Infrared absorption in hydrogen-bonded complexes and absorption of an excess electron in hydrogen-bonded solvents

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Abstract

A comparison was made between the theories of IR absorption in hydrogen-bonded complexes and near-IR and visible absorption of an excess electron in hydrogen-bonded solvents. The near-IR and visible absorption spectra of excess electrons in water, alcohols, amines and alkanes were calculated in terms of electron–vibron coupling. The role of the hydrogen bond on electron stabilization and solvation is discussed.

Keywords: Infrared spectrometry; Excess-electrons; Hydrogen-bonded complexes; Hydrogen-bonded solvents; Infrared absorption

The IR absorption spectrometry of hydrogen-bonded (H-bonded) complexes and near-IR and visible absorption of an excess electron have many common features. It will be shown that the theoretical formalism to describe the band broadening mechanisms is very similar in both instances. Moreover, the vibrational dynamics of H bonds play an important role in localization, electron attachment, stabilization and solvation of an excess electron generated by radiolysis or photoionization in H-bonded solvents.

Various theoretical approaches have been proposed to understand the origin of most of the characteristic spectroscopic properties of IR absorption in H-bonded complexes. The various theoretical approaches used in the treatment of the stretching mode $\nu(XH)$ in H-bond complexes may be classified as the weak coupling limit [1–5] and strong coupling limit [6–8].

The weak coupling of the system to the bath is treated through perturbation theory and it can be used only for weak H-bonded complexes. For medium-strong and strong H-bonded complexes the interactions are sufficiently strong that the vibrational relaxation (dephasing) cannot generally be treated through perturbation theory. In the strong coupling limit, the Hamiltonian in the excited vibrational state depends linearly (or non-linearly) on the external coordinate $Q$ coupled to the internal vibrational mode $q$. This term is called the strong coupling term.

In the strong coupling method, the Hamiltonian is diagonalized by performing a canonical transformation. For weak coupling of an H-
bonded system to a bath, the cumulant expansion approach is usually used, assuming that the coupling is a purely classical stochastic Gaussian process for which the cumulant expansion may be truncated beyond second order.

Substantial progress has been made in elucidating the physical nature of this coupling. Two main relaxation mechanisms have been proposed. One of these considers broadening mechanism of the band as the direct dipolar interaction of the dipole moment of the complex to the local fluctuating electric field produced by the solvent dipoles as proposed Zundel and co-workers [9], or of the dipole moment of the proton donor and the dipole moment produced by the H bond as proposed Abramczyk [5,10] in the complex regarded as a non-rigid supermolecule. The other is an indirect relaxation mechanism caused by the anharmonic coupling of the high-frequency $\nu_{s}(X-H)$ stretching mode to the low-frequency hydrogen bridge vibration $\nu_{e}(X-H \cdots Y)$ [1-4,7-8]. The IR band shape of the mode is controlled by the dynamics of the bridge motion $(X-H \cdots Y)$.

Both the weak and strong coupling theories can be classified according to the level of approximation in treating the dynamics of the bridge. Bratos [1] assumed that the time dependence of the coupling of the $\nu_{e}$ mode to the environment (bath) is suppressed (static limit). The $X \cdots Y$ bridge is regarded as a Brownian oscillator obeying the Langevin equation in the model of Robertson and Yarwood [3] or the generalized Langevin equation in the model of Sakun [4]. The interaction of the oscillator with bath is ignored, so that the $X \cdots Y$ length is allowed to oscillate without damping in the gas phase in the Marechal-Witkowski model [7].

More recently, an approach by Boulil et al. [11] has been reported, which is a fully quantum mechanical theory and the coupling to the bath is described as intermolecular resonance energy exchange with the molecules of the inert solvent (bath). This model is able to connect the Marechal-Witkowski approach in the gas phase and the theories in the liquid phase.

For medium-strong and strong H-bonded complexes it is believed that additional IR band-shaping mechanisms are efficient: Fermi resonances between $\nu_{s}$ and combinations or overtones (e.g., the doubly excited in-plane hydrogen bending and the doubly excited out-of-plane hydrogen bending), mechanical and electrical anharmonicity of the mode itself, a double-well potential governing the motion of the proton stretching vibration, causing tunnelling of the proton to the acceptor $Y$.

