THE JOURNAL OF CHEMICAL PHYSICS **133**, 164509 (2010)

Isotope effects in liquid water by infrared spectroscopy. IV. No free OH groups in liquid water

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(Received 22 June 2010; accepted 5 October 2010; published online 25 October 2010)

The presence of free OH (OH not H-bonded) in bulk water is a key element for the determination of its molecular structure. The OH covalent bond infrared (IR) absorption is highly sensitive to the molecular environment. For this reason, IR spectroscopy is used for the determination of free OH. A workable definition of this is obtained with methanol (MeOH) in hexane where minute quantities of free OH are present. These absorb at 3654 cm^{-1} (a 27 cm^{-1} redshift from the gas position) with a full width at half height of 35 cm^{-1}. The IR spectrum of water between room temperature and 95 °C does not display such a band near 3650 cm^{-1}. This indicates that we do not see, in the IR spectra, the "free" OH group. From this we conclude that it is not present in liquid water at least down to the 1000 ppm level which is the limit of detectivity of our spectrometer. Other spectroscopic considerations of methanol and water in acetonitrile solutions indicate that weak H-bonds are also not present in liquid water. © *2010 American Institute of Physics*.
[doi:10.1063/1.3505321]

I. INTRODUCTION

The structure of liquid water made the top list of the 125 unsolved scientific questions listed for the Science 125th anniversary issue in 2005.[1] More recently, Nature stated in one of its editorials that "*No one really understands water*."[2] The search is not over and the struggle to determine the molecular nature of this vital substance is ongoing. The hydrogen bond network is an intrinsic part of liquid water that creates some molecular ordering. Proton hopping is another feature as important as H-bonds.[3] Often neglected, this phenomenon is easily observed in infrared (IR) when D_2O is mixed with H_2O: H and D permute at a fast rate in the femtosecond time scale forming HDO. The signature of this is unmistakably characterized by a deformation band in the IR.[4] With proton hopping there is, by necessity, bond breaking: O—H valence bonds and H-bonds. These have a life time of 0.1–10 ps.[5] However, these bonds are broken only fleetingly leaving a virtual null balance of "free" OH (not giving an H-bond) in liquid water.[6] This unceasing proton exchange is responsible for some liquid water characteristics and to some OH stretching band broadening observed in IR.

A review of the structure of liquid bulk water (thereafter liquid water) from that proposed by Bernal and Fowler[7] in 1933–1967 was made by Cabana and Jolicoeur.[8] It is said that the use of different spectroscopic techniques produced opposite conclusions about the presence of free OH in liquid water. Each oxygen atom of the molecules is the site of two H-bond acceptors and the two hydrogen atoms can be two donors of H-bonds. If one of these does not make an H-bond it leaves the OH group free. In 1986, Giguère *et al.* with Raman spectra arrived at the conclusion that there are very little of them.[9] In our 2002 IR study of some 60 odd solutions of H_2O/D_2O mixtures we arrived at the same conclusion.[4] However, in 2005 another group arrived at the conclusion that at least 8% of the water molecules have free OH groups at 25 °C.[10] Maréchal reviewing the situation in 2008 indicated that very few of them are present.[11]

In the theoretical realm, molecular dynamics simulation (MDS) is a powerful analytical tool that could solve the problem. Some MDS studies determined that, for liquid water, the mean number of H-bonds per molecule varies between 3.2 and 4.[12,13] Recent MDS indicated that the number of four H-bonded water molecules varies between 36% and 67%.[14] These values which depend on H-bonding definitions leave a number of nonfully bonded water molecules. Others determined that hydrogen bonding is partly covalent.[15–18] Furthermore, MDS has not incorporated in their models the well established phenomenon of proton hopping. Due to this, the three atoms of H_2O do not belong to the same molecule for a long period of time. Because of this the water molecule cannot be considered rigid. This is a major drawback that limits MDS ability to adequately model the real liquid water situation. The consequence of this is that MDS has not yet been able to evaluate satisfactorily the presence of free OH groups in liquid water with the consequence that the contradictory experimental results were not solved. This may come from an imprecise definition of free OH.

Understanding the structure of liquid water is certainly not simple.[2,19] However, the presence of free OH in liquid water is a fundamental question that has to be addressed. If present, many organizations could contain them: monomers, dimers, trimers, oligomers, cyclic structures, etc. All these

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0021-9606/2010/133(16)/164509/8/$30.00

models will have free OH groups. An adequate definition of free OH that would make consensus could solve the problem. Because of the weak nature of H-bonds to which we add proton hopping, free OH groups are sometimes considered to be present in non-negligible amounts in liquid water. Moreover, the concentration of these is believed to increase with temperature.[10] Nevertheless, the presence of these has not been established unambiguously at room temperature and even less at higher temperatures.

Intermolecular coupling significantly modifies local vibrational mode frequencies.[13] Since IR spectroscopy is very sensitive to the molecular environment it is an excellent probe of the water local structure.[4] The numerous studies of OH containing molecules (including H_2O and D_2O) in hydrophilic and hydrophobic environments that we have made almost never showed free OH.[4,20–23] One rare exception showed the presence of minute amounts of free OH.[24] This is unraveled later on.

