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The structure and vibrational spectra of proton solvates in solution

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Contents

I.	Introduction	901
II.	The origin of the hypothesis that the H_3O^+ ion is the simplest stable proton hydrate	901
III.	The hydroxonium ion in the solid phase	902
IV.	The hydroxonium ion in the liquid phase	902
V.	The proton dihydrate $H_5O_2^+$	903
VI.	The $H_5O_2^+$ ion in solutions	904
VII.	The continuous absorption in the IR spectra of solutions of acids. Initial interpretation	905
VIII.	Differentiation of the spectra of proton disolvates from the spectra of solutions	906
IX.	Calculation of the IR spectra of proton disolvates	907
X.	Interpretation of the continuous absorption in the IR spectra of solutions of acids and strong bases	908
XI.	The structure of the solvated proton and the catalytic properties of acids	909
XII.	Conclusion	910

Abstract. The experimental and theoretical studies on the structure and properties of the simple stable proton hydrate are surveyed. It is shown that the hydrate is the ion $(H_2O\cdots H\cdots OH_2)^+$. The mechanism of the generation of the continuous absorption observed in the IR spectra of solutions of acids and strong bases is examined. It has been found that a common feature of the structures of all stable proton solvates — the ions $(A\cdots H\cdots A)^{\pm}$ — is the presence in the latter of a symmetrical hydrogen bridge, the properties of which hardly depend on the nature of the ligand A. The constancy of the parameters of the hydrogen bridge provided a basis for the creation of a unique quantitative theory of the catalytic action of acids and bases. The bibliography includes 103 references.

I. Introduction

The physicochemical and catalytic properties of solutions of acids are determined mainly by the presence in the latter of protons, which appear on dissociation of the acid. In solution the protons form stable solvates, the structure and principal properties of which do not change on further solvation.[1] The simplest stable proton solvates actually participate in the majority of the processes occurring in solutions of acids. Special mention should be made of the fact that they play a primary role in homogeneous acid catalysis. In the chemical reactions of organic and inorganic compounds, stable proton solvates act as reactants and ionising agents, forming various intermediate complexes. Thus they participate in the equilibrium and nonequilibrium stages of the acid-catalytic process.

The simplest stable proton solvate is the stable chemical species formed on interaction of the dissociated proton with a specific number of solvent molecules. The properties and structure of the 'excess' solvent molecules solvating it hardly differ from those of the molecules of the pure solvent (the 'free' molecules). The desolvation of the simplest stable proton solvate leads to a rearrangement of its structure and of the system of its chemical bonds, which is manifested by a marked alteration of its properties.

II. The origin of the hypothesis that the H_3O^+ ion is the simplest stable proton hydrate

The problem of the determination of the stoichiometric compositions and structures of the simplest stable proton solvates in solutions arose long before the appearance of the physical methods which make it possible to achieve this. As long ago as the past century it was known that, when salts and especially acids are dissolved in water, heat is evolved, indicating strong binding of the solute to water. In 1886, Arrhenius and van't Hoff showed that many salts and acids decompose into ions in an aqueous medium.[1,2] Hence it was possible to conclude that the high heats of solution of acids in water are due to the formation of stable proton hydrates.

On the basis of the above considerations and also data on the kinetics of esterification in aqueous alcoholic systems, Hantzch and Caldwell[3] and Goldschmidt and Ulby[4] postulated as early as 1907 that the dissociation of an acid in water results in the formation of the hydroxonium ion H_3O^+. The firm establishment of this view was in many respects promoted by the proton theory of acids established independently by Brønsted[5] and Lowry.[6] According to this theory, the interaction of an acid and water takes place as follows:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- .$$

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At that time, there were no data whatsoever indicating the simultaneous addition of several molecules to the proton. This was also the reason why the vast majority of investigators had no doubt that the simplest proton hydrate was always the hydroxonium ion.

The concept of the H_3O^+ ion, which existed for decades, became generally accepted and the appearance in the literature of alternative hypotheses was entirely ignored. An extremely instructive situation arose as a result of this. In the 1950s, it was already possible to identify proton hydrates with the aid of physical methods and to estimate their geometrical parameters. Nevertheless, the efforts of all investigators were directed not to the establishment of the composition and structure of the simplest stable proton hydrate but to the search for H_3O^+ in the solid and liquid phases. Experimenters therefore made a special selection of the conditions under which only the hydroxonium ion could be formed (naturally the appearance of any other proton hydrates was impossible under these circumstances). Such conditions are fulfilled when there is not more than one water molecule for each dissociated proton.

III. The hydroxonium ion in the solid phase

The above approach was used in studies designed to detect and identify the H_3O^+ ion in the solid phase with the aid of resonance and diffraction methods. This made it possible to obtain data on its structure and properties. The first hypothesis of the existence of an ion with three equivalent O–H bonds was put forward in 1924 on the basis of the results of crystallographic studies on perchloric acid monohydrate and ammonium perchlorate, which demonstrated that these substances are fully isomorphous.[7] The structure of the hydroxonium ion in the solid phase (in crystalline strong acid hydrates) was established a quarter of a century later, after the NMR method had become available. It was shown that[8,9] the H_3O^+ ion in the crystalline monohydrates of perchloric, nitric, and sulfuric acids is a pyramid with three O–H bonds 0.98–1.02 Å long and apical angles of ~115° (Fig. 1*a*).

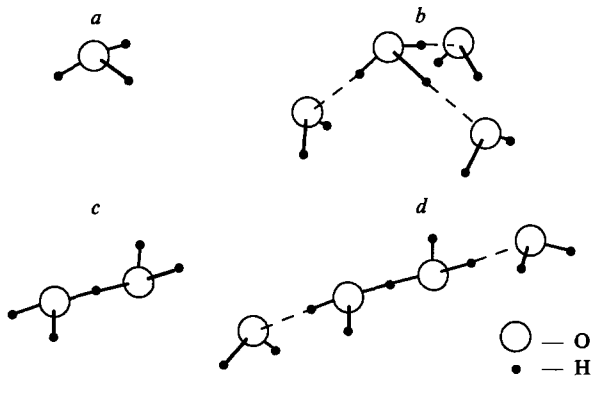


Figure 1. The structures of proton hydrates: (*a*) the hydroxonium ion H_3O^+; (*b*) the hydroxonium ion trihydrate $H_9O_4^+$; (*c*) the proton dihydrate $H_5O_2^+$; (*d*) the proton tetrahydrate $H_9O_4^+$.

The vibrational frequencies of the H_3O^+ ion in the crystalline monohydrates of hydrogen halides and also of nitric, perchloric, and sulfuric acids were measured by IR spectroscopy.[10–12] The frequencies for different crystals, assigned to the vibrations of the hydroxonium ion, differ significantly. The scatter of the deformation and stretching vibrational frequencies can reach several tens or hundreds of reciprocal centimetres respectively. Such a considerable difference between the frequencies does not conflict with the theory of vibrations because the influence on the H_3O^+ ion of the surrounding anions is different in different systems.[13] In individual cases, the influence of the anion is so strong that the hydroxonium ion loses its initial C_{3v} symmetry.

Evidently the distortion of the geometry of the H_3O^+ ion under the influence of the surrounding anions is smaller the lower the charge density on the latter, i.e. the larger their ionic radii. The frequencies observed in the $H_3O^+ \cdot ClO_4^-$ crystal (3220, 2820, 1670, and 1020 cm^{-1}), in which the charge density on the ClO_4^- anion and hence the distortion of the structure of the hydroxonium ion should be smallest, can therefore be most legitimately adopted as the vibrational frequencies of the H_3O^+ ion unperturbed by anions.[14] By analogy with the isoelectronic ammonia molecule and other molecules of the type XH_3, these vibrations were interpreted as follows:[10] $\nu_1 = 2820\ cm^{-1}$, $\nu_2 = 1020\ cm^{-1}$, $\nu_3 = 3220\ cm^{-1}$, and $\nu_4 = 1670\ cm^{-1}$.