The theoretical aspects of strong H-bonded complexes have been discussed in several papers [2,12]. The IR band shape theories of strong H bonds could explain not only the facts that the band is very broad, much more intense and shifted to lower wavenumbers compared with the position of the free band, but also a well defined structure, especially Evans windows and A, B and C bands. Bratos and Ratajczak [2] have shown that Fermi resonances results in the A, B and C bands whereas Hofacker et al. [13] have pointed out that the theoretical intensities for this mechanism for carboxylic acids deviate drastically from the experimental intensity pattern. Recently, a model has been proposed [14] that is intended to cover the gap between weak and strong H-bonded complexes. A model was presented in which the IR band shape theories for weak and strong H bonds becomes the particular cases of the general description. It is assumed that the proton motion occurs in a single- or double-potential well and is accompanied by the anharmonic coupling to the low-frequency stretching mode of the bridge $\nu_{e}(X-H \cdots Y)$. The stretching mode $\nu_{s}(XH)$ is coupled to the $\nu_{e}(X-H \cdots Y)$ mode and the strong coupling limit theory has been used to describe this interaction. The low-frequency mode $\nu_{e}(X-H \cdots Y)$ is damped by the environment undergoing intermolecular resonant energy exchange with the molecules of the solvent. The interaction between the $\nu_{e}(X-H \cdots Y)$ and the environment is responsible for the time evolution of the coupling strength between $\nu_{s}(XH)$ and $\nu_{e}(X-H \cdots Y)$. Both the potential well shape and the strength of the coupling are randomly modulated with time. The two lowest states of a potential well are weakly coupled to the solvent (Markovian approach). The fluctuations of the potential well and the vibrational energy levels arising from the
direct coupling to the environment are described by the stochastic Liouville equation.

This physical mechanism underlying the IR $\nu_a(XH)$ absorption band width with a fully quantum mechanical description and discussion in terms of “Franck-Condon progression” is in analogy with the case of vibronically broadened electronic bands in molecules. This analogy is even greater for the case of electronic absorption of an excess electron trapped in a solvent. Recently, an absorption band-shape theory of an excess electron in condensed media has been proposed [15]. The theoretical details can be found elsewhere [15–20]. Here an outline is presented of the analogy between the IR band broadening of the vibrational mode $\nu_a(XH)$ and visible band broadening of an excess electron (Table 1).

If one considers an electronic transition $n = 0 \rightarrow 1$ of an excess electron and a vibrational motion $v = 0 \rightarrow 1$ in an adiabatic approximation, it is stated that in both instances similar theoretical formalism can be used. The fast motion of an electron coordinate $r$ is coupled with the slow motion of vibration $q$ of the molecule being a trapping site or belonging to the cavity that has been formed around the electron. However, this vibrational motion, which is slow in comparison with an electron, becomes the fast motion $q$ for the H bond, because it is coupled with the low-frequency mode of the hydrogen bridge $Q$.

Additional mechanisms of band broadening are also similar: the direct dephasing of electronic frequencies due to the statistical variety of an electron environment plays the same role as the direct dephasing of vibrational frequencies of vibrational bands. Tunnelling, although it cannot be excluded, seems not to influence the band widths much in either instance. Band broadening due to the different potential wells of the ground and an excited state (different frequencies in the ground and excited states) can be formally de-

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**TABLE 1**

Analogy between solvent-broadened vibrational line shape in H-bonded complexes and vibronically broadened electronic band profile of an excess electron

<table>
<thead>
<tr>
<th>Excess electron</th>
<th>H-bonded complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^- \cdots X-H$</td>
<td>$X-H \cdots Y$</td>
</tr>
<tr>
<td>$q$</td>
<td>$q$</td>
</tr>
<tr>
<td>$n = 0 \rightarrow 1$ of electrons</td>
<td>$v = 0 \rightarrow 1$ of $X-H$ vibration</td>
</tr>
<tr>
<td>Fast motion</td>
<td>Slow motion</td>
</tr>
<tr>
<td>$r_{\text{electrons}} = r$</td>
<td>$q$</td>
</tr>
<tr>
<td>Electron eigenfunctions: $\psi_0(r, q), \psi_1(r, q)$</td>
<td>$\psi_0(q), \psi_1(q)$</td>
</tr>
<tr>
<td>Energy eigenvalues: $E_0(q), E_1(q)$</td>
<td>$E_0(q), E_1(q)$</td>
</tr>
<tr>
<td>$\frac{\delta E_0}{\delta q} = 0$</td>
<td>$\frac{\delta E_0}{\delta Q} = 0$</td>
</tr>
<tr>
<td>Coupling mechanism</td>
<td>Additional band broadening mechanisms</td>
</tr>
<tr>
<td>(a) Direct dephasing of electron states by solvent</td>
<td>(a) Direct dephasing of vibrational states by solvent</td>
</tr>
<tr>
<td>(b) Tunnelling of an excess electron</td>
<td>(b) Tunnelling of proton</td>
</tr>
<tr>
<td>(c) Fluctuations during transition due to different potential wells in the ground and the first excited states</td>
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</table>
scribed in both instances as a fluctuation with time of the parameters characterizing the energy potential well in which the transition occurs.

