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Isotope effects in liquid water by infrared spectroscopy

Jean-Joseph Max^{a)} and Camille Chapados^{b)}

Département de Chimie-Biologie, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada G9A 5H7

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The light and heavy liquid water (H_2O-D_2O) mixtures in the 0-1 molar fraction were studied in the mid-infrared by Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy. Five principal factors were retrieved by factor analysis (FA). When D_2O is mixed with H_2O , the HDO formed because of the hopping nature of the proton (H or D) results in three types of molecules in equilibrium. Because of the nearest-neighbor interactions, the three molecules give rise to nine species. Some of the species evolve concomitantly with other species giving the five principal factors observed. We present the spectra of these factors with their abundances. The calculated probability of the species present at different molar fractions which when the concomitant species are combined gives the observed abundances. To appreciate clearly the difference between the principal spectra, a Gaussian simulation of the bands was made. Because of the numerous components that make up the stretch bands, they are not very sensitive to changes in composition of the solutions; nevertheless, they do indicate the presence of new entities other than the pure species. The deformation bands, more sensitive to such changes than the stretch bands, clearly indicate the presence of the three types of molecules as well as of intermediate species. These bands are sensitive to the two hydrogen bonds on the oxygen atom that a reference molecule makes with its nearest-neighbors, but not to the hydrogen bonds that the nearest-neighbors make with the next nearest neighbors. © 2002 American Institute of Physics. [DOI: 10.1063/1.1448286]

I. INTRODUCTION

Although many organic substances are completely miscible in water, they rarely make ideal mixtures. Alcohol (R– OH) is a good example. The high molecular weight alcohols (7 C and more) are not soluble in water; as the number of carbons is decreased, solubility increases, becoming more and more ideal. An illustration of this is found in an IR study of 1-propanol and water where we have shown that these substances do not form ideal mixtures even though they are completely miscible.¹ The lowest molecular weight alcohol is water (H–OH), an ideal solution difficult to study. To observe the interaction of HOH with HOH, we choose its closest parent, heavy water (DOD). Since the object of this paper is to study aqueous ideal mixtures, we choose H₂O and D₂O mixtures so as to bring other problems inherent to this ideal mixture system to the surface.

The hydrogen atoms in a water molecule are not fixed to one molecule but can migrate to neighboring molecules. The same is true for the deuterium in heavy water. Consequently, the H or D atoms in a mixture of light and heavy water will switch with the atoms of neighboring molecules to form a third species, HDO.²⁻⁴ The study of H_2O-D_2O mixtures is not as easy as it first seems because HDO cannot be isolated. We cannot buy a bottle of HDO as we can for H_2O and D_2O . Even though HDO cannot be isolated chemically, can it be observed spectroscopically? This would appear easy to do at first glance. HDO abounds in a H_2O-D_2O mixture. Therefore, the HDO spectrum was obtained by subtracting 25% of each spectrum of H_2O and of D_2O from the spectrum of an equimolar H_2O-D_2O mixture.² The resulting HDO spectrum shows sigmoids in the deformation regions of the parent molecules, suggesting that either the spectral subtraction was not adequate or that other species are present in the mixture. Since heavy water and deuterated compounds are used extensively in the study of biological compounds,⁵⁻⁷ and since D_2O is an important economic commodity,⁸ it is worth examining the H_2O-D_2O system again. The purpose of this paper is to expose the difficulties we encountered in such a study and to describe the techniques and methods we devised to overcome them.

IR spectroscopy is a technique permitting the different species present in solution to be identified and their abundances to be determined.^{9–21} However, because of the presence of strong hydrogen bonds that shift the IR bands from their free molecule (gas phase) positions, the absorptivity of the vibrational modes are enhanced (see Ref. 22 and references therein). Hence, OH stretch vibrations are strong absorbers, making IR transmission measurements of aqueous solutions difficult to obtain.²³ Light water (H₂O) is then a very poor IR solvent because it is a strong absorber over most of the range from the near infrared to the far infrared.

Heavy water is often used to replace ordinary water when it absorbs in regions of interest to the solute (e.g., amide A, B, and I bands of proteins) and when the isotopic substitution has no effect on the solute other than the band displacement resulting from the exchange of the labile protons.²⁴ The IR study in light and heavy water of chloro-

^{a)}Current address: Scientech R&D, 247 Thibeau, Cap-de-la-Madeleine, (QC), Canada G8Y 6X9.

^{b)}Author to whom correspondence should be addressed. Electronic mail: Camille Chapados@uqtr.ca

phyll photosystem II and glycine are examples of the use of proteins and amino acids, respectively (see Refs. 6, 7, and references therein). In IR and neutron diffraction studies, isotopic substitution is often used in aqueous solutions to distinguish the OH groups of the solute from those of the solvent, or to determine the hydration shells.^{25,26} However, the disproportionation effect in the H₂O–D₂O mixtures, which comes from the particular influences that deuterium and hydrogen have on oxygen, is the cause of the differences between the two molecules.^{27–31} Therefore, the use of isotopic substitution in water used as a solvent²⁶ could result in noticeable perturbations in its molecular vibrations.

Other than a shift in the IR bands, heavy water (D_2O) behaves similarly to light water in the infrared. In H_2O-D_2O mixtures, however, the formation of HDO complicates the situation. With such handicaps, the logical position would be to find an alternative to such a solvent. The problem is that there is none because water is the natural solvent of all biological molecules and is present in all biological events. It is also omnipresent in our world and every substance on earth comes in contact with it.

Raman spectroscopy is a way to overcome the difficulty due to the strong IR absorbance of liquid water, given that the Raman signal of the OH stretch vibrations are weaker than the corresponding IR absorption.³² On the other hand, attenuated total reflectance (ATR) configuration allows the complete mid-IR spectra of aqueous systems to be obtained with high precision and reproducibility.7,9-19,21,33 We have developed an adequate quantitative method using ATR that provides consistently reliable results as long as the following basic requirements are met: (1) a proper crystal is used whose refractive index is sufficiently different from that of the solution;¹⁰ (2) the IR beam is at a proper angle of incidence; (3) the ATR crystal is of adequate length. When these conditions are satisfied, the IR-ATR spectra reflect the system's chemical changes.¹⁰ When we used this technique to study alkali halide aqueous solutions as well as several acidbase titrations,^{7,11–19,21} we found that water forms stable clusters with the ions when a binary salt (NaCl, KCl), a strong acid (HCl) or a strong base (NaOH) is dissolved in it.^{11–14,17,19,21} With this technique, we detected the formation of complexes in aqueous phosphoric and sulfuric acids;^{15,16,18} some of these complexes had previously been deduced only from thermodynamic measurements.

In previous studies, we applied principal factor analysis (FA) to a series of IR spectra to determine the abundances of the species. This type of analysis is suited to cases where some of the species can easily be obtained from a set of experimental spectra. Other methods of applying FA can be used³⁴ that usually result in abstract spectra; these can then be transformed into real spectra by more demanding methods.^{20,35}

The purpose of the present study is to apply the technique mentioned above to analyze the mid-IR spectra of H_2O-D_2O mixtures to determine: (i) the number of species; (ii) their abundances; (iii) their compositions; and (iv) the hydrogen bonding network.

II. EXPERIMENTAL AND DATA TREATMENT

A. Chemicals and solutions

Heavy water (Aldrich Chemical Co., purity >99.9 at % D) was used without further purification. Deionized water was used for light water. Light and heavy water were used to prepare the mixtures. Each sample was prepared by weighing the proper quantities in a 5.0 ml volumetric flask. A series of 63 samples ranging from pure light water to pure heavy water was prepared, the composition of which is given in Table I. This table gives the species concentrations, the D mole fraction $(\chi_D \equiv [D_2O]/([H_2O] + [D_2O]))$, where the concentrations are initial concentrations), and the measurement temperatures.

B. IR measurements

The IR measurements were obtained using a model 510P Nicolet FTIR spectrometer with a TGS detector. Two KBr windows isolated the measurement chamber from the outside. The samples were contained in a Circle cell (Spectra-Tech, Inc.) equipped with a ZnSe crystal rod (8 cm long) in an ATR configuration (the beam is incident at an angle of 45° with the rod's axis and makes 11 internal reflections of which 9 are in contact with the liquid sample). The spectral range of this system is $6500-670 \text{ cm}^{-1}$. The spectra were taken under nitrogen flow to ensure low CO2 and water vapor residues in the spectrometer. Each spectrum represents an accumulation of 500 scans at 4 cm^{-1} resolution. The measurements were made at 27.1 ± 1.2 °C. The cell was carefully dried before each measurement. Since model 510P is a single-beam spectrometer, a background was taken with the cell empty before measuring each sample.

The IR measurements consisted in obtaining the ATR background intensity, R_0 , and the ATR sample intensity, R. The ratio of R/R_0 is the intensity I for the spectral range being studied. Thereafter, the 3023 data points, $[I(\tilde{\nu}) \text{ vs } \tilde{\nu} (\text{in cm}^{-1})]$ of each spectrum were transferred to a spread-sheet program for numerical analysis. The intensities I were then transformed to absorbances, $\log(1/I)$ (abbreviated in some cases as a.u.). A small baseline shift (less than 0.01 a.u.) was made to obtain a null mean absorbance in the 5700–5500 cm⁻¹ region, where light²³ and heavy water do not absorb.

