" of the rotational structure of the ν_B sub-bands.

Energy and elasticity of the H-bond. The values of $D_0(D_e)$ that is the energies of the dissociation of a free H-complex from its ground state (from the potential minimum), have been determined for the hydrogen bond for the first time (only a few have as yet been determined); the values, given in Table 5, were found from the measured "absolute" intensity of the lines in the spectrum of the equilibrium gas. This new and fundamental information (which will probably increase), combined with the highly accurate spectral parameters of the complexes, provides a fundamentally important supplement to ordinary thermodynamic and spectral data on H-bonds (plentiful for the condensed phase, but not for the gas phase).

Table 5. Dissociation energies of hydrogen bonds, from high-resolution spectra.

H-complex	Dissociation energy[a], kcal mol^{-1}		Spectrum	Refs.
	D_0	D_e		
HCN·HF	4.51 (26)	6.23 (38)	MB	[74]
»	4.96 (5)	6.87 (11)	i.r.	[90]
HCCCN·HF	4.87 (17)	5.59 (21)	MB	[91]
CH_3CN·HF	6.23 (14)	6.93 (21)	MB	[92]
HF·HF	2.97 (11)	4.56 (28)	i.r.	[93]
HCl·HCl	1.23 (6)	2.27 (25)	i.r.	[93]

[a] D_0 and D_e—measured from the lowest level and from the potential energy minimum.

The stretching force constant of the H-bond k_σ is determined accurately from the centrifugal stretching of the H-complex from the rotational spectrum.[74] A large number of "rotational" k_σ have now been obtained (an example is given in Table 4); these values are apparently more reliable than the previous isolated determinations of ("vibrational") k_σ from the frequency of the ν_σ bands, difficult to observe, in the far infrared region of the spectrum. Far infrared spectroscopy is also developing successfully (see for example the published review†), and a significant breakthrough is possible with the appearance of tunable lasers. Because of the difference in the selection rules, the two types of spectra should usefully supplement one another.

Comparison of the published[75] values of k_σ shows a mutual proportionality of the k_σ values in corresponding series of complexes AH.B (Fig. 7), similar to the proportionality of the enthalpies of the H-bonds.[94] As in the work cited,[94] it is possible to express this mutual independence of the proton-donor (P) and electron-donor (E) functions in the H-bond of any two partners, $(AH)_i$ and B_j, as the product $(k_\sigma)_{ij} = k_{11}P_iE_j$, where k_{11} is the normalisation to the standard H-complex with $P_1 = E_1 = 1$. A key question in this extension of the product rule[94] to k_σ is whether the two P and E scales (the scale constructed from ΔH in the liquid phase[94] and the new scale constructed from k_σ for the free H-complexes) coincide. For example, the electrophilic character of hydrogen fluoride (P = 1.9) estimated from k_σ (Fig. 7) is greater than that estimated from ΔH (P = 1.5 [94]) (this is only a preliminary estimate without conclusions). In general, the new data make it possible to compare on a more reliable basis two different measures of the strength of the H-bond, namely the dissociation energy and the quasi-elastic constant.

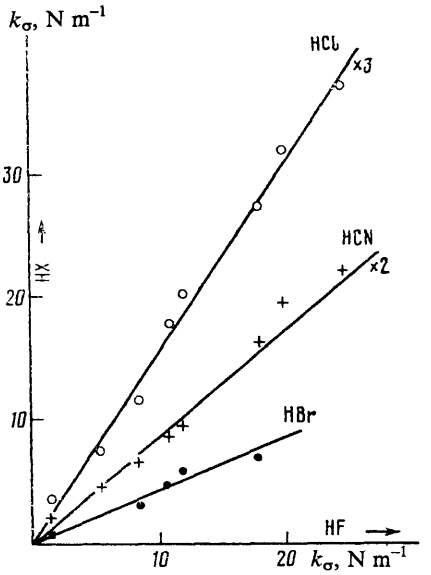


Figure 7. Relationship between the force constants of H-bonds of different proton donors HX with indentical protonophiles B in the gas phase, constructed from the data of Legon and Millen.[75]

Dipole moments. The extremely accurate dipole moment of a H-complex from measurements of the Stark effect in the microwave spectrum is the projection of μ on the prolate top axis; the total moment μ is established less accurately, because of the poor determination of the perpendicular components. For H_2S.HF, for example, the projection μ_a = 2.6239(17) D, and μ = 2.80(7) D.[73] To separate the induced moment $\Delta\mu$, it is necessary to subtract from μ_a the projections of the moments of the sub-molecules AH and B, not for the equilibrium configuration of the H-complex but with appropriate averaging with respect to the zeroth amplitudes. In spite of the difficulty of taking account of the non-rigidity of the H-complex in this way, the non-additivity of the dipole moments of the partners in the H-complex, that is the appearance of an additional excess moment $\Delta\mu$ (Table 4), has been reliably established.

†E Knozinger, O Schrems in J R Durig (Editor) *Vibrational Spectra and Structure*, Elsevier, 1987, Chapter, 3, p. 142

In some cases, the quantity $\Delta\mu$ can be attributed to the polarisation of one partner by the other, but in other cases this explanation is insufficient. For example, in $H_2S.HF$, $\Delta\mu$ is 0.2–0.6 D greater than that from the calculated polarisation and "...this contribution is very probably due to the charge transfer characteristic of the donor–acceptor model".[73]

In the particular case of the centrosymmetric protonophiles N_2 and NCCN, it is possible to estimate the redistribution of charge within the protonophile resulting from the H-bond. Movement of the two symmetrical N nuclei, identical in this case, is excluded, and the electrical asymmetry of the protonophile in the H-complex is revealed. The calculated N → N charge transfer is 0.025 e (see the paper by Legon and Millen[74] for more details). This means that not much can be expected from the traditional estimation of the values of $\Delta\mu$ for H-complexes in solutions from a simple vector scheme. The model of a "rigid" complex in this case is even less favourable, since at room temperature the deformations are much greater than in a cold molecular beam.

