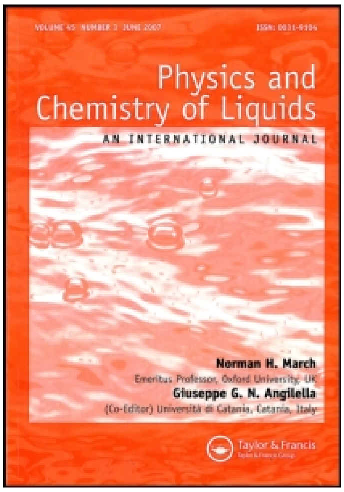

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Structure of Water in Microemulsions Investigated by Raman Scattering†

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Measurements of Raman intensity of the O—H stretching band in microemulsions give experimental evidence of the existence of a layer of water whose structural properties differ from those of bulk water.

The measurements are performed with an isotopic substitution method, which allows a careful evaluation of various contributions. The depth of the layer can be evaluated, and the structural situation of water is discussed in the frame of the current theories.

1 INTRODUCTION

It is well known that the properties of water change drastically near the interfaces, and that water is very small capillaries or tiny bubbles exhibits properties different from those of bulk water.[1] In such a problem two main questions arise: the first one concerns the depth of the layer of water, in some sense bonded to the interface, and whose properties differ from those of bulk water: the second one is the characterization of the structure of bonded water in comparison with that of bulk water.

Microemulsions are physical systems that can be fruitfully investigated for such purposes. In microemulsions, in fact, the water is dispersed in oil as very small droplets, whose dimensions range from 25 Å to 100 Å depending on the water concentration. Systems of this kind have been extensively investigated during the past years with a large variety of techniques, and at present they can be quite well characterized.[2–8] As a general rule they behave as follows: at very low concentrations of water, the system consists of small

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droplets of water, surrounded by a layer of surfactant and co-surfactant, dispersed in oil. The radius of the droplets increases as the concentration of water is increased. At a certain water concentration the system undergoes a structural transition, the water now being dispersed as thin rods.

Increasing again the water concentration, another structural transition takes place: the system becomes stratified, being formed of alternating layers of oil and water. Ultimately at higher concentration of water the microemulsion is inverted, now being formed of oil droplet dispersed in water.

The evaluation of the droplet radius as a function of concentration as well as the critical concentrations at which the structural transitions occur are well known, from a variety of experiments (as, for example, light scattering,[9,10,4,11] dielectric properties,[12,13] viscosity measurements,[14,4,15], acoustic absorption,[16] small angle neutron scattering[17,18] and so on.).

In the present paper we try to investigate the structural properties of water in microemulsion, by studying the Raman spectra of water, mainly in the region of the O—H stretching. It is well known that the O—H stretching is very sensitive to the structural properties of the system, and recently by such a technique an extensive study of structural properties of water in electrolytic solutions has been carried out.[19]

We use microemulsion prepared from *n*-dodecane (as the oil phase) potassium oleate as surfactant and hexanol as co-surfactant. The aqueous phase is normal water and heavy water as will be discussed in Section 2. The method of preparation can be found in Refs. 8, 10.

The Raman spectra are taken using a Spex Ramalog 5, together with an Ar-laser operating at 5145 Å wavelength, with a mean power of 100 mW. All the measurements are performed at the constant temperature of 20°, the sample being thermostated in a modified Harney–Miller cell.

2 EXPERIMENTAL PROCEDURE

Our goal is the experimental detection of the O—H stretching spectrum of water in microemulsions. However it is to be noted that the presence of hexanol in the microemulsion jeopardizes noticeably the situation.