C. Factor analysis (FA)

Factor analysis of a spectral data set is a process by which the principal factors of an evolving system can be identified and their concentrations obtained from derived multiplying factors (MFs). An evolving system is a system that is modified when a parameter such as temperature, pressure, concentration, or in this case the molar faction, is varied. However, when two or more species evolve simultaneously with the varying parameter, FA cannot separate them because the relative concentrations of two or more species remain constant. It may then happen that the principal factors retrieved by FA contain more than one molecular species. Such a situation was observed in aqueous solutions of pro-

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TABLE I. Concentrations, molar fraction, measurement temperatures, and final MFs retrieved of the H_2O-D_2O mixtures.

| [D ₂ O] | [H ₂ O] | | | | | Final MI | Fs | |
|--------------------|--------------------|----------------|-----------|------------------|-------|----------|-------|------------------|
| ±0.4% (M) | ±0.4% (M) | $\chi_D^{(a)}$ | Т (°С) | H ₂ O | HDO' | HOD° | HDO" | D ₂ O |
| 0.00 | 54.971 | 0.0000* | 27.14 | 1.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.629 | 54.271 | 0.0115 | 27.31 | 0.954 | 0.046 | 0.002 | 0.000 | 0.000 |
| 0.961 | 54.071 | 0.0175 | 27.48 | 0.928 | 0.071 | 0.002 | 0.000 | 0.000 |
| 1.462 | 53.563 | 0.0266* | 27.92 | 0.893 | 0.105 | 0.004 | 0.000 | 0.000 |
| 1.991 | 53.095 | 0.0361 | 28.04 | 0.853 | 0.140 | 0.008 | 0.000 | 0.000 |
| 2.465 | 52.542 | 0.0448* | 28.23 | 0.830 | 0.156 | 0.016 | 0.000 | 0.000 |
| 2.965 | 51.996 | 0.0539 | 27.27 | 0.794 | 0.194 | 0.015 | 0.000 | 0.000 |
| 3.510 | 51.625 | 0.0637 | 27.42 | 0.763 | 0.211 | 0.028 | 0.001 | -0.002 |
| 4.022 | 51.152 | 0.0729 | 27.42 | 0.736 | 0.234 | 0.031 | 0.001 | 0.000 |
| 4.506 | 50.693 | 0.0816 | 27.87 | 0.707 | 0.258 | 0.036 | 0.001 | -0.001 |
| 4.983 | 50.079 | 0.0905* | 28.07 | 0.681 | 0.270 | 0.046 | 0.003 | -0.001 |
| 5.524 | 49.476 | 0.1004 | 28.20 | 0.644 | 0.305 | 0.046 | 0.005 | -0.001 |
| 6.027 | 48.933 | 0.1097 | 28.29 | 0.617 | 0.318 | 0.057 | 0.005 | 0.000 |
| 6.458 | 48.715 | 0.11/1 | 26.29 | 0.611 | 0.315 | 0.069 | 0.006 | 0.000 |
| 0.968 | 48.157 | 0.1264 | 26.50 | 0.577 | 0.328 | 0.078 | 0.007 | 0.000 |
| × 009 | 47.803 | 0.1358* | 20.77 | 0.559 | 0.342 | 0.089 | 0.008 | 0.000 |
| 0.000 0.475 | 47.145 | 0.1432 | 27.22 | 0.550 | 0.302 | 0.094 | 0.010 | 0.000 |
| 0.47J 8.061 | 40.077 | 0.1537 | 27.22 | 0.308 | 0.372 | 0.105 | 0.010 | 0.000 |
| 0.501 | 40.131 | 0.1027 | 27.37 | 0.463 | 0.395 | 0.105 | 0.013 | -0.000 |
| 9.959 | 45 115 | 0.1750 | 27.30 | 0.403 | 0.300 | 0.136 | 0.014 | -0.002 |
| 10 909 | 44 223 | 0.1000 | 26.25 | 0.412 | 0.370 | 0.152 | 0.023 | 0.002 |
| 11.921 | 43.592 | 0.2147 | 26.53 | 0.379 | 0.408 | 0.176 | 0.030 | 0.000 |
| 12.970 | 42.120 | 0.2354 | 26.64 | 0.342 | 0.414 | 0.196 | 0.040 | 0.002 |
| 13.975 | 41.128 | 0.2536* | 26.80 | 0.304 | 0.419 | 0.222 | 0.040 | 0.003 |
| 14.952 | 39.797 | 0.2731 | 27.47 | 0.271 | 0.419 | 0.238 | 0.053 | 0.003 |
| 15.973 | 39.798 | 0.2895 | 27.43 | 0.250 | 0.415 | 0.252 | 0.065 | 0.004 |
| 17.072 | 37.887 | 0.3106 | 27.41 | 0.219 | 0.406 | 0.274 | 0.084 | 0.005 |
| 17.918 | 37.223 | 0.3250 | 27.44 | 0.202 | 0.396 | 0.289 | 0.094 | 0.005 |
| 19.045 | 35.987 | 0.3466 | 26.50 | 0.184 | 0.376 | 0.309 | 0.110 | 0.011 |
| 20.189 | 34.704 | 0.3678* | 26.70 | 0.165 | 0.362 | 0.324 | 0.124 | 0.013 |
| 22.441 | 32.528 | 0.4083 | 27.02 | 0.117 | 0.332 | 0.350 | 0.163 | 0.028 |
| 25.011 | 29.971 | 0.4549* | 27.30 | 0.081 | 0.294 | 0.364 | 0.205 | 0.045 |
| 27.326 | 27.686 | 0.4967 | 27.38 | 0.062 | 0.250 | 0.373 | 0.250 | 0.062 |
| 29.850 | 25.619 | 0.5381* | 27.44 | 0.038 | 0.212 | 0.368 | 0.293 | 0.091 |
| 32.181 | 22.755 | 0.5858 | 27.22 | 0.028 | 0.166 | 0.348 | 0.345 | 0.125 |
| 34.519 | 20.596 | 0.6263* | 27.29 | 0.010 | 0.137 | 0.329 | 0.370 | 0.170 |
| 37.066 | 17.698 | 0.6768 | 27.29 | 0.007 | 0.092 | 0.288 | 0.409 | 0.230 |
| 39.323 | 15.618 | 0.7157 | 27.43 | 0.005 | 0.064 | 0.248 | 0.421 | 0.275 |
| 40.269 | 14.467 | 0.7557* | 27.44 | 0.000 | 0.060 | 0.236 | 0.428 | 0.310 |
| 41.551 | 13.342 | 0.7301 | 27.51 | 0.002 | 0.040 | 0.211 | 0.431 | 0.340 |
| 42.405 | 12.101 | 0.7708 | 27.50 | 0.000 | 0.030 | 0.191 | 0.423 | 0.363 |
| 44 206 | 10.605 | 0.7902 | 26.93 | 0.001 | 0.029 | 0.159 | 0.428 | 0.415 |
| 45.427 | 9.482 | 0.8273* | 27.15 | 0.001 | 0.016 | 0.128 | 0.409 | 0.487 |
| 46.678 | 8.271 | 0.8495 | 27.47 | 0.000 | 0.012 | 0.110 | 0.375 | 0.533 |
| 47.691 | 7.302 | 0.8672 | 27.46 | 0.000 | 0.011 | 0.086 | 0.361 | 0.579 |
| 47.963 | 6.725 | 0.8770 | 27.46 | 0.000 | 0.008 | 0.075 | 0.348 | 0.604 |
| 48.838 | 6.088 | 0.8892* | 27.58 | 0.000 | 0.007 | 0.056 | 0.341 | 0.631 |
| 49.239 | 5.605 | 0.8978 | 26.58 | 0.000 | 0.002 | 0.060 | 0.315 | 0.659 |
| 49.783 | 5.030 | 0.9082 | 26.63 | 0.000 | 0.005 | 0.046 | 0.289 | 0.693 |
| 50.384 | 4.445 | 0.9189 | 26.82 | 0.001 | 0.004 | 0.035 | 0.266 | 0.718 |
| 51.006 | 3.887 | 0.9292* | 26.91 | 0.000 | 0.002 | 0.031 | 0.239 | 0.753 |
| 51.504 | 3.349 | 0.9389 | 27.16 | 0.000 | 0.002 | 0.021 | 0.208 | 0.789 |
| 52.130 | 2.777 | 0.9494 | 27.11 | 0.000 | 0.005 | 0.0138 | 0.173 | 0.813 |
| 52.555 | 2.223 | 0.9594* | 27.10 | 0.000 | 0.003 | 0.011 | 0.152 | 0.848 |
| 53.104 | 1.675 | 0.9694 | 27.13 | 0.000 | 0.001 | 0.008 | 0.120 | 0.873 |
| 53.699 | 1.108 | 0.9798 | 26.04 | 0.000 | 0.000 | 0.007 | 0.079 | 0.922 |
| 53.784 | 0.830 | 0.9848* | 26.23 | 0.000 | 0.000 | 0.003 | 0.063 | 0.929 |
| 54.040 | 0.568 | 0.9896 | 26.29 | 0.000 | 0.000 | 0.003 | 0.042 | 0.954 |
| 54.422 | 0.250 | 0.9954 | 20.38 | 0.000 | 0.000 | 0.001 | 0.019 | 0.978 |
| 54.520 | 0.142 | 0.9974 | 20.70 | 0.000 | 0.000 | 0.001 | 0.010 | 0.984 |
| 54.520 | 0.000 | 1.0000 | 20.07 | 0.000 | 0.000 | 0.000 | 0.000 | 0.773 |

 ${}^{a}\chi_{D} \equiv [D_2O]/[H_2O] + [D_2O];$ the labeled values (*) are the experimental spectra shown in Fig. 1.



FIG. 1. ATR-IR spectra of H_2O-D_2O mixtures. Shown are 18 out of the 63 spectra taken. The sample compositions are given in Table I.

panol and in aqueous solutions of sucrose, where some hydrated species could not be sorted from the principal factors obtained by FA.^{1,36}

FA was performed with the spreadsheet program using the following iterative procedure: $^{15,16}(1)$ H₂O and D₂O were used first as principal spectra along with HDO obtained from a (1:1) H_2O and D_2O mixture; (2) a set of realistic MFs were chosen with which to multiply the principal spectra and form a sum $[\Sigma(MF \times principal spectra)];$ (3) the sums were compared to the experimental spectra and the resulting residues minimized in accordance with a least-squares fit procedure; (4) the presence of nonzero residues serve to identify another principal spectrum that is then added to the previous principal spectra and the procedure is repeated from step (1) until the residues are minimized. With the number of factors in the system determined, these final MFs are multiplied by the sample principal spectra concentrations to give the species concentrations. The presence of negative or inadequate concentrations is taken as a sign that the principal spectra are not orthogonal; an adequate procedure is used to render them orthogonal. The final MFs were then obtained and the orthogonal principal spectra (eigenspectra) and final concentrations determined.

III. RESULTS AND DISCUSSION

A. IR-ATR spectra

Of the 63 experimental IR-ATR spectra taken of the H_2O-D_2O mixtures, 18 are presented in Fig. 1 (identified by * in Table I). The large number of solutions was necessary to obtain several spectra at low and high D molar fractions where only two water molecular types are prevalent. The series of spectra presents regular evolving characteristics: the H_2O spectrum (Fig. 1) shows the broad intense $v_{1,3}$ band of water from 3700 to 2800 cm⁻¹, the weak broad combination band at 2115 cm⁻¹, the v_2 band at 1638 cm⁻¹, and the strong absorption that starts near 1100 cm⁻¹ due to the libration band situated near 670 cm⁻¹. The counterpart D_2O bands are situated, respectively, at 2700–2200, 1550, 1205 cm⁻¹, and near 800 cm⁻¹.

As H₂O is replaced by D₂O in the mixture, the 3700– 2800 cm⁻¹ band decreases to the profit of the 2750–2200 cm⁻¹ one. The H₂O deformation band at 1638 cm⁻¹ decreases to the profit of the 1450 cm⁻¹ band until D and H are in equal concentrations, whereupon this band also decreases to the profit of the 1205 cm⁻¹ band. The 1450 cm⁻¹ band is assigned to the deformation mode of the newly formed molecule, HDO (δ_{HOD}).^{2,4} The stretch bands of this molecule appear where the parent molecules absorb.