THE INFLUENCE OF HYDROGEN BONDING ON THE LOCALIZATION, ELECTRON ATTACHMENT, STABILIZATION, SOLVATION, DYNAMICS OF THE LOCALIZATION AND SPECTROSCOPIC PROPERTIES OF AN EXCESS ELECTRON IN HYDROGEN BOND-FORMING MATRICES

Despite much experimental and theoretical interest, the influence of H bonding on the localization, electron attachment, stabilization, solvation, dynamics of the localization and spectroscopic properties in bulk liquid ammonia, water and other matrices and also in small clusters remains unclear. The theoretical calculations should be of help in finding the sites of preferential attachment within a molecular cluster and to establish whether an electron forms the cavity with the electron in the centre through breaking the existing H-bond structure, is attached to pre-existing groups of the molecules with free OH or NH bonds or does not break the H-bond structure being attached as an additional electron in the diffuse solvent anionic complex.

In order to answer these questions, three main structures have been considered for the H-bonded solvents: the electron localized in the cavity [21,28]; the solvated diffuse anionic complex [29–34]; and the polaron [35].

The structures with the electron in the cavity are currently most favoured but the question remains of what the structure of the cavity is and what the sites of preferential attachment within a molecular cluster are. In the framework of the cavity models, dipole-oriented [22,28,36] and H bond-oriented [37–42] structures have been considered for H-bond solvents. Alcohols seem to ignore the H-bond, creating a dipole-oriented cavity [28]. In contrast, the H bond-oriented cavities seem to exist in water, ammonia and amines [23,27,38–42]. Experimental electron spin resonance results [24], molecular dynamic simulations and some ab initio calculations [22,33,34,40,41,43] suggest that six protons in OH or NH bonds are directed towards the electron localized at the centre of the \((\text{H}_2\text{O})_6^-\) or \((\text{NH}_3)_6^-\) cavity. The results of Newton [22] showed that the cavity seems to be formed by the free OH or NH groups and fully H-bonded molecules do not appear to offer especially favourable trapping sites.

The theoretical calculations are consistent with the nozzle beam studies [44] where an increase in signal intensity at \(n = 6\) is observed. However, most unexpected is the detection of \((\text{H}_2\text{O})_2^-\) dimers [44], because it seemed that only larger clusters are required for both water and ammonia for trapping of the electron.

Despite ab initio results for the electron in the negatively charged clusters which depend strongly on the diffuseness of the basis set, a few marked differences in the structure of the hydrated and ammoniated electron can be observed: the size of the cavity for \(\text{NH}_3\) is calculated to be 3.9 Å whereas that for water is 2.6 Å [22]; the breathing force constant of the \(e_{\text{an}}^-\) cavity is markedly smaller than that of the \(e_{\text{aq}}^-\) cavity; the ammoniated electron is calculated to be appreciably less strongly bound than the hydrated electron or even unbound electron relative to the isolated electron and six ammonia molecules [22]; the electron spin density on the proton in water is positive whereas in ammonia it is negative [22–23,36]; and ammonia clusters of any size do not form well-bound excess electron surface states [39].

