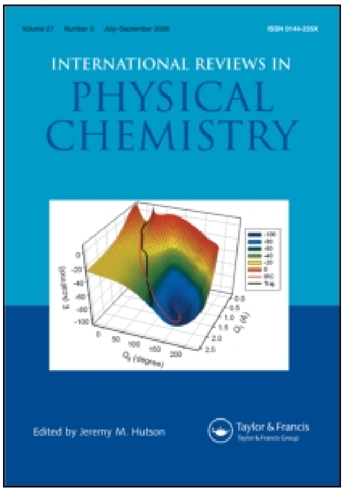

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The structure and vibrational spectra of proton hydrates: $H_5O_2^+$ as a simplest stable ion

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Ability to form a strong quasisymmetric H-bond is a fundamental property of the proton. This H-bond determines the stability of the proton hydrates and acid–base complexes, which defines the specific features (catalytic, electrochemical, etc.) of acidic solutions. The protonated water dimer $H_5O_2^+$ can be treated as a simplest stable proton hydrate in aqueous acid solutions. Its lifetime is larger than characteristic times of the stretching and bending vibrations, and it behaves as an individual ion with unique and distinctive structure and IR/Raman spectra. $H_5O_2^+$ is characterised by specific structural and spectroscopic properties which only slightly depend on further hydration: short $O\cdots O$ distance (<2.45 Å), IR-intensive band near $1720\,cm^{-1}$ and Raman intensive line around $500\,cm^{-1}$. The broad continuous IR absorption is a characteristic feature of the $H_5O_2^+$ ion in a strongly solvating medium, particularly, in acid solutions. $H_5O_2^+$ is a distinct chemical unity that participates in the equilibrium and non-equilibrium stages of the acid catalysed processes. The H_3O^+, $H_7O_3^+$ and $H_3O^+(3H_2O)$ ions are short-lived species in acid solutions. H_3O^+ and $H_7O_3^+$ exist as the individual entities in liquid phase under special conditions.

Keywords: proton hydrates; hydrogen bond (H-bond); infrared (IR) and Raman spectra; MD simulations; models of continuous absorption

Contents

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1. Introduction

The problem of the determination of the stoichiometric compositions and structures of the simplest stable proton solvates arose long before the appearance of the physical methods which make it possible to achieve this. In the end of the nineteenth century it was known that, when salts and acids are dissolved in water, heat is evolved, indicating binding of the solute to water. In 1886, Arrhenius and van't Hoff showed that many salts and acid decompose into ions in an aqueous medium [1]. Hence it was possible to conclude that the high heats of acid solution in water are due to the formation of the stable proton hydrates. Taking into account this phenomenon as well as the data on kinetics of esterification in aqueous alcoholic solutions, Hantzch and Caldwell [2] and Goldschmidt and Ulby [3] postulated in 1907 that the dissociation of an acid in water results in the formation of the hydronium ion H_3O^+. The firm establishment of this hypothesis was promoted by the proton theory of acids established independently by Brønsted [4] and Lowry [5]. According to this theory, the interaction of an acid with water takes place as follows:

$$HA + H_2O \rightleftarrows H_3O^+ + A^-. \qquad (1)$$

However, there were no data whatsoever indicating the simultaneous addition of several water molecules to the proton at that time. This is why the H_3O^+ ion was considered as the simplest stable proton hydrate.

The concept of the H_3O^+ ion became generally accepted and the appearance of the alternative hypotheses was simply ignored. This led to an extremely specific situation. In the 1950s, it was already possible to identify proton hydrates using different physical methods and to estimate their geometrical parameters. Nevertheless, most of the scientists tried to verify the H_3O^+ hypothesis instead of careful investigation of the simplest stable proton hydrate structure in molecular crystals and solutions. Experiments were usually performed under the special conditions in which only H_3O^+ ion could be formed while the appearance of any other proton hydrates was impossible. Such conditions are fulfilled in the case of the 1 : 1 ratio of the water molecule to the proton. It was usually assumed that the H_3O^+ ion is the simplest proton hydrate even in the presence of an excess of water. What were the reasons for this assumption? First of all, the H_3O^+ hypothesis was very tractable and widely used in interpreting experimental results. For a long period of time, the IR-active band at $\sim$1700 cm^{-1} in acid solutions has been erroneously assigned to the ν_4 band of H_3O^+ [6]. Finally, results of some theoretical studies supported this hypothesis. Huckel's [7] paper has been frequently quoted in the literature. According to this study, the addition of a water molecule to the proton results in the formation of an ion with three equivalent O–H bonds with the enthalpy of formation $\sim$170 kcal mol^{-1}. On the other hand, the theoretical study of Huggins [8] was rarely discussed. It was supported in the latter paper that the proton can be strongly hydrated by the two water molecules in aqueous solutions of acids. This results in the formation of the $H_5O_2^+$ ion with the strong symmetric $O \cdots H^+ \cdots O$ fragment, in which the H-bond is significantly shorter than that in liquid water. For a very long period of time, Huggins model, that is the $H_5O_2^+$ ion, was applied for the gas phase, while the Huckel model, that is the H_3O^+ ion, was used for acid solutions.

Approximately at the same time, a continuous absorption of acid or base solutions in the range from $\sim$800 to 3500 cm^{-1} was detected [9]. It complicated assignment of the bands caused by vibrations of the proton hydrates. Interpretation of the vibrational spectra of acid and base aqueous solutions required explanation of the origin of this phenomenon.

In essence, accurate experimental evidences of structure of the simplest stable proton hydrates in solutions were required. Search for such evidences was confronted with a number of difficulties. To obtain data on spectral features of the proton hydrates required precision methods for recording infrared and Raman spectra, their high photometric accuracy and reproducibility of the spectra from one experiment to another. For example, requirements on IR spectroscopy consisted in a creation of an absorbing layer of a sample of an acid on 1–5 μm thick with an assured temperature control of the sample. One should take into account that acid solutions are corrosive liquids and selection of a material for cell windows transparent in the necessary frequency range is rather limited (germanium, silicon). These difficulties were overcome by the early 1960s when, along with an improvement of classic technique of IR absorption spectroscopy, Farenfort brought IR frustrated total internal reflection (FTIR) and Harrick brought frustrated multiple internal reflection (FMIR) spectroscopy into practice [10]. It gave an opportunity to record high-quality IR spectra of solutions of acids and bases under temperature control of the sample and an accurate allowance for the cell absorption. In the middle of 1960, Raman spectroscopy was developed. The combined use of IR/Raman spectroscopy appeared to be a powerful tool for investigations of the proton hydrates due to different symmetry of these ions.

Summing up, the detailed experimental investigations of the structure and spectroscopic properties of the protonated water clusters have become possible since the end of 1960s. Theoretical methods are widely used to study the structure, relative stability and vibrational spectra of protonated water clusters/proton hydrates in the gas and condensed phases. Harmonic frequencies and IR intensities are usually evaluated in the double adiabatic approximation. It is of limited applicability to strong H-bonded systems because of mechanic [11] and electric anharmonicity [12]. Due to technical limitations, direct quantum–mechanical computations of the IR spectra of acid solutions are impossible at present. This is why theoretical models of the structure and spectra of the proton hydrates have not been completed yet.

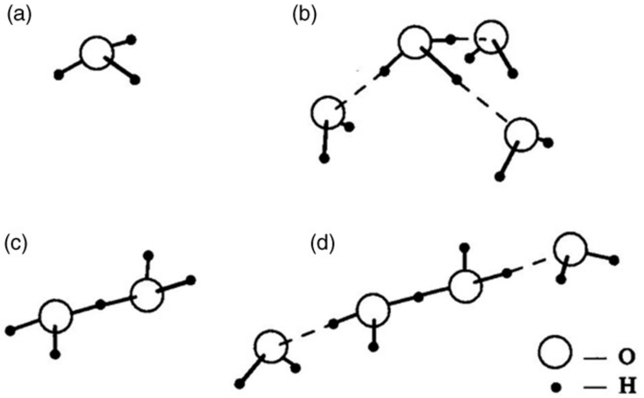

Figure 1. The structure of the selected proton hydrates: (a) the hydronium ion H_3O^+; (b) the hydronium ion trihydrate $H_3O^+(3H_2O)$; (c) the protonated water dimer $H_5O_2^+$ and (d) the partially hydrated protonated water dimer $H_5O_2^+$ $(2H_2O)$.

