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Infrared spectroscopy of acetone–water liquid mixtures. II. Molecular model

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In aqueous acetone solutions, the strong bathochromic shifts observed on the OH and CO stretch infrared (IR) bands are due to hydrogen bonds between these groups. These shifts were evaluated by factor analysis (FA) that separated the band components from which five water and five acetone principal factors were retrieved [J. Chem. Phys. **119**, 5632 (2003)]. However, these factors were abstract making them difficult to interpret. To render them real an organization model of molecules is here developed whose abundances are compared to the experimental ones. The model considers that the molecules are randomly organized limited by the hydrogen bond network formed between the water hydrogen atoms and the acetone or water oxygen atoms, indifferently. Because the oxygen of water has two covalent hydrogen atoms which are hydrogen-bonded and may receive up to two hydrogen atoms from neighbor molecules hydrogen-bonded to it, three types of water molecules are found: OH_2, OH_3, and OH_4 (covalent and hydrogen bonds). In the OH stretch region these molecules generate three absorption regimes composed of ν_3, ν_1, and their satellites. The strength of the H-bond given increases with the number of H-bonds accepted by the oxygen atom of the water H-bond donor, producing nine water situations. Since FA cannot separate those species that evolve concomitantly the nine water situations are regrouped into five factors, the abundance of which compared exactly to that retrieved by FA. From the factors' real spectra the OH stretch absorption are simulated to, respectively, give for the ν_3 and ν_1 components the mean values for OH_2, 3608, 3508; OH_3, 3473, 3282 and OH_4, 3391, 3223 cm^{-1}. The mean separations from the gas-phase position which are respectively about 150, 330, and 400 cm^{-1} are related to the vacancy of the oxygen electron doublets: two, one, and zero, respectively. No acetone hydrate that sequesters water molecules is formed. Similarly, acetone produces ten species, two of which evolve concomitantly. Spectral similarities further reduce these to five principal IR factors, the abundance of which compared adequately to the experimental results obtained from FA. The band assignment of the five-acetone spectra is given.
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I. INTRODUCTION

The molecular spectroscopic study of aqueous acetone presented in Paper I (hereafter I) showed that this system, though apparently simple, is very complex.[1] There, the experimental attenuated total reflectance (ATR-IR) spectra of three series of solutions—low, intermediate, and high water contents—were reported. Factor analysis (FA) using spectral windowing retrieved ten principal factors (five water and five acetone). The ten factors evolving independently as a function of concentration must be considered separately to determine the molecular organization of the mixture. This could not be done in Paper I because the ten principal factors retrieved did not represent pure species (different the ones from the others) and the multiplying factors (MFs, related to the species abundances or concentrations) were abstract.

Because FA cannot separate concomitant evolving species, the ten factors retrieved represent the minimum number of species in the system. In order to determine the exact number of species in the solutions and interpret the different IR factors retrieved by FA, we evaluate the mixtures by considering the water and acetone molecules in a random organization, constrained only by the hydrogen bonding between the molecules: all labile hydrogen atoms are H-bonded to oxygen from either acetone or water. In this system, the water molecules are twice H-bond donors and twice H-bond acceptors while the acetone molecules are only twice H-bond acceptors. The species distributions as a function of concentration are determined. After regrouping the species that evolve concomitantly and whose spectra are differently perturbed, the number of spectroscopically different species and their abundances are determined. The resulting distributions are compared with the MFs obtained from FA of the IR spectra. This operation will ensure that the ten principal factors are exclusive the ones from the others and that their MFs are real. This provides real spectra that are used to determine the molecular organization of the species.

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II. THEORETICAL CONSIDERATIONS

A. Factor analysis (FA): Orthogonalization procedure

Experimental spectra are obviously real. The first step in the FA procedure aimed to retrieve the principal factors necessary to describe the entire set of experimental spectra was reported in I. The principal spectra retrieved by FA by separating water and acetone absorption (Figs. 6 and 8 in I) are real spectra that are not necessarily exclusive one from the others. In other words, these spectra are not spectra of orthogonal species or factors. (The expression ''orthogonal spectra'' cannot be used because the integral of the product of two real spectra is not zero, see Appendix A.) In order to give a molecular interpretation to the isolated species, it is necessary to have spectra of orthogonal factors so that the band assignments are unique. Therefore, a second step is necessary to render them orthogonal and the MFs real. Although orthogonal factors are not necessary for FA to work, they are necessary to interpret the results in terms of molecular organizations since orthogonalization generates real abundances and real spectra of pure species.

Simple procedures are not effective in obtaining these orthogonal factors. Consequently, more elaborate procedures are needed. First, given the number of principal factors separated by FA, it is necessary to develop a predictive model that consists of identifying the spectral characteristics of the different species. Note that these species are by definition orthogonal species since they are exclusive one from the others. Using these orthogonal species, the expected MFs (from the equilibrium between them) are calculated. Since FA cannot separate species that evolve concomitantly, their MFs must be added to form a single factor that can be compared to the experimental one. From the obtained MFs' distribution, the spectra of the principal orthogonal factors are obtained from the set of experimental spectra and the whole series of experimental MFs recalculated (see Appendix B). Finally, calculated and experimental MF series are compared. When a close match between them is obtained, the FA procedure that gives real MFs and spectra of orthogonal factors is complete.

B. Determination of the water and acetone species and their abundances

In I, factor analysis applied with spectral windowing on aqueous acetone spectra yielded five water and five acetone principal spectra. These were identified in the OH and C═O stretch regions, respectively. The strong overlap between water ν_2 and acetone ν_3 prevented us from using the water deformation region. In the following, a detailed analysis of the perturbing factors acting on the two OH stretch modes of water is presented.

1. Determination of the water species

The different water species that can be separated by FA were determined by considering the environmental factors that influence the O–H stretching vibrations. The water O–H stretch bands, which are due primarily to the vibration of the covalent bond formed by the hydrogen and oxygen atoms, are situated in the 3400 cm^{-1} region. Compared to the gas-phase situation, the spectrum of liquid water is considerably modified due to the formation of a hydrogen bond network. From the lone molecule situation (gas phase), the hydrogen bonding in liquid water strongly red-shifts the O–H stretch band about 400 cm^{-1} (or ~0.88 times), accompanied by a considerable increase in intensity.[2–6] Breaking or weakening some hydrogen bonds decreases the red shift and the intensity.[7] The liquid water OH red shift can be compared to that of the isotopic shift: Substituting D for H red-shifts the band by about 1000 cm^{-1} (or ~0.7 times), while substituting ^{18}O for ^{16}O shifts the band by about 200 cm^{-1} (or ~0.94 times).

Although the OH groups act as H-bond donors, the OH stretch band shifts considerably to higher frequencies (from the pure water position) when the water oxygen does not accept any H-bond (leaving two free electron pairs on the oxygen atom). In I, we concluded that the hydrogen bonds accepted by the water oxygen strongly weaken its two OH valence bonds. This must be considered when analyzing the OH stretch band displacements. Therefore, depending on the number of hydrogen bonds accepted by the water molecules, these can be divided into three types of water species—OH_2, OH_3, and OH_4 (covalent and hydrogen bonds considered)—that generate three absorption regimes.[8]

Since FA retrieved five principal water factors, the three types of water species must be further divided by considering the situation of the next neighbors. A central water molecule whose two hydrogen atoms are hydrogen-bonded (being H-bond donors) to the oxygen atoms of two neighboring molecules that can either be water or acetone. Since the latter H-bond acceptors already accept one H-bond each (from the central water molecule), the oxygen of these molecules can accept one or two H-bonds, giving each of the three types of water species three subspecies: (1,1), (1,2), or (2,2), for a total of nine water species (Table I). In this Table, the water species are identified as e_1 to e_9, along with their species abbreviation $H_2O^{i\,j\,k}$, where *i*, which can be 0, 1, or 2, represents the number of H-bonds *accepted* by the central molecule (H_2O) and *j* and *k*, which can be 1 or 2 (since these molecules already accept one H-bond from the central H_2O molecule), those *accepted* by its two H-bond acceptors molecules. Figure 1 illustrates the scheme of water species e_5 ($H_2O^{1\,1\,2}$ in the ellipse). This water molecule accepts one H-bond (from another water molecule) and gives two H-bonds to surrounding water or acetone molecules. Four combinations are possible. Acetone and water as H-bond acceptors are inscribed in trapezoids and square boxes, respectively (only the significant H-bonds are drawn). The squares and trapezoids are interchangeable without modifying the central water molecule spectral characteristics. In solution, as water concentration increases, water increasingly turns into H-bond acceptors, the oxygen of which can accept one or two H-bonds.

2. Calculation of the abundances of the different water species

To form an ideal solution with water, a solvent must accept H-bonds from water as easily as water itself. Since acetone and water are completely miscible, we make the fol-

TABLE I. Different water species in aqueous acetone.

Species	Number of H-bonds accepted by the central HOH i (=0, 1 or 2)	Number of H-bonds accepted by the O^j neighbor (O^j acceptor: water or acetone) j (=1 or 2)	Number of H-bonds accepted by the O^k neighbor (O^k acceptor: water or acetone) k (=1 or 2)	Species symbol[a] $H_2O^{i\,j\,k}$
e_1	0	1	1	$H_2O^{0\,1\,1}$
e_2	0	1	2	$H_2O^{0\,1\,2}$
e_3	0	2	2	$H_2O^{0\,2\,2}$
e_4	1	1	1	$H_2O^{1\,1\,1}$
e_5[b]	1	1	2	$H_2O^{1\,1\,2}$
e_6	1	2	2	$H_2O^{1\,2\,2}$
e_7	2	1	1	$H_2O^{2\,1\,1}$
e_8	2	1	2	$H_2O^{2\,1\,2}$
e_9	2	2	2	$H_2O^{2\,2\,2}$

[a] i from column 2; j and k from column 3 and 4, respectively.
[b] Illustrated in Fig. 1.

lowing hypothesis: Water and acetone oxygen atoms are equivalent hydrogen bond acceptors. Such a postulate was made to explain the methanol–water mixtures.[9] With this postulate, the different water species abundances are calculated from a probabilistic mixture of water and acetone molecules. The probability (equivalent to the molar fraction) of the nine water species in the water–acetone system (Table I) is obtained with

$$P_{H_2O^{i,j,k}} = P_{H_2O^i} \times \frac{P_{O^j} P_{O^k}}{P^2_{O^2} + P^2_{O^1} + P_{O^1} \times P_{O^2}}, \tag{1}$$

where $P_{H_2O^i}$ is the probability of the central water accepting i H-bonds (that is to have $2-i$ lone pairs of electrons on its oxygen atom), and P_{O^j} and P_{O^k} are the probabilities of neighbor H-bond acceptor oxygen atoms, either water or acetone, accepting j and k H-bonds, respectively. Because of the symmetry of water, the denominator in Eq. (1) represents the only three different cases (j,k) that can be separated, which are (1,1), (1,2), and (2,2).

