Unusual strong broadening of some absorption bands in the IR spectra of organic molecules bonded with H^+ in disolvates $[L–H^+–L]$

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An unusual feature has been detected in the IR spectra of the proton disolvates $L–H^+–L$, namely strong broadening of the absorption bands of molecular groups of the organic ligand L directly bonded with H^+.

Broad absorption continua in the frequency range 200–3000 cm^{-1} and strong broadening of absorption bands are general unusual features of the IR spectra of proton hydrates in water and organic solutions. A number of theories explaining them by intrinsic properties of proton hydrates[1–4] or by the effect of molecules in the nearest environment[5,6] have been suggested. However, they cannot comprehend all known experimental data.

The main structural unit of proton hydrates is the dihydrate $[H_2O–H^+–OH_2]$, that is the $H_5O_2^+$ cation, or the monohydrate $[H_2O\cdot H^+\cdot L_1]\cdot n$L, where L_1 is An^- or an organic base[7,8]. Since both cations belong to the general class of homoconjugated $L\cdot H^+\cdot L$ and heteroconjugated $L_1\cdot H^+\cdot L_2$ proton disolvates, a study of the IR spectra of different proton disolvates can give a new insight to the understanding of the IR spectra of proton hydrates.

This paper presents data on unusual features in the IR spectra of disolvates of a strong acid $[L\cdot H^+\cdot L]\cdot FeCl_4^-$, where L is acetone, butyl acetate (BA), tributyl phosphate (TBP), ethanol or diethyl ether in CCl_4 solutions. All disolvates were obtained by passing dry gaseous HCl through 0.2 M $FeCl_3$ solutions in CCl_4 containing an organic base L in the molar ratio $L/FeCl_3 = 2$. The reaction $HCl + FeCl_3 + 2L \rightarrow L_2H^+FeCl_4^-$ results in the formation of an acid disolvate. The IR data shows that the solutions do not contain free ligand L, and $FeCl_3$ is quantitatively transformed into $FeCl_4^-$ ions. Anhydrous reagents of the chemically pure grade were used. Organic bases were additionally purified to remove trace water by universally known methods. The solutions were prepared and poured into an IR cell in a dry box. The IR spectra were recorded on a Bruker IFS-113v FTIR spectrometer in the range 4000–200 cm^{-1} using a vacuum cell with silicon windows.

The IR spectra of all disolvates contain very broad and intense bands of in-plane deformations $\delta(OHO) \approx 1500$ cm^{-1} and antisymmetric stretching vibrations $\nu_{as}(OHO) \approx 920$ cm^{-1} of the central OH^+O fragment with a very strong H-bond and a triply degenerate band $\nu_3(F_2)$ at 383 cm^{-1} of tetrahedral $FeCl_4^-$ anions. The shape of the $\nu_3(F_2)$ band is almost undistorted. This means that the degeneration is practically not removed because the $FeCl_4^-$ anion interacts with the L_2H^+ cation very weakly.

The main distinctive feature of the IR spectra of L_2H^+ cations is an unusual behaviour of the absorption bands of the ligand atomic groups that are directly bonded with the proton H^+. For instance, in the spectrum of $(BA)_2H^+$ cations there are no typical strong ν_{as} and ν_s bands of stretching vibrations of COO groups in butyl acetate molecules, but there is a very broad band at 1575 cm^{-1}, which can be attributed to ν_{as}(COO) (Figure 1). Since this band is strongly overlapped with the others, its width at the half height can be estimated as ≥ 65 cm^{-1}. The band at 1304 cm^{-1}, which slightly appears above the contour of the ν_{as}(OHO) and δ(OHO) absorption bands, can be attributed to ν_s(COO).

In the spectrum of $(Me_2CO)_2H^+$ the intense narrow band ν(C=O) is absent as well, while the ν(C–C) band at 1250 cm^{-1} is shifted to the high-frequency region by 31 cm^{-1}. This indicates that acetone molecules are bonded with H^+ very strongly. Therefore, the frequency ν(C=O) will be significantly lowered. There is only one band with a frequency of 1595 cm^{-1}, which can be attributed to ν(C=O),[†] but its width is unusually large (Figure 1, Table 1).