In the mixture spectra (Fig. 1), isosbestic points are observed at 2750 and 1250 cm^{-1} , and quasi-isosbestic points are seen near 2180 and 1150 cm^{-1} . The isosbestic points indicate a regular transformation of the water bands into deuterated ones, although the quasi-isosbestic points suggest that other species may be present.

B. Simple spectral analysis

Because the variation of the intensity and band maxima are often used in the spectral analysis of mixtures, we analyzed these parameters in the H_2O-D_2O mixture spectra.

1. Integrated intensity of O–H and O–D stretch bands

The number of O–H valence bonds in the sample is proportional to the product of the sample molar concentration with the probability of finding a hydrogen atom attached to an oxygen atom (P_H). Therefore, from Eq. (A2) (see Appendix A), if the integrated intensity of these vibrations is independent of neighboring water molecules, the integrated intensity of the O–H stretch band will be proportional to χ_D . The same situation exists for the O–D stretch vibration. For all experimental spectra, we calculated the integrated intensity in the 3700–2750 and 2750–2160 cm⁻¹ ranges for ν_{OH} and ν_{OD} , respectively. The results given in Fig. 2(A) show that both integrated intensities are linear functions of χ_D . This indicates that the integrated ν_{OH} and ν_{OD} intensities are not affected by neighboring isotopic water molecules.

2. Band maxima variations

Figure 2(B) shows the position of ν_{OH} and ν_{OD} band maxima as a function of χ_D . Both maxima vary linearly, over the range 3340–3406 cm⁻¹ in the first case, and over the range 2505–2473 cm⁻¹ in the second case. These linear relationships suggest the presence of two OH species and two OD species. This could implicate $(2 \times 2 =)4$ species, but indicates that at least three species are present should one combine equally with OH and OD to form one species different from that of pure H₂O and pure D₂O.

Figures 2(C), 2(D), and 2(E) show the position as a function of χ_D of the HOH, HOD, and DOD deformation bands, respectively. Between $\chi_D = 0$ and 0.5, ν_{max} of δ_{HOH} increases linearly from 1639 to 1651 cm⁻¹ (steps are due to the finite spectral sampling of 1.92 cm⁻¹ giving a resolution of 4 cm⁻¹ following Shannon's theorem), a variation of 13 cm⁻¹ [Fig. 2(C)]. Between $\chi_D = 0.5$ and 0.8, ν_{max} of δ_{HOH} remains constant. Thereafter the position of this band cannot be determined exactly because its intensity is weak (less than 4% of that of pure water), and other bands become increasingly



FIG. 2. Spectral features of the experimental spectra. (A), ν_{OH} (Δ) and ν_{OD} (O) integrated intensity. Band maxima of (B) $\nu_{OH}(\Delta)$ and $\nu_{OD}(O)$, (C) δ_{HOH} , (D) δ_{HOD} , and (E) δ_{DOD} .

important in this spectral region. For D₂O, ν_{max} of δ_{DOD} decreases linearly in steps from 1218 to 1206 cm⁻¹, a variation of 12 cm⁻¹ [Fig. 2(E)].

The situation of HDO is more complex. The band sandwiched between the δ_{HOH} (1638 cm⁻¹) and δ_{DOD} (1207 cm⁻¹), which cannot be assigned to H₂O or D₂O, is assigned to δ_{HOD} (Fig. 1). The ν_{max} of δ_{HOD} , which occurs at χ_{D} = 0.5 is 1446 cm⁻¹. At low and high χ_{D} , the ν_{max} positions are not reliable because the intensities are weak and components of the other species are important. The ν_{max} are reliable only between χ_{D} =0.1 and 0.9. At lower and higher values, ν_{max} increases from 1447 to 1455 cm⁻¹ for a variation of 8 cm⁻¹ on both sides.

The OH and OD stretch bands and the three clearly visible deformation bands of H₂O, HDO, and D₂O indicate the presence of these three molecules. For H₂O and D₂O, the 13 and 12 cm⁻¹ variation of ν_{max} of the deformation bands would indicate the presence of intermediate species of H₂O and D₂O between HDO and H₂O on one side and D₂O on the other side. The very weak variation of ν_{max} of δ_{HOD} with χ_D and the band being situated between the other two may not be indicative of supplementary species.

Although crude, this analysis would suggest the presence of five spectroscopically different entities. To sort them, we proceeded in sequence: first, the HDO spectrum was obtained from the H_2O-D_2O equimolar solution spectrum; second, FA was made on all solution spectra with three factors to retrieve the supplementary species; third, FA was made with five principal factors.

C. Factor analysis using three principal factors

1. Determination of a third specie

Pure H_2O and pure D_2O are obviously two principal factors in the series and are obtainable in pure form. The third species, HDO, cannot be obtained in pure liquid form since it exists solely in equilibrium with H_2O and D_2O , as described by the equation,^{2,37}

$$H_2O + D_2O \rightleftharpoons 2HDO. \tag{1}$$

The thermodynamic equilibrium constants, K_e , is

$$K_e = \frac{[\text{HDO}]^2}{[\text{H}_2\text{O}][\text{D}_2\text{O}]},\tag{2}$$

where K_e values found in the literature at 25 °C ranged from 3.76 to 3.94.^{27–31}

The "pure" HDO spectrum had been obtained previously by subtracting 0.25 H₂O spectrum and 0.25 D₂O spectrum from an equimolar H_2O-D_2O solution spectrum.² Because it presents sigmoïdal features near the deformation bands of the parent molecules, the resulting spectrum cannot be considered exact. Such features are not due to optical effects produced by the ATR configuration since they are still present in the real and imaginary parts of the refractive index spectra (*n* and *k*).² The sigmoidal features indicate that too much of the H₂O and D₂O spectra have been subtracted from the equimolar spectrum. Bearing this in mind and using the condition of no negative band previously used,^{1,7,11-19,36} we obtained the HDO spectrum by subtracting $0.18 \times \text{pure H}_2\text{O}$ spectrum and $0.18 \times \text{pure } D_2O$ spectrum from the equimolar H₂O-D₂O spectrum. The resulting spectrum normalized to 55.13 M (Ref. 38) was identified as that of HDO and is shown in Fig. 3(A) with those of H₂O and D₂O.

2. Multiplying factors (MF)

The spectra of H₂O, HDO, and D₂O shown in Fig. 3(A) are orthogonal since each spectrum is of a pure molecular species. These spectra served to determine the MFs of the different experimental spectra (Fig. 1) using FA. The results, given as a function of χ_D in Figs. 3(B), show a regular pattern for the three species, indicating that the species chosen yield coherent results.

3. Residues

The residues obtained from the difference between experimental and calculated spectra were divided into two regions in Fig. 3(C). $\chi_D < 0.5$ and $\chi_D > 0.5$. The residues are not zero, and show a regular pattern near the OH and OD stretch bands and near the HOH, HOD, and DOD deformation bands. These results suggest the presence of other species in the solutions.

We verified that introducing a fourth principal factor into FA did not decrease the residues significantly, but adding a fifth one did. We then concluded that at least five principal factors were necessary to perform FA on the 63 experimental spectra.



FIG. 3. FA results with three eigenspectra: (A) ATR-IR spectra of H₂O (bottom), HDO (middle), and D₂O (top); (B) MFs retrieved; (C) Residues of the difference between experimental spectra (Fig. 1) and calculated spectra (Σ MF×principal spectrum) at χ_D <0.5 and χ_D >0.5. (χ is the molar fraction).

D. Factor analysis using five principal spectra

Pure H_2O and D_2O are obviously the two first principal factors. Three other principal factors must be determined.

1. Determination of the three remaining factors

A first step in the analysis was undertaken to determine the variation path of the five MFs retrieved by FA. The composition of the three unknown factors could then be determined.

Since the equimolar H₂O–D₂O mixture contains more than three species, we chose to start with the extreme differences in concentration—those samples should be the least complicated to study. In the $\chi_D < 0.05$ mixture, the relative molar amount of D₂O at equilibrium is expected to be less than $(0.05)^2 = 0.0025$ (see Appendix A); the solution would contain principally H₂O with around $[2 \times 0.05 \times (1-0.05) \approx]0.10$ molar ratio of HDO. The first unknown factor contains H₂O and HDO, a species that we call HDO'.³⁹

To determine the composition of HDO', we choose the experimental spectrum at $\chi_D = 0.027$. The operation of maximizing the subtraction of the pure water spectrum from the experimental result was monitored near 1638 cm⁻¹ subject to the constraint that there be neither a negative band nor a sigmoid absorption in this region. The MFs determined for pure H₂O and HDO' were 0.892 and 0.108, respectively. Similarly, the experimental spectrum at $\chi_D = 0.985$ was assumed to contain only two species: D₂O and the second unknown factor that we call HDO''. The subtraction of the heavy water spectrum from the experimental one, which was monitored near 1205 cm⁻¹, gave 0.930 and 0.070 for the MFs of pure D₂O and HDO'', respectively.

The third unknown factor, which we named HDO°, was obtained from the mixture at $\chi_D = 0.497$ (Ref. 40) by subtracting the spectra of the four other factors determined previously from the experimental spectrum, monitoring the maximum extent of the subtraction in the three deformation regions. The MFs subtracted were 0.062, 0.25, 0.25, and 0.062 for H₂O, HDO', HDO'', and D₂O, respectively. The MF of HDO° is therefore 0.376.

The small MF values of HDO' and HDO" (0.108 and 0.070, respectively) resulted in a low signal to noise ratio for the corresponding eigenspectra. To compensate for this, we translated the information gained with two easily identified principal factors to more concentrated solutions than initially utilized. The abundances of the two factors being higher provides a better signal to noise ratio. This is presented in the next section.

2. Principal factors with high signal to noise ratios

The precision of FA was increased by minimizing the residues using matrix multiplication with the five eigenspectra previously determined and with the experimental spectra at $\chi_{\rm D}$ =0.000, 0.054, 0.497, 0.949, and 1.000 (Table I). The eigenspectra matrix \mathbf{S}^{P} was obtained from the matrix of the five experimental spectra \mathbf{S}_{exp}^{P} from the relation,

$$\mathbf{S}^{P} = \mathbf{S}_{\text{exp}}^{P} \times \mathbf{P}^{-1},\tag{3}$$

where **P** is the matrix of the MFs of the five experimental spectra (at $\chi_D = 0.000$, 0.054, 0.497, 0.949, and 1.000) obtained from the five principal spectra determined in the preceding section. The **P** matrix is given in Table II.

