

# Infrared spectroscopy of acetone–water liquid mixtures. I. Factor analysis

Jean-Joseph Max<sup>a)</sup> and Camille Chapados<sup>b)</sup>

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

(Received 25 September 2002; accepted 20 June 2003)

Acetone and water mixtures covering the whole solubility range were measured by Fourier transform infrared attenuated total reflectance spectroscopy. In this system, only water can supply the hydrogen atoms necessary for hydrogen bonding. Using spectral windowing with factor analysis (FA), 10 principal factors were retrieved, five water and five acetone. Hydrogen bonding is observed on the carbonyl stretch band as water is introduced in the solution, redshifting the band further from its gas position than that observed in pure liquid acetone. This indicates that the hydrogen bonding is stronger than the acetone dipole–dipole interactions because it overrides them. A water molecule isolated in acetone is twice H bonded through its two H atoms; although both OH groups are H-bond donors, the OH stretch band is less redshifted ( $\sim 138\text{ cm}^{-1}$ ) than that of pure liquid water ( $\sim 401\text{ cm}^{-1}$ ). This is attributable to the two lone electron pairs remaining on the oxygen atom that sustain a large part of the OH valence bond strength. Hydrogen bonds on the water oxygen weaken both its OH valence bonds and modify the OH stretch band when water is added to the solution. The oxygen atoms of both water and acetone can accept 0, 1, and 2 H bonds given by water to yield three water and three acetone situations. Since these six situations are far less than the 10 principal factors retrieved by FA, other perturbations must be present to account for the difference. Although acetone and water are intermingled through H bonds, hydrates in the sense of an acetone molecule sequestering a number of water molecules or altering the H-bonding water network are not present because the principal factors evolve independently. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600438]

## I. INTRODUCTION

Because nonpolar liquids have relatively weak and isotropic interactions, binary mixtures of them are relatively simple to understand. Mixtures of polar liquids are more complex because dipole–dipole and dipole-induced dipole moments perturb the molecules considerably.<sup>1</sup> Among polar liquids, alcohols and water create complicated situations because the OH groups that form hydrogen bonds (H bonds) act as donor, acceptor or concurrently. Because of its importance, water has fueled enormous efforts to understand its solvation properties.<sup>2</sup> In spite of these efforts, a general model that would explain all the properties of water has not yet been found.<sup>3</sup> This indicates that our knowledge of aqueous binary systems is not complete and consequently leads to ambiguous interpretation of ternary and higher systems.

The water oxygen atom has two covalent hydrogen atoms that form hydrogen bonds with neighbor molecules and two nonbonding orbitals to which two hydrogen atoms from other neighbor molecules can be hydrogen bonded. Consequently, a water molecule can have four hydrogen bonds. Hence, the high density of H bonds forming a tridimensional network is responsible for the exceptional physical, chemical, and biological properties of liquid water.<sup>4</sup> In ice and liquid water, the small H<sub>2</sub>O molecule held by numerous di-

rectional H bonds gives a tetrahedral organization around its oxygen atom.<sup>5,6</sup> This model was used to calculate its IR spectrum.<sup>7</sup> The question that comes to mind is how can such a “highly organized liquid” still be a fluid?<sup>4</sup>

An H bond is obtained when an H from a donor group like a hydroxyl is attached to an H-bond acceptor from another group. The donor and acceptor groups can be either on the same molecule or on different molecules.<sup>8</sup> Infrared (IR) spectroscopy is a good method to use for observing this interaction because the stretch band of the donor group is significantly redshifted accompanied by a considerable intensity increase.<sup>8</sup> The IR spectra of alcohols and their solutions were used to establish Luck’s notation of OH free and OH bonded:<sup>9</sup> in the equilibrium  $\text{OH}_{\text{free}} + \theta_{\text{free}} \rightleftharpoons \text{OH}_{\text{H bond}}$ , where  $\theta_{\text{free}}$  represents a non-H-bonded lone electron pair and  $\text{OH}_{\text{free}}$  represents an OH group not H bonded. We have adopted the same notation.

The purpose of the present work is to add new results that will shed some light on the nature of H bonding in a binary aqueous system by studying mixtures that cover the full water molar fractions, but with limited H bonding possibilities. The acetone–water system is well suited for this because (1) pure acetone contains no labile hydrogen that can form H bonds, (2) only the water hydrogen atoms can make H bonds with the oxygen atoms of either water or acetone in acetone–water mixtures, and (3) the water and acetone IR bands are very distinct. Therefore, as the sole hydrogen bond donor molecule, water will limit the possi-

<sup>a)</sup>Current address: Scientech R&D, 247 Thibeau, Cap-de-la-Madeleine, (QC), Canada G8Y 6X9; Electronic mail: jjmax@scientech-rd.com

<sup>b)</sup>Author to whom correspondence should be addressed; Electronic mail: Camille\_Chapados@uqtr.ca

bilities of the hydrogen-bonding network and consequently facilitate the analysis of this system.

Because of the high absorptivity of the OH stretch band of water, the IR transmission spectra are difficult to obtain.<sup>10</sup> The attenuated total reflection (ATR) method is a suitable alternative by providing good quality IR spectra of water mixtures with high precision and reproducibility.<sup>4,5,11–30</sup> Furthermore, we have shown in Ref. 17 that the ATR spectra reflect the chemical changes in aqueous solutions without the need to transform them into the real and imaginary parts of the refractive indices [ $n(\nu)$  and  $k(\nu)$ ] as long as certain basic requirements are met: (1) a proper crystal whose refractive index is far from that of the solution; (2) a proper angle of incidence for the IR beam; (3) a crystal of adequate length.

In this paper, we present the ATR–IR spectra of a series of acetone–water mixtures on which factor analysis (FA) was performed. We looked first at diluted mixtures (water in acetone and acetone in water), and then at the complete range. This allowed us to (1) sort out the principal factors, (2) obtain their spectra and abundances, and (3) estimate the presence of “free” OH in the mixtures.

## II. EXPERIMENTAL WORK AND DATA TREATMENT

### A. Chemicals and solutions

Acetone (Laboratory Mat purity >99.5% w/w, water content  $\leq 0.5\%$ ) was used without further purification. Deionized water was used to prepare the mixtures. Three series of samples were obtained: (1) low water content in acetone (water molar fraction  $\chi_w < 0.24$ ); (2) low acetone content in water ( $\chi_w > 0.80$ ); (3) whole concentration range ( $0.00 < \chi_w < 1.00$ ). The first series was obtained with 140 mL liquid acetone to which was added pure water in steps up to 10.7 mL. The second series was obtained with 100 mL pure liquid water to which acetone was added in step up to 100.1 mL. The third series was obtained with 40 mL liquid acetone to which pure water was added in steps up to 205 mL. The sample compositions of the three series are given in Tables I–III, respectively. The water molar fractions obtained directly from the volumes considering both components to be “neat” components are given in these tables (the relationships between component volumes, concentrations and molar fractions are given in Appendixes A and B). Later on, the values were corrected to take into account the small water content (0.5% determined by IR) of the “neat” acetone used.

### B. IR measurements

The IR measurements were obtained using a model 510P Nicolet FTIR spectrometer with a DTGS 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  $45^\circ$  with the rod’s axis and makes 11 internal reflections of which nearly 6.6 are in contact with the liquid sample). The spectral range of this system is 5700 to  $650\text{ cm}^{-1}$ . The spectra were taken under nitrogen flow to ensure low  $\text{CO}_2$  and water va-

TABLE I. Water molar fraction of acetone aqueous mixtures at low water concentration.

Sample number	Water molar fraction ( $\chi_w$ )	
	From volumes	Corrected <sup>a</sup>
1	0.0000	0.0166
2	0.0029	0.0194
3	0.0058	0.0222
4	0.0129	0.0291
5	0.0200	0.0359
6	0.0338	0.0492
7	0.0472	0.0622
8	0.0602	0.0749
9	0.0729	0.0872
10	0.0973	0.1108
11	0.1204	0.1333
12	0.1424	0.1546
13	0.1633	0.1749
14	0.1832	0.1943
15	0.2022	0.2128
16	0.2376	0.2473

<sup>a</sup>Corrected for the residual water in the solvent (see text).

por residues in the spectrometer. Each spectrum represents an accumulation of 500 scans at  $2\text{ cm}^{-1}$  resolution ( $0.965\text{ cm}^{-1}$  sampling interval). The measurements were made at  $27.1\text{ }^\circ\text{C} \pm 0.3\text{ }^\circ\text{C}$ . The cell was carefully dried before each measurement series. Model 510P being a single-beam spectrometer, a background reference was taken with the empty cell before measuring the spectra of the samples. These were obtained by circulating the liquid mixture into the cell (approximately 1 mL volume) at a rate of  $0.5\text{ mL min}^{-1}$ .

The IR measurements consisted in obtaining the ATR background and sample spectra,  $R_0$  and  $R$ , respectively. The ratio of  $R/R_0$  is the intensity  $I$  for the spectral range being

TABLE II. Water molar fraction of acetone aqueous mixtures at low acetone concentration.