V. Solvation of the H-bond

The influence of a solvent on neutral H-bonds is qualitatively similar to its influence on ionic bonds, but is weaker than in the case of acid–base equilibria; in particular, it does not reverse the sequences of the strengths of acids and bases. This is partly due to the narrower range of liquids, not including associated liquids (water etc.). In addition, the magnitude of the influence differs considerably.[95] Non-polar $(AH)_n$ rings remain almost unchanged on going from the gas phase to solution; the liquid environment has no significant influence on the H-bond in this extreme case of the formation of a non-dipolar associate. At the same time, polar dimers AH.B undergo fairly marked changes in solution; the solvation effect may be greater than the primary effect of free H-bond formation. Finally, in the extreme case where the strength of the H-bond of the polar dimer AH.B is close to its limit, solution or condensation leads qualitative changes, bringing about the transformation of the molecular complex AH.B into the "conjugate" complex $A^-.H^+B$ or into the salt. The subsequent discussion deals mainly with the non-ionising solvation of the H-bond, and ionising solvation is mentioned only briefly.

Available data on the energy of H-bonds in the gas phase are insufficient for a reliable comparison with their energy in the more extensively studied liquid phase. A clearer picture of the influence of the medium on the H-bond is given by an analysis of the infrared spectra. Infrared spectroscopic data show that the solvation of a complex always leads to an increase in the strength of the H-bond.[94–96] According to these data, the transfer of a gaseous associate to the condensed phase: 1) lowers the frequency of the stretching vibrations ν_S (Table 6), 2) increases the frequency of the deformations ν_B, and 3) increases the absolute intensity of the vibrations ν_S. Each of these changes is a reliable spectral indication of an increase in the strength of the H-bond.[83,97] They all show quantitative consistency, that is they correspond to the same increase in the strength of the H-bond.[95] Thus dissolving free $FH.NCCH_3$ in acetonitrile lowers the ν_S frequency by 350 cm^{-1} (Table 6), and simultaneously displaces the ν_B band from 587 cm^{-1} to 750 cm^{-1}.[96] According to published correlations,[97] both displacements correspond to an increase in the energy of the H-bond from 5 kcal mol^{-1} to 8 kcal mol^{-1}. When gaseous $(CF_3)_2CHOH.NH_3$ is dissolved in dichloroethane, the intensity of ν_S increases by 10^5 cm $mmol^{-1}$;[95] this corresponds to an increase in the energy of the H-bond by ~4 kcal mol^{-1}, and is also consistent with the increase in $\Delta\nu$ from 500 cm^{-1} to 970 cm^{-1} (Table 6).

Table 6. Displacement $\Delta\nu = \nu_0^0 - \nu$ of the ν_S bands for various H-complexes in the gas phase and in liquids (solution in CCl_4 and in the liquid base B).[80,95,98–102]

Complex AH.B[a]	Δν, cm⁻¹			Complex AH.B[a]	Δν, cm⁻¹		
	gas	CCl_4	B		gas	CCl_4	B
CH_3OH.	(3682)[b]			$(CF_3)_3COH$.	(3630)		
Dimer	90	154	200[c]	Nitrile	275	390	480
Polymer	300	342	340	Water	280	372	—
Nitrile	58	107	141	Oxiran	355	440	—
Ether	123	184	175	m-Ether	440	565	—
Acetone	90	156	166	DMSO	610	820	1010
Pyridine	210	320	425	Pyridine	900	1150	1450
Ammonia	177	310	375[d]	Ammonia	750	—	—
TEA	370	460	438	CF_3COOH.	(3589)		
CF_3CH_2OH.	(3657)			Dimer	510	560	—
Nitrile	104	166	203	HF.	(3961)		
Oxiran	141	207	—	Dimer	80	—	—
Ether	220	268	267	Polymer	500	520	550
THF	220	289	312	Nitrile	300	485	650
Pyridine	370	530	580	m-Ether	500	—	740
Ammonia	310	540	—	Ether	575	740	750
$(CF_3)_2CHOH$.	(3646)			HCl.	(2886)		
Nitrile	148	250	326	Nitrile	155	275	335
Water	150	260	—	m-Ether	316	486	—
Oxiran	235	320	—				
Ammonia	500	760	970[d]				

[a] The names of the bases B are abbreviated: nitrile = acetonitrile; ether and m-ether = diethyl and dimethyl ethers; TEA = triethylamine; [b] the frequencies ν_0^0 of free AH in the gas phase are given in brackets; [c] in chloroform; [d] in dichloroethane.

The decrease in the ν_S wavenumber in solution has been most extensively studied; it was first observed by Allerhand and Schleyer[98] (although the authors cited did not attribute it to an increase in the strength of the H-bond), and was confirmed in subsequent experiments[95,96,99–109] and is shown in Table 6. The solvation effect depends not so much on the polarity of the medium as on the polarity of the associate and the dimensions of the partner molecules.[95] The solvation displacements $\Delta\nu_S = \nu_S(\text{gas}) - \nu_S(\text{solution})$ in highly polar solvents (acetonitrile, DMSO) is only ~70% greater than $\delta\nu_S$ in the "inert" CCl_4, and in a given medium the displacements for polar complexes are ten times those for non-polar complexes (Table 6).

