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Raman and FTIR spectroscopic study on water structural changes in aqueous solutions of amino acids and related compounds

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Abstract

Structural changes of water in aqueous solutions of glycine, alanine, ammonia, amines (methyl-, ethyl-, propyl-, and *n*-butylamine), carboxylic acids (formic, acetic, propionic, and *n*-butyric acid), KF and 1-hexansulphonic acid sodium salt have been analysed using FTIR and Raman difference spectroscopy. Isotropic and anisotropic Raman spectra, as well as the rho-spectra, have been calculated. The OH stretching region of the amino acid difference spectra shows changes in defined frequency regions which can be attributed to electrostatic and hydrophobic interactions as well as to hydrogen bonding. Point charges affect the symmetry of the water molecules, while for hydrophobic interaction no symmetry changes in the water molecules are observed. © 1997 Elsevier Science B.V.

Keywords: Raman and FTIR difference spectroscopy; Rho-spectra; Water structure; Amino acids; Electrolytes

1. Introduction

In vibrational spectroscopy, the study of water has a long standing history. From these investigations, several proposals have evolved to explain the structure of water. In the early 70s, water was seen from the thermodynamical point of view as a medium that is composed of clusters of variable sizes, built up and broken in time (flickering clusters) [1]. Spectroscopic investigations of the structure of water explained the liquid on the level of a single water molecule. Two major explanations were established. One explanation sees the water in a hydrogen bonding network with other water molecules. The broad bands in the OH stretching region found for water are explained in terms of a continuous distribution of geometrically and energetically distorted molecules (continuous model) [2]. The other model distinguishes between completely and partially hydrogen-bonded water. Both types are in equilibrium with each other (mixture model) [3] and are distributed over a wide range of geometrical and thus energetical structures. Within this model, solutes would change the population between the individual types of water, rather than altering the symmetry of the water molecules (population effect).

The effect of solutes on the structure of water has also been intensively investigated by vibrational spectroscopy. Point charges have been introduced to water to analyse hydration shells and their effect on the water band envelope in the OH stretching region

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[4,5] in terms of structure making and breaking properties [6]. Organic molecules and water were diluted in well-defined stoichiometric ratios to correlate the bands in the OH stretching region with a special type of interaction [7,8]. The interaction of water with the hydrophobic parts of molecules is also discussed in the literature [9,10].

Generally, absorbance spectra or Raman intensity spectra have been used. Only in a few studies has difference spectroscopy been applied to assess the structural alterations of water caused by the solutes [11,12]. The use of difference spectroscopy in analysing the functioning of biological molecules, and especially the role of water in this [13], needs a basic understanding of difference spectra in the OH, NH, and CH stretching region. Changes on a large or small scale in this spectral region, having their origin in altered water molecules, may then be properly interpreted.

In this study, we analysed how water is affected by glycine and alanine at their isoelectric points in aqueous solution focusing on the wavenumber region above 2800 cm^{-1}. In an earlier study, we assessed whether changes in the OH stretching region of these amino acids and related compounds could be corrected by simulation of their IR and Raman spectra [14]. In the present study, we suggest a structural interpretation of the data we found. To assess the contribution of the functional groups of the amino acids (carboxylic and amino group, and the hydrophilic tail), several model compounds like carboxylic acids and primary amines, with increasing aliphatic chains, were analysed. Also, spectra from aqueous KF solutions, as well as aqueous 1-hexansulphonic acid sodium salt (HSA–Na) solutions, were recorded. We are able to show that every type of interaction, i.e. electrostatic, hydrophobic, or hydrogen bonding, causes changes at different parts of the band envelope in the OH stretching region.

2. Experimental

Commercial chemicals with the highest available degree of purity (from Sigma, Merck-Schuchardt, Riedel de Haën, all from Germany; Fluka Chemie, Switzerland; BDH Chemicals, Toronto, Canada; Fisher Scientific Company, Fair Lawn, NJ, USA, and Aldrich Chemical Comp. Inc., Milwaukee, Wis. USA) were used. Aqueous solutions of alanine (pH 6.1) and glycine (pH 6.1), of aliphatic acids (formic (pH 1.7), acetic (pH 2.3), propionic (pH 2.4) and butyric acid (pH 2.4)), and of ammonia (pH 12.2), amines (methylamine (pH 12.7), ethylamine (pH 12.8), propylamine (pH 12.9) and butylamine (pH 13.0)) as well as KF (1 M, pH 7.9; 2 M, pH 8.0) and HSA–Na (1 M, pH 7.6; 4 M, pH 7.9) were prepared. Purified water (conductivity 0.006 milli-Siemens) was obtained from a MILLIPORE System.