Sample number	Water molar fraction ( $\chi_w$ )	
	From volumes	Corrected <sup>a</sup>
1	1.0000	1.0000
2	0.9973	0.9973
3	0.9949	0.9949
4	0.9925	0.9925
5	0.9901	0.9901
6	0.9853	0.9853
7	0.9805	0.9805
8	0.9758	0.9758
9	0.9689	0.6890
10	0.9598	0.9598
11	0.9508	0.9508
12	0.9399	0.9399
13	0.9313	0.9313
14	0.9208	0.9208
15	0.9105	0.9106
16	0.9004	0.9006
17	0.8906	0.8908
18	0.8716	0.8718
19	0.8533	0.8537
20	0.8029	0.8036

<sup>a</sup>Corrected for the residual water in the solvent (see text).

TABLE III. Water molar fraction of acetone aqueous mixtures ( $\chi_w$ ).

Sample number	Water molar fraction ( $\chi_w$ )	
	From volumes	Corrected <sup>a</sup>
1	0.0000	0.0166
2	0.0925	0.1062
3	0.1694	0.1808
4	0.2342	0.2440
5	0.2897	0.2981
6	0.3377	0.3450
7	0.3796	0.3860
8	0.4165	0.4221
9	0.4492	0.4543
10	0.5048	0.5089
11	0.5503	0.5536
12	0.5880	0.5909
13	0.6341	0.6364
14	0.6710	0.6728
15	0.7099	0.7113
16	0.7473	0.7483
17	0.7811	0.7819
18	0.8107	0.8113
19	0.8360	0.8365
20	0.8595	0.8598
21	0.8843	0.8846
22	0.9107	0.9108
23	0.9214	0.9215
24	0.9298	0.9299
25	0.9386	0.9387
26	0.9543	0.9544
27	1.0000	1.0000

<sup>a</sup>Corrected for the residual water in the solvent (see text).

studied. Thereafter, the 5237 data points of [ $I(\tilde{\nu})$  versus  $\tilde{\nu}$  (in  $\text{cm}^{-1}$ )] for each spectrum were transferred to a spreadsheet program for numerical analysis. The intensities  $I$  were transformed into absorbance units,  $\log(1/I)$  (abbreviated in some cases as a. u.). No baseline shift was necessary because the mean absorbance in the  $5700\text{--}5500\text{ cm}^{-1}$  region was near 0.002 a. u. (in water-rich mixtures), which corresponds to the reported water intensity in this region.<sup>10</sup>

### C. Factor analysis (FA)

Factor analysis of a spectral data set is a process by which evolving system principal factors 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, molar fraction, etc., is varied. However, when two or more species evolve simultaneously in a constant ratio, FA cannot separate them. In such cases, the principal factors contain more than one species as in aqueous solutions of propanol,  $\text{D}_2\text{O}$ , and sucrose.<sup>11,13,29</sup> In spite of these shortcomings, FA is a powerful method that was successfully used to study many aqueous systems.<sup>13,22–29</sup> We will use it to obtain the acetone-water species.

The first step in the FA procedure is to recover the principal factors necessary to describe the entire set of experimental spectra. This was achieved by the following iterative procedure: (a) the choice in the set of experimental spectra of two principal factors (the pure and most concentrated species); (b) subtraction of these factors each multiplied by the

highest MFs possible from the experimental spectra to minimize the residues; (c) these are evaluated to obtain any emerging pattern that signals the presence of a supplementary species [the spectrum of this species becomes an additional principal factor and the procedure is repeated from step (b)]; (d) when no other supplementary factor can be introduced that minimizes significantly the residues, the FA procedure is complete. At this stage the number of principal factors, their spectra and abundances are determined. Since these factors are not automatically exclusive one from the others, the next step is to render them exclusive and make the MFs real. This step is system dependent and different stratagems can be used. For this acetone–water system, the one that we used will unfold in a subsequent paper (Paper II). For the present FA study, the exclusive factors are not needed.

## III. RESULTS AND DISCUSSION

The whole spectra of aqueous acetone solutions at low, high, and intermediate concentrations are analyzed first. Next, the spectra are tackled by parts: first, the water bands and second, the acetone ones.

### A. Aqueous acetone spectra in the whole $4000\text{--}700\text{ cm}^{-1}$ range

#### 1. Low water content in acetone ( $\chi_w < 0.24$ )

This series with low water content in acetone (Table I) was made to study the water  $\nu_{\text{OH}}$  band starting from a situation where the acetone molecules surrounding each water molecule isolate them from one another. At these concentrations, the only possible hydrogen bonds are those between the water OH groups and the acetone–carbonyl groups.

(a) *Experimental IR spectra*: Figure 1(A) shows 16 IR–ATR spectra of water–acetone mixtures. Apart from the small bands at  $3414$  and near  $3455\text{ cm}^{-1}$ , assigned, respectively, to acetone  $2\nu_3$  and  $\nu_3 + \nu_{17} + \nu_{19}$ , the absorption in the  $3700\text{--}3100\text{ cm}^{-1}$  region comes from the OH stretch of water. The  $3615\text{ cm}^{-1}$  and  $3520\text{ cm}^{-1}$  bands still observed in “neat” acetone [lower spectrum in Fig. 1(A)] are due to minute quantities of water ( $<0.5\%$ ). At the high acetone concentrations, the CO and CC stretch bands ( $\nu_3$  and  $\nu_{17}$ ) are saturated (ATR–a.u. $>2$ ) and cannot be used in the analysis. When water is added to the solution, the other acetone bands show some variations indicative of several acetone species. In Fig. 1(A), the vertical lines at  $3615$ ,  $3520$ , and  $3414\text{ cm}^{-1}$  were drawn to follow the evolving spectral features. With increasing water concentration, the  $\nu_3$  and  $\nu_1$  water bands near  $3615$  and  $3520\text{ cm}^{-1}$  are lowered and a new band emerges near  $3250\text{ cm}^{-1}$ . At  $3414\text{ cm}^{-1}$ , the  $2\nu_3$  band of acetone is slightly modified indicating that the water molecules perturb the acetone molecules.

(b) *Water content in “neat” acetone*: To evaluate the water content in “neat” acetone ( $\chi_w = 0.000$ , from volumes) we integrated in Fig. 1(A) the absorption in the  $3700\text{--}3500\text{ cm}^{-1}$  limit (this range avoids the  $3414\text{ cm}^{-1}$  acetone band). The Fig. 1(B) trace indicates that Beer’s law is valid up to around  $2.0\text{ M}$  water. Extrapolating to zero gives a  $0.52\%$  ( $\pm 0.02$ , w/w) water content in the “neat” acetone. The other solution concentrations were corrected accordingly (Table I).

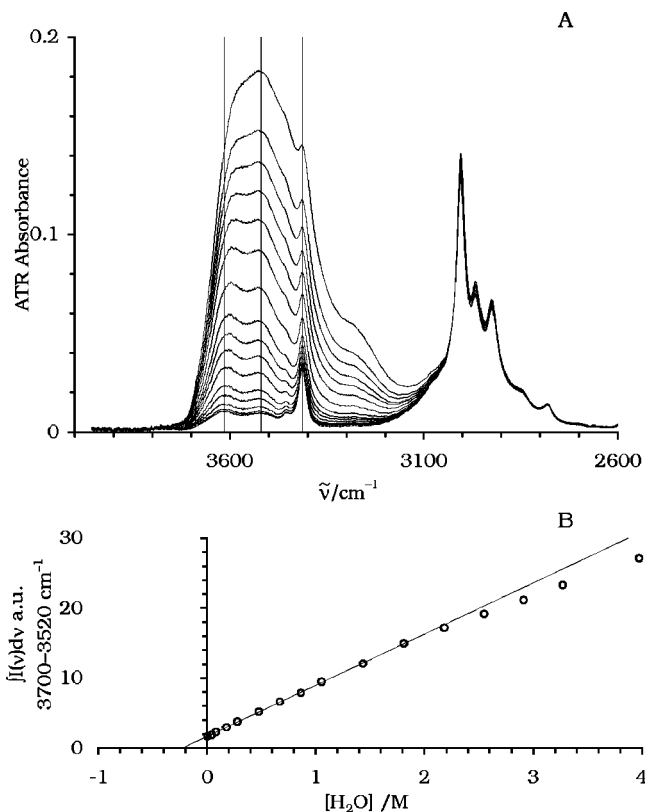


FIG. 1. IR spectra of the low water content in acetone–water mixtures (Table I for sample compositions). (A) O–H and C–H stretch regions; (B) integrated intensity of OH stretch band. Note in (A) the vertical lines are at 3615, 3520, and 3414  $\text{cm}^{-1}$ .

(c) *FA of the spectra of low water content in acetone:* Not considering the intensity factor, the OH bands in the top and bottom spectra in Fig. 1(A) are very different from one another. This indicates that at least two water species are present in the solutions. These together with pure acetone make at least three species in this series of mixtures.