In fact in the microemulsion the contribution to the OH stretching band comes not only from the water, but also from the OH groups of hexanol. In order to overcome such a difficulty we prepare the microemulsions with heavy water. In such a way, as far as the structural properties of water are concerned, we are faced only with the OD band. Another difficulty arises the noticeable contribution to the spectra of the CH's stretching, that falls in a spectral region between the OH and OD band. However, the comparison

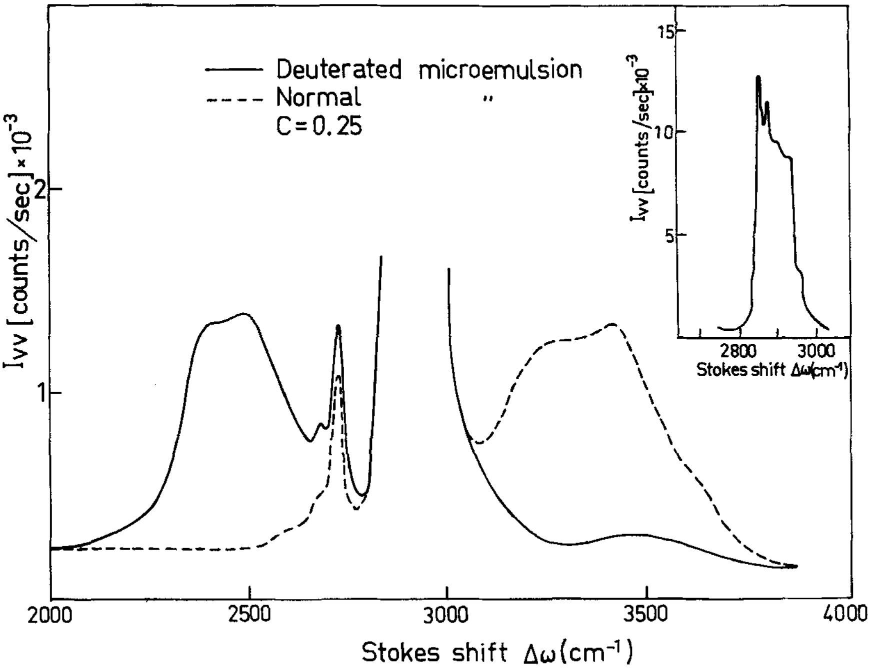

FIGURE 1 Raman spectra of microemulsion with heavy (continuous line) and light (dashed line) water at $c = 0.25\ V_{\text{water}}/V_{\text{total}}$ concentration. In the inset the CH band is shown.

between spectra taken in microemulsion prepared both with normal and heavy water allows us to subtract unwanted contributions quite easily.

As an example we show in Figure 1 the Raman spectra, in the range between 2000 and 3800 cm^{-1}, taken in a microemulsion prepared with normal water (full line) and heavy water (dashed line). Two procedures, in principle, are possible: the subtraction of the OH band in the H_2O microemulsion of the contributions given both by the OH group of hexanol and by the CH group, such contributions being evaluated from the spectra of D_2O microemulsion.

On the contrary one can subtract from the OD band in the D_2O microemulsion the contribution of the CH groups evaluated from the microemulsion. We prefer to follow the second procedure because:

i) The CH contribution in the range 2800–3000 cm^{-1} is of paramount magnitude, so that even a small mistake in the normalization procedure can give rise to large errors.

ii) The OH band contains two unwanted contributions, namely CH and OH from hexanol.

As a rule we prepare two microemulsions at the same volume fraction of water, normal and heavy. It is to be noted that we use, as surfactant, anhydrous potassium oleate, instead of potassium hydrate and oleic acid, as usual, in order to avoid the unwanted presence of H_2O in the microemulsion prepared with D_2O.

Our experimental results show that the spectral shape of the CH bands remains unchanged both in normal and heavy water, microemulsion, and also at various water contents. Then we can use the part of the spectra in the neighbourhood of 2800 cm^{-1} to normalize the Raman intensity of the two microemulsions, and to subtract the CH contribution (evaluated from the H_2O spectrum) to the OD band. An example is shown in Figure 2. The goodness of the procedure can be seen by comparing the resulting OD band with that obtained in the case of pure D_2O: the details of the band masked in the microemulsion by the CH contribution, clearly appear after subtraction. In the sequel we discuss the O—D stretching band, and its behaviour at different water concentrations. In the sequel we discuss isotropic spectra, obtained from experimental results by the equation, $I_{is} = I_{VV} - \frac{4}{3}I_{VH}$.