Raman spectra were recorded with a SPEX 1403

Table 1
Band assignments of water vibrations found in the OH stretching region of Raman and IR spectra

Raman [18]	Band assignment[a]	Raman [3]	Band assignment[b]	Raman, this work	IR	Band assignment
3627	ν_w	3635	ν_{free} tri	3632	3604	ν_{free}
3551	ν_{ww}	3545	ν_{bonded} tri	3562	3527	ν_{bonded} tri
3480	Antisym. vib. of sym. bonded water (only Aniso)	3455	ν_3 tetra (only Aniso)	3486		ν_3 (only Aniso)
3411	ν_b	3400	ν_{1B} tetra	3388	3382	$2\nu_2$ and
approx. 3300	Overtone $2\nu_2$	3215	ν_{1A} tetra	3212	3209	ν_1 (+ ν_3 in IR)
3241	ν_d				3095	Residual due to band anharmonicity

[a]Water molecules with asymmetry in hydrogen bond strength: 'bonded', ν_b, and 'weakly bonded', ν_w, frequency. Water molecules with symmetric hydrogen bonding: symmetric OH stretch, ν_d, and symmetric stretch of a weakly dibonded species, ν_{ww}.

[b]Water molecules coordinated with three other water molecules (tri): free OH stretching unit of water, ν_{free} tri, and a bonded OH stretching unit, ν_{bonded} tri. Water molecules coordinated with four other water molecules (tetra): asymmetric mode, ν_3 tetra, and Fermi doublet of the symmetric mode ν_1 and overtone of the ν_2 splitted into ν_{1A} tetra and ν_{1B} tetra.

spectrometer, equipped with RCA 31034 photo tube and an Elscint photon counting system [15]. The light source was a Spectra Physics Argon Ion Laser (514.5 nm) with a laser power of 1.5–2 W on the sample. We used a divided spinning cell after Kiefer [16]. Spectra have been recorded at 3 cm^{-1} resolution (240 μm slits), and their isotropic and anisotropic intensities calculated [17] and normalized to the particle density of water. Then the difference against the spectrum of pure water was taken. For demonstration purposes, all isotropic and anisotropic Raman difference spectra have been smoothed with a 21-point Savitzky–Golay smoothing function. The contour of the isotropic and anisotropic spectra between 3800 cm^{-1} and 2800 cm^{-1}, the OH stretch vibrations of water, was curve-fitted by superposition of five gaussian subbands, particular vibrational transitions broadened by the variation of inter- and intramolecular interactions. The gaussian components are given in Table 1 and compared to bands found in the literature. Rho-spectra have been calculated from the parallel and perpendicular polarized Raman intensities.

FTIR spectra were recorded on either Bruker 113v (University of Alberta, Canada) or Bruker 120HR (University of Copenhagen, Denmark) instruments using a cylindrical ATR accessory (Circle-Cell, Spectra Tech. Inc.). After normalization to the particle density of water, "molar cross section" spectra were calculated from averaged spectra. Details of the calculation have been given elsewhere [19,20]. Differences in the molar cross section spectra of solutions against those of the pure water spectrum were taken [14]. The spectral resolution for all IR spectra was 2 cm^{-1}.

3. Results and discussion

3.1. Spectra of pure water

The IR absorbance spectrum of water in the OH-stretching region from 3800 to 2800 cm^{-1} with band maxima is shown in Fig. 1a. The band centres listed in Table 1 are found by applying a curve fitting routine on the band envelope. This technique positions an additional band at 3527 cm^{-1}. Fig. 1b shows the isotropic and anisotropic Raman spectra of water in the same wavenumber region, as mentioned above. Real time measurement of both isotropic and anisotropic spectra eliminates the difficulty of establishing a baseline in order to determine the dispersion of the depolarization ratio (in the following, this is called the "rho-spectrum" (see also Refs. [21],[22])) (Fig. 1c).