Among the numerous studies on the Raman spectra of the hydroxonium ion in the solid state, mention should be made of the communications[15,16] in which the Raman spectra of the $H_3O^+ \cdot SbCl_4^-$, $H_3O^+ \cdot Cl^-$, and $H_3O^+ \cdot Br^-$ were published. The frequencies of the fundamental vibrations of the H_3O^+ ions in these crystals had the following values respectively: 3509, 3463, 1604, and 1095 cm^{-1}; 2900, 2700, 2570, 1605, and 970 cm^{-1}; 2895, 2630, 2525, 1650, 1615, and 970 cm^{-1}.

Since the $SbCl_4^-$ anion has the largest radius, the spectrum of the H_3O^+ ion in the $H_3O^+ \cdot SbCl_4^-$ crystal is closest to that of the unperturbed symmetrical hydroxonium ion. With decrease in the radius of the anion, the splitting of the second (2700 and 2570 cm^{-1}) and then also the third (1650 and 1615 cm^{-1}) vibrational frequencies of the H_3O^+ ion, associated with the loss of the C_{3v} symmetry by the latter, is observed. The occurrence of such splitting indicates unambiguously that, in frequency terms, the second and third vibrations of the unperturbed H_3O^+ ion (3463 and 1604 cm^{-1} for the $H_3O^+ \cdot SbCl_4^-$ crystal) are degenerate stretching (ν_3) and deformation (ν_4) vibrations respectively. This assignment agrees fully with results of measurements of the degree of depolarisation of the lines considered.[15,16]

Thus the interpretation of the vibrations of the H_3O^+ ion based on the Raman spectra is better founded that the assignment based solely on the isoelectronic nature of the H_3O^+ ion and the NH_3 molecule. In contrast to the free ammonia molecule,[17] the highest-frequency vibration of the hydroxonium ion proved to be the symmetrical stretching vibration (ν_1) and not the degenerate stretching vibration (ν_3). From the standpoint of the theory of vibrations, such inversion of the frequencies is possible. The ratio of the ν_1 and ν_3 frequencies depends on the angle between the X–H bonds and on the force constant for their interaction.[18]

Analysis of the literature data shows that towards the 1980s the structures and spectra of proton hydrates had been investigated in detail only in those cases where not more than one water molecule corresponded to each acid proton, i.e. when only the H_3O^+ ion could be formed in the system. The question of the composition and structure of the simplest stable proton hydrate in systems with a stoichiometric water : proton ratio greater than 1 : 1 was not considered at all. Investigators assumed that the simplest stable proton hydrate is always the hydroxonium ion even in the presence of an excess of water.

IV. The hydroxonium ion in the liquid phase

It is impossible to obtain quite such detailed data on the structure of the H_3O^+ ion in solution as in the solid phase. In the study of the structures of the molecular formations in a liquid, the X-ray and neutron diffraction methods as well as the NMR method yield little information (owing to the thermal motion of the molecules and ions). The conclusions reached concerning the structure of the simplest proton hydrate in aqueous solutions of acids were therefore based solely on the study of their IR spectra.

Three absorption bands with maxima near 2900, 1750, and 1205 cm^{-1} (2170, 1400, and 960 cm^{-1} in the case of the deuterio-analogues) have been recorded in the IR spectra of aqueous solutions of HCl, HBr, HNO_3, $HClO_4$, and H_2SO_4.[19–21] The observed bands were located near those of the H_3O^+ ion in the

solid phase. They were therefore assigned to the vibrations of the hydroxonium ion without additional studies. Here no account was taken of the fact that the vibrations of this ion, which according to the theory should be active simultaneously in the IR and Raman spectra,[18] were detected only in absorption spectra. All attempts to record hydroxonium lines in the Raman spectra of the above aqueous solutions were unsuccessful.[12,22]

However, on passing to liquid systems in which only the hydroxonium ion may be formed (with the ratio water : acid = 1:1) the picture changes sharply. Thus the Raman spectrum of a solution of the equimolar $H_2O-HSbCl_4$ mixture in dichloroethene exhibits all four lines of the H_3O^+ ion: 3560 (ν_1), 3510 (ν_3), 1600 (ν_4), and 1095 cm^{-1} (ν_2).[23] The reliability of the assignment of the observed lines to the corresponding vibrations of the H_3O^+ ion has been confirmed, as in the spectra of the crystalline monohydrates (see above), by the splitting of the degenerate vibrational frequencies (3510 and 1600 cm^{-1}) following the replacement of the $SbCl_4^-$ anion by smaller anions (Cl^- and Br^-).

Summarising the foregoing, it must be emphasised that the H_3O^+ ion has been detected only in those solid and liquid systems where only one water molecule corresponded to each acid proton. On the other hand, the conclusion that this ion is present in dilute aqueous solutions of acids clearly conflicted with the theory of vibrational spectra. Nevertheless, the concept of the H_3O^+ ion as the simplest stable proton hydrate in aqueous solutions of acids was not questioned.

Together with the experimental data listed above, the theoretical results conflicting with this idea also remained disregarded. Since the 1930s, the study by Hückel, who showed that the addition of a water molecule to the proton results in the formation of an ion with three equivalent O–H bonds the enthalpy of formation of which is ~170 kcal mol^{-1},[24] has been frequently quoted in the literature. On the other hand, nobody discussed the theoretical study by Huggins,[25] which was carried out at approximately the same time. On the basis of quantum-chemical estimates, the hypothesis was put forward in the latter study that in aqueous solutions of acids the dissociated proton can be strongly hydrated by two water molecules. This results in the formation of the symmetrical ion $H_5O_2^+$, in which the hydrogen bond is significantly shorter (2.55 Å) than in liquid water (Fig. 1*b*). According to Huggins' view, this ion is in fact the principal form of the hydrated proton.

V. The proton dihydrate $H_5O_2^+$

The first experimental results indicating that the simplest stable proton hydrate in aqueous solutions is not the hydroxonium ion were obtained by Eigen.[26,27] He estimated the kinetic diameter of the proton hydrate from measurements of the rate of recombination of the H^+ and OH^- ions in water and found it to be ~9 Å. This is very close to the size of the hydroxonium ion trihydrate $H_9O_4^+$, which has the C_{3v} symmetry like the H_3O^+ ion (Fig. 1*b*). The hypothesis that the simplest stable proton hydrate is the $H_9O_4^+$ ion, put forward on the basis of the above agreement, was confirmed also by certain indirect data. However, more careful measurements of the rate constants for the recombination of the H^+ and OH^- ions showed[28] that in reality they are almost twice as high as the values obtained by Eigen.[27] It followed from these data that the diameter of the proton hydrate should be ~5 Å and not 9 Å.[29] This value of the diameter of the simplest proton hydrate in aqueous solutions does not agree with the size of not only the H_3O^+ ion but also the $H_9O_4^+$ ion. Nevertheless the concept of the $H_9O_4^+$ ion, which was very popular in the 1950s and 1960s, can still be encountered in isolated communications even at the present time.

Since the beginning of the 1960s, experimental data began to appear in the literature from which it followed that in aqueous acid solutions the proton is bound firmly to two water molecules. The formation of the stable proton dihydrate was first established as a result of an analysis of the changes in the IR spectrum of a polymeric film of poly(styrenesulfonic acid) occurring when it is moistened.[30] In aqueous solutions of strong acids, such dihydrates were detected in a study of the kinetics and mechanisms of the hydrolytic reactions of organic compounds.[31] Later their presence in solutions was confirmed by IR spectroscopy.[32] The above data demonstrated incontrovertibly that the simplest stable proton hydrate in aqueous solutions has the composition $[H\cdot 2H_2O]^+$. However, there was no information about its molecular structure in solution, stability, and energetic stability.