Liquid water is made of OH_4 entities in a tetrahedral arrangement.[4] Two hydrogen atoms are covalently bonded and two hydrogen atoms are H-bonded to the oxygen atom. However, the H atoms are in permutation at a fast rate with surrounding molecules. This will move the molecules in ways as to bring indetermination in the organization of the liquid structure. Therefore, the object of this paper is to: first, define free OH for liquid water by obtaining its IR spectral signature (position and band width); second, search in the IR spectrum of liquid water at all viable temperatures for the presence of this band; third, determine its abundance. Similarly, many water models contain “weak” H-bonds. These have to be defined and looked for. For this we use model systems consisting of H_2O and MeOH in acetonitrile because these systems absorb in the region where bands have been assigned to weak H-bonded water. Therefore, the fourth objective is to determine their presence and abundance. The global objective of this paper is not to determine the structure of water but to add clear-cut pieces that will aid in its determination. These are the determination of free OH groups and weak H-bonds in liquid water.

II. EXPERIMENTAL

A. Chemical and solutions

Heavy water (Sigma-Aldrich Canada Ltd, Oakville, ON, Canada, purity >99.9 atom% D), methanol (Fisher Scientific, high performance liquid chromatography grade purity >99.9% w/w, water content <0.1%), methanol-OD (Aldrich Chemical Co., purity >99.8 atom% OD), hexane (Fisher Scientific Canada, Montreal, QC, Canada, Spectranalyzed, purity >99.9% w/w, water content <0.02%), and acetonitrile (Fisher Scientific Canada, Optima grade, purity >99.9%, water content <0.01%). De-ionized and freshly distilled water was used for light water. Light and heavy water were used to prepare HDO mixtures.

B. IR measurements

The IR measurements were obtained using a model 510P Nicolet FT-IR spectrometer with a deuterium triglycine sulfate detector. The spectral range was $5500-650\ \mathrm{cm}^{-1}$. Two KBr windows isolated the measurement chamber from the outside. The samples were contained in a Circle cell (SpectraTech, Inc.) equipped with a ZnSe crystal rod (8 cm long) in an attenuated total reflection (ATR) configuration. The beam is incident at an angle of 45° with the rod axis and makes 11 internal reflections. Depending on the cell used, 6.6 or 3.3 reflections were in contact with the sample. These were determined with water.[25] The spectra were taken under a nitrogen flow to ensure low CO_2 and water vapor in the spectrometer. Each spectrum represents an accumulation of 500 scans at $2\ \mathrm{cm}^{-1}$ resolution ($0.965\ \mathrm{cm}^{-1}$ sampling interval). The measurements were made at $27.1 \pm 0.3\ ^\circ\mathrm{C}$. The cell was carefully washed and dried before each measurement series. Model 510P being a single-beam spectrometer, a background reference was taken with the empty cell before measuring each sample.

The IR measurements consisted in obtaining the ATR background and sample interferograms. These are transformed into spectral intensities R_0 and R, respectively. The ratio of R/R_0 is the intensity I of the spectrum. Thereafter, the 5029 data points $\{I(\tilde{\nu})$ versus $\tilde{\nu}(\mathrm{in\ cm}^{-1})\}$ of each spectrum were transferred to a spreadsheet program for numerical analysis. The intensities I were transformed into absorbance units, $\log(1/I)$ (abbreviated in some cases as a.u.). Sometimes a small baseline shift (less than 0.004 a.u.) was necessary to obtain a null mean absorbance in the $5500-5400\ \mathrm{cm}^{-1}$ region where the samples do not absorb.

III. RESULTS

A. Situation of liquid water

Figure 1(a) shows a liquid water spectrum ($4000-700\ \mathrm{cm}^{-1}$) obtained at room temperature by ATR.[4,22] The broad intense absorption band between 3700 and $2700\ \mathrm{cm}^{-1}$ is related to the OH stretch vibrations of water. Figure 1(b) shows an expanded view of the OH stretch region of water from room temperature to $95\ ^\circ\mathrm{C}$. The vertical lines are the gas phase position of water asymmetric (ν_3) and symmetric (ν_1) stretch vibrations which is the likely region of free OH in the liquid. The pure liquid spectra show a broad band spanning from 3740 to $3480\ \mathrm{cm}^{-1}$ that increases in intensity with temperature but remains weak in relation to the massive H-bonded OH band downstream near $3400\ \mathrm{cm}^{-1}$ [Fig. 1(a)]. The broad weak band ($\sim 3600\ \mathrm{cm}^{-1}$) is often assigned to free OH, weak H-bonds or molecules with a low degree of connectivity.[10] Is this the band of free OH bonds or weak H-bonds of liquid water?