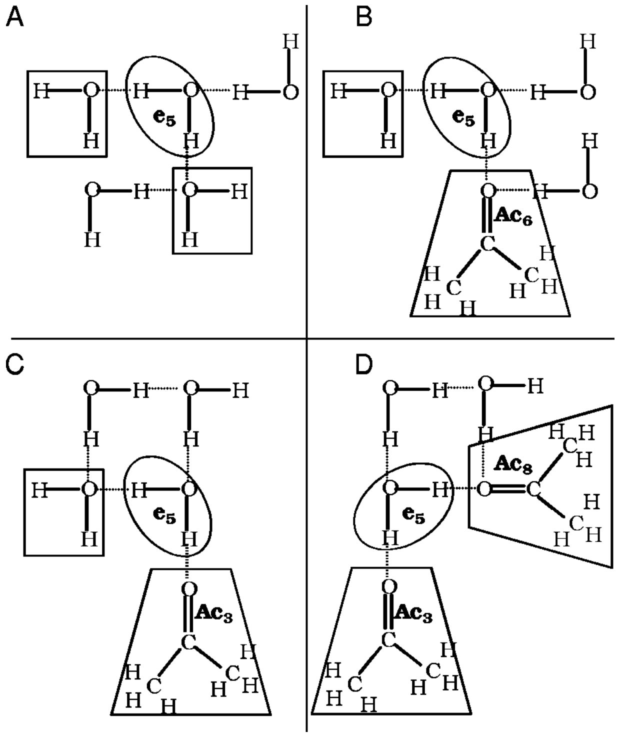

FIG. 1. Two-dimensional representation of the four possible configurations of water species e_5 ($H_2O^{1,1,2}$) in aqueous acetone, see Table I.

Since the acetone and water oxygen atoms are equivalent in their ability to accept H-bonds from water, the oxygen atoms accepting i H-bonds are distributed between water and acetone following their molar fraction, that is

$$P_{H_2O^i} = \chi_w \times P_{O^i}, \tag{2}$$

where P_{O^i} is the probability of an oxygen atom (from acetone or water) accepting i H-bonds. To evaluate P_{O^i}, we consider that for the central water molecule and its neighbors there is no *a priori* reason for all three oxygen atoms (O^i where $i=0,1,2$) to have the same probability. Consequently, the equilibrium between the oxygen atoms and its equilibrium constant are subject to disproportionation, giving the following relations:

$$(-O^2) + (-O^0) \rightleftharpoons 2(-O^1), \tag{3}$$

$$K_O = \frac{[-O^1]^2}{[-O^2][-O^0]}, \tag{4}$$

without and with disproportionation, the equilibrium constant, K_O, will be equal or different than 4, respectively.

Although the idea that all labile hydrogen atoms will form H-bonds when enough acceptors are present is still the object of debate,[5] we consider it valid for the acetone–water mixture in the whole concentration range. This is verified below.

Let r_H be the ratio of the number of H-bond donors over H-bond acceptors in the mixture. The case that represents an excess H-bond acceptor situation is evaluated by $r_H \leqslant 1$. We have

$$r_H = \frac{[H]}{\Sigma_z z \times [O^z]} = \frac{2[H_2O]}{2[Ac] + 2[H_2O]} = \frac{c_w}{c_{Ac} + c_w} = \chi_w, \tag{5}$$

TABLE II. Distribution of the water species in aqueous acetone into principal factors.

Species	Species abbreviation[a] $H_2O^{i\ j\ k}$	Number of H-bonds accepted $=i+j=k$	Principal factor		Species proportion in one factor
			Water type[b]	Symbol	
e_1	$H_2O^{0\,1\,1}$	2	$OH_2\}$	w_1	
e_2	$H_2O^{0\,1\,2}$	3	OH_2	w_2	1
e_4	$H_2O^{1\,1\,1}$	3	OH_3		K_O
e_3	$H_2O^{0\,2\,2}$	4	OH_2	w_3	1
e_5	$H_2O^{1\,1\,2}$	4	OH_3		K_O
e_7	$H_2O^{2\,1\,1}$	4	OH_4		K_O
e_6	$H_2O^{1\,2\,2}$	5	OH_3	w_4	1
e_8	$H_2O^{2\,1\,2}$	5	OH_4		1
e_9	$H_2O^{2\,2\,2}$	6	$OH_4\}$	w_5	

[a] From Table I.

[b] The subscripts indicate the number of H (valence and H-bond) attached to the oxygen atom.

where [H] represents the labile hydrogen concentration, z the number of H-bonds that the different oxygen can accept, c_w and c_{Ac} the water and acetone concentrations and χ_w the water molar fraction. The probability of oxygen being of the three different types is

$$P_{\mathrm{O}^0}=\alpha(1-\chi_w)^2, \tag{6}$$

$$P_{\mathrm{O}^1}=2\times\beta\chi_w(1-\chi_w), \tag{7}$$

$$P_{\mathrm{O}^2}=\gamma\chi_w^2, \tag{8}$$

where α, β, and γ are disproportionation functions.[10] Equation (4) is related to Eqs. (6)–(8) by

$$K_{\mathrm{O}}=\frac{(P_{\mathrm{O}^1})^2}{P_{\mathrm{O}^2}\times P_{\mathrm{O}^0}}. \tag{9}$$

Equations (6)–(9) have previously been reported for the disproportionation between H and D in the H_2O–D_2O mixtures.[10] Equations (1) and (2) give

$$P_{H_2O^{1,1,1}}=\chi_w\times\frac{(P_{\mathrm{O}^1})^3}{P_{\mathrm{O}^2}^2+P_{\mathrm{O}^1}^2+P_{\mathrm{O}^1}\times P_{\mathrm{O}^2}} \tag{10}$$

and

$$P_{H_2O^{0,1,2}}=\chi_w\times\frac{P_{\mathrm{O}^0}\times P_{\mathrm{O}^1}\times P_{\mathrm{O}^2}}{P_{\mathrm{O}^2}^2+P_{\mathrm{O}^1}^2+P_{\mathrm{O}^1}\times P_{\mathrm{O}^2}}. \tag{11}$$

Combining Eqs. (9)–(11), one obtains

$$\frac{P_{H_2O^{1,1,1}}}{P_{H_2O^{0,1,2}}}=K_{\mathrm{O}}. \tag{12}$$

This relation indicates that species $H_2O^{1,1,1}$ and $H_2O^{0,1,2}$ (e_4 and e_2, Table I) evolve together and cannot be separated by FA. They give the principal factor w_2. In the same way, we have

$$\frac{P_{H_2O^{1,1,2}}}{P_{H_2O^{2,1,1}}}=\frac{P_{H_2O^{2,1,2}}}{P_{H_2O^{1,2,2}}}=1 \tag{13}$$

and

$$\frac{P_{H_2O^{1,1,2}}}{P_{H_2O^{0,2,2}}}=K_{\mathrm{O}}. \tag{14}$$

Equations (12)–(14) indicate that several water species remain in the same proportion throughout the whole mixing range so that FA cannot sort them out. These water species must be regrouped into a single principal factor. As a result, the nine water species described in Table I give the five principal factors in Table II. FA can sort these.

Taking from Ref. 10 the disproportionation functions

$$\alpha=\frac{1+\left(1-\frac{K_{\mathrm{O}}}{4}\right)(1-2\chi_w)-\sqrt{\left[1+\left(1-\frac{K_{\mathrm{O}}}{4}\right)(1-2\chi_w)\right]^2-4(1-\chi_w)^2\left(1-\frac{K_{\mathrm{O}}}{4}\right)}}{2(1-\chi_w)^2\left(1-\frac{K_{\mathrm{O}}}{4}\right)}, \tag{15}$$

$$\beta\chi_w=1-\alpha(1-\chi_w), \tag{16}$$

$$\gamma\chi_w^2=\alpha(1-\chi_w)^2-(1-2\chi_w), \tag{17}$$

and Eqs. (1) and (2), the nine water species (Table I) probabilities (≡molar fractions) were calculated. From the comparison between the experimental results and the theoretical calculations, K_{O} was found to be 2.5. With this value, the species probabilities obtained are illustrated in Fig. 2.

Figure 2(A) displays the probability of species e_1 (water

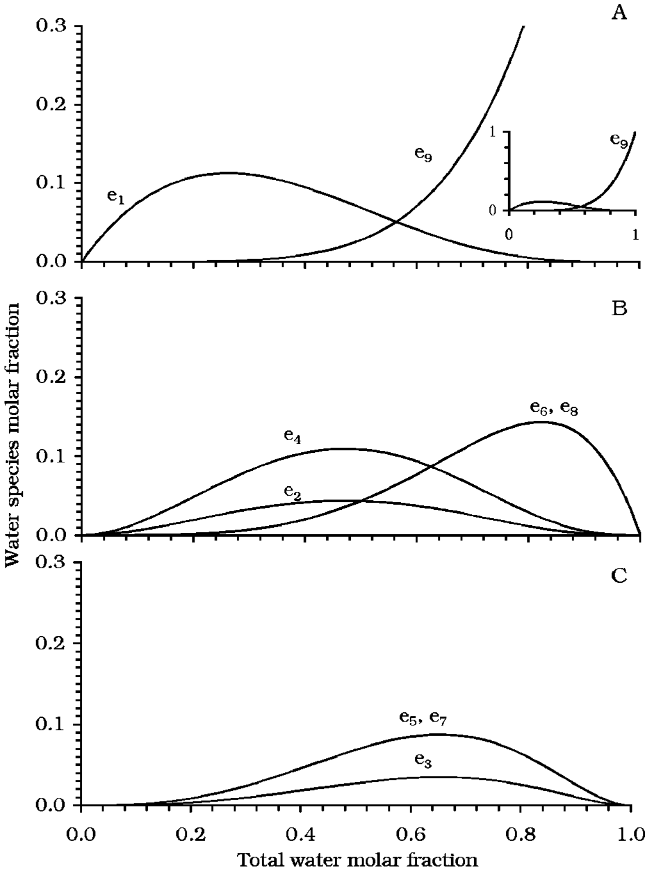

FIG. 2. Probability (≡ in molar fraction) of the nine water species (e_1–e_9) in the acetone–water mixtures as a function of total water molar fraction (see text). Note: Species e_6 and e_5 have the same probabilities as species e_8 and e_7, respectively.

isolated in acetone) and e_9 (pure water). From Eq. (12), the ratio of species e_2 to e_4 is 2:5 [Fig. 2(B)]. From Eq. (13), that of species e_6 to e_8 is 1:1 [Fig. 2(B)]. Finally, from Eqs. (13) and (14), the ratio of species e_3 to e_5 to e_7 is 2:5:5 [Fig. 2(C)]. Figure 2 clearly shows the evolving characteristics of each species. In Table II, the species (e_1 to e_9) with similar evolving patterns are combined and related to the experimental factors (w_1 to w_5). The nine species provide five factors.

3. Acetone species determination

Similarly, the different acetone species that can be separated by FA were determined by considering the environmental factors that influence the acetone carbonyl stretching vibration. In I, FA applied to the acetone 1800–700 cm^{-1} spectral region gave five principal acetone factors, their relative abundances and molar spectra [in I, Figs. 8(B) and 8(A), respectively]. These results dealt with spectra of nonexclusive factors (which do not represent pure species or factors). Although exclusive factors are not necessary for FA to work, they are necessary to obtain the pure component spectra in order to interpret them. A detailed analysis of the perturbing factors affecting the acetone carbonyl vibration is made in the following section.