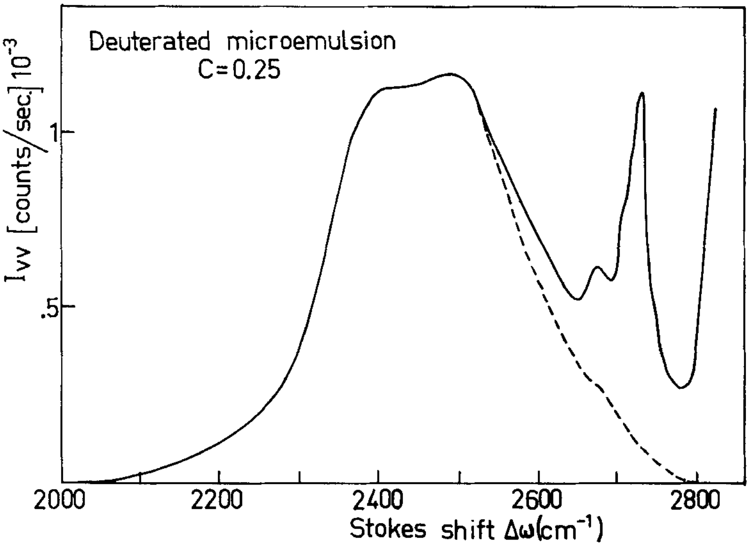

FIGURE 2 Raman spectrum of $c = 0.25$ V_{water}/V_{total} deuterated microemulsion (continuous line). The dashed line is the resulting OD band after subtraction of the CH contribution.

3 DISCUSSION OF EXPERIMENTAL RESULTS

We investigate microemulsions with the following water concentration (volume of water/total volume): $c = 0.12, 0.25, 0.32, 0.44, 0.55, 0.80$. At the first three concentrations the microemulsion consists of microsphere of water of 25 Å, 62 Å and 86 Å radius respectively. The values of the radii are estimated at each concentration, on the basis of various data taken from literature[18,10,20,5] the 0.44 concentration corresponds to rods of water.

The 0.55 concentration corresponds to the layered system. The concentration of 0.80 corresponds to the inverted phase, in which small droplets of oil are dispersed in water.

In the present work a detailed discussion is made for the case of water microsphere. It will be seen that the conclusions agree well with the result, concerning the layered system. In the case of inverted microemulsion ($c = 0.80$) the OD spectrum is practically indistinguishable from that of pure water, as is expected. As far as the microemulsion at $c = 0.44$ (rods) is concerned, the system exhibits birefringence and the Raman spectra cannot be interpreted in a simple way.

In Figure 3 we report the O—D bands, evaluated as mentioned before, for pure D_2O and for the microemulsions at $c = 0.12$, 0.25, 0.32. The drastic difference between pure water and microemulsions is quite evident, and furnishes a direct evidence of the peculiar structural situation of water in very small droplets.

In order to treat our data quantitatively, we make the hypothesis that in a microsphere of radius r, there exists a boundary layer of depth d of "bounded water," whose structural properties, and therefore Raman spectrum, differs from that of "bulk water." Therefore the Raman spectrum will be the sum of two contributions, bulk water and bonded water, the relative