The proton is unique in chemistry by virtue of its atomic mass and electronic size. Because of the latter it exerts an intense electric field on its surrounding. Therefore, it cannot remain free under ordinary conditions. In the case of aqueous acids, it must be combined with the solvents. Different water protonated clusters are widely used to describe hydration processes in acid solutions. There are the hydronium ion H_3O^+, the Zundel ion $H_3O^+(H_2O)$, the protonated water dimer $H_5O_2^+$, the protonated water trimer $H_7O_3^+$ and the Eigen ion $H_9O_4^+$ (Figure 1). It should be noted that the $H_9O_4^+$ formulation is misleading because it does not distinguish between the fully hydrated H_3O^+ and the partially hydrated $H_5O_2^+$, cf. Figure 1(b) and (d). This is why the $H_3O^+(3H_2O)$ formulation will be used in the review for the Eigen ion. To differentiate between these cations, the simplest stable proton hydrate should be defined. This definition was introduced by Sokolov [13]. According to it, the proton hydrate can be treated as a stable species if

(1) it behaves as an individual ion with unique and distinctive structure and IR/Raman spectra;
(2) its specific structural and spectroscopic properties slightly depend on further hydration.

Results of the most distinguished experimental and theoretical studies of the protonated water clusters/proton hydrates in the gas and condensed phases are discussed in the review. The main attention is paid to the structural and spectroscopic properties of the systems under consideration. Detailed analysis of continuous absorption of acid or base solutions as well as the mechanism of proton transfer in polar solvents is beyond the scope of the present review.

2. Historical background

The first experimental results indicating that the simplest stable proton hydrate in aqueous solutions is not the hydronium ion were obtained by Eigen [14]. 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 to be ~9 Å. This is very close to the size of the $H_3O^+(3H_2O)$ ion, which has the C_{3v}/C_3 symmetry, similar to the H_3O^+ ion. The hypothesis that the simplest stable proton hydrate is the $H_3O^+(3H_2O)$ ion, put forward on the basis of the above experiment, and 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 [15] that in reality they are almost twice as high as the value obtained by Eigen [14]. It followed from these data that the diameter of the proton hydrate should be ~5 Å [16]. This value of the diameter of the simplest proton hydrate fits to the size of the $H_5O_2^+$ ion. It should be stressed that the lifetime of $H_3O^+(3H_2O)$ has not been estimated. Characteristic features of this ion in aqueous acid solution were not described in literature. Nevertheless, the concept of the $H_3O^+(3H_2O)$ ion was extremely popular in the 1950s and 1960s and is still very popular in the community performing the MD simulation of the proton transfer in polar solvents [17].

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. A continuous absorption in the spectra of acid solutions was recorded in the near IR region (4000–8000 cm^{-1}) [18]. Overtone and combined vibrations of the OH groups (~5150 and ~6900 cm^{-1}) locate in this region. Optical density of these bands was found to be proportional to ($[H_2O]_0-2[HCl]_0$), where $[H_2O]_0$ and $[HCl]_0$ are the analytical concentrations of water and HCl, respectively. Therefore, the hydration number inferred for proton from the spectral data in the above-indicated frequency range amount to 2 [13]. Unfortunately, this fact was not related to the structure of the hydrated proton.

A large series of studies on the continuous absorption has been carried out by Zundel and co-workers [19] since the end of 1960s. One of the first he assumed (the first was Ackermann [9]) was that this phenomenon is caused by delocalisation of the positive or negative charge in the solvate complex. It has been shown [20] with the aid of a novel experiment that the appearance of the continuous absorption requires the hydration of the acid proton by two water molecules. Zundel's [19,21] interpretation of the continuous absorption is based on the following assumptions:

1. Vibrational spectra of aqueous solutions of acids and strong bases contain the same vibrational bands, which are not caused by fundamental vibrations of the H^+ or OH^- hydrates;
2. The lifetime of the H_3O^+ ion (which is the simplest proton hydrate in Zundel view) is so short that its vibrations cannot be recorded by the IR spectroscopy;
3. The $H_3O^+(3H_2O)$ ion is the most stable ion-molecular species which vibrations are detected in the IR spectrum of the solution (Figure 2).

On the basis of these assumptions, Zundel proposed a model of the proton hydration in solution. Its essential features are the following: the $H_3O^+(H_2O)$ cation does exist in acid solutions. This species is not the simplest stable ion but an unstable group, which is incapable of entering into chemical reactions as an integral whole/entity. The proton in this cation is rapidly exchanged between the two water molecules, occupying one of the boundary positions:

$$(H_2OH^+\cdots OH_2) \rightleftarrows (H_2O\cdots H^+OH_2). \tag{2}$$

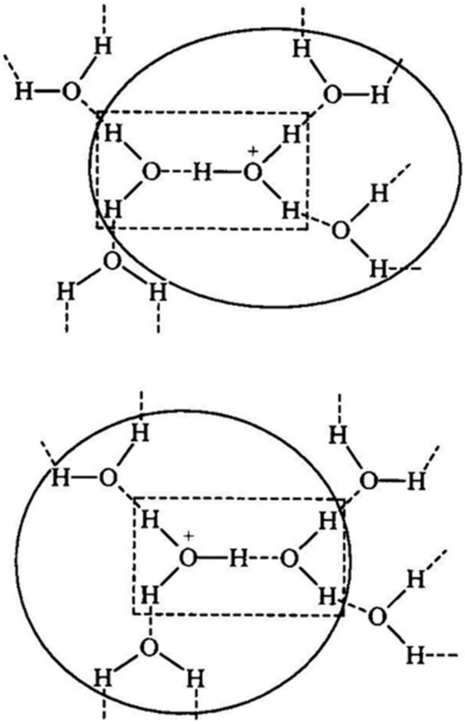

Figure 2. The molecular structure of the proton hydrate according to Zundel data [19]. The $H_3O^+(3H_2O)$ ion is shown within the circumscribed region.

Assumptions (1)–(3) were based on the results of the studies [9,22,23] which subsequently proved to be erroneous:

(1) IR spectra of aqueous solutions of strong acids and bases, for example, aqueous HCl and KOH solutions are quite different. Their spectra are characterised by different bands caused by the fundamental transitions of the H^+ and OH^- hydrates [13].

(2) The H_3O^+ ion does exist in aqueous solutions under special conditions [13]. Its vibrational spectra can be recorded by the IR spectroscopy in aqueous acid solutions [24].

(3) Zundel assumption of the extremely short lifetime of the proton hydrates was supported by the unfortunate misprint committed by Bell [25] in his well-known monograph 'Proton in Chemistry'. Bell wrote on page 23 of his book: 'Assignment of the vibrational spectra observed in aqueous acid solutions to hydronium ion seems to be dubious at present. The lifetime of a species must be at least $1/(3 \times 10^{10} \times 1205) = 3 \times 10^{-13}$ s for the vibrational frequency of 1205 cm^{-1}, to be revealed. Here Bell made an arithmetical error, because the actual result of calculation is $\sim 3 \times 10^{-14}$ s [26]. This misprint, unfortunately, was reproduced in the translated versions of the monograph.

It should be stressed, that the Zundel model treats the $H_3O^+(H_2O)$ ion as the simplest unstable proton hydrate in which the proton is rapidly exchanged with the adjacent water molecule, see Equation (2). The $H_3O^+(H_2O)$ cation is often called as the Zundel cation [27]. It differs strongly from $H_5O_2^+$. This is why definition of $H_5O_2^+$ as the Zundel cation [28] seems to be incorrect.

3. Protonated water clusters in molecular crystals and the gas phase

The nature of the interactions of the simplest proton hydrates with water molecules is central to the study of acidic solutions. In assessing the effect hydration (the solvent), it is natural to consider first the strong interactions of the cation with the nearest water molecules and then examine the structure modifications and energy effects arising at longer distances.

In the gas phase, the mass spectrometric technique and vibrational spectroscopy enable one to study the interaction of the cation with a varying number of 'inner sphere' molecules in the absence of bulk of the solvent. The structure of clusters under investigation may be computed by *ab initio* or DFT methods with relatively large basis sets. In molecular crystals, the structure and vibrational spectra of the simplest proton hydrates can be investigated experimentally.