The 1731 cm^{-1} of the acetone (abbreviated in some cases as Ac) carbonyl in the gas phase[11] is red-shifted to 1712 cm^{-1} (ATR position) in pure liquid. It is assumed that dipole–dipole intermolecular interaction, being the sole possibility, is responsible for this shift.[12] On the other hand, when labile hydrogen atoms are available, they strongly perturb the CO stretch vibrations whose IR bands are red-shifted from the liquid acetone position.[13] In aqueous mixtures, water is the only molecule that can provide these labile hydrogen atoms. Two mechanisms are responsible for a bathochromic shift: Dipole–dipole interactions and H-bondings. Based on these premises, we divided the acetone molecules into three types of species, depending on the number of H-bonds accepted by the acetone carbonyl, AcCO^0, AcCO^1, and AcCO^2, for respectively, 0, 1, and 2 H-bonds accepted.

Since five principal acetone factors were retrieved by FA, the three types of acetone species had to be further divided. The acetone carbonyl group can accept two H-bonds. In aqueous acetone, these come from water whose oxygen atom can also accept 0, 1, or 2 H-bonds. The resulting ten different possible situations are identified in Table III (Ac$_1$ to Ac$_{10}$).

4. Calculation of the abundance of the different acetone species

Similarly to the case of the water species, the acetone species occurrences were evaluated from their solution prob-

TABLE III. Different acetone species in aqueous acetone.

Species	Number of H-bonds accepted by acetone i (=0, 1 or 2)	Number of H-bonds accepted by O^j neighbor j (=0, 1 or 2)	Number of H-bonds accepted by O^k neighbor k (=0, 1 or 2)	Species symbol AcCO$^{i\,j\,k}$	Degree of perturbation on ν_{CO} $(i+j+k)$
Ac$_1$ (pure acetone)	0	NA[a]	NA[a]	AcCO^0	0
Ac$_2$	1	0	NA[a]	AcCO$^{1\,0}$	1
Ac$_3$	1	1	NA[a]	AcCO$^{1\,1}$	2
Ac$_4$	1	2	NA[a]	AcCO$^{1\,2}$	3
Ac$_5$	2	0	0	AcCO$^{2\,0\,0}$	$(1+1=)2$
Ac$_6$	2	0	1	AcCO$^{2\,0\,1}$	$(1+2=)3$
Ac$_7$	2	0	2	AcCO$^{2\,0\,2}$	$(1+3=)4$
Ac$_8$	2	1	1	AcCO$^{2\,1\,1}$	$(2+2=)4$
Ac$_9$	2	1	2	AcCO$^{2\,1\,2}$	$(2+3=)5$
Ac$_{10}$ (lone acetone in water)	2	2	2	AcCO$^{2\,2\,2}$	$(3+3=)6$

[a] NA, not appropriate.

ability. For the formation of hydrogen bonds, the premises used for water (Secs. 1 and 2) were used for acetone: (a) The number of H-bonds accepted by the oxygen (acetone or water) determines their ability to form H-bonds; (b) all three types of O^i ($i=0,1,2$) are in equilibrium [Eq. (3)], giving constant K_O [Eq. (4)]. Evaluating the probability ($\equiv$ molar fraction) of the ten species (Table III), we have

$$P_{AcO^{i,j,k}}=P_{AcO^i}\Bigg[1-\Bigg(\{1-\delta_{2,i}-\delta_{0,i}\}\Bigg\{1-\frac{P_{H_2O^i}}{P_{H_2O}}\Bigg\}\Bigg)\Bigg]$$

$$\times\Bigg[1-\Bigg(\{1-\delta_{0,i}-\delta_{1,i}\}$$

$$\times\Bigg\{1-\frac{P_{H_2O^i}\times P_{H_2O^k}}{\Sigma(P_{H_2O^i}\times P_{H_2O^k})}\Bigg\}\Bigg)\Bigg], \tag{18}$$

where P_{AcO^i}, $P_{H_2O^i}$, and P_{H_2O} are the probabilities for acetone and water species, and water of any type, respectively. The symbol $\delta_{j,k}$ is the Kronecker symbol ($=0$ when $k\neq j$, and 1 when $k=j$) and

$$\Sigma(P_{H_2O^j}\times P_{H_2O^k})=P^2_{H_2O^0}+P^2_{H_2O^1}+P^2_{H_2O^2}+P_{H_2O^0}$$

$$\times P_{H_2O^1}+P_{H_2O^0}\times P_{H_2O^2}$$

$$+P_{H_2O^1}\times P_{H_2O^2}. \tag{19}$$

Using Eq. (2), Eq. (18) becomes

$$P_{AcO^{i,j,k}}=(1-\chi_w)P_{O^i}[1-\{(1-\delta_{2,i}-\delta_{o,i})$$

$$\times(1-P_{O^i})\}]\Bigg[1-\Bigg\{(1-\delta_{0,i}-\delta_{1,i})$$

$$\times\Bigg(1-\frac{P_{O^j}\times P_{O^k}}{\Sigma(P_{O^i}\times P_{O^k})}\Bigg)\Bigg\}\Bigg], \tag{20}$$

where $\Sigma(P_{O^j}\times P_{O^k})$ is defined in the same way as $\Sigma(P_{H_2O^j}\times P_{H_2O^k})$ following Eq. (19).

Using value $K_O=2.5$ previously determined and Eqs. (19) and (20) as well as those in Sec. 2, the ten acetone species relative probabilities ($\equiv$molar fraction) were calculated. These are presented in Fig. 3.

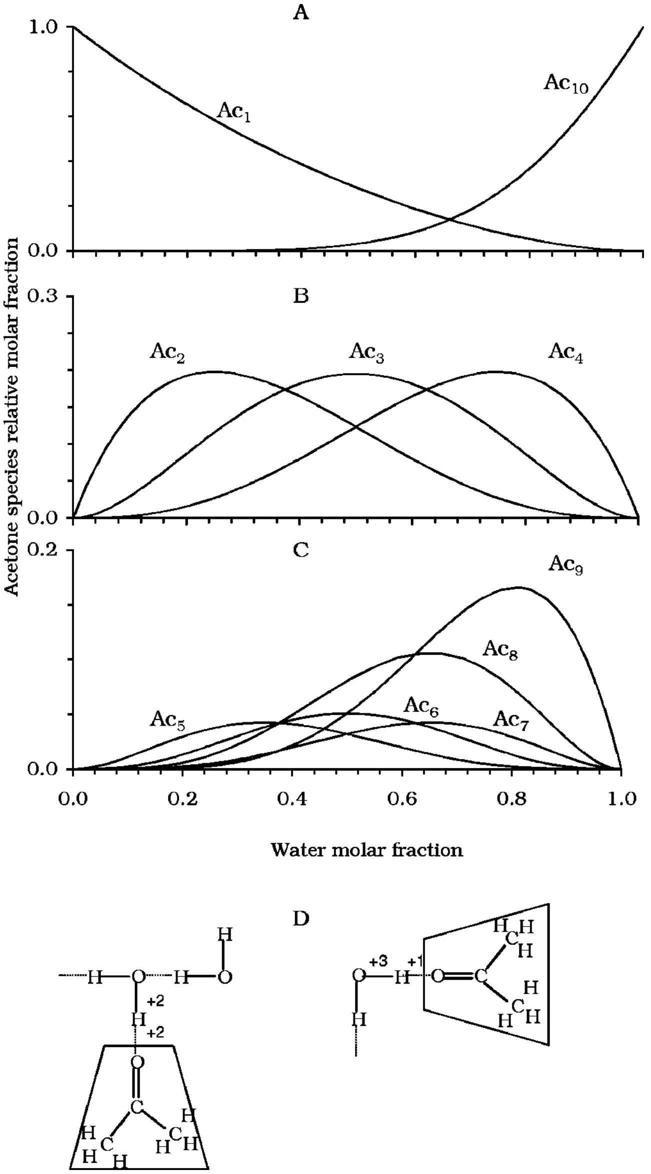

FIG. 3. Acetone species in aqueous acetone. A–C, probabilities of the ten species (Ac_1-Ac_{10}) as a function of total water molar fraction (see text). D, two examples in a two-dimensional representation of situations where a C═O bond is submitted: Left, to a "+2" perturbation (Ac_3) and right to a "+1" perturbation (Ac_2) (see text).

5. Recombination of the acetone species

Since five acetone factors were observed, the ten acetone species had to be recombined. After similar development, as in Sec. 2, we obtain

$$\frac{P_{AcO^{2,1,1}}}{P_{AcO^{2,0,2}}}=\frac{[Ac_8]}{[Ac_7]}=K_O. \tag{21}$$

Being related by a constant, the two species in Eq. (21) evolve simultaneously and must be recombined. The ten species give nine observables. However, since the red shift of the carbonyl group is much less important than that of the OH group (34 versus 433 cm^{-1}) it indicates that the nine observables are restricted to a small spectral region. This will limit their separations by FA. Figure 3 shows that the abundances of species Ac_5 and Ac_6 are low (<5%) and species Ac_4 and Ac_3 evolve almost simultaneously as Ac_9 and Ac_6, respectively. We regroup these species to give six factors. Since this number is one more than the five retrieved, a particular strategy was developed so that the comparison of the FA results could be made with the probabilistic model. The strategy will unfold later.

III. EXPERIMENT

ATR-Fourier-transform infrared (FTIR) spectral data of aqueous acetone used in the present study were reported in I.

IV. RESULTS AND DISCUSSION

Sixteen of the 27 spectra of water–acetone mixtures in the entire solubility range are presented in Figs. 4(A)–4(C). In I, FA was applied to the 4000–1800 cm^{-1} region where water absorbs strongly and acetone absorbs weakly, and to

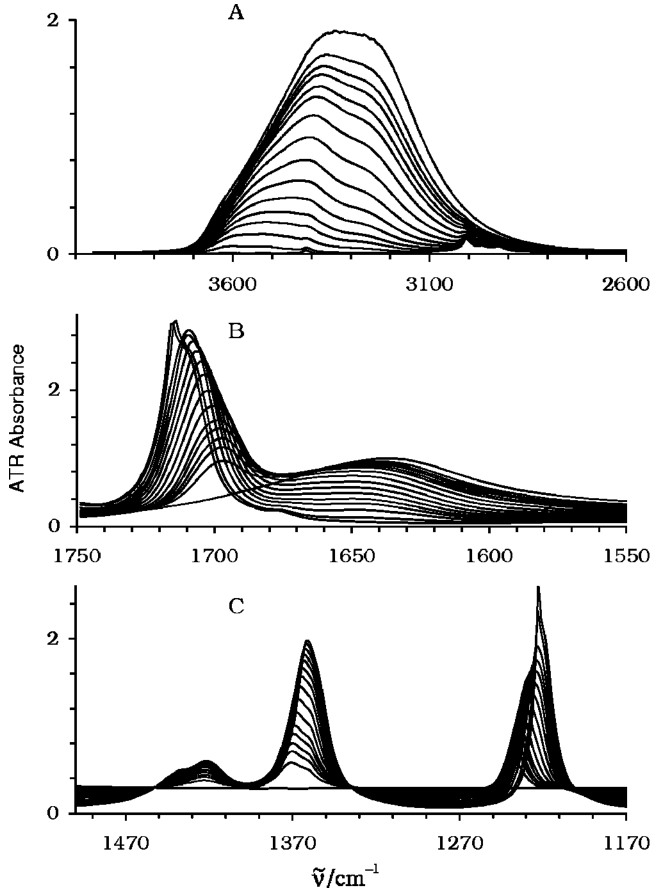

FIG. 4. Sixteen of 27 ATR-IR spectra of acetone–water mixtures in the whole solubility range. (A) O–H and C–H stretch regions; (B) acetone C=O stretch (ν_3) and water deformation (δ_{HOH}) regions; (C) δ_{CH3} and CC stretch (ν_{17}) regions.