A second problem is the role of H-bond interactions on the dynamics of the electron localization and stabilization. Barnett et al. [39] investigated by molecular simulation experiments very early stages following excess electron injection in ammonia and water. They started from the system in which an electron is initially attached to an equilibrated neutral cluster in the ground electronic state in the pre-existing trapping sites due to the process of multi-phonon non-radiative transitions [45] or as a result of the charge-induced polarization [46–48]. The H-bond interactions play a role in the first stage of the dynamic of excess electron migration (0.15–4 ps for the ammonia clusters and 0.15–1.2 ps for water) during the reorganization in the vicinity of the electron with the NH or OH bonds pointing to the
centre of the excess electron as a final result. In the next step, migration of the electron towards the centre of the cluster occurs, characterized by polaron-like dynamic evolution. The processes of the excess electron migration are slower in ammonia than in water. The question arises of what the major interaction is that is responsible for the equilibrium structures suggested by molecular dynamics simulations and electron spin resonance of the solvated electron in H-bonded solvents. Clark and Illing [23] suggested that the major interaction, apart from the spin polarization, is H bonding with the localized electron as a donor to the antibonding $\sigma^*_{OH}$ or $\sigma^*_{NH}$ orbitals in water and ammonia.

RESULTS AND DISCUSSION

As mentioned in the Introduction, a theory of the absorption spectrum of an excess electron has recently been proposed [15]. The theoretical development considers the contribution to the absorption band profile from the coupling of the excess electron with the vibrational intramolecular modes of the matrix, inhomogeneous broadening due to the statistical variety of trapping sites and tunnelling. The vibrational coupling between the excess electron and the solvent molecules modifies the equilibrium structure by the selective attachment to the intramolecular vibrational modes of the molecules forming the trap (in terms of the "cavity" or the "solvated anion" model). The vibrational coupling is treated in the framework of the strong coupling limit theory.

Theoretical spectra were calculated in the visible and near-IR range of the electron solvated in water, alcohols, ammonia, amines, ethers and alkanes. The comparison between the theory and experiment suggests that the coupling between the excess electron and the intramolecular modes of the solvent plays the dominant role on the absorption bands of the excess electron in both the visible and the near-IR regions. The model generates the peak position, the width and the asymmetry of the visible (equilibrated) spectra of the solvated electron in water, methanol, ammonia, methylamine, trimethylamine, propane and 3-methylpentane with good accuracy.

It has been shown that the band widths arise from the combination of the vibronic bands due to the coupling of the electron with the low-frequency modes: torsional $\nu_t$ or bending $\nu_b$ modes. Some of the results are given in Figs. 1–5. In matrices that form H bonds, an excess electron is coupled with the torsional mode, at 710 cm$^{-1}$ for water, 320 cm$^{-1}$ for ammonia and 370 cm$^{-1}$ for methylamine. The only exception is methanol,
where the electron is coupled with the bending mode $\nu_b$ (C–OH) at 1345 cm$^{-1}$. In non-H-bonded solvents an excess electron is coupled with the bending modes lying at low frequencies: The $\nu_b$ (C–N–C) mode at 365 cm$^{-1}$ for trimethylamine, $\nu_b$ (C–O–C) at 440 cm$^{-1}$ for diethyl ether, $\nu_b$ (C–C–O) at 596 cm$^{-1}$ for tetrahydrofuran, $\nu_b$ (CCC) at 323 cm$^{-1}$ for propane-d$_8$ and $\nu_b$ (CCC) at 444 cm$^{-1}$ for 3-methylpentane. From this selective attachment deductions can be made about the geometry of the cavity or the preferential sites on an anion.

It is well known that in H-bond complexes the stretching $\nu_s$ and the torsional $\nu_t$ modes are the most sensitive on H-bond interaction. Taking this fact into account, it was concluded that the absorption spectra in water, ammonia and methylamine should be ascribed to the electrons in H bond-oriented cavities, whereas in alcohols, ethers, alkanes and trimethylamine to the electrons in dipole-oriented cavities. The vibronic bands are broadened by the coupling of the intramolecular modes $\nu_t$ or $\nu_b$ with the low-frequency modes of the bath. In H-bonded matrices these are the modes of the hydrogen bridges. It was found that the inhomogeneous broadening due to the distribution of solvent environments plays a minor role on the band shapes. The short-time dynamics probed by the spectral band shape is not affected by tunnelling.

The results linked to the near-IR absorption (transient band) led to the conclusion that the IR spectra of excess electrons in alcohols have a different origin to those in water and aqueous glasses. In alcohols there are two kinds of trapped electrons, which are distinctly different in nature. The visible-absorbing electrons are associated with the OH traps in alcohol matrices [coupling
with the bending mode \( \nu_b(\text{OH}) \) whereas the IR-absorbing electrons are trapped in the alkyl group (coupling with the \( \text{CH} \) stretching modes) (Fig. 6).

