IR ν$_s$(XH) ABSORPTION BAND SHAPE OF H-BONDED COMPLEX IN CONDENSED MEDIA. II. NUMERICAL CALCULATIONS OF THE PROFILES

Halina ABRAMCZYK

Technical University, Institute of Applied Radiation Chemistry, Wroblewskiego 15, 93-590 Lodz, Poland

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The IR absorption band profiles of H-bonded complexes in the spectral range 600–3600 cm$^{-1}$ have been calculated in terms of the theory presented in the accompanying paper. We have considered the IR band profiles as a function of strength of the H-bond, the influence of the environment on the band shape and the effect of fluctuations of the energy potential well, in which the vibrational transition of the ν$_s$(XH) mode occurs.

1. Introduction

In the last decade, considerable attention has been given to study the shape of IR hydrogen stretching bands of hydrogen bonded systems in all phases. There are two groups of theories. One of these proposes an indirect mechanism of relaxation through the anharmonic coupling of the high-frequency ν$_s$(XH) mode to the low-frequency stretching bridge motion ν$_a$(XH...Y) [1–5]. The other is direct coupling of the dipole moment of the complex to the electric field produced by the charges and dipoles of the solvent [8–10]. The former one is especially useful for the gas phase to explain the vibrational substructure of the band profile. The latter one is often applied to explain a continuous IR absorption observed in many systems of the type (BH...B)$^+$ and (BH...B)$^-$ in acid and base solutions in liquid phase. One of the important theoretical questions is, are the vibrational structure and continuum the extreme case of the same mechanism or is each of them governed by a different mechanism? In other words, is the continuum observed in a broad frequency range the result of the statistical distribution of the positions of the bands determined by the special arrangement of the H-bonds interacting with the ions and dipoles of the environment as proposed by Zundel [11] or is it a special case of the anharmonic coupling between the ν$_s$ and ν$_a$ modes? The other question is, why in contrast to the continuous absorption in amorphous systems, broad bands are usually observed in crystals with H-bonds of the same type (BH...B)$^+$ and (BH...B)$^-$. Is it possible to describe all phases within the framework of the same band-broadening mechanisms?

In the preceding paper [12] we have discussed in detail mechanisms contributing to the vibrational phase coherence relaxation of the stretching ν$_s$(XH) mode in hydrogen-bonded complex and the effect of this dynamics on IR band shapes. We have proposed as the dominant broadening mechanism: the anharmonic coupling of the ν$_s$ mode to the external, low-frequency stretching mode ν$_a$ of the bridge in the presence of fluctuations of the energy potential and energy levels arising from the direct coupling to the bath. For strong H-bonds, a double-minimum potential may exist and tunneling leading to a superposition of the bands, whose origins will be displaced from one another has been taken into account in our paper.

The purpose of the present paper is to examine to what extent the experimental IR band shapes of weak and strong hydrogen bonds in gases, liquids and solids can be understood in terms of the theory presented in our previous paper [12].
2. Numerical calculations of the IR absorption band shape

In the framework of the linear response theory the infrared absorption coefficient is expressed as

$$\alpha(\omega) = \frac{2\pi\omega}{3\hbar cnV} \left[ 1 - \exp(-\beta\omega) \right] \int_{-\infty}^{\infty} \langle \hat{M}^+(t)\hat{M}(0) \rangle \exp(i\omega t) \, dt,$$

where $\hat{M}$ denotes the dipole moment of the sample, $V$ its volume, $\omega$ is the frequency of the incident radiation, $n$ is the refractive index. The absorption coefficient is expressed in (mol/l) cm$^{-1}$ units. We have calculated in paper I [12] that the dipole correlation function $\langle \hat{M}^+(t)\hat{M}(0) \rangle$ is given by