(d) *Determination of the principal factors:* Two principal species may be sufficient to explain the experimental spectra at  $\chi_w \ll 1$ . To separate these we proceeded as follows: let  $i$  and  $j$  be the two different mixture indices with  $\chi_w^i < \chi_w^j \ll 1$  (hence  $(\chi_w^j - \chi_w^i) \ll 1$ ). Let  $S_1$  (pure acetone) and  $S_2$  be the spectra of the two principal species and the  $a$ 's their respective concentration at  $\chi_w \ll 1$ . We therefore have

$$S_i = a_1^i S_1 + a_2^i S_2 \quad \text{and} \quad S_j = a_1^j S_1 + a_2^j S_2. \quad (1)$$

From the condition  $\chi_w^i < \chi_w^j \ll 1$ , we deduce that

$$a_1^i > a_1^j \quad \text{and} \quad a_2^i < a_2^j. \quad (2)$$

Hence, we have

$$S_i - \frac{a_2^i}{a_2^j} S_j = S_1 \left( a_1^i - a_1^j \frac{a_2^i}{a_2^j} \right)$$

$$\text{and} \quad S_j - \frac{a_1^j}{a_1^i} S_i = S_2 \left( a_2^j - a_2^i \frac{a_1^j}{a_1^i} \right) \quad (3)$$

with

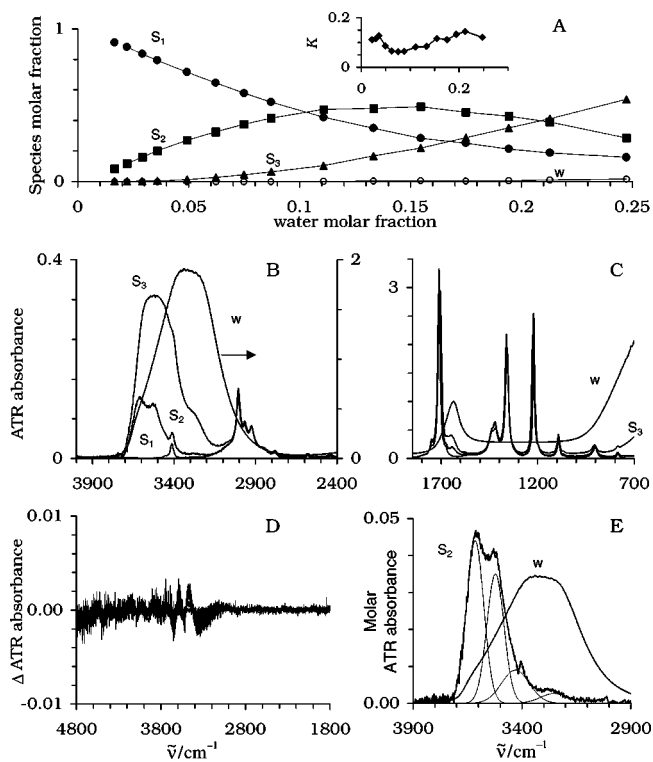


FIG. 2. The result of FA on the low water content in acetone–water mixtures. (A) Species molar fraction as a function of total water molar fraction (inset, equilibrium constants,  $K$ , see text). (B), (C) principal spectra (D) residues. (E) Gaussian simulation of species  $S_2$ . Note in (A) the lines are eye guides.  $S_1$ , pure acetone;  $S_2$  and  $S_3$ , acetone–water species; and  $w$ , pure water.

$$\frac{a_1^i}{a_1^j} > 1 > \frac{a_2^i}{a_2^j}, \quad (4)$$

that is

$$a_1^i - a_1^j \frac{a_2^i}{a_2^j} > 0. \quad (5)$$

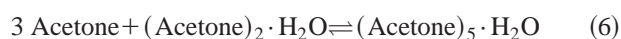
Therefore, a good pure acetone spectrum ( $S_1$ ) can be obtained by subtracting from a spectrum at water molar fraction  $\chi_w^i \ll 1$  the next one in the series with  $\chi_w^j < \chi_w^i \ll 1$ . This last spectrum is multiplied by a positive coefficient [Eq. (5)] less than unity. The resulting spectrum normalized to 13.6 M acetone represents pure liquid acetone. With Eq. (3), the spectrum of the second principal species ( $S_2$ ) was obtained in the same way. Repeating the procedure with three pairs of experimental spectra (with  $\chi_w^i < \chi_w^j \ll 1$ ) and averaging the results gave the spectra  $S_1$  and  $S_2$  in Figs. 2(B) and 2(C). A third principal species was retrieved by FA (Sec. II C) from which a small quantity of the pure water spectrum was subtracted. The result normalized to 13.6 M acetone yielded spectrum  $S_3$  [Figs. 2(B) and 2(C)].

The molar fractions of  $S_1$ ,  $S_2$ , and  $S_3$  as a function of water molar fraction are presented in Fig. 2(A). The residues [Fig. 2(D)] obtained from the difference between calculated and experimental spectra are sufficiently low ( $< 4$  m.a.u.) to indicate that the three principal species are sufficient to describe the spectra in the 0.000–0.247 M range.

TABLE IV. Composition of the six principal species retrieved in aqueous acetone at low water content and at low acetone content, respectively.

Species	Acetone content	Water content	Molar ratio	Water molar fraction	Acetone molar fraction
$S_1$	13.48±0.15 M	0.03±0.08 M	1.00:0.00		0.995±0.005
$S_2$	13.46±0.20 M	2.69±0.20 M	5.0±0.5:1.0		0.830±0.015
$S_3$	13.60±0.35 M	7.00±0.35 M	1.94±0.18:1		0.660±0.018
$S_4$	13.60±0.15 M	21.60±0.30 M	1.00:1.60±0.06	0.614±0.006	
$S_5$	6.485±0.020 M	32.70±0.15 M	1.00:5.04±0.05	0.835±0.002	
$S_6$	0.00 M	55.30 M	0.00:1.00	1.000	

(e) *Species equilibrium*: The molecular composition of  $S_1$ ,  $S_2$ , and  $S_3$  are given in Table IV. The acetone to water ratio are 1:0, 5:1, and 2:1, respectively. Pure liquid water is also present in minute quantities, but is not considered here. The thermodynamic equilibrium between the three species is



with the equilibrium constant  $K$ :

$$K = \frac{[(\text{Acetone})_5 \cdot \text{H}_2\text{O}]}{[\text{Acetone}]^3 [(\text{Acetone})_2 \cdot \text{H}_2\text{O}]} = \frac{[S_2]}{[S_1]^3 \times [S_3]} \quad (7)$$

The equilibrium constant  $K$  was evaluated using the species concentrations retrieved by FA [Fig. 2(A) inset]. The near constant value obtained ( $0.10 \pm 0.04 \text{ L}^3 \text{ mol}^{-3}$ ) indicates that the procedure is correct. In the region 0 to 0.1 water molar fraction, the pure acetone concentration is near 13.5 M; the concentration ratio  $[S_3]/[S_2]$  at around 0.4% indicates that the amount of  $S_3$  is negligible compared to  $S_2$ . This justifies disregarding  $S_3$  to obtain spectrum  $S_2$  [through Eq. (3)], which is established to be pure. However, it is not possible to ensure that  $S_3$  [Figs. 2(B) and 2(C)] does not contain higher water content species.

(f) *Water molecule isolated in acetone*: The water absorption in species  $S_2$  necessitates some consideration. The pure acetone spectrum ( $S_1$ ) was partly subtracted from the  $S_2$  spectrum [Fig. 2(B)] and the result normalized to 1 M water. The result presented in Fig. 2(E) shows a glitch near  $3415 \text{ cm}^{-1}$  because the use of  $S_1$  resulted in a non perfect subtraction of the  $\nu_{\text{CO}}$  overtone of acetone. This glitch does not interfere with subsequent operations.

The Gaussian simulation of the  $S_2$  spectrum is shown in Fig. 2(E) with the pure water spectrum as a comparison (trace  $w$ ). The component positions are given in Table V. The two principal absorption bands situated at  $3615$  and  $3522 \text{ cm}^{-1}$  are assigned to  $\nu_3$  and  $\nu_1$  of isolated water molecules in acetone. These components are approximately  $140 \text{ cm}^{-1}$  redshifted relative to their gas positions and approximately  $260 \text{ cm}^{-1}$  blueshifted relative to the liquid positions. The full width at half-height (FWHH) of the isolated and pure liquid species is  $93$  and  $195 \text{ cm}^{-1}$ , respectively (Table V). Two small bands situated at  $3430$  and  $3250 \text{ cm}^{-1}$  not presently assigned indicate the presence of other water species in small amount.

“Free” OH groups are thought to exist in pure liquid water.<sup>9</sup> Their amount decreases rapidly when adding molecules that have excess H-bond acceptor lone electron pairs on their oxygen as in methanol.<sup>9</sup> Consistent with reported work on alcohol–water mixtures and other related work,<sup>9(a)</sup> acetone, as a strong hydrogen acceptor, will make hydrogen bonds with all available water molecules in a water-poor solution. Consequently, water molecules with a “free” OH group cannot exist in such situations. This means that all the OH groups available in the mixtures are hydrogen bonded to an acetone oxygen atom. However, the OH stretch band of water surrounded by acetone is much less redshifted [Fig. 2(E),  $S_2$ ] than that of the pure liquid water situation [Fig. 2(E),  $w$ ]. For  $S_2$ , all the hydrogen atoms are bonded to the acetone carbonyls. However, the strong hydrogen bonding causes much less redshift than that of pure water where the molecules give either the same number of hydrogen bonds

TABLE V. Position (in  $\text{cm}^{-1}$ ), full-width at half height (FWHH in  $\text{cm}^{-1}$ ), and molar intensities (in ATR–IR a.u.) of the IR Gaussian components of the water absorbance in principal factors  $S_2$  in aqueous acetone.