3.1. *Frequencies of the fundamental transitions*

The simplest protonated water cluster, the H_3O^+ hydronium ion, has been known since the early 1920s and has been studied in crystalline acid monohydrates $H_3O^+X^-$, where X^- is different counterions, by IR and Raman spectroscopy [29–32], and by X-ray [31,33] methods. Fundamental transitions of the cation in the $H_3O^+ClO_4^-$ crystal are given in Table 1. The distortion of the H_3O^+ structure is negligible in this crystal and the vibrational spectrum of H_3O^+ is closest to that of the unperturbed cation (C_{3v} symmetry). Assignment of the vibrational bands of H_3O^+ was made by analogy with the isoelectronic ammonia molecule (Figure 3). In many crystals, the influence of the counterion is so strong that the H_3O^+ loses its initial C_{3v} symmetry. As a result, the splitting of the degenerate stretch (ν_3) and bending (ν_4) vibrations is observed [34]. Vibrational spectra of the protonated water dimer in molecular crystals $H_5O_2^+Y^-$, where Y^- is different counterions, were studied by IR, Raman and INS spectroscopy [34–36]. The $H_5O_2^+$ ion has approximately C_{2h} symmetry in different crystals [37]. Fundamental transitions of the cation in the $H_5O_2^+ClO_4{}^-$ crystal are given in Table 1. One can see that the IR spectra of the ions are different in the 2000–3000 cm^{-1} frequency region. Vibrations of the $O\cdots H\cdots O$ fragment of $H_5O_2^+$ locate below 2000 cm^{-1}. However, the IR intensity of the $O\cdots H\cdots O$ bending modes is quite low. The Raman spectra of the ions differ strongly below 1000 cm^{-1}. The $O\cdots O$ symmetric stretching mode of the $H_5O_2^+$ ion locates in this region.

Vibrational spectra of the $H_3O^+(3H_2O)$ and $H_5O_2^+$ clusters with Ar and Ne are measured in the frequency region above 1000 cm^{-1} [38]. IR spectra of the bare H_3O^+ and $H_5O_2^+$ ions are also available [39–45]. Fundamental transitions of the H_3O^+ and $H_5O_2^+$ ions in the bare cations as well as in the $H_3O^+(3H_2O) * Ar$ and $H_5O_2^+ * Ne$ complexes are given in Table 2. The spectra of bare $H_5O_2^+$ are probably more perturbed than the Ar/Ne tagged spectra due to high intensity of laser pulse and the requirement that the molecule absorb multiple photons to dissociate [46–48]. Assignment of the photodissociation

Table 1. Frequencies of the fundamental transitions (cm^{-1}) of the H_3O^+ and $H_5O_2^+$ ions in $H_3O^+ClO_4^-$ and $H_5O_2^+ClO_4^-$ crystals*.

$H_3O^+ClO_4^-$			$H_5O_2^+ClO_4^-$			
IR [32]	Raman [32]	Assignment	IR [35]	Raman [35]	INS [36]	Assignment
3220	3250	Degenerate stretch (ν_3)	3340	3370, 3300	–	OH stretches of the terminal waters, ν_w(OH)
			3220	3205, 3180		
2820	2808	Symmetric stretch (ν_1)	–	–	–	
1670	1649	Degenerate bending (ν_4)	1770	1800–1700	1800	HOH bending, $\sigma(H_2O)$
			1680		1720	
–	–	–	1490	1400	1560	O$\cdots$H$\cdots$O bending, σ(OHO) and γ(OHO)
			1270	–	1320	
1020	1024*	Symmetric bending (ν_2)	1080	1050	1120	The parallel shared proton vibration, ν_{as}(OHO)
					1200	
–	–	–	–	637*	448	O$\cdots$H$\cdots$O symmetric stretch, ν_s(OHO)

Note: The most intensive bands in the Raman spectra are marked by asterisks.

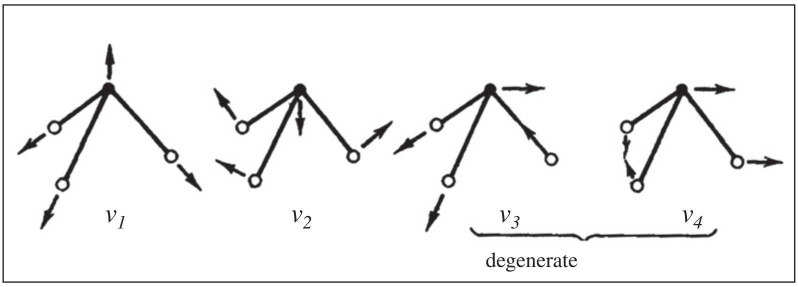

Figure 3. Normal vibrations of H_3O^+.

spectrum of the $H_5O_2^+ * Ne$ complex has been recently done by Meyer and co-workers [47,48].

The following conclusions can be made from the data presented in Tables 1 and 2.

(1) Frequencies of the stretches modes ν_1 and ν_3 of H_3O^+ are extremely sensitive to the environmental effects because the cation undergoes appreciable distortion upon hydration. This is why there is no clear correlation between the frequencies of the ν_1 and ν_3 modes in the bare H_3O^+ ion and the ion in $H_3O^+(3H_2O)$.

(2) Environmental effects change strongly the frequencies of the OH stretches of the terminal water molecules $\nu_w(OH)$ and cause a red shift of the parallel shared proton vibration, $\nu_{as}(OHO)$ of $H_5O_2^+$. The frequency of the bending mode $\sigma(H_2O)$ is hardly affected by environment and can be described in harmonic approximation fairly well [46,49]. Moreover, it is insensitive to the position of the shared proton in the $H_5O_2^+ * RG_n$ ($RG = Ar$, Ne and $n = 1$–5) complexes [46]. The latter can be described by a rescaled symmetry variable $\delta = [0.5 * r(O \cdots O) - r(O \cdots H^+)]/r(O \cdots O)$ [50] or asymmetry of H-bond $q = r(O \cdots O)/2 - r(O \cdots H^+)$ [51]. In the bare $H_5O_2^+$ cation $\delta \sim 0$ ($q \sim 0$) and $\sigma(H_2O) = 1741\,cm^{-1}$, while in the $H_5O_2^+ * Ar$ cluster $\delta \sim 0.1$ ($q \sim 0.09\,Å$) and $\sigma(H_2O) = 1758\,cm^{-1}$. Location of the $\sigma(H_2O)$ mode $\sim 1740\,cm^{-1}$ is unique to $H_5O_2^+$ because the bending vibrations of the H_3O^+ ion and dangling water molecules in larger protonated water clusters, such as $H_3O^+(3H_2O)$, appear as very sharp bands near $1600\,cm^{-1}$ [52].

(3) The band near $2600\,cm^{-1}$ is caused by the OH stretches of the $H_3O^+(3H_2O)$ cation and may be treated as the Eigen signature [38].

3.2. *Proton hydration in the gas phase*

Kebarle and co-workers [53] performed a series of novel investigations of the following gas-phase reactions:

$$H^+(n-1)H_2O + H_2O = H^+(nH_2O). \tag{3}$$

It was shown that the heat of addition (ΔH) of a water molecule to the hydronium ion is $31.6\,kcal\,mol^{-1}$. The energy of the addition of the second ($19.5\,kcal\,mol^{-1}$) and subsequent water molecules is significantly smaller, decreasing monotonously with increase of their

Table 2. Frequencies of the fundamental transitions (cm^{-1}) of the bare H_3O^+ and $H_5O_2^+$ ions and the ions in the $H_3O^+(3H_2O) * Ar$ and $H_5O_2^+ * Ne$ complexes.

H_3O^{+a} [39–42]	$H_3O^+(3H_2O) * Ar$ [38]		$H_5O_2^{+c}$ [43,44]	$H_5O_2^+ * Ne$ [46]	
3530	2655	Degenerate stretch (ν_3)	3684, 3609	3683, 3603	OH stretches of the terminal waters, ν_w(OH)
3491	–	Symmetric stretch (ν_1)	–	–	–
3390^b					
1639	~1600	Degenerate bending (ν_4)	–	1878, 1763	H_2O bending, $\sigma(H_2O)$
			1741		
954	~1050	Symmetric bending (ν_2)	1043	1047	The combinational band of the O$\cdots$H$\cdots$O symmetric stretch, ν_s(OHO) and wagging motion^d
526^b					
–	–	–	921	928	The parallel shared proton vibration, ν_{as}(OHO)^d

Notes: [a] The IR intensity ratios for the fundamental ν_3, ν_1, ν_4 and ν_2 bands of H_3O^+ are about 13 : 1 : 3 : 11.

[b] The ν_1 and ν_2 vibrations are subject to a double-well potential [40,41], the frequencies of the $1^- \leftarrow 0^+$ and $1^+ \leftarrow 0^-$ bands are given, respectively.

[c] Location of the O$\cdots$H$\cdots$O bending vibrations is not clear.