$$G(t, P) = \langle \hat{M}^+(t)\hat{M}(0) \rangle = \left( \frac{\partial M}{\partial q} \right)^2 \sum_{\gamma=0}^{\infty} \epsilon_2(\gamma) \sum_{m=1}^{4} \left( \sum_{\alpha=0}^{\gamma} \sum_{j=0}^{\gamma} \sum_{k=0}^{\gamma} \sum_{l=0}^{\gamma} \sum_{q=0}^{\gamma} A_{\gamma\alpha\gamma} C_{\gamma\alpha\gamma} \langle B_{\gamma\alpha}^m \rangle + \sum_{\alpha=\gamma+1}^{\infty} \sum_{j=0}^{\gamma} \sum_{k=0}^{\gamma} \sum_{l=0}^{\gamma} \sum_{q=0}^{\gamma} A_{\gamma\alpha\gamma} C_{\gamma\alpha\gamma} \langle B_{\gamma\alpha}^m \rangle \right),$$

where

$$A_{\gamma\alpha\gamma} = \left( \frac{l!}{q!} \frac{\gamma!}{(\alpha-k)!(\alpha-j)!(\gamma-\alpha+k)!(\gamma-\alpha+j)!} \right)^2.$$

$$<B_{\gamma\alpha}^m> = f_m \exp\left\{-i[\langle \omega_0 \rangle + \langle \omega_m \rangle - 2\alpha_0^2\omega_0 + (\gamma-\alpha)\omega_{00}]t \right\} \exp\left\{-[(\gamma-\alpha)+2q+2j])\Gamma t/2 \right\} \times \exp\left\{-2\alpha^2[\tau_0^2\exp(-t/\tau_0) - 1] + \tau_0 t \right\} \exp\left\{-b^2[\tau_b^2\exp(-t/\tau_b) - 1] + \tau_b t \right\}.$$

All of the other symbols in eqs. (2)–(5) have been explained in paper [12]. The correlation function $G(t, P)$ depends on the following molecular properties $P$: the angular frequency $\langle \omega_0 \rangle$ of the free species of the $\nu(XH)$ mode, the angular frequency $\omega_0$ of the low-frequency stretching mode of the bridge $\nu_m$, the anharmonic coupling constant $\alpha_0$, which reflects the strength of the coupling between the high-frequency stretching mode $\nu(XH)$ of hydrogen bonded species and the $\nu_a$ mode of the bridge. This parameter characterizes the strength of the H-bond in the framework of the used model. The damping parameter $\Gamma$ reflects the strength of the coupling between the solvent and the stretching mode of the bridge. The parameter $\Gamma$ describes the influence of the solvent on the $\nu(XH)$ mode exerted indirectly through the disturbing of the H-bond bridge motion. For perfectly isolated H-bonded complex $\Gamma$ is equal to zero. In fact, however, the environment of the H-bond may affect also directly the position, intensity and the band shape. This effect may play an important role for strong H-bonds in polar solvents because of the high polarizability of the H-bonds. The electric fields of the solvent molecule dipoles, as well as the anion fields change the potentials of the H-bond protons and destroy their symmetry. Thus, the direct interaction with solvent cause the energy levels fluctuations of proton in Born–Oppenheimer energy potential. This effect enters into our model through the parameter $a$, which is the average value of the frequency jump caused by fluctuations of the potential due to molecular motions of the solvent. The correlation time $\tau_a$ is the inverse of the probability per unit time of making a jump $a$ and reflects the timescale of the molecular motions of the solvent. There is another factor, maybe much more important, resulting in the fluctuations with time of the potential well. The proton in the H-bond is coupled not only with $\nu_b$ but with all of the external vibrations of the bridge, which have not been taken into account in the anharmonic coupling constant $\alpha_0$. The interaction of the other external modes with the mode causes that the energy potential of the ground and excited vibrational state is characterized by different equilibrium geometries. Thus, the vibrational transition from one energy surface to another may be regarded as the transition in the same potential well fluctuating with time, where the timescale of the fluctuations is given by $\tau_b = \langle \omega_0 \rangle^{-1}$. This effect enters into the model
through the parameter $b$, which is the average value of the vibrational frequency jump caused by the fluctuations of the energy potential due to interactions with the external modes other than $\nu_0$. Some of these quantities may be obtained from experiment as $\omega_{bo}$, $\tau_a$ and $\tau_b$ or reasonably estimated as $a$ or $\Gamma$. The others can be considered as adjustable parameters. The $f_n$ factors in eq. (5) provide the information about transition moments $\langle n | q | m \rangle$ and depend on the average, static energy potential, in which the proton motion occurs. They can be obtained from ab initio SCF or model calculations like the standard Somorjai and Hornig procedure [13]. We have used the harmonic approximation, in which the transition moment is expressed as

$$f_i = q_i^2 = \hbar/2m\langle \omega_i^2 \rangle,$$

where $m$ is the reduced mass of the $\nu_i(\text{XH})$ mode.