The distinction between the two kinds of trapped electrons has been indicated by many workers [49–52] and the present results support their conclusions. In contrast, the IR absorption in water has a different origin. There is only one kind of trap in water, the OH trap. The visible band is associated with the electron coupled with the torsional mode \( \nu_t (710 \text{ cm}^{-1}) \) whereas the IR band is due to the electron in the same trap coupled to the stretching mode \( \nu_s(\text{OH}) \) (at 3651 \text{ cm}^{-1} for \( \text{H}_2\text{O} \) and 2660 \text{ cm}^{-1} for \( \text{D}_2\text{O} \)). The coupling with \( \nu_s(\text{OH}) \) or \( \nu_s(\text{OD}) \) becomes weaker with time when an electron reaches the stages closer to equilibrium, which results in a decrease in the IR absorption.

Strong evidence in favour of this interpretation is the failure to detect IR absorption in \( \text{H}_2\text{O} \) at
low temperatures in contrast to D$_2$O matrices. This seemed surprising because the molecular structures including the ability to form H bonds are very similar in both matrices and the depth of the electron potential well should be nearly the same. The model is able to explain it on the basis of the different vibrational properties of protiated and deuterated matrices.

It has been shown that the absorption in the near-IR region for the coupling with $\nu_s$(OH) is much weaker than in D$_2$O for the coupling with $\nu_s$(OD). It should be stressed that the differences between H$_2$O and D$_2$O are not the result of any arbitrary change in parameters. The results in Fig. 7 were calculated for the same set of molecular properties. The only different parameter that causes the different spectrometric behaviour of H$_2$O and D$_2$O is the frequency of the vibrational stretching mode $\nu_s$(OH) ($\omega_{\text{ag}} = 3651$ cm$^{-1}$ for H$_2$O and 2660 cm$^{-1}$ for D$_2$O) which was taken from IR experiments. Hence the isotope effect on the absorption spectra is not the result of any arbitrary reparametrization, but comes from the coupling between the excess electron with the same mode $\nu_s$(OH) having different frequencies on deuteration.

The vibrational coupling of the electron is able not only to explain the appearance of the IR-absorbing band in D$_2$O and its absence in H$_2$O matrices at low temperatures, but also to reproduce the difference in the band widths and the peak positions of the visible bands in H$_2$O and D$_2$O. Further evidence in favour of this interpretation is the finding that the conversion e$_\text{IR}$ $\rightarrow$ e$_\text{vis}$ is observed in alcohols but not or to a much lesser extent in water. The conversion in alcohols is possible due to the different traps responsible for the IR and visible absorption. In water there exists only one kind of trap, which means that the idea of conversion loses its sense.

Conclusions

The results provide strong arguments [16–20] that the dynamics of the excess electron are governed by vibrational properties of matrices in which the electron is trapped. It has been indicated which vibrational modes are coupled with an excess electron in typical matrices. It has been shown that in H-bonded matrices the vibrational modes which are the most sensitive on H-bond formation, i.e., the stretching mode $\nu_s$ and the torsional mode $\nu_t$, are coupled with an electron. The coupling with the high-frequency stretching mode $\nu_s$ determines the absorption of the transient band in the near-IR region whereas coupling with the low-frequency torsional mode $\nu_t$ determines the absorption of the equilibrium band in the visible range. This suggests that an electron is involved in some kind of H-bond interaction with the solvent molecules forming an H-bonded trap.

In other matrices dipolar interactions between the solvent molecules and an electron seems to determine the spectrometric properties of the absorption bands of an electron. In this instance the electron is coupled with the vibrational modes, which strongly modifies the dipole moments of the molecules like bending modes. However, many details, some of which are fundamental, remain to be elucidated. The critical point is not that a fit of the experimental spectra is achieved, but what physical insight about the band shape can be gained from this theory in its present form. In addition, the experimentally measured spectra of the solvated electron were readily reproduced in the past by a wide range of sometimes mutually exclusive ad hoc models. Further work on the applications of the theory to a variety systems is necessary to establish whether its derived parameters show physically sensible trends and to clarify its physical implications concerning the band shape.

REFERENCES