The five principal spectra obtained with Eq. (3) and normalized to the pure water concentration (55.13 M) are shown in Fig. 4(A). With these principal spectra, FA was then applied to the 63 experimental spectra. The MFs retrieved are given in Fig. 4(B) and in Table I. The vertical lines in the figure indicate the molar fractions at which the eigenspectra were determined. The MFs of the five species show regular

TABLE II. Multiplying factors (MFs) of the five experimental spectra S_{exp}^{P} used to obtain the matrix *P* (see text).

| $\chi_{ m D}$ | 0.000 | 0.054 | 0.497 | 0.949 | 1.000 | |
|----------------------|-------|-------|-------|-------|-------|-----|
| 1st principal factor | 1.000 | 0.794 | 0.062 | 0.000 | 0.000 | ≡ P |
| 2nd principal factor | 0.000 | 0.194 | 0.250 | 0.005 | 0.000 | |
| 3rd principal factor | 0.000 | 0.015 | 0.373 | 0.014 | 0.000 | |
| 4th principal factor | 0.000 | 0.000 | 0.250 | 0.173 | 0.000 | |
| 5th principal factor | 0.000 | 0.000 | 0.062 | 0.813 | 0.993 | |

evolving patterns, indicating that FA proceeded correctly. In Fig. 4(B), the continuous lines are obtained from calculations discussed in Sec. III E 2.

The residues from the differences between experimental and calculated spectra are given in Fig. 4(C). The integrated squared intensity of the difference spectra were less than one-30th that obtained with three principal factors (Fig. 3). The remaining residues do not show as regular a pattern as in the previous case. In Fig. 4(D), we compare the integrated squared intensity of the residues with the mean temperature difference at which the sample spectra were recorded. Since the two curves are correlated, we can relate the remaining residues [Fig. 4(C)] to a temperature variation between the spectra. Furthermore, the amplitude and shape of the residues are similar to those reported for a temperature variation of $1.2 \,^{\circ}C$,⁴¹ which is the temperature stability of our system.

We concluded from the above FA that five principal factors are present in the H_2O-D_2O mixtures: H_2O ; HDO'; HDO° , HDO'', and D_2O . No other principal factors could be observed given the limit of the present experimental precision. The nature and composition of the five principal factors can now be determined.

3. Composition of the five principal factors

The composition of the five eigenspectra of Fig. 4(A)was calculated with Eq. (3). The composition of the samples that gave the experimental spectra S_{exp}^{P} was multiplied by the inverse matrix \mathbf{P}^{-1} to obtain the composition corresponding to the eigenspectra. Spectrum **a** is that of water; spectrum **b** is that of HDO' composed of a H₂O-HDO 1:1 mixture (the absence of δ_{D_2O} band near 1205 cm⁻¹ indicates that D_2O is not present); spectrum d is that of HDO" made up of a D₂O-HDO 1:1 mixture (the absence of $\delta_{\rm H_2O}$ band near 1640 cm^{-1} indicates that H₂O is not present); and spectrum **e** is that of D_2O . The situation of spectrum c (HDO°) is more complex: the IR bands centered near 1640, 1455, and 1205 cm^{-1} indicate the presence of the three molecular types of water: H_2O , HDO, and D_2O in the ratio 1:4:1. The resulting compositions of the five principal factors are reported in Table III. No situation exists where a "pure" HDO spectrum could be retrieved because H2O and D2O molecules are present in the HDO° factor, which are slightly different from that of "pure" H₂O and D₂O, and which evolve simultaneously with "pure" HDO. Note that we used Eq. (1) with $K_e = 4.0$ for calculating the HDO composition in the HDO', HDO°, and HDO" spectra because the disproportionation effects which influence the constant are very small and can be neglected (see Appendix A).



FIG. 4. FA results using five eigenspectra. (**A**), ATR-IR spectra of: H_2O , **a** (bottom), **b**, **c**, **d**, and D_2O , **e**. Each spectrum is shifted 1 a.u. from the preceding one. (**B**) MFs retrieved (symbols). Full lines come from the theoretical calculations (see text). Light vertical lines indicate where the principal spectra were determined. (**C**) Residues of the difference between experimental (Fig. 1) and calculated spectra using five principal factors at $\chi_D < 0.5$ and $\chi_D > 0.5$. Same presentation as in Fig. 3. (**D**) Integrated intensity of the residues (O, bottom trace) and temperature variation of the spectra (\times , top trace).

E. Interpretation of the five species retrieved

The results of FA on the series of 63 IR spectra of mixtures of H₂O and D₂O indicate that five principal factors are present in the samples (Fig. 4). Two of these factors are pure H_2O and D_2O , labeled H_2Oa and D_2Oe , respectively. The a and e tags indicate the evolving factors; the others are b, c, and d. Most of molecules in liquid water have 4 hydrogen bonds with 4 neighboring water molecules of the same type^{42,43} (see Appendix B). The spectra in Fig. 4(A) indicate that pure water (H_2Oa) and factors **b** and **c** contain H_2O molecules because the bands observed at 1638, 1649, and 1654 cm⁻¹, respectively, can only be assigned to $\delta_{\rm H_2O}$. Factors \mathbf{c} , \mathbf{d} , and \mathbf{e} contain D_2O molecules because the bands observed at 1214, 1212, and 1207 cm⁻¹, respectively, can only be assigned to δ_{D_2O} . We first address the question of evaluating the difference in the H₂O molecular environment that could induce a perturbation of the H₂O deformation band near 1638 $\rm cm^{-1}$

1. Environmental influence on the H₂O deformation vibration

The oxygen of water can make four bonds with H and/or D atoms: two covalent bonds and two hydrogen bonds. The five situations possible are illustrated at the bottom of Fig. 5, where valence and hydrogen bonds are not distinguished. Depending on the neighboring molecules, several situations exist. These are schematically illustrated in Fig. 5 (top) by a two-dimensional water network where each water molecule $(H_2O, HOD, and D_2O)$ is represented in a square box. Each box is linked to four different boxes through four hydrogen bonds (dotted lines). The boxes are identified by a column letter and a line number, as in a crossword puzzle. For example, the situation in pure liquid water is depicted by box C2 because the nearest-neighbors to the H_2O (H_2Oa) in the box are 4 H₂O molecules. The two hydrogen atoms of H₂Oa are hydrogen bonded to the oxygen atoms of two neighboring H₂O molecules (D2 and C3) while the oxygen atom of H_2Oa is hydrogen bonded to two hydrogen atoms of two other neighboring H₂O molecules (B2 and C1).

When few HDO molecules are present in the solution, as in E3, the H and D of an HDO molecule are hydrogen bonded to the oxygen atoms of H_2O in F3 and E4, respectively. The perturbation on H_2O in E4 is of first order because its oxygen is now hydrogen bonded to both a H and a D atom. The oxygen in HDO is hydrogen bonded to two nearest-neighbor H_2O molecules in D3 and E2 via two hydrogen atoms. The perturbation on the D3 molecule is considered second order because the hydrogen atoms are always hydrogen bonded to an oxygen atom of a neighboring water molecule.

2. Probability evaluation of the different cases

While Fig. 5 illustrates only part of the situation, Table IV lists all possible combinations that a reference water molecule can have with four neighboring water molecules (H₂O, HDO, or D₂O). Table IV enumerates the $(2^4=)$ 16 possible combinations of 4 ordered elements with H and D that a reference **HOH** molecule situated at the center can make

TABLE III. Composition of the five principal factors in H₂O-D₂O mixtures.

| Spectrum [Fig. 4(A)] | Initial cor | ncentration | Concer | | | |
|-------------------------|-------------------------|-------------------------|-------------------------|------------|-------------------------|--|
| | H ₂ O (M) | D ₂ O (M) | H ₂ O (M) | HDO (M) | D ₂ O (M) | Molar ratios ^a H ₂ O:HDO:D ₂ O |
| a H ₂ O | 55.13 | 0.00 | 55.13 | 0.00 | 0.00 | 1:0:0 |
| b HDO' | 41.33 | 13.83 | 27.51 | 27.65 | 0.00 | 1:1:0 |
| c HDO° | 27.56 | 27.42 | 9.19 | 36.65 | 9.14 | 1:4:1 |
| d HDO" | 13.80 | 41.53 | 0.00 | 27.60 | 27.72 | 0:1:1 |
| e D ₂ O | 0.00 | 55.13 | 0.00 | 0.00 | 55.13 | 0:0:1 |

^aThe evaluation of HDO abundance was obtained using Eq. (1) and $K_e = 4.00$.

with the two water molecules H-bonded to its oxygen atom. One OH valence bond of this molecule is directed toward the top of the table, making a hydrogen bond with an oxygen atom of a water molecule (OH_2 , OHD, or OD_2). Similarly, the other OH valence bond is directed toward the bottom of the table.

Listed to the left and right of the reference HOH molecule in Table IV are two columns containing the different combination of HOH, DOD, HOD, and DOH molecules whose H or D makes a hydrogen bond with the oxygen of the reference molecule. Depending on the hydrogen bond made with the oxygen atom of the reference molecule, three different situations may be distinguished with the letters **a**, **b**, and **c** [it will be shown later that the letters **a**, **b**, and **c** refer to the spectra in Fig. 4(A): **a**, an H of the molecules in both left and right columns are hydrogen bonded to the reference molecule O (combination #1, 3, 13, and 15; e.g., C2, E5, and C4 in Fig. 5); **b**, an H from the left and a D from the right or vice versa are hydrogen bonded to the reference molecule O (combination #2, 4, 5, 7, 9, 11, 14, and 16; e.g., E4 and E8 in Fig. 5); c, a D of the molecules in both left and right columns are hydrogen bonded to the reference molecule O (combination #6, 8, 10, and 12; e.g., F10 in Fig. 5). The three different situations in the case of a central HOH molecule are indicated in the column entitled $H_2O(1)$ at the right of Table IV. Similarly, the columns headed HOD (2) and D_2O (3) are for the HOD reference water molecule, giving species b, c, and d, and the **DOD** reference water molecule participating in the spectra c, d, and e in Fig. 4. Therefore, for each of the three central molecules (HOH, HOD, or DOD), three possibilities were identified, resulting in $(3 \times 3 =)$ 9 different species. For H_2O these are 1a, 1b, and 1c (C2, F3, and F10 in Fig. 5). Similarly, for HDO these are 2b, 2c, and 2d (F5, F6, and F9), and for D_2O these are 3c, 3d, and 3e (E9, G6, and G8). Four of the nine species evolve simultaneously with other species, giving five principal factors (a, b, c, d, and e). This will be demonstrated below.

The abundances of the nine different species identified above are related to their probabilities identified in Table IV. The degeneracy of each of the 16 combinations depicted in Table IV has to be determined. Any one water molecule (HOH, HOD or DOD) cannot be distinguished from other similar molecules. HOH and DOD have a C_{2v} symmetry, while that of HOD is C_s . Therefore, each situation involving an HOH or a DOD molecule H-, or D-bonded to the oxygen of the center water molecule must be counted twice, since the equivalence of their two possible molecular orientations renders them indistinguishable. The degeneracy numbers are listed in Table IV. As an example, in combination 1 two water molecules are involved; each is twice degenerate, for a total degeneracy of 4. The disproportionation effect, in which H and D are not considered equivalent (in terms of probability), has been invoked by some authors in their studies of H₂O–D₂O mixtures.^{27–30} We demonstrate in Appendix A that this phenomenon can be neglected in the present circumstances.