[d] The doublet-band absorption around 1000 cm^{-1} is fully reproduced and explained in terms of coupling of the parallel shared proton vibration to wagging motion of the water molecules and the O$\cdots$H$\cdots$O symmetric stretch [47].

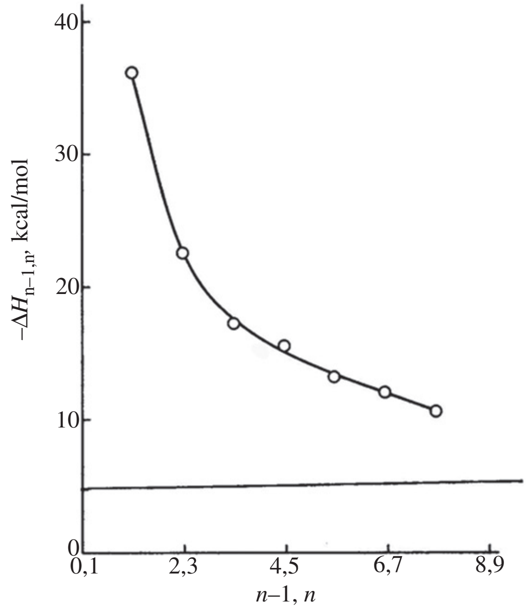

Figure 4. Enthalpy changes, $\Delta H_{n-1,n}$, for reaction (3) proceeding in the gas phase. Enthalpy of the H-bond formation in bulk water is given by the dotted line [55].

number (Figure 4). It should be noted that the entropy term does not play an essential role in the considered processes [54]. ΔH equals to 19.5 kcal mol^{-1} for $n=2$ and is around 10 kcal mol^{-1} for $n=7$ [53]. It means that the H-bond in the $H_5O_2^+$ ion is extremely strong while the H-bond between $H_5O_2^+$ and a water molecule is ~17.9 kcal mol^{-1}. The latter value is typical for strong H-bonds occurring in the carbon acid dimers.

Widely excepted models [17,19,25,28,38] assume that the hydrated proton forms the symmetrical structure $H_3O^+(3H_2O)$. The question arises whether the Eigen ion has an exceptional stability. Results of the mass spectrometric studies [54] clearly demonstrate that $H_3O^+(3H_2O)$ is not exceptionally stable, since its equilibrium concentrations are not prominent but fit the general concentration distribution in the cluster. In contrast to the Eigen ion, a preference for the cluster NH_4^+ $(4NH_3)$ is indicated by the results shown in Figure 5. According to it, the NH_4^+ forms an inner shell of four NH_3 molecules, which in the tetra-ammoniate state forms a compact but uncrowded structure [56]. The build-up of a distinct outer shell leads to a drop off in the $-\Delta H_{4,5}$ value (Figure 5). The structure of the NH_4^+ ion slightly changes upon solvation [57]. In contrast to NH_4^+, hydration of the hydronium ion leads to the formation of the new species, the $H_5O_2^+$ ion. These examples show the principle difference in the structure and relative stability of the $H_3O^+(nH_2O)$ and NH_4^+ (nNH_3) clusters in the gas phase.

Enthalpy changes, $\Delta H_{n-1,n}$, for reaction $H_5O_2^+(n-1)H_2O+H_2O=H_5O_2^+(nH_2O)$ evaluated in Librovich *et al.* [58] using the data of Kebarle and co-workers [53] is given in Figure 6. According to it, the water molecules belonging to the proton hydration sphere differ from the molecules in bulk water up to $n \sim 9$. This conclusion is supported by the

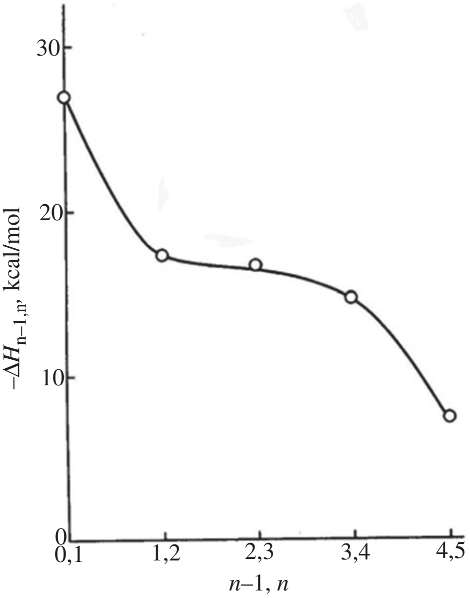

Figure 5. Enthalpy changes, $\Delta H_{n-1,n}$, for reaction $NH_4^+(n-1)NH_3 + NH_3 = NH_4^+(nNH_3)$ proceeding in the gas phase.

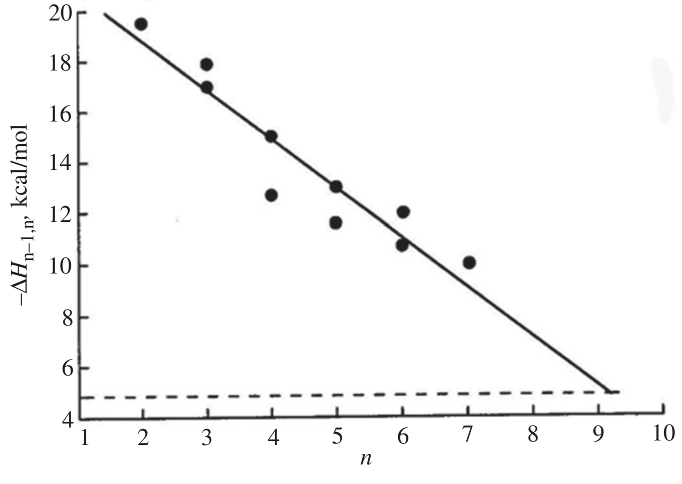

Figure 6. Enthalpy changes, $\Delta H_{n-1,n}$, for reaction $H_5O_2^+(n-1)H_2O + H_2O = H_5O_2^+(nH_2O)$ proceeding in the gas phase. Enthalpy of the H-bond formation in bulk water is given by the dotted line [55].

results of the spectroscopic study of the gas-phase protonated water clusters, $H^+(mH_2O)$, $m = 2$–11 [38]. It was found in Headrick *et al.* [38] that the clusters of the size range 9 to 11 display very broad background absorption throughout the entire 2300–3000 cm^{-1} range, reminiscent of the excess proton spectrum in bulk water.

3.3. $H_3O^+nH_2O$ versus $H_5O_2^+(n-1)H_2O$: relative stability of the cations

Relative stability and the IR spectra of the protonated water clusters were studied experimentally [44,53,59,60] and theoretically [51,61–63]. These data enables one to investigate the equilibrium in the following model gas-phase reactions:

$$H_2O^+(nH_2O) \leftrightarrow H_5O_2^+(n-1)H_2O, \text{ where } n = 1, \ldots, 5 \tag{4}$$

For $n = 1$ and 2, the equilibrium shifts to the right-side of the equations:

$$H_3O^+(H_2O) \rightarrow H_5O_2^+ \tag{5a}$$

$$H_5O_2^+(H_2O) \rightarrow H_7O_3^+ \tag{5b}$$

It has been established by mass spectrometric studies [53] that the reactions (5a) and (5b) are exothermic by 19.5 and 17.9 kcal mol^{-1}, respectively. Indeed, the IR spectrum of the protonated water dimer contains the bands of the $H_5O_2^+$ ion only, while this ion is absent in the IR spectrum of the protonated water trimer.

For $n = 3$ the equilibrium shifts to the left-side of the equation:

$$H_3O^+(3H_2O) \leftarrow H_5O_2^+(2H_2O) \tag{6}$$

Conversion from $H_3O^+(3H_2O)$ to $H_5O_2^+(2H_2O)$ requires ~2 kcal mol^{-1}. The gas-phase spectrum of the protonated water hexamer cluster shows the presence of the both structures; see Figure S4 in Jieli and Aida [63]. Equation (6) describes conversion from the Eigen ion to the partially hydrated $H_5O_2^+$ cation. This equilibrium attracts considerable attention in the MD simulations of proton transfer in acidic solvents [27,50,64–70] and in the gas phase [51,61–63].

For $n = 4$, a large number of different conformers with similar stability were computed [51,63]. Neither of them corresponds to the hydrated H_3O^+ or $H_5O_2^+$ cations.