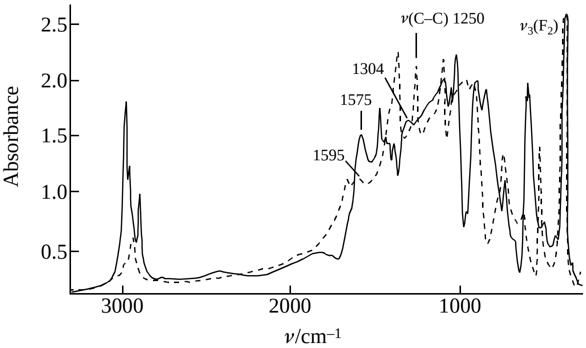

Figure 1 IR spectra of carbon tetrachloride solutions of $(BA)_2H^+FeCl_4^-$ (solid line) and $(Me_2CO)_2H^+FeCl_4^-$ (dotted line). The spectrum of CCl_4 is subtracted.

There are all the known TBP bands in the IR spectrum of the $(TBP)_2H^+$ cation with the exception of the intense ν(P=O) band (Figure 2). If the contour of the overlapped bands δ(OHO) and ν_{as}(OHO) is separated into the two symmetric components $\delta(OHO) = 1455$ cm^{-1} and $\nu_{as}(OHO) = 920$ cm^{-1} in order to describe the resulting shape correctly, a third component, a very broad and intense band at 1100 cm^{-1}, should be added. Obviously, the latter should be attributed to the disappeared ν(P=O) band. Despite the fact that the frequency and, especially, the half-width of this band (~190 cm^{-1}) should be considered as approximate values, they are indicative of an unusually strong broadening. Indeed, if one compares the half-widths of ν(P=O) bands of TBP molecules bonded to electron acceptors of different strengths (Table 1), one can see that a decrease of the ν(P=O) frequency does not lead to a regular broadening of the bands with the exception of the symmetric hydroxonium ion in $[H_3O^+\cdot 3TBP]FeCl_4^-$. For the latter, the nature of the broadening can be the same as that for the disolvate $[H^+\cdot 2TBP]FeCl_4^-$, but occurring less markedly. No significant broadening of the bands ν_{as}(COO) of butyl acetate and ν(C=O) of acetone with decreasing frequency of the C=O group linked with the electron

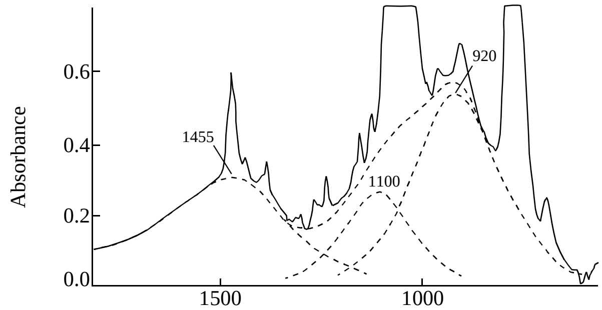

Figure 2 IR spectrum of the $[H^+\cdot 2TBP]FeCl_4^-$ disolvate. The bands $\delta(OHO) = 1457$ cm^{-1} and $\nu_{as}(OHO) = 920$ cm^{-1} and the band at 1100 cm^{-1}, which is attributed to 'disappeared' ν(P=O), are marked by a dashed line.

[†] The other narrow band at 1660 cm^{-1} has too low intensity. Furthermore, it is not sensitive to the addition of a small quantity of water; thus, it cannot be attributed to ν(C=O) of the disolvate $(Me_2CO)_2H^+$.

Table 1 The ν(X=O) band frequencies and widths at the half height ($\Delta\nu_{1/2}$) in the IR spectra of ‘free’ ligands L and ligands linked with electron acceptors.

Compound	Solvent or solution composition	ν(P=O)/cm^{-1}	$\Delta\nu$(P=O)/cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	Reference
TBP	100% TBP	1274[a]	—	58[b]	
$(TBP\cdot 2H_2O)_n$	100% TBP, satur. with H_2O	1248	26	42	10
$[H_5O_2^+\cdot 2TBP\cdot 2H_2O]FeCl_4^-$	TBP	1218	56	22	8
$[H_3O^+\cdot 3TBP]FeCl_4^-$	TBP	1195	79	58	7
$UO_2Cl_2\cdot 2TBP$	CCl_4	1177	97	22	11
$[H^+\cdot 2TBP]FeCl_4^-$	CCl_4	1100	174	~190	This work
		ν(COO)/cm^{-1}	$\Delta\nu$(COO)/cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	
Butyl acetate	1.5 M in CCl_4	1742	—	20	
BA·*p*-NP[b]	CCl_4	1707	35	21	12
$[H^+\cdot 2BA]FeCl_4^-$	CCl_4	1575	167	≥ 65	This work
		ν(C=O)/cm^{-1}	$\Delta\nu$(C=O)/cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	
Acetone	0.8 M in CCl_4	1718	—	13	
$[H^+\cdot nH_2O\cdot mMe_2CO]FeCl_4^-$	CCl_4	1684	34	14	This work
$[H^+\cdot 2Me_2CO]FeCl_4^-$	CCl_4	1590	128	≥ 94	This work

[a] The overlapped band of some non-equivalent P=O groups of TBP isomers. [b] H-complex of butyl acetate and *p*-nitrophenol.

acceptor is observed as well. It is only in the IR spectra of disolvates $H^+\cdot 2L$ that the broadening of the bands ν(X=O) is so significant that it can be called anomalous.

