SMALL AMPLITUDE COLLECTIVE PROTON MOTIONS IN WATER NETWORKS - APPLICATION TO ICES, CLATHRATES AND AQUEOUS SOLUTIONS

J. Green, A. Lacey, M. Sceats

To cite this version:
J. Green, A. Lacey, M. Sceats. SMALL AMPLITUDE COLLECTIVE PROTON MOTIONS IN WATER NETWORKS - APPLICATION TO ICES, CLATHRATES AND AQUEOUS SOLUTIONS. Journal de Physique Colloques, 1987, 48 (C1), pp.C1-53-C1-58. <10.1051/jphyscol:1987108>. <jpa-00226238>

HAL Id: jpa-00226238
https://hal.archives-ouvertes.fr/jpa-00226238
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SMALL AMPLITUDE COLLECTIVE PROTON MOTIONS IN WATER NETWORKS - APPLICATION TO ICES, CLATHRATES AND AQUEOUS SOLUTIONS

J.L. GREEN, A.R. LACEY and M.G. SCEATS

Department of Physical Chemistry, University of Sydney, Sydney, N.S.W. 2006, Australia

Résumé. Une caractéristique de la spectroscopie Raman de l'eau en relation avec le mouvement collectif de petite amplitude des protons, est employée pour étudier la structure de réseau de l'eau liquide, des glaces, semiclathrates, alcools, electrolytes et des mélanges H₂O/H₂O₂.

Abstract. A feature in the Raman spectrum of water networks, assigned to small amplitude collective proton motions, is used to probe the network structure in ices, liquid water, H₂O/H₂O₂ mixtures, semiclathrates, alcohols and electrolytes.

1. Introduction

The OH stretching spectrum of water is strongly perturbed by the strength of hydrogen bonding [1]. However, the stretching motions of adjacent molecules are strongly coupled [2] as expected for a transition which exhibits a large transition dipole moment. This complexity was circumvented by study of the OH stretching motions in heavily deuterated systems [2], where the OH oscillators are mechanically decoupled from the surrounding OD oscillators. Their spectrum exhibits the range of OH stretching frequencies induced by the variation of the hydrogen bonding, i.e. inhomogeneous broadening. Data thus obtained provide a probe of the character of the hydrogen bonding and have been used to develop structural models of liquid water [3].

In this paper recent experiments will be reviewed in which the spectrum of coupled OH oscillators is studied. Whereas the decoupled spectrum provides information on the singlet bond distribution, the coupled spectrum is influenced by higher order distribution functions which more directly reflect the structure of the networks and hydrogen bond correlations.

2. Collective Proton Motions in Defect-Free Tetrahedral Networks

The ices are continuous tetrahedral networks [4]. The strong coupling of OH oscillators in ice I was first revealed by Haas and Hornig [5] who observed the coupling between adjacent OD oscillators O-D...O-D in dilute D₂O/H₂O ice I. The consequences of this coupling on the spectrum of H₂O ice I was pointed out by Whalley [2]. Calculations by Rice and coworkers [6-8] have shown that the observed infrared and Raman spectra can be modelled to a high precision, and have confirmed that the spectrum is dominated by intermolecular coupling. A feature of the spectrum is the appearance in the low frequency edge of the In Raman spectrum of an intense band due to the in-phase collective motion of the OH oscillators [9]. It is this feature that we will use as a probe of the collective motions. As shown in Figure 1, this band appears, albeit broader, in the spectrum of amorphous solid water H₂O(as) and, with reduced intensity, in liquid water.
Consider the linewidth, $\Delta$, of the in-phase collective band in ice I. This has been measured by Sivakumar et al [9], and is fitted to the form

