

The molecular structure of liquid water delivered by absorption spectroscopy in the whole IR region completed with thermodynamics data

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ABSTRACT

Absorption spectra of liquid water at various temperatures in the whole IR region ($0 < \tilde{\nu} < 4000 \text{ cm}^{-1}$) are obtained from ATR spectra recorded in the mid-IR region combined with absorption spectra measured in the FIR region. They can be accurately decomposed over two independent spectra. The spectra of the two kinds of H_2O (D_2O) molecules they suppose are defined as fulfilling spectroscopic constraints and as being in accordance with thermodynamic values. Their enthalpy difference $H^e - H^s$ is found equal to 11.8 kJ mol^{-1} for ordinary water and 12.2 kJ mol^{-1} for heavy water. H_2O (D_2O) molecules of lower enthalpies H^s , greater than the enthalpy of H_2O or D_2O molecules in ices by 1.3 kJ mol^{-1} , display vibrations that resemble those of H_2O (D_2O) molecules in ice. Molecules with enthalpies H^e reorient without breaking their H-bonds as H^e appears greater than the potential barrier for rotations around their symmetry axes.

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1. Introduction

Liquid water, by far the most abundant liquid on Earth, which we everyday use, drink, live in, etc., is one of the less understood liquid at molecular level even if H_2O is a particularly simple and stable molecule. It displays, however, such an exceptional ability to establish numerous hydrogen bonds (H-bonds in the following) that their relative arrangements and their dynamics are particularly numerous and difficult to describe. Ice is a solid with each H_2O molecule establishing H-bonds on two neighbor H_2O molecules and accepting two from two other neighbor H_2O molecules. The basic arrangement of these molecules is that of a regular tetrahedron and the number of H-bonds is as great as that of covalence bonds, an exceptional situation. IR spectroscopy, the most sensitive and powerful method to detect hydrogen bonds and define their strengths, clearly shows that in liquid water nearly all O–H groups establish H-bonds, with consequently the number of “free” O–H groups remaining very small [1–3]. It indicates that liquid water keeps a nearly as dense H-bond network as ice together with this basic tetrahedral structure that can, however, be more disordered. The question then arises: how does this hyperdense H-bond network, is so modified in liquid water that it allows fluidity, which combined with this density of H-bonds, is at the origin of all exceptional properties of water? Many experimental methods and theoretical approaches have been used to answer this question, but up to now no definitive conclusion has been drawn.

Despite its great interest absorption IR spectroscopy, a basic method widely used by Chemists, has been scarcely used in the case of water, due to inherent difficulties that lead to that paradoxical situation that IR spectra of liquid water are less known than those of many other much less common liquids. The reason is that liquid water displays in the mid-IR region exceptionally strong absorption bands with particularly great absorption coefficients k . It makes usual experimental absorption setups hard to use because samples should be much thinner, typically a few μm thick, if one wishes to avoid catastrophic saturations of bands. It explains why Raman spectroscopy, which is much less sensitive to H-bonds than IR spectroscopy and therefore much more easily avoids saturation of bands, has for long been used instead of IR spectroscopy for the study of liquid water, at the price, however, of a significant loss in the signal to noise ratio. IR absorption spectra of water are also much harder to exploit than IR spectra of other less absorbing liquids, where the refraction index n can be well approximated by a constant value on the whole range of wavenumbers $\tilde{\nu}$. As a consequence reflections on the surfaces of the transparent windows that hold the liquid water sample appear in the spectra in the form of a constant shift of the baseline that does not depend on $\tilde{\nu}$ and can consequently be easily subtracted to obtain the absorbance $\lg(I_0(\tilde{\nu})/I(\tilde{\nu}))$ of the sample alone (I_0 and I are the IR intensities at the input and output of the sample). This is no longer true for liquid water where n , which is related to k by Kramers–Kronig relations, strongly varies in spectral regions of strong absorbance $k(\tilde{\nu})$ and reflections at the window-sample interfaces can no longer be easily eliminated, as they now induce an appreciable and complicated distortion of the baseline. An Attenuated Total Reflection

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(ATR) setup may consequently appear preferable to usual absorption setups for obtaining precise values of optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$ and therefore of absorbance [4,5]. With such a setup the intensities of the IR beam $I_0(\tilde{\nu})$ and $I_p(\tilde{\nu})$ at the input and output of a transparent crystal immersed in water are precisely measured [6]. Unfortunately real crystals are not transparent for $\tilde{\nu}$ smaller than some 600 cm^{-1} . As the knowledge of ATR intensities in this far IR (FIR) region is necessary to calculate either optical constants or absorption spectra (also called transmission spectra), methods have been devised to minimize the effects of this absence of transparency [7] or hypotheses have been made to approximate their values in the FIR region [8]. But to the best of our knowledge, precise absorption spectra of liquid water in the whole IR region ($0 < \tilde{\nu} < 4000\text{ cm}^{-1}$), where all fundamental $0 \rightarrow 1$ vibrational transition appear, do not exist in the literature, except for spectra at room temperature [9] or for the limited spectral region where ν_s bands (O–H stretch modes in the region $2700\text{--}3600\text{ cm}^{-1}$ and O–D stretch in the region $2000\text{--}2800\text{ cm}^{-1}$ for liquid water) appear. Even if these ν_s bands constitute an invaluable source of information for H-bonded systems, they are not sufficient to deduce a complete picture of the structure and dynamic of liquid water, because other important vibrational bands such as librational bands are missing. In Section 2 of this article we describe a method to obtain absorption spectra in this whole spectroscopic region at various temperatures that encompass the region where water is a liquid, for both ordinary and heavy waters. The accuracy of these spectra will enable us to perform a quantitative analysis of their variations with temperature, which will make a basis to formulate a detailed proposition for the molecular structure of liquid water.