In the calculations we have assumed that the proton motion occurs in a single minimum potential and there is no tunneling. So, it means, that we have put all $f_n$ (except $f_1$) and $\langle \omega^m \rangle$ in eq. (5) as equal to zero. We have taken the following values for the quantities $P$: $\langle \omega_i^2 \rangle = 3600 \text{ cm}^{-1}$, $\omega_{bo} = 150 \text{ cm}^{-1}$, $\alpha_0$ is changing progressively as $-1.2$, $-1.5$, $-2.0$, $-2.5$, $-3.0$, $\Gamma = 60$ and $150 \text{ cm}^{-1}$, $\tau_a = 1.0 \times 10^{-12} \text{ s}$, $\tau_o = 1.47 \times 10^{-13} \text{ s}$. The reduced mass $m$ is taken for the diatomic oscillator O–H and is equal to $1.5745 \times 10^{-27} \text{ kg}$.

3. Results and discussion

The results of numerical calculations of the IR absorption coefficient $\alpha(\omega)$ according to the eqs. (1), (2) are presented here. First, for illustrative purposes we have shown the interplay between the various factors, which effect the band shape. In fig. 1 we have shown the IR profile as a function of the anharmonic coupling constant $\alpha_0$, which reflects the strength of the H-bond complex. An inspection of the figure shows that the IR band profile changes progressively, when the coupling constant increases. For weak H-bond ($\alpha_0 = -1.2$) the profile is a set of relatively narrow lines peaked at

Fig. 1. The absorption intensity $I(\omega) = \alpha(\omega)/N_k(\hbar M/\hbar q)^2$ of the $\nu_i(\text{XH})$ band as a function of the anharmonic coupling constant $\alpha_0$. $\langle \omega_i^2 \rangle = 3600 \text{ cm}^{-1}$, $\omega_{bo} = 150 \text{ cm}^{-1}$, $\Gamma = 60 \text{ cm}^{-1}$, $a = 0.0$, $b = 0.0$. 

The absorption intensity $I(\omega)$ of the $v(XH)$ band as a function of the anharmonic coupling $\omega_0 = -1.2 \text{ and } 1.5$, $\langle \omega_b \rangle = 3700 \text{ cm}^{-1}$, $\omega_{\text{lo}} = 150 \text{ cm}^{-1}$, $\Gamma = 60 \text{ cm}^{-1}$, $\alpha = 0.0$, $b=0.0$ (---) and $b=500.0 \text{ cm}^{-1}$ (-----), $\tau_s = 1.47 \times 10^{-15} \text{ s}$.

$$\omega_{\text{res}} = \langle \omega_b \rangle - 2\alpha^2 \omega_0 + (\gamma - \alpha) \omega_0.$$  \hspace{1cm} (7)