The probability of each of the three different species of HOH in each sample may now be calculated. The species H_2Oa is encountered in combination 1, 3, 13, and 15 (Table IV). Therefore, we have

$$P_{H_2Oa} = \frac{P_{H_2O}}{4} (4P_{H_2O}^2 + 4P_{H_2O} \times P_{HDO} + P_{HDO}^2), \qquad (4)$$

where P_{H_2Oa} is the probability for one water molecule to be of type H_2Oa , and where P_{H_2O} and P_{HDO} are given by Eqs. (A3) and (A4). In Eq. (4), the first term P_{H_2O} represents the probability that the reference molecule (the center molecule in Table IV) is a H_2O molecule. The dividing factor 4 was introduced to take into account the 2×2 number of independent permutations of the right and left atoms (H or D) of the right and left side water molecules. The numerical factors inside the parenthesis (4, 4, and 1) are the degeneracy numbers (Table IV).

Equation (4) reduces to

$$P_{H_2Oa} = \frac{P_{H_2O}}{4} (2P_{H_2O} + P_{HDO})^2.$$
(5)

The probabilities for one water molecule to be of the type H_2Ob , H_2Oc were evaluated in the same way from data in Table IV,

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FIG. 5. Top: Two-dimensional representation of the hydrogen bond network in the H_2O-D_2O mixtures. Each square contains one water molecule (with H or D). Full and dotted lines represent covalent and hydrogen bonds, respectively. Bottom: The five principal factors where two bonds are covalent bonds and the other two are H-bonds (see text).

$$P_{H_2Ob} = \frac{P_{H_2O}}{2} [4P_{H_2O} \times P_{D_2O} + P_{HDO} \times (2 - P_{HDO})]$$
(6)

and

Ρ

$$H_{2OC} = \frac{P_{H_2O}}{4} (2P_{D_2O} + P_{HDO})^2.$$
(7)

The six remaining probabilities were deduced from Eqs. (5) to (7) and from Table IV,

$$\mathbf{P}_{\mathrm{HDOb}} = \mathbf{P}_{\mathrm{H}_{2}\mathrm{Oa}} \frac{\mathbf{P}_{\mathrm{HDO}}}{\mathbf{P}_{\mathrm{H}_{2}\mathrm{O}}},\tag{8}$$

$$P_{HDOc} = P_{H_2Ob} \frac{P_{HDO}}{P_{H_2O}},$$
(9)

$$P_{\text{HDOd}} = P_{\text{H}_2\text{Oc}} \frac{P_{\text{HDO}}}{P_{\text{H}_2\text{O}}},\tag{10}$$

TABLE IV. Relation between a reference HOH molecule and neighboring molecules in H₂O–D₂O mixtures.

| Combi- nation number | Left molecule H-bonded to reference molecule | - | OH2 | H-bonded to OHD | | Þ | Right molecule H-bonded to reference molecule | Species related to H ₂ O (1) | and evolvir reference i HOD (2) | ng factors molecule ° D ₂ O (3) | Number of degenerate situations for each reference molecule |
|----------------------------|---|-------|-----|-----------------|----|------|--|--|--|---|--|
| | | | | | | | · | 1 | | 20 | 4 |
| 1 | H-O-H | •••• | | | | •••• | | 1a 11 | 20 | 3C 24 | 4 |
| 2 | | •••• | | | | •••• | | 10 | 20 | 50 20 | 2 |
| 5 | | •••• | | | | •••• | | 1a 16 | 20 | 24 | 4 |
| 4 | | | | | | •••• | | 10 15 | 20 | 2d | 4 |
| 5 | | | | | | | | 10 | 20 | 3a | 4 |
| 0 | | •••• | e | 8 | | | | 10 15 | 20 | 34 | 2 |
| 0 | | | | i L | | •••• | | 10 | 20 | 30 | ۲ ۸ |
| 0 | | | C | Ş | | •••• | | 10 | 20 20 | 3e 2d | 4 |
| 9 | | •••• | Ę | | | •••• | | 10 | 20 | 30 20 | 2 |
| 10 | | •••• | | | | •••• | | 10 | 20 | 3e 24 | 1 |
| 11 | | ••••• | | | | •••• | | 10 | 20 | 30 2- | 1 |
| 12 | | •••• | | | | •••• | ····D=O=D | HC L | 20 | 3e | 2 |
| 13 | | •••• | | | | •••• | | 12 | 20 | 3C 24 | 2 |
| 14 | | | | | | | | 10 | 20 | 30 2- | 1 |
| 15 | | | | | | | | 1a 11 | 20 | 3C | 1 |
| 16 | D-0-H··· | | ~ | ~ | _ | •••• | ···D-0-D | 10 | <u>2c</u> | 30 | 2 |
| | | | DD₂ | HC | H2 | Dif | ferent species | <u>1a, 1b, 1c</u> | <u>2b, 2c, 2d</u> | <u>3c, 3d, 3e</u> | |
| | | _ | | Ŭ | | | Total different species: | | 9 | | |
| | | | | | | N | umber of evolv | ing factors | (a, b, c, c | d, e) = 5 | |

^aH–O–H is the reference molecule (1) which can be replaced by HOD (2) and DOD (3) depending on the situation considered.

^bOne **H** of the central molecule is H-bonded to an O of either OH_2 , OHD, or OD_2 . The H or D of the neighboring molecule does not influence the number of species (see text).

^cThe numbers refer to the reference molecule and the letters a, b, c, d, and e to the evolving factors. Vg, the species 1b and 2b evolve simultaneously as a function of χ_D and cannot be separated by FA.

and

$$P_{D_2Oc} = P_{H_2Oa} \frac{P_{D_2O}}{P_{H_2O}},$$
(11)

$$P_{D_2Od} = P_{H_2Ob} \frac{P_{D_2O}}{P_{H_2O}},$$
 (12)

$$P_{D_2Oe} = P_{H_2Oe} \frac{P_{D_2O}}{P_{H_2O}}.$$
 (13)

The numerical values computed with Eqs. (5)–(13) are plotted as functions of χ_D in Fig. 6. Adding the abundances of all species with the same letter (**a**=1a; **b**=1b+2b; **c** =1c+2c+3c; **d**=2d+3d; and **e**=3e), the total relative amount of species **b**, **c**, and **d** were computed using Eqs. (6)–(12) and plotted in Fig. 4(B) (full lines) along with the experimental results. The experimental results with their errors are on the theoretical calculated lines. The experimental errors correspond to the symbol sizes in the figure $(\sim \pm 0.003)$.

Using Eqs. (4), (6), and (8) together with Eqs. (A3)–(A5), and neglecting the reported disproportionation (i.e., $\alpha = \beta = \gamma = 1$), one obtains

$$\mathbf{P}_{\mathrm{HDOb}} = \mathbf{P}_{\mathrm{H}_{2}\mathrm{Ob}} \,. \tag{14}$$

In the same way, it is easily demonstrated that

$$\mathbf{P}_{\mathrm{H}_{2}\mathrm{Oc}} = \mathbf{P}_{\mathrm{D}_{2}\mathrm{Oc}},\tag{15}$$

$$\mathbf{P}_{\mathrm{HDOd}} = \mathbf{P}_{\mathrm{D}_{2}\mathrm{Od}},\tag{16}$$

and

$$P_{HDOc} = 4P_{H_2Oc}.$$
 (17)

Therefore, species 1b and 2b remain in the same 1:1 proportion whatever may be the value of χ_D . The same situation prevails for species 2d and 3d. Finally, species 1c, 2c,



FIG. 6. Probability of different species in the H_2O-D_2O mixtures. (A) D_2O species: D_2Oc ; D_2Od ; and D_2Oe ; (B) HDO species: HDOb; HDOc; and HDOd; (C) H_2O species: H_2Oa ; H_2Ob ; and H_2Oc .

and 3c remain in the 1:4:1 proportion independently of the value of χ_D . These properties fully explain the reason why only five principal factors were retrieved by FA when nine species are present in the H₂O–D₂O mixtures. FA sort as a single factor the species that evolve simultaneously.

Furthermore, the results obtained by FA on the 63 H_2O-D_2O mixture spectra are well supported by a simple probabilistic model. The nine water species are included in the five principal factors. This relation can be explained as follows: each oxygen atom forms four bonds with the hydrogen or deuterium atoms, two covalent bonds and two hydrogen bonds. Principal factor a is related to an oxygen atom with four bonds to hydrogen atoms, i.e., water (1a in Fig. 5, e.g., B2, C3, D4, and E5). Principal factor b is related to an oxygen atom with three bonds to hydrogen atoms and one bond to a deuterium atom (1b and 2b in Fig. 5, e.g., B4, E2, E3, and F5). Species 1b and 2b are not necessarily hydrogen bonded to one another (e.g., B4), but evolve simultaneously [they have the same probability, Eq. (14)]. Principal factor **c** is related to an oxygen atom with two bonds to hydrogen atoms and two bonds to deuterium atoms (1c, 2c, and 3c in Fig. 5, e.g., B5, B7, C5, and G3). Species 1c, 2c, and 3c are not necessarily hydrogen bonded to one another, but evolve simultaneously [Eq. (15) and (17)]. The concentration of specie 2c is four times that of specie 1c [Eq. (17)]. Principal factor **d** is related to an oxygen atom with one bond to a hydrogen atom and three bonds to deuterium atoms (species 2d and 3d in Fig. 5, e.g., B8, D8, D9, and G10). Species 2d and 3d evolve simultaneously [Eq. (16)]. Finally, principal factor e is related to an oxygen atom with four bonds to deuterium atoms, i.e., heavy water (specie 3e in Fig. 5, e.g., B9, B10, C8, and G8).

The probability model confirms that principal factor **b** [Fig. 4(A)] is related to a 1:1 H₂O–HDO mixture. In the same way, principal factor **d** [Fig. 4(A)] is related to a 1:1 D₂O–HDO mixture. Finally, principal factor **c** [Fig. 4(A)] is related to a 1:4:1 H₂O-HDO–D₂O mixture. This agrees with the composition that was ascribed to the five principal factors in Sec. III D 3 (Table III). The different types of water molecules that are included in principal factors **b**, **c**, and **d** are not necessarily hydrogen bonded to one another (Fig. 5).

IR spectroscopy allows a direct measurement of the species present in liquid solutions, as opposed to other methods, such as vapor pressure measurements³⁰ where solution composition is determined by indirect measurements. Five of the nine species anticipated were detected in the present experiments. With variations of temperature and/or pressure, the disproportionation effect could be made to yield values of α , β , and γ different from 1 (see Appendix A). Equations (14)– (17) would not be valid in that case, and all nine water species in the H₂O–D₂O mixtures could be sorted.

