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Infrared spectra of water. II : Dynamics of H$_2$O(D$_2$O) molecules

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Abstract. — Spectra of $\varepsilon''$ (imaginary dielectric constant) of water in the IR region, obtained as described in a previous article by using attenuated total reflection (ATR) techniques, are analyzed. Criteria are presented which allow us to define, on the basis of spectroscopical arguments only, the low temperature spectrum $\varepsilon''(T_L)$ and the high temperature spectrum $\varepsilon''(T_H)$ on which any spectrum at temperature $T$, in the range $-5$ °C to $80$ °C, may be decomposed. These spectra display novel features: their $\nu_s$ bands (intramolecular stretch) have shapes which have great similarities in both spectra ; the $\delta$ band (intramolecular bend) of the high temperature spectrum $\varepsilon''(T_H)$, has a simple shape with no apparent structure, which may be approximated, with a good precision, by a Lorentzian curve. A discussion of the origin of these features reveals a new picture of water at a molecular level: it is made of H$_2$O molecules which either perform rotations of a vibrational character (librations) around their three axes and appear in $\varepsilon''(T_L)$ or perform rotations around their C$_2$ symmetry axis $z$ of a diffusional (relaxational) character. H$_2$O molecules of the latter type appear in $\varepsilon''(T_H)$. Their concentration reaches $\approx 35$% at 0 °C (1 atm.) and $\approx 90$% at 100 °C (1 atm.). They have rotational energies around $z$ greater than the maximum of the potential energy governing this rotation. Around their other two axes they perform librations which qualitatively do not differ from those performed by molecules appearing in $\varepsilon''(T_L)$. The estimated correlation time, or average time during which phase coherence of $\delta$ vibrations in these molecules is kept, falls in the range $10^{-14}$-$10^{-13}$ s, as deduced from the Lorentzian shape of the $\delta$ band in $\varepsilon''(T_H)$. The analysis of these spectra also indicates that the $\nu_s$ band borrows its intensity from $\nu_s$ via a cubic term in the vibrational potential.

1. Introduction.

Water is a species which exhibits many paradoxes. Its constituent molecule, H$_2$O, for instance, is one of the simplest and most stable molecules. Yet it has a very particular electronic structure which looks quite ordinary but has far lying consequences: it has as many non-bonding orbitals as valence orbitals. This is at the origin of an extremely high density of H-bonds in water, which makes it an exceptional liquid. A part of the paradox is that we certainly better understand how this exceptional density of H-bonds is at the origin of exceptional
properties of water [1] than how H₂O molecules manage, with these numerous directional H-bonds, to keep water a liquid, even if a complex liquid [2]. Another paradox is that, although one of the most familiar species which has been studied by all available techniques, its IR spectra were up to recently poorly known and no systematic dependence of these spectra upon such parameters as temperature or H/D isotopic composition were reported. Using an ATR cell, we have been able to obtain good quality IR spectra of water, which are described in a preceding article [3] (which will be denoted I in the following) and to study their dependence upon these two parameters. Let us stress that ATR spectra in the IR region are spectra of bulk water, as it consists of making absorption on the evanescent wave only which gets out of a crystal. As this evanescent wave extends over a region of the size of the wavelength, that is, several microns in our case, ATR spectra are spectra of a film of this thickness, with negligible surface effects which disappear at a distance of the order of 1 nm [4].

The aim of this article is to analyze these IR spectra of water, in view of getting some insight into the disposition and dynamics of H₂O molecules in water. One of the main results described in I is that any spectrum \( \varepsilon''(T) \) \((-5 °C < T < 80 °C; \varepsilon'' \) is the imaginary dielectric constant of water) may be decomposed into any two spectra \( \varepsilon''(T_0) \) and \( \varepsilon''(T_1) \) following the equation:

\[
\varepsilon''(T) = \varepsilon''(T_0) - a(T, T_0, T_1) \times [\varepsilon''(T_0) - \varepsilon''(T_1)]. \tag{1}
\]

In these equations we have not explicited, for simplicity, wavenumbers \( \tilde{\nu} \), but we shall keep in mind that the \( \varepsilon''(T) \) represent spectra. This form implies the presence of several isothesbic points in various bands of the spectra which appear at all wavenumbers \( \tilde{\nu} \) where \( \varepsilon''(T_0) = \varepsilon''(T_1) \). The presence of such isothesbic points has been previously recognized in \( \nu_s \) Raman bands [5-7] or 2 \( \nu_s \) NIR (near infrared) bands [8-10].

In the range of temperatures considered, the variations of \( a(T, T_0, T_1) \) with \( T \) are well described by a quadratic approximation. When \( T_0 \) is taken equal to 0 °C and \( T_1 \) to 75 °C, which we shall suppose in the rest of the article, \( a(T, T_0, T_1) \), which we shall simply write \( a(T) \) then obeys the equation:

\[
a(T) = a(T, 0,75) = [(T - T_0)/(T_1 - T_0)] \times \{1 - 0.2 \times [(T - T_1)/(T_1 - T_0)] \}. \tag{2}
\]

These equations (1) and (2) are valid whatever the H/D isotopic composition, under the condition that all \( \varepsilon''(T) \) in equation (1) stand for spectra having the same H/D composition.