The medium has its weakest influence on non-dipolar cyclic associates, that is $(RCOOH)_2$, $(ROH)_4$, and $(HF)_6$.[95] The displacement of their ν_S band in solution is only 10–15% of the displacement $\Delta\nu^0$ in the gas, and the spectra of $(RCOOH)_2$ are similar to the gas-phase spectra not only in solution but also in crystals.[103–105] A surprising feature is that the ν_S bands of the gaseous cyclic formations $(CH_3OH)_4$ and $(HF)_6$ also undergo almost no displacement in liquid methanol and hydrogen fluoride (Table 6). In these associated liquids, the original rings undoubtedly are not preserved, and undergo rearrangement to give polymeric chains $(AH...)_n$, but the change in the long-range order of the H-bonds

does not influence the H-bond itself. This is consistent with the recently observed fact[107] that the infrared spectra of associated alcohols is independent of their concentration in solution (above ~1 M).

This absence of change in the spectra and hence in the H-bonds in $(AH...)_n$ is observed with a marked increase in the dielectric constant ε of the medium from 1 in the gas to 85 in liquid HF. Thus ε does not influence the H-bond, and correlations between its strength and ε are not significant. A similar lack of sensitivity to the environment is shown by the non-dipolar centrosymmetric ion $(FHF)^-$; in different media from water to the crystal, the frequency $\nu = 2500$ cm^{-1} changes by only $\pm 2\%$.[107,108] On the other hand, the formally symmetrical ion $(ClHCl)^-$ is sensitive to its environment.[109]

In contrast to the non-dipolar $(AH)_n$, the strongest interaction with a solvent is undergone by the highly polar dimers AH.B of small molecules (NH_3, CH_3CN, HF, CH_3OH). The wavenumber displacements $\Delta\nu_S$ of these dimers are much greater in the liquid phase, and are sometimes more than twice those for the gas phase, so that the solvation displacement reaches 100–140% of the primary displacement $\Delta\nu^0$, and its absolute magnitude reaches about 500 cm^{-1} (Table 6). Thus the effect of solvation of the H-complex by an aprotic solvent may be greater than the primary effect of H-bond formation. In these cases, the conclusions that the H-complex is independent of the environment and that a local H-bond A–H...B is formed are extremely approximate.

The solvation is stronger, the more polar the partner molecules in the complex and the smaller their size.[95] Thus for the complexes of NH_3 and $N(C_2H_5)_3$ with methanol (Table 6), the displacement $\Delta\nu$ in CCl_4 solution increases by 75% and 25% respectively. The "exposed" ammonia is solvated more strongly than triethylamine, which has undergone "intramolecular solvation". This means, in particular, that the electronic effects of the substituents are greatest in the gas and are levelled out in the liquid, to an extent which is greater, the more active the medium. Thus the picture of the change in the acid–base equilibria in solution examined above (section II) is partly repeated. The factors *P* and *E* characterising the ability to form a H-bond should also depend on the medium, so that, in particular, the proposed[94] extrapolation of the values of *P* and *E* from the solution to the gas is inaccurate. Thus in the gas phase, ammonia is a weaker electron donor than pyridine, whereas in CCl_4 solution the two compounds are comparable in this respect (see $\Delta\nu$ in Table 6), and in a more polar medium, reversal of the relative strengths of these compounds should be expected.

An environment of an H-bond which is similar to it increases its strength by a further factor of 2 compared with that given by the maximum solvation of a polar dimer A–H...B by an aprotic solvent. The change from the free dimer A–H...AH to the polymer $(AH...)_n$ (in the gas or in the liquid) increases $\Delta\nu$ by a factor of 4–6, from 90 cm^{-1} to 300 cm^{-1} and 500 cm^{-1} for methanol and hydrogen fluoride respectively (Table 6); the enthalpy of the H-bond also shows a corresponding increase, from ~3 kcal mol^{-1} in the dimers to 5.5 kcal mol^{-1} and 7 kcal mol^{-1} in the polymers.[83,93,97]

In this long-familiar cooperative effect, which was first proposed to explain the characteristics of liquid water,[110] the group AH, which gives up its proton for H-bond formation, attracts a neighbouring proton more strongly, and by accepting the neighbouring proton it gives up its own proton more readily. Thus charge transfer (polarisation) in a single H-bond AH...A–H partly extends to the sequence $(A–H...)_n$ formed. The effect is extinguished comparatively rapidly along the chain; the frequency ν_S decreases considerably on going from the dimer to the tetramer of an alcohol, and the subsequent multimers are spectrally indistinguishable. The cooperative effect (the non-additivity of the H-bonds) cannot be attributed to the sum of the paired interactions, but the effect is reproduced by calculation of triple interactions.[77] It is the cooperative effect that makes chains of alternating H-bonds such widely encountered structural elements in associated liquids and crystals, in particular those of alcohols and carbohydrates.[83,111]

The contrast between the solvation of polar and non-polar H-complexes indicates additional electrostatic polarisation of the dipolar H-complex by its environment. It resembles the "reactive field effect" in the Onsager model, but probably only outwardly. The only significant interaction is that with the closest solvation layer, which is not characterised by the volume macroparameters of the medium, including the value of ε.