$$\Delta_0 + \frac{\Delta}{\exp(h\nu/kT) - 1}$$

The frequency $\nu$ is 200 cm$^{-1}$, and corresponds to the 0-0 stretching region of the translational spectrum [10]. The collective mode scatters off the translational optical phonons. The width of the uncoupled OH oscillator spectrum in D$_2$O is only weakly temperature dependent [9] and is primarily attributed to inhomogeneous broadening arising from proton disorder in ice I. This width extrapolated to 0 K is 25.8 cm$^{-1}$. The experiments show that $\Delta_{\text{OH}} > \Delta_0$, with $\Delta_0 = 19$ cm$^{-1}$ and this we attribute to motional narrowing of the collective mode. The OH stretching excitation, a vibron, moves rapidly through the network at low temperatures and the spectrum is unperturbed by the inhomogeneous distribution. In principle, the linewidth near 0 K should approach a $\delta$-function. The scattering due to optical and acoustic motions is frozen out as $T \to 0$ K because the in-phase mode lies at the low energy edge of the vibron density of states. The residual width $\Delta_0$ of the collective band could be due to inhomogeneous broadening arising from lattice disorder. This width extrapolated to 0 K is 25.8 cm$^{-1}$. The experiments show that $\Delta_{\text{OH}} > \Delta_0$, with $\Delta_0 = 19$ cm$^{-1}$ and this we attribute to motional narrowing of the collective mode.

The elegant codeposition experiments of Devlin and coworkers [12, 13] have allowed measurement of the spectrum of intact H$_2$O molecules in D$_2$O ice I. The role of Fermi resonance has been deduced from these spectra [14] and the coupling element $W$ is 60 cm$^{-1}$. In the coupled spectrum the impact of Fermi resonance is less pronounced, but we suggest that it could be the source of the residual width at 0 K of the in-phase collective mode, by the irreversible process of excitation of the bending overtone on one molecule followed by fission into bending excitations on adjacent molecules or excitation of the librational modes. The linewidth is given by Fermi's Golden rule, $2\hbar^2 \rho(\nu_0)/\mathcal{M}$, where $\rho$ is the overtone density of states. The residual width is consistent with a density of states at $\nu_0$ of $4.2 \times 10^{-4}$ cm$^{-1}$, which is in reasonable agreement with the simulations of the liquid water spectrum [15] in which the bending overtone density of states at 3086 cm$^{-1}$ is calculated to be $1.3 \times 10^{-3}$ cm$^{-1}$. The results suggest that the Gaussian form for $\rho$ used in simulations [7] falls off too rapidly. It is also possible that the combined density of states of bending and librational modes should be used. If our hypothesis is correct, the OH stretching vibrational lifetime in ice I is 0.6 ps.

The width of the vibron band is estimated from $2(\nu_{\text{OH}} - \nu_0)$ where $\nu_{\text{OH}}$ is the frequency of the decoupled oscillator and $\nu_0$ that of the in-phase collective mode. For ices I, II, III and V, H$_2$O(as) and liquid water the vibron bandwidth spans a range of 300-400 cm$^{-1}$. The similarity of these widths suggests that the magnitude of the resonance coupling between OH oscillators is the same in all these tetrahedral networks. This is confirmed by analysis of the spectra of proton ordered ices II and IX, which yields a coupling force constant [17] in agreement with that required to model the ice I spectrum. While the vibron bandwidth of the networks with severely distorted hydrogen bonds is slightly less than that of ice I,

![Fig. 1: The Raman spectrum of water, H$_2$O(as) and ice.](image)
It is clear that the collective behaviour is not sensitive to the network topology for tetrahedral networks, a conclusion borne out in calculations of the spectrum of H$_2$O(as)[18,19].