F. Thermodynamic equilibrium of H₂O–D₂O liquid mixtures

Equation (1) represents chemical equilibrium in the gas phase. For the liquid phase, with the five principal factors obtained by FA of the H₂O–D₂O mixtures, we calculated the total amount of H₂O, D₂O, and HDO; this permitted us to evaluate the equilibrium constant K_e [Eq. (2)] for different $\chi_{\rm D}$. These results are plotted in Fig. 7(A) (\bigcirc symbols), where the upper and lower curves from the median symbols are the error limits when an error level of ± 0.003 is applied on all MFs. The mean value of K_e was found to be 4.16 ± 0.30 in the 0.1 $< \chi_{\rm D} < 0.9$ range. Some concentrations were not obtained with sufficient precision outside these limits. The constant is, within experimental error, the same as that obtained by vapor measurements.²⁷⁻³⁰ However, since we know that there are more than three species in the solutions, this result has limited value other than for purposes of comparison.

The five principal species retrieved by FA from the mid-IR spectra of H₂O-D₂O mixtures, which are designated by the letters **a** to **e** [Fig. 4(A)], can be summarized as follows: **a**, H_2O (OH₄); **b**, HDO' (OH₃D); **c**, HDO° (OH_2D_2) ; **d**, HDO'' (OHD_3) ; and **e**, D_2O (OD_4) . The symbols in parentheses are the effective principal factors observed with IR. The notation OX_4 (where X=H or D) indicates that two bonds are covalent and two are hydrogen bonds. For example, the principal factor **b**, OH₃D, corresponds to two situations: (1) H-O-H (two OH covalent bonds) with two hydrogen bonds on the oxygen (one O···H and one O···D); (2) H-O-D (one OH and one OD covalent bonds) with two hydrogen bonds on the oxygen (two $O \cdots H$). In liquid water, proton hopping (or tunneling) occurs at a very fast rate,⁴⁴ so that the OH₃D grouping frequently passes from one situation to the other. Furthermore, due to the individual molecular rotation and proton hopping the three following equilibria take place in a H₂O–D₂O mixture:

$$OH_4 + OH_2D_2 \rightleftharpoons 2OH_3D, \tag{18}$$



FIG. 7. Experimental (\bigcirc) and theoretical values of the equilibrium constants (A) for the equilibrium Eq. (1); (B) equilibrium Eq. (18); (C) equilibrium Eq. (19); and (D) equilibrium Eq. (20) (see text). In (A), the high and low continuous lines from the central terms indicate the error margin.

$$OH_3D + OHD_3 \rightleftharpoons 2OH_2D_2, \tag{19}$$

$$OH_2D_2 + OD_4 \Longrightarrow 2OHD_3,$$
 (20)

whose equilibrium constants are

$$K_1 = \frac{[\mathrm{OH}_3\mathrm{D}]^2}{[\mathrm{OH}_4][\mathrm{OH}_2\mathrm{D}_2]},\tag{21}$$

$$K_2 = \frac{[\mathrm{OH}_2\mathrm{D}_2]^2}{[\mathrm{OH}_3\mathrm{D}][\mathrm{OH}\mathrm{D}_3]},\tag{22}$$

$$K_2 = \frac{[\text{OHD}_3]^2}{[\text{OH}_2\text{D}_2][\text{OD}_4]}.$$
 (23)

With the principal spectra normalized to the same concentration (55.13 M), the MFs are transformed into concentrations that can be substituted into Eqs. (21)–(23) to evaluate the three constants. The results are given in Figs. 7(B), 7(C), and 7(D), where the mean constant values are 2.65, 2.25, and 2.65 for K_1 , K_2 , and K_3 , respectively. The deviation points calculated where the concentrations of the species are low are not reliable (at the limits of the curves). The experimental values with their experimental errors fall on the theoretical ones (horizontal lines) calculated from the probability equations [Eqs. (5)–(13)]. This indicates that disproportionation is not observed on the mixture spectra, and justifies the approximation, $\alpha = \beta = \gamma = 1$, used in the present study.

 $OH_iD_{(4-i)}$ is an average description where all possible forms have almost equal probability because they change rapidly from one form to the other. For instance, OH_3D represents from time to time $H_2O-(H,D)$ or $HDO-(H)_2$, each one is transforming into the other by exchanging covalent bonds to hydrogen-bonds at the rate of ~1 ps.⁴⁴ In OH_3D grouping, there is an equal possibility that the two covalent bonds give either H_2O and HDO molecules (see details below for OH_2D_2 grouping). This is why the composition of **b** species was found to be 1:1 H_2O :HDO. Furthermore, from Eq. (6), (A3)–(A5) and considering $\alpha = \beta = \gamma = 1$, one obtains

$$P_{\rm H_2Ob} = 2\chi_{\rm D}(1-\chi_{\rm D})^3.$$
(24)

Equation (24) together with Eq. (14) gives the total probability of species \mathbf{b} ,

$$P_{\mathbf{b}} = 4\chi_{\rm D}(1 - \chi_{\rm D})^3.$$
(25)

Equation (25) exactly represents the probability of OH_3D grouping, that is the probability for an oxygen to be surrounded by three H and one D atoms. The transformation from $H_2O-(H,D)$ into $HDO-(H)_2$ through proton hopping in a chain of neighboring water molecules ("proton wires")^{45,46} at a rate in the order of 1 ps does not permit the spectral separation between both molecular species. This fast proton hopping could be partly responsible for the broadness of the OH stretch bands in liquid water (1 ps corresponds roughly to a bandwidth of 33 cm⁻¹). The same analysis can be applied to the five $OH_iD_{(4-i)}$ species, showing that

$$P_{a} = (1 - \chi_{D})^{4}, \tag{26}$$

$$P_{c} = 6\chi_{D}^{2}(1 - \chi_{D})^{2}, \qquad (27)$$

$$P_{d} = 4\chi_{D}^{3}(1 - \chi_{D}), \qquad (28)$$

and

$$\mathbf{P}_{\mathbf{e}} = \chi_{\mathbf{D}}^4. \tag{29}$$

The numerical results obtained with Eqs. (25)-(29) correspond exactly to the results obtained with Eqs. (5)–(13) for the five spectroscopic factor abundances. However, the $OH_iD_{(4-i)}$ representation indicates that the oxygen atom environments (i.e., the four atoms bonded to it: two covalent bonds and two hydrogen bonds) produce the spectroscopic species or entities which justify the equilibrium Eqs. (18)– (20). For example let H1, H2, D1, and D2 of the OH_2D_2 grouping be the four atoms that surround the oxygen. Two atoms make the covalent bonds which determine the molecule that produces the bending vibration. The six combinations possible for both covalent bonds are OH1H2, OH1D1, OH1D2, OH2D1, OH2D2, and OD1D2. The first molecule is H_2O , the four middle ones are HDO, and the last one is D_2O giving the ratio 1:4:1 that was found for the spectroscopic species c.





FIG. 8. Gaussian fitting in the OH and OD stretch regions of the principal spectra: (a) $H_2O(\equiv OH_4)$; (b) $HDO'(\equiv OH_3D)$; (c) $HDO^\circ(\equiv OH_2D_2)$; (d) $HDO''(\equiv OHD_3)$; (e) $D_2O(\equiv OD_4)$; (top) residues. Note that for OX_4 (where X=H or D) two bonds are covalent bonds and two are hydrogen bonds.

G. Band simulation and band assignments: Decomposition with Gaussian profiles

In an effort to obtain some spectroscopic evidence of the nine species in the H₂O-D₂O mixture solutions, we proceeded with the band simulation of the principal spectra. We started by fitting the band contours with Gaussian profiles. Although the Gaussian profile is not the best one to simulate IR spectra, it worked reasonably well in the case of H_2O-D_2O . We also tried the Voigt and the Lorentzian profiles, as well as products of the Gaussian and Lorentzian profiles. These proved no more useful than the Gaussian profile because the experimental bands are wide, intense, and composed of many components that are not all separated. Using all the spectral features as indicative of the presence of components as well as the bands observed in the far-IR spectra of liquid water and heavy water,47 we determined the number of components and their positions in the H2O-D2O principal spectra.

The simulation of the five principal spectra in the H_2O-D_2O mixtures is presented in Figs. 8 and 9 for the regions 5500–2000 cm⁻¹ and 2600–600 cm⁻¹, respectively. Spectra **a**, **b**, **c**, **d**, and **e** are for H_2O ($\equiv OH_4$), HDO' ($\equiv OH_3D$), HDO° ($\equiv OH_2D_2$), HDO" ($\equiv OHD_3$), D_2O ($\equiv OD_4$), respectively. [The OX₄ (where X=H or D) terms



FIG. 9. Gaussian fitting of the principal spectra in the combination and deformation: (a) $H_2O(\equiv OH_4)$; (b) $HDO'(\equiv OH_3D)$; (c) HDO° ($\equiv OH_2D_2$); (d) $HDO''(\equiv OHD_3)$; (e) $D_2O(\equiv OD_4)$; (top) residues. Same note as in Fig. 8.

were previously defined.] The position and assignment of the bands are given in Table V.

The low values of the residues given at the top of Figs. 8 and 9 are a sign that the spectrum simulations were reasonably good. While it is also clear that there is room left for improvement, this would require better quality spectra and many additional components (their number, band shapes, and bandwidths). We do not have access to this information at present for liquid water.

Nonetheless, the H_2O and D_2O spectra contain the same number of components with the bands of D_2O shifted relative to that of H_2O due to the isotopic displacement. The intermediate species **b** contains the spectra of HDO and H_2O , but with the components slightly displaced compared to the parent molecules. The same is true of species **d** that contains the spectra of HDO and D_2O . The species **c** contains the spectrum of HDO, D_2O , and H_2O with the components displaced from that of the four other species. We found no component that could be assigned to species other than the five observed.