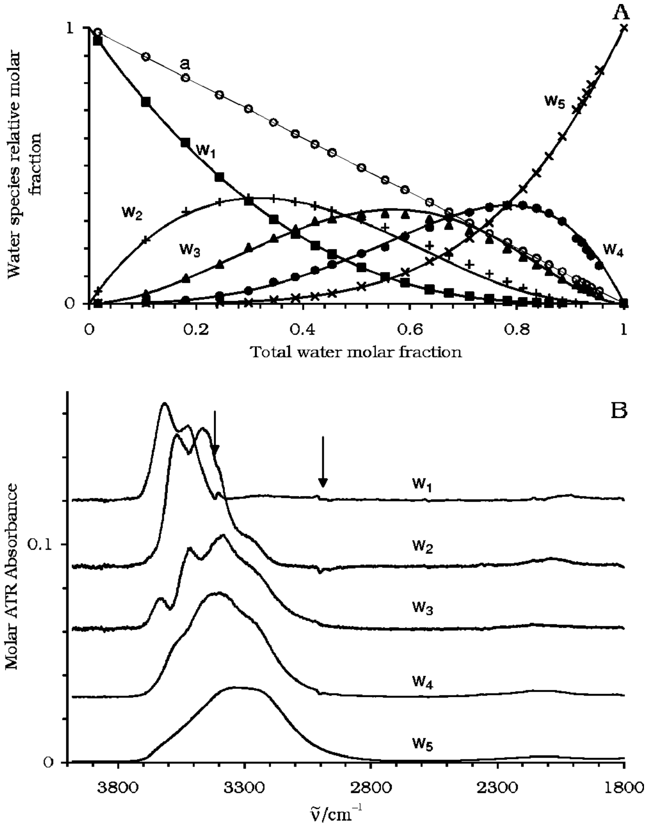

FIG. 5. Principal orthonormal water factors in the of acetone–water mixtures. (A) Water species molar fractions: the symbols are from FA and the lines from the probabilistic model; (B) principal spectra: $\mathbf{w}_1$–$\mathbf{w}_4$, water species in acetone; $\mathbf{w}_5$, pure water. Note: the arrows in (B) indicate acetone glitches resulting from the pure acetone spectrum subtraction.

the 1800–700 cm^{-1} region where the reverse takes place. Using this spectral windowing, ten principal factors (five water and five acetone) where retrieved by FA. These ten species do not evolve concomitantly as a function of concentration and must be considered independently in order to establish the chemical interpretation of the mixture organization.

A. Water species in water–acetone mixtures

In the 4800–1800 cm^{-1} region, the water OH band stands out as the principal feature [$\nu_{\max}=1.9$ a.u., Fig. 4(A)]. Although weak the carbonyl $2\nu_3$ and CH stretch, respectively, near 3410 cm^{-1} (0.03 a.u.) and 2900 cm^{-1} (0.14 a.u.) are easily identified. Since these bands are little displaced with different acetone concentrations, they were subtracted with the pure acetone spectrum normalized to the proper concentrations. The weak sigmoid residues resulting from the procedure do not interfere with the OH band analysis.

Factor analysis applied to the resulting spectra revealed five principal water factors. Their molar spectra and relative abundances are given in I [Figs. 6(B) and 6(A), respectively]. These results dealt with spectra of nonorthogonal principal factors, the orthogonalization of which could not be achieved using standard techniques.

1. Water principal factor spectra

a. Orthogonalization procedure: Obtaining pure component spectra. The relationship between concentrations and molar fractions reported in Appendix B of I was used to transform the water molar fraction into water concentration so that Beer's law could be applied. In addition, this relationship is easier to follow since the concentrations are obtained directly when the principal spectra MFs are expressed in molar absorbance. Also, the spectra of the pure components were obtained using matrix conversion (Appendix B).

b. Real water species molar fraction and orthogonalization of the water principal spectra. After the probability-calculated species (e_i) are merged into the five orthogonal principal factors (w_i, Table II), their intensities are adjusted by parameterizing the principal factor abundances with K_{O} obtained from Eqs. (3) and (4). Using Eqs. (15)–(17), (19)–(21), and relation (B3) taken from I and the numerical value of K_{O}, we calculate MFs for $\mathbf{S}_{\exp}^{P}$ represented by matrix $\mathbf{P}'$. Further use of Eq. (B8) (Appendix B and Ref. 14) gives the principal factor abundance (MF$'$) that is compared with the theoretical results. The best fit presented in Fig. 5(A) was obtained using $K_{\mathrm{O}}=2.5\pm1.5$. On this figure, the calculated values (full lines) are consistent with the experimental ones (symbols) obtained by FA. This indicates that the model proposed is adequate.

An equilibrium constant of 2.5 indicates that Eq. (3) is slightly left displaced. That is the oxygen atoms accepting

TABLE IV. MFs obtained from probability calculations (matrix P').

Factor	Water molar fraction of the experimental spectra 0.0166	0.1062	0.2440	0.4543	0.8598	1.0000
a[a]	13.591	13.305	12.761	11.555	5.620	0.000
w_1	0.218	1.157	1.894	1.722	0.062	0.000
w_2	0.010	0.363	1.510	3.234	0.714	0.000
w_3	0	0.056	0.590	2.976	4.051	0.000
w_4	0	0.004	0.112	1.331	11.171	0.000
w_5	0	0	0.013	0.357	18.480	55.441[b]

[a] Factor a represents all types of acetone species.
[b] See Ref. 15.

only one H-bond ($-O^1$) are a little less abundant than those accepting zero or two H-bonds ($-O^0$ and $-O^2$). Stated differently, an oxygen accepting one H-bond is a slightly stronger H-bond acceptor than one that does not accept any.

In conclusion, (1) nine different water species are the number of species in the acetone–water mixtures; (2) the grouping of these species into five principal factors is supported by experimental results; (3) the transformation of abstract MFs (taken from I) into real ones is adequate and (4) the orthogonalization procedure is satisfactory.

c. The spectra of the five orthogonalized water principal factors. The principal water factors obtained using $\mathbf{P}'$ (Table IV) are orthogonal. Their spectra are shown in Fig. 5(B), where the letters (w_1–w_5) identifying the factors are the same as those in Table II. The spectra of the orthogonal factors [Fig. 5(B)] have more features than that of the non-orthogonal ones (I). Some weak glitches observed on the spectra near 3410, 3006, 2965, and 2920 cm^{-1} (arrows on the figure) derive from the use of the pure acetone spectrum in the subtraction procedure. This subtraction is not perfect because the acetone bands are slightly displaced in aqueous solutions. These glitches being weak do not interfere with the water species evaluation.

2. Simulation of the OH stretch bands of the water principal spectra

To best compare the different water principal spectra in Fig. 5(B), they were simulated using Gaussian shapes. Other shapes were tried with no better results, so we opted to use this profile. Since the band enhancement procedures do not work on the spectra in this figure, we cannot determine the exact number of components in the OH stretch region. However, based on previous experience, we present the best possible fit in Fig. 6.[10,16] The component characteristics are listed in Table V. The two principal water absorbance components in this region are assigned to fundamental vibrations ν_3 and ν_1. To these components are added the satellite components originating mostly from the external modes (translations and rotations) coming from the far-IR.[10,16,17] These absorptions form a typical water-type cohort called an absorption regime. Since we identified three types of water (OH_2, OH_3, and OH_4), each one having its own set of bands, we have three regimes that we label 1, 2, and 3, respectively. The neighbors and next neighbors which modify the absorption regimes in synchronization further perturb these regimes.

a. Principal factor w_5 (pure water). We start with principal factor w_5, pure water (species e_9, Tables I and II), not because it is a simple system but because the OH stretch band simulation into components has been the object of previous publications where the rationale for the band simulations is given.[8,10,18] The two main components at 3389 and 3222 cm^{-1} are assigned to ν_3 and ν_1 of water, respectively (Table V). The molecules are completely hydrogen-bonded. The two hydrogen atoms of a central water molecule are hydrogen-bonded to the oxygen of neighboring molecules and one hydrogen of two other neighbor molecules is hydrogen-bonded to the oxygen of the central molecule, forming an OH_4 type of water molecule.[10] The many other components retrieved are assigned to combination bands (Table V). The broadness of the components indicates that they probably contain sub-components, but these could not be retrieved lacking discriminating criteria. All these components form regime 3 of water absorption.

b. Principal factor w_1. Next we tackle water principal factor w_1 because its spectrum is the sharpest and its components are at the highest frequencies of the series. The spectrum of this factor was simulated with two components situated at 3618 and 3518 cm^{-1} (Fig. 6). Since this principal factor is retrieved from the low water molar fraction region [Fig. 5(A)], it is related to species e_1 [Fig. 2(A)] identified as an OH_2 type water (Table II). The two components are assigned easily to ν_3 and ν_1, respectively. Very little satellite absorption is observed on this spectrum because each water molecule is isolated from the others. This impedes the formation of hydrogen bonding between the water molecules, which considerably decreases the band formation in the far-IR. Having no band to combine with, the fundamental bands have no satellite band. The absorption pattern observed for factor w_1 forms regime 1 of water absorption.

The ν_3 and ν_1 components of OH_2 at 3618 and 3518 cm^{-1} are red-shifted from the gas-phase positions (3756 and 3657 cm^{-1}),[11] but blue-shifted from pure liquid positions (3389 and 3222 cm^{-1}, Table V). The red shift of around 140 cm^{-1} from the gas position confirms that the water molecules of factor w_1 are twice H-bond donors. Even with these H-bonds given, the OH stretch band is at relatively

TABLE V. Position (in cm^{-1}), full width at half height (FWHH in cm^{-1}), and molar intensities (in ATR-IR a.u.) of the IR Gaussian components of the five water principal factors in aqueous acetone.