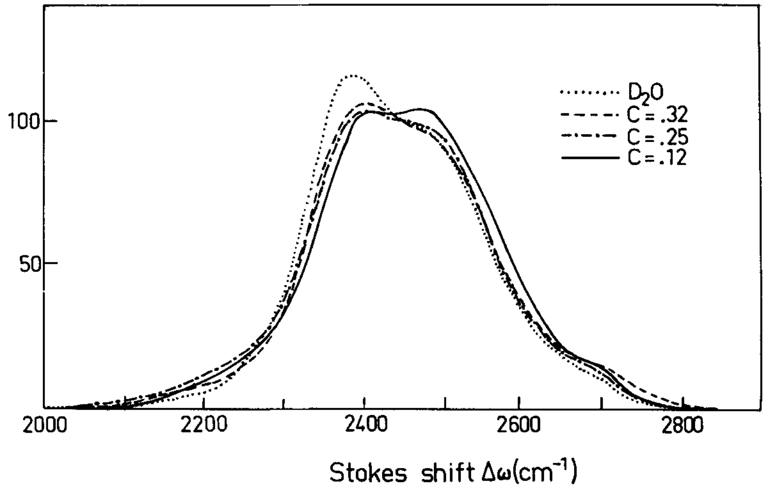

FIGURE 3 Isotropic Raman spectra ($I_{is} = I_{vJ} - \frac{4}{3} I_{VH}$ for microemulsions at different values of C.

amount of the two contributions being $[(r - d)/r]^3$ and $1 - [(r - d)/r]^3$ respectively?

In such a model the spectra referring to microspheres of 62 and 86 Å ($c = 0.25$ and 0.32) could be obtained by "adding" some amount of the spectrum of pure D_2O to the spectrum referring to the 25 Å microspheres ($c = 0.12$). In other words one could write:

$$\left.\begin{aligned} F_{62}(\omega) &= \alpha_{62} F_{D_2O}(\omega) + (1 - \alpha_{62}) F_{25}(\omega) \\ F_{86}(\omega) &= \alpha_{86} F_{D_2O}(\omega) + (1 - \alpha_{86}) F_{25}(\omega) \end{aligned}\right\} \tag{1}$$

where $F(\omega)$ are normalized spectra.

Actually, experimental data can be fitted to a very good accuracy with Eq. (1), and the fit furnishes the value of $\alpha_{62} = 0.37 \pm 0.02$ and $\alpha_{86} = 0.50 \pm 0.02$.

Now let us call γ_{25} the contribution of pure water in the spectrum referring to the 25 Å microspheres, i.e.

$$F_{25}(\omega) = \gamma_{25} F_{D_2O}(\omega) + (1 - \gamma_{25}) F_B(\omega) \tag{2}$$

where $F_B(\omega)$ is the (unknown) spectrum of the "bonded" water. Then a straightforward calculation shows that the contribution of pure water in the F_{62} and F_{86} spectra will be given by:

$$\left.\begin{aligned} \gamma_{62} &= \alpha_{62} + \gamma_{25}(1 - \alpha_{62} \\ \gamma_{86} &= \alpha_{86} + \gamma_{25}(1 - \alpha_{86} \end{aligned}\right\} \tag{3}$$

In turn the γ values can be related to the radius r of microspheres and to the depth d of the layer of bonded water, as mentioned before:

$$\gamma = \left(\frac{\pi - d}{\pi}\right)^3 \tag{4}$$

One obtains the following relation between the values of c, the radius r of microspheres and the depth d of the layer, expressed in Å:

$$\alpha = \frac{(1 - d/\pi)^3 - (1 - \mathrm{d}/25)^3}{1 - (1 - d/25)^3} \tag{5}$$

In Figure 4 we plot α vs r with d as a parameter. From such a contribution, and given the experimental values of α for the microspheres of 62 and 86 Å, it is easy to determine the value of d to a good accuracy. It results $d = 16.6$ Å. Such a result is in good agreement with values cited in literature for the depth of water bonded to interfaces.[1]

If we apply an analogous procedure to the spectrum of the microemulsion at $c = 0.55$ (layered system), we get for d a value of 22 Å. It seems therefore that in the case of a plane interface the thickness of "bonded" water is a bit larger than in the case of spherical interface.