To settle the problem we need a good definition of free OH absorption. Water with its two OH groups which is soluble in only a few organic solvents is not the best candidate. Methanol ($H_3C—O—H$) with its CH_3 group and its sole OH group is a better candidate for the following reasons. The CH_3 group that has replaced one water hydrogen atom makes it far more soluble in organic solvents than water which gives many situations where free OH could occur. The OH group with its labile H makes only one H-bond although the oxygen atom with its two free electron pairs that can receive two H-bonds makes it a strong H-bond acceptor. The covalent OH group produces only one IR OH

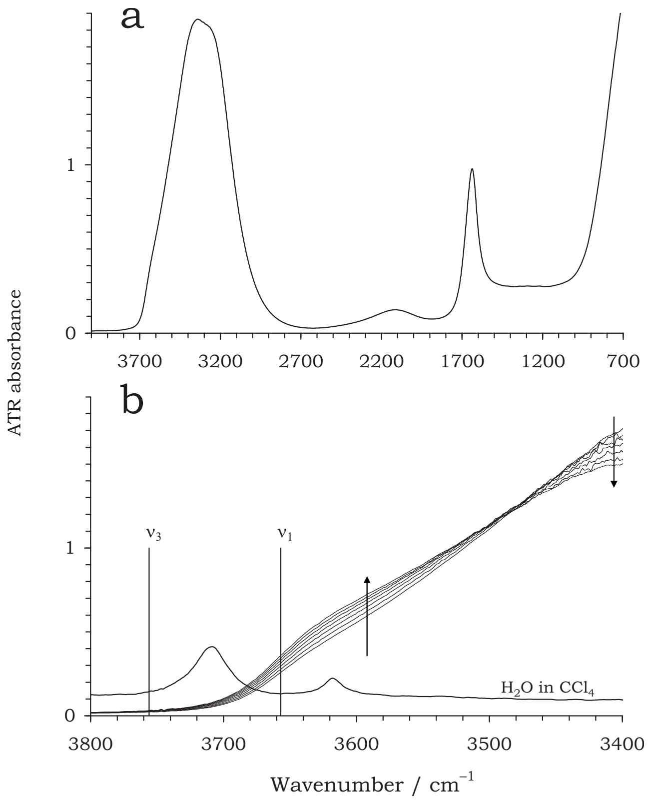

FIG. 1. IR-ATR spectra of liquid water. (a) 4000–700 cm^{-1} region at 27 °C. (b) Expanded region (3800–3400 cm^{-1}) at seven temperatures from 29 to 95 °C (arrows indicate the temperature increase). At the bottom is the spectrum of H_2O diluted in CCl_4 (in arbitrary units). The water gas positions are indicated by vertical lines.

stretch band whereas water has two. This simplifies the interpretation of IR measurements of the OH stretch.

B. Spectroscopic definition of free OH groups

1. Free OH band from methanol in n-hexane

Methanol monomers are observed in CCl_4 solutions.[26,27] Because of its tetrahedral symmetry (T_d), the net dipole of CCl_4 is zero. However, the C—Cl bond has a large dipole and large polarizability that perturb locally neighboring molecules. Hexane has also a net dipole near zero. However, its aliphatic groups are much weaker dipoles than the C—Cl bonds. Because of this, hexane is less aggressive toward the solute than CCl_4. We recently determined the behavior of methanol in hexane.[23,24]

Figure 2(a) shows the experimental IR-ATR spectra of methanol in n-hexane with the hexane spectrum subtracted at mole fractions from 0.004 to 0.016. The CH groups are situated near 2900 cm^{-1}; the massive absorption band near 3300 cm^{-1} is the absorption of the H-bonded OH groups.

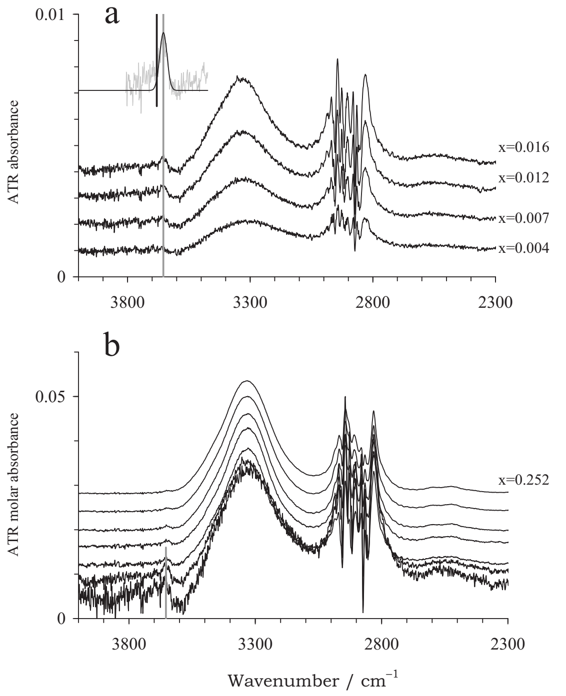

FIG. 2. IR-ATR spectra of methanol in n-hexane with the solvent spectrum subtracted. (a) Original spectra at, from top to bottom, 0.016, 0.012, 0.007, and 0.004 mol fraction. (b) Methanol molar spectra from 0.252 to 0.007 mol fraction. For clarity, the spectra are separated. Inset (top) experimental free OH spectrum (gray line from MeOH/Hex) with a Gaussian fitting (black line); thick vertical black line is the gas phase position (3681 cm^{-1}).