Studies on the proton dihydrate in the crystalline phase proved more informative. Thus it followed from crystallographic data that, when a water molecule adds to the H_3O^+ ion, the structure of the entire hydrate undergoes a major rearrangement. This results in the formation of the $H_5O_2^+$ ion with a shortened symmetrical (or quasi-symmetrical) O···H···O bond. On further hydration of this ion, its structure hardly changes and the length of the hydrogen bridge always remains 2.4–2.5 Å.[26]

The IR and Raman spectra of the $H_5O_2^+$ ion in the solid phase have been investigated thoroughly.[33,34] The results obtained by Picotin et al.[33] are presented in Figs 2 and 3. Crystals of $H_5O_2^+\cdot SbCl_6^-$, $H_5O_2^+\cdot GaCl_4^-$, and $H_5O_2^+\cdot GaBr_4^-$, as well as their deuterio-derivatives were chosen as the objects of study. The selection of crystals with large anions ensured the least distortion of the geometry of the $H_5O_2^+$ ion, so that its spectra are fairly close to those of the free ion (Figs 2 and 3). Analysis of the vibrational frequencies of the initial and deuteriated crystals showed that only the vibrations of the proton dihydrates are manifested in the region above 500 cm^{-1}. We may note that the

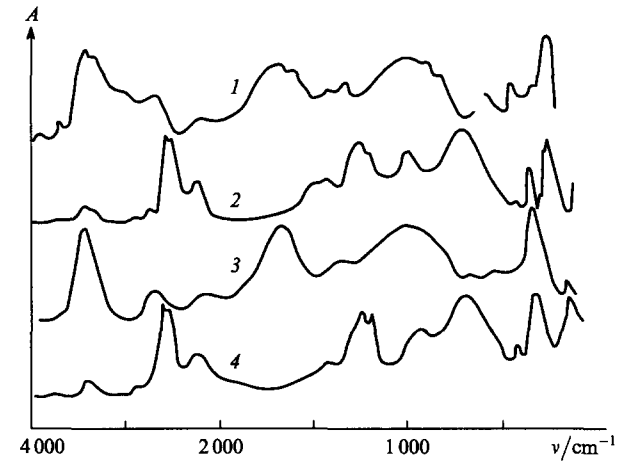


Figure 2. IR spectra of the crystals of $H_5O_2^+\cdot SbCl_6^-$ (curve *1*), $D_5O_2^+\cdot SbCl_6^-$ (curve *2*), $H_5O_2^+\cdot GaBr_4^-$ (curve *3*), and $D_5O_2^+\cdot GaBr_4^-$ (curve *4*) according to the data of Picotin et al.[33]

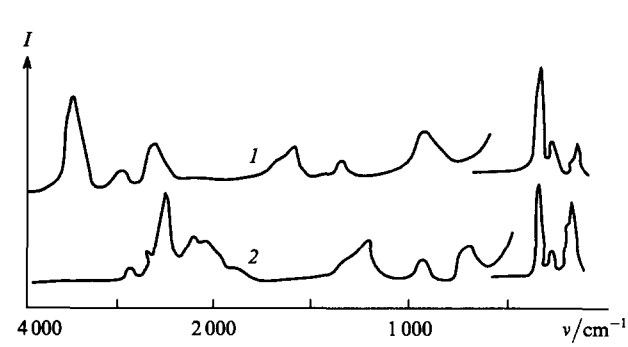


Figure 3. Raman spectra of the crystals of $H_5O_2^+\cdot SbCl_6^-$ (curve *1*) and $D_5O_2^+\cdot SbCl_6^-$ (curve *2*) according to the data of Picotin et al.[33]

IR spectrum of the $H_5O_2^+$ ion (Fig. 2) contains significantly more components than the Raman spectrum (Fig. 3). However, the marked overlap of the bands precludes the determination of not only their positions but also their total number.

The spectrum of the $H_5O_2^+$ ion has a much more elaborate structure and is better resolved when it is recorded by the inelastic neutron scattering method. Such a spectrum (Fig. 4) has in fact been obtained[35] for the ionic crystal of $(H_5O_2^+)_3(PW_{12}O_{40}^{3-})$. In the frequency range 350 – 1800 cm^{-1}, it is possible to note in this spectrum 28 vibrational bands in the form of inflections or distinct peaks. The selection rules for the absorption, Raman, and incoherent inelastic neutron scattering spectra are different, so that comparison of these spectra is legitimate only as regards the frequencies of their bands.

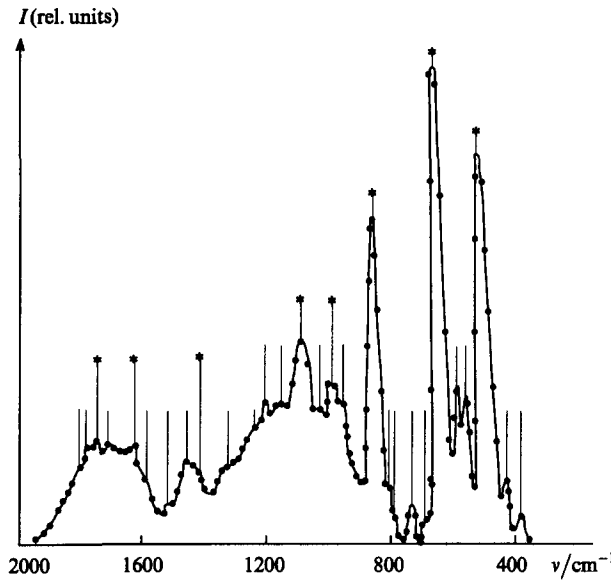


Figure 4. The spectrum of the incoherent inelastic neutron scattering by a crystal of $(H_5O_2^+)_3(PW_{12}O_4^{3-})$ according to the data of Kearley et al.[35]

Interesting results have been obtained in the study of proton hydration in the gas phase. Kebarle and coworkers performed a series of novel investigations[36,37] of gas-phase reactions of the type

$$H^+(H_2O)_{n+1} + H_2O \rightleftharpoons H^+(H_2O)_n .$$

It was shown that the heat of addition of a water molecule to the hydroxonium ion in the gas phase is 31.6 kcal mol^{-1}.[37] This greatly exceeds the energies of the strongest hydrogen bonds, indicating the stability of the $H_5O_2^+$ ion formed. The energy of the addition of the third and subsequent water molecules to the proton is significantly smaller, decreasing monotonically with increase in their number (Fig. 5).

The above investigations[36,37] stimulated a whole series of theoretical studies of the structure and the shape of the potential energy surface of the hydrated proton $H^+(H_2O)_n$. As a result, it was established that the energy of the addition of a H_2O molecule to the H_3O^+ ion is 32 kcal mol^{-1}.[38] This value agrees well with experimental data.[37] It has also been shown that a linear symmetrical hydrogen bond with an equilibrium O···O distance of 2.39 Å corresponds to the energy minimum of the $H_5O_2^+$ ion.[38] The potential energy curve for the central proton has a very flat minimum — when the proton is displaced by 0.3 Å, the potential energy hardly changes. For fixed O···O distances, significantly exceeding the equilibrium value, the cross-section through the potential energy surface along the O···H coordinate has two minima. The calculations of Kraemer and Diercksen[38] have been confirmed in other studies (see, for example, Kollman and Allen[39] and Yukhnevich et al.[40]).