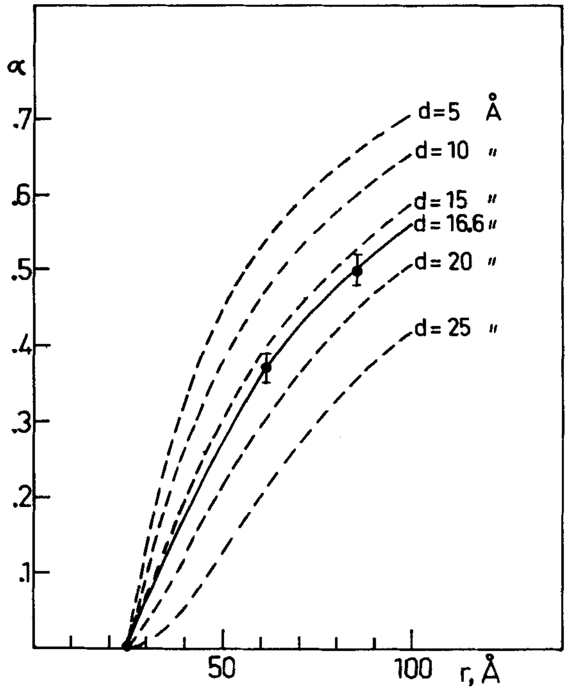

FIGURE 4 Relationship between bulk water, fraction α, radius of microbubble r and layer depth d.

4 THE SPECTRUM OF BONDED WATER

Once the amount of "bonded" water is known, it is easy to subtract from the Raman spectra the contribution of the bulk water, in order to obtain the O—D stretching spectrum of bonded water. Actually such a spectrum is almost identical to the spectrum of the microemulsion at $c = 0.12$ (see Figure 3). In such a case, in fact, only 4% of water in the microspheres is "bulk" water.

As mentioned before, a modification of the spectral shape of the O—D stretching Raman-band, indicates a modification in the structure of water. However the kind of modification can be specified only if one assumes a precise model for the structure of water. Now the general problem of the structure of water at present is far from a definite solution. Actually there are various proposed models, that can be roughly divided into two main categories.[21]

i) Continuous theory, in which a net of bonds is assumed, with broken bond and distortions that behave as continuous variables.

ii) Discrete theory, in which a finite, small number of coexisting structures is assumed.

Recently, a new model that, in a sense, is intermediate between the abovementioned models[22,23] has been proposed. In such a model molecules of water are divided into five groups, according to the number of hydrogen bonds (from zero to four). Then, in the frame of a bond-percolation calculation, it is shown that tetrabounded molecules tend to clusterize, so that water