For $n = 5$, the equilibrium shifts to the right side of the equation:

$$H_3O^+(5H_2O) \rightarrow H_5O_2^+(4H_2O) \tag{7}$$

The $H_5O_2^+$ $(4H_2O)$ ion corresponds to the global minimum, while the $H_3O^+(5H_2O)$ ion is a local-minimum structure. Conversion from $H_5O_2^+$ $(4H_2O)$ to $H_3O^+(5H_2O)$ requires ~0.4 kcal mol^{-1} [51,61–63]. Indeed, the gas-phase spectrum of the protonated water hexamer shows the presence of the fully hydrated protonated water dimer $H_5O_2^+$ $(4H_2O)$; see Figure S6 in Jieli and Aida [63].

According to Jiang *et al.* [59], the $H_5O_2^+$ containing isomers become more stable than their H_3O^+ counterparts for protonated water clusters with a size of $n \geq 5$. On the other hand, a distinct band near the Eigen signature at 2600 cm^{-1} is reestablished at $n = 9$ [38].

Results of the experimental and theoretical studies of the structure and IR spectra of the gas-phase protonated water clusters may be summarised as follows:

(1) Formation of the first coordination sphere slightly changes the $O \cdots O$ distance and the frequency of the bending mode $\sigma(H_2O)$ of the $H_5O_2^+$ cation. These values are practically the same in the $H_5O_2^+$ ion, its partially hydrated form $H_5O_2^+(2H_2O)$ and the fully hydrated protonated water dimer $H_5O_2^+(4H_2O)$.

(2) Formation of the first coordination sphere changes strongly the structure and IR spectrum of the Eigen ion, $H_3O^+(3H_2O)$. There is no clear correlation between the frequencies of the $H_3O^+(3H_2O)$ ion and its partially hydrated form $H_3O^+(5H_2O)$.

4. Protonated water clusters in liquid phase

4.1. *H_3O^+ in liquid phase: the 1 : 1 system*

It is impossible to get quite such detailed data on the structure of the H_3O^+ ion in solution as in molecular crystals. The X-ray and neutron diffraction methods as well as the NMR method yield little information in acid solutions due to the fast exchange between protons and water molecules. NMR can be efficiently applied in the studies of the special systems, in which the proton exchange is practically suppressed (Section 4.3). The conclusions reached concerning the structure of the simplest proton hydrate in acid solutions 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 deuterium analogues) have been recorded in the IR spectra of aqueous solutions of HCl, HBr, HNO_3, $HClO_4$ and H_2SO_4 [71,72]. The observed bands were located near those of the H_3O^+ ion in molecular crystals (Table 1). They were therefore assigned to the vibrations of the hydronium ion without additional studies. All attempts to record hydronium lines in the Raman spectra of the acid solutions were unsuccessful [29,73]. This fact was simply ignored. However, on passing to liquid systems in which the H_3O^+ ion does exist (with the ratio acid : water = 1 : 1) situation changes sharply. The Raman spectrum of a solution of the equimolar H_2O–$HSbCl_4$ mixture in dichloroethene exhibits four lines 3560, 3510, 1600 and 1095 cm^{-1} [74] which correspond to the frequencies of the fundamental transitions ν_3, ν_1, ν_4 and ν_2 of H_3O^+ in the gas phase and molecular crystals (Tables 1 and 2). The reliability of the assignment of the observed lines to the corresponding H_3O^+ vibrations has been confirmed by the splitting of the degenerate vibrational frequencies (3510 и 1600 cm^{-1}) following the replacement of the $SbCl_4^-$ anion by the smaller anions (Cl^- и Br^-) [75,76].

It should be noted that the ratio acid : water = 1 : 1 is only a necessity criterion for existence of the H_3O^+ ion. The IR spectrum of a saturated solution of the equimolar H_2O–HCl mixture in SO_2 clearly shows the band at ~1720 cm^{-1} [77]. It was attributed [78] to the $(H_2O \cdots H^+ \cdots OSO)$ ion with the strong quasisymmetric H-bond.

According to Stoyanov *et al.* [79], the existence of the H_3O^+ ion in organic solvents requires the formation of three more-or-less equivalent, medium-to-strong H-bonds with solvent or counterion. Only solvents with the basicity range, chlorocarbons to tributyl phosphate, are suitable. The range includes benzene, which has unexpectedly strong π interactions with the O–H bonds of H_3O^+. There are three requirements of the counterion. It must have very low proton-acceptor ability, be relatively non-polarisable and have high chemical stability [76].

Summarising the foregoing, it must be emphasised that the H_3O^+ ion has been detected in those solid and liquid systems where only one water molecule corresponded to each acid proton. The presence of H_3O^+ has to be detected by IR and Raman spectra and should be verified by stoichiometric data. On the other hand, the conclusion that this ion is present in dilute aqueous solutions of acid clearly conflicted with the theory of vibrational spectra [78].

4.2. $H_5O_2^+$ in acid solutions in the access of water

The acid-catalysed reactions of organic compounds in aqueous solutions usually proceed in access of water. Definition of the mechanism of these reactions is a fundamental aim of physical organic chemistry. Knowledge of the amount and the structure of intermediate complexes of reactant molecules with catalyst entities are required for this. The relative concentrations of these complexes were determined by using thermodynamic parameters (acidity functions and activities of catalyst components). The structure of the strong H-bonded systems was obtained from the vibrational spectra. Results of the most pronounced works are described below.

According to Librovich *et al.* [80], a new band around 1700 cm^{-1} appears in the IR spectrum of the HCl aqueous solution with the increase of the acid concentration. The optical density of the band is proportional to the amount of the HCl added. (This band was erroneously assigned to the H_3O^+ ion [6,72,77].) Detailed analysis of the structure of the proton hydrates in the HCl aqueous solutions is impossible due to excess of water. It was suggested [34] that continuous IR absorption of the aqueous HCl solution is caused by the presence of $H_5O_2^+$.

The IR spectra of aqueous H_2SO_4 solutions were obtained by the method of frustrated total internal reflections (FTIR) in Maiorov *et al.* [81]. This system was chosen for the following reasons:

(1) The IR spectrum of pure H_2SO_4 shows no absorption in the 1500–2000 cm^{-1} frequency range;
(2) The IR spectra were obtained for pure water and for aqueous H_2SO_4 solutions with concentrations ranging from 4.96 to 99.99%.

Dilution of the acid with water led to appearance of the wide band with ν_{max} around 1665 cm^{-1} (Figure 7). Dilution from 99.99 to 90% H_2SO_4 did not shift it. Outside this concentration interval, ν_{max} is located at 1700 cm^{-1}. Below the 61% acid, the new band appears at 1645 cm^{-1}, which corresponds to the bending vibrations of water (Figure 7).

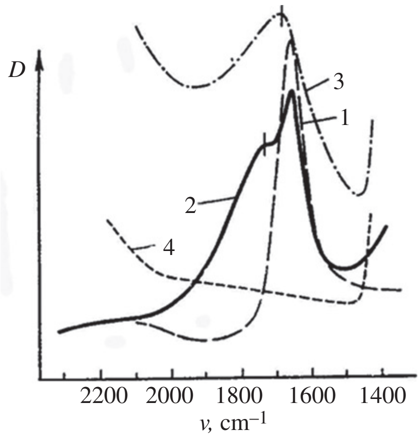

Figure 7. FTIR IR spectra for aqueous H_2SO_4 solutions at 30°C: (1) H_2O; (2) 39.8% H_2SO_4; (3) 90% H_2SO_4 and (4) 99.1% H_2SO_4.

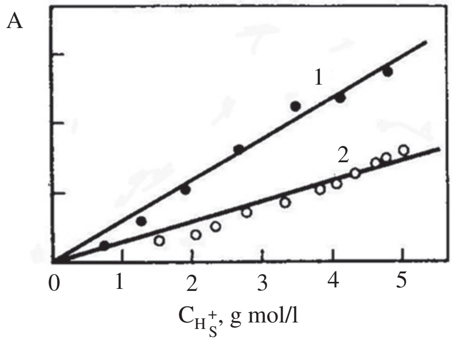

Figure 8. Variation of the optical density of the HOH bending $\sigma(H_2O)$ band (A) for bound water with the concentration of solvated proton ($C_{H_S^+}$) : (1) dilution of water with the acid, 0 stands for pure water and (2) dilution of the acid with water, 0 stands for 99.99% acid.