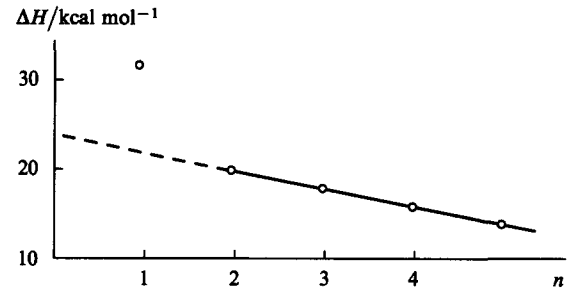


Figure 5. Variation of the heat of addition of a water molecule (ΔH) to the proton hydrate $H^+(H_2O)_n$ with the composition of the latter (n), according to the data of Kebarle et al.[36]

Nonempirical calculations for the hydrates $H_3O^+ \cdot (H_2O)_n$ with $n = 0-4$ showed[41] that the $H_9O_4^+$ ion has a stable chain structure with a central symmetrical hydrogen bond (Fig. 1*d*). The O···O distance (2.36 Å) then proves to be the same as in the $H_5O_2^+$ ion. This result was unexpected to Newton and Ehrenson,[41] who believed that the simplest stable proton hydrate is the hydroxonium ion and that $H_9O_4^+$ represents H_3O^+ hydrated by three water molecules, i.e. has the C_{3v} symmetry (Fig. 1*b*). Thus the results of quantum-chemical calculations led to the same conclusions as the results of the experimental studies examined above: first, the existence of the stable ion $(H_2O\cdots H\cdots OH_2)^+$ with a strong symmetrical hydrogen bond is energetically favoured and, second, the structure and properties of this ion are almost independent of the surrounding molecules.

VI. The $H_5O_2^+$ ion in solutions

The claim that the simplest stable proton hydrate in aqueous solutions is the symmetrical ion $(H_2O\cdots H\cdots OH_2)^+$ was first made on the basis of the analysis of the IR spectra of such solutions.[42] It was shown[42] that, despite the fact that the vibrational frequencies of the H_3O^+ and $H_5O_2^+$ ions are fairly similar (Table 1), these ions may be identified by comparing the IR and Raman spectra of the system investigated.

Table 1. The vibrational frequencies (cm^{-1}) of proton hydrates in IR (IRS) and Raman (RS) spectra.

H_3O^+ (C_{3v})		$H_5O_2^+$ (C_s)	
IRS	RS	IRS	RS
			460
1100	1100	1170	–
–	–	1370	–
1600	1600	1710	1710
2900	2900	2900	2900
3500	3500	3500	3500

The concept formulated by Librovich et al.[42] permitted an approach from a single standpoint, to the consideration of various physicochemical properties of aqueous solutions of acids. By employing it, it has been possible to account for the experimental hydration numbers of protons in aqueous solutions,[32] the kinetics and mechanisms of acid-catalytic hydrolytic reactions,[31,43] and a number of other features. It also made it possible to establish the ionic-molecular composition of the sulfuric acid – water system.[44]

The results of diffraction measurements on aqueous HCl solutions have been published,[45] showing that the O···O distance is shortened and equal to 2.52 Å. The authors attributed it to the complex $H_2O \cdot H_3O^+$. However, taking into account the data

considered above, one must recognise that such a short distance is more likely to be characteristic of the $H_5O_2^+$ ion.

The $H_5O_2^+$ ion has also been detected in the liquid phase by high-resolution NMR.[46] When an equimolar amount of water was added to a solution of octanesulfonic acid in a mixture of deuteriohalomethanes (Fig. 6, spectrum *1*), the bands of the H_3O^+ ion were recorded (Fig. 6, spectrum *2*). The addition of an excess of water to the solution led to a sharp weakening of these bands and the appearance of two new narrow lines with a 1:4 intensity ratio (Fig. 6, spectrum *3*). These lines are due to the central and terminal protons of the symmetrical ion $(H_2O\cdots H\cdots OH_2)^+$.

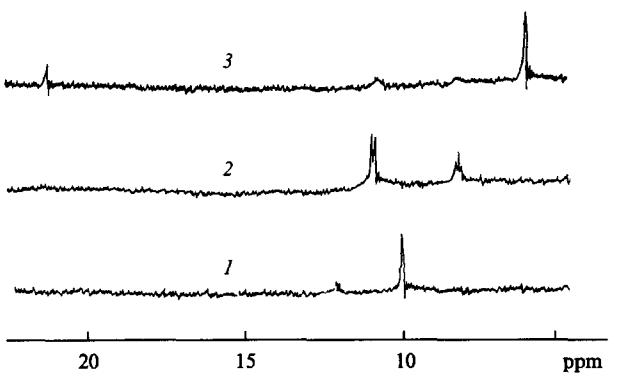


Figure 6. NMR spectra of dilute solutions of $H_2O-HSO_4C_8H_{17}$ mixtures in deuteriohalomethanes according to Golubev's data[46] for different $H_2O:HSO_4C_8H_{17}$ ratios: (*1*) 0:1; (*2*) 1:1; (*3*) 2:1.

Solutions of the $CF_3SO_3H-H_2O$ and $HI-H_2O$ mixtures in an inert solvent (CCl_4) diluted to 10^{-2} M have been investigated by IR spectroscopy.[47] For the acid:water = 1:1 ratio, the bands of the hydroxonium ion were observed in the spectrum of the solution (Fig. 7, spectrum *1*). Following an increase in the water concentration to give the ratio 1:2, the spectrum changed sharply (Fig. 7, spectrum *2*). Further addition of water to the system did not affect the IR absorption curve.

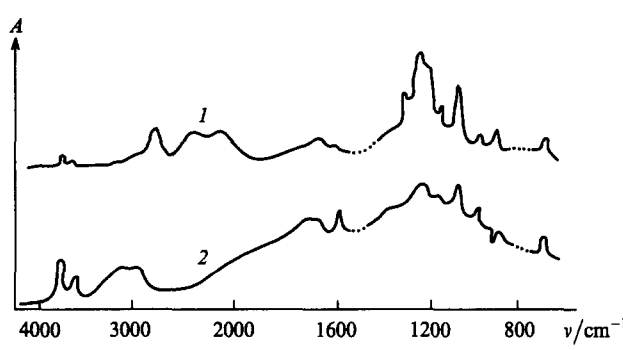


Figure 7. IR spectra of the $H_2O-HSO_3CF_3-CCl_4$ ternary system according to data of Dogonadze et al.[47] for different molar component ratios: (*1*) 1:1:50; (*2*) 2:1:50.

Artificially created systems, fairly remote from aqueous acid solutions, have been studied.[46,47] Nevertheless, the results obtained demonstrated unambiguously the following most important features of the interactions of the proton with water molecules in solution.

1. The hydroxonium ion exists in the liquid phase only when there is not more than one water molecule per acid molecule.

2. With increase in the water content in the system, a chemical reaction between H_3O^+ and H_2O and not simple hydration of the H_3O^+ ion takes place in the system. It is accompanied by a rearrangement of the bonds and the formation of the symmetrical ion $H_5O_2^+$.

3. The hydration of the $H_5O_2^+$ ion (to give a water:acid ratio in excess of 2:1) does not alter its structure.

VII. The continuous absorption in the IR spectra of solutions of acids. Initial interpretation

The determination of the molecular structure of the simple proton solvate in solutions is indissolubly linked to the study and interpretation of its vibrational spectra. Until recently, such interpretation involved considerable difficulties. The point is that the IR spectra of all systems in which proton dihydrates (as well as other proton disolvates formed via a strong symmetrical hydrogen bond) are present exhibit an intense continuous absorption (CA) in the range from ~3500 to 800 cm^{-1}. The positions and intensities of individual, usually indistinct, maxima on the contour of this continuum depend on the composition of the test solution. A significant factor proves to be not only which species, other than the proton disolvate $(A\cdots H\cdots A)^{\pm}$, are present in solution but also what molecules A solvate the proton.[48]

The continuous absorption in the spectra of solutions of acids and strong bases was first recorded in the near infrared (4300–6700 cm^{-1}) and it was immediately established that its optical density is proportional to the acid or alkali concentration in solution.[49,50] Much later a similar spectroscopic phenomenon was observed also in the region of the fundamental vibrational frequencies of the molecules.[51,52] Ackermann,[52] who was the first to detect a continuous absorption in this region, assumed that it is due to the delocalisation of the positive or negative charge in the solvate complex. Subsequently, the continuous absorption observed in the spectra of numerous aqueous and nonaqueous solutions was vigorously studied by various investigators.[53–57]