	H_2O gas[b] position	Mean position	OH_2 $w_1\equiv e_1$			OH_2, OH_3 $w_2\equiv e_2+e_4$			OH_2, OH_3, OH_4 $w_3\equiv e_3+e_5+e_7$			OH_3, OH_4 $w_4\equiv e_6+e_8$			OH_4 $w_5\equiv e_9$: pure H_2O		
			Position	FWHH	Int.	Position	FWHH	Int.	Position	FWHH	Int.	Position	FWHH	Int.	Position	FWHH	Int.
$\nu_3+\nu_{L2}$									3760	300	0.0003	3700	300	0.0002	3730	310	0.0004
						3695	100	0.0020									
$\nu_1+\nu_{L2}$												3647	70	0.0035	3620	105	0.0052
$\nu_3+\nu_{T2}$												3588	70	0.0085	3528	135	0.0100
ν_3	3756																
$\nu_3(OH_2)$		3608	3618	94	0.0424	3576	94	0.0482	3631	84	0.0115						
$\nu_3(OH_3)$		3473				3447	151	0.0443	3466	150	0.0087	3505	150	0.0175			
$\nu_3(OH_4)$		3391							3395	190	0.0340	3388	190	0.0354	3389	195	0.0289
Ac residue		3410,3006 2965,2920															
$2\cdot\nu_2$			3400	75	0.0014				3390	76	0.0040	3285	150	0.0030			
ν_1	3657																
$\nu_1(OH_2)$		3508	3518	94	0.0313	3480	94	0.0138	3527	84	0.0220						
$\nu_1(OH_3)$		3282				3281	151	0.0105	3280	150	0.0055						
$\nu_1(OH_4)$		3223							3226	190	0.0143	3222	190	0.0222	3222	195	0.0279
Residue			3222	260	0.0025												
ν_1-ν_{T1}									3042	150	0.0011	3045	150	0.0035	3079	135	0.0060
ν_3-ν_{L2}															2974	135	0.0035
ν_1-ν_{L2}												2870	300	0.0008	2840	135	0.0014
ν_3-ν_{L1}															2685	135	0.0007
ν_1-ν_{L1}															2583	115	0.0004
ν_2	1595														1638	81	0.0162
ν_{L1}[a]															613	341	0.0446
ν_{L2}[a]															395	300	0.0154
ν_{t1}[a]															183	148	0.0155
ν_{t2}[a]															50	80	0.0031
Integrated intensity (4000–2500 cm^{-1})					8.8			15.6			18.0			17.6			16.3

[a] Zelsmann (Ref. 17) from fitted components obtained from transmission measurements at 0 °C.
[b] Reference 11.

high frequency. The absorption in this frequency region was assigned previously to ‘‘free’’ OH oscillators.[19–22] However, in the present case, OH_2 molecules are surrounded by acetone, a strong H-bond acceptor, which will form H-bonds with all available labile hydrogen atoms. Moreover, the full width at half height (FWHH) of these bands at 94 cm^{-1} makes them too wide to be free OH oscillators. Also, if these were present, we would have four components forming two absorption regimes: A ν_3, ν_1 pair for the single H-bond donor species and another ν_3, ν_1 pair for the twice H-bonded species. Since we observe only two components they cannot be assigned to free OH oscillators. These arguments indicate clearly that OH_2 twice H-bonded is the perfect candidate for the water absorption species at 3618 and 3518 cm^{-1}.

Anti-cooperativity had been invoked to explain the small bathochromic shift of the OH stretching of water isolated molecules. However, similar lower bathochromic shifts were observed for methanol diluted in different H-bond acceptors. The methanol OH stretch position is situated at: 3681 cm^{-1} in the gas phase,[11] 3328 cm^{-1} in liquid,[11] 3500 cm^{-1} in dioxane,[23] 3530 cm^{-1} in acetonitrile,[24] and 3509 cm^{-1} in acetone (unpublished ATR measurements). These shifts from the gas position are 353, 180, 150, and 172 cm^{-1}, respectively. In the three last systems, each isolated methanol molecule having a single OH group can give only a single H-bond (and accept none because methanol molecules are isolated the ones from the others). Therefore, because of this unique H-bond with methanol, no anti-cooperativity can take place. However, the bathochromic shift of the methanol OH vibration is far less than that usually expected in a strong H-bonding situation. Similarly, anti-cooperativity cannot be used to explain the small red shift observed in water isolated in acetone since the bathochromic shift is similar to that observed in organic methanol solutions. The small bathochromic OH shifts are explained by the situation of the OH groups that do not accept any H-bond.

c. Principal factor w_2. The ν_{OH} band of spectrum w_2 (Fig. 6) is separated into four principal components situated at 3576, 3447, 3480, and 3281 cm^{-1} (Table V). This water principal factor, w_2, is related to two water species, e_2 and e_4 (Table II), that generate two absorption regimes. The 3576 cm^{-1} component has the highest position: Its bandwidth (94 cm^{-1}) is the same as ν_3 of OH_2 of species e_1 (factor w_1). Consequently, we assign this component to ν_3 of regime 1 generated by species e_2. The red shift of 42 cm^{-1} compared to that of spectrum w_1 ($\equiv e_1$) is explained by the situation of the H-bond acceptors where one of these accepts a single H-bond (O^1) and the other accepts two H-bonds (O^2), whereas in species e_1 the H-bond acceptors accept only a single H-bond (O^1) (Table II). In the same way, the 3480 cm^{-1} component is assigned to ν_1 of OH_2 (species e_2): Its bandwidth is the same as ν_3 and the spacing $\nu_3-\nu_1$ is the same as that of OH_2 of species e_1 (factor w_1). The ν_3, ν_1 intensity ratio in spectrum e_2 of w_2 is different from that

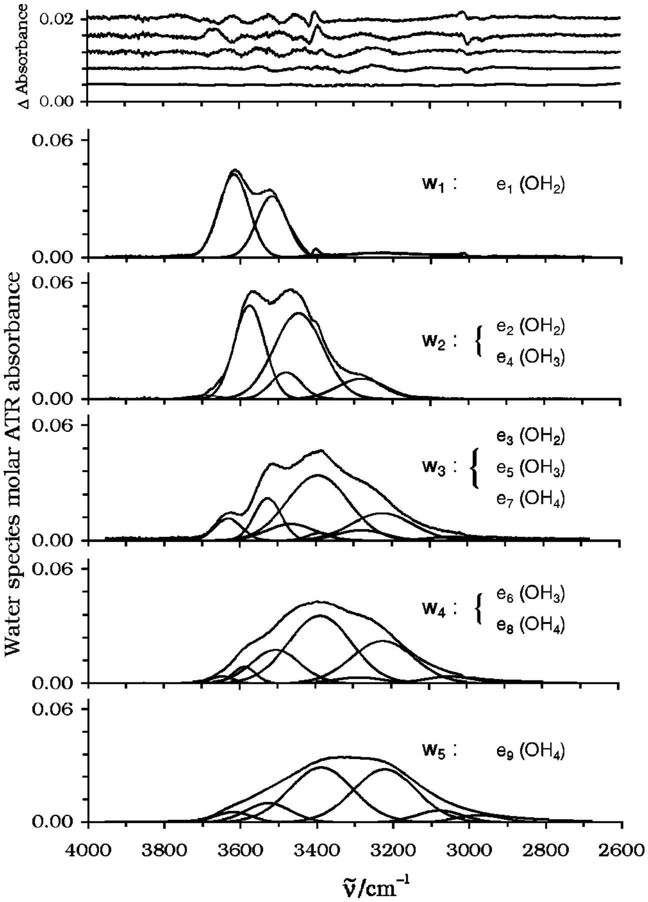

FIG. 6. Gaussian simulation of the five principal water spectra of Fig. 5(B): w_1–w_4, water species in acetone; w_5, pure water.

observed for e_1 of w_1. Although the difference may come from an imperfect simulation, it may also originate from differences in environment in the two cases. A change in environment has been observed to cause strong modifications in the intensity ratio of H_2O ν_3, ν_1 bands.[25] Due to different lone electron pair numbers on both oxygen accepting the H-bond from the central water molecule (e_2), the molecular symmetry of this species is less than that of species e_1, which can in turn decrease the ν_1 intensity (symmetric OH stretch) of this species to the benefit of its ν_3 intensity (antisymmetric OH stretch).

The two remaining components at 3447 and 3281 cm^{-1} are assigned, respectively, to ν_3 and ν_1 of absorption regime 2 generated by species e_4, which is an OH_3 water type. The spacing between the components is 166 cm^{-1} and their bandwidths are 151 cm^{-1}. The positions, spacing and bandwidths make this regime more like regime 3 (OH_4) than regime 1 (OH_2) (Table V). Therefore, it must be concluded that an H-bond accepted produces a stronger perturbation of the OH stretching oscillator than does an H-bond given. The symmetry decrease of an e_4 water species (with a single lone pair of electrons left) produces a ν_1 intensity decrease to the benefit of ν_3.

d. Principal factor w_4. The ν_{OH} band of spectrum w_4 (Fig. 6) is separated into seven components situated between 3710 and 2850 cm^{-1}. This water principal factor is made of OH_3 and OH_4, forming species e_6 and e_8 (Table II) that generate two absorption regimes. The two species have an extensive hydrogen bonding network that should generate many bands in the far-IR and consequently produce many satellite components in the fundamental region. The intensity of these satellites is weaker than that of fundamentals ν_3 and ν_1 and the position of the OH_3 components is at higher frequency than that of OH_4. Using these characteristics, the assignment of the w_4 components was made and is presented in Table V.

The three most intense w_4 components are situated at 3505, 3388, and 3285 cm^{-1} (Fig. 6). The 3505 cm^{-1} component is assigned to ν_3 of the OH_3 absorption regime. The ν_1 of this regime is difficult to identify because the most likely candidate, the 3285 cm^{-1} component, is too far away from ν_3. This leaves the absorption of ν_1 buried in the much stronger component at 3388 cm^{-1}. The 3285 cm^{-1} component is assigned to $2\nu_2$. The 3388 and 3222 cm^{-1} components are assigned, respectively, to ν_3 and ν_1 of the OH_4 absorption regime with a separation between the two components of 166 cm^{-1}. This band separation and the bandwidth of 190 cm^{-1} of the w_4 components is due to the extensive hydrogen bonding of this principal factor.

e. Principal factor w_3. The ν_{OH} band of spectrum w_3 (Fig. 6) is separated into eight components situated between 3710 and 2800 cm^{-1}. Although the spectrum of this factor has more spectral features than the other factors, the components strongly overlap, making the separation between them difficult and likely incomplete. To illustrate this difficulty, the small component situated at 3390 cm^{-1} that cannot be easily separated into the three regimes described below is assigned to $2\nu_2$. The water principal factor w_3 is made of OH_2, OH_3, and OH_4, forming species e_3, e_5, and e_7, respectively (Table II), that generate three absorption regimes.

The e_3 species made of OH_2 do not accept H-bonds from other water molecules. Because of this, ν_3 and ν_1 of this regime are on the high frequency side of the band. We assign the 3631 and 3527 cm^{-1} bands to, respectively, ν_3 and ν_1 of e_3/w_3 absorption regime 1 (Table V). The separation between the components and their bandwidths are similar to species e_1 of factor w_1. The small positions and relative intensity differences are explained by the difference in neighbor situations: H_2O^{011} and H_2O^{022} for the e_1 and e_3 species, respectively (Table II).

The e_5 species, made up of OH_3, is more H-bonded to other water molecules than the e_3 species, but less so than the e_7 species (Table II). As a result, the absorption of the e_3 species is at the center of the band. We assign the 3466 and 3280 cm^{-1} bands to, respectively, ν_3 and ν_1 of e_5/w_3 absorption regime 2 (Table V). The band separation of 186 cm^{-1} is correct and the relative intensity adequate. This band separation and the large bandwidth indicate that this species is largely hydrogen-bonded to other water molecules.

Finally, the e_7 species, made up of OH_4, is more H-bonded to other water molecules than the w_3 species (Table II). As a result, the absorption of the e_7 species occupies the lower frequency part of the band. We assign the 3395 and 3226 cm^{-1} bands to respectively ν_3 and ν_1 of e_7/w_3 absorption regime 3 (Table V). The component separation of 169 cm^{-1} is correct and the band's relative intensity adequate. Once again, the separation between the component and the large bandwidths indicate that this species is largely hydrogen-bonded to other water species.