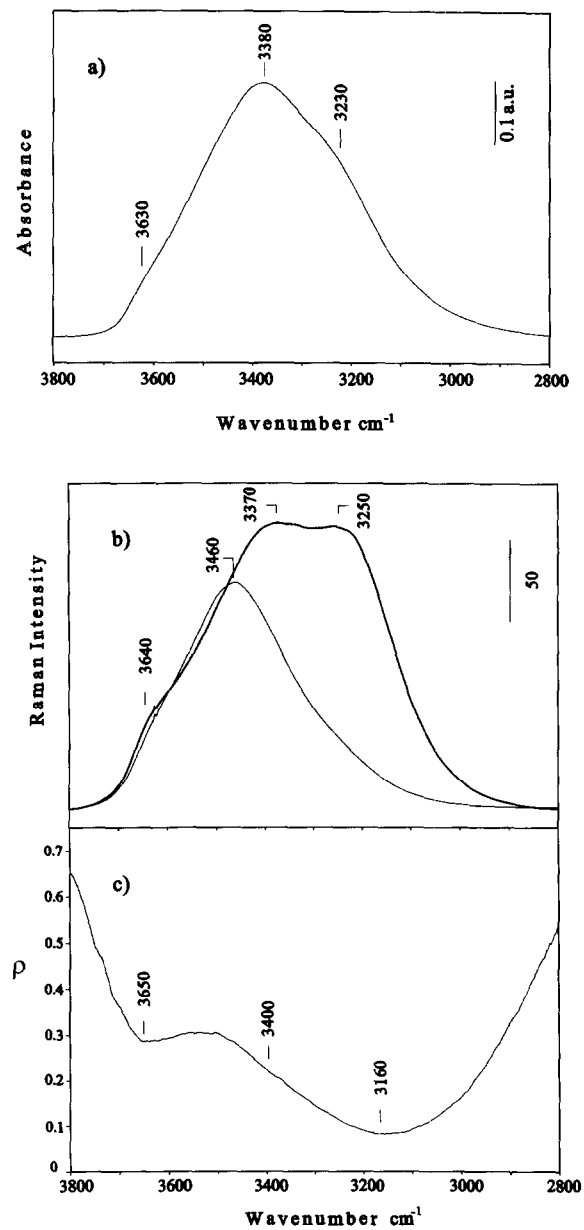

Fig. 1. (a) IR absorbance spectrum of pure water in the region 3800 cm^{-1}–2800 cm^{-1}. (b) Isotropic (——) and anisotropic (——) Raman spectra of pure water, and (c) the resulting rho-spectrum in the same wavenumber region.

We find that the rho-spectrum is composed of two gaussian features with minima at 3650 cm^{-1} and 3160 cm^{-1}. A third feature might be hidden around 3400 cm^{-1} according to the second expected member of the Fermi doublet. The highest value of rho between the two minima is reached around 3500 cm^{-1}. At the high frequency tail, rho reaches 0.65 at 3800 cm^{-1} while the background rho should be 0.75.

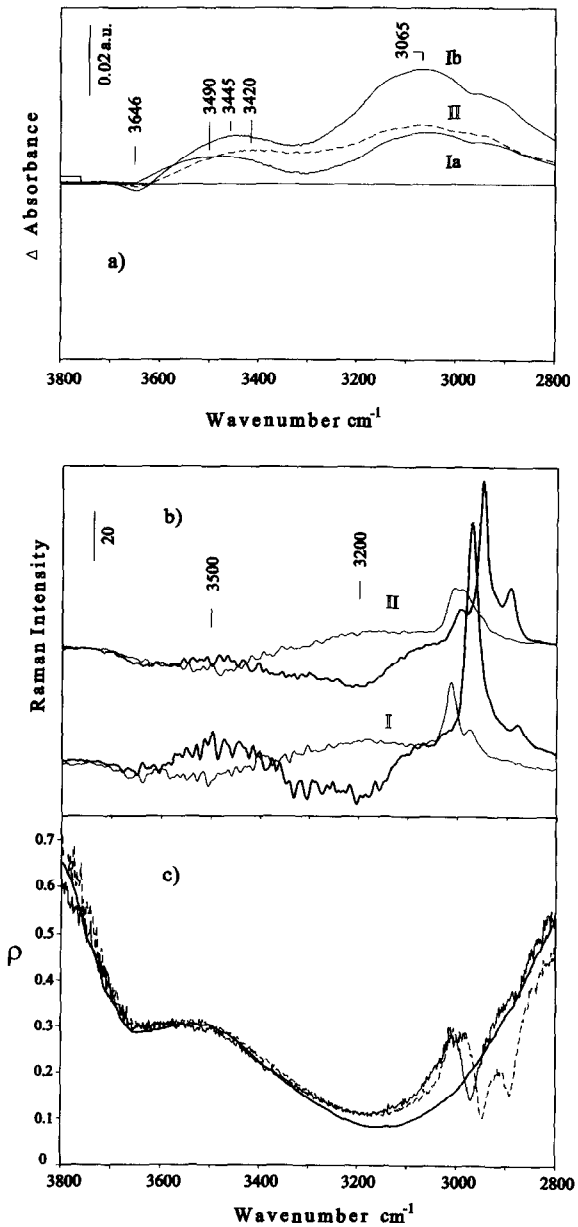

Fig. 2. Difference spectra of aqueous solutions of glycine (I, and Ia, 1 M; Ib, 2 M) and alanine 1 M (II, - - -) against pure water: (a) IR and (b) isotropic (——) and anisotropic (——) Raman difference spectra. (c) Rho-spectra: (——) pure water, aqueous solution of (——) glycine and (- - -) alanine.