A large series of studies on the continuous absorption has been carried out by Zundel and coworkers.[30,57–60] Some of their results are extremely interesting. Thus it has been shown[30] with the aid of a novel experiment that the appearance of the continuous absorption requires that the solution contains a dissociated proton bound to two water molecules. On the other hand, it must be said that in his studies Zundel's aim was not to obtain the spectrum of the ion 'in a pure form'. He confined himself to the analysis of the spectra of mixtures in terms of the transmittance scale (see, for example, Fig. 8). This made it impossible for him to draw inferences about the details of the spectral absorption curve for the ion under consideration and hence about its molecular structure. We may also note that Zundel based his concept concerning the mechanism of proton hydration both on incontrovertible experimental data and on the results of studies[27,51,52] which proved subsequently to be erroneous. For this reason, the explanation which he proposed for the causes of the appearance of the continuous absorption[58] appears unconvincing. As a result of Zundel's many publications,

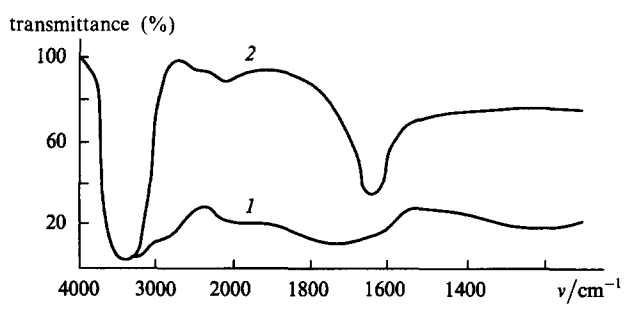


Figure 8. IR spectra of a 10 M HCl solution in H_2O (curve *1*) and of water (curve *2*) according to the data of Schioberg and Zundel.[57]

his view became well known and we shall therefore consider it in detail.

Zundel based his interpretation of the continuous absorption on the following assumptions:[58]

1. The spectra of aqueous solutions of acids and strong bases contain the same vibrational bands.

2. The lifetime of the H_3O^+ ion (which is the simplest proton hydrate in Zundel's view) is so short that its vibrations cannot be recorded by IR spectroscopy.

3. The most stable ion-molecule formation, the vibrations of which are manifested in the IR spectrum of the solution, is the $H_9O_4^+$ ion (Fig. 9).

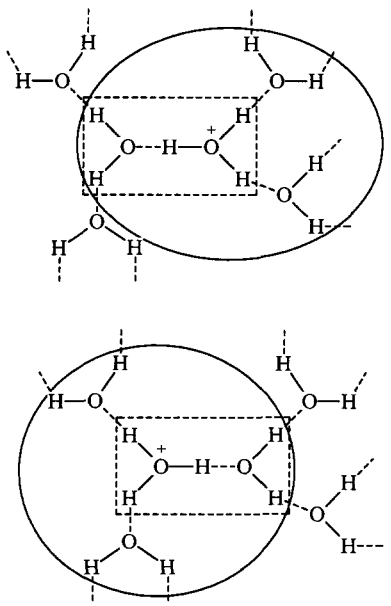


Figure 9. The molecular structure of the proton hydrate according to Zundel's data.[58] The $H_9O_4^+$ ion is shown within the circumscribed region.

On the basis of the assumptions listed,† Zundel proposed a model of the proton hydration in solution, the essential features of which reduce to the following. The $H_5O_2^+$ group (not the simplest stable ion but an unstable group which is incapable of entering into chemical reactions as an integral whole) exists in aqueous solutions of acids. The proton in this group is rapidly exchanged between the two water molecules, occupying one of the boundary positions:

$$(H_2OH^+\cdots OH_2) \rightleftharpoons (H_2O\cdots H^+OH_2).$$

The transfer of the proton, which is located in a potential well with two minima, takes place as a result of the fluctuations of the electric field generated by the environment of the $H_5O_2^+$ group. The ultrahigh polarisability of the hydrogen bond (this property of the O···H···O bond is simply postulated) plays a special role in this process. According to this model (which has not undergone significant changes since that time[59,60]), the continuous absorption arises by virtue of the appearance of additional transitions during the tunnelling of the proton through the central potential barrier.

Together with the explanation of the origin of the continuous absorption examined above, other treatments of this spectroscopic phenomenon have been proposed.[61-65] Like Zundel's hypothesis, they are all based on the hypothesis of a strong interaction between the bridging proton and the medium. For example, it has been shown[65] that the experimentally observed broad absorption region may arise as a result of the interaction of the vibrations of the central proton in the $H_5O_2^+$ ion with the low-frequency vibrations of the surrounding ligands (the proton–phonon theory). This approach made it possible to describe the isotope effects and to account for the presence of the continuous absorption in the IR spectra of solutions of strong bases. The simplest stable solvated ion in such solutions has the structure $(HO\cdots H\cdots OH)^-$.

However, in the studies by Golubev, Denisov,[47] and Pankov and coworkers[66] published at the beginning of the 1980s, it was shown that the initial postulate, on which all the proposed theories were based, conflicts with experiment. In these investigations, studies were made of the IR spectra of the ion $(H_2O\cdots O\cdots OH_2)^+$ in a water–acid–carbon tetrachloride ternary system[47] and of the complex $(RO_H\cdots H\cdots O_HR)^+$ in a alcohol–acid–aprotic solvent (CCl_4 and CH_2Cl_2) system.[66] It was established that, even when the solvation effects are reduced to a minimum, the shape of the contour and the intensity of the continuous absorption in the spectrum of the ion $(A\cdots H\cdots A)^\pm$ remain the same as in polar solvents. In other words, the continuous absorption is not caused by the influence of the medium but is due to the intrinsic internal properties of the ions with a symmetrical hydrogen bond.

The data obtained in the above studies[47,66] made a most important contribution to understanding the phenomenon under consideration, on the one hand, and posed a new major problem before investigators, on the other. It was now necessary to explain all the characteristics of the continuous absorption in the vibrational spectra of solutions of acids and strong bases listed above on the basis of the properties of a molecular system consisting of a small number of atoms (only five in the case of the $H_3O_2^-$ ion). The successful solution of this problem, i.e. the establishment of a quantitative relation between the properties of the individual structural elements of the proton disolvate and its vibrational spectrum, would make it possible not only to understand the mechanism of the appearance of the continuous absorption but also to determine the structure of the ion $(A\cdots H\cdots A)^\pm$.

Evidently, the solution of the problem formulated requires more accurate information about the nature of the vibrations of the proton disolvate, i.e. on the experimental side it was necessary to effect a transition from the spectra of mixtures to the individual spectra of ions, and on the theoretical side the consideration of the monocoordinate O···H···O bridge had to be replaced by allowance for all the degrees of freedom of the vibrational system investigated. A formulation of this kind was achieved by a number of investigators.[40,48,67-71]

VIII. Differentiation of the spectra of proton disolvates from the spectra of solutions

In practice, the structure of the simplest proton hydrate in solution may be established only by investigating its IR spectrum. It is therefore necessary to measure this spectrum as thoroughly as possible. Thus, in the case of strongly absorbing liquids, to which aqueous solutions also belong, the IR spectra must be measured not by the transmittance technique but by the multiple distorted total internal reflection (MDTIR) technique.[72] The high accuracy of the measurement of the spectrum is especially important in cases such as the resolution of the spectrum into components or the differentiation of the spectrum of a particular molecule from the spectrum of a mixture.

From the standpoint of the correctness of the primary spectroscopic measurements, mention may be made of the studies of Yukhnevich et al.[48] and Maiorov and Librovich.[71] Using the MDTIR method, these investigators obtained, with a highly satisfactory accuracy, the absolute spectroscopic absorption coefficients of aqueous and methanol solutions of hydrogen

† These postulates conflict with experimental data in Refs 11, 15, 19, 46, and 48, in Refs 15, 19, and 23, and in Refs 28, 29, and 42 respectively.