The absolute magnitude of the solvation effect increases regularly with increase in the strength of the H-bond, but changes little relative to the latter.[95] Thus the weak methanol dimer and the strong hetero-dimer $(CF_3)_3COH.NC_5H_5$ in the gas phase are characterised by displacements $\Delta\nu_S$ = 90 cm^{-1} and 900 cm^{-1} respectively, which in solution increase to 150–200 cm^{-1} and 1200–1500 cm^{-1} (Table 6). Further increase in the "polarisation" of AH.B probably leads finally to proton transfer to give the conjugate complex (ion pair) $A^-.H^+B$, and then the separated ion pair $A^-||H^+B$. The values of ΔH also increase regularly,[112] but the changes in the spectrum are not regular, and on the contrary change sign sharply at the hypothetical point corresponding to the "quasi-symmetrical" H-bond A..H...B.[113,114] This phenomenon is not observed in free H-complexes. On the contrary, gaseous hydrochloric acid contains (in addition to free molecules) only the molecular complex $H_2O.HCl$,[74] and, similarly, the vapours over the ionic salts NH_4CN or NH_4Cl contain the molecular complexes $H_3N.HCN$ [114] or $H_3N.HCl$.‡ Intra-complex proton transfer in $H_3N.HCN$ is convincingly excluded by the detection of the semi-deuteriated complex $H_3N.DCN$ in the infrared spectrum in the gas phase (by the usual method).[114] Free associates apparently exist only as the molecular complexes AH.B; ion pairs do not exist in the free form, and are stabilised only by intermolecular interaction with the environment. Each acid AH possibly has its own stability limit or, in other words, proton transfer threshold. Thus hydrogen fluoride retains its proton both in water (pK = 3.45) and in strong bases[96] with a H-bond energy of not less than 15 kcal mol^{-1} (estimated from spectral data[96]). The energies of the H-bonds formed by organic OH acids may also reach 11–15 kcal mol^{-1} before the base is protonated. The proton transfer threshold for HCl, HBr, and CH-acids, however, does not exceed 5–7 kcal mol^{-1}, and molecular complexes of these acids with a higher bond energy are not known.

The energies of solvation of H-bonds can be considered. The enthalpies of dimerisation of carboxylic acids decrease considerably in solution,[83] but this fact cannot be generalised, the conclusion cannot be extended to polar complexes AH.B, and this cannot be regarded as a decrease in the strength of the H-bond in the dimer (as is sometimes done). The decrease in ΔH is due entirely to the solvation of the monomer (see below), and does not contradict what has been said above. The ΔH values measured in different media relate to different states of not only the H-complex but also the "free" partners, and spectral estimates of the H-bond in these media

‡ A C Legon, D J Millen *Chem. Phys. Lett.*, 1988, **147** 484

implicitly assume that there is no change in the state of the free partners; this difference in the states of the products of dissociation of the H-bond must be borne in mind.

The usual notation for complex formation AH + B ⇄ AH.B is applicable only to the gas phase, and does not take account of the influence of the medium. The qualitative model of the effect of the medium S includes two opposed factors: 1) to combine the two solvated partners AH(S) and B(S) into the H-complex it is necessary to "squeeze out" part of the solvation layer of each partner, leading to a decrease in ΔH, and 2) the overall solvation layer "compresses; the H-complex, increasing ΔH in the medium S. The overall effect of the solvent may have either sign, although the former (decrease) predominates most frequently. According to Iogansen,[94] the "desolvation" of the AH molecule involves the replacement of the weak H-bond (H-interaction) with the solvent by a stronger bond with B. The reaction in solution should therefore be described as follows:

$$AH \cdot S + B(S) \rightleftarrows AH \cdot B(S) + S, \quad (9)$$

where (S), as usual, denotes the "S environment" (the interaction B(S) is not taken into account, since there is no specific model). The solvent SD is regarded as a direct participant in reaction (9); it makes an additive (negative) contribution to the enthalpy of the reaction which is proportional to its electron-donor power E_S^0.[94] Appreciable electron-donor power is shown by all compounds up to the extremely inert perfluorohydrocarbons; the noble gases also form H-bonds with strong electrophiles AH (see above). CCl_4, traditionally used in infrared spectroscopy, is far from the most "inert";[115,116] for example, the energy of the H-bond which it forms with HF is ~2 kcal mol^{-1} (ν_S is displaced by 110 cm^{-1}).

Thus according to the model, the decrease in ΔH in solution is related to the fact that complex formation to give AH.B unavoidably breaks down the H-interaction AH.S. The magnitude of the latter is proportional to the product of two independent parameters:[94] the proton-donor power of the acid AH (P_i) and the electron-donor power of the solvent molecule S (E_S^0):

$$\delta_1 \Delta H = 6.4 P_i E_S^0. \quad (10)$$

Eqn. (10) predicts that the solvent will make an additive contribution to the enthalpy of reaction (9). The strength of the H-interaction AH.S can be determined not only using Eqn. (10) but also from the increase in the intensity of the ν_S infrared band in solution (compared with the gas phase AH), determined by "spectral calorimetry".[97] The direct determination of $\delta_1 \Delta H$ by the usual methods is difficult, because of the need to distinguish the "non-specific" interaction.

The increase in the strength of the H-bond of the dimer AH.B as a result of the polarising action of the medium can be estimated only from the ν_S frequencies. The extension to the solvation displacements of the published correlations[97] (which assumes that they are also applicable in the gas phase) leads to the expression

$$\delta_2 \Delta H = 0.055 \delta \nu_s / -\Delta H^0. \quad (11)$$

The accuracy of the prediction (11) must be examined carefully, because of the limitations of the correlations[97] and their "transfer" to the gas; independent data are consistent with Eqn. (11), but are few in number.