For medium–strong H-bonds ($\alpha_0 = -2.0$) the vibrational structure becomes less clearly defined leading to the relatively broad band with some substructure features. For medium–strong H-bonds ($\alpha_0 = -2.5$ and $3.0$) the band intensity increases considerably and the bands become structureless and very broad with the half width about $1000 \text{ cm}^{-1}$. The profile is distinctly asymmetric with a steeper slope at the low-frequency side. The results presented in fig. 1 have been calculated for the same influence of the environment ($\Gamma = 60 \text{ cm}^{-1}$) and the static energy potential without any fluctuations ($b=0$). In figs. 2 and 3 we have shown the effect of the energy fluctuations ($b=500 \text{ cm}^{-1}$) due to the change of the potential well during the jump from the ground to the first excited vibrational state. We can see that the fluctuations in the energy potential shape lead to a smoothed absorption band. The absorption bands lose their substructure much faster as compared with those in fig. 1. It is worth emphasizing that for weak H-bonds in the gas phase, when the interactions with the solvent are very weak, the
vibrational substructure can totally disappear if the fluctuations of the energy potential due to the coupling with the external bridge motions are large. However, despite of smoothing of absorption profile the fluctuations of the potential shape do not lead to the continuous IR absorption for strong H-bonds. In fig. 1 we have considered a relatively weak influence of the environment on the IR absorption band. This will certainly be true for inert solvents, while polar solvents have a strong influence on the proton motion in H-bonds. This influence is extremely significant for strong H-bonds of type (BH...B)⁺ and (BH...B)⁻ in amorphous systems because of the high polarizability of the band. We can take this effect into account by increasing the damping parameter \( \Gamma \). The results are presented in fig. 4 for \( \Gamma \) equal to 150 cm⁻¹. We can see that the interaction of the H-bond complex with the solvent lead to the significant changes of the intensity distribution of the profiles both for weak and strong H-bonds as compared with the fig. 1. For weak H-bonds the profiles lose their vibrational structure. For medium–strong and strong H-bonds (\( \alpha_0 = -2.5 \) and \( -3.0 \)) the IR absorption becomes a continuous absorption in a broad frequency range.

It means that the same mechanism as for weak H-bonds, i.e. the anharmonic coupling between \( v \) and \( v_0 \) when the bridge mode is coupled to the environment allow understand the origin of the continuous absorption without supposing any additional mechanism. The spectra in figs. 1–3 are not intended to suggest the existence of any discrete classes of H-bonds. On the contrary, the evolution of the band widths and shapes with increasing the coupling constant \( \alpha_0 \) has definitely a continuous character. Figs. 1–3 were selected out of this continuity only because they are typical representatives which were in the past approached by different types of interpretations.

The bands as in figs. 1a and 1b are observed for complexes of ethers with hydrogen halides and some other complexes in the gas phase [14]. In fig. 5 we have shown the experimental spectrum of hydrogen fluoride–dimethylether system in the gas phase compared with the theoretical one calculated from the our model. The free H–F vibration \( \langle \omega_0 \rangle \) is taken as 3960 cm⁻¹ [16], the low-frequency stretching bridge vibration \( \omega_{00} \) measured from the far-infrared spectrum in the gas phase as 185 cm⁻¹ [17]. The band consists of a central maximum, which is accompanied on both sides by weaker submaxima at very similar distances.

Figs. 4a and 4b are typical profiles for moderately strong H-bonds in water, alcohols, phenols, oximes in liquid phase. In fig. 6 we have compared the experimental profile [18] with theoretical one for methanol.

The theoretical spectrum was normalized to the experimental value of the absorption coefficient at maximum,

![Fig. 4. The absorption intensity \( I(\omega) \) of the \( \nu(XH) \) band as a function of the anharmonic coupling constant \( \alpha_0 \). \( \omega_{00} = 3600 \text{ cm}^{-1} \), \( \omega_{00} = 150 \text{ cm}^{-1}, \Gamma = 150 \text{ cm}^{-1}, a = 0.0, b = 0.0 \).]
because we do not know $\partial M/\partial q$. The value of $\partial M/\partial q$ calculated from this is 57.29 D/Å what means that the model predicts quite well the absolute value of the band intensities. As we can see, the model generates the absorption band of methanol with fair accuracy. It is worth noticing that the additional band at the low-frequency side usually interpreted as the band from trimer or higher polymers [18] appears in the theoretical spectrum as a natural consequence of the vibronic progression for the isolated dimer.