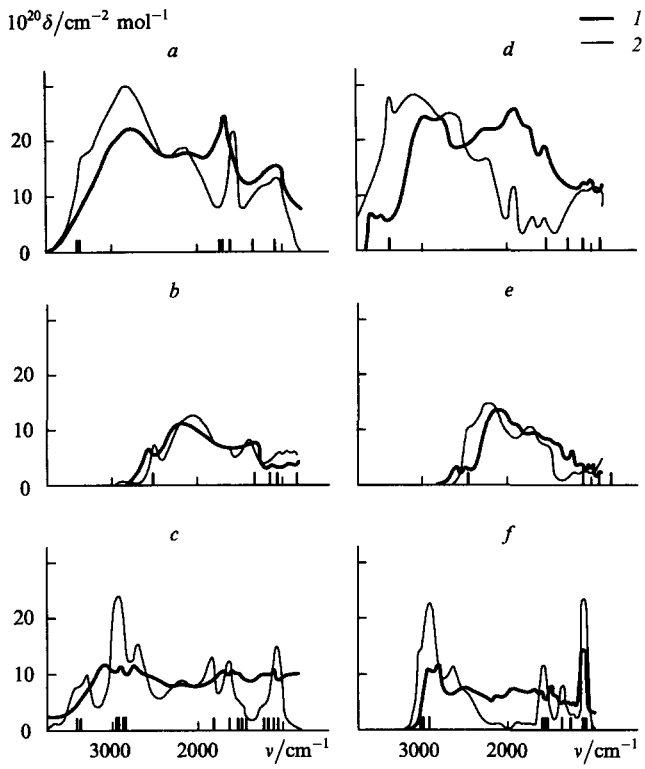


Figure 10. The measured (curves *1*) and calculated (curves *2*) IR spectra of proton disolvates according to the data of Yukhnevich et al.[48]: (*a*) $H_5O_2^+$, (*b*) $D_5O_2^+$; (*c*) $(CH_3OH)_2H^+$; (*d*) $H_3O_2^-$; (*e*) $D_3O_2^-$; (*f*) $(CH_3O)_2H^-$.

chloride and potassium hydroxide. This made it possible to differentiate for the first time the spectra of the ions $H_5O_2^+$, $D_5O_2^+$, $(CH_3OH)_2H^+$, $H_3O_2^-$, $D_3O_2^-$, and $(CH_3O)_2H^-$ 'in a pure form' by measuring the spectra of a series of auxiliary systems (Fig. 10).

In the differentiation of the spectra of positively charged ions, acid–solvent systems with known ion-molecular compositions and known molar absorption coefficients of the system were selected. The spectra of the ions $(A\cdots H\cdots A)^+$ were found directly by subtracting from the IR spectrum of the solution the absorptions due to the solvent molecules and the acid anions. The differentiation of the vibrational spectra of the negatively charged ions involved much greater difficulties. The point is that the spectrum of the solvent molecules (water and methanol respectively), which strongly solvate the $H_3O_2^-$ and $(CH_3O)_2H^-$ ions present in the solution, differs appreciably from the spectrum of the pure solvent.[73,74] Therefore, in determining the spectra, estimates were made of the position, width, and intensity of the ν_{OH} band of the H_2O and CH_3OH molecules solvating the ions $(A\cdots H\cdots A)^-$. As a result, the accuracy of the absorption cross-sections obtained for ions with a negative charge (~30%) proved to be significantly lower than for the positively charged ions (~15%).

IX. Calculation of the IR spectra of proton disolvates

Interpretation of the IR spectra of proton disolvates requires allowance for their highest-order vibrations.[47,66] In other words, the mechanism of the appearance of the continuous absorption must be analysed in terms of the anharmonic approximation of the theory of the vibrations of polyatomic molecules. This approach has been used in the calculation and analysis of the IR spectra of the ions $(A\cdots H\cdots A)^{\pm}$ in a number of studies.[40,48,67–70] Proton disolvates differing significantly in composition—$H_5O_2^+$, $D_5O_2^+$, $(CH_3OH)_2H^+$, $H_3O_2^-$, $D_3O_2^-$, and $(CH_3O)_2H^-$—were chosen as the objects of study. This made it possible to determine the influence of the ionic charge, of the nature of the ligand, and of deuteriation on the shape of the continuous absorption contour.

For the calculation of the spectra of the systems listed above, it was also necessary to know, together with the properties of the ligand molecules, also the geometrical, energetic, and electrooptical parameters of the O···H···O bridges. The authors of the studies under consideration based the determination of the above parameters on the data concerning the ions $(A\cdots H\cdots A)^{\pm}$ already available at the time. In view of the importance of the characteristic properties of these ions for the understanding of the nature of the continuous absorption, we shall consider them in detail.

The study of the kinetics of the gas-phase chemical reactions leading to the formation of the ions $(A\cdots H\cdots A)^{\pm}$ showed that the energy of the addition of the second solvating molecule to the proton is virtually unchanged (31 ± 2 kcal mol^{-1}) for several tens of compounds investigated, in which the molecule A is water, an alcohol, acid, ester, ketone, or aldehyde.[34,75–78] The invariance of the bond energy of the symmetrical hydrogen bridge in all the systems containing it was confirmed by the results of numerous quantum-chemical calculations.[76,79–82] All the available experimental data[83–88] as well as the results of calculations by various methods[79–82,89,90] showed that the length of the O···H···O bridge (2.4–2.55 Å) also depends little on the structure of the molecules solvating the proton. The results of quantum-chemical calculations[48,68] demonstrated that the force constants, the atomic charges, and the dipole moments of the bonds in the O···H···O fragment are independent of the nature of the ligand (Table 2). The last two of the characteristics indicated are determined by the ionic charge.

Table 2. Parameters of the symmetrical hydrogen bridge O···H···O (data of Yukhnevich et al.[48]).

Parameter	$H_3O_2^-$	$H_5O_2^+$	$(CH_3O)_2H^+$	$(CH_3OH)_2H^+$
$R_{O\cdots H}$/Å	1.207	1.197	1.212	1.203
$F_{O\cdots H}$/ mdyn Å^{-1}	2.35	2.0	2.62	2.48
$F_{O\cdots H,\ O\cdots H}$/ mdyn Å^{-1}	1.76	1.50	1.99	1.79
$F_{O\cdots H\cdots O}$/ mdyn Å^{-1}	0.16	0.13	0.16	0.10
Q_O/electric charge units	−0.84	−0.42	−0.67	−0.42
Q_H/electric charge units	0.36	0.41	0.36	0.40
$\mu_{O\cdots H}/\mu_{OH(H_2O)}$	1.33	0.63	1.30	0.75

There have been few experimental studies devoted to the nature of the potential energy surface of proton disolvates.[87,88] However, in the case of the ion $[(C_2H_5O)_2O\cdots H\cdots O(C_2H_5)_2]^+$, investigated for this purpose, as well as the ion $H_5O_2^+$,[38–40] the central proton is located in a symmetrical potential well with one minimum. This conclusion was reached on the basis of the results of studies of a single crystal of the etherate $(C_2H_5)_2O\cdot HZnCl_3$ by X-ray diffraction and ^1H NMR.[87,88]

The IR spectra of the ions $H_5O_2^+$, $D_5O_2^+$, $(CH_3OH)_2H^+$, $H_3O_2^-$, $D_3O_2^-$, and $(CH_3O)_2H^-$ have been calculated, taking into account the kinematic, dynamic, and electrooptical anharmonicities of the vibrations, by a variational method[91] in accordance with a general algorithm. No adjustment of the calculated frequencies and intensities of the absorption bands to achieve agreement with experimental spectra of specific ions was carried out. All the parameters of the O···H···O bridges needed to calculate the spectra of the test systems were found with the aid of

a semiempirical model for the description of the dynamic and electrooptical properties of the hydrogen bond[92] or by means of quantum-chemical calculations.[48,68]

The absorption spectra of the proton disolvates calculated in this way are presented in Fig. 10. The positions of the fundamental vibrational bands are designated by vertical lines. The complete set of the calculated frequencies of the $H_5O_2^+$ ion in the range 200–1800 cm^{-1} is presented in Table 3. The table shows that the average deviation of the calculated fundamental vibrational frequencies from the frequencies of the most intense lines in the inelastic neutron scattering spectrum[35] is ±18 cm^{-1} (which corresponds to the accuracy achieved by a modern theory of the vibrations of polyatomic molecules[18]).