As the methanol concentration is increased this band increases without much modification.[24] The molar spectra [Fig. 2(b)] indicate that almost all the MeOH OH groups are H-bonded. A small narrow band is observed at 3654 cm^{-1}. It increases slightly with concentration [Fig. 2(a)]. Nonetheless, its relative intensity decreases [Fig. 2(b)] and at $x=0.252$ (2.335M) its intensity is almost null (<20 mM). This band position is 27 cm^{-1} redshifted from that of the gas (Table I). Since the bathochromic shift is due to weak van der Waals interactions we assigned the 3654 cm^{-1} band to free OH groups of methanol monomers. At very low concentration: $x=0.004$ (32 mM) a very small fraction of the OH groups are free. As the methanol concentration is increased the free OH relative abundance decreases steadily until $x=0.252$ and thereafter is negligible. The MeOH free OH band with a full width at half height (FWHH) of 35 cm^{-1} is situated at 3654 cm^{-1} [Fig. 2(a) insert]. In CCl_4 the MeOH free OH band is 37 cm^{-1} shifted from the gas phase position with a FWHH of 40 cm^{-1} (Table I). Here, the small bathochromic shift increase (10 cm^{-1}) from that of hexane comes from the higher electronegativity of the chloride atoms than that of hexane hydrogen atoms which is almost zero. The larger FWHH in CCl_4 solutions is due to the almost spherical structure of the solvent which gives the MeOH libration movement more leeway than hexane. Hexanol in hexane shows also a small free OH band with a bathochromic shift of 25 cm^{-1} and a FWHH of 30 cm^{-1}.[24] The shift is the same as for methanol but the lower FWHH is due to smaller libration movements. Notwithstanding the small differences in the three situations presented, the definition of alcohol free OH is the following: an IR band situated near 3650 cm^{-1} (a redshift of around 30 cm^{-1} from the gas position) with a FWHH of near 35 cm^{-1}.

2. Free OH band in liquid water

With the free OH band characteristics determined we looked at the situation of liquid water. Figure 1(b) illustrates the region of interest for water at several temperatures from

TABLE I. IR band positions of water (H_2O, HDO, and D_2O) and methanol (MeOH, MeOD): gas, liquid, and in solution in hexane, CCl_4, and acetonitrile.

	Gas[a]			In hexane[b]			In CCl_4 [c]				Sat. in aromatic compounds[d]					Very diluted in MeCN[e]					Liquid[f]			
Vibration mode	$\tilde{\nu}$ (cm^{-1})	ν_3-ν_1	H/D ratio	$\tilde{\nu}$ (cm^{-1})	Shift from gas	FWHH[g] (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	Shift from gas	ν_3-ν_1	FWHH (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	H/D ratio	Shift from gas	ν_3-ν_1	FWHH (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	H/D ratio	Shift from gas	ν_3-ν_1	FWHH (cm^{-1})	$\tilde{\nu}$ (cm^{-1})	H/D ratio	Shift from gas	ν_3-ν_1
ν_3 H_2O	3756						3708	48		30	3678		79		36	3657		99		77	3389		367	
ν_{OH} HDO	3707										3633		74		22	3578		129		77	3426		281	
ν_{OH} MeOH	3681			3654	27	35	3644	37		40						3542		139		85	3328		353	
ν_1 H_2O	3657	99					3618	39	90	15	3591		66	87	23	3542		115	115	77	3222		435	167
ν_3 D_2O	2788		1.347								2730	1.347	58			2697	1.356	91		56	2546	1.331	242	
ν_{OD} HDO	2727		1.359								2668	1.362	59			2631	1.360	96		62	2492	1.375	235	
ν_{OD} MeOD	2718		1.354													2617	1.353	101		63	2467	1.349	251	
ν_1 D_2O	2671	117	1.369								2626	1.367	45	104		2592	1.367	79	105	56	2476	1.301	195	70
ν_2 H_2O	1595															1632		−37		40	1638		−43	
ν_2 HDO	1402		1.138													1430	1.141	−28		40	1446	1.133	−44	
ν_2 D_2O	1178		1.354													1200	1.360	−22		26	1207	1.357	−29	
ν_2 HDO/ ν_2 D_2O			1.190														1.192					1.198		
Comments	Free OH (no H-bond)			Free OH (no H-bond but with van der Waals int.)			Free OH (no H-bond but with van der Waals and dipole interactions)				OH bonded to πe^- (weak H-bond)					OH bonded to MeCN only (strong H-bonds: ROH···N)					Bonded OH (Strong H-bonds: OH···O;H···OH)			
Solubility				Water not soluble; MeOH phase separation			Water microsoluble (0.008M); MeOH soluble				Water, very slightly soluble					Water and methanol, completely soluble								

[a] Reference 30.
[b] Reference 24.
[c] This work and Refs. 26 and 27.
[d] Reference 35.
[e] This work.
[f] Reference 4.
[g] FWHH: Full width at half height.

room temperature to 95 °C. Note that the complete H_2O/D_2O mid-IR ATR spectra are given in Ref. 22. Figure 1(b) shows a broad featureless weak band situated between 3720 and 3480 cm^{-1} (ν_{max} at $\sim$3600 cm^{-1}) that increases slightly with temperature. This small band remains weak and never becomes as intense as the H-bonded band at 3350 cm^{-1}. Figure 1(b) also displays the spectrum of free OH of water dissolved in CCl_4 where the characteristic H_2O ν_3 and ν_1 bands are evident. There is no evidence of these bands in the pure water spectrum and no evidence of the free OH characteristics given above for MeOH in hexane. From these details we conclude that free OH is not present in the bulk of liquid water from room temperature to as high as 95 °C. Since the detection limit of our IR spectrometer is 0.001 a.u. it sets at 0.1% the upper concentration limit of free OH in water which is 0.10M in the $\sim$55M of pure water (110M of OH). This indicates that, if free OH is present in liquid water, it is less than 0.1%.