IV. CONCLUSION

The molecules H_2O , HDO, and D_2O are present in the H_2O-D_2O solutions where they form a complex mixture. Each water molecule has two covalent bonds and can make

TABLE V. Position (in cm⁻¹), full width at half height (FWHH in cm⁻¹), and intensities (in ATR-IR abs. units) of the IR Gaussian components of liquid H_2O , HDO', HDO', HDO', HDO', and D_2O .

| | a: H ₂ O | | | b: HDO' | | | c: HDO ^o | | | d: HDO" | | | e: D ₂ O | | |
|--|---------------------|------|-------|----------|-------|-------|---------------------|------|-------|----------|------|-------|---------------------|------|-------|
| | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. |
| $\overline{\nu_3 + \nu_2 + \nu_{T1}}$ H ₂ O | 5160 | 240 | 0.015 | 5160 | 240 | 0.009 | | | | | | | | | |
| $2\nu_3 D_2 O$ | | | | | | | 5015 | 250 | 0.006 | | | | 5050 | 600 | 0.003 |
| $3\nu_2$ H ₂ O | 4920 | 240 | 0.005 | 4940 | 240 | 0.013 | | | | 4880 | 250 | 0.008 | | | |
| $3\nu_2 - \nu_{T1} H_2O$ | 4640 | 240 | 0.002 | 4640 | 240 | 0.005 | | | | | | | | | |
| $\nu_3 + \nu_{L,T} H_2 O$ | 4350 | 310 | 0.002 | 4350 | 310 | 0.006 | | | | 4410 | 310 | 0.004 | | | |
| $\nu_3 + \nu_{L1} H_2 O$ | 4000 | 310 | 0.010 | 4000 | 310 | 0.008 | 3880 | 310 | 0.012 | 4020 | 310 | 0.009 | | | |
| $3v_2 + v_{T1} D_2 O$ | | | | | | | | | | | | | 3833 | 170 | 0.015 |
| $\nu_3 + \nu_{L2} H_2 O$ | 3730 | 310 | 0.280 | 3735 | 310 | 0.018 | 3700 | 105 | 0.010 | 3760 | 310 | 0.013 | | | |
| $3\nu_2$ D ₂ O | | | | | | | 5700 | 105 | 0.010 | | | | 3660 | 200 | 0.004 |
| $v_1 + v_{12} H_2 O$ | 3620 | 105 | 0.280 | 3618 | 105 | 0.215 | 3601 | 105 | 0.221 | 3599 | 105 | 0.073 | 2000 | 200 | 0.001 |
| $v_1 + v_{12} + u_2 = 0$ | 3528 | 135 | 0.544 | 3522 | 141 | 0.490 | 3518 | 105 | 0.194 | 3529 | 105 | 0.062 | | | |
| $v_3 + v_{12} = D_2 O^2 v_{OU}$ | | | | | | | | | | | | | 3420 | 360 | 0.005 |
| V ₀ | | | | | | | 3426 | 191 | 0.880 | 3421 | 198 | 0.650 | 0.20 | 200 | 0.000 |
| v_2 H ₂ O v_{OII} | 3389 | 195 | 1.560 | 3389 | 198 | 1.330 | | | | | | | | | |
| , 3 1120, 7 OH | | | | | - / • | | 3300 | 196 | 0.862 | 3300 | 196 | 0.190 | | | |
| ν_1 H ₂ O | 3222 | 195 | 1.490 | 3236 | 198 | 0.950 | 3215 | 140 | 0.075 | | | | | | |
| 1 2 - | | | | | | | 3120 | 130 | 0.149 | 3135 | 135 | 0.063 | | | |
| $\nu_2 + \nu_{1T} D_2 O$ | | | | | | | | | | | | | 3070 | 270 | 0.006 |
| $v_1 - v_{T1} H_2 O$ | 3079 | 135 | 0.309 | 3079 | 135 | 0.140 | | | | | | | | | |
| $\nu_{1} - \nu_{11} = \frac{1}{2} = \frac{1}{2}$ | 2974 | 135 | 0.183 | 2974 | 135 | 0.150 | | | | | | | | | |
| $2\nu_2$ HOD | | | | | | | 2965 | 210 | 0.125 | 2955 | 165 | 0.061 | | | |
| $\nu_1 - \nu_{1,2}$ H ₂ O | 2840 | 135 | 0.067 | 2840 | 135 | 0.075 | 2826 | 120 | 0.018 | 2840 | 125 | 0.025 | | | |
| $\nu_2 + \nu_{12} D_2 O$ | | | | | | | | | | | | | 2820 | 200 | 0.021 |
| $\nu_3 - \nu_{11} H_2 O$ | 2685 | 135 | 0.027 | 2662 | 135 | 0.060 | | | | | | | | | |
| $\nu_2 + \nu_{T1} D_2 O$ | | | | | | | | | | 2684 | 55 | 0.030 | 2678 | 81 | 0.415 |
| $v_2 + v_{T2} D_2 O$ | | | | | | | 2620 | 135 | 0.395 | 2621 | 140 | 0.533 | 2618 | 81 | 0.363 |
| $v_1 - v_{11} H_2 O$ | 2583 | 115 | 0.021 | | | | | | | | | | | | |
| $\nu_1 D_2 O$ | | | | | | | | | | | | | 2546 | 141 | 1.290 |
| $\nu_{\rm OD}$ | | | | 2509.5 | 159 | 0.980 | 2491.5 | 164 | 1.372 | 2494 | 153 | 1.256 | | | |
| $\nu_{2} + \nu_{1T} H_{2}O$ | 2460 | 135 | 0.333 | | | | | | | | | | | | |
| $\nu_1 + \nu_{T1} D_2 O$ | | | | | | | | | | | | | 2476 | 81 | 0.603 |
| $\nu_1 D_2 O$ | | | | | | | 2397 | 140 | 0.400 | 2385.7 | 130 | 0.705 | 2393 | 141 | 1.640 |
| $\nu_2 + \nu_{11} H_2 O$ | 2340 | 135 | 0.023 | 2351 | 135 | 0.075 | | | | | | | | | |
| $v_1 - v_{T2} D_2 O$ | | | | | | | 2277 | 115 | 0.160 | 2260 | 95 | 0.160 | 2290 | 81 | 0.191 |
| | | | | 2288 | 156 | 0.052 | | | | | | | | | |
| $v_3 - v_{L2} D_2 O$ | | | | | | | | | | | | | 2232 | 81 | 0.180 |
| $v_1 - v_{L2} D_2 O$ | | | | | | | 2170 | 90 | 0.020 | 2155 | 90 | 0.037 | 2161 | 100 | 0.090 |
| $v_2 + v_{L2} + v_{T2}$ H ₂ O | 2115 | 350 | 0.140 | 2117 | 350 | 0.105 | 2114 | 250 | 0.065 | | | | | | |
| $v_3 - v_{L1} D_2 O$ | | | | | | | | | | 2071 | 180 | 0.047 | 2060 | 150 | 0.039 |
| $\nu_1 - \nu_{\rm IT} D_2 O$ | | | | | | | | | | | | | 1840 | 190 | 0.022 |
| 1 21 2 | | | | 1815 | 250 | 0.100 | 1844 | 280 | 0.107 | 1844 | 260 | 0.076 | | | |
| $\nu_2 + \nu_{T1} H_2 O$ | 1815 | 170 | 0.065 | | | | | | | | | | | | |
| $\nu_2 + \nu_{\rm LT} D_2 O$ | | | | | | | | | | | | | 1740 | 230 | 0.012 |
| | | | | | | | | | | 1721 | 95 | 0.021 | | | |
| $\nu_2 + \nu_{T2} H_2 O$ | 1710 | 85 | 0.183 | 1721 | 85 | 0.076 | 1700 | 65 | 0.058 | | | | | | |
| $\nu_2 H_2O$ | 1638 | 81 | 0.900 | 1649 | 80 | 0.560 | 1654 | 65 | 0.213 | | | | | | |
| $v_2 + v_{L2} + v_{T2} D_2 O$ | | | | | | | 1560 | 250 | 0.060 | 1567 | 160 | 0.088 | 1555 | 235 | 0.105 |
| $\nu_2 - \nu_{T2} H_2 O$ | 1551 | 85 | 0.220 | 1542 | 85 | 0.200 | 1583 | 65 | 0.052 | | | | | | |
| $\nu_2 + \nu_T$ HOD | | | | | | | 1515 | 67 | 0.100 | 1535 | 65 | 0.012 | | | |
| ν_2 HOD | | | | 1455 | 75 | 0.610 | 1446 | 76 | 0.540 | 1460.5 | 70 | 0.525 | | | |
| $\nu_2 - \nu_T$ HOD | | | | | | | 1407 | 65 | 0.050 | 1410 | 65 | 0.047 | | | |
| $\nu_2 - \nu_{T1} H_2 O$ | 1446 | 180 | 0.190 | | | | | | | | | | | | |
| | | | | 1379 | 140 | 0.185 | 1362 | 250 | 0.275 | 1368 | 210 | 0.156 | | | |
| $\nu_2 + \nu_{T1} D_2 O$ | | | | | | | | | | | | | 1344 | 180 | 0.046 |
| $\nu_2 + \nu_{T2} D_2 O$ | | | | | | | 1264 | 48 | 0.023 | 1267 | 48 | 0.064 | 1265 | 52 | 0.112 |
| $\nu_2 D_2 O$ | | | | | | | 1214 | 55 | 0.250 | 1211.6 | 50 | 0.556 | 1207 | 55 | 0.957 |
| $\nu_2 - \nu_{\rm L2} ~{\rm H_2O}$ | 1190 | 380 | 0.277 | 1157 | 420 | 0.260 | | | | | | | | | |
| $\nu_2 - \nu_{T2} D_2 O$ | | | | | | | 1156 | 48 | 0.050 | 1153 | 48 | 0.090 | 1154 | 52 | 0.115 |
| $\nu_2 - \nu_{T1} D_2 O$ | | | | | | | | | | | | | 1110 | 100 | 0.130 |
| | | | | | | | 1086 | 210 | 0.235 | 1085 | 210 | 0.155 | | | |
| | | | | | | | 970 | 100 | 0.055 | | | | | | |

TABLE V. (Continued.)

| | a: H ₂ O | | | b: HDO' | | | c: HDO ^o | | | C | i: HDO" | | e: D ₂ O | | |
|-------------------------------------|---------------------|------|-------|----------|------|-------|---------------------|------|-------|----------|---------|-------|---------------------|------|-------|
| | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. | Position | FWHH | Int. |
| $\overline{\nu_2 - \nu_{L1} H_2 O}$ | 950 | 170 | 0.169 | | | | | | | | | | | | |
| $v_2 - v_{L2} D_2 O$ | | | | | | | | | | 930 | 115 | 0.050 | 926 | 360 | 0.235 |
| | | | | | | | 813 | 260 | 0.278 | 838 | 350 | 0.165 | | | |
| $\nu_{\rm LT} \; {\rm H_2O}$ | 831 | 120 | 0.180 | 839 | 240 | 0.160 | | | | | | | | | |
| $v_2 - v_{L1} D_2 O$ | | | | | | | | | | | | | 785 | 100 | 0.039 |
| | | | | | | | | | | 719 | 180 | 0.480 | | | |
| $\nu_{\rm L1}~{\rm H_2O^a}$ | 686 | 344 | 2.470 | 613 | 341 | | | | | | | | | | |
| | | | | | | | 590 | 341 | 1.800 | 500 | 341 | 0.810 | | | |
| $\nu_{\rm LT}~{\rm D_2O}$ | | | | | | | | | | | | | 520 | 200 | 0.370 |
| $\nu_{L1} D_2 O^a$ | | | | | | | | | | | | | 449 | 340 | 1.240 |
| ν_{L2}^{a} | 395 | 300 | 0.850 | | | | | | | | | | 315 | 208 | 0.790 |
| ν_{t1}^{a} | 183 | 148 | 0.860 | | | | | | | | | | 177 | 140 | 0.830 |
| ν_{t2}^{a} | 50 | 80 | 0.170 | | | | | | | | | | 50 | 80 | 0.180 |

^aZelsmann (Ref. 47) from fitted components obtained from transmission measurements at 0 °C.

four H-bonds: two through the H or D and two with the oxygen. On the oxygen of a reference molecule (H₂O, HDO, and D₂O) are four bonds: two covalent and two H-bonds. Because of the hopping nature of the proton (and proton-D), the bonds are continually changing. The proximity of neighboring molecules causes nine different combination or species in the mixtures. These are: (1) H₂O-(H)₂; (2) H₂O-(H,D); (3) H₂O-(D)₂; (4) HDO-(H)₂; (5) HDO-(H, D); (6) HDO-(D)₂; (7) D₂O-(H)₂; (8) D₂O-(H,D); (9) D₂O-(D)₂. The abundances of the species depend on the initial concentrations of the parent molecules.