Assignment	$\text{H}_2\text{O}$ gas <sup>b</sup> position	Species $S_2$			Shift from gas position	Pure water <sup>a</sup>			Shift from gas position
		Position	FWHH	Int.		Position	FWHH	Int.	
$\nu_3$ ( $\text{OH}_{\text{free}}$ )	3756								
$\nu_1$ ( $\text{OH}_{\text{free}}$ )	3657								
$\nu_3$ ( $\text{OH}_2$ )		3615	93	0.0440	141				
$\nu_1$ ( $\text{OH}_2$ )		3522	93	0.0350	135				
		3430	150	0.0083					
		3250	150	0.0027					
$\nu_3$ ( $\text{OH}_4$ )						3389	195	0.0289	367
$\nu_1$ ( $\text{OH}_4$ )						3222	195	0.0279	435

<sup>a</sup>Reference 13.

<sup>b</sup>Reference 33.

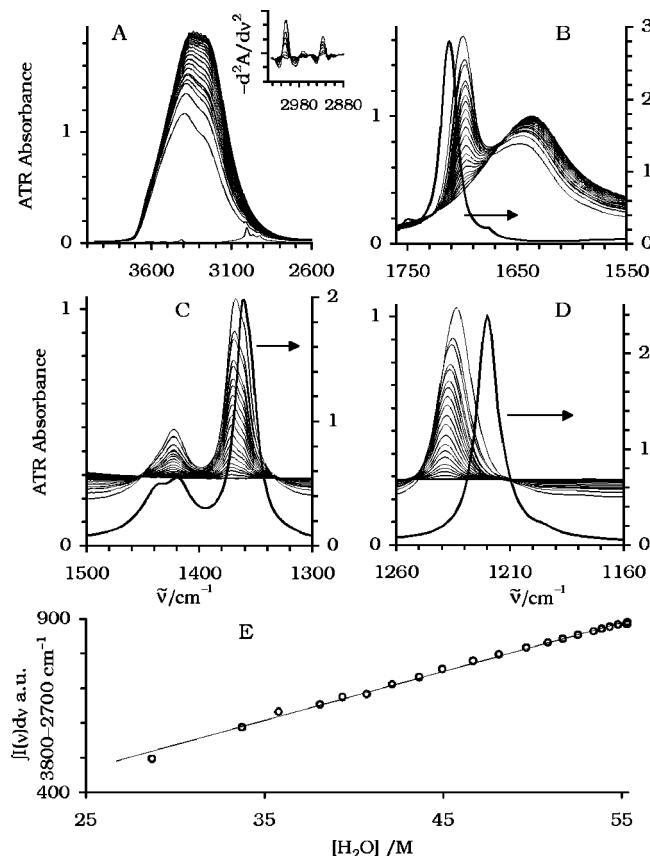


FIG. 3. IR spectra of low acetone content in acetone–water mixtures (Table II for sample composition). (A) O–H and C–H stretch regions (inset, second derivatives of  $\nu_{\text{CH}}$ ); (B) acetone CO stretch ( $\nu_3$ ) and water deformation ( $\delta_{\text{HOH}}$ ) region; (C)  $\delta_{\text{CH}_3}$  region; (D)  $\nu_{\text{CC}}$  region ( $\nu_{17}$ ); and (E) integrated intensity of  $\nu_{\text{OH}}$ . Note in (B)–(D) the heavy lines are for pure acetone, scale at right.

or less. Similar situations of strong hydrogen-bonding acceptors like dioxane and acetonitrile have also been reported.<sup>14,31</sup>

## 2. Low acetone content in water ( $\chi_w > 0.80$ )

The series of low acetone content in water (Table II), was made to study the water  $\nu_{\text{OH}}$  band in situations where each water molecule is surrounded by other water molecules with few acetone molecules nearby. The interactions between acetone molecules are minimal.

(a) *Experimental IR spectra*: Figures 3(A)–3(D) show the IR–ATR spectra of low acetone content in water along with the spectrum of pure liquid acetone ( $S_1$ , Sec. III A 1). Starting from the pure water spectrum (top one), the OH stretch band [Fig. 3(A)] is blueshifted as acetone is added to water; its intensity is decreased and some new spectral features become apparent. The acetone CO stretch [ $\nu_3$ , Fig. 3(B)] is redshifted by nearly  $15 \text{ cm}^{-1}$  (at  $1697 \text{ cm}^{-1}$ ) from its pure liquid ATR position ( $1712 \text{ cm}^{-1}$ ) due to hydrogen bonding. The CC stretch band of acetone ( $\nu_{17}$ ) passes from  $1220 \text{ cm}^{-1}$  in the pure liquid to  $1238 \text{ cm}^{-1}$  in the solutions [Fig. 3(D)]. This  $18 \text{ cm}^{-1}$  blueshift is interpreted as a strengthening of the CC bond as a consequence of the weakening of the CO bond.

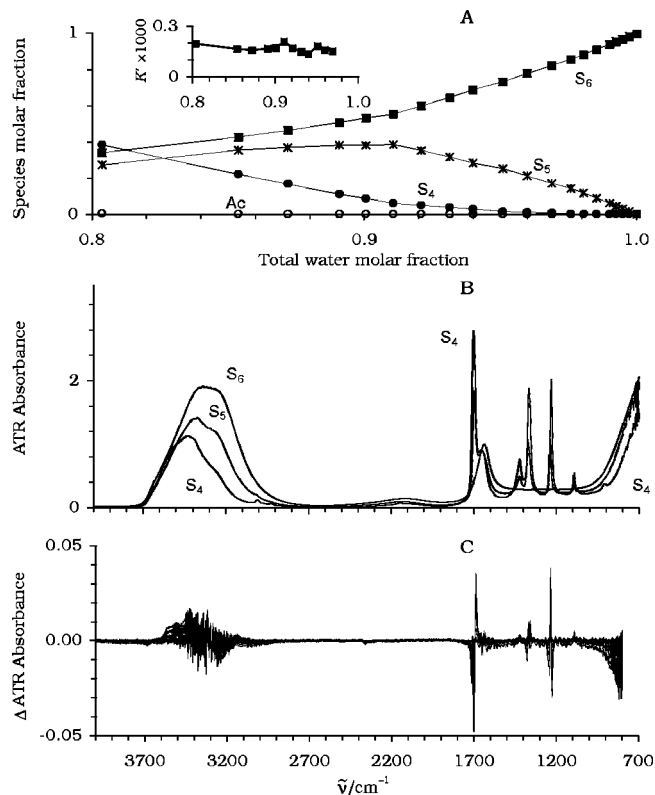


FIG. 4. The result of FA on the low acetone content in acetone–water mixtures. (A) Species molar fraction (inset, equilibrium constants,  $K'$ , see text); (B) principal spectra; (C) residues.  $S_4$  and  $S_5$ , acetone–water species;  $S_6$ , pure water; Ac, pure acetone.

Because of the intense OH stretch band, the CH stretch bands are difficult to observe directly; their second derivatives were then obtained [inset in Fig. 3(A)]. These bands are progressively redshifted as acetone is added to water. Similarly, the  $\text{CH}_3$  deformation bands of acetone [Fig. 3(C)] are slightly modified as acetone is added to water. These results indicate that the  $\text{CH}_3$  groups of acetone are slightly affected by water.

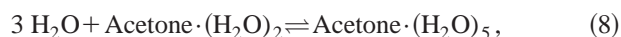
Figure 3(E) shows the OH stretch band integrated intensity of water ( $3800\text{--}2700 \text{ cm}^{-1}$ ) as a function of water concentration. The monotonic relationship obtained indicates that the measurements are accurate. The proportionality coefficient obtained in this concentration range is  $14.10 \text{ ATR a.u. L mol}^{-1}$ . This value, which is almost 10% lower than that of pure water ( $888/55.30 = 16.06 \text{ ATR a.u. L mol}^{-1}$ ), indicates a slightly higher OH stretch band integrated intensity in this concentration range.<sup>32</sup> This indicates the presence of another water species in the solution.

(b) *FA on the spectra of low acetone content in water*: We retrieved three principal factors by FA in the low acetone content aqueous spectra. Pure liquid water is clearly one ( $S_6$ ); pure liquid acetone is another, but was not considered here because of its minute amount (Table II). The spectrum of the second principal factor ( $S_5$ ) was obtained with Eq. (3). The procedure was applied using four pairs of spectra. By averaging the results, the first two principal spectra were obtained [Fig. 4(B)]. Spectrum  $S_5$  was not normalized to  $13.6 \text{ M}$  acetone to avoid having the water spectrum go off

scale. Since the retrieved  $S_6$  spectrum was the same as that of pure water obtained directly, we concluded that the procedure worked adequately. A third principal species ( $S_4$ ) was obtained by the procedure given in Sec. II C. After subtracting a minute amount of the pure acetone spectrum, the resulting spectrum was normalized to 13.6 M acetone [Fig. 4(B)]. The species molar fractions are presented in Fig. 4(A).