Since the broad 3600 cm^{-1} water band [Fig. 1(b)] cannot be assigned to free OH groups, can it be assigned to weak OH intermolecular bonds? Methanol and water diluted in acetonitrile (CH_3CN) are used to answer this question.

C. Bathochromic displacement of H-bonded species in solutions

For species containing O—H and N—H groups, the bathochromic shift of the stretching vibrations from the gas phase position is related to the strength of H-bonds.[28] To verify this we looked at the IR spectra of methanol and water diluted in acetone ($(CH_3)_2C{=}O$) and in acetonitrile ($CH_3C{\equiv}N$) because both solvents are strong H-bond acceptors and both solutes are completely soluble in these organic solvents.[29]

1. Methanol in acetonitrile

Figure 3(a) illustrates the IR-ATR spectra (4000–2300 cm^{-1}) of methanol (OH and OD) in acetonitrile at low mole fraction (<1%, with the solvent spectrum subtracted). The OH and OD stretch vibrations are situated at 3542 and 2617 cm^{-1} for MeOH and MeOD, respectively. These are 139 and 101 cm^{-1} redshifted from gas phase positions[30] and 214 and 150 cm^{-1} blueshifted from the pure liquid positions (Table I). At these low concentrations MeOH and MeOD molecules are monomers; giving their single H-bond to one solvent molecule and accepting none from other alcohol molecules. The high position of the singly bonded species (H-bond donor) is explained by the free lone electron pairs on the oxygen atom: the alcohol concentration is not high enough to permit association of two alcohol molecules to form a dimer. Similar results were reported for methanol in acetone.[29] From this we conclude that the bathochromic displacement of the OH (OD) groups depends not only on the labile hydrogen but also on the available oxygen electron lone pairs.[20,29] When these are free the frequencies will be high at 3542 and 2617 cm^{-1} for the OH and OD bonds, respectively. The bathochromic shift from the gas phase position is not great even though these H-bonds are strong (the solvent is a strong H-bond acceptor). However, when the oxygen receives one labile hydrogen the vibration shifts to 3328 and 2467 cm^{-1}, respectively.

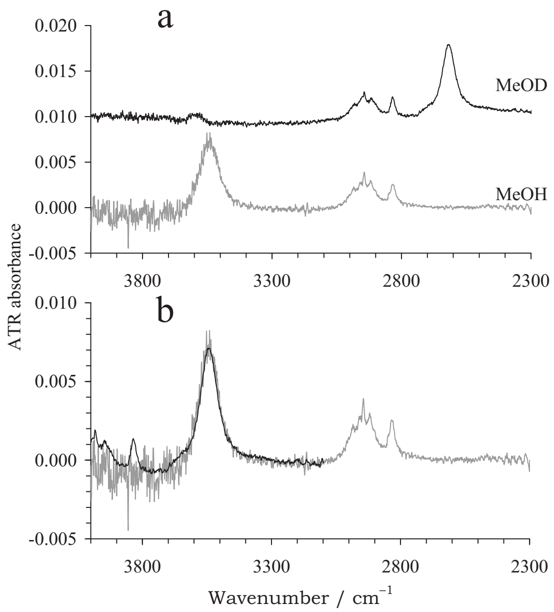

FIG. 3. IR-ATR spectra of methanol in acetonitrile (0.007 mol fraction) with solvent subtracted. (a) Bottom, MeOH (gray line); top, MeOD (black line, shifted 0.01 ATR-AU); (b) Superposition of the MeOD spectrum [from frame (a)] with the original frequencies (2960–2290 cm^{-1}) multiplied by 1.353 on the MeOH spectrum (4000–2300 cm^{-1}).

Figure 3(b) displays the OH and OD stretch bands of methanol isolated in acetonitrile; the OD frequency scale is multiplied by 1.353. This scaling factor is close to the OH/OD isotopic factor of

$$1.373\left(\text{from}\sqrt{\frac{2.014}{2.014+15.999}\times\frac{1.008+15.999}{1.008}}\right)$$

and to that of H_2O and D_2O spectra obtained at different temperatures (1.350).[22] This relation indicates that the shift upon isotopic substitution is solely due to the labile hydrogen.