If the action of the solvent on an associate is slight, as with $(RCOOH)_2$, Eqn. (10) describes the total effect of the solvent. Thus the changes in $-\Delta H$ for the dimerisation of trifluoroacetic acid in solution, calculated using Eqn. (10) coincide with the measured values (Table 7), that is the H-interaction is the main component of the solvation of the acid monomer; the van der Waals interaction is weak and approximately the same for different solvents (see Table 7). The measured and calculated values of $-\Delta H$ for the dimerisation of other acids in different solvents show similar agreement;[105] in benzene, the energy of solvation of the "free" acid reaches 4 kcal mol^{-1}.

Table 7. Enthalpies of dimerisation and solvation of trifluoroacetic acid in different media, kcal mol^{-1}.

Medium	Dimerisation		Solvation of the monomer	
	measured (Ref.117)	calculated from Eqn. (10)	measured (Ref.117)	calculated from Eqn. (10)[a]
Gas	—	(7.0)[b]	—	—
Cyclohexane	5.8 (3)	5.72	2.3 (4)	1.28
Carbon tetrachloride	4.6 (2)	5.13	3.4 (6)	1.87
Benzene	(3.7)[c]	2.94	5.2 (6)	4.06
1,2-Dichloroethane	3.5 (4)	3.10	5.3 (6)	3.90

[a] Only H-interaction; [b] accepted value; [c] estimated by analogy.[117]

An example can be used to illustrate the increase in the strength of a H-bond in the non-polar CCl_4, or more accurately the positive contribution δ_2 calculated using Eqn. (11) from the experimental frequencies in Table 6. For three typical dimers, namely the non-polar $(RCOOH)_2$ and the polar methanol.ether and (smaller) methanol.ammonia, this increase in strength has values of about 0.3, 0.8, and 1.5 kcal mol^{-1} respectively, or 4, 25, and 40% of the energy of complex formation in the gas phase. With the opposed contribution δ_1, the expected change in $-\Delta H$ is appreciably negative in the first case (Table 7), close to zero in the second, and positive in the third (0.7 kcal mol^{-1}). In polar media, the same increase in the strength of the H-bond δ_2 may be appreciably greater, reaching 60–70%. Finally, the greatest increase in the strength of the H-bond by 3–4 kcal mol^{-1} or more than 100% is observed in an associated liquid, or more accurately a polymeric associate (see above). The results of direct measurements of ΔH in undiluted polar bases in general are consistent with the above spectral estimates. Although data have been obtained for the unique case of self-associates, the most interesting and illuminating data for the highly polar H-complexes of small molecules in different environments have not been obtained.

VI. Summary

Thus the analysis of published data has shown that the variety of theoretical and experimental approaches to the solution of the problem of the influence of the medium on acid–base equilibria not only reveals definite qualitative regularities but also makes it possible to take quantitative account of the influence of specific solvation. Considerable progress in the understanding of the role of hydrogen bonds can be expected from the study of ionic dimers and clusters in the gas phase and in relatively inert media. Further studies of the solvation of neutral H-complexes are required; it may be hoped

that the observed similarity in the influence of solvation on hydrogen bonds and acid–base equilibria will be described quantitatively. Important information on the role of the medium will be provided by a more extensive combination of quantum-chemical calculations for dimers and small clusters with the methods of molecular dynamics and Monte Carlo methods, which make it possible to take account of the contribution of hundreds of solvent molecules.

An important direction of future studies will probably be the development of a single approach to charged and neutral associates. The "complementary nature" of the information makes their comparison difficult; for ion–molecule complexes, a large amount of data has been obtained on their energy of formation, whereas for neutral complexes, a large amount of data has been obtained on their structure and spectral properties.

The task of research workers in physical organic chemistry and various branches of spectroscopy should be to build bridges between acid–base equilibria in the gas phase, molecular and ionic hydrogen bonds, and their solvation in different media.

While the present manuscript was being prepared for publication, a number of new papers which must be included were published.

Data on the energy of anionic H-complexes (O^-, Cl^-, N^-, S^-)[118] and complexes of carbanions,[119] and on their hydration in the gas phase, have been published. Two papers[120,121] have been devoted to the application of previously examined approaches to biological systems (proteins and enzymes). Finally, an experimental and theoretical study of the gas-phase CH-acidity in aromatic and heterocyclic compounds has been carried out.[122]

A linear relationship has been established[123] between the proton and carbon basic strength ($CH_3A \rightarrow CH_3^+ + A^-$) in the gas phase. The observed deviations in an aqueous medium have been analysed. Experimental methods and statistical thermodynamic calculations have been used to study isotopic effects in the hydration of gas-phase ions, and it has been concluded that "light" water coordinates preferentially to both cations and anions.[124] Data have been published[125] on the acidity of a number of radical-cations in the gas phase and in DMSO, and the influence of solvation on the $pK_{HA}^{+\cdot}$ values has been discussed. A method has been proposed[126] for the theoretical calculation of pK_a for organic compounds in water by a combination of non-empirical and Monte Carlo calculations.

Without attempting to list the large number of gaseous complexes for which new studies have been carried out, the development of spectra studies may be noted. These are being extended to multimers (clusters) and in particular to linear homo- and hetero-trimers,[127] where the cooperative effects of two "conjugated" H-bonds A–H...A–H...A–H have been observed. The isomerism of the structure of molecular complexes, that is the two minima of the potential energy of the relative orientation of the partners AH and B, has been more effectively studied. For example, in addition to the T-shaped complex $HCN.CO_2$ with an N...C bond, the less stable complex NCH...OCO has been observed (see the paper by Klots and co-workers[128] and references therein).