The residues, obtained from the difference between experimental and calculated spectra using the principal factors, are shown in Fig. 4(C). Because of the strong absorptivity of acetone  $\nu_3$  and  $\nu_{17}$  bands, the residues are not zero near 1700 and 1230  $\text{cm}^{-1}$ . Except for these two bands, the residues are very small, indicating that the three principal factors are sufficient to account for all the species present in this series of low acetone content acetone mixtures.

(c) *Species equilibrium*: The molecular composition of  $S_4$ ,  $S_5$ , and  $S_6$  are given in Table IV. Their acetone to water molar ratios are 1:1.60, 1:5, and 0:1, respectively. The equilibrium equation and constant are



$$K' = \frac{[\text{Acetone} \cdot (\text{H}_2\text{O})_5]}{[\text{H}_2\text{O}]^3 [\text{Acetone} \cdot (\text{H}_2\text{O})_2]} \equiv \frac{[S_5]}{[S_6]^3 \times [S_4]}. \quad (9)$$

The  $K'$  values plotted in Fig. 4(A) insert give an average value of  $(0.17 \pm 0.05) \times 10^{-3} \text{L}^3 \text{mol}^{-3}$ . With the water concentration ( $c_w = 55.3 \text{M}$ ), the ratio of  $[S_4]/[S_5]$  is calculated at nearly 4%. Although this indicates that spectrum  $S_5$  contains almost 4% of spectrum  $S_4$ , both can be used as principal factors since these need not be exclusive in FA.

### 3. Whole solubility range of acetone in water ( $0.0 \leq \chi_w \leq 1.0$ )

Sections III A 1 and III A 2 indicated that aqueous acetone could be described at each end of the concentration scale by the formation of complexes. Hence one could conclude, as in the case of aqueous acetonitrile,<sup>12</sup> that aqueous acetone is a nonhomogenous mixture. If true, this hypothesis must be valid over the entire concentration range.

Twenty-seven spectra of the water–acetone mixtures in the whole solubility range (Table III) are presented in Figs. 5(A)–5(D). The water  $\nu_{\text{OH}}$  integrated intensity between 3800–2700  $\text{cm}^{-1}$  [Fig. 5(E)] gives a linear relationship ( $16.60 c_w - 2.174$ ). The proportionality coefficient, which is comparable to that of water ( $888/55.30 = 16.06 \text{ a.u. L mol}^{-1}$ ), could indicate that a single water species is present in the solutions. However, at least four different water species were retrieved in the preceding sections. This indicates that the integrated band intensity is not the best method to determine the number of species in a solution. FA was then tried with four, five, six, and seven principal factors. In each case, strong residues indicated that these trials were unsuccessful.

In previous studies dealing with the acid–base titration, FA permitted the retrieval of up to 10 species although only six were present simultaneously and single species could be found in some parts of the titration curves.<sup>15,21–23</sup> In this aqueous acetone system, the use of more than six principal factors decreased the accuracy of the retrieved MFs without

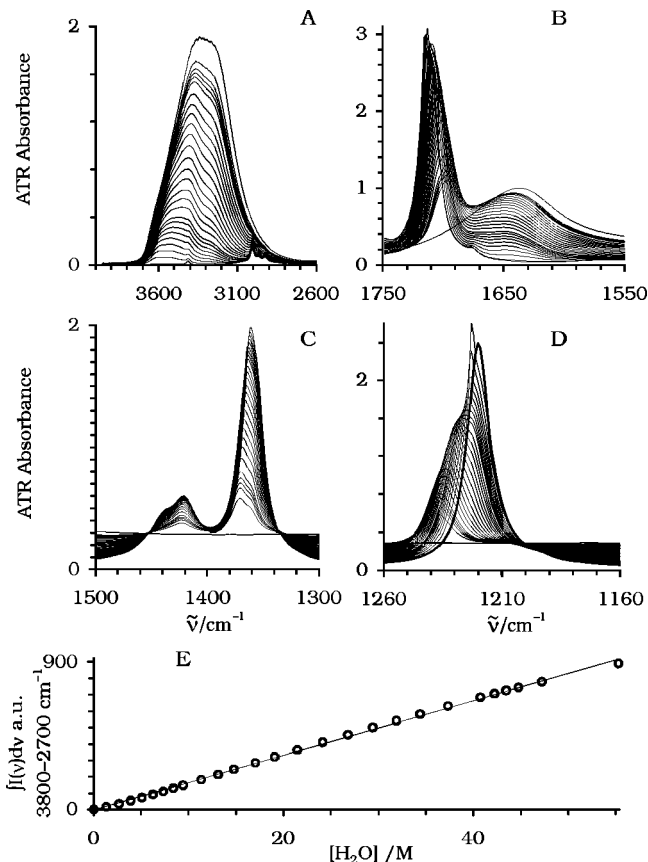


FIG. 5. IR spectra of acetone–water mixtures in the whole solubility range (Table III for sample composition). (A) O–H and C–H stretch regions; (B) acetone CO stretch ( $\nu_3$ ) and water deformation ( $\delta_{\text{HOH}}$ ) region; (C)  $\delta_{\text{CH}_3}$  region; (D) CC stretch region ( $\nu_{17}$ ); and (E) integrated intensity of  $\nu_{\text{OH}}$ .

significantly reducing the residues. Consequently, more than six principal species must be present simultaneously and no single species is present except at the limits of the concentration range. Hence, since FA using the entire spectrum did not provide a satisfactory solution, we had to modify our approach.

### B. Water and acetone treated separately

Since more than six species are present simultaneously in the aqueous acetone system, by targeting separately the water and acetone species, the factor separation is made easier because the water and acetone species absorb in different spectral ranges with much different absorptivities. FA was then applied to the 4000–1800  $\text{cm}^{-1}$  region where water absorbs strongly and acetone absorbs weakly. Thereafter, it was applied to the 1800–700  $\text{cm}^{-1}$  region where the acetone features are the strongest. This targeting maximize the information of water species in one region and of the acetone species in the other region without unnecessary data that contain little information of the targeted species.

#### 1. Factor analysis of water species in the 4800–1800 $\text{cm}^{-1}$ region

In the 4800–1800  $\text{cm}^{-1}$  region [Fig. 1(A)], the strongest acetone absorption occurs in the CH stretch (3100–2700

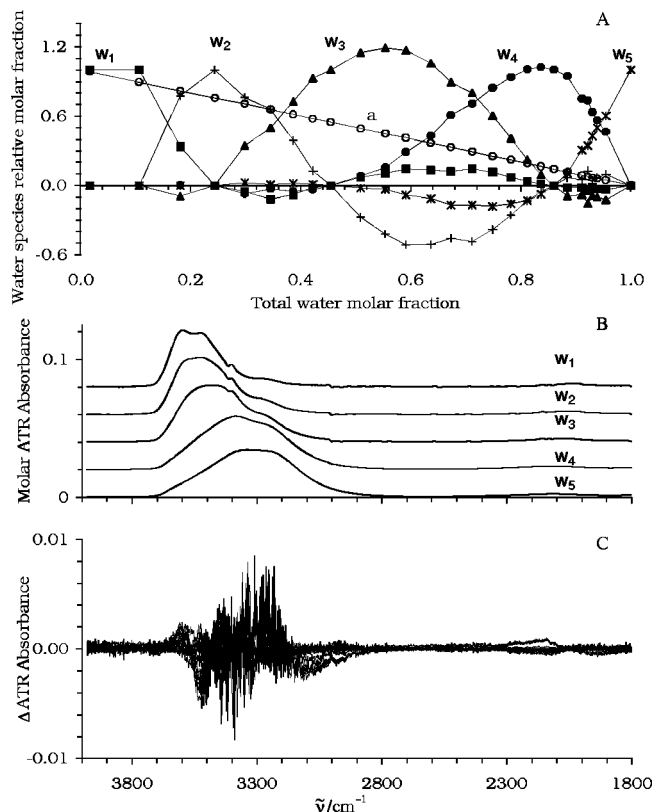


FIG. 6. FA results applied to the 4000–1800  $\text{cm}^{-1}$  spectral region ( $\nu_{\text{OH}}$  of water) of acetone–water mixtures in the whole solubility range (acetone absorption bands subtracted). (A) Abstract water species molar fractions (symbols, from MFs; lines are eye guides); (B) real spectra of nonexclusive principal factors; (C) residues,  $w_1$ – $w_4$ , water acetone species;  $w_5$ , pure water;  $a$ , total acetone.

$\text{cm}^{-1}$ ) and  $2\nu_3$  ( $\sim 3410 \text{ cm}^{-1}$ ) bands with intensities 0.14 and 0.03 a.u., respectively. These are far less intense than water absorption in this region [maximum intensity, 1.9 a.u., Fig. 5(A)]. Since the acetone bands are not much displaced for the different solutions (Fig. 1), they were subtracted with the pure acetone spectrum normalized to the proper concentrations. This resulted in low intensity sigmoid features that do not interfere with the water analysis.