The extent of the collective mode character is defined by the relative contribution of the in-phase collective mode to the 1$_R$ Raman spectrum. We have devised [20] a spectral stripping procedure for extraction of this quantity in cases where in-phase collective mode is not well resolved, such as in liquid water (Figure 1). The polarization ratio I$_R$/I$_L$, for the remainder of the spectrum does not vary significantly with frequency, and is very close to that of uncoupled oscillators. Presumably this arises from cancellations of contributions due to the complex phase relationships among the OH oscillators in these modes. The collective spectrum $I_C(\omega)$ is thus defined by $I_R(\omega) - a^{-1}I_L(\omega)$ where $a$ is an adjustable parameter determined by fitting the high frequency shoulder to minimize $I_C(\omega)$ in this region. The value of $a$ is typically 0.21±0.02 [20]. The area, $C$, of $I_C(\omega)$ relative to $1_R(\omega)$ is taken to be a measure of the collective character. Spectra of ice I at a wide range of temperatures were thus analysed [20] and the value of $C_{\text{ice}}$ was found to be 0.54±0.03 with no temperature dependence. This implies that the thermal disorder, which leads to an increase in the linewidth of the in-phase collective mode with increasing temperature [9], does not reduce the extent of the collective motion, but merely causes a scattering of the vibron modes by interaction with the lattice phonons. The value of $C$ for H$_2$O(as) is the same as that of ice I [20] showing that the collective character is not affected by the topological disorder of H$_2$O(as), nor by a modest increase in the short range disorder [9].

The collective character of the motion can be strongly perturbed by the introduction of defects which cause the OH oscillator frequencies to lie outside the vibron bandwidth. The upper limit to the vibron band is about 3500 cm$^{-1}$ for all the tetrahedral networks, while the lower limit is about 3100 cm$^{-1}$. Broken hydrogen bonds have stretching frequencies above 3500 cm$^{-1}$ and because they lie outside the vibron band they act as defects with respect to the collective stretching motions. In ice I the concentration of broken bonds is too small to influence the collective motions. However the effect of deuteration is to introduce mass defects which vibrate near 2400 cm$^{-1}$. The intensity of the collective band thus decreases with increasing OD mole fraction $p_{OD}$, and the results [21] can be fitted by $C_{\text{ice}}(1-p_{OD})^2$. This is expected because the collective motions arise from a coupling of nearest neighbour OH oscillators. If $C$ for all defect free tetrahedral networks is 0.54 then we propose that for networks with intrinsic defects of mole fraction $p_I$, that $C = C_{\text{ice}}(1-p_I)^2$. Thus a measurement of $C$ can be used to estimate $p_I$. In the absence of mass defects, we can assume that in most cases the defects will arise from broken hydrogen bonds with OH stretching frequencies above 3500 cm$^{-1}$ as required by the magnitude of the vibron band. Thus $p_I$ can be broadly interpreted as the mole fraction of broken hydrogen bonds. This is the concept used to analyse the defective network of liquid water in the next section. Alternatively, when other molecules are added, it is possible that a new network topology will arise, characterized by water molecules with a lower coordination number, hence a lower value of $C$.

3. Liquid Water - A Random Network with Defects

It has been proposed that liquid water can be regarded as a continuous random network [3]. However, the lifetime of a configuration of water molecules is small and the random network must be defective. As water is cooled, the defect density decreases and the behaviour of the thermodynamic and transport properties of water exhibit increasingly anomalous behaviour [22,23] suggesting approach towards a thermodynamic singularity, near $T_S = -45^\circ$C. As water is cooled at 1 atm towards $T_a$ there are increasing fluctuations between configurations of water molecules with similar energies but significantly different densities. The well known anomalous properties of water in the normal liquid regime stem from a residue of the behaviour exhibited in the supercooled region. The structural origin of the behaviour of liquid water remains the centre of much debate.