The choice of \( T_0 = 0 °C \) and \( T_1 = 75 °C \) is well suited to describe experimental results. These temperatures and corresponding spectra \( \varepsilon''(T_0) \) and \( \varepsilon''(T_1) \) have, however, no special physical meaning. In view of obtaining a description of the structure and dynamics of H₂O(D₂O) molecules in water, we shall instead of these spectra take as a basis for the decomposition of spectra at temperature \( T \) (Eq. (1)) spectra \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) which are the spectra which would be observed at very low and very high temperatures respectively if phase transitions did not occur before such temperatures could be experimentally reached. These spectra \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \), which then have a physical meaning, are defined by their decomposition on the experimentally known spectra \( \varepsilon''(T_0) \) and \( \varepsilon''(T_1) \) (Eq. (1)), that is, by their \( a(T_L) = a(T, T_0, T_1) \) and \( a(T_H) = a(T, T_0, T_1) \). With such a basis, we have:

\[
\varepsilon''(T) = \varepsilon''(T_L) - \alpha(T) \times [\varepsilon''(T_L) - \varepsilon''(T_H)] \tag{3}
\]

with the concentration of « defect » molecules, that is the proportion of molecules contributing to \( \varepsilon''(T_H) \) given by:

\[
\alpha(T) = a(T, T_L, T_H) = [a(T) - a(T_L)]/[a(T_H) - a(T_L)]. \tag{4}
\]
Let us mention that $\alpha$ does not only depend on temperature $T$ but also depends on pressure, as pressure has been shown to have an effect similar to that of temperature [11]. As spectra described in article I were obtained at 1 atm. this $p$ dependence of $\alpha$ will not be considered in this article. Let us also note that the quadratic development of $a(T)$ in equation (2) is of no use to define $a(T_L)$ and $a(T_H)$, and consequently $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$, as this development is largely insufficient for extrapolations to very low and very high temperatures. The problem, which will be discussed in section 2.1 will then be to find criteria which will allow us to define these quantities. Once defined a spectroscopic analysis of various bands of $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ will be performed in subsequent subsections. In section 3a dynamical description for the arrangement of $\text{H}_2\text{O}(\text{D}_2\text{O})$ molecules in water, which incorporates novel features revealed by this analysis, will be proposed.

2. Analysis of $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$.

2.1 DETERMINATION. — The decomposition of the 2 $\nu_s$ band, as obtained in the NIR region, into several Gaussian bands has been proposed by Luck and Ditter [8] and constituted the first quantitative attempt to analyze this band and get a picture of water at the molecular level. The decomposition on a Gaussian basis is, however, at the origin of a lack of flexibility which makes it hard to use when one wishes to improve the precision. Some attempts to directly define the low temperature and high temperature components of Raman $\nu_s$ bands from experimental spectra have been later proposed [6, 12]. Such a procedure avoids decomposition on bands having a predetermined form. As described previously (Eqs. (1)-(4)) IR spectroscopy is particularly well adapted to it, and, in order to define $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ we shall be able to use spectroscopic criteria only, discarding thermodynamical ones which seem to be less precise. The first criterion which we shall use is that these spectra have no negative parts. It implies $a(T_L) > -1.1$ and $a(T_H) < 2.1$ for spectra of any isotopic composition. With the latter value the $\nu_s$ band (Fig. 1) of $\varepsilon''(T_H)$ has nevertheless quite an unfamiliar dip at $3150$ cm$^{-1}$ which makes it unreasonable. The absence of this dip requires $a(T_H) < 1.7$. We may furthermore reasonably postulate that the decomposition of any spectrum $\varepsilon''(T)$ on $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ is valid up to $100^\circ$C (we have checked it up to $80^\circ$C). It implies $a(T_H) > 1.25$ by extrapolating equation (2) up to $T = 100^\circ$C. In order to have a better determined value for this quantity, we may appeal to Raman spectra which exhibit strongly decreasing $\nu_L$ (libration) bands when the temperature is raised [5]. It is then reasonable to assume that the $\nu_L$ band in the Raman equivalent spectrum of $\varepsilon''(T_H)$ has a very weak intensity which is equivalent to assuming that the intensities of $\nu_L$ Raman bands mainly originate from « lattice water molecules », which appear in $\varepsilon''(T_L)$ in IR spectra. The concentration of these molecules is $1 - \alpha(T)$ (Eq. (3)). Taking the intensities of these Raman $\nu_L$ bands at $T_0 = 0^\circ$C and $T_1 = 75^\circ$C to be proportional to 0.225 and 0.076 [5] respectively, we have using equations (2) and (4):

$$[1 - \alpha(T_0)]/[1 - \alpha(T_1)] = 0.225/0.076 = a(T_H)/[a(T_H) - 1].$$

(5)

It gives $a(T_H) = 1.5$ which is the value which we shall adopt. Let us note that with this value (and with any higher value) $\varepsilon''(T_H)$ has a very weak negative part in the region 2350-2700 cm$^{-1}$ It may be due to some small temperature dependence of $\varepsilon''(T_H)$ which remained up to now undetected, and which introduces negative values originating from a derivative of this bandshape or, equivalently, to a (small) temperature dependence of the centers of « $\delta + \nu_L$ » (the bands which fall in this region) in $\varepsilon''(T_H)$.