In an analysis of accurate spectral data on interatomic distances, Legon and Millen[129] revealed the "course" of the isotopic effect in the H-bond. The replacement of H by D decreases the zero-point amplitudes of hydrogen, both tranverse and longitudinal; the first increases, and the second decreases, the strength of the H-bond (as in the excitation of the vibrations ν_B and ν_S). With increase in the strength of the H-bond, the first contribution, which changes in the same sense as the "flexibility" of the H-bond, decreases, whereas the second, which changes in the same sense as the anharmonicity of ν_S, increases. Thus the overall isotopic effect may change sign: the deuterium bond is stronger than the proton bond for weak H-bonds, but is weaker in the case of strong H-bonds.

The new far infrared laser spectroscopy has demonstrated its promising possibilities in the interpretation of the complex rotational–tunnel spectrum of the water dimer.[130] As a result of the observation of the ν_B vibrations, it is also applicable in principle to cyclic non-dipolar (so that there is no rotational spectrum) associates — dimers and multimers $(AH)_n$.

References

1. M I Kabachnik *Usp. Khim.*, 1979, **48** 1523 [English translation in *Russ. Chem. Rev.*, 1979(9)]
2. R W Taft *Progr. Phys. Org. Chem.*, J W Wiley, New York, 1983, **14** 247
3. L M Epshtein *Usp. Khim.*, 1979, **48** 1600 [English translation in *Russ. Chem. Rev.*, 1979(9)]
4. L M Epshtein *Vodorodnaya Svyaz'* (The Hydrogen Bond), Izd. Nauka, Moscow, 1981, p. 255
5. L N Bykova, S I Petrov *Usp. Khim.*, 1970, **39** 1631 [English translation in *Russ. Chem. Rev.*, 1970(9)]
6. L N Bykova, S I Petrov *Usp. Khim.*, 1972, **41** 2065 [English translation in *Russ. Chem. Rev.*, 1972(11)]
7. F G Bordwell, J C Branca, D L Hughes, W N Olmstead *J. Org. Chem.*, 1980, **45** 3311
8. A G Kozachenko, E I Matrosov, M I Kabachnik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2440
9. M K Chantooni, I M Kolhoff *J. Phys. Chem.*, 1976, **80** 1306
10. F G Bordwell, R J McCallum, W N Olmstead *J. Org. Chem.*, 1984, **49** 1424
11. B A Korolev *Zh. Obshch. Khim.*, 1980, **50** 841
12. K M Dyumaev, B A Korolev *Usp. Khim.*, 1980, **49** 2065 [English translation in *Russ. Chem. Rev.*, 1980(11)]
13. R P Bell *The Proton in Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1977, p. 83
14. N S Golubev, G S Denisov, V M Shraiber *Vodorodnaya Svyaz'* (The Hydrogen Bond), Izd. Nauka, Moscow, 1981, p. 212
15. G S Denisov, A I Kul'bida, V M Shraiber *Molekulyarnaya Spektroskopiya* (Molecular Spectroscopy), Izd. Leningrad. Gos. Univ., Leningrad, 1982, p. 123
16. S E Odinokov *Doctoral Thesis,* Moscow State University, Moscow, 1983
17. A Streitwieser, E Juaristi, L L Nebenzahl *Comprehensive Carbanion Chemistry,* Elsevier, New York, 1980, Ch. 7
18. O A Reutov, I P Beletskaya, K P Butin *CH-kisloty* (CH-Acids), Izd. Nauka, Moscow, 1980, Chapter 1
19. D A Bors, M J Kaufman, A Streitwieser *J. Am. Chem. Soc.*, 1985, **107** 6975
20. M J Kaufman, S Gronert, A Streitwieser *J. Am. Chem. Soc.*, 1988, **110** 2829, 2843
21. F G Bordwell, G E Drucker, N H Andersen *J. Am. Chem. Soc.*, 1986, **108** 7310
22. T I Lebedeva, E S Petrov, M I Terekhova, A I Shatenshtein *Dokl. Akad. Nauk SSSR,* 1975, **225** 357
23. E S Petrov, M I Terekhova, A I Shatenshtein *Zh. Obshch. Khim.*, 1974, **44** 1118
24. T I Lebedeva, E S Petrov, A I Shatenshtein *Zh. Org. Khim.*, 1977, **13** 905