Table 3. Experimental[35] and calculated[48] vibrational frequencies (cm^{-1}) of the $H_5O_2^+$ ion in the range 0–2000 cm^{-1}.

No.	Experiment	Calculation	No.	Experiment	Calculation
1	1800		14	1080[a]	1093[a]
2	1775	1770[a]	15	1030	1026
3	1730[a]	1742[a]	16	982[a]	1021
		1721	17	955	1015
4	1710	1711	18	836[a]	833[a]
		1672			
		1644	19	805	
5	1610[a]	1622[a]	20	785	
		1603			
		1602			
6	1580	1577	21	730	724[a]
7	1515	1509	22	685	
		1503			
		1502	23	616[a]	673[a]
8	1450	1446	24	590	
9	1425[a]	1415	25	560	
		1403	26	494[a]	498[a]
		1363			497[a]
10	1325	1350	27	430	
11	1240	1256	28	380	
12	1205	1246			
13	1150				

[a] The fundamental vibrational frequency.

Analysis of the calculated IR spectra of the ions investigated established two characteristic features. Firstly, the majority of the vibrations of the proton disolvates and primarily the vibrations of the hydrogen bridge are not localised in one coordinate. Their modes, determined by the structure of the ion, are individual.[48,69] Secondly, in the region where the continuous absorption is observed experimentally the spectra of all the ions considered contain tens (40–300) compound vibrational bands and overtones, the intensities of many of which (30%–60%) are comparable to those of the fundamental vibrational bands.[67–70]

Detailed study of the influence of various anharmonic parameters on the nature of the calculated spectra of the ions $(A\cdots H\cdots A)^{\pm}$ showed that the presence in the latter of a large number of intense combination bands is a consequence of the electrooptical anharmonicity of the vibrations of the O···H···O fragment. Furthermore, it has been possible to establish unambiguously that only two nonequivalent electrooptical parameters make a decisive contribution (~85%) to the overall intensity of the higher-order vibrational bands in the spectra of proton disolvates.[70] The causes of the appearance of intense overtone vibrational bands in the spectra of the ions $(A\cdots H\cdots A)^{\pm}$ were analysed by considering the modes and intensities of the vibrations of the hydrogen bridge O···H···O. Such analysis made it possible to establish that the vibrations of the O···H···O fragment, in which the central proton shifts simultaneously along and across the direction of the hydrogen bond, are anomalously intense and to understand why precisely these vibrations are so intense.[69]

Analysis of the coefficients in the expansion of the anharmonic eigenfunctions of the vibrational energy levels in terms of the harmonic basis functions made it possible to explain why the intense combination bands in the spectra of proton disolvates are so numerous. It was found that the strong kinematic interaction of the coordinates of the hydrogen bridge with other coordinates of the ions $(A\cdots H\cdots A)^{\pm}$ causes the displacement of the proton along or across the hydrogen bond to occur in more than half of their fundamental vibrations, while the simultaneous shift in both directions indicated occurs in virtually every third overtone vibration. These composite vibrations and overtones are in fact active in the absorption spectrum.[48,69]

Thus it follows from the calculations that the continuous absorption in the spectra of proton disolvates may be due to the presence in the range 800–3700 cm^{-1} of a large number of overlapping intense higher-order vibrational bands. The appearance of such bands is caused by the intrinsic properties of the ions $(A\cdots H\cdots A)^{\pm}$ and in the first place by the electrooptical anharmonicity of the O···H···O fragment and the strong interaction of the coordinates of the hydrogen bridge with the internal coordinates of the ligand.

X. Interpretation of the continuous absorption in the IR spectra of solutions of acids and strong bases

The results of the comparison of the calculated and measured absorption cross-sections of the ions $H_5O_2^+$, $D_5O_2^+$, $(CH_3OH)_2H^+$, $H_3O_2^-$, $D_3O_2^-$, and $(CH_3O)_2H^-$ (Fig. 10, Table 4) demonstrated the validity of the explanation of the nature of the continuous absorption proposed by Yukhnevich et al.[48] It is seen from the spectra presented in Fig. 10 and the data in Table 4 that the calculation made it possible to reproduce on the whole correctly the overall form of the spectral curves and the integral absorption of all the ions in the frequency range considered and also to reproduce correctly the changes in the spectra of the $H_5O_2^+$ and $H_3O_2^-$ ions occurring on isotopic substitution.

Table 4. The absolute absorption intensities of the proton disolvates (I) and their isotopic ratios (I_H/I_D) according to the data of Yukhnevich et al.[48]

Ion	Calculation		Experiment		Frequency range/cm^{-1}
	I/D^2 Å^{-1}	I_H/I_D	I/D^2 Å^{-1}	I_H/I_D	
$H_3O_2^-$	87	2.8	62 ± 13	2.6 ± 0.8	3700–900
$D_3O_2^-$	31		24 ± 5		2700–900
$H_5O_2^+$	96	2.5	130 ± 14	3.1 ± 0.5	3700–900
$D_5O_2^+$	38		42 ± 5		2700–800
$(CH_3O)_2H^-$	66		82 ± 17		3700–900
$(CH_3OH)_2H^+$	84		131 ± 14		3700–900

Yet another confirmation of the concept concerning the origin of the continuous absorption under discussion is the fact that, when the $H_5O_2^+$ and $H_3O_2^-$ ions are deuteriated, their integral absorption (the average for both ions) diminishes by a factor of 2.85 ± 0.5 (Table 4). This value agrees well with the calculated value 2.65 (Table 4). However, it can correspond neither to the isotopic ratio of the fundamental vibrational intensities of the O–H bond nor to the ratio of the intensities of the first overtone vibrations. According to the theory of vibrations,[18] in the former case the isotopic ratio should be 1.84, while in the latter it should be 3.39. The experimental

isotopic intensity ratio (2.85) can be explained by averaging the values (1.84 and 3.39) for several fundamental and first overtone vibrations.

Thus the published data show that the continuous absorption in the spectra of acids and strong bases is caused by the intrinsic vibrations of the simplest stable proton solvates. The solvates themselves are stable charged species with a symmetrical hydrogen bridge O···H···O, the properties of which are almost independent of the nature of the ligand.

XI. The structure of the solvated proton and the catalytic properties of acids

The equilibrium stage involving the protonation of the organic compound which subsequently undergoes chemical reaction plays an important role in homogeneous acid catalysis. The degree of protonation of the organic compound depends on the catalytic activity of the acid solution and primarily on the acidity function of the solution. It was assumed for a long time that the protonation of the organic molecule B involves the transfer to the latter of a proton from the acid medium and the formation of the protonated form BH^+. It was postulated that BH^+ is the simplest stable proton solvate, the addition to which of a second and subsequent solvent molecules does not alter its structure. However, as early as 1980 it was already established[93] that in many cases the protonation of the molecule of compound B is a reaction involving the substitution of a water molecule in the $H_5O_2^+$ ion by a molecule of B:

$$(H_2O\cdots H\cdots OH_2)^+ + B \rightleftharpoons (H_2O\cdots H\cdots B)^+ + H_2O. \qquad (1)$$

The radical revision of the ideas concerning the mechanism of the catalytic action of acids was caused by the finding that the protonated form of the organic molecule in solutions is usually not the BH^+ ion but the $(H_2O\cdots H\cdots B)^+$ ion.[94] The new concept, elucidating the characteristic features of this mechanism, was based on the constancy of the enthalpy of formation of proton disolvates[34,75-78] and the independence of the parameters of the symmetrical hydrogen bridge on the nature of the molecules solvating the proton.[48,68,79-90] Understanding the fact that the properties of the central ···H··· fragment, which is common to a wide range of compounds, determine not only the nature of their vibrational spectra but also their behaviour and chemical reactions made it possible to solve the following fundamental problem in homogeneous acid catalysis.