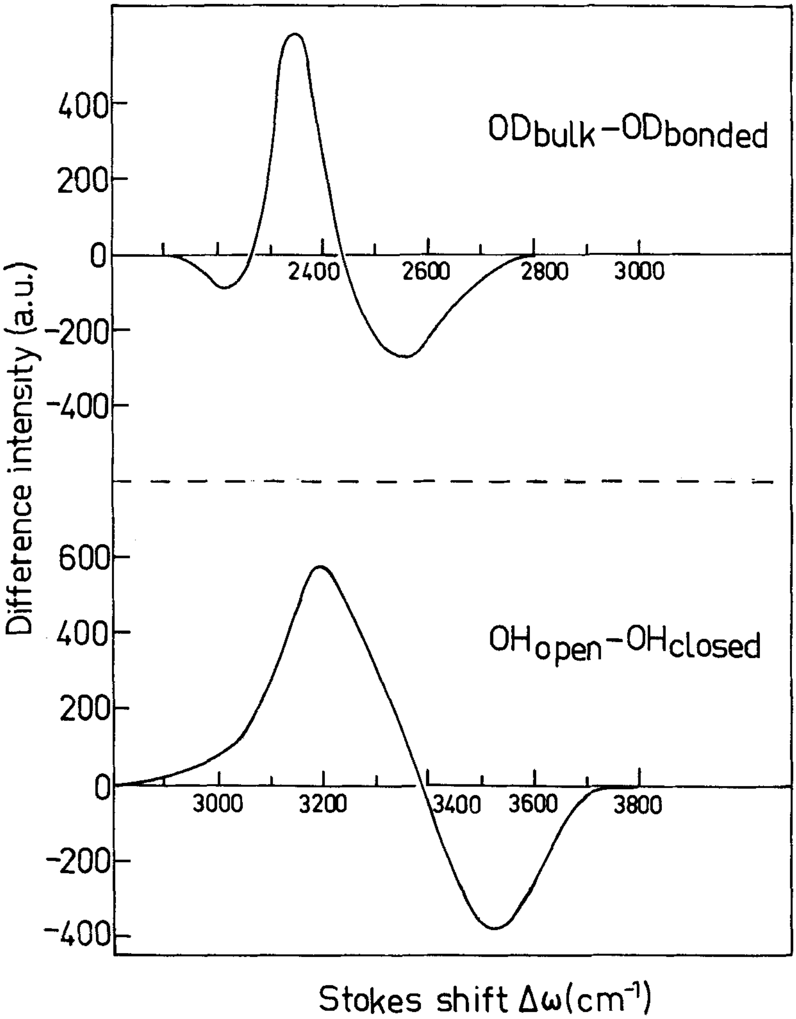

FIGURE 5 Difference between spectra of OH stretching: upper part: case of microemulsion, lower part: case of supercooled water.

molecules can be divided into two classes: open water, in which a regular tetrahedral structure exists, and closed water that behaves like a continuum, being the mixing of all the molecules but the tetrabonded. Recent Raman measurements, performed from $T = 80°C$ to supercooled water at $T = -30°$, showed that the latter model can be fruitfully employed, and gives information about the Raman spectra that would be attributed to "open" and "closed" water.[24]

Unfortunately, such measurements have been performed in normal (H_2O) water, so that spectral shape cannot be directly compared to D_2O spectra. As a qualitative comparison we show in Figure 5 the difference between the O—H stretching spectra in "closed" and "open" normal water[24] together with the difference between the O—D stretching in bonded and bulk water of the present measurement. Although the implied range of frequency is different in the two cases, a close similarity in the behaviour of the two curves can be shown.

In the frame of the above-mentioned model, such a circumstance would imply that water bonded to interface has a larger content of "closed" water than in the bulk. In other words the interaction of water with the surface, partially destroys the structure of water, giving rise to a more compact, more disordered phase.

The same conclusion can be reached in the frame of the "discrete" models.[25,26] As an example one can decompose the O—D stretching band in four contributions, both in the case of bulk and bonded water. The four contributions are attributed to hydrogen bonded 2370 (Simm.), 2510 (Antisimm.) and non-hydrogen bonded 2610 (Simm.), 2670 (Antisimm.).

Then the comparison between bulk and bonded water shows that the contribution centred at 2370 is considerably lowered in the bonded water, again indicating a loss of order.

As a final comment, we would also mention recent works on the behaviour of O—H stretching in electrolytic solutions.[19] The presence of electrolyte noticeably alters the structure of water, giving rise to a modification in the shape of the O—H band that turns out to be quite similar, although more relevant, to that shown by bonded water in the present measurement.

Again, such a circumstance leads to the conclusion that bonded water suffers a loss of structure, and, in a sense, indicates an analogy between water bonded to surface and hydration water in an electrolytic solution.

5 CONCLUDING REMARKS

Raman measurement performed in microemulsion prepared both with normal and heavy water allows a careful evaluation of the O—D stretching band. The study of the evolution of the O—D band as a function of water concentration, and therefore of the radius of the microbubbles in which water is partitioned, leads to the following conclusion:

i) The structural properties of water stored in microsphere, change as the radius of microsphere changes.

ii) Experimental results can be fully explained assuming the existence of a boundary layer of water with a structure different from that of bulk water. There are therefore, direct evidence of the existence of such a layer.

iii) Experimental results also allow the evaluation of the thickness of the bonded layer; it turns out to have a depth of 16.6 Å in case of spherical surfaces and of 22 Å in case of plane surface. Such values are in quite good agreement with those cited in literature.

iv) As far as the structure of bonded water is concerned, Raman spectra indicate a more compact structure, together with a lower amount of order. Such a conclusion seems quite general, independently from the model assumed for the water structure itself, and agrees with results obtained in electrolytic solutions.