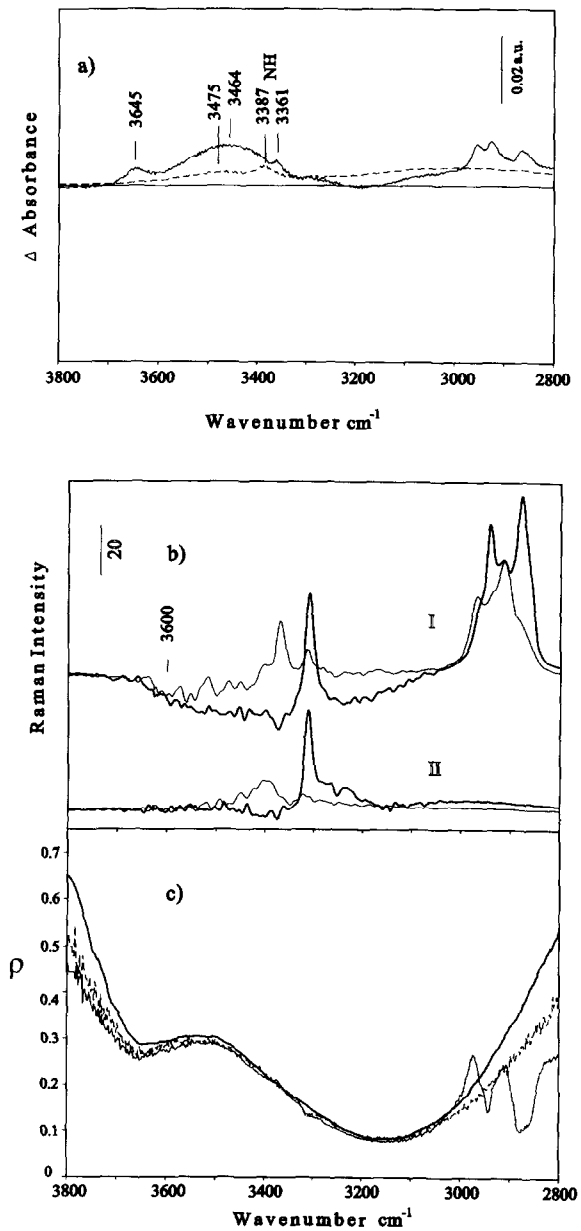

Fig. 3. Difference spectra of 1 M aqueous solutions of butylamine (I and ——) and ammonia (II and - - -) against pure water: (a) IR and (b) isotropic (——) and anisotropic (——) Raman difference spectra. (c) Rho-spectra: (——) pure water, aqueous solution of (——) butylamine and (- - -) ammonia.

On the low frequency side of the band envelope, rho reaches 0.54 at 2800 cm^{-1}, although Raman intensities seem to have dropped completely to zero at this point. Analysing the rho-spectrum reveals two very important results: i) the vibrational contour extends far beyond the frequency range that is expected from intensity spectra, and ii) there is a second minimum on the high frequency side for the "free" OH oscillator of water.

3.2. Amino acids

IR difference spectra of aqueous solutions of glycine (1 and 2 M) and alanine (1 M) are shown in Fig. 2a. The difference spectra are positive over the entire frequency range with maxima near 3500 cm^{-1} (glycine 1 M 3490 cm^{-1}, and 2 M 3445 cm^{-1}, and alanine 1 M 3420 cm^{-1}) and approx. 3100 cm^{-1}. The maxima at approx. 3100 cm^{-1} are higher in intensity than the maxima around 3500 cm^{-1} for each of the difference spectra, indicating strong hydrogen bonding. The intensities of the 1 M and 2 M glycine solutions are proportional to concentration. At 3646 cm^{-1}, all difference spectra of the amino acids in water show weak minima, indicating the loss of "free" OH oscillators. The minimum around 3300 cm^{-1} is believed to arise from population shifts into molecular assemblies that absorb at higher and lower frequencies. Bands of CH_2 and CH_3 stretch character do not express themselves clearly between 3000 and 2900 cm^{-1}. Also, no NH stretching vibrations are resolved [10].

The isotropic Raman difference spectra of the amino acid solutions (1 M) (Fig. 2b) display maxima around 3500 cm^{-1} and minima around 3200 cm^{-1}. This combination, maximum at 3500 cm^{-1}, minimum at 3200 cm^{-1}, is reversed in the anisotropic difference spectra. In contrast to the IR spectra, bands for the CH-stretching vibrations are observed in their Raman spectra.

Rho-spectra of 1 M aqueous solutions (Fig. 2c) are almost identical with those for pure water above 3400 cm^{-1}, except that the rho values for the glycine solution are slightly lower than those for water around 3500 cm^{-1}. As a consequence of the above-mentioned iso–aniso intensity shifts and strong hydrogen bonding, the rho of glycine and alanine solutions are higher than that for pure water below 3400 cm^{-1}.