The 3542 cm^{-1} band position of methanol in acetonitrile is lower than that of free OH but higher than the 3328 cm^{-1} position of the liquid which is more bonded (Table I). This intermediate position indicates that the OH group is neither free nor fully bonded. However, the two species are completely miscible. Since there is no hindrance between the methanol molecules and those of acetonitrile the H of the OH group is strongly bonded to the N of acetonitrile with the O receiving no H since the methanol molecules are surrounded by acetonitrile molecules. The H-bonding is strong despite the band high frequency. We assign the 3542 cm^{-1} band to the OH group H-bonded to acetonitrile with the MeOH oxygen receiving no hydrogen from other MeOH molecules. The 85 cm^{-1} FWHH of the band is also intermediate between the 35 cm^{-1} of the free OH groups and the 200 cm^{-1} of the fully bonded species.[29] The intermediate bandwidth substantiates the above assignment. This also agrees with the 3542 cm^{-1} band of methanol in CCl_4 that was assigned to dimers.[26] In these the OH hydrogen of the

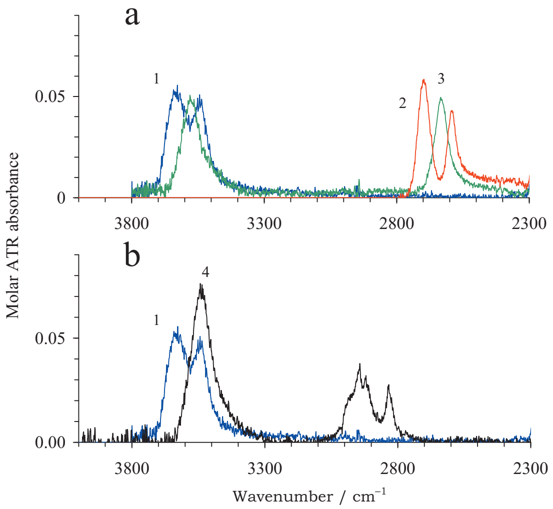

FIG. 4. Comparison of molar IR-ATR spectra of isolated water and methanol in acetonitrile (0.010 mol fraction). (a) H_2O (1), D_2O (2), and HDO (3). (b) H_2O (1) and MeOH (4).

first molecule makes an H-bond with the oxygen of the second molecule but the oxygen of the first accepts none.

2. Water isotopic mixtures in acetonitrile

At low water mole fraction (less than 1%) of aqueous acetonitrile, the water molecules are surrounded by acetonitrile molecules. To obtain the pure HDO spectrum from the isotopic mixture spectra, these are subtracted from the H_2O and D_2O spectra. Figure 4(a) shows the IR-ATR spectra of the stretching bands of pure H_2O, HDO, and D_2O monomers in acetonitrile. The spectra show two well resolved bands assigned to ν_3 and ν_1 the asymmetric and symmetric stretch vibrations, respectively. The deformation bands (ν_2) are situated at 1632, 1430, and 1200 cm^{-1}, respectively. These positions are close to that of the pure liquids. The pure HDO spectrum is easy to separate from the H_2O/D_2O dilute mixtures in MeCN. This is different from the pure liquid H_2O/D_2O mixtures where the spectral separation is difficult.[4] This clearly indicates that H_2O, HDO, and D_2O molecules at low mole fraction in MeCN are surrounded only by MeCN molecules. Similar results were obtained for water (H_2O) in acetone.[20] Table I lists the positions of the water stretching and deformation bands. As for methanol in acetonitrile, the water stretching bands are redshifted from the gas phase positions but much less than in the pure liquid species.

In Fig. 4(a) and Table I we note that ν_{OH} and ν_{OD} of HDO/MeCN are near ν_1 of H_2O and D_2O, respectively. This situation is different than that in gas phase whereas the HDO bands are situated half way between ν_1 and ν_3 (Table I). In the HOD solution the two vibrations are to some degree coupled whereas they are not in the gas phase. This indicates that all water molecules surrounded by hydrophilic solvent molecules have their labile hydrogen atoms H-bonded. Moreover, ν_3 and ν_1 of H_2O in MeCN are lower than that of the gas or that in CCl_4 solutions but much higher than that of the pure liquid (Table I). Because of this, the 3657 and 3542 cm^{-1} water bands cannot be assigned to free OH groups. In a strong bonding situation, the relatively high position is attributed to the water oxygen atoms whose lone electron pairs are free. Anti- or noncooperativity[31,32] is sometimes assumed to explain the small bathochromic shift of ν_3 and ν_1 of H_2O as observed in acetone. Since similar bathochromic shifts are observed for methanol (one OH) and water (two OH) isolated in acetonitrile or acetone: anticooperativity cannot be the cause. The bathochromic OH shift is the consequence of the formation of an H-bond between the OH labile hydrogen atoms and MeCN with the methanol or water oxygen atoms free of H-bond.[33]

Figure 4(b) illustrates the molar IR-ATR OH stretch of MeOH/MeCN and H_2O/MeCN. The MeOH OH stretch band is located at the same position as that of water ν_1 (Table I). Hence, one cannot simply use either methanol or HOD OH bands as generic water OH bands: care must be taken in the assignment of the OH bands. The bands of HDO diluted in H_2O or D_2O must be used with caution when assigning the pure H_2O and D_2O bands: one has to consider the parent molecules with the surrounding milieu.

Figure 4(b) shows another interesting phenomenon of solutes in acetonitrile. The intensity of the MeOH OH stretch band (located exactly at water ν_1) is nearly twice that of water ν_1. Integrated intensities of the OH stretch absorption of MeOH and H_2O are almost equal. However, MeOH has one single OH while water has two. Hence, the methanol OH absorbs twice as much as that of water. On the contrary, the OH (OD) of HOD absorbs as much as that of H_2O (D_2O) in CH_3CN [Fig. 4(a)]. This comparison indicates that OH absorptivities of methanol and alcohols in general are different from that of water.[25] Therefore, intensity relations between these molecules must be made, if necessity dictates, with caution.