Factor analysis applied to the resulting spectra revealed five principal water factors. Their molar spectra and relative abundances are given in Figs. 6(B) and 6(A), respectively. The minimal residues obtained [Fig. 6(C)] indicated that FA worked satisfactorily. Therefore, five water principal factors are sufficient but necessary to account for the water absorption in the whole concentration range. Negative MF values in Fig. 6(A) indicated abstract abundances. These need to be made positives to interpret them.

To render the five water spectra in Fig. 6(B) exclusive one from the others, we tried second derivatives and Fourier self-deconvolution enhancement procedures to monitor the subtractions. Our efforts were unsuccessful because the massive absorptions contain too many large overlapping components. In such situations, these techniques generate artifacts without real band enhancement. Since the procedure to render the five water factors exclusive one from the others re-

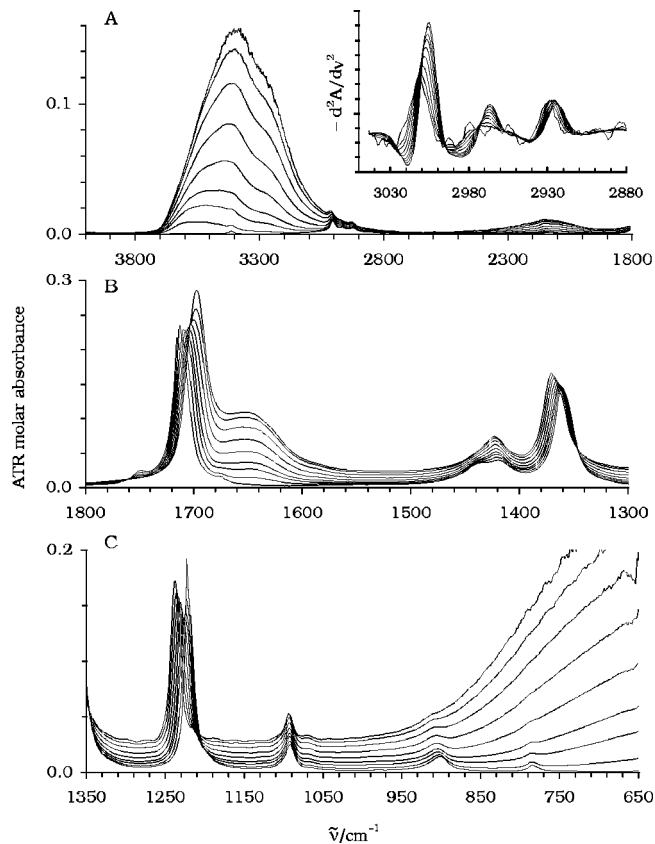


FIG. 7. Nine of the 26 IR spectra of acetone–water mixtures in the whole solubility range (Fig. 5) after the pure water spectrum subtraction and normalization to 1 M acetone. Inset, second derivative spectra in the  $\nu_{\text{CH}}$  region.

quired a detailed analysis of the perturbation, it will be presented in a subsequent paper (Paper II of this study).

## 2. Factor analysis of acetone species in the 1800–700 $\text{cm}^{-1}$ region

Figure 7 contains nine of the 26 acetone–water mixture spectra obtained over the whole solubility range (Fig. 5) following subtraction for pure water and normalization to 1 M acetone. The absorption in the 3400, 1650, and below 1000  $\text{cm}^{-1}$  regions is due to the remaining water species.

In frame (A) of Fig. 7, we observe weak CH stretch bands situated in the far wing of the much stronger OH stretch band of water. To observe them more clearly, second derivatives were obtained (inset). With increasing acetone concentrations, the CH bands redshift (conversely, they blue-shift with increasing water concentrations). These shifts show clearly the evolving character of the CH stretch bands. In very dilute acetone in water, the two discernible bands at 3014 and 2930  $\text{cm}^{-1}$  [Fig. 7(A), inset] are close to the gas phase positions at 3018.5 and 2937  $\text{cm}^{-1}$ , respectively.<sup>33</sup> This indicates that the van der Waals interactions operating on the  $\text{CH}_3 \cdots \text{CH}_3$  groups in liquid acetone are hindered in very dilute aqueous acetone where acetone molecules are isolated one from the other. Although the CH stretch band shifts are interesting,<sup>34</sup> their study lies outside the scope of the present work and are the object of ongoing research.



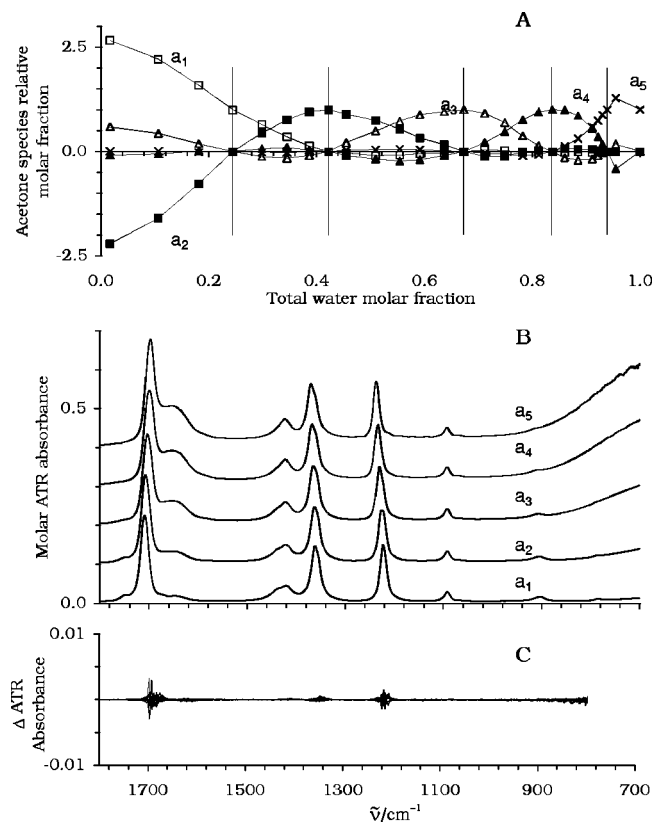


FIG. 8. FA results applied to the 1800–700  $\text{cm}^{-1}$  spectral region of acetone–water mixtures in the whole solubility range (pure liquid water spectrum subtracted). (A) Abstract acetone species molar fractions (symbols, from MFs; lines are eye guides); (B) real spectra of nonexclusive factors; (C) residues,  $a_1$ , pure acetone;  $a_2$ – $a_5$ , aqueous acetone species.

In frames (B) and (C) (Fig. 7), the other acetone bands are clearly visible in the 1800–650  $\text{cm}^{-1}$  region. Although less spectacular than in the case of water, these spectra show the evolving character of the acetone bands with the increasing water content of the solutions.

Factor analysis applied to the molar acetone spectra revealed five principal factors. Their relative abundances and molar spectra are given in Figs. 8(A) and 8(B), respectively. The low residues obtained in Fig. 8(C) indicated that FA worked satisfactorily. Therefore, five acetone principal factors are sufficient but necessary to account for the acetone absorption over the whole concentration range. Negative MF values in Fig. 8(A) indicated abstract abundances because the retrieved spectra are not exclusive one from the others.

Again, exclusive spectra are not necessary for FA to work, but they are necessary to give them a molecular interpretation. Our efforts to render the five acetone spectra in Fig. 8(B) exclusive one from the others were unsuccessful because of the presence of closely overlapping components. The spectral separation needing a detailed analysis of the perturbation will be presented in Paper II.

Table VI lists the position of the six principal acetone bands observed in the nonexclusive principal acetone spectra [Fig. 8(B)]. Decreasing the acetone concentration in aqueous acetone lowers the C=O stretching frequency while increasing the frequency of the five remaining acetone vibrations. This is interpreted as a progressive release of the C=O valence strength (due to hydrogen bonds accepted) which in turn increases the strength of the other valence bonds.

Since the carbonyl band of pure liquid acetone (abbreviated in some case as Ac) is redshifted from the gas phase position, passing from 1731 (Ref. 33) to 1712  $\text{cm}^{-1}$  (ATR position, Table VI), it is assumed that dipole–dipole intermolecular interaction, being the sole possibility, is responsible for the shift.<sup>35</sup> The CO bond dipole moment vectors of nearest neighbors in the liquid tend to be oriented in an antiparallel manner.<sup>1</sup> On the other hand, when labile hydrogen atoms are available, they strongly perturb the CO stretch vibrations whose IR bands are redshifted.<sup>36</sup> Adding water to acetone increases the redshift to 1698  $\text{cm}^{-1}$  (34  $\text{cm}^{-1}$  from the gas position) for the worst case (Table VI). This increase (almost double the redshift from gas to liquid phase) indicates that the hydrogen-bonding perturbations between acetone and water molecules are stronger than the dipole–dipole interactions between acetone molecules. We have observed the opposite effect in acetonitrile–water mixtures.<sup>12</sup>

In aqueous acetone, water is the only molecule that can provide labile hydrogen atoms. Two mechanisms are responsible for the bathochromic shift: dipole–dipole interactions and H bondings. Based on these premises, the acetone molecules can be divided into three types of species depending either on the number hydrogen bonds it accepts or on the number of free electron pairs remaining on the acetone carbonyl oxygen. From this, the interpretation of three different acetone species should have been easy. However, FA revealed five different acetone factors in the acetone–water mixtures. To reconcile this difference and determine the exact number of species present in aqueous acetone solutions requires that the abstract abundances be made real and the

TABLE VI. Position of the acetone nonexclusive principal factors in aqueous acetone.