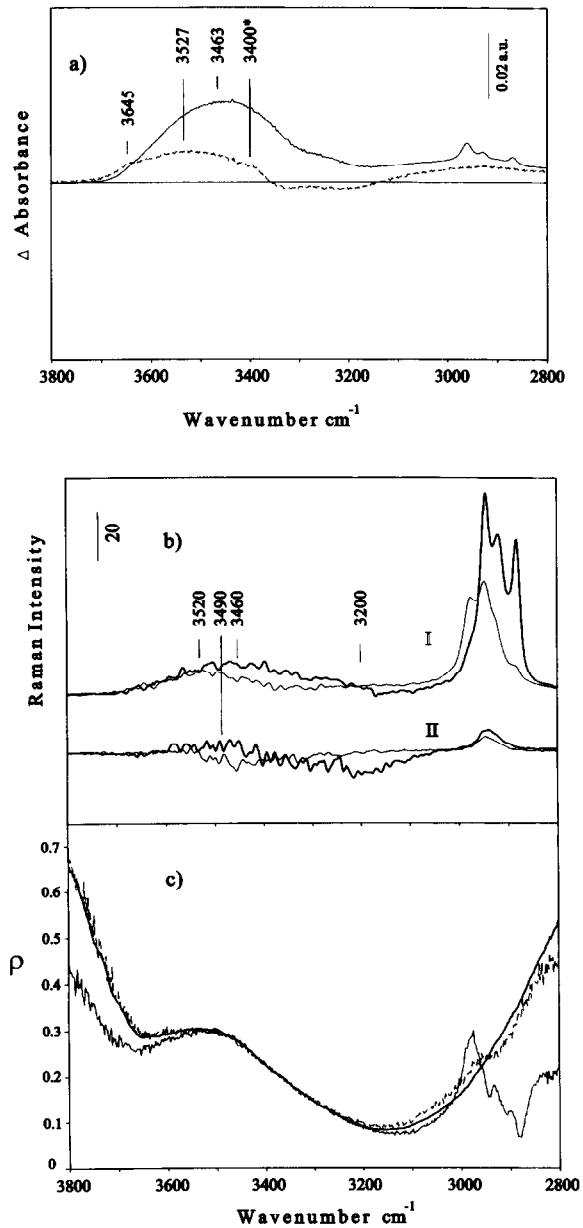

Fig. 4. Difference spectra of 1 M aqueous solutions of butyric (I and ——) and formic (II and - - -) acid against pure water: (a) IR and (b) isotropic (——) and anisotropic (——) Raman difference spectra. (c) Rho-spectra: (——) pure water, aqueous solution of (——) butyric and (- - –) formic acid. * in a): OH stretching vibration of carboxylic acid functionality.

3.3. Amines and carboxylic acids

In order to assess the individual effects of the aliphatic residues on the water structure, we analysed the aqueous solutions of both amines and carboxylic acids with increasing chainlength. At 1 M concentration, their dissociation is minimal so that we can neglect contributions of either carboxylate or ammonium ions. The functional group allows a reasonable solubility in water without reaching any critical micelle concentration (cmc) of the solutes.

The IR difference spectra of the amines (Fig. 3a) and carboxylic acid solutions (Fig. 4a) against pure water have major intensity gains around 3450 cm^{-1} with increasing chainlength. Thus, the shift of the maximum at 3500 cm^{-1} to lower wavenumbers going from 1 M to 2 M glycine solution (see Fig. 2a) must be interpreted in terms of increasing intensity around 3450 cm^{-1} due to an increased number of molecules with hydrophobic structrure. In the difference spectra of the amines, a weak positive band appears around 3645 cm^{-1} with increasing chainlength. A band at this wavenumber is also found in the difference spectrum of formic acid solution against pure water (Fig. 4a). Due to weak intermolecular hydrogen-bonding, the maxima around 3100 cm^{-1} are only slightly different in intensity for the two types of solutes.

Especially for ammonia (Fig. 3b, II), the isotropic and anisotropic Raman difference spectra hardly deviate from zero. The asymmetric (anisotropic spectrum) and symmetric (isotropic spectrum) NH stretching vibrations are clearly seen. Increasing chainlength for the carboxylic acids separates the isotropic and anisotropic Raman intensity at around 3400–3450 cm^{-1} (Fig. 4b, I and II). Below 3200 cm^{-1}, the anisotropic intensity is higher than the isotropic intensity (see also the 4 M HSA–Na solution (Fig. 6b)).

The depolarization ratio for both solutes (Fig. 3c and Fig. 4c) follows closely that of pure water from 3000 to 3600 cm^{-1}. Thus, intensity changes around 3500 cm^{-1} observed in the IR and Raman spectra