The Raman spectra of liquid water at 1 atm were obtained in the range $-28^\circ$C to $90^\circ$C, and values of $C$ were obtained [20] using the procedures described in Section
2, and the results are plotted in Figure 2. The most important feature of the results is that they linearly extrapolate to the value of ice I and \( H_2O(\text{as}) \) near the temperature \( T_s \) of the purported thermodynamic singularity. From the analysis of Section 2 we would conclude that \( \rho_1 \rightarrow 0 \) as \( T \rightarrow T_s \). It should be noted that homogeneous nucleation to ice I prevents experiments in the vicinity of \( T_s \) and the range of extrapolation is large. Furthermore, it should not be construed that the configuration of water is tending to ice I like structures (6 membered rings) as \( T \rightarrow T_s \) but rather to a low density continuous tetrahedral network.

The data obtained at 1 atm do not reveal the full complexity of liquid water. Studies at constant density are more revealing. Raman spectra of water under tension in sealed capillaries were obtained and analysed. In this case the density of water is approximately constant, 18.2 cm\(^3\)mol\(^{-1}\) below 30\(^\circ\)C. The values of \( C \) obtained in this study (a collaborative project with Dr. R. Speedy) are also plotted in Figure 2 for a sample with an OD mole fraction of 0.18. At temperatures below 20\(^\circ\)C the value of \( C \), hence \( \rho_1 \), does not change significantly. This indicates that the defects are strongly coupled to the density, insofar as the configurational composition of the liquid is temperature independent under conditions of constant volume. The data of Figure 2 emphasize the importance of performing studies at approximately constant volume conditions. Water under tension (e.g. -210 bar at 9.12\(^\circ\)C for the sample in Figure 2) and in the supercooled region exhibits an amplification of the anomalous properties of water to such an extent that they are reflected by observable changes in spectroscopic properties in the OH stretching region. Further studies are required to verify these results.

4. Chemical defects in Water Networks - \( H_2O_x/H_2O \) Solutions

The properties of aqueous solutions are extremely important. If pure water is to be viewed as a detective random network [3], then one of the primary questions concerning aqueous solutions relates to the effect of solutes on the water structure. There can be no single answer to this question because of the wide variety of behaviour exhibited and often classified as structure "making" or "breaking". The simplest class of solutes are those which can themselves be incorporated into the network. Such an example is \( H_2O_2 \). This molecule adds an excess of two lone pairs for each peroxide molecule, such that each OH oscillator should, in principle, be unperturbed in \( H_2O-H_2O_2 \) networks because strong O-H...O bonds can always be formed. The uncoupled oscillator spectrum of mole fraction \( x = 0.56 \) of \( H_2O_2 \) in water shows a distribution of OH stretching frequencies which is not dissimilar to that of pure water and, although the detailed interpretation is not clear, the spectra indicate that the hydrogen bonds in these mixtures are similar in strength to those in liquid water. The Raman spectra of \( H_2O_x/H_2O \) mixtures over a wide range of compositions and temperatures have been obtained and the small amplitude collective proton motions are analysed to yield values of \( C(X)(T) \). In all
cases $C_x(T)$ was reduced from that of $H_2O$ indicating a breakdown of the collective character attributed to structure breaking.

Two regimes of behaviour were observed as a function of mole fraction $x$ of $H_2O$. For $x<0.08$, the data generally follows a $(1-mx)$ behaviour with $m=2-3$ indicating that each $H_2O$ creates approximately two to three defects in the network of $O-H$ oscillators. For higher values of $x$, the dependence tends to a weaker $(1-x)$ dependence and we interpret this in terms of network reconstruction. Solid solutions of $H_2O/H_2O_2$ exhibit a complex phase diagram and the crystal structures of $H_2O_2:2H_2O$ and $H_2O_2$ are characterized by networks which have a lower coordination than the tetrahedral networks of pure $H_2O$. The number of nearest neighbour oscillators are reduced, and it follows that the vibron bandwidth will decrease. Furthermore, for an approximately invariant distribution of oscillator frequencies a proportionally larger fraction will fall outside the vibron bandwidth thereby reducing $C$. We suggest that the decrease of $C$ at high mole fractions of $H_2O_2$ is associated with reconstruction of the network topology to that of a network of lower connectivity. It is interesting to note that $H_2O_2$ also gradually suppresses the density fluctuations of water [25] over the range in which we observe defect behaviour ($x<0.1$) and is completely quenched in the reconstruction regime.