In (I) we have indicated that $a(T_L)$ should be less than $-0.6$. For values of $a(T_L)$ less than $-1.1$ negative values localized on the high frequency side of the $\nu_s$ band appear which can
hardly be justified, even with the assumption that $\varepsilon''(T_L)$ has a hidden temperature dependence, because they are too localized to come from a derivative bandshape. We shall choose $a(T_L) = -0.8$ as the most representative. An argument supporting the choice of this value will be given in section 2.3. As may be seen in figure 2 variations of $a(T_L)$ modify the intensity of the $\nu_s$ band without changing its position and shape significantly.

In the following, spectra $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ will correspond, unless otherwise indicated, to these values $a(T_L) = -0.8$ and $a(T_H) = 1.5$. The latter value for $a(T_H)$ relies on quantitative arguments. That for $a(T_L)$ is only the most reasonable. It consequently does not preclude choosing, if justified, other values. As will be seen these will, nevertheless, not modify our conclusions in a significant manner. With these values we find, using equation (4), that the concentration $\alpha$ of H$_2$O defect molecules, represented by their spectra $\varepsilon''(T_H)$, at the temperature of fusion $T_F = 0 ~^\circC$ is:

$$\alpha(T_F) = 0.35.$$  

(6)

In the same way (Eq. (4)) the concentration $\alpha(100)$ of defect molecules at 100 °C is found to be equal to 0.89. The adoption of different values for $a(T_L)$ would lead to no significant changes for these values, especially for $\alpha(100)$, as long as they stay within the limits compatible with the absence of negative parts in $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$.

2.2 $\nu_s$ BANDS. — These correspond to stretching vibrations $\bar{O}$-H--\bar{O} which have been extensively studied in Raman and NIR spectroscopies. One novel point appears in IR spectra in

Fig. 1. — Spectra $\varepsilon''(T_H)$ of ordinary water calculated using equation (1) with $a(T_H) = a(T_H, T_0, T_1) = 1.25$ (thick line), $a(T_H) = 2.05$ (thin line), $T_0 = 0 ~^\circC$ and $T_1 = 75 ~^\circC$. Denominations of bands are indicated.
Fig. 2. — Spectra $\varepsilon''(T_L)$ of ordinary water calculated using equation (1) with $a(T_L) = a(T_0, T_1) = -0.6$ (thick line), $a(T_L) = -1.3$ (thin line), $T_0 = 0^\circ$C and $T_1 = 75^\circ$C.

the conventional region. It is illustrated in figure 3 where we have represented $\varepsilon''(T_L)$, for both ordinary and heavy water, in the region where $\nu_s$ bands are displaid. In the same figure spectra $\varepsilon''(T_H)$, multiplied by a factor of 2 and shifted towards lower frequencies of 100 cm$^{-1}$ for ordinary water and 80 cm$^{-1}$ for heavy water are also represented. It clearly appears that, for both types of water, $\nu_s$ bands have shapes in $\varepsilon''(T_L)$ which are similar to those in $\varepsilon''(T_H)$, except for some submaxima or subminima. In heavy water a marked dip in $\varepsilon''(T_L)$ at 2440 cm$^{-1}$ falls at twice the frequency of the maximum of the bending $\delta$ band (1220 cm$^{-1}$). This dip coincides with a maximum in the shifted spectrum $\varepsilon''(T_H)$, where the $2 \delta$ band appears then as a separate shoulder, marked by an arrow. This strongly suggests, as already proposed [13], that this dip in $\varepsilon''(T_L)$ is due to a Fermi resonance of $\nu_s$ with $2 \delta$ since, when falling around a maximum, Fermi resonances create a dip whereas they appear as shoulders when occurring on the slope of a band [14, 15], as in $\varepsilon''(T_H)$. This argument is strengthened by the fact that for HDO spectra this band clearly appears as a separate band at $\approx 2900$ cm$^{-1}$ (twice the wavenumber of the $\delta_{HDO}$ band), as noted earlier in IR spectra [3, 16] and Raman spectra [17, 18]. We conclude that in the absence of Fermi resonances $\nu_s$ bands of heavy water would have similar shapes in $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ (they would remain shifted by 80 cm$^{-1}$). This conclusion is strongly supported by the analysis of spectra due to isolated HDO molecules [19] where single peaked $\nu_s$ bands in $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ are really superposable. This clearer situation holds because features due to Fermi resonances appear as an easily identifiable separate band in this case.

The same features are certainly present in the spectra of ordinary water (Fig. 3) but are less apparent. It may be due to a relatively more important magnitude of intermolecular vibrational
energies concerning \( \nu_s \) vibrations situated on two different \( \text{H}_2\text{O} \) molecules which are H-bonded. It nevertheless remains that, with the exception of small variations in curvatures which may be attributed to Fermi resonances, the shape of \( \nu_s \) in \( \epsilon''(T_L) \) is not much different from that in \( \epsilon''(T_H) \), which is an important point in this article.