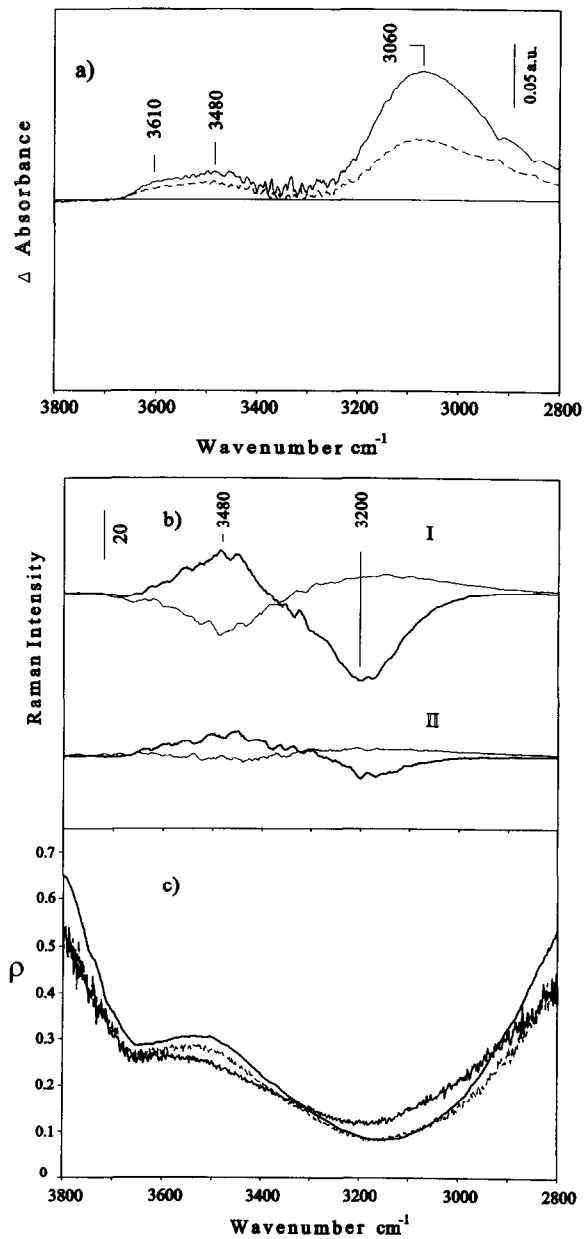

Fig. 5. Difference spectra of aqueous solutions of KF 1 M (- - -, II) and 2 M (——, I) against pure water: (a) IR and (b) isotropic (——) and anisotropic (——) Raman difference spectra. (c) Rho-spectra: (——) pure water, 1 M (- - -) aqueous solution of KF and 2 M solution (——). The KF solution spectra in a) were recorded on a Nicolet 5PC (purged with dry air (dew point – 70°C)) using an open-boat ATR accessory. The KF solution spectrum was subtracted interactively against a pure water spectrum by minimizing the water band at 2300 cm^{-1}. The difference spectrum was smoothed by a 15-point Savitzky–Golay smoothing function. Deionized water was used from a PURITE system (Oxon, UK) with reversed osmosis.

are not coupled with changes in the symmetry of water molecules.

3.4. KF and HSA–Na

KF is representative of solutes forming strong hydrogen bonding and, of course, with no hydrophobic part. The difference spectra of 1 M and 2 M aqueous KF solutions against pure water (Fig. 5) have features in common with the difference spectra of amino acid solutions (see Fig. 2): i) a weak maximum at 3500 cm^{-1} in the IR spectra, which is, however, resolved into two bands at 3610 cm^{-1} and 3480 cm^{-1} in both 1 M and 2 M difference spectra, and ii) a maximum near 3100 cm^{-1} (Fig. 5a) which is more intense than the maximum at 3500 cm^{-1}. In the HSA–Na difference spectra (Fig. 6), we find a maximum around 3473 cm^{-1} which narrows and shifts to higher frequencies (3486 cm^{-1}) on going from 1 M to 4 M solution. This might be caused by more and more water molecules mostly facing the sulphonium groups. Due to the weaker electronegativity and increased number of possible orientations for water molecules around the sulphonium group, no bands are resolved within the broad maximum.

In the isotropic Raman difference spectra of KF solutions against water, intensity gains are also found around 3480 cm^{-1} and intensity losses around 3200 cm^{-1}. The intensity in the anisotropic spectra shows the opposite behaviour, with a neg./pos. contour around 3480 cm^{-1} (–)/3200 cm^{-1} (+). This pattern parallels the one for the 1 M HSA–Na solution (Fig. 6b). For the 4 M solution of HSA–Na, isotropic and anisotropic Raman difference spectra show a maximum at the same wavenumber (3500 cm^{-1}). Both rho-spectra of KF and HSA–Na solutions at higher concentrations flatten out around 3500 cm^{-1} in favour of lower rho values. Lower rho values than for water also in the rho-spectrum of 1 M glycine solution around 3500 cm^{-1} must therefore be interpreted as an equivalent affect of the carboxylate group of glycine on the water structure.