25. I S Antipin, A N Vedernikov, A I Konovalov *Dokl. Akad. Nauk SSSR,* 1985, **283** 139
26. I S Antipin, A N Vedernikov, A I Konovalov *Zh. Org. Khim.,* 1985, **21** 1355; 1986, **22** 446; 1989, **25** 3
27. S G Lias, J F Liebman, R D Levin *J. Phys. Chem. Ref. Data,* 1984, **13** 695
28. *Gas Phase Ion Chemistry,* Acad. Press, New York, 1979
29. I A Koppel' *Reakts. Sposobn. Org. Soed.,* 1987, **24**(3) (87) 261
30. M Fujio, R T McIver, R W Taft *J. Am. Chem. Soc.,* 1981, **103** 4017
31. E M Arnett, B Chawla, L J Bell, et al. *J. Am. Chem. Soc.,* 1977, **99** 5729
32. E M Arnett, B Chawla *J. Am. Chem. Soc.,* 1979, **101** 7141
33. M M Meot-Ner, L W Sieck *J. Am. Chem. Soc.,* 1983, **105** 2956
34. A D Headley *J. Am. Chem. Soc.,* 1987, **109** 2347
35. Y K Lau, P Kebarle *Can. J. Chem.,* 1981, **59** 1515
36. M Taagepera, D J De Frees, W J Hehre, R W Taft *J. Am. Chem. Soc.,* 1980, **102** 424
37. G Caldwell, M D Roozeboom, J P Kiplinger, J E Bartmess *J. Am. Chem. Soc.,* 1984, **106** 4660
38. W J Hehre, C F Pau, A D Headley, et al. *J. Am. Chem. Soc.,* 1986, **108** 1711
39. E M Arnett, L E Small, R T McIver, J S Miller *J. Am. Chem. Soc.,* 1974, **96** 5638
40. S Ikuta, P Kebarle, G M Bancroft, et al. *J. Am. Chem. Soc.,* 1982, **104** 5899
41. Y K Lau, P Kebarle *J. Am. Chem. Soc.,* 1976, **98** 7452
42. S K Pollack, J L Delvin, K D Summerhays, R W Taft *J. Am. Chem. Soc.,* 1977, **99** 4583
43. Y K Lau, K Nishizawa, A Tse, et al. *J. Am. Chem. Soc.,* 1981, **103** 6291
44. B E Mills, R L Martin, D A Shirley *J. Am. Chem. Soc.,* 1976, **98** 2380
45. R S Brown, A Tse *J. Am. Chem. Soc.,* 1980, **102** 5222
46. R V Hodges, F A Houle, J L Bauchamp, et al. *J. Am. Chem. Soc.,* 1980, **102** 932
47. J Catalan, O Mo, P Pezez, M Yañez *J. Chem. Soc., Perkin Trans. II,* 1982, 1409
48. J C Bollinger, R Houriet, C W Kern *J. Am. Chem. Soc.,* 1985, **107** 5352
49. J Catalan, J L G De Paz, M Yanez *J. Am. Chem. Soc.,* 1988, **110** 2699
50. R Yamdagni, P Kebarle *J. Am. Chem. Soc.,* 1973, **95** 3504
51. W R Davidson, J Sunner, P Kebarle *J. Am. Chem. Soc.,* 1979, **101** 1675
52. P Kebarle, W R Davidson, M A French, et al. *Discuss. Faraday Soc.,* 1977, **69** 220
53. J W Larson, T B McMahon *J. Am. Chem. Soc.,* 1983, **105** 2944
54. J W Larson, T B McMahon *J. Am. Chem. Soc.,* 1984, **106** 517
55. G W Caldwell, M D Rozeboom, J P Kiplinger, J E Bartmess *J. Am. Chem. Soc.,* 1984, **106** 4661
56. J W Larson, T B McMahon *J. Am. Chem. Soc.,* 1987, **109** 6230
57. M M Meot-Ner *J. Am. Chem. Soc.,* 1984, **106** 1257, 1265
58. C V Speller, M M Meot-Ner *J. Phys. Chem.,* 1985, **89** 5217
59. M M Meot-Ner, L W Sieck *J. Phys. Chem.,* 1985, **89** 5222
60. M M Meot-Ner, L W Sieck *J. Am. Chem. Soc.,* 1986, **108** 7525
61. T B McMahon, P Kebarle *J. Am. Chem. Soc.,* 1986, **108** 6502
62. P J Desmeules, L C Allen *J. Chem. Phys.,* 1980, **72** 4731
63. J Gao, D S Garner, W L Jorgensen *J. Am. Chem. Soc.,* 1986, **108** 4784
64. J E Del Bene, M J Frisch, J A Pople *J. Phys. Chem.,* 1985, **89** 3669
65. T Zeegers-Huyskens *J. Mol. Struct.,* 1986, **135** 93
66. W R Davidson, J Sunner, P Kebarle *J. Am. Chem. Soc.,* 1979, **101** 1675
67. P Kebarle, W R Davidson, J Sunner, S Meza-Hojer *Pure Appl. Chem.,* 1979, **51** 63
68. P Kebarler *Ann. Rev. Phys. Chem.,* 1977, **28** 455
69. Y K Lau, P P S Soluja, P Kebarle *J. Am. Chem. Soc.,* 1980, **102** 7429
70. S Yamabe, T Minato, K Hirao *Can. J. Chem.,* 1983, **61** 2227
71. C E Klots *J. Phys. Chem.,* 1981, **85** 3585
72. J Bromilow, J L M Abboud, C B Lebrilla, et al. *J. Am. Chem. Soc.,* 1981, **103** 5448
73. T R Dyke *Top. Curr. Chem.,* 1984, **120** 85
74. A C Legon, D J Millen *Chem. Rev.,* 1986, **86** 635
75. A C Legon, D J Millen *Acc. Chem. Res.,* 1987, **20** 39
76. K I Peterson, G T Fraser, D D Nelson, W Klemperer *Intermolecular Interactions Involving First Row Hydrides* (Edited by R J Bartlett, D Reidel) Publ. Co., New York, 1985, p.217
77. A Beyer, A Karpfen, P Schuster *Top. Curr. Chem.,* 1984, **120** 1
78. R K Thomas *Proc. Roy. Soc. (London),* 1971, **325A** 133
79. R K Thomas *Proc. Roy. Soc. (London),* 1975, **344A** 579
80. D J Millen *J. Mol. Struct.,* 1983, **100** 351
81. A V Iogansen *Izv. Akad. Nauk SSSR, Ser. Fiz.,* 1989, **53** 1741
82. N D Sokolov, V P Sakun *Sovremennye Problemy Kvantovoi Khimii* (Present-Day Problems in Quantum Chemistry), Izd. Nauka, Leningrad, 1987, p. 57
83. G C Pimentel, A L McClellan *The Hydrogen Bond* (Translated into Russian), Izd. Mir, Moscow, 1964
84. L Schriver, A Burneau, J P Perchard *J. Chem. Phys.,* 1982, **77** 4926
85. G P Ayers, A D E Pullin *Spectrochim. Acta,* 1976, **32A** 1629
86. K C Janda, J M Steed, S E Novick, W Klemperer *J. Chem. Phys.,* 1977, **67** 5162
87. A D Buckingham, P W Fowler *Can. J. Chem.,* 1985, **63** 2018
88. B I Stepanov *Zh. Fiz. Khim.,* 1945, **19** 507; 1946, **20** 408
89. N Sheppard *Hydrogen Bonding* (Edited by D Hadzi), Pergamon Press, London, 1958, p. 85
90. B A Wofford, M E Eliades, S G Lieb, J W Bevan *J. Chem. Phys.,* 1987, **87** 5674
91. A C Legon, D J Millen, H M North *J. Chem. Phys.,* 1987, **86** 2530
92. A C Legon, D J Millen, H M North *Chem. Phys. Lett.,* 1987, **135** 303
93. A S Pine, B J Howard *J. Chem. Phys.,* 1986, **84** 590
94. A V Iogansen *Teor. Eksp. Khim.,* 1971, **7** 302
95. A V Iogansen *Dokl. Akad. Nauk SSSR,* 1987, **297** 1151
96. M Couzi *Ph. Doct. These.,* Bordeaux, 1970
97. A V Iogansen *Vodorodnaya Svyaz'* (The Hydrogen Bond), Izd. Nauka, Moscow, 1981, p. 112
98. A Allerhand, P Schleyer *J. Am. Chem. Soc.,* 1963, **85** 371
99. I H Reece, R L Werner *Spectrochim. Acta,* 1968, **24A** 1271
100. A V Iogansen, G A Kurkchi, V M Furman, et al. *Zh. Prikl. Spektrosk.,* 1980, **33** 302
101. A V Iogansen, G A Kurkchi, O V Levina *Zh. Prikl. Spektrosk.,* 1973, **18** 676
102. T A Iskanderov, Ya M Kimel'fel'd, E M Smirnova, A V Iogansen, et al. *Optika i Spektrosk.,* 1986, **61** 988
103. S Bratoz, D Hadzi, N Sheppard *Spectrochim. Acta,* 1956, **8** 249