Water in acetonitrile at low concentration shows near 3600 cm^{-1} two well defined components with FWHH of 77 cm^{-1} spanning from 3700 to 3400 cm^{-1} assigned to ν_3 and ν_1 of water H-bonded to acetonitrile [Fig. 4(a) and Table I]. Although the low intensity band in pure water [Fig. 1(b)] covers almost the same spectral region (3740–3480 cm^{-1}) the fundamental characteristic of the two bands (ν_3 and ν_1) is not observed. Because of this and because the pure water 3600 cm^{-1} absorption is a low intensity featureless band it cannot be assigned to ν_3 and ν_1 of free water and not even to weakly H-bonded water. Therefore, our previous assignment to a combination band ($\nu_1+\nu_{L2}$) must be maintained.[4] In this context, it may be important to recall that the IR spectrum of liquid water displays intense combination bands [Fig. 1(a)]. For example, the well accepted broad band near 2115 cm^{-1} is assigned to a combination of the deformation and libration modes. Furthermore, the pseudoplateau between 1500 and 900 cm^{-1} is the manifestation of several combination bands involving the deformation and far IR (FIR) bands.[4] Therefore, such combination bands are also present in the massive band near 3400 cm^{-1} that includes the OH fundamental vibrations but they are often neglected.[10,12,15–18,30,34] However, a detailed analysis requires the entire IR spectrum from FIR to near IR.[25]

3. Bathochromic displacement of H-bonded species in solutions

The broad OH stretch band of water ($3700-2700\ \mathrm{cm}^{-1}$) is often assigned to a continuous distribution of H-bonded OH groups having different O—O distances. The terms *continuous distribution* is imprecise due to ill defined hydrogen bond. The OH stretch frequency is related to the O—O distance from one oxygen molecule to another oxygen molecule.[19,28] Similarly for acetonitrile solutions, the O—N distances are involved. Hence, strong H-bonds would have O—N distances in a limited range that should produce sharp bands. Figures 3 and 4 and Table I indicate that for methanol and water isolated in acetonitrile, the strong H-bonding situation gives higher frequencies and narrower bands than that in the pure liquid situation [Fig. 1(a)]. Is this a contradiction? If the high frequency of the OH (water and methanol) H-bonded to acetonitrile nitrogen atom comes from a weaker H-bond than that in pure liquid then a larger variety of O—N distances should be produced. This would bring a broader band than that of the fully H-bonded situation. Figure 4(b) shows that the FWHH span of both ν_3 and ν_1 of H_2O/MeCN are $170\ \mathrm{cm}^{-1}$ (FWHH of individual bands are $77\ \mathrm{cm}^{-1}$) whereas the pure H_2O OH bands covers $420\ \mathrm{cm}^{-1}$ [Fig. 1(a)]. This indicates that the traditional relation made between OH stretch frequencies and the O—N distance where the highest frequency comes from the longest intermolecular distance[28] is not valid for liquids.

Furthermore, the position of the OH band of methanol H-bonded to acetonitrile ($CH_3OH\cdots N\equiv CCH_3$) is $3542\ \mathrm{cm}^{-1}$. From Nakamoto *et al.*[28] relation between OH stretch frequencies and the O—N distances this would give an O···N distance longer than 4.0 Å (it goes out of scale in Ref. 28) giving an H-bond length above 3.0 Å (the methanol or water covalent O—H distance is 1.0 ± 0.1 Å). Since a strong H-bond made of H—N should have a distance of 1.5–1.6 Å (Ref. 28) giving a maximum total of less than 2.6 Å, something is wrong (compared to >4.0 Å). For methanol and water dissolved in acetone we have obtained similar results although the O—O distances (O—H···O) are involved. Furthermore, the position of this band is very similar in both acetone (O—H···O) and acetonitrile (O—H···N) which indicates a similar behavior and H-bonding situation. This in turn is not compatible with Nakamoto *et al.* relations. From this we gather that Nakamoto *et al.*[28] relations which were obtained from crystallographic data on solids are not transferable to liquids.

Water is sparingly soluble in aromatic solvents making it an ideal system to study weak H-bonds. The IR spectra of H_2O, HDO, and D_2O have been obtained by Gentric *et al.*[35] in six solvents: benzene, toluene, p-xylene, mesitylene, α-methyl-naphthalene, and thiophene. Since the positions differed but little in the six solvents we averaged them and present the values in Table I. H_2O and D_2O form two bands separated by approximately $100\ \mathrm{cm}^{-1}$ assigned to ν_3 and ν_1, respectively. This is comparable to those obtained in the gas phase and in CCl_4 and MeCN solutions (Table I). ν_3 of H_2O in CCl_4, aromatic compounds, and MeCN redshifts from the gas position by 48, 79, and $99\ \mathrm{cm}^{-1}$, respectively. The shifts of the other mode are similar or higher. Recall that water is sparingly soluble in CCl_4 and in the aromatic compounds whereas it is fully soluble in MeCN. The $48\ \mathrm{cm}^{-1}$ displacement of water in CCl_4 is due to van der Waals and dipole moments interactions; the $79\ \mathrm{cm}^{-1}$ displacement of water in aromatic compounds is due to H-bonding between the hydrogen atoms and aromatic π electrons.[35,36] These form weak H-bonds. Because of this the aromatic compounds dissolve only sparingly water. The $99\ \mathrm{cm}^{-1}$ displacement of water in MeCN is due to strong H-bonds between the hydrogen atoms and the N atoms which, however, dissolve completely water. One can pass from pure water to pure acetonitrile without any phase separation. The spectra presented in Fig. 4 are for low water concentrations in MeCN. In these, the water O atoms receive no H from neighbor water molecules. This explains the relatively high position of the OH stretch band compared to the liquid but lower than that in the aromatic compounds (Table I). Therefore, in MeCN, the H_2O ν_3 at $3657\ \mathrm{cm}^{-1}$ indicates strong H-bonding situation despite the relative high frequency. In more concentrated water solutions,[37] the OH stretch bands shift to lower frequencies because the water oxygen atoms receive H atoms from neighbor water molecules through H-bonding.