5. Semiclathrates - A model for Hydrophobic Hydration Networks

Clathrate structures are characterized by a continuous tetrahedral water network [26] as in the ices, and exhibit collective small amplitude proton motions similar to that in ice I. The semiclathrate of tetra n-butyl ammonium hydroxide [27] has been studied using the techniques described above. We have studied the crystal, the liquid, the supercooled liquid and its aqueous solutions. This type of clathrate was chosen for study because it is a convenient model for understanding hydrophobic hydration, which is of considerable importance for understanding biological structures. The semiclathrate crystal has a broad distribution of hydrogen bond lengths, and thus exhibits a broad distribution of decoupled $OH$ stretching frequencies. However the in-phase collective band is well established and has a value of $C=0.48$. This is close to the value expected for a defect free tetrahedral network, perhaps with a defect density of 0.06. Upon melting there is a large increase in the decoupled oscillator spectrum above 3500 cm$^{-1}$ corresponding to broken bonds, and $C$ in the coupled spectrum is reduced to 0.27, suggesting a defect probability of 0.30. In this case the fluid properties arise from extensive breaking of the hydrogen bonds; indeed, more so than in the melting of ice. However, upon dilution with $H_2O$, $C$ rises again to a value larger than that of bulk water at the same temperature, as shown in Figure 3. We attribute this behaviour to network restabilization in which each solute molecule establishes its own ordered hydration shell, perhaps with a separated layer of water molecules between the hydration shells of neighbouring solutes, in comparison to the shared hydrated water molecules of the parent clathrate. The dilution data provide information on network reconstruction during hydrophobic aggregation.

6. Alcohols and Electrolytes

Water-alcohol solutions exhibit a wide variety of thermodynamic [28] and transport behaviour which is poorly understood in terms of structural properties. We have studied aqueous solutions of ethanol, isopropanol and t-butanol with a view to determining the effect of these molecules on the liquid water random network structure. The series was chosen because it represents a progressive increase in the size of the hydrophobic alkane region. The neat alcohols exhibit very small $OH$ stretching collective character because the number of nearest neighbour $OH$ oscillators is limited and the vibron bandwidth is less than the disorder.

Measurements of $C(x,t)$ show that for $x<0.16$ ethanol and i-propanol are accommodated into the network with insignificant change in the collective character. This implies that these alcohols neither introduce broken hydrogen bond defects, nor destroy the tetrahedral character of the network. On the other hand, the t-butanol increases the value of $C$ relative to that of pure water, and the largest value of $C$ is similar to that of the comparable semi-clathrate discussed in the previous section. This suggests that the solution properties of t-butyl alcohol [29] arise
from formation of clathrate-like cages.

Finally, studies have been completed on LiCl electrolyte solutions. These solutions quench the anomalous properties of water [30,31] and, as for H$_2$O/H$_2$O mixtures, we have observed a decrease in the collective band character. This is attributed to breaking up of the tetrahedral structure of the water network.

7. Conclusions

In this paper we have reviewed the basic concepts which explain the observation of a strongly polarized band in the $\tilde{\nu}_2$ Raman spectrum of water networks in terms of an in-phase collective OH stretching spectrum. We have demonstrated that this region of the spectrum can be used as a probe of the network structure by application to a variety of aqueous solutions. The introduction of solutes may change the collective character depending on whether it promotes the network structure, by reducing the network defect probability, or breaks the network structure. The latter may occur either by the introduction of extra defects in the form of broken hydrogen bonds or by reconstruction of the network into one of lower connectivity than the tetrahedral networks of pure water systems. This work was supported by the Australian Research Grants Scheme. JLG acknowledges the award of a Commonwealth Postgraduate Scholarship.

References