The similarity of the HSA–Na and KF solutions can be explained by the low critical micelle concentration (cmc = 6.2×10^{-1} mol l^{-1} [23]) of HSA–Na. In the concentrations studied here, HSA–Na is present in the form of micelles in aqueous solution. The micelles exclusively present their sulphonic groups to the bulk water. The difference spectra and rho-spectra of both solutes therefore represent the effect of electrostatic interaction on the water structure. The strong hydrogen bonding indicated by higher rho-values below 3200 cm^{-1} for the HSA–Na solution could be explained by

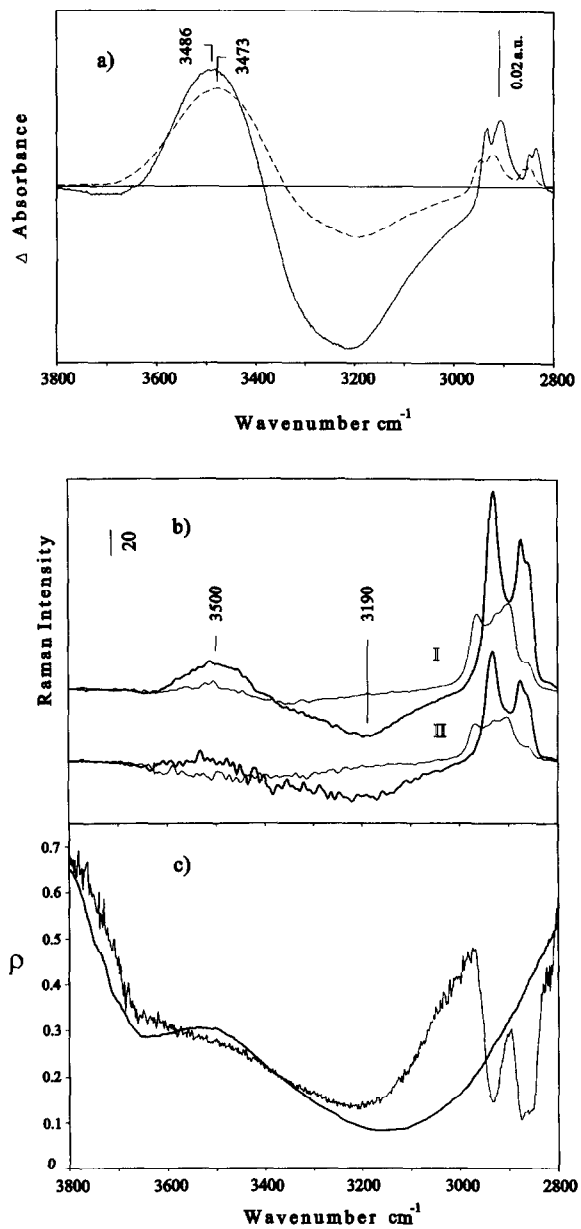

Fig. 6. Difference spectra of aqueous solutions of HSA–Na: 1 M (II and - - -) and 4 M (I and ——) against pure water: (a) IR and (b) isotropic (——) and anisotropic (——) Raman difference spectra. (c) Rho-spectra: (——) pure water, 4 M (——) aqueous solution of HSA–Na.

water molecules attached or trapped in the so-called Stern– and Gouy–Chapman double layers of the micelles [24].

3.5. Charged groups, hydrophobic interaction, hydrogen bonding

Whenever water molecules face a solute, the type of interaction can be either electrostatic or hydrophobic, as well as hydrogen bonding. The selection of solutes in this study allows correlation of each type of interaction with changes in the band envelope of the OH stretching region of water. Discussion of the rho-spectra allows distinction between population effects and structural effects.

When facing charged groups like carboxylate (amino acids at their I.P.), sulphonic or fluoride ions, positive intensity around 3600–3450 cm^{-1} is found. For groups with low electronegativity (i.e. carboxylic groups) and high polarizability, the band is broad. For charges with high electronegativity and low polarizability like fluoride, this maximum is resolved into two bands. For all the solutes mentioned, the rho-spectra display higher or equivalent rho values on the high frequency side of the 3500 band and lower rho values on the low frequency side (flattening out). This is typical for a pair of antisymmetric and symmetric vibrational bands in a spectrum. Therefore water appears to conserve C_{2v} symmetry, including more or less contributions from other possible geometries around the negative charges. For the carboxylic acid solutions, almost no deviation from C_{2v} water is found. The density of the negative charge of the functional group must be equivalent to one of the oxygen atoms of water, leaving the water molecules next to the carboxylic acid group in the same symmetry as in the bulk water.

We want to mention that the water bands found in aqueous solution coincide with those bands found in the spectral region above 3400 cm^{-1} in binary mixtures of water and organic solutes in inert solvents [8]. Our spectra indicate that the first shell of water around those solutes mentioned in this study is similar to water arrangements in these binary mixtures, and hence causes equivalent vibrational bands.