\subsection*{2.3 \( \delta \) bands. — These are bands which correspond to the bending vibration within an \( \text{H}_2\text{O} \) molecule (the \( \nu_2 \) band in the gas phase). They have been scarcely studied up to now, except in some Raman spectra where it has been noted that they become narrower when the temperature is raised [5]. This effect appears in a more quantitative manner in IR spectra (Figs. 4 and 5) where \( \epsilon''(T_L) \) and \( \epsilon''(T_H) \) are drawn in the region \( \tilde{\nu} \approx 2000 \text{ cm}^{-1} \). We may then see that the most striking feature is found in \( \epsilon''(T_H) \) where \( \delta \) bands have Lorentzian shapes of the form:

\[
\mathcal{L}_H(\tilde{\nu}) = P_H/\pi \mu_H \left\{ 1 + \left[ (\tilde{\nu} - \tilde{\nu}_H)/\mu_H \right]^2 \right\}
\]

with \( P_H = 40 \text{ cm}^{-1}, \quad \tilde{\nu}_H = 1.637 \text{ cm}^{-1} \) and \( \mu_H = 34 \text{ cm}^{-1} \) for ordinary water and \( P_H = 29 \text{ cm}^{-1}, \quad \tilde{\nu}_H = 1.206 \text{ cm}^{-1} \) and \( \mu_H = 21 \text{ cm}^{-1} \) for heavy water.

The \( \delta \) band in \( \epsilon''(T_L) \) keeps a marked peak at a somewhat higher wavenumber (1.650 cm\(^{-1}\) for ordinary water and 1.210 cm\(^{-1}\) for heavy water) but exhibits asymmetric features and is wider. This tendency is not unexpected as, when going to ice an even wider band appears with no apparent peak at all [20]. We may suspect this \( \delta \) band in water to be composed of two bands, as clearly appears in the case of HDO molecules [19]. This is on the limit of detection, however, in our present case of \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \) molecules.
Fig. 4. — \(\epsilon''(T_L)\) (thick line) and \(\epsilon''(T_H)\) (thin line) of ordinary water. The dotted spectrum represents \(\epsilon''(T_L)\) where Gaussian bands (Eq. (8)) simulating \(2\nu_L\) and \(\delta + \nu_L\) have been subtracted. The thin line spectrum marked by an arrow is the spectrum obtained after subtraction of the Lorentzian curve (Eq. (7)) from \(\epsilon''(T_H)\).  

This \(\delta\) band of \(\epsilon''(T_L)\) is superimposed on an overtone of \(\nu_L\) and also overlaps the \(\delta + \nu_L\) band in ordinary water. In order to obtain a rough approximate bandshape for \(\delta\) (Fig. 4) we subtract from the experimental band in \(\epsilon''(T_L)\) the two Gaussian bands of the form:

\[
G(\tilde{\nu}) = P \left\{ \exp - 1/2 \left[ (\tilde{\nu} - \bar{\nu})/\sigma \right]^2 \right\}/\sigma \sqrt{2\pi}
\]

with \(P = 66\,\text{cm}^{-1}\), \(\bar{\nu} = 1300\,\text{cm}^{-1}\) and \(\sigma = 260\,\text{cm}^{-1}\) for the overtone band and \(P = 22\,\text{cm}^{-1}\), \(\bar{\nu} = 2165\,\text{cm}^{-1}\) and \(\sigma = 170\,\text{cm}^{-1}\) for the \(\delta + \nu_L\) band. We do not assign any special meaning to these Gaussian bands. In our present state of knowledge, they simply represent the best simple empirical simulation for these overlapping bands. The resulting spectrum is drawn in dotted line in figure 4. Its integrated intensity \(P_L\), center of intensity \(\bar{\nu}_L\) and width \(\sigma_L\) (\(\bar{\nu}_L\) and \(\sigma_L\) are respectively the normalized first and second centered moments of the resulting \(\delta\) band, while \(P_L\) is its moment of order zero) may then be measured and these quantities represent the rough characterization of the \(\delta\) bandshape in \(\epsilon''(T_L)\) which is allowed by this empirical procedure. They are then found to be equal to \(P_L = 42\,\text{cm}^{-1}\), \(\bar{\nu}_L = 1625\,\text{cm}^{-1}\), \(\sigma_L = 98\,\text{cm}^{-1}\). These estimated values of first moments of the \(\delta\) band in \(\epsilon''(T_L)\) will be useful in section 3.

The same procedure is applied to the \(\delta\) band of \(\epsilon''(T_L)\) in heavy water (Fig. 5). The \(\nu_L\) overtone is then better approximated by an empirical band of the form:

\[
C(\tilde{\nu}) = P/2 \sigma \cosh \left\{ \pi/2 [(\tilde{\nu} - \bar{\nu})/\sigma] \right\}
\]

with \(P = 22\,\text{cm}^{-1}\), \(\bar{\nu} = 2165\,\text{cm}^{-1}\) and \(\sigma = 170\,\text{cm}^{-1}\).
Fig. 5. — \( \varepsilon''(T_L) \) (thick line) and \( \varepsilon''(T_H) \) (thin line) of heavy water. The dotted spectrum represents \( \varepsilon''(T_L) \) where the band simulating \( 2 \nu_L \) (Eq. (9)) has been subtracted. The thin line marked by an arrow is the spectrum obtained after subtraction of the Lorentzian curve (Eq. (7)) from \( \varepsilon''(T_H) \).

which has a character somewhat intermediate between a Gaussian and a Lorentzian [21], while the \( \langle \delta + \nu_L \rangle \) band is not subtracted because of its smaller overlap with \( \delta \). The first moments of the remaining \( \delta \) band (dotted spectrum in Fig. 5), from which a constant baseline has been subtracted are then \( P_L = 33 \text{ cm}^{-1}, \quad \tilde{\nu}_L = 1190 \text{ cm}^{-1}, \quad \sigma_L = 65 \text{ cm}^{-1} \).