Mode (approximate description)	Gas <sup>a</sup> $\text{cm}^{-1}$	Pure liquid $\text{cm}^{-1}$	$a_2$ $\text{cm}^{-1}$	$a_3$ $\text{cm}^{-1}$	$a_4$ $\text{cm}^{-1}$	$a_5$ $\text{cm}^{-1}$	$a_5$ shift from liquid $\text{cm}^{-1}$	$a_5$ shift from gas $\text{cm}^{-1}$
$\nu_3$ (CO str)	1731	1712	1707.5	1703.5	1700	1698	14	33
$\nu_4$ ( $\text{CH}_3$ d-def)	1435	1438						
$\nu_{15}$ ( $\text{CH}_3$ d-def)	1410	1420				1423.5	–3.5	–13.5
$\nu_5, \nu_{16}$ ( $\text{CH}_3$ s-def)	1363.5	1362	1364	1366	1369	1371	–9	–7.5
$\nu_{17}$ (CC str)	1215.5	1223	1227	1231	1234	1237	–14	–21.5
$\nu_{22}$ ( $\text{CH}_3$ rock)	1090.5	1092.5	1093	1093	1093	1093.5	–1	–3

<sup>a</sup>Reference 33.

nonexclusive spectra rendered exclusive. This is the object of a subsequent paper (Paper II).

### C. Cooperativity, anticooperativity in aqueous acetone

In hydrogen bonding systems, the concept of cooperativity has been invoked when an enhanced situation results in a greater than normal redshift in the OH stretch frequency.<sup>37</sup> Conversely, anticooperativity occurs for a smaller redshift than normal situation.

#### 1. H-bonding anticooperativity

A water molecule isolated in acetone forms two H-bonds with acetone molecules. The water OH stretch bands are situated at 3615 and 3522  $\text{cm}^{-1}$  (Table V). Since these nearly 140  $\text{cm}^{-1}$  bathochromic shifts from the gas positions are less than half the value observed in pure liquid water ( $\sim 400 \text{ cm}^{-1}$ ) it was attributed to anticooperativity.<sup>38</sup> However, similar low bathochromic shifts were observed for methanol diluted in different solvents. The methanol OH stretch position is situated at 3681  $\text{cm}^{-1}$  in the gas phase;<sup>33</sup> 3328  $\text{cm}^{-1}$  in the liquid phase;<sup>33</sup> 3500  $\text{cm}^{-1}$  in dioxane;<sup>39</sup> 3530  $\text{cm}^{-1}$  in acetonitrile;<sup>31</sup> and 3509  $\text{cm}^{-1}$  in acetone (unpublished ATR measurements). These shifts from the gas position are 353, 180, 150, and 172  $\text{cm}^{-1}$ , respectively. In the three solution systems, each isolated methanol molecule having a single OH group can give only a single H bond (and can accept none because the methanol molecules are isolated). Therefore, because of this unique H bond with methanol, no anticooperativity can take place. However, the bathochromic shift of the methanol OH vibration is far less than that expected in a strong H-bonding situation. Consequently, anticooperativity cannot be used to explain the small redshift observed in water acetone mixtures since the water OH stretch band bathochromic shift is similar to that observed in methanol organic solutions.

#### 2. H-bonding cooperativity

The concept of cooperativity of hydrogen bonds<sup>31,38–41</sup> applied to methanol implies that one or both of the oxygen lone electron pairs are mobilized. Similar cooperativity effects attributed to cation–oxygen interactions have been observed for different cations with decreasing cooperative effect:<sup>40</sup>  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ . Since cooperativity decreases with increasing cation size it was attributed to the interactions between a cation and an oxygen lone pair.<sup>38</sup> The water OH groups with partial positive charge on the hydrogen atoms and partial negative charge on the oxygen form strong dipoles. The H atom is smaller than  $\text{Li}^+$ , so that the combined effects of the smaller (partial) charge of the H atom and its smaller size should produce a cooperative effect at least similar to that of the smallest cation ( $\text{Li}^+$ ). Therefore, one can assume that an H bond to an oxygen atom will produce a relatively strong cooperativity effect. Consequently, an OH group giving a strong H bond should have an increased bathochromic shift when simultaneously accepting an H bond.

### 3. Bathochromic shift of the OH valence bond due to H-bond accepted

When water is added to acetone–water mixtures, opposite variations of acetone stretching frequencies are observed (Table VI). These indicate that when acetone accepts an H bond (through the mobilization of a lone pair on its oxygen atom), its C=O valence strength is decreased, which in turn increases the strength of other acetone valence bonds (Table VI). Similar effects are expected for water: an H bond accepted by its oxygen will release both its OH valence bonds whose stretching frequency will be lowered. Although this lowered frequency was attributed to “cooperativity” between H bonds, it is merely due to the weakening of the OH valence bond since cooperativity necessarily involves both accepted and given H bonds. Hence, the observed lowering of the OH frequency due to an accepted H bond on the oxygen atom should not be referred to as a “cooperative” effect because the OH stretching frequency is lowered due to the weakening of its valence bond (as for the C=O bond in acetone). The OH bond weakening is due to two interactions: the H bond given by the hydrogen and the H bond accepted by the oxygen. Depending on the solution mixtures, these can occur individually or together on a given oxygen.

### D. Interpretation of the five water and five acetone factors

From the above arguments (Sec. III C), the fact that an OH group is acting as a hydrogen-bond donor is not solely responsible for its strong bathochromic shift. For water surrounded by acetone, the small bathochromic shift is attributed to the availability of the water oxygen free electron pairs ( $\theta_{\text{free}}$ ). Consequently, as the water content is increased in the solution, the hydrogen bonds accepted by the water–oxygen weakens both OH valence bonds. This is observed by lowering their stretching frequencies. Hence, depending on the number of hydrogen bonds accepted by the water molecule, or inversely depending on the number of free electron pairs on the oxygen atom, the water molecules can be divided into three types of water species:  $\theta_{\text{free}} = 2$ ,  $\theta_{\text{free}} = 1$ , and  $\theta_{\text{free}} = 0$ , which will produce three absorption regimes (numbers indicate that 2, 1, and 0 free electron pairs are left on the oxygen). These regimes composed of  $\text{H}_2\text{O } \nu_3$ ,  $\nu_1$ , and their satellites have previously been identified in aqueous acetonitrile.<sup>12</sup> Since five principal water factors were retrieved in aqueous acetone by FA, the three types of water species must be further divided. As for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  mixtures,<sup>13</sup> this additional separation necessitates the evaluation of a random H-bond network organization. For the particular situation of aqueous acetone, this will be done in Paper II.

## IV. CONCLUSION

FA using spectral windowing to separate water and acetone absorption gave 10 principal factors (5 water and 5 acetone), whereas FA applied to the whole spectral range could not. Therefore, these 10 species do not evolve concomitantly as a function of concentration and must be considered distinct in order to establish the chemical interpreta-

tion of the mixture organizations. Due to the individual evolving character of the five acetone and five water factors retrieved, we arrive at the conclusion that hydrates in the sense of an acetone molecule either by sequestering a number of water molecules or through alterations in the H-bond water network are not present in aqueous acetone.

The interpretation of ten principal factors is not easily done from purely spectroscopic considerations. Three forces are at play in the acetone–water mixtures: dipole–dipole interactions, hydrogen-bonding, and hydrophobic interactions.<sup>1,6</sup> The last of these was observed on the CH stretching bands that are blueshifted as water is introduced in the solution. The dipole–dipole interactions are observed through the redshift of the carbonyl stretch band when acetone passes from the gas phase to the liquid phase. Hydrogen bonding is observed on the water bands and on the carbonyl stretch band. As water is introduced in the solution, the CO band redshift is greater than in the pure liquid situation. This indicates that the hydrogen bonding is stronger than the dipole–dipole interactions in acetone because it overrides them.

Although both OH groups act as H-bond donors when water is isolated in acetone (a strong H-bond acceptor), the OH stretching bathochromic shift from the gas position is far less than that observed in pure liquid water. This is attributed to the two lone electron pairs remaining on the oxygen atom (no H bond accepted in this situation). As water is introduced in the solution, the hydrogen bonds accepted by the water oxygen strongly weakens both its OH valence bonds and must be taken into account when analyzing the OH stretch band displacements. Depending on the number of H bonds the water molecule accepts (0, 1, or 2), three types of water molecules are found in acetone mixtures. Similarly for acetone, three types of molecules are found. Since five water factors and five acetone factors were retrieved by FA, these six types of species are submitted to other perturbations that requires detailed analysis. This, in turn, indicates that FA is sensitive enough to sort out the latter perturbations thus making FA a useful tool for chemical interpretation of solutions. However, detailed analysis of the FA results necessitates real species abundances and exclusive spectra. To obtain these, simple procedures did not work. Consequently, more elaborate procedures that necessitate the evaluation of a random organization model will be done in Paper II. Only at the end of that paper will a complete molecular model emerge.