IV. CONCLUSION

Methanol in hexane forms almost exclusively H-bonded species; a few errant monomers are observed which display an absorption band that is unambiguously assigned to free OH groups (not H-bonded). These are situated at $3654\ \mathrm{cm}^{-1}$ with a FWHH of $35\ \mathrm{cm}^{-1}$. The $27\ \mathrm{cm}^{-1}$ redshift from the gas phase position indicates van der Waals interactions. In pure liquid water we found no band with such characteristics even at 95 °C. With a detection limit is 0.001 a.u. the upper limit of free OH in liquid water is set at 0.1%.

Furthermore, in mixtures of H_2O and D_2O, HDO is formed instantaneously through proton hopping. IR detects easily this species by its deformation band which is situated between that of H_2O and D_2O.[4] However, also because of proton hopping, HDO cannot be isolated chemically. Moreover, a detailed factor analysis of the light and heavy water mixtures of IR spectra revealed five factors identified as OH_4;OH_3D;OH_2D_2;OHD_3;OD_4 that have two coordinate bonds and two accepted H-bonds. Note that the three intermediate species cannot be isolated chemically but their IR spectra were obtained. Note also that since we could observe these that comes from proton hopping free OH groups, which also come from proton hopping, could have been observed. We did not.

From the above arguments we conclude that, if present in liquid water, free OH groups would be much less than 0.1%. This is in agreement with the fact that hydroxyl groups have a high propensity to form H-bond with acceptors and receive H-bond from donors. Therefore methanol molecules easily aggregate in hexane even at very low concentration. It seems logical that in a friendly milieu like water with as many H-bonding acceptor sites as labile H atoms, water molecules will share all their hydrogen atoms with neighbor water molecules through H-bonding.

At low MeOH concentration in MeCN the OH stretch band is situated near 3542 cm^{-1}. This band is assigned to labile hydrogen atoms H-bonded to the solvent (a strong acceptor). Even if the position is high compared to that of the pure liquid ($\sim 3300\ \mathrm{cm}^{-1}$) it is nevertheless 139 cm^{-1} redshifted from the free OH situation (gas phase). Because MeCN is a strong H-bond acceptor it makes a strong H-bond with methanol despite the band high frequency. The small redshift of 139 cm^{-1} from the gas phase is not related to weak H-bonds but to the lack of H-bond on the methanol oxygen atoms. As for methanol, water at low concentration in MeCN absorbs at 3657 and 3542 cm^{-1} (Fig. 4 and Table I). The ν_3 and ν_1 bands of water in MeCN are clearly resolved. Although this position is high compared to that of pure liquid ($\sim 3310\ \mathrm{cm}^{-1}$) the H-bonding is strong. Since the weak band near 3600 cm^{-1} of pure water [Fig. 1(b)] does not have the ν_3 and ν_1 band characteristics it cannot be assigned to free water monomers or even to weak H-bonds.

The situation of methanol and water in acetonitrile (and in acetone)[20,29] seems contrary to the textbook explanation of the bathochromic displacement due to H-bonds. In textbooks, the OH band displacements (from the gas phase positions) are linked to the H-bond strength: the larger the displacement the stronger the H-bond.[28] The present results discard this relation for solutions involving hydrophilic liquids. Therefore, the relations obtained for solids cannot be extrapolated to solutions and pure liquids. For these, at least, we have to revise our notion of H-bonding.

Since the objective of this paper is not to determine the molecular structure of liquid water but to determine the presence of free or weakly bound OH groups in the liquid we arrive at the conclusion that liquid water contains very little, if at all, free OH groups and weak H-bonds. The consequence of this is that monomers, dimers, trimers, oligomers, and cyclic structures are little present if at all in the bulk of liquid water. MDS modelers should incorporate these premises into their models that should contain no free OH groups. This severely limits the models but is a challenge to modelers to generate a genuine model that has some bearing with reality. The outcomes confronted to experimental results would bring us closer to framing the big picture of the molecular organization of liquid water. Although the puzzle of the molecular organization of water is not yet complete, the pieces that we are adding are decisive ones.

ACKNOWLEDGMENTS

This work was supported in part by a grant from the Natural Sciences and Engineering Research of Canada (NSERC).

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