The bands of molecular group linked with H^+ in $H^+\cdot 2L$, which contain only single C–C and C–O bonds, are changed much more significantly since their oscillations strongly interact and are not characteristic. Thus, in the IR spectra of $(Et_2O)_2H^+$ both the ν_{as}(C–O–C) band and the bands of stretching C–C vibrations are not observed. Similarly, the stretching C–O and C–C vibrations are not detected in the spectrum of $(EtOH)_2H^+$. However, the spectra of both of the disolvates contain the bands of stretching and bending vibrations of CH_2 and Me groups.

Thus, if L is bonded to H^+ *via* an X=O group with a double bond whose vibrations interact weakly with those of coupled single bonds, as is the case, for example, in the disolvates $(Bu–O–)_3P=O–H^+–\ldots$ or $(Me–)_2C=O–H^+–\ldots$, the ν(X=O) band is broadened so significantly that it becomes difficult to detect it in the IR spectra. Meanwhile, the stretching vibrations of ordinary bonds coupled with the X=O group (P–O in TBP, C–C in acetone) are observed as bands of normal width.

If L is linked with H^+ *via* a molecular group containing only ordinary bonds, as is the case, for example, in $(Me–CH_2–)_2O–H^+–\ldots$ of $[Et_2O\cdot H^+\cdot Et_2O]$ or in $Me–CH_2–O(H)–H^+–\ldots$ of $[EtOH\cdot H^+\cdot EtOH]$, not only the bands of stretching vibrations of the single bonds nearest to H^+ (C–O–C in Et_2O or C–O in ethanol) but also the bands of C–C bonds coupled with them, are not observed in the IR spectra. The stretching OH vibration of the disolvate $(EtOH)_2H^+$, observed as a broad band at 3271 cm^{-1} is the only exception.

The following explanation can be proposed for the unusual broadening of some absorption bands in the IR spectra of organic molecules L in the disolvates $[LH^+L]$ weakly perturbed by an anion. The potential energy curve of the proton in L_2H^+ has two minima with so low a barrier between them that it does not reach the energy of the ground vibration state.[2–5,9] As a result, the minimum becomes broad and flat, and H^+ in the ground vibrational state is delocalised in the spatial region A–B (Figure 3). If the rates of the H^+ migration within this region and of the 0→1 vibration transition are comparable, for example, for a C=O group, the width of the ν(C=O) band grows significantly. In other words, a fast change of the proton charge location within the A–B region induces similar changes in the electron density of the C=O bond. As a result, the force constant and the shape of the potential energy curve of the proton are changed with the same frequencies as the spatial location of the proton. This leads to the multiplicity of 0→1 (as well as 1→2, *etc.*) transition energies and to a significant broadening of the absorption bands. If the group linked with H^+ is X=O with a highly characteristic frequency (weakly interacting with the frequencies of coupled single bonds), the modulating effect of H^+ on the force constants of the bonds does not spread beyond the X=O bond. However, if the vibrations of a molecular group of the ligand L linked with H^+ interact strongly with each other (the COO group, C–O–C and C–C vibrations, *etc.*), the specific influence of H^+ is spread on the two nearest coupled bonds.

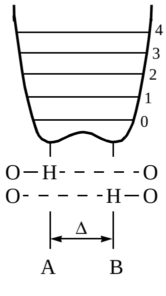

Figure 3 The double minimum of the potential energy function of the bridged proton in the O–H$^+$–O fragment of disolvates L_2H^+ is approached to a single broad and flat bottom. The proton in the ground state (v = 0) is delocalised within the A–B region.

In the proton dihydrate $[H_2O–H^+–OH_2]\cdot nH_2O$, there is the same specific effect of a delocalised proton on the nearest O–H···O groups formed by the $H_5O_2^+$ cation and water molecules. This may be a fundamental reason for the appearance of the main feature of the IR spectra of proton hydrates in aqueous and organic solutions and solids: strong broadening of the bands and extended absorption known as continuous background absorption.

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