Variation of the absorbance of the HOH bending vibration band (A) for bound water with the total concentration of the solvated protons is given in Figure 8. The ratio of the absorbance values in access of water and in the concentrated acid is 2. These observations can be accounted for in the following manner. Dilution of the acid leads to the formation of the $H_2O \cdots H^+ \cdots OR$ ions, where OR is H_2SO_4, H_2SO^- or their complexes with water. Here HOH bending vibrations $\sigma(H_2O)$ are limited to the H_2O group of the ions. Further addition of water gives rise to the formation of the $H_2O \cdots H^+ \cdots OH_2$ ions. Association of the $H_5O_2^+$ ions is different from the association of the $H_2O \cdots H^+ \cdots OR$ ions and the ν_{max} band shifts in passing from 90% H_2SO_4 to the 61% acid. Below the 61% acid, pure water appears in the acid solution. Continuous absorption was detected for the concentrated H_2SO_4 solutions. The $H_5O_2^+$ ions are absent in these conditions [81] while H_3O^+ does not cause this phenomenon. It was suggested that the continuous absorption in the concentrated H_2SO_4 solutions is caused by the $H_2O \cdots H^+ \cdots OR$ ions with strong quasisymmetric H-bonds.

Non-ionised acid ($\sim 2.5\,\text{g mol l}^{-1}$) exists in the equimolar H_2SO_4–H_2O mixture, see Figure 9 [82]. It means that the equilibrium $H_2SO_4 + H_2O \rightleftarrows H_3O^+ + HSO_4^-$ does not completely shift to the right, as was assumed previously [83]. In the access of water, the following equilibrium arises: $H_2SO_4 + 2H_2O \rightleftarrows H_5O_2^+ + HSO_4^-$. Due to it, the $H_5O_2^+$ ion is generated. Hence, the mechanism of sulfonation of organic compounds was revealed [84].

Conception of the simplest stable proton solvate $H_5O_2^+$ enables one to reveal the mechanism of the hydrolytic reactions of organic compounds in aqueous acid solutions. This reaction resembles a rate-limiting stage of acid-catalytic processes. It was assumed for a long time that the protonation of the organic molecule B was described by the following scheme: $B + H^+ \rightleftarrows BH^+$, where BH^+ is the simplest proton solvate, the addition to which a second and subsequent solvent molecules does not alter its structure. However, as early as 1980 the continuous in the IR spectrum of the BH^+ system was detected. It implies the appearance of the strong H-bonded species with a quasisymmetric $B \cdots H^+ \cdots O$ fragment. The following scheme of the hydrolytic reactions of organic compounds in aqueous acid solutions was suggested:

$$B + (H_2O \cdots H \cdots OH_2)^+ \rightleftarrows (B \cdots H \cdots OH_2)^+ + H_2O. \tag{8}$$

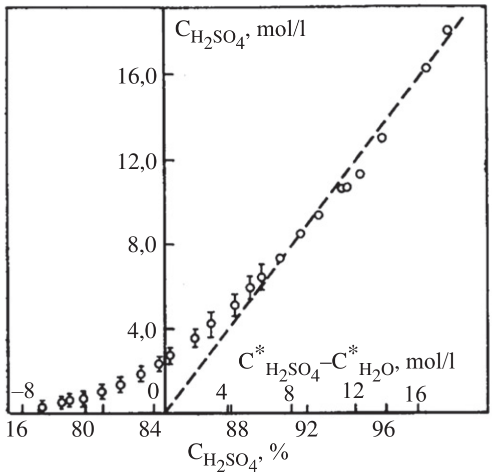

Figure 9. Dilution of the pure H_2SO_4 with water. $C_{H_2SO_4}$ stands for the acid concentration, estimated from the experimental spectrum, while $C^*_{H_2SO_4}$ and $C^*_{H_2S}$ are the analytical concentrations of the acid and water, respectively.

In other words, this reaction resembles the substitution of the water molecule in $H_5O_2^+$ by the B molecule. The mechanism of acid-catalytic processes was revisited and the Hammet acidity function H_0, was discovered and the limits of its applicability were established [85].

Kinetic equation of the acid-catalytic reaction of esterification [86] is written as:

$$W = K_{\text{eff}}\ [B]\ [H_5O_2^+] \tag{9}$$

where W is a rate of the reaction, K_{eff} – an effective rate constant, [B] – concentration of the substrate (esters, amides, etc.) and $[H_5O_2^+]$ – concentration of $H_5O_2^+$ that is extracted from the equilibrium composition of the acid–water mixture. Equation (9) agrees nicely with the experimental data [86].

The papers discussed in this section, give indirect information on the structure of the protonated water dimer. On the other hand, they unambiguously indicate that $H_5O_2^+$ is the simplest stable proton hydrate, which participates in the equilibrium and non-equilibrium stages of the acid-catalytic processes.

4.3. *H_3O^+ versus $H_5O_2^+$ in liquid phase*

The H_3O^+ ion does exist in condensed phase in special cases, when not more than one water molecule corresponds to each acid proton (Sections 3.1 and 4.1). The question is 'What is happened in the presence of an excess of water'? To answer this question, special experimental studies were done.

The H_3O^+ ion was investigated by high-resolution NMR in a mixture of an equimolar amount of water with octanesulfonic acid in freons [87]. The spectrum of the ion is given in Figure 10. The addition of an excess of water led to a sharp weakening of these bands and the appearance of two new narrow lines with a 1 : 4 intensity ratio (Figure 10). These lines are due to the shared proton and four hydrogens of the terminal water molecules of $H_5O_2^+$.

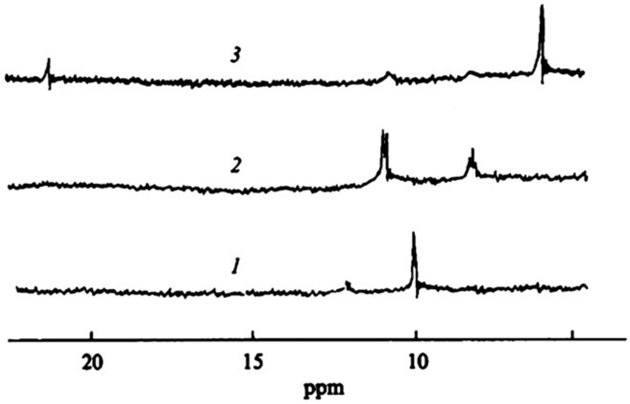

Figure 10. NMR spectra of dilute solutions of H_2O–$HSO_4C_8H_{17}$ mixtures in deuteriohalomethanes for different $H_2O:HSO_4C_8H_{17}$ ratios: (1) 0 : 1; (2) 1 : 1 and (3) 2 : 1.

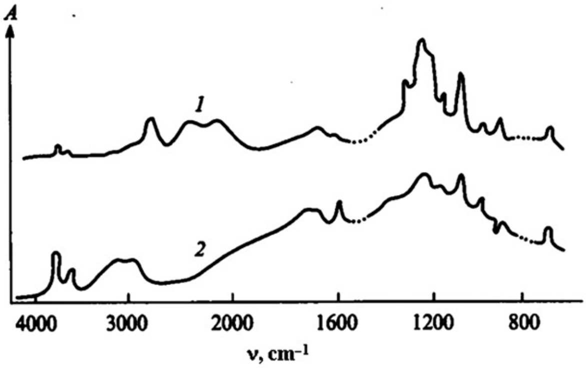

Figure 11. IR spectra of the H_2O–HSO_3CF_3–CCl_4 ternary system for different molar components ratios: (1) 1 : 1 : 50 and (2) 2 : 1 : 50.

Solutions of the CF_3SO_3H/H_2O and HI/H_2O mixtures in an inert solvent (CCl_4) delituted to 10^{-2} M have been investigated by IR spectroscopy [34]. For the acid : water = 1 : 1 ratio, the bands of the H_3O^+ ion were observed in the spectrum (Figure 11). Increase in the water concentration to the ration 1 : 2 leads to the sharp change of the spectrum in the 1500–3000 cm^{-1} and the appearance of continuous absorption (Figure 11), due to the formation of the $H_5O_2^+$ ion. Further addition of water did not affect the IR absorption curve.

According to Librovich *et al.* [88], the most convincing information about the nature of the proton hydrates in liquid phase can be obtained using both IR absorption and Raman scattering methods simultaneously, rather than only IR as in Giguère [6] and Giguère and Turrell [72]. A comparison between the IR and Raman spectra of aqueous HCI solutions performed in ref. [78] demonstrated that the observed bands cannot be assigned to H_3O^+ ion. Both these observations and theoretical calculations shows that the bands observed in

Table 3. Vibrational frequencies of the proton hydrates in liquids and solids (cm^{-1})[a].