Hydrophobicity gains importance with increasing aliphatic chainlength and increasing solute concentration. For the IR difference spectra, positive intensity around 3500–3400 cm^{-1} evolves in all cases [9]. Despite the intensity changes observed in the IR and polarized Raman spectra, the rho-spectra remain very much unchanged compared with pure water. Spectral differences in the 3500–3400 wavenumber region, including band shifts and intensity changes without depolarization changes, may be interpreted in terms of population effects within the framework of the mixture model. The band at 3645 cm^{-1}, found especially in the difference spectra of amine solutions, has not been observed in difference spectra of the other solutes with aliphatic chains. We conclude that the band at 3645 cm^{-1} in the amine spectra is mainly caused by water molecules facing the amino group *and* the neighbouring aliphatic tail. A similar band at around 3680 cm^{-1} was found in water/methanol mixtures [7]. Low pH values like those found for carboxylic acids probably hinder the existence of a "free" oscillating OH-unit of a water molecule which should cause a band around 3645 cm^{-1}.

Hydrogen bonding causes OH stretch vibrations to shift dramatically to lower frequencies. Intense broad bands around 3200 and 3100 cm^{-1} are present in the IR spectra of aqueous solutions of all amino acids, KF and HSA–Na studied here. Hydrogen bonding is also accompanied by an increase in the dipole moment of XH oscillators and a decrease in the polarizability, accordingly. Thus we find stronger IR absorbance and weaker Raman scattering. The rho-spectra indicate a partial loss of symmetry of water below 3200 cm^{-1}.

4. Conclusion

Amino acids exhibit spectral contours in the OH stretching region of water at their isoelectric point for three types of interactions: electrostatic, hydrophobic and hydrogen bonding. Independent of the solute, each type of interaction causes structural alteration of neighbouring water molecules. The water OH stretching band envelope will be affected in well-defined frequency ranges: point charges affect the wavenumber region above 3400 cm^{-1}, hydrophobic entities cause intensities changes around 3400 cm^{-1}, and bands around 3100 cm^{-1} originate from strong hydrogen bond formation.

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References

[1] H.S. Frank, W.-Y. Wen, Discuss. Faraday Soc. 24 (1957) 133–140.
[2] J. Schiffer, D.F. Hornig, J. Chem. Phys. 49 (1968) 4150–4160.
[3] W.F. Murphy, H.J. Bernstein, J. Phys. Chem. 76 (1972) 1147–1152.
[4] T.T. Wall, D.F. Hornig, J. Chem. Phys. 47 (1967) 784–792.
[5] G.E. Walrafen, J. Chem. Phys. 55 (1971) 768–792.
[6] M.H. Brooker, in: R.R. Dogonadze, E. Kálmán, A.A. Kornyshev, J. Ustrup (Eds.), The Chemical Physics of Solvation, Part B. Spectroscopy of Solvation, Elsevier, Amsterdam, 1986, Chap. 4, p. 119–187.
[7] D.N. Glew, N.S. Rath, Can. J. Chem. 49 (1971) 837–856.
[8] S.O. Paul, T.A. Ford, Spectrochim. Acta 37A (1981) 415–420.
[9] D. Hecht, L. Tadesse, L. Walters, J. Am. Chem. Soc. 114 (1992) 4336–4339.
[10] D. Hecht, L. Tadesse, L. Walters, J. Am. Chem. Soc. 115 (1993) 3336–3337.
[11] S. Subramanian, H.F. Fisher, J. Phys. Chem. 76 (1972) 84–89.
[12] M. Moskovits, K.H. Michaelian, J. Am. Chem. Soc. 102 (1980) 2209–2215.
[13] W.B. Fischer, S. Sonar, T. Marti, H.G. Khorana, K.J. Rothschild, Biochemistry 33 (1994) 12757–12762.
[14] W.B. Fischer, H.H. Eysel, O.F. Nielsen, J.E. Bertie, Appl. Spectrosc. 48 (1994) 107–112.
[15] G. Bertsch, Dissertation, University of Heidelberg, 1982.
[16] W. Kiefer, J.A. Topp, Appl. Spectrosc. 28 (1974) 26–34.
[17] H.H. Eysel, J.E. Bertie, J. Raman Spectrosc. 19 (1988) 59–64.
[18] J.R. Scherer, M.K. Go, S. Kint, J. Phys. Chem. 77 (1973) 2108–2117.
[19] J.E. Bertie, H.H. Eysel, Appl. Spectrosc. 39 (1985) 392–401.
[20] (a) J.E. Bertie, H. Harke, M.K. Ahmed, H.H. Eysel, Croatica Chim. Acta 61 (1988) 391–404. (b) J.E. Bertie, M.K. Ahmed, H.H. Eysel, J. Phys. Chem. 93 (1989) 2210–2218.
[21] K. Cunningham, P.A. Lyons, J. Chem. Phys. 59 (1973) 2132–2139.
[22] C.I. Ratcliffe, D.E. Irish, J. Phys. Chem. 86 (1982) 4897–4905.
[23] J. Bandrup, E.H. Immergut (Eds.), Polymer Handbook, 2nd edn., John Wiley and Sons, New York, 1975.
[24] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975, Chap. 2, p. 19–41.