The intensity ratios of the three absorption regimes (e_3, e_5, and e_7) are consistent with the expected intensity obtained from probability (1, K_O, and K_O, Table II). The differences are explained by the complexity due to the presence of three pairs of overlapping components and by the satellite bands that further complicate the absorption.

3. Water types in aqueous acetone

In aqueous acetone, depending on the number of hydrogen atoms (valence and H-bonded) surrounding the oxygen of a water molecule, three water types exist: OH_2, OH_3, and OH_4. The neighbor molecules influence these water types by dividing each into three subspecies, for a total of nine water species. Pure water is one of the species. The other eight species appear as acetone is added to the solution. Following a random organization, the abundances of these types are determined, indicating that some species evolve concomitantly, yielding five principal factors. These were observed in the IR-FA separated ATR spectra of the solutions after the principal factors were separated. Then, after principal factor orthogonalization, the comparison between calculated and experimental results was excellent. This indicates that the model developed for water in aqueous acetone is valid and that the procedure to prove it is adequate.

Furthermore, the band simulation with several components yielded three absorption regimes for the three water types. The assignments of the components to the nine subspecies prove the adequacy of this model, further justifying it. Each absorption regime yields two principal bands, ν_3 and ν_1, to which satellite components are added. Our assignment greatly differs from the one recently proposed where four separated bands in the massive OH stretch absorption of salt solutions are assigned to different size clusters.[26] However, our assignment is consistent with our previous study of ten salt aqueous solutions and H_2O/D_2O mixtures.[16,27] The ν_3, ν_1 pair assignment is evident for the situation of isolated water molecules in acetone. It is possible to follow the ν_3, ν_1 pair (or regime) from the non-H-bonded oxygen of water (OH_2) situation to the once and twice H-bonded situations (OH_3 and OH_4). These observations further justify our assignment of the OH stretch bands of liquid water.

The pure water spectrum (w_5) covers the whole 3800–2800 cm^{-1} region (Fig. 6) while the other water species spectra (w_1 to w_4) cover only a part of this region. As expected from FA, any effort to reconstruct the w_5 spectrum with the w_1 to w_4 spectra was unsuccessful, even when the satellite bands were not considered. This confirms that the pure water spectrum is not an amalgamation of the other water species spectra and that pure water is a genuine species that is orthogonal to the others.

A fundamental point to take into consideration is the importance of the oxygen atom on the central water molecule and its neighbors. The oxygen of the central water molecule can have two, three and four hydrogen atoms surrounding it and consequently can have two, one and zero free electron pairs. The oxygen of neighbor molecules hydrogen-bonded to the central water molecule, either water or acetone, can have one or zero free electron pair accepting zero or one more hydrogen bond from a next neighbor. Since all these situations produce a different water spectrum, it is of prime importance to consider the situation of the oxygen atoms in all hydrogen-bonded species in order to evaluate the hydrogen-bonding network.

With the randomly mixed solutions used in the present paper, we can calculate the number of ‘‘isolated’’ water molecules at any total water molar fraction. An isolated water molecule is one that gives two H-bonds to acetone molecules but accepts none (because they can only be furnished by other water molecules). This water molecule is of type e_1, that is, OH_2 (Table II). As an example, at $\chi_w = 0.30$ we calculate that 37.0% of the water molecules are of type e_1. From these we must eliminate those giving one or both H-bonds to other water molecules since they produce water dimers or higher oligomers. Since the oxygen from acetone and water has the same ability to accept H-bonds, the amount of isolated water molecules is obtained by multiplying the total amount of type e_1 water molecules twice by the molar fraction of acetone, that is $(1-\chi_w)$. The result, at $\chi_w = 0.30$, was $(37.0\times0.70\times0.70=)$ 18%. This result is similar to that obtained by neutron diffraction for methanol–water mixtures at the same molar fraction: 13%.[28]

B. Acetone species in the water–acetone mixtures

1. Regrouping the species random distribution into principal factor abundances

FA applied to the spectra of aqueous acetone in the 1800–700 cm^{-1} region revealed five principal factors. The probabilistic model gives ten species, two of which evolve simultaneously giving nine observables. Because FA cannot sort these, they are regrouped following the perturbations on the C═O groups which is evaluated by scaling the displacement of the acetone CO stretch band (ν_3) since a weakening of the C═O bond red-shifts the band. This is done by evaluating the strength of the H-bond accepted by acetone: The weaker the given H-bond is the stronger the O–H valence bond is. We attribute an arbitrary number representing the O–H valence strength +3, +2, +1, in relation to respectively 0, 1, and 2 H-bonds accepted by the oxygen of this O–H group. Hence, we attribute numbers +1, +2, and +3 to the strength of the H-bond accepted by acetone (and therefore to the C═O perturbation) in relation to the number of H-bonds accepted by the O–H group, respectively.

To illustrate the above scheme we give in Fig. 3(D) two examples in a two-dimensional representation. *Left*, the oxygen of the water donor molecule (to acetone) is once hydrogen bonded, therefore gives a +2 H-bond strength producing a+2 perturbation on the C═O ketone. *Right*, the oxygen of the water donor molecule accepts no hydrogen bond, hence having a +3 O–H valence strength that entails a +1 perturbation on the C═O.

With this scheme, a rough estimate of the H-bond perturbation on the C═O ketone is made. When two H-bonds are accepted by the carbonyl, the perturbations are added. Although rough—because it does not consider the acetone–acetone dipole–dipole interactions—this method scales the

TABLE VI. Distribution of the acetone species in aqueous acetone into principal factors.

Species abbreviation $AcCO^{i\,j\,k}$	Degree of perturbation on ν_{CO}[a]	Acetone species	Principal factor
$AcCO^{0}$	0	$Ac_1\}$	$\mathbf{a_1}$
$AcCO^{1\,0}$	1	Ac_2	$\mathbf{a_2}$
$AcCO^{1\,1}$	2	$\frac{1}{2}Ac_3$	
$AcCO^{2\,0\,0}$	2	$\frac{1}{2}Ac_5$	
$AcCO^{1\,1}$	2	$\frac{1}{2}Ac_3$	$\mathbf{a_3}$
$AcCO^{1\,2}$	3	Ac_4	
$AcCO^{2\,0\,0}$	2	$\frac{1}{2}Ac_5$	
$AcCO^{2\,0\,1}$	3	Ac_6	
$AcCO^{2\,0\,2}$	4	$\frac{1}{2}Ac_7$	
$AcCO^{2\,1\,1}$	4	$\frac{1}{2}Ac_8$	
$AcCO^{2\,0\,2}$	4	$\frac{1}{2}Ac_7$	$\mathbf{a_4}$
$AcCO^{2\,1\,1}$	4	$\frac{1}{2}Ac_8$	
$AcCO^{2\,1\,2}$	5	Ac_9	
$AcCO^{2\,2\,2}$	6	$Ac_{10}\}$	$\mathbf{a_5}$

[a] From Table III, the degree of perturbation of ν_{CO} is equal $i+j+k$.

H-bonding perturbations on the C═O stretching vibration. The degree of perturbation on ν_{CO} for the ten carbonyl situations is given in Table III. With these and the species distribution (Fig. 3), the regrouping is made in Table VI. The result is presented in Fig. 7(A), where the full lines and symbols are the calculated and experimental results, respectively. The fit between probability calculations and FA of curves $\mathbf{a_1}$ (pure acetone) and $\mathbf{a_5}$ (lone acetone) is excellent. That of curves $\mathbf{a_2}$, $\mathbf{a_3}$, and $\mathbf{a_4}$ are close matches. Although not as good as for $\mathbf{a_1}$ and $\mathbf{a_5}$, they are nevertheless acceptable.

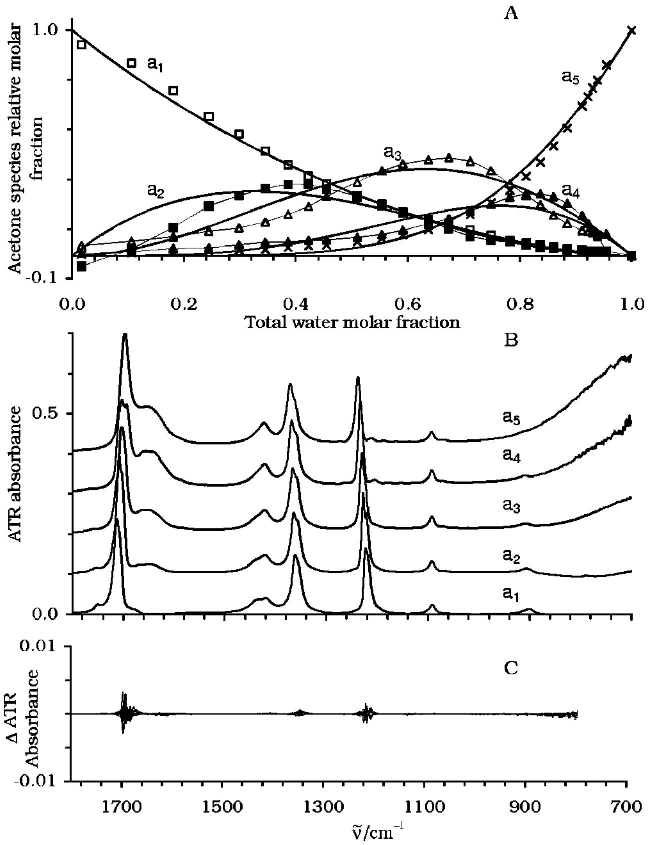

FIG. 7. Principal orthonormal acetone factors in the acetone–water mixtures. (A) Relative molar fractions (the symbols are from FA and the lines from the probabilistic model); (B) principal spectra (shifted 0.1 a.u. from each other); (C) residues. $\mathbf{a}_1$, pure acetone; $\mathbf{a}_2$–$\mathbf{a}_5$, aqueous acetone species.

2. IR spectra of the five orthogonal acetone principal factors

With the now real species distribution, the five principal acetone factors retrieved by FA are orthogonal in a five-dimensional space.[29] Their spectra are presented in Fig. 7(B) ($\mathbf{a_1}$–$\mathbf{a_5}$) and the band assignment given in Table VII. Figure 7(C) gives the residues obtained from the recombination of the principal spectra with the MFs [Fig. 7(A)]. Since these are weak it indicates that FA and orthogonalization procedure worked adequately. Consequently, the results are reliable.

Although the five acetone species spectra [Fig. 7(B)] look alike, they are related to orthogonal factors. Spectrum $\mathbf{a_1}$ is the pure acetone spectrum and has no water band. With the other species we notice that water ν_2 and ν_L near 1650 and below 900 cm^{-1}, respectively, increase from spectrum $\mathbf{a_2}$ to spectrum $\mathbf{a_5}$, reflecting the fact that the number of water molecules surrounding the acetone molecules increased as the water content of the solution increased. The intensities of the other acetone bands are almost constant, but their positions are shifted (Table VII).