A new type of absorption pattern is found in H-bonds of medium strength in the gas, liquid and solid states (fig. 1c). It is characterized by the appearance of several or even many submaxima laying on the lower-frequency side extending of several hundreds cm$^{-1}$. The most investigated examples are the carboxylic acids, imidazole, amine hydrohalides and pyridine–phenol complexes. Figs. 1d and 1e show typical patterns for stronger H-bonds. Such spectra have very large band width over 1000 cm$^{-1}$ (metal dihydrogen phosphates and arsenates, organophosphoric and phosphinic acids, selenic acids, complexes of carboxylic acids with oxo-bases). However, the characteristic trio of bands A, B, C on the high-frequency side for realistic systems does not appear in the model. The calculated spectra seems to support the Claydon–Sheppard mechanism of creation of the A, B, C bands [19]. The $\nu_c(XH)$ complex band is essentially a broad absorption that extends over the whole region in which the A, B, C bands appear. The broad band is composed, as we have shown, of a number of unresolved components arising from the anharmonic coupling of the $\nu_B$ and $\nu_c$ vibrations. The overtones of the bending modes may interact by Fermi resonances with the components of the broad band having similar wave numbers. Since the intensity of the overtones is low a window is cleaved in the broad absorption band.

Figs. 4d and 4e represent the continuum for the easily polarizable complexes (BH...B)$^+$ and (BH...B)$^-$ in liquid phase. Such spectra are observed for the solutions of HCl, HI, H$_2$SO$_4$, benzene sulfonic, benzene phosphonic acids in water, biopolymers, non-aqueous solutions of methane sulfonic acid and toluene sulfonic acid in DMSO and methanol, imidazole, pyrazole dissolved in water and protonated with HCl, hydrolysis protons in salts of polystyrene sulfonic acid in water, ethanol and methanol on chromium oxide [11].

4. Conclusions

The purpose of this paper is to answer whether various groups of typical absorption patterns in H-bond complexes in gas, liquid and solid phase, which were in the past approached by different types of interpretations, can be explained in the framework of the same theoretical model. We have shown that for weak coupling of the
low-frequency stretching mode with environment the band consists of a central maximum which is accompanied on both sides by weaker submaxima at very similar distances as is observed in the gas phase. For stronger coupling with environment the bands become structureless and broader as is observed in moderately strong H-bonds. For the polarizable H-bonds of type (BH...B)$^+$ and (BH...B)$^-$ in liquids the strength of the coupling with environment increases considerably what is the reason for the occurrence of the continuum. In contrast, in crystals containing polarizable H-bonds of the same type, the strength of the coupling with environment is smaller than in liquids taking into account the order with almost all H-bonds in the same potential well and instead of the continuum discrete but usually very broad bands are observed.

One of the goals of this paper was to answer what is the reason for the 1R continuum observed in solutions and other amorphous systems in which polarizable H-bonds are present. Our conclusion is the same as proposed by Zundel [11] that the continuity is caused by various interaction effects of these H-bonds with their environment. However, the mechanism of the influence of the environment on the spectra is quite different. Zundel [11] assumes that the continuum indicates that either the ground state or an excited state or both have a continuous energy level distribution. They suppose that the electric fields of the ions and the dipole fields of the solvate and solvent molecules near the H-bonds have a large distribution in amorphous systems. The continuity of energy levels distribution comes into being as a result of the induced dipole interaction with easily polarizable H-bonds. The large polarizability of hydrogen bonds is explained in terms of tunneling approximation considering a single H-bond with a double-minimum potential in an electrical field.

The large absorbance of these continua is explained by the large transition moments with polarizable H-bonds. The continuum due to the coupling with the bond stretching vibrations or with other vibrations of the solvent molecules is of minor importance in their model.

In our model, the strong coupling with the intramolecular vibrations (especially with $\nu_v$) is the main reason of the continuum and the large absorbance.

The influence of the environment is introduced indirectly through the coupling of the mode with bath. The intramolecular vibrations are modified by the environment, which in turn effect the frequency of the $\nu_v(XH)$ mode.

This mechanism permits to explain the continuum without assuming tunneling what seems to be important, taking into account that no single experiment exists proving unambiguously the $\nu_v(XH)$ spectral effect of this mechanism in dense phases. To conclude, we have shown that the model proposed in the previous paper [12] seems to generate the widths, intensities and the characteristic features in all phases with fair accuracy.

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References