We see that \( \delta \) bands in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) have comparable intensities \( P_L \) and \( P_H \). As \( P_L \) slightly varies when a different \( a(T_L) \) is chosen for the definition of \( \varepsilon''(T_L) \), this has been a criterion for taking \( a(T_L) \approx 0.8 \). The reason is that the intensities of these \( \delta \) bands are hardly affected by the environment [3, 19]. It is then logical to think that they have the same intensities in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \).

The centers of intensities \( \tilde{\nu}_L \) and \( \tilde{\nu}_H \) of \( \delta \) bands in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) differ by some 10 cm\(^{-1} \) with \( \tilde{\nu}_L \) being smaller than \( \tilde{\nu}_H \). This is somewhat surprising as \( \delta \) bands are found at higher wavenumbers when the strength of H-bonds increases [22]. As H-bonds in \( \varepsilon''(T_L) \) are certainly not weaker than those in \( \varepsilon''(T_H) \), this effect is attributed to a residual component of the \( \nu_L \) overtone which is visible on the low frequency side of the dotted spectra in figures 4 and 5. With this rough procedure it looks useless to go deeper into this analysis but, as a conclusion of this subsection we may retain that, within an accuracy of 10 cm\(^{-1} \), centers of intensity of \( \delta \) bands in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) are the same.

The width of \( \delta \) bands in \( \varepsilon''(T_L) \) is most probably the manifestation of a modulation of the force constant governing the \( \delta \) vibrations by some low frequency intermolecular modes of the same symmetry as \( \delta \) in an H\(_2\)O (D\(_2\)O) molecule. Good candidates for such modes are the O-O-O bending modes which fall in the 50 cm\(^{-1} \) region [17, 23]. Such a modulation leaves the integrated intensity of the band unaltered [24].
2.4 \( \delta + \nu_L \) BANDS. — These are bands whose maxima in \( \varepsilon''(T_L) \) fall around 2 150 cm\(^{-1}\) for ordinary water and 1 610 cm\(^{-1}\) for heavy water. There is some ambiguity when assigning them as \( \delta + \nu_L \) bands in IR or Raman spectra [13, 25], and it is the aim of this subsection to examine it. The possibility that they are a \( 3 \times \nu_L \) overtone band has been discussed in the case of ice [20]. An argument against this attribution is that these bands have similar shapes, and particularly comparable widths, in \( \varepsilon''(T_L) \) and in the spectrum of ice. The main but not significant differences are found in a somewhat larger intensity in ice accompanied by a shift of some 50 cm\(^{-1}\) towards higher wavenumbers. It does not reflect the situation of \( \nu_L \) bands whose maxima are much more separated: they are found at 650-700 cm\(^{-1}\) in \( \varepsilon''(T_L) \) and at 850-900 cm\(^{-1}\) in the case of ice, which implies that the maxima of \( 3 \times \nu_L \) differ by a quantity much greater than 50 cm\(^{-1}\) between \( \varepsilon''(T_L) \) and the spectrum of ice.

The attribution to \( \delta + \nu_L \) is not, however, so straightforward. For symmetry reasons it cannot be the consequence of a mechanical anharmonicity such as a modulation of the force constant of the \( \delta \) mode by terms linear in the coordinates for \( \nu_L \), as is usual for \( \nu_L \) bands of H-bonded systems [15, 24]. The reason is that in a tetrahedral symmetry, such as experienced by a particular H\(_2\)O molecule in ice where such a band exists, none of the three \( \nu_L \) librations of this molecule has a symmetry representation which would make the corresponding potential completely symmetrical. A complementary argument is that in this case this band would get its intensity from the \( \delta \) band, and would correspond to a 00 \( \rightarrow \) 11 transition, while the \( \delta \) band itself would correspond to a 00 \( \rightarrow \) 10 transition (the set of bands \( \delta \) and \( \delta + \nu_L \) is in this case most comparable to electronic bands with Franck-Condon structures [24, 26]). The center of intensity of this \( \delta \) band is then that of all 00 \( \rightarrow \) 1 \( n \) transitions and would consequently fall at 1 870 cm\(^{-1}\) for ordinary water. This is not a common value [22], especially when compared with that in the gas phase at 1 595 cm\(^{-1}\) [27]. Furthermore, it would then be hard to understand how \( \delta \) bands (00 \( \rightarrow \) 10 transition) fall at the same position in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) (Sect. 2.3) whereas the \( \delta + \nu_L \) band (00 \( \rightarrow \) 11 transition) is shifted by some 100 cm\(^{-1}\) between these two spectra and is appreciably less intense in \( \varepsilon''(T_H) \) than in \( \varepsilon''(T_L) \) (Fig. 5).

Another possibility would be that this \( \delta + \nu_L \) band is a consequence of «electrical anharmonicity» (presence of non-linear terms in vibrational coordinates in the dipolar moment). The presence of qualitatively similar bands in Raman spectra, however, makes this assumption unlikely, since then polarizability derivatives, instead of dipolar moment derivatives, trigger transitions.