Aqueous HCl solution [90]	$H_5O_2^+$ in solids [89]	Assignment	H_3O^+ in solution [76]	Assignment
–	–	–	3560; IR, R	Symmetric stretch, ν_1
2900; IR, R	3000; IR, R	$\nu_w(OH)$	3510; IR, R	Degenerate stretch, ν_3
1710; IR, R	1720; IR, R	HOH bending, $\sigma(H_2O)$	1600; IR, R	Degenerate bending, ν_4
1370; IR[b]	1370; IR	$O \cdots H \cdots O$ bending, $\gamma(OHO)$	–	–
1170; IR	1040; IR	The parallel shared proton vibration, $\nu_{as}(OHO)$	1100; IR, R	Symmetric bending, ν_2
460; R	475; R	$O \cdots H \cdots O$ symmetric stretch, $\nu_s(OHO)$	–	–

Notes: [a] Activity of the band in IR and Raman spectra is labelled by IR and R, respectively.
[b] This band is observed in the $D_5O_2^+$ ion also (1030 cm^{-1}) [90].

IR and Raman spectra can be assigned to the vibrations of ion ($H_5O_2^+$) involving a strong hydrogen bond. This ion was suggested to be the simplest proton hydrate occurring in aqueous solutions of strong acids. It can be seen from Table 3 that the $H_5O_2^+$ spectrum in solids [89] is quite similar to the proton hydrate spectrum in the HCl aqueous solution. On the other hand, the latter remarkably differs from that of the H_3O^+ ion in solution [76]. Summing up, an unambiguous identification of the H_3O^+ ion requires the simultaneous consideration of the IR and Raman spectra.

4.4. $H_7O_3^+$ and $H_3O^+(3H_2O)$ in liquid phase

These ions exist as the individual protonated water clusters in a crystalline environment [91,92]. Study of the stepwise bonding of water molecules to H^+ in weakly basic solvents (benzene and dichloroethane) with weakly basic anions (carborane counterions) shows that $H_7O_3^+$ behaves as an individual ion with unique and distinctive structure and IR spectra [93]. The excess proton gets localised between three oxygen atoms. Experimental fingerprint for this ion in liquid water has not been detected yet.

To the best of our knowledge, the structure and vibrational spectra of the $H_3O^+(3H_2O)$ ion in liquid phase has not been published yet.

4.5. $H_5O_2^+$ as a simplest stable ion

Results described in this section demonstrated unambiguously the following important features of the proton interaction with water molecules in solution.

(1) The H_3O^+ ion may exist in the liquid phase when there is not more than one water molecule per acid molecule. When there is an increase of water content in the system, a chemical reaction between H_3O^+ and H_2O occurs, see Equation (5a). This process cannot be treated as simple hydration of the H_3O^+ ion because a rearrangement of the bonds and angles resulted in the formation of $H_5O_2^+$.

(2) The protonated water dimer can be treated as a simplest stable proton hydrate in the aqueous acid solution. Its lifetime is larger than the characteristic times of the stretching and bending vibrations. $H_5O_2^+$ behaves as an individual ion with unique and distinctive structure and IR/Raman spectra. It is characterised by specific structural and spectroscopic properties which only slightly depend on further hydration: short $O \cdots O$ distance (<2.45 Å), IR-intensive band near $1720\,\mathrm{cm}^{-1}$ and Raman intensive line around $500\,\mathrm{cm}^{-1}$.

(3) Further increase in water content leads to successive formation of the $H_7O_3^+$, $H_3O^+(3H_3O)$ and $H_5O_2^+(4H_3O)$ cations. The latter can be considered as the fully hydrated $H_5O_2^+$ cation, of which specific structural and spectroscopic properties slightly change upon formation of the first coordination sphere. In contrast to $H_5O_2^+$, the $H_7O_3^+$ and $H_3O^+(3H_3O)$ ions should be treated as the short-lived particles for which lifetime is so short that their vibrations cannot be recorded by IR/Raman spectroscopy in acid solution.

(4) In the gas phase, organic solvents and zeolite micropores, the size and structure of the simplest stable protonated water cluster is determined by specific properties of the system under consideration. Main factors are the size of the

cluster and absence of the counterion in the gas phase [44,59,60], the basicity of solvent and special requirements of the counterion in organic solvents [79,93], the size of the micropore and the number of the acidic Brönsted sites in zeolite [94,95].

5. MD simulations of the protonated water clusters in liquid phase

There is considerable published literature on the subject; for reviews, see, for example, [96–98]. The present summary is not designed to provide exhaustive coverage; rather, a brief overview is presented of selected results and ideas focusing on three aspects, (a) the debate on the relative contributions of the protonated water forms to the acid solutions; (b) interpretation of the IR spectra and (c) the criterion used to differentiate between the protonated water forms.

Simulation techniques have provided considerable insight into the solvation dynamics of the hydrated proton. Particularly, the equilibrium between different protonated water forms might be modelled. In the *ab initio* MD study by Tuckerman *et al.* [64], the $H_3O^+(3H_2O)$ cation has been found in *ca* 60% of the snapshots, the rest being populated by various intermediate proton-transferred states resembling $H_5O_2^+$. A similar contribution of the $H_5O_2^+$ species (*ca* 40%) has been found in the multistate empirical bond study by Vuilleumier and Borgis [65], on the basis of both the geometrical criterion of classification ($r(O \cdots O) < 2.45$ Å) and the occurrence of proton-transferred process in a specified amount of time (50 fs). Changing the proton-transferred observation time, however, significantly influenced the proportion of both hydrated proton forms and the difficulty of discrimination between two unambiguous structures has been pointed out. This problem has been addressed in the paper by Asthagiri *et al.* [68], where the dominant proton complex in an *ab initio* MD run has been identified as a slightly asymmetric $H_5O_2^+$ cation. Smiechowski and Stengret [52] studied spectra of HDO isotopically diluted in an aqueous acid solution. The analysis was carried out with the help of *ab initio* calculations on protonated water clusters with two to eight water molecules. They identified 'an asymmetric variant of the regular $H_5O_2^+$ cation' as a dominant hydrated proton species in solution. The *ab initio* MD study of HCl solutions by Heuft and Meijer [99] employed structural analysis based on the concept of embedded cluster species, $H_7O_3^+$ was suggested as the dominant local structure element (~50%), with the $H_5O_2^+$ and the $H_3O^+(3H_2O)$ cations corresponding to ~30 and 15%, respectively.

Different DFT functionals were used in the considered *ab initio* MD simulations, namely Becke 88-Lee-Yang-Par (BLYP) [50,67,70,99] and Perdew-Burke-Ernzerhof (PBE) [68]. According to Vener *et al.* [95], BLYP and PBE give different values for the $O \cdots O$ distances in the protonated water clusters. The average distance difference is around 0.04 Å.The use of PBE instead of BLYP in the MD simulations of the protonated water clusters in acid solutions changes the $H_3O^+(3H_2O)$ and $H_5O_2^+$ ratio. This explains the different results obtained in the previous MD simulations of the relative contributions of the protonated water forms to the acid solutions.

Molecular simulations have also allowed computation of vibrational spectrum, usually in the form of vibrational density of state or the IR spectrum [65,66]. The prevailing conclusion has been that the protons in E-type cluster contribute to the 3150–2500 cm^{-1} spectral range, while the spectral signature of the central proton in the $H_5O_2^+$ cation is an intense absorption in the 1800–1000 cm^{-1}. In simulations of the IR spectrum [65,66], the linear approximation for the dipole moment function was used. However, MP2 computations of the dipole moment surface in $H_5O_2^+$ [12] clearly show that this approximation has limited applicability to the strong H-bonded systems.

From the above discussion, one gets a sense that the obtained results depend crucially on the criterion used to differentiate between the protonated water clusters. In our opinion, to separate a continuum of states of the hydrated proton in acid solutions to H_3O^+-like or $H_5O_2^+$-like components one has to consider the Raman spectrum. Indeed, the H_3O^+-like species are characterised by sharp lines around 1100 cm^{-1}, while the $H_5O_2^+$-like cation has very intensive line $\sim$500 cm^{-1}. Unfortunately, the Raman spectrum has not been computed in the considered papers.

6. Theoretical models of continuous absorption in acid solutions

Continuous absorption of aqueous acid and base solutions was first observed by Ackermaann [9]. To interpret this phenomenon, different theoretical models were suggested in literature. The most promising models are considered below.