Raman spectra of water in the entire vibrational region $0 < \tilde{\nu} < 4000\text{ cm}^{-1}$ have put into evidence the existence of isosbestic points [10]. All spectra at various temperatures display the same (scattering) intensity at the particular wavenumbers of these isosbestic points. The set of IR spectra presented in this paper confirms the existence of such isosbestic points around 600 , 1600 , 1680 , and

3550 cm^{-1} (see Fig. 1). The greater signal to noise ratio of IR spectra however allows a more quantitative analysis, based on the observation that will be made that the whole series of spectra can be well decomposed over two independent spectra that are both linear combinations (additions with various coefficients) of experimental spectra. This will not appear as a hypothesis or a supposition but as an experimental result that cannot be ignored and constitutes a solid starting point for the analysis of these spectra. It strongly suggests the existence of two kinds of H_2O molecules in liquid water, a point that can be discussed and has indeed been the object of passionate discussions where the alternative explanation to the existence of these two kinds of H_2O molecules is a continuous distribution of H-bond frequencies in liquid water [11], a proposition that has been formulated on the basis of a consideration of ν_s modes (O–H... stretch) only and not of all vibrational modes. In our opinion opposing these two approaches is meaningless because they are not exclusive: the ν_s band of simple H-bonded systems with a single type of H-bond, such as found in gases, is broad, revealing continuous distributions of H-bond frequencies due to intermolecular vibrations of the two molecules linked by the H-bond [6]. Such a distribution broadens for systems with H-bonds or H-bonded molecules of various kinds. The existence of two kinds of H_2O molecules in liquid water is therefore compatible with a continuous distribution of H-bonds, as each type of H_2O molecules conveys with it a continuous and appreciably broad distribution of H-bonds. In the same way, starting the analysis of experimental results by considering first the H-bond continuous distribution may be fully legitimate, in particular for results other than spectroscopic ones, but does not *a priori* excludes the presence of two types of H_2O molecules.

The set of absorption spectra at various temperatures obtained as described in Section 2 are analyzed in Section 3. It starts with this decomposition over two independent spectra that is first put into evidence. The search for the spectrum of H_2O molecules that would be the only ones at very low temperatures and for the spectrum of H_2O molecules that would be predominant at very high temperatures is then discussed in this same Section 3. This is the logical proceeding after this finding of the decomposition over two basic spectra. In the course of this search spectroscopic criteria are defined but are found insufficient for a complete definition of these spectra. Well-known thermodynamical properties are then invoked that allow a definition of the spectra of “low-temperature” H_2O molecules that are compared to the spectrum of H_2O molecules of ice, and of the spectra of “high-temperature” H_2O molecules. The enthalpies of these two kinds of molecules are measured in the course of this analysis. A discussion of all these results is presented in Section 4 that allows to propose a structure for these two types of H_2O molecules together with a proposition that concerns one of the most exceptional properties of liquid water: the variations of its density with temperature. In Section 5 conclusions are drawn.

2. Absorption spectra of water

In this section, we combine former experimental ATR spectra in the mid-IR region recorded at temperatures ranging from the limit of the supercooled region ($-4\text{ }^\circ\text{C}$ for ordinary water, $0\text{ }^\circ\text{C}$ for heavy water) up to $80\text{ }^\circ\text{C}$ with former absorption spectra in the FIR region recorded in the same range of temperatures. It allows obtaining accurate enough absorption spectra in the whole IR region that extends from nearly zero wavenumbers up to the near IR region, with a resolution close to 2 cm^{-1} over 8192 points. In order to do this we use a procedure adapted from Bertie-Eysel's iteration procedure [4], calculating in a first step an “enlarged experimental” ATR spectrum $atr^e(\tilde{\nu})$ at temperature T equal to the experimental one

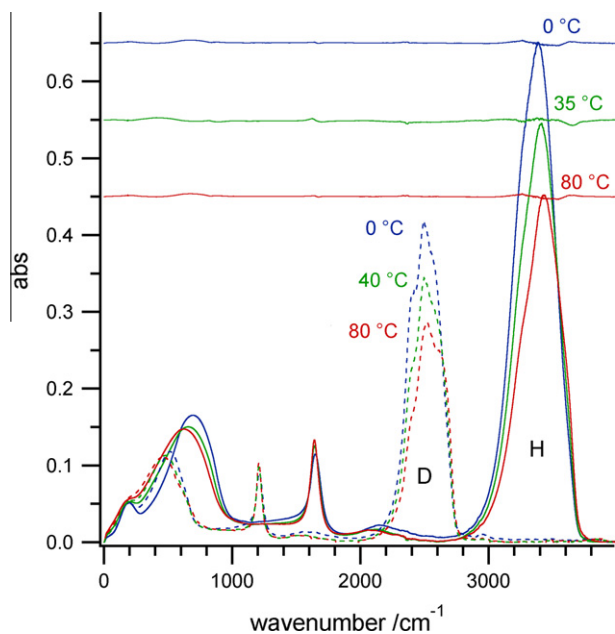


Fig. 1. Absorption spectra of samples $1\text{ }\mu\text{m}$ thick of ordinary water (full lines, “H” inside ν_s bands) and heavy water (dotted line, “D” inside ν_s bands) at three selected temperatures indicated on top of ν_s bands. Flat spectra are residual decomposition spectra over the two spectra $S^l(\tilde{\nu})$ and $S^h(\tilde{\nu})$ (Eq. (6)) for ordinary water at same temperatures as indicated. They are offset for clarity, so as to be positioned near the maximum of the ν_s band of their corresponding absorption spectrum.

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