References

1. J. Clifford, in *Water, a Comprehensive Treatise.* (F. Franks, Plenum Pub. Corp., New York, London. 1975).
2. S. I. Ahmad, K. Shinoda, and S. Friberg, *J. Coll. and Interf. Sci.*, **47**, 1, 32 (1974).
3. A. Graciaa, J. Lachaise, A. Martinez, and A. Rousset: (a) *C. R. Acad. Sci. Paris t*, **285** *B* 295 (1977); (b) *C. R. Acad. Sci. Paris t*, **286** B 157).
4. S. Ballaro', F. Mallamace, F. Wanderlingh, D. Senatra, and G. Giubilaro, *J. Phys.*, **C12**, 4729 (1979).
5. L. M. Prince, *J. Coll. and Interf. Sci.*, **52**, 182 (1975).
6. E. Ruckenstein and J. C. Chi, *J. Chem. Faraday Trans., II*, **71**, 1690 (1975).
7. E. Ruckenstein, *J. Coll. and Interface Sci.*, **66**, 369 (1978).
8. K. Shinoda and S. Friberg, *Adv. in Colloid and Interf. Sci.*, **4**, 2881 (1975).
9. D. Attwood, L. R. J. Currie, and P. H. Elworth, *J. Coll. and Interf. Sci.*, **46**, 255 (1974); *J. Coll. and Interf. Sci.*, **46**, 249 (1974).
10. S. Ballaro', F. Mallamace, and F. Wanderlingh, *Optics Comm.*, **25**, 2 144 (1978).
11. G. Fourche' and A. M. Belloq, *C.R. Acad. Sci Paris t*, **289** B 261 (1979).
12. M. Clausse, *Colloid and Polym. Sci.*, **255**, 40 (1977).
13. D. Senatra and G. Giubilaro, *J. Coll. and Interf. Sci.*, **67**, 448 (1978), *J. Coll. and Interf. Sci.*, **67**, 457 (1978).
14. K. D. Dreher, W. B. Hogarty, and R. D. Sydansk, *J. Coll. and Interf. Sci.*, **57**, 2, 379 (1976).
15. S. Matsumoto and P. Sherman, *J. Coll. and Interf. Sci.*, **30**, 525 (1969).
16. S. Ballaro', F. Mallamace, and F. Wanderlingh, *Phys. Lett.*, **77**A, 2, 3, 198 (1980).
17. M. Dvolaitzky, L. Guyot, M. Lagues, J. P. Le Pesant, R. Ober, C. Sauterey, and C. Tauping, *J. Chem. Phys.*, **69**, 7, 3279 (1978).
18. C. Taupin, J. P. Cotton, R. Ober, *J. Appl. Cryst.*, **11**, 613 (1978).
19. F. Aliotta, M. P. Fontana, G. Maisano, P. Migliardo, and F. Wanderlingh, *Optica Acta*, **27**, 931 (1980).
20. J. H. Schulman and D. P. Riley, *J. Colloid Sci.*, **4**, 383 (1948).
21. D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water.* (Oxford Univ. Press, Oxford, 1969).

22. H. E. Stanley, *J. Phys. A*, **12**, 12, L329 (1979).
23. H. E. Stanley and J. Teixeria, *J. Chem. Phys.*, **73**, 3034 (1980).
24. G. Maisano, F. Mallamace, P. Migliardo, F. Wanderlingh, and G. D'Arrigo, to be published (1981).
25. D. F. Irish and M. H. Brooker, "Raman and infrared spectral studies of electrolytes." In *Adv. in Raman and Infrared Spectr.* Edited by R. J. H. Clark and R. E. Hester (Heyden and Sons, London, 1976), vol. 2, pp. 212–311.
26. G. E. Walrafen, "Raman and infrared spectral investigation of water structure," in *Water, a Comprehensive Treatise.* Edited by F. Franks (Plenum Pub. Corp., New York, London, 1972), vol 1, pp. 151–214.