1. The physical significance of the Hammett acidity function H_0 was discovered and the limits of its applicability were established. Previously, the use of this function was based on the postulate that the mechanisms of the protonation in acid solutions of stable compounds (indicators) and of the reacting organic molecule are the same.[95] This postulate had no physical justification, since no common properties embracing indicators and organic compounds with different structures and chemical compositions were known.

It has been shown[93] that Hammett's postulate holds only in those cases where the molecules of compound B are protonated via reaction (1). In other words, an obligatory condition for its validity is the presence in the proton solvate of a symmetrical hydrogen bridge with invariant parameters. A number of conditions must be fulfilled for the protonation of the molecule of compound B to occur in accordance with the scheme indicated.[96] Firstly, the acid–base interaction in the solution must go to completion, i.e. positively charged proton solvates must be formed in it. Secondly, the molecules solvating the proton must have lone pairs ensuring the formation of a symmetrical hydrogen bond. Thirdly, it is necessary that the heat of addition of a proton to a molecule of compound B (the proton affinity) should be greater than the proton affinity of the water molecule (i.e. >170 kcal mol^{-1}) but less than 197 kcal mol^{-1}.[96] For heats of addition of a proton to a molecule of compound B exceeding 197 kcal mol^{-1}, the preconditions for the fulfilment of Hammett's postulate vanish and protonation leads to the formation of the BH^+ ion.

2. Quantitative relations between the acidity functions of acid solutions and the thermodynamic activities of water have been obtained. It has been shown[94] that, when equilibrium (1) obtains in the solution of an acid, then the Hammett acidity function H_0 should be formulated as follows:

$$H_0 = -\lg\left(a_{H^+}\, a_{H_2O}\frac{f_B}{f_{BHOH_2^+}}\right), \qquad (2)$$

where a represents the thermodynamic activities of the corresponding species and f represents the activity coefficients.

The fundamental difference between Eqn (2) and the formulation adopted earlier for H_0 is the presence in the former of the activity of water. This made it possible to account for the long established fact[95,97] that the quantity $H_0 + \lg a_{H_2O}$ is independent of the activity of the anion in solution, while the ratio of the activity coefficients is the same for organic compounds having different structures, provided that Hammett's hypothesis holds. It has also been shown[94] that, in those cases where equilibrium (1) obtains, the degrees of protonation and the basicity constants $K_{BHOH_2^+}$ should be calculated in virtually the same way as for the previous ideas concerning the structure of the protonated form:

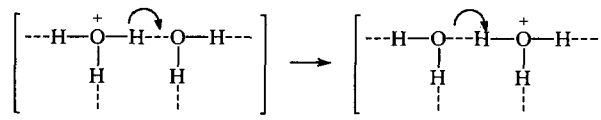
$$H_0 = pK_{BHOH_2^+} + \lg\left(\frac{c_B}{c_{BHOH_2^+}}\right),$$

$$K_{BHOH_2^+} = \frac{a_B a_{H_5O_2^+}}{a_{BHOH_2^+}\, a_{H_2O}}.$$

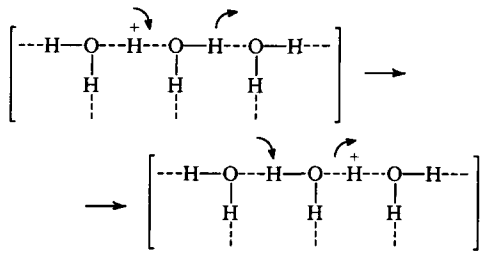
3. An explanation has been proposed for the difference between the gas-phase and liquid-phase acidities observed for many compounds. A large number of organic compounds, forming the $BHOH_2^+$ ion both in the gas and liquid phases, fall within the range of the energies for the addition of a proton to a molecule of compound B indicated above.[98] However, the mech-anisms of the protonation of a series of compounds in the gas and liquid phases are different (a substitution reaction with formation of the $BHOH_2^+$ ion takes place in the gas phase, while the BH^+ ion is formed in the liquid phase).[96] A difference between the gas-phase and liquid-phase acidities is observed in precisely such cases. Hence the above difference is caused not by the influence of the medium on the activity coefficients of the forms B and BH^+ but by the different mechanisms for the protonation of the organic molecule in the liquid and gas phases.[96]

4. The mechanism of the hydrolytic reactions of organic compounds was established. It has been shown[43] that ions with symmetrical hydrogen bonds may participate as the reactants in the rate-limiting stages of acid-catalytic processes. However, only the stoichiometric composition of the intermediate complexes could be inferred from the kinetic data. In order to establish the mechanism of the rate-limiting stage of the reaction, it was also necessary to know the structures of the reacting species. The information obtained about the structures of the simplest stable proton hydrates in aqueous solutions of strong acids made it possible to establish the structure of the intermediate complex in the hydrolytic reactions. This permitted the understanding of the detailed mechanism of the rate-limiting stage in these reactions.[99]

5. The mechanism of the proton conduction in aqueous solutions of acids was revised. On the basis of the concept of the H_3O^+ ion, it had been assumed previously that the anomalously high mobility of the proton in such cases can be explained by the Grotthus relay mechanism.[26,95]



However, in reality the simplest stable proton hydrate in aqueous solutions of acids is the $H_5O_2^+$ ion. In this case, charge transfer without disturbing the structure of the solution is possible only for a synchronous transfer of two protons in accordance with the mechanism:[100,101]



Such a transfer is equivalent to the migration of a proton from one potential well to another, overcoming a barrier of ~2.4 kcal mol^{-1}.[102]

An analogous mechanism of the transfer of a negative charge (a proton defect) can be put forward for aqueous solutions or bases, where the simplest stable hydrate of the hydroxide ion is $(HO\cdots H\cdots OH)^-$.[65]

XII. Conclusion

The history of the development of ideas concerning the structure of the simplest stable proton hydrate shows how important is the correct understanding of the relation between the molecular structures of the test objects and their properties recorded experimentally.

The main outcome of studies carried out over many years, the different stages of which have been examined consecutively in the present review, is the establishment of the structures and properties of the simplest stable proton solvates in solutions of acids and strong bases. Such solvates are the ions $(A\cdots H\cdots A)^{\pm}$ with a symmetrical hydrogen bridge, the properties of which are almost independent of the nature of the ligand A. The broad region of continuous absorption observed in the IR spectra of proton disolvates is due to the electrooptical anharmonicity and the noncharacteristic nature of their vibrations.

The elucidation of the characteristic features of the mechanism of the vibrations of systems containing strong symmetrical hydrogen bonds led to a deeper understanding of the process involving the establishment of their IR spectra. Together with the interpretation of the continuous absorption, which has been confirmed experimentally, it also made it possible to achieve a simple explanation, having a clear physical significance, of the 'anomalous' dependence of the vibrational frequencies of such systems on the isotopic composition.[103]

The level of knowledge concerning the structures and properties of the simplest stable proton solvates achieved at the present time has made it possible to abandon the purely empirical relations in the determination of the mechanisms of acid–base catalytic reactions and to construct a unique quantitative theory of the catalytic action of acids and bases. The satisfactory foundations and the clear-cut definition of the limits of the applicability of this theory have made it possible to employ it successfully in order to account for the known experimental facts and to predict the conditions for the occurrence of various physicochemical processes in solutions.

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