The novel point conveyed by IR spectra is that the ratio of the intensities of these \( \delta + \nu_L \) bands in \( \varepsilon''(T_L) \) and \( \varepsilon''(T_H) \) is of the same order of magnitude as that of their \( \nu_L \) bands (Fig. 3). It strongly suggests that the \( \delta + \nu_L \) band is a consequence of a mechanical anharmonicity appearing in the form of a cubic term (the lowest order anharmonic term) in the potential coupling the coordinates of the \( \delta \), \( \nu_L \) and \( \nu_L \) modes. Such terms are of the same nature as those responsible for Fermi resonances [24, 26]. It implies that this \( \delta + \nu_L \) band borrows its intensity from \( \nu_L \) but that its position is mainly defined by the position of \( \delta + \nu_L \).

3. Interpretation.

IR spectra are compatible with the now standard picture of water which emerged from NIR [8, 9] and Raman spectra [5, 12, 17, 28-30] and describes water as a mixture of «basic water molecules», that is H\(_2\)O molecules which are at the origin of \( \varepsilon''(T_L) \), and «defect» molecules at the origin of \( \varepsilon''(T_H) \). This description offers the advantage of retaining the possibility to explain why distances typical of a tetrahedral ordering of O atoms (as found in
ice) are kept in water, as shown by X-ray and neutron diffraction techniques [31-35]. These defect molecules are here to ensure that water is a liquid, as basic water molecules are thought to aggregate and form patches of rather rigidly bonded molecules, as deduced from these diffraction experiments and from Raman spectra [36] in the supercooled region, while defect molecules are thought to be less bonded. The usual description of the nature of these defect molecules, as deduced from Raman and NIR spectroscopy, however, displays some incompatibilities with novel features revealed by IR spectrometry, particularly those concerning $\nu_5$ and $\delta$ bands of $\varepsilon''(T_H)$. I shall first discuss these incompatibilities, before proposing a new picture for these defect molecules which is compatible with bands in $\varepsilon''(T_H)$.

Defect molecules have been described as H$_2$O(D$_2$O) molecules keeping one strong H-bond (of the same nature as H-bonds linking basic water molecules) and one weaker H-bond which may be a « bifurcated » H-bond [37, 38] or even a broken H-bond [8, 9]. The difficulty with such descriptions is that there is not one type of defects, but there are two which are complementary and in equal number, as they are created in pairs, a point already noted [38]. In order to illustrate this point let us think of a defect molecule consisting of one « strong » H-bond and one broken H-bond. Its complementary defect is an H$_2$O molecule establishing two « strong » H-bonds with its O-H groups but accepting only one H-bond on its two lone-pairs. These complementary defects cannot contribute to $\varepsilon''(T_L)$, as this would imply $\alpha(T)$ (Eq. (3)) to be less than 0.5. This is an impossible condition to satisfy since at $T_1 = 75^\circ$C (or $a(T_1) = 1$) it implies $a(T_H) + a(T_L) > 2$, using equation (4). As seen in section 2.1 this cannot be obtained with $a(T_L)$ and $a(T_H)$ satisfying even the less severe conditions ($-1.1 < a(T_L) < 0.6$ and $1.25 < a(T_H) < 2.1$) which are necessary for $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ to display no negative parts.

These complementary defects consequently should contribute to $\varepsilon''(T_H)$. The presence of two kinds of defects, however, is in contradiction with what is seen in IR spectra as the $\delta$ band of $\varepsilon''(T_H)$ is a narrow band with no structure. The assumption that both kinds of defects give the same narrow $\delta$ band at same wavenumber is untenable, as defects consisting of one strong and one weakened H-bond give asymmetrical $\delta$ bands [39] while complementary defects which have two equivalent strong H-bonds give symmetrical $\delta$ bands at higher wavenumbers [22]. Furthermore we would then expect $\delta$ bands in $\varepsilon''(T_H)$ to be at lower wavenumbers than $\delta$ bands in $\varepsilon''(T_L)$ which is not what has been found in section 2.3. Finally a rapid interchange of the two kinds of defects, which might explain the Lorentzian shape of $\delta$ in $\varepsilon''(T_H)$ can be rejected on the basis that it strongly depends on the concentration $\alpha$ of defects, which is in contradiction with $\varepsilon''(T_H)$ (and also $\varepsilon''(T_L)$) being temperature independent.

Similar difficulties arise with $\nu_5$ bands for which it is hard to understand how bands due to two kinds of defect molecules, as in $\varepsilon''(T_H)$, have shapes similar (Sect. 2.2) to bands originating from one kind of molecules only, as in $\varepsilon''(T_L)$.

Another difficulty of such a model is that it predicts $\nu_L$ librational bands to appear at significantly lower wavenumbers in $\varepsilon''(T_H)$ than in $\varepsilon''(T_L)$. This does not seem to be what happens as this difference is of 100 cm$^{-1}$ only (Fig. 4), which is also visible as a shift of this order of magnitude between maxima of « $\delta + \nu_L$ » bands between $\varepsilon''(T_L)$ and $\varepsilon''(T_H)$ (Fig. 3) and is described in the literature as a small shift only of these $\nu_L$ bands with temperature [25, 40].