The gas and liquid (ATR) phase positions of the acetone CO band (ν_3) are situated at 1731 and 1712 cm^{-1}, respectively. A shift of 19 cm^{-1} on a carbonyl ketone indicates strong intermolecular dipole–dipole interactions, the only perturbation possible in liquid acetone. The CO bond dipole moment vectors of nearest neighbors in the liquid tend to be oriented in an antiparallel manner.[2] Adding water to acetone increases the red shift to 1697 cm^{-1} (34 cm^{-1} from the gas position) in the worst case (Table VII). This increase (almost double the red shift from gas to liquid phases) indicates that the hydrogen bonding perturbations between acetone and water molecules are stronger than the dipole–dipole interactions between acetone molecules. This is not always the case since we observed the opposite on the CN stretch band of acetonitrile–water mixtures.[8]

The residues [Fig. 7(C)], obtained from the difference between the FA calculated spectra and the experimental spectra, show weak glitches near 1712, 1369, and 1210 cm^{-1}. These glitches correspond, respectively, to ν_{CO}, ν_{CC}, and δ_{CH} acetone strong bands. These glitches indicate the nonperfect behavior of these groups when submitted to environmental changes. Since these second order effects are weak but real, they could be used to study these perturbations but spectra with higher resolution and higher signal-to-noise ratio would be needed. This is an ongoing project.

C. Comparison between water and acetone principal factor abundances

In the acetone–water system, a comparison between the five water principal species molar fractions [Fig. 5(A)] and

TABLE VII. Position (in cm^{-1}) and assignment of the bands of the five acetone principal spectra.

Symmetry species	Approximate type of vibration	Gas[a]	$AcCO^0$ a_1 pure acetone	a_2	a_3	a_4	$AcCO^{2\,2\,2}$ a_5 isolated acetone
$2\,\nu_3$			3412				
$\nu_1,\ \nu_{13}$	CH_3 d-str	3018.5	3005	3006	3008	3012	3014
ν_{20}	CH_3 d-str	2972	2965	2967	2970	∼2972	
$\nu_2,\ \nu_{14}$	CH_3 s-str	2937	2924	2924	2926	2928	2930
$2\,\nu_{15}$			2845	2845	∼2845		
$\nu_3+\nu_{22}$			2780	2780	2775	2770	2770
			∼2700				
$\nu_{16}+\nu_{17}$			2578	2584	2589	2591	2595
$\nu_3+\nu_7$			∼2503	∼2503	2495		
$2\,\nu_{17}$			2443	2445	2450	∼2450	∼2450
$\nu_{16}+\nu_{18}$			2262	2264	2272	∼2272	
$2\,\nu_{22}$			2145	2148	2150	2150	2160
$\nu_{17}+\nu_{18}$			2120	2120	∼2100	2100	∼2095
$\nu_2+\nu_L H_2O$				∼2060	∼2100	∼2115	∼2130
$\nu_7+\nu_{17}$			2000	2008	2014	2020	
$\nu_7+\nu_{22}$			1885	1886			
$\nu_{16}+\nu_{23}$			1830	∼1850	∼1850		
$\nu_{15}+\nu_8$			1795	1800	1805	∼1810	∼1815
$\nu_{17}+\nu_{19}$			1750	1752	1757	1765	∼1767
				∼1720	∼1713		
ν_3	CO str	1731	1712	1709	1702	1703	1697
				1704		1694	
$\nu_7+\nu_{18}$			1676	1668	∼1660	1658	
$\nu_2 H_2O$							∼1650
$\nu_2 H_2O$				1647	1650	∼1641	∼1640
			1560	1580	1584	1587	∼1585
ν_{21}	CH_3 d-def	1454					
ν_4	CH_3 d-def	1435	1436	1439	∼1439	∼1440	∼1445
ν_{15}	CH_3 d-def	1410	1420	1421	1422	1422	1423
$\nu_5,\ \nu_{16}$	CH_3 s-def	1363.5	1361	1365	1366	1368	1371
			∼1355	1357	∼1359	1360	∼1362
							1297 ?
				1270	∼1270	1262	1273 ?
				1245		∼1243	∼1250
ν_{17}	CC str	1215.5	1223	1228	1231	1233	1238
			1220	1222	∼1225		
							1212
ν_3-ν_{23}			1195	1200 ?	∼1203	1206	
						1178 ?	1185
					1145	1153	
			1125	1127	1123	1129	
ν_{22}	CH_3 rock	1090.5	1092	1093	1093	1093	1094
ν_6	CH_3 rock	1066[b]	1062	1066	1068	1069	1070
			1040	1040 ?	∼1041 ?		
$\nu_8+\nu_{23}+\nu_{24}$			980	986	∼990	∼985	
ν_3-ν_7			∼920	∼930	942		
ν_{18}	CH_3 rock	891	901	906	908	910	∼913
ν_7	CC str	777	785	788			
ν_{19}	CO ip-bend	530					
ν_8	CCC def	385					
ν_{23}	CO op-bend	484					
ν_{24}	Torsion	109					

[a] Reference 11.

[b] Raman.

those of the five acetone species [Fig. 7(A)] reveals similar patterns but with significant differences. To bring these out, we plotted in Fig. 8 the species concentration as a function of total water concentration (which, following the Beer's law, will produce proportional absorbance). In frames where two curves are drawn ($\mathbf{a_i}$ and $\mathbf{w_j}$ for acetone and water species, respectively), these look alike yet are different. The ratios between the two curves (**r**) show these differences even more clearly. If the two quantities were directly related, the **r** curves would be horizontal lines. This is not the case. How can that be, since we have used the same solutions to generate the principal spectra (five for the water species and five

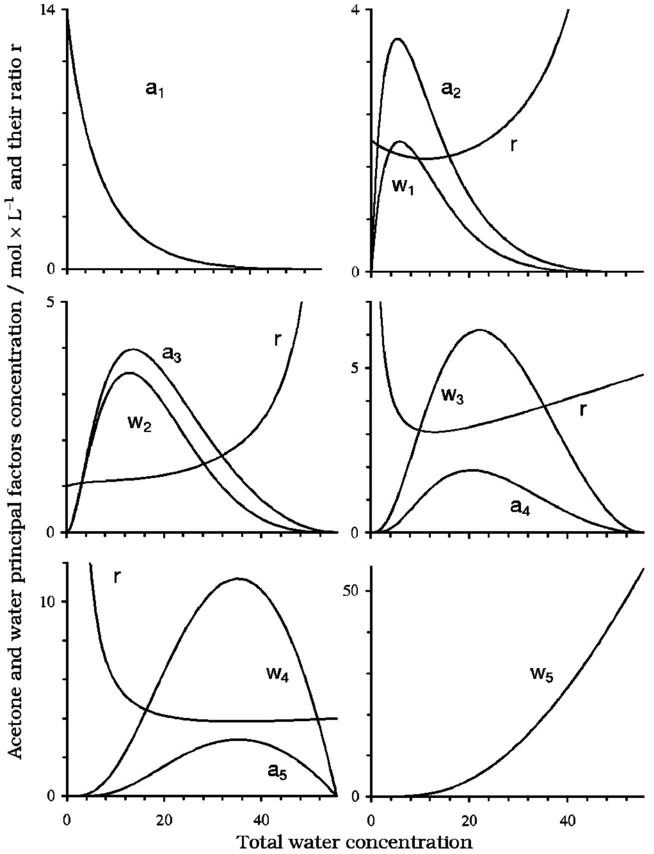

FIG. 8. Comparison between acetone and water principal factor concentrations as a function of total water concentration. The frames bring together one water and one acetone factor with similar abundances. The traces (*r*) are the ratio between both factors in the frame. $\mathbf{a}_1$, pure acetone; $\mathbf{a}_2$–$\mathbf{a}_5$, acetone–water species; $\mathbf{w}_1$–$\mathbf{w}_4$, water–acetone species; $\mathbf{w}_5$, pure water.

for the acetone species)? To understand this apparent paradox, we have to look at the neighbor and next neighbor situations.

In the simplest situation obtained in very low acetone concentration in water, the surroundings of the CH_3 groups are little perturbed since CH_3 stretch bands are only slightly displaced in a water environment. We will, therefore, be concerned only with the CO group surrounded by water molecules. Due to the equal capability of acetone and water to accept H-bonds (from water), the acetone molecule will accept two H-bonds. This results in a lack of two H-bonds (those that are given to the acetone molecule) for the remaining water molecules. Because of hydrogen hopping, the free electron pair (the lack of H-bonds accepted) cannot be located on a particular water oxygen atom. Thus, the position of the acetone molecule cannot be related to specific water molecules. In the mixture, two water molecules have a free electron pair because of accepting one H-bond (not two, as with all other water molecules). One of these is sketched in Fig. 9.

In water, the CO group of the lone acetone molecule has two electron pairs that will accept two H-bonds. In a water-rich mixture, almost all the water molecules accept two H-bonds ($H_2O^{2\,2\,2}$); this is species e_9 producing principal factor $\mathbf{w}_5$ (Table II). The two H-bonds accepted by the acetone molecule come from water molecules that accept two

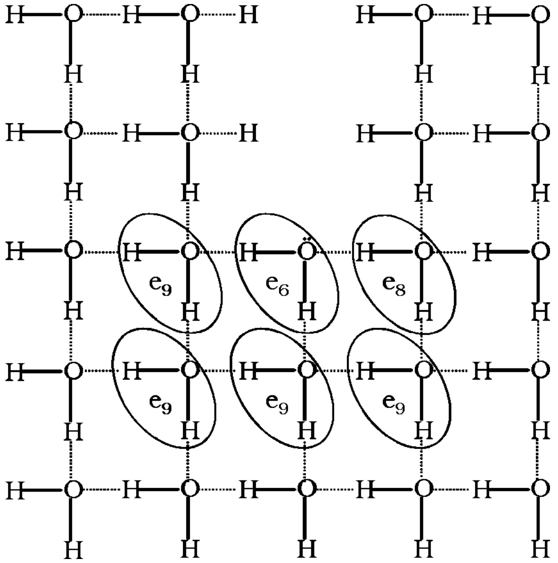

FIG. 9. Two-dimensional schematic representation of the water H-bond network perturbation at very low acetone concentration in water. Note the lone electron pair on the oxygen in e_6.

H-bonds themselves ($AcCO^{2\,2\,2}$); this is species Ac_{10} producing principal factor a_5 (Table VI).

In the mixture, the two hydrogen bonds between the acetone and water molecules will leave two water molecules with a lone electron pair each ($H_2O^{1\,2\,2}$); they are e_6 species (Table I). Figure 9 sketches the situation in two dimensions for one of these two water molecules. They accept a single H-bond from other surrounding water molecules that accept two themselves ($H_2O^{2\,1\,2}$); the latter are e_8 species (Table I) since they are connected to ordinary water molecules (e_9 in Fig. 9). The e_6 and e_8 water molecules form principal factor $\mathbf{w}_4$ (Table II).

Thus, an a_5 acetone molecule, which is surrounded by water molecules will perturb four of them, giving a 1–4 ratio of acetone to perturbed water molecules. This could be interpreted as an acetone tetrahydrate if the four water molecules were interacting directly with acetone. This is not the case because the perturbed water molecules are not necessarily neighbors to the acetone molecules. Furthermore, the acetone molecules do not locally perturb the water H-bond network. Consequently, it is not possible to speak of an acetone tetrahydrate. This explains why two sets of species are present in aqueous acetone, one for water and one for acetone, each set producing different evolving principal factors, $\mathbf{w}_4$ and $\mathbf{a}_5$, respectively (Fig. 8). For the more concentrated acetone solutions, the same logic can be put forward but is rendered more difficult due to the overlapping situations as ratios $a_2 : w_1$, $a_3 : w_2$ and $a_4 : w_3$ in Fig. 8 illustrate.