#### APPENDIX A: RELATIONSHIP BETWEEN COMPONENT CONCENTRATIONS AND WATER MOLAR FRACTIONS

By definition, water molar fraction ( $\chi_w$ ) is

$$\chi_w = \frac{c_w}{c_w + c_{AC}}, \quad (\text{A1})$$

where  $c_w$  and  $c_{AC}$  are the molar concentrations of water and acetone, respectively. Expressed in molar numbers  $n_w$  and  $n_{AC}$  contained in a volume  $V$ , Eq. (A1) becomes

$$\chi_w = \frac{\frac{n_w}{V}}{\frac{n_w}{V} + \frac{n_{AC}}{V}} = \frac{n_w}{n_w + n_{AC}} \quad (\text{A2})$$

that can be transformed to obtain

$$n_w = \frac{\chi_w}{(1 - \chi_w)} n_{AC}. \quad (\text{A3})$$

Replacing the molar numbers by volumes introduced in the sample ( $V_w$  and  $V_{AC}$ ), neat liquid densities ( $d_w$  and  $d_{AC}$ ) and molar mass gives

$$V_w = \frac{\chi_w}{(1 - \chi_w)} \times \frac{M_w}{M_{AC}} \times \frac{d_{AC}}{d_w} V_{AC}. \quad (\text{A4})$$

Starting with a given neat acetone volume,  $V_{AC}$ , Eq. (A4) gives the water volume necessary to obtain the desired water molar fraction.

#### APPENDIX B: RELATION BETWEEN ACETONE CONCENTRATION AND WATER MOLAR FRACTION

With the Handbook data<sup>42</sup> and complementary measurements, the relation between water and acetone concentrations was found to be almost linear, with a slight second-order variation:<sup>43</sup>

$$c_w = a_0 + a_1 c_{AC} + a_2 c_{AC}^2. \quad (\text{B1})$$

Combining Eqs. (A1) and (B1), gives

$$a_2 (\chi_w - 1) c_{AC}^2 + [\chi_w + a_1 (\chi_w - 1)] c_{AC} + a_0 (\chi_w - 1) = 0. \quad (\text{B2})$$

The solution of Eq. (B2) in  $c_{AC}$  is

$$c_{AC} = \frac{a_1 - \frac{\chi_w}{1 - \chi_w}}{2a_2} \left[ -1 + \sqrt{1 - \frac{4a_0 a_2}{\left(a_1 - \frac{\chi_w}{1 - \chi_w}\right)^2}} \right]. \quad (\text{B3})$$

<sup>1</sup>D. S. Venables, A. Chiu, and C. A. Schmuttenmaer, *J. Chem. Phys.* **113**, 3243 (2000); **113**, 3249 (2000).

<sup>2</sup>D. S. Venables and C. A. Schmuttenmaer, *J. Chem. Phys.* **113**, 11222 (2000).

<sup>3</sup>A. K. Soper, *Science* **297**, 1288 (2002).

<sup>4</sup>Y. Maréchal, *J. Chem. Phys.* **95**, 5565 (1991).

<sup>5</sup>Y. Maréchal, in *Hydrogen Bond Networks*, edited by M.-C. Bellissent-Funel and J. C. Doré (Kluwer Academic, Dordrecht, 1994).

<sup>6</sup>M. Ferrario, M. Haughney, I. R. McDonald, and M. L. Klein, *J. Chem. Phys.* **93**, 5156 (1990).

<sup>7</sup>J. Bandekar and B. Curnutte, *J. Mol. Spectrosc.* **58**, 169 (1975).

<sup>8</sup>A. D. Buckingham, *J. Mol. Struct.* **250**, 111 (1991).

<sup>9</sup>(a) W. A. P. Luck, *Angew. Chem., Int. Ed. Engl.* **19**, 28 (1980); (b) W. A. P. Luck, H. Borgholte, and T. Habermehl, *J. Mol. Struct.* **177**, 523 (1988).

<sup>10</sup>D. M. Wieliczka, S. Weng, and M. R. Querry, *Appl. Opt.* **28**, 1714 (1989).

<sup>11</sup>J.-J. Max, S. Daneault, and C. Chapados, *Can. J. Chem.* **80**, 113 (2002).

<sup>12</sup>J.-J. Max and C. Chapados, *Can. J. Anal. Sci. Spectrosc.* **47**, 72 (2002).

<sup>13</sup>J.-J. Max and C. Chapados, *J. Chem. Phys.* **116**, 4626 (2002).

<sup>14</sup>V. A. Sirotkin, B. N. Solomonov, D. A. Faizullin, and V. D. Fedotov, *J. Struct. Chem.* **41**, 997 (2000).

<sup>15</sup>J.-J. Max, M. Trudel, and C. Chapados, *Appl. Spectrosc.* **52**, 226 (1998).

<sup>16</sup>I. S. Kislina, V. D. Maiorov, N. B. Librovič, and M. I. Vinnik, *Russ. J. Phys. Chem.* **50**, 1676 (1976).

<sup>17</sup>J.-J. Max and C. Chapados, *Appl. Spectrosc.* **53**, 1045 (1999).

- <sup>18</sup>J.-J. Max, M. Trudel, and C. Chapados, *Appl. Spectrosc.* **52**, 234 (1998).
- <sup>19</sup>J.-J. Max and C. Chapados, *Appl. Spectrosc.* **53**, 1601 (1999).
- <sup>20</sup>J.-J. Max and C. Chapados, *Appl. Spectrosc.* **52**, 963 (1998).
- <sup>21</sup>J.-J. Max and C. Chapados, *Can. J. Chem.* **78**, 64 (2000).
- <sup>22</sup>J. Baril, J.-J. Max, and C. Chapados, *Can. J. Chem.* **78**, 490 (2000).
- <sup>23</sup>J.-J. Max, C. Ménichelli, and C. Chapados, *J. Phys. Chem. A* **104**, 2845 (2000).
- <sup>24</sup>J.-J. Max and C. Chapados, *J. Chem. Phys.* **113**, 6803 (2000).
- <sup>25</sup>C. Ménichelli, J.-J. Max, and C. Chapados, *Can. J. Chem.* **78**, 1128 (2000).
- <sup>26</sup>J.-J. Max, S. de Blois, A. Veilleux, and C. Chapados, *Can. J. Chem.* **79**, 13 (2001).
- <sup>27</sup>J.-J. Max and C. Chapados, *J. Chem. Phys.* **115**, 2664 (2001).
- <sup>28</sup>J. E. Bertie and Z. Lan, *Appl. Spectrosc.* **50**, 1047 (1996).
- <sup>29</sup>J.-J. Max and C. Chapados, *J. Phys. Chem. A* **105**, 10681 (2001).
- <sup>30</sup>J. E. Bertie and Z. Lan, *J. Phys. Chem. B* **101**, 4111 (1997).
- <sup>31</sup>S. Singh, D. Schiöberg, and W. A. P. Luck, *Spectrosc. Lett.* **14**, 141 (1981).
- <sup>32</sup>To compensate the lower proportionality coefficient the OH stretch band integrated intensity of the second water species is higher than that of pure water it replaces when increasing acetone concentration.
- <sup>33</sup>T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume* (National Bureau of Standards, Washington, DC, 1972).
- <sup>34</sup>K. Hermansson, *J. Phys. Chem. A* **106**, 4695 (2002).
- <sup>35</sup>A. D. Buckingham, *Can. J. Chem.* **38**, 300 (1960); R. A. Nyquist, C. L. Putzig, and D. L. Hasha, *Appl. Spectrosc.* **43**, 1049 (1989).
- <sup>36</sup>G. C. Pimentel and A. L. McLellan, *The Hydrogen Bond* (W. H. Freeman, San Francisco, 1960).
- <sup>37</sup>G. A. Jeffrey, *An Introduction to Hydrogen Bonding* (Oxford University Press, New York, 1997).
- <sup>38</sup>W. A. P. Luck, D. Klein, and K. Rangsiwatananon, *J. Mol. Struct.* **416**, 287 (1997).
- <sup>39</sup>L. England, D. Schiöberg, and W. A. P. Luck, *J. Mol. Struct.* **143**, 325 (1986).
- <sup>40</sup>H. Kleeberg, G. Heinje, and W. A. P. Luck, *J. Phys. Chem. A* **90**, 4427 (1986).
- <sup>41</sup>W. A. P. Luck, *J. Mol. Struct.* **448**, 131 (1998).
- <sup>42</sup>R. C. Weast, *Handbook of Chemistry and Physics*, 57th ed. (CRC, Cleveland, 1976).
- <sup>43</sup>We obtained in Eq. (B1):  $a_0 = 55.387 \text{ mol L}^{-1}$  (a value close to that of pure water);  $a_1 = -3.602$  (a value around 10% less than that of acetone to water molar ratio); and  $a_2 = -0.0344 \text{ L mol}^{-1}$ .