3.1 DYNAMICS OF DEFECT MOLECULES. — From this discussion it may be concluded that only one type of defect molecules exists and appears in $\varepsilon''(T_H)$. These defect molecules cannot be much different from basic water molecules because their $\nu_5$ bands keep many features of the $\nu_5$ bands of the basic water molecules. Furthermore the Lorentzian shape of their $\delta$ bands implies that some of their vibrations, in some way coupled to $\delta$, has a diffusional character. The most straightforward way to fulfill these requirements is to suppose that these defect H$_2$O
molecules are molecules whose energy levels for their rotations around their axis $z$ ($z$ is the bisector of the two O-H directions in the plane of the molecule) are above the maximum of the potential energy governing these rotations and consequently display a diffusional character for their rotations around this $z$ axis, while keeping a vibrational character for their rotations around their two other axes (they still perform librations around $x$ and $y$). Basic water molecules have, on the contrary, rotational energies (around $z$) below this maximum and consequently perform librations around their three axes, which is certainly a particularity of water. This description adopts the same physical basic picture as that proposed by Robinson and coworkers [41, 42]. It differs somewhat from it with the identification of the rotation around $z$ as being responsible for the apparition of defect molecules, whereas Robinson and coworkers identify it as that of lower frequency with no particular attribution.

This particular choice of the $z$ axis comes from the fact that for any H$_2$O molecule a rotation of $\pi$ around this axis leaves the rotational potential unchanged, while it requires a rotation of $2\pi$ around the other two axes. Furthermore when the H$_2$O molecule considered experiences, as in ice, an environment of tetrahedral symmetry, the force constants for these three rotations are the same around equilibrium (zero rotation), because of the linearity of H-bonds. It implies that the curvatures of the three potentials are the same around their equilibrium positions in that case. From these two properties we deduce that, in a tetrahedral environment, the potential maximum for a rotation of $\pi/2$ around $z$ is much lower than the potential maxima for rotations of $\pi$ around the other two axes. When the environment of the molecule considered no longer keeps a tetrahedral symmetry, these maxima may be strongly modified, but the periodicities of the three rotations do not change, and for the great majority of molecules, if not all, the maximum of the potential around $z$ remains much lower than the maxima of the potentials around the other two axes. We may then have molecules with their rotational energies around $z$ above the maximum of the potential governing this rotation, while the rotations around the other two axes remain under the maxima of the corresponding potentials, thus retaining a vibrational character for these two rotations.

We may then easily understand the apparent discrepancy that $\nu_L$ bands exhibit between IR and Raman spectra [43]: the IR bands change only little when the temperature is raised [25, 40], while the Raman bands have their intensities which dramatically decrease [5], keeping their shapes and positions unchanged. The behavior of the IR $\nu_L$ band may be understood when one realizes that in a tetrahedral symmetry the dipole moment has no linear terms in coordinates describing rotations around $z$, because of the parity. These bands are consequently not very sensitive to rotations around $z$ even when the environment no longer keeps this tetrahedral symmetry (in the average it has this symmetry). They consequently do not suffer an abrupt change when such rotations are altered, as when passing from basic water molecules to defect molecules. They are consequently not very sensitive to the concentration of defect molecules, and display small changes only when the temperature is varied. This is not true for Raman $\nu_L$ bands where polarizability has terms linear in coordinates describing rotations around $z$ in a tetrahedral symmetry and are consequently much more sensitive to the concentration of defect molecules.

3.2 DISCUSSION. — From the preceding section it appears that basic water molecules are not so much characterized by the fact that they are four-bonded but by the fact that they experience rotations of a vibrational character, which may also in principle be achieved by molecules held by three bonds instead of four. These molecules certainly have a small contribution in the fluidity of water. They have some similarities with H$_2$O molecules in ice as $e^\circ(T_L)$ displays some similarities with the IR spectrum of ice I [20, 44]. The main difference is that they certainly form much less cyclic structures of H$_2$O molecules, and in that sense they may be closer to molecules found in amorphous solid water [45], where H-bonds are thought to be
more bent than in ice. They may aggregate in clusters of finite size [31-36]. Defect molecules are those molecules which display rotations around their \( z \) axes of a diffusional character. They consequently have only part of the properties of molecules of a normal liquid, which perform diffusional rotations around their three axes.

The description presented here is strictly valid in the range of temperatures investigated, that is between \(-5 \) °C and \( 80 \) °C. It is likely to remain valid in the deep supercooled region where the significant mechanism expected in this region is the increase in structuration of basic water molecules aggregates. At temperatures higher than \( 80 \) °C we expect the validity of this description to remain justified on a shorter range of temperatures, because the concentration of broken H-bonds, which may display cooperative properties, certainly becomes more and more appreciable. Such broken H-bonds are certainly present in the range \(-5 \) °C, \( 80 \) °C, in \( \varepsilon"(T_H) \) and also in \( \varepsilon"(T_L) \), but not in a quantity sufficient to appear as the major feature. They have been detected in NIR spectra [10, 46, 47] which is a region where they can be detected with a much greater sensitivity than in the conventional IR region, where the intensities related to \( \nu_s \) vibrations may be smaller by one order of magnitude for broken H-bonds as compared to strong H-bonds.