V. CONCLUSION

By evaluating first and second order perturbations of OH and C=O stretching vibrations of water and acetone in aqueous acetone we obtained nine water and ten acetone species. Considering the oxygen atom and the hydrogen atoms (valence and H-bond) surrounding it, water in aqueous acetone is made of three types of water: OH_2, OH_3, and OH_4.

These depend on the number of H-bonds accepted by the water molecules, which are 0, 1, and 2, respectively. Each type produces a distinguishable OH stretch absorption regime composed of ν_3 and ν_1 (mean values for OH_2, 3608, 3508; OH_3, 3473, 3282, and OH_4, 3391, 3223 cm^{-1}, respectively) with several satellite components. Depending on the neighbor situations related to the number of H-bonds accepted by the neighboring oxygen atoms (1 or 2), each type of water further modulates the OH absorption regime. The probabilistic model developed for randomly organized mixtures of acetone and water molecules have both the same capabilities to accept H-bonds but are limited by the H-bond network gave ten acetone and nine water species. The evaluation of the species' abundances shows that some of the water species evolve concomitantly as a function of water concentration, producing five principal factors. These corresponded to factors retrieved from the IR spectra by FA using spectral windowing. Each of the five principal water spectra is a particular combination of the three regimes. Pure water and isolated water in acetone have only one absorption regime each. For the three other situations, more than one regime makes up the spectra.

The ten acetone species yielded nine principal factors, the abundances of which vary as a function of water molar fraction. Because of the small shift of the C═O stretch band, only five principal factors are retrieved by FA from the IR spectra. Nevertheless, based on similarity considerations, the combination of the species' abundances calculated from probability correspond to those retrieved from IR. This indicates that the assumed mixture organization is satisfactory.

In aqueous acetone the molecular model is as follows: (1) The molecules form an extensive hydrogen bond network; (2) when water molecules are close one to the others, hydrogen hopping occurs; (3) oxygen atoms from both acetone and water are equally likely to accept H-bonds from water; (4) when free electron pairs on the oxygen atoms are in excess, all labile hydrogen atoms form H-bonds; (5) the molecules are almost randomly organized, restricted only by the hydrogen bond network: No preferred complexes are present in aqueous acetone; (6) although the OH groups act as H-bond donors, the OH stretching bathochromic shift from the gas position increases with increasing number of H-bonds accepted by the oxygen atom; (7) the H-bond strength increases a little with increasing number of H-bonds accepted by the oxygen atom of the H-bond donor.

Three forces are at play in acetone–water mixtures: Dipole–dipole interactions, hydrogen bonding, and hydrophobic interactions.[2,9] The last of these was observed on the CH stretching bands that are blue-shifted as water is introduced into the solution.[1] The dipole–dipole interactions were observed through the red shift of the carbonyl stretch band when acetone passed from the gas phase to the liquid phase. Hydrogen bonding was also observed on the carbonyl stretch band as water was introduced into the solution, red-shifting the band further. This indicates that hydrogen bonding is stronger than dipole–dipole interactions in acetone because it overrides them.

Since the presence of free OH was inferred from an evaluation of IR spectra of aqueous acetonitrile solutions,[20,30] and since that species was not found by others,[8,19] we carefully looked for it in the water–acetone mixtures where such an entity would exist. We found none because acetone scavenges them all.

Our work sheds some light on a widely used and apparently simple system: The acetone–water solution. It turns out to be quite complex. This indicates that simple aqueous systems, whose organization is taken for granted, must be reevaluated. Since our work provides a new method of evaluation of the nature of H-bonding in aqueous solutions, it could in time lead to a comprehensive model of liquid water that could explain all its physico-chemical properties. Furthermore, our study of aqueous acetone by FA on ATR-IR spectra yields an enormous quantity of information using a relatively simple analytical technique that has several advantages when compared to more expensive and complicated analytical methods like neutron diffraction.

APPENDIX A: ORTHOGONALIZATION

1. Spectral orthogonality

The most useful coordinate systems are orthogonal since they are related to distinct factors.[31] It is practical to use an orthogonal system to perform FA on spectroscopic data. Since this does not provide real factors, these must be rendered real in order to interpret them. Therefore, usual factor analysis of a set of spectra of multicomponent mixtures yields n orthogonal spectra,[32] giving orthogonal vector representations of transformed spectra of pure components.[33] Various methods of constructing an orthogonal set out of a given set of linearly independent vectors are available,[34–36] of which the Gram–Schmidt and the Schweinler–Wigner orthogonalization procedures are preferred.[35] These orthogonalization procedures applied to absorbance spectra necessarily yield abstract spectra.[34,36]

Since real absorbance spectra have only positive values, any pair of real spectra cannot be orthogonal consistent with the usual mathematical orthogonality condition. As a simple example, consider the spectra of pure water and pure acetone. These spectra are not orthogonal, even if both species are pure and, therefore, fully exclusive one from the other. However, the two spectra can be transformed into orthogonal abstract spectra by a simple linear transformation. Furthermore, a set of abstract orthogonal spectra (S_1,S_2) is easily obtained from any set of real spectra (S_a,S_b). However, the orthogonal set of spectra is far from unique and it is easily shown that it may represent virtual nonorthogonal species that are nonexclusive one from the others.

In short, mathematical spectral orthogonalization cannot provide real spectra and cannot be used as a criterion to prove that a set of spectra represent pure species. Nonetheless, factor analysis that gives abstract factors is very useful because it gives the number of components in mixtures.

2. Real spectra of orthogonal species

When both the concentrations and identities of the components in a mixture are unknown, it is not possible to obtain by analytic methods the pure components spectra.[32] When the number of components in a mixture is known—either directly or by factor analysis—then the dimension of the vector space in which all the mixtures can be represented is known giving a set of orthogonal spectra. The problem then is to obtain the appropriate linear combination of these orthogonal spectra to yield the pure component real spectra.[32] Also, the abundance of the pure components in the mixture must be real (no negative values). These conditions are necessary to interpret the spectra in molecular terms.

In the present work, both spectra of pure liquid water and acetone are obtained experimentally giving real non orthogonal spectra (consistent with the definition). Both species are pure components (exclusive one from the other) and, therefore, are orthogonal species. Any partial subtraction of one from the other produces negative bands and/or sigmoïdal features, which indicates that the resulting spectrum is an abstract spectrum.

3. The H_2O–D_2O mixture: An example

A first step in the FA procedure is the determination of the number of principal factors. Each principal factor defines an individual dimension in the chemistry space of the mixtures. The case of light-heavy water mixtures is a good example.[10] When H_2O and D_2O are mixed, HDO is produced.[37–39] However, HDO being in equilibrium with H_2O and D_2O cannot be obtained pure. The spectrum of ‘‘pure’’ HDO is usually obtained by taking three spectra, pure H_2O, pure D_2O and an equal mixture of the two, then subtracting the spectra of the pure species from that of the mixture gives the HDO spectrum.[37] However, the resulting spectrum showed sigmoids which is an indication that the mixture contained more than three species. In Ref. 10, we showed that it contained five principal factors because of the interactions of the neighbor molecules. In H_2O–D_2O mixtures, only two spectra are known from experimental measurements: Pure H_2O and pure D_2O. By considering the neighbor and next-neighbor situations we found that nine different water species were present. Therefore, light–heavy water mixtures belong to a nine-dimensional chemical space that has nine orthogonal species (axes). Since some of the nine species evolve concomitantly when the D_2O concentration is changed, FA cannot sort their IR spectra. Thus only five principal IR factors were obtained: Two represent the pure single species: H_2O and D_2O; two represent two species each and the last one represents three water species. These five factors, being exclusive the ones from the others, are orthogonal factors.

4. The case of aqueous acetone

In I, we obtained five water and five acetone principal factors for aqueous acetone. This formed a 10-dimensional space. As for the light–heavy water mixtures study[10] we made an evaluation of the perturbations on the carbonyl and water oxygen atoms. This gives nine water species in aqueous acetone for a nine-water dimension in the acetone–water chemistry space. However, abundance calculations showed that some of the nine water species vary concomitantly making them impossible to separate. This reduces the chemistry space effectively occupied by aqueous acetone to five water dimensions.

APPENDIX B: RESIDUES FOLLOWING SPECTRAL MATRIX MANIPULATIONS

To obtain the spectra of the pure principal components with real spectra and MFs, it is necessary to modify the principal spectra obtained in Paper I. Since this is achieved through matrix transformations, we ensure here that the residues are not altered by these manipulations. This exercise indicates that it is not necessary to repeat the full FA procedure when the principal spectra ($\mathbf{S}^P$) are modifed, provided that these are obtained from the same set of experimental spectra ($\mathbf{S}^P_{\mathrm{exp}}$) selected from the whole set of experimental spectra ($\mathbf{S}_{\mathrm{exp}}$).[14] In matrix notation, $\mathbf{S}^P_{\mathrm{exp}}$ giving spectra ($\mathbf{S}^P$) of nonorthogonal principal factors and selected MFs of the experimental spectra used as principal factors ($\mathbf{P}$)

$$\mathbf{S}^P_{\mathrm{exp}} = \mathbf{S}^P \times \mathbf{P} \tag{B1}$$

and

$$\mathbf{S}_{\mathrm{exp}} = \mathbf{S}^P \times \mathbf{MF}. \tag{B2}$$

Let $\mathbf{S}^{P'}$ represent the matrix made of the molar spectra of the principal orthogonal factors, we have the relation

$$\mathbf{S}^P_{\mathrm{exp}} = \mathbf{S}^{P'} \times \mathbf{P}'. \tag{B3}$$

Inverting Eq. (B1) gives

$$\mathbf{S}^P = \mathbf{S}^P_{\mathrm{exp}} \times \mathbf{P}^{-1}. \tag{B4}$$

Introducing Eq. (B3) into Eq. (B4) gives

$$\mathbf{S}^{P'} \times \mathbf{P}' \times \mathbf{P}^{-1} = \mathbf{S}^P. \tag{B5}$$

Finally replacing $\mathbf{S}^P$ in Eq. (B2) with that in Eq. (B5) gives

$$\mathbf{S}_{\mathrm{exp}} = \mathbf{S}^{P'} \times \mathbf{P}' \times \mathbf{P}^{-1} \times \mathbf{MF} \tag{B6}$$

and

$$\mathbf{S}_{\mathrm{exp}} = \mathbf{S}^{P'} \times \mathbf{MF}, \tag{B7}$$

with

$$\mathbf{MF}' = \mathbf{P}' \times \mathbf{P}^{-1} \times \mathbf{MF}. \tag{B8}$$

Equation (B8) proves that the residues are not modified when the principal factors are different than from originally determined but calculated with the same experimental spectra.

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[15] The matrix $\mathbf{P}'$ values obtained are listed in Table IV. There, the molar concentration of factor w_5 (pure water) is 55.441 mol L^{-1}. This value is a little higher than the value 55.304 mol L^{-1} given in Tables II and III of Ref. 1. The slight difference (0.3%) comes from the quadratic approximation used for the relation between water and acetone concentrations [from I, Appendix B, Eq. (B1)].

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