From the IR-ATR spectra of the 63 solutions that we took, five principal factors were retrieved by FA giving their spectra and their abundances. The four remaining species that could not be sorted evolve simultaneously with one or two others within one of the five principal factors. Species that evolve simultaneously cannot be sorted by FA. Of the nine species, seven are grouped into three spectroscopically different entities. These entities plus the two parent molecules (H₂O and D₂O) yield five principal irreducible orthogonal factors. These are (a) H₂O-(H)₂; (b) H₂O-(H,D) and HDO-(H)₂ in the 1:1 ratio; (c) H₂O-(D)₂, HDO-(H, D), and D₂O-(H)₂ in the ratio 1:4:1; (d) HDO-(D)₂ and D₂O-(H,D) in the ratio 1:1; and (e) D₂O-(D)₂.

An increase in the disproportionation between the species in the H_2O-D_2O solutions would lead to a better separation of all nine species. This could be obtained with better quality spectra through higher resolution and better temperature stability than the ones presented here. A temperature and/or pressure study might also retrieve all nine species. No hydrates in the sense of sequestering a particular arrangement were observed. As well, no cluster of pure HDO was observed. Consequently, the spectrum of HDO with some of the parent molecules could be observed and retrieved, but not the pure HDO spectrum.

The OH:OD stretch bands of light and heavy water are not very sensitive to the presence of HOD, but deformation bands are. These were found to be sensitive to the two hydrogen bonds on the oxygen atom of the reference molecule, but less sensitive to the hydrogen bond that the second neighbor makes with the third neighbors. In liquid water as observed by IR, the focus point is on the oxygen atom around which the protons (H or D) turn as in a merry-goround. The model of liquid water is made with OX_4 (with X=H or D). With the oxygen atom two X make two covalent bonds and two X make two hydrogen bonds. These four bonds are continually exchanging at a fast rate.

The nine different species present in the H_2O-D_2O solutions were modeled using a simple probabilistic model. Combining the species that evolve simultaneously gave the five principal factors that were spectroscopically identified. This result provides a better description of the liquid water situation than the three species previously identified. The five principal factors identified by their IR spectra and their abundances provide a good understanding of the species present in the solutions. This is important for those working with H_2O-D_2O mixtures in the preparation of biological and chemical samples, and for those who use infrared spectroscopy as an analytical tool for the quantification of heavy water in the nuclear industry.

APPENDIX A: DISPROPORTIONATION EFFECTS

Disproportionation effects have been reported in H_2O-D_2O mixtures with the equilibrium Eq. (1).²⁷⁻³⁰ These effects were determined by comparing the deviation of the equilibrium constant K_e [Eq. (2)] from the ideal value of 4, the value that would be obtained if both H and D atoms were found covalently linked to an oxygen atom with equal probability. In this Appendix, we will evaluate the effects of the reported disproprotionation on the concentration of the three types of water molecules in the H_2O-D_2O mixtures. Let us consider one liter of a mixture initially made up of *n* moles of H_2O and *m* moles of D_2O . The D molar fraction is given by $\chi_D = [D_2O]/([H_2O] + [D_2O])$, so that $\chi_D = m/(n+m)$. Let P_D and P_H be the probability that an atom attached to a given oxygen atom be deuterium or hydrogen, respectively. We then have

$$P_{\rm D} = \chi_{\rm D} \tag{A1}$$

and

$$\mathbf{P}_{\mathrm{H}} = 1 - \chi_{\mathrm{D}} \,. \tag{A2}$$

Therefore, the probability for a water molecule of the mixture at equilibrium to be H_2O , HDO or D_2O is given by

$$P_{\rm H_2O} = \alpha (1 - \chi_{\rm D})^2, \tag{A3}$$

$$P_{\rm HDO} = 2\beta \chi_{\rm D} (1 - \chi_{\rm D}), \qquad (A4)$$

$$P_{D_2O} = \gamma \chi_D^2, \tag{A5}$$

where α , β , and γ are correction functions of χ_D that have been introduced to take into account the disproprotionation in Eq. (1). Without it, $\alpha = \beta = \gamma = 1$. The equilibrium constant is then

$$K_e = \frac{[\text{HDO}]^2}{[\text{H}_2\text{O}][\text{D}_2\text{O}]} = \frac{(\text{P}_{\text{HDO}})^2}{\text{P}_{\text{H}_2\text{O}}\text{P}_{\text{D}_2\text{O}}}.$$
 (A6)

Using Eqs. (A3)–(A5), Eq. (A6) may be written as follows (excluding $\chi_D=0$ and 1):

$$4\beta^{2}\chi_{\rm D}^{2}(1-\chi_{\rm D})^{2} = K_{e}\alpha\gamma\chi_{\rm D}^{2}(1-\chi_{\rm D})^{2}.$$
 (A7)

At equilibrium, the solution is made up of H_2O , HDO or D_2O . Therefore,

$$P_{H_2O} + P_{HDO} + P_{D_2O} = \alpha (1 - \chi_D)^2 + 2\beta \chi_D (1 - \chi_D) + \gamma \chi_D^2 = 1.$$
(A8)

Let x be the number of moles of HDO obtained in a liter of the mixture at equilibrium. The number of remaining H₂O and D₂O moles are n-x/2 and m-x/2. Hence, we have

$$P_{H_2O} - P_{D_2O} = \frac{n - \frac{x}{2}}{n + m} - \frac{m - \frac{x}{2}}{n + m} = \frac{n - m}{n + m} = 1 - 2\chi_D.$$
(A9)

Combining Eqs. (A3), (A5), and (A9) one obtains

$$\gamma \chi_{\rm D}^2 = \alpha (1 - \chi_{\rm D})^2 - (1 - 2\chi_{\rm D}).$$
 (A10)

Combining Eqs. (A3), (A4), (A8), and (A10), one obtains

$$\beta \chi_{\rm D} = 1 - \alpha (1 - \chi_{\rm D}). \tag{A11}$$

Substituting Eqs. (A10) and (A11) into Eq. (A7) and solving for α , one obtains

$$\alpha = \frac{1 + \left(1 - \frac{K_e}{4}\right)(1 - 2\chi_{\rm D}) - \sqrt{\left[1 + \left(1 - \frac{K_e}{4}\right)(1 - 2\chi_{\rm D})\right]^2 - 4(1 - \chi_{\rm D})^2 \left(1 - \frac{K_e}{4}\right)}}{2(1 - \chi_{\rm D})^2 \left(1 - \frac{K_e}{4}\right)}.$$
(A12)

Functions β and γ are obtained by substituting Eq. (A12) into Eqs. (A11) and (A10). A numerical example of the correction functions α , β , and γ is presented in Fig. 10 for the case $K_e = 3.74$.²⁷ This example indicates that the correction functions are very close to unity, justifying the approximation obtained by using the direct probability relations ($\alpha = \beta = \gamma = 1$). By studying the limiting values of the function α when χ_D approaches 0 and 1, one obtains

$$\lim_{\chi_{\rm D}\to 0} \alpha = 1 \tag{A13}$$



$$\lim_{\chi_{\rm D}\to 1} \alpha = \frac{4}{K_e}.$$
 (A14)

In the same way,

$$\lim_{\chi_{\rm D} \to 0} \gamma = \frac{4}{K_e} \tag{A15}$$

and

$$\lim_{\chi_{\rm D}\to 1} \gamma = 1. \tag{A16}$$

Finally,

$$\lim_{\chi_D \to 0} \beta = \lim_{\chi_D \to 1} \beta = 1.$$
(A17)

The extreme value of β is obtained when $\chi_D = 0.5$ by

$$\beta_{\text{extreme}} = \beta_{(\chi_{\text{D}}=0.5)} = \frac{2}{1 + \sqrt{\frac{4}{K_e}}}.$$
 (A18)

From the above results, we calculated the concentration deviations for the different types of water molecule at the maximum deviation of HDO for which $\chi_D = 0.5$, yielding $\alpha = \gamma = 1.017$ and $\beta = 0.983$. These results indicate a concen-



FIG. 10. Correction functions α , β , and γ when the disproportionation function K_e is 3.74 (see text).

tration variation of 1.7% compared to no disproportionation. The approximation obtained with $\alpha = \beta = \gamma = 1$ gives a deviation for the MFs of $0.25 \times 0.017 = 0.004$ for H₂O and D_2O , and $0.5 \times 0.017 = 0.008$ for HDO. These deviations are within our experimental errors. A temperature stability better than 0.05 K would be needed to observe the disproportionation effect in H₂O-D₂O mixtures.

APPENDIX B: "FREE" OH IN AQUEOUS SOLUTIONS

From a near-IR study of methanol–water mixtures, it has been reported that around 13% of liquid water OH are nonhydrogen bonded and constitute "free" OH.48 This amount represents a high quantity of defects in the liquid water network. Roughly (13 M/50 M=) 26% of the water molecules would have only three hydrogen bonds. Using the integrated intensity of the O-H stretching vibrations in the gas phase which is about 7% of that in the liquid,⁴⁹ the determination of the structure of acetonitrile-water mixtures was made.⁵⁰ Recent work in our laboratory on the same mixtures showed that the molar O-H stretching integrated intensity remained approximately constant throughout the solubility range (unpublished). This indicates that very little free OH groups are in the aqueous solutions. Although this important issue cannot be settled here, a rough estimate would indicate that less than 1% of the water molecules have less than four hydrogen bonds. Work is in progress on this system and others to answer this fundamental question of the quantity of free OH in aqueous solutions.

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- $^{39}\mbox{Because species }\mbox{H}_2\mbox{Ob}$ and HDOb are present simultaneously, they were identified as H2O·HDO when first observed as a spectroscopic species. However, as shown in Sec. III E 2, species H₂Ob and HDOb are always present in the same proportion, but they are not necessarily hydrogen bonded together (see case F5 in Fig. 5). This indicates that the two species do not form a pair (or a hydrate), and justifies the label HDO' rather than H₂O·HDO.
- 40 At $\chi_D \!=\! 0.497,$ the mixture contains the maximum amount of HDO which gives the most intense spectrum of this species.
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