104. M Haurie, A Novak *J. Chim. Phys. Phys. Chim. Biol.*, 1965, **62** 137
105. A A Mashkovskii, V A Yakina, V P Glazunov, S E Odinokov *Zh. Prikl. Spektrosk.*, 1978, **28** 724
106. J N Finch, E R Lippincott *J. Phys. Chem.*, 1957, **61** 894
107. E Spinner *Austr. J. Chem.*, 1977, **30** 1167
108. C J Chunnilall, W F Sherman *J. Mol. Struct.*, 1982, **80** 121
109. J C Evans, G Y-S Lo *J. Phys. Chem.*, 1966, **70** 11
110. H S Frank, W Y Wen *Discuss. Faraday Soc.*, 1957, **24** 133
111. G A Jeffrey, S Takagi *Acc. Chem. Res.*, 1978, **11** 264
112. E N Gur'yanova, I P Gol'dshtein, T I Perepelkova *Usp. Khim.*, 1976, **45** 1568 [English translation in *Russ. Chem. Rev.*, 1976(10)]
113. S E Odinokov, A A Mashkovskii, V P Glazunov, A V Iogansen, et al. *Spectrochim. Acta, Part A*, 1976, **32** 1355
114. W J Jones, R M Seel, N Sheppard *Spectrochim. Acta, Part A*, 1969, **25** 385
115. D N Shchepkin *Optika i Spektrosk.*, 1965, **19** 709
116. A V Iogansen, E V Broun *Optika i Spektrosk.*, 1966, **20** 42
117. S D Christian, T L Stevens *J. Phys. Chem.*, 1972, **76** 2039
118. M M Meot-Ner *J. Am. Chem. Soc.*, 1988, **110** 3854
119. M M Meot-Ner *J. Am. Chem. Soc.*, 1988, **110** 3858
120. M M Meot-Ner *J. Am. Chem. Soc.*, 1988, **110** 3071
121. M M Meot-Ner *J. Am. Chem. Soc.*, 1988, **110** 3075
122. M M Meot-Ner, S A Kafafi *J. Am. Chem. Soc.*, 1988, **110** 6297
123. J I Brauman, Ch Ch Hau *J. Am. Chem. Soc.*, 1988, **110** 5611
124. J W Larson, T B McMahon *J. Am. Chem. Soc.*, 1988, **110** 1087
125. F G Bordwell, J P Cheng *J. Am. Chem. Soc.*, 1989, **111** 1792
126. S Jorgensen, M Briggs *J. Am. Chem. Soc.*, 1989, **111** 4190
127. R S Ruoff, T I Emilsson, C Chuang, et al. *J. Chem. Phys.*, 1989, **90** 4069; 1988, **89** 138
128. T D Klots, R S Ruoff, H S Gutowsky *J. Chem. Phys.*, 1989, **90** 4216
129. A C Legon, D J Millen *Chem. Phys. Lett.*, 1988, **147** 484
130. K L Busarow, R C Cohen, G A Blake, et al. *J. Chem. Phys.*, 1989, **90** 3937; 1988, **89** 1268