6.1. *Proton tunnelling in the Zundel cation $H_3O^+(H_2O)$*

It was shown by Zundel and Metzger [20], that this continuum is caused by the presence of the proton dehydrate $H_3O^+(H_2O)$. The proton is rapidly exchanged between the two water molecules in this cation, see Equation (2). The proton transfer/tunnelling occurs in the double-minimum potential of the $OH^+ \cdots O$ fragment. This process is driven by the fluctuations of the electric field generated by the environment of the Zundel cation $H_3O^+(H_2O)$. The ultrahigh polarisability of the hydrogen bond (this property of the $OH^+ \cdots O$ fragment is simply postulated) plays a special role in this process. According to this model (which has not undergone significant changes since that time [100]), the continuous absorption arises by virtue of the appearance of additional transitions during the proton tunnelling through the potential barrier. To explain the observed anomalously broad (width 2000 cm^{-1}) IR band resulting from the stretching vibration of the shared proton, it was assumed that thermal fluctuations of the medium shift the proton vibrational levels up to $\sim$2000 cm^{-1}. However, the broadening in this case cannot exceed kT [101], where the value serves as a quantitative measure of the average random change in the proton-medium interaction energy. Hence, at room temperature, the corresponding bandwidths appear to be no larger than 200 cm^{-1} by order of magnitude, independently of the form of proton potential curve.

This model contradicts to experimental data. It was found [102] that intensity of the continuous absorption band does not depend on temperature. On the other hand, thermal fluctuations of the medium do depend on it.

6.2. *The 'proton–phonon' model*

This model was suggested in Librovich *et al.* [103]. Its detailed description is given elsewhere [101]. According to this model, broad spectra arise when light absorption induces not only purely proton excitation, but also combinational transitions involving excitation of the low-frequency vibrations of the system. An intense sideband of ~2000 cm^{-1} half-width could arise only if the proton–phonon coupling is sufficiently strong and if many intense combinational transitions occur in the system, that is, if the phonon subsystem is large. An analogous spectral broadening mechanism is known to act in doped crystals. The optical spectrum of an impurity centre in a crystal consists of a narrow 'zero-phonon peak' (purely electrostatic transition) and a broad phonon-assisted sideband. The stronger electron–phonon coupling, the broader and more intense is the sideband. The experimental vibrational spectrum of the $O\cdots H^{+}\cdots O$ fragment resembles the above electronic spectrum. The hydrated proton in water was considered as an impurity in a quasicrystalline medium. Accordingly, the relatively narrow band near 1200 cm^{-1} was treated as a zero-phonon band corresponding to the purely protonic transitions, and the broad continuous absorption as a phonon sideband, which arises due to various combinations of phonon excitations in the solvate complex. The theoretical absorption curve was found to be in a good agreement with experiment at reasonable values of the parameters involved.

However, it was shown later, that the continue absorption is observed in an alcohol–acid–aprotic solvent system [34]. The solvation effects are reduced to a minimum in this system. It implies that the continuum absorption is not caused by environmental effects but is due to the intrinsic properties of the strong H-bonded systems with the quasisymmetric $O\cdots H^{+}\cdots O$ fragment.

6.3. *Mechanical and electric anharmonicity of the* $O\cdots H^{+}\cdots O$ *fragment*

According to Yukhnevich *et al.* [34], continuous absorption is caused by the properties of the $O\cdots H^{+}\cdots O$ fragment itself rather than by environmental influence. Thus, the nature of this phenomenon needed a conceptually new explanation. This aim was solved in Yukhnevich *et al.* [104]. In this article, the absorption spectra of the $H_5O_2^{+}$, $D_5O_2^{+}$ and $(CH_3OH)_2H^{+}$ ions were extracted from IR spectra of acid solutions and detailed analysis of these spectra was performed taking into account the kinetic, dynamic and electro-optical anharmonicities of the proton vibrations. The set of ions chosen for the study provided the possibility to compare the spectra of the cation and its isotopically different analogue as well as the hydrated and solvated proton forms. A good agreement between the calculated and experimental data (Figure 12), without using any kind of fitting, indicates that the proposed model is applicable for spectra calculations of the strong H-bonded systems with a quasisymmetric $O\cdots H^{+}\cdots O$ fragment. All the parameters of the $O\cdots H^{+}\cdots O$ fragment needed to calculate the spectra were found with the aid of quantum-chemical calculations or a semi-empirical model for description of the dynamic and electro-optical parameters of the strong H-bond. Analysis of the computed IR spectra of the ions under consideration established two characteristic features. It was found that in the region where the continuous absorption is observed experimentally, the spectra of all ions contain tens of (40–300) combinational transitions and overtones. Relative intensity of these bands is comparable to that of the fundamental transitions. It is caused by electric anharmonicity of the $O\cdots H^{+}\cdots O$ fragment. It was established that the continuous absorption in the spectra of proton hydrates is due to the presence of a large number of overlapping intense higher order vibrational bands in the 800–3700 cm^{-1} frequency region. The appearance of such bands is caused by the intrinsic properties of the ions with strong H-bond and quasisymmetric $O\cdots H^{+}\cdots O$ fragment and strong coupling between shared

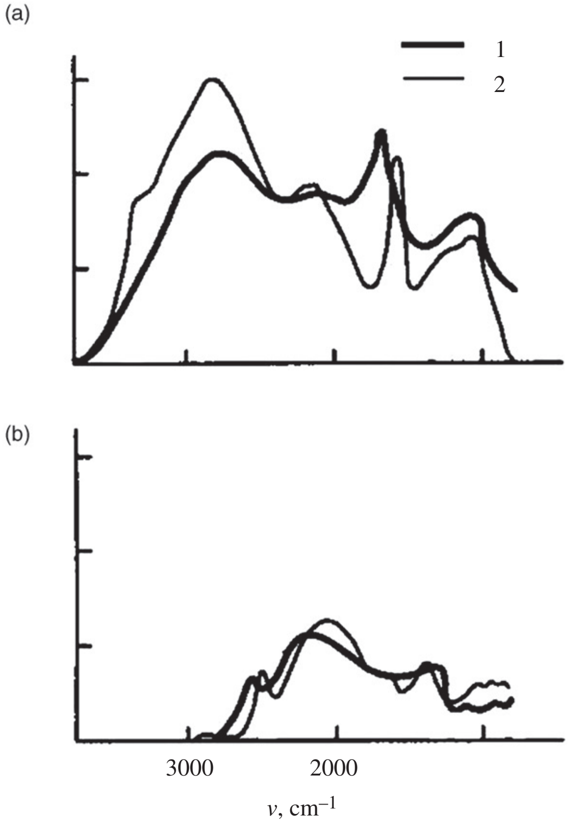

Figure 12. The measured (curve 1) and calculated (curve 2) IR spectra of the proton hydrates: (a) $H_5O_2^+$ and (b) $D_5O_2^+$.

proton motion and the internal coordinates of the ligand. It should be noted that the described model does not contradict the experimental data.

The above-mentioned models lead to some valuable insights. However, they use the parameters that were found from fitting the experimental data. This is why these models should be treated as semi-empirical.

7. Conclusions

The present review may be summarised as follows:

(1) The H_3O^+ ion may exist in the liquid phase when there is not more than one water molecule per acid molecule. Unambiguous identification of H_3O^+ in acid solutions requires consideration of the Raman spectrum because the ion is characterised by very intensive Raman line around $1100\,\mathrm{cm}^{-1}$. Hydration of the H_3O^+ ion causes a rearrangement of the bonds and angles resulting in the formation of $H_5O_2^+$.

(2) The $H_5O_2^+$ cation can be treated as the simplest stable proton hydrate in the aqueous acid solution. Its lifetime is larger than the characteristic times of the

stretching and bending vibrations and it behaves as an individual ion with unique and distinctive structure and IR/Raman spectra. $H_5O_2^+$ is characterised by specific structural and spectroscopic properties which slightly depend on hydration: short O···O distance (<2.45 Å), IR-intensive band near 1720 cm^{-1} and Raman intensive line around 500 cm^{-1}.

(3) $H_7O_3^+$ behaves as an individual ion with unique and distinctive structure and IR spectra in weakly basic solvents (benzene and dichloroethane) with weakly basic anions (carborane counterions). Experimental fingerprint for this ion in liquid water has not been detected yet.

(4) The $H_9O_4^+$ formulation often used for the Eigen ion is misleading because it does not distinguish between the fully hydrated hydronium ion, $H_3O^+(3H_2O)$, and the partially hydrated protonated water cluster, $H_5O_2^+(2H_2O)$. This is why the $H_3O^+(3H_2O)$ formulation should be used for the Eigen ion.

(5) The existence of discrete $H_3O^+(3H_2O)$ ions in the liquid phase has not been confirmed experimentally. The Eigen ion is a short-lived species in acid solutions.

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