From the magnitude of the width \( \mu_H \) of the Lorentzian curve describing the \( \delta \) band in \( \varepsilon"(T_H) \) (Sect. 2.3) we may estimate the correlation time \( \tau_c \), or average time during which the coherence of the \( \delta \) vibrations in defect molecules is kept. Let \( \sigma_H \) be the width (second centered moment) of this \( \delta \) band if we could freeze all rotations and intermolecular vibrations of molecules. It is likely that some of these intermolecular displacements are responsible for this width (through a modulation of the force constant of \( \delta \), for instance), as it cannot be due to resonance vibrational energy transfers between \( \delta \) vibrations situated on neighbour molecules. When varying the environment of \( \text{H}_2\text{O} \) molecules by isotopic dilution, such \( \delta \) bands appear in the form of derivative-like bands [3, 19] which are characteristic of bands which modify their centers, but not their intensities and widths. In contrast, the effect of resonance vibrational energy transfers would be to alter the widths of these bands upon isotopic dilution, which is not the effect observed. We may then write, using Kubo's theory of lineshapes [48]:

\[
\mu_H = 2 \pi \tau_c \sigma_H^2
\]  

(10)

with \( 2 \pi \tau_c \sigma_H \ll 1 \) (rapid modulation condition — the factor \( 2 \pi \) comes from the fact that \( \mu_H \) and \( \sigma_H \) are expressed in \( \tilde{\nu} \) instead of \( \omega \)). We deduce \( \sigma_H \gg \mu_H \). As it is reasonable to expect \( \sigma_L \ll \sigma_H \), where \( \sigma_L \) is the width of the \( \delta \) band in \( \varepsilon"(T_L) \) which we have seen to be of the order of \( 3 \nu_H \) (Sect. 2.3) for both ordinary and heavy water, we deduce that \( \sigma_H \) has a value falling between \( \mu_H \) and \( 3 \mu_H \). From these extreme values we deduce, using equation (10) with \( \mu_H \approx 35 \text{ cm}^{-1} \).

\[
10^{-13}/2 \pi < \tau_c \ll 10^{-12}/2 \pi \text{ (in seconds)}.
\]  

(11)

This \( T_2 \)-type correlation time is certainly too short to be measured by NMR experiments [2]. In principle it falls into the possibilities of Raman spectroscopy, but has apparently not been measured using this technique. It corresponds to \( \delta \) making a small number of oscillations only before loosing phase coherence. It is likely to be in someway connected to the diffusive nature of rotations around \( z \). The precise mechanism by which it is connected, however, remains unknown. Finally, let us note that a \( T_1 \)-type relaxation mechanism, corresponding to a finite lifetime \( 1/(2 \pi \mu_H) \) for the first excited state in \( \delta \) would give the same order of magnitude \( (\approx 10^{-13} \text{ s}) \) for this lifetime. We think it less likely to occur as it would imply a much smaller \( \sigma_H (\ll \mu_H) \) to obtain a Lorentzian shape, which would be hard to correlate with a \( \tilde{\nu}_L \) (the center of the \( \delta \) band) unchanged when passing from \( \varepsilon"(T_L) \) to \( \varepsilon"(T_H) \).
4. Conclusion.

The analysis of IR spectra, obtained using ATR techniques and which display a good signal-to-noise ratio, revealed novel features: the $\nu_s$ bands display similar shapes between $\epsilon''(T_L)$ and $\epsilon''(T_H)$; the $\delta$ band of $\epsilon''(T_H)$ is narrow with no apparent structure. It has a Lorentzian shape centered at the same wavenumber as the unsymmetrical $\delta$ band of $\epsilon''(T_L)$. The interpretation of these features allowed us to propose a description for the dynamics of H$_2$O(D$_2$O or HDO) molecules in water which starts from the same physical mechanism as that proposed by Robinson and coworkers [41, 42] but differs somewhat from it in its development. It classifies molecules into two types which are called basic water molecules and defect molecules. This does not differ from previous spectroscopic studies whose main conclusions are consequently adopted. We are, however, able to be more precise for what concerns the nature and dynamics of both kinds of molecules. Basic water molecules are those molecules which perform rotations around their three axes having a vibrational character (librations), while rotations around the axis of symmetry $z$ of defect molecules have a diffusional liquid-like character. This special role attributed to the $z$ axis does not appear in Robinson and coworkers' model. These properties also differ from those proposed earlier, especially for defect molecules which were thought of as being molecules having broken or strongly weakened H-bonds. In the range of temperatures considered ($-5^\circ C < T < 80^\circ C$) broken or strongly weakened H-bonds do not seem to play any special role. This might, however, not be the case at higher temperatures or pressures.

Let us note that, although our central arguments concern intramolecular vibrational bands which we have obtained using ATR techniques, we have invoked results concerning intermonomer bands such as libration bands. As our spectra were limited to $\tilde{\nu} \geq 650 \text{ cm}^{-1}$ we saw only part of these bands and have consequently been obliged to appeal to older spectra in the FIR region. Such spectra are scarce and certainly amenable to better quality using modern equipment which has made great progress. It will in particular be very useful to verify that the decomposition of intermonomer vibrations follow the same decomposition as that of intramonomer bands (Eqs. (1) and (2)), which is not a priori true, as parts of $\epsilon''(T_L)$ and $\epsilon''(T_H)$ in the FIR region might display temperature variations. It will be the aim of subsequent experiments to look at this point.

This article has been devoted to the analysis of the variations of IR spectra of water with temperature. In forthcoming articles [19, 49] I shall analyze their variations with deuterium concentration. This will allow the determination of various mechanical parameters, such as intra and intermolecular coupling energies or Fermi resonance energies of various vibrations. Let us finally note that the interest of obtaining precise IR spectra of water extends beyond that of conveying information on the structure and dynamics of H$_2$O molecules in pure water, as it may allow to apply IR spectroscopy to the vast domain of aqueous solutions, particularly the domain of molecular biology, where IR spectroscopy has scarcely been used outside narrow spectral windows where water does not absorb.

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