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The supramolecular structure of liquid water and quantum coherent processes in biology

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Abstract. Vibrational spectroscopy provides a powerful tool to understand the molecular structures. When applied to the liquid water, this technique reveals so many details which can also shed a light on the supramolecular arrangement of the most ubiquitous of the substances. In particular, the two fluid model of water, proposed several decades ago, finds experimental evidence. Moreover, some fundamental parameters calculated in the realm of the theory of Quantum ElectroDynamics applied to liquid water can be actually measured showing an excellent agreement with the theory. This allows to add a dynamical origin to the mixed cluster model of water well known by the biologists for fifty years and opens the way to the dawn of a real quantum biology.

1. Introduction

The study and the comprehension of the dynamics of water have been often thought to be at the basis of most outstanding problems in modern biology, such as protein folding and the fast communication pathways between biological molecules. Several models of liquid water have been proposed so far, starting from the suggestive two-phase picture proposed by Roentgen in 1892. Some decades later, Linus Pauling introduced the concept of the hydrogen bond (HB), and the properties of the continuum were explained by a network formed of HBs and distorted by the temperature. For many decades, water has been described as a collection of independent molecules whose cohesion was only secured by short-range forces. Long-range cohesion was explained by introducing the concept of a statistically interconnected network that consisted of random HBs that were subject to continuous restructuring as a result of thermal collisions. The widespread diffusion of the computer modelling and the very smart calculation capability of contemporary informatics have been the basis of a considerable number of Molecular Dynamic (MD) simulations. The one most commonly applied are derived from non-polarisable model of water which consists of three or four interaction sites located on the atomic centres of oxygen and hydrogen, the fourth being located along the H-O-H bisector. Using this conceptual framework it is possible to calculate the component of the electric field exerted on the proton by all the surrounding molecules and projected onto the OH covalent bond. The emerging picture is that water is made up of a single population of absorbers whose energy varies continuously. However, if the MD is not dynamic in nature then it cannot provide a dynamic scenario. Moreover by fitting a number of different sets of experimental data, it has been shown that all the anomalies of liquid water may be explained in terms of domains of different density. Such a model assumes the



existence of two states that have different specific volumes at a given pressure p and temperature T . In this paper we explore the features of the IR spectra of liquid water with the aim to show that the experimental results obtained by several experimentalists can hardly be discussed and strongly suggest the existence of two kinds of H_2O molecules in liquid water. Moreover these two kinds of molecules can be attributed to the two quantum levels system described by Giuliano Preparata and coworkers in their theory formulated in last two decades.

2. The vibrational spectrum of water

The IR spectrum of liquid water is composed by two bands, one centred around 1650 cm^{-1} having a Gaussian line shape and another much wider ranging from 3000 to 3800 cm^{-1} (see fig. 1). The first one has been attributed to the bending motion of the H_2O molecule, while the latter to the stretching vibrations. For many decades this spectrum has been used both to support and to confute the two-phase nature of liquid water and its opposite, the continuum picture. Theories of the two-phase nature were first proposed in the 19th century by Roentgen but they were discarded according to the statement of Bernal and Fowler in 1933 that molecules having the same thermodynamic properties cannot show any differences in the behaviour. More recently computer simulations have been extensively used to check models calibrated against sets of experimental data (e.g. radial distribution function, heat of vaporization). However, none of the existing models is able to reproduce the dynamic properties of the liquid such as the rate of formation of H-bonds and even the vibrational spectrum is obtained by Molecular Dynamics (MD) only with the use of “ad hoc” hypothesis. The MD modelling of the shapes of the H_2O IR and Raman spectra and their simple temperature dependencies could seem to support the continuum model of water [1, 2, 3]. According to the viewpoint of liquid-state statistical mechanics the continuum picture emerges quite naturally in case the system is at a sufficiently high temperature and low density in order to assume the mutual independence of the component molecules so that the ensemble of molecules should be described by a density matrix. In case of “isolated” chromophores, the transition frequency of a vibrational mode will fluctuate on some characteristic time scale. In case this time rate is sufficiently slow the line shape will be simply the distribution of the frequencies, at the opposite, when the rate is much higher, the effect of fluctuation dynamics will appear into the spectrum and the line shape will be narrower than the distribution of the frequencies. However, in case of liquid water the situation is quite more complicated because of the intermolecular and intramolecular coupling. One recently proposed solution calculates the line shape as a distribution of time averaged frequencies where the time of averaging is a parameter obtained by fitting the experimental line shape [4]. However, a careful inspection of the line shape does not show a unique Gaussian line, actually it is well known that the broad absorption peak from 2800 to 3800 cm^{-1} , attributed to the OH stretching mode, can be deconvoluted into line shapes which are usually assigned to different bond ordering parameters [5]. The deconvolution in sub-bands could be done mathematically in infinitely many ways; this is a trivial consequence of the central limit theorem which states that independent random variables (in the present case the number of H-bonds) are normally distributed, i.e. tend to be distributed around a mean value. However every hypothesis should be physically reasonable and experimentally proved. Moreover, the inspection of the second derivative of the IR spectrum reveals three minima located respectively to 3200 , 3400 and 3600 cm^{-1} and the mean squared error χ^2 of the deconvolution in three sub-bands is much smaller than in case of a single Gaussian fit. Thus it can be safely assumed that the best deconvolution of the stretching peak is done by using three (Gaussian) substructures respectively located at approximately 3200 , 3400 and 3600 cm^{-1} . It is quite interesting to address the problem of the dependence of the peaks on the co-ordination of the involved molecules by comparing the spectroscopic features of gaseous, liquid and solid water. It is apparent that in vapour, where molecules can be assumed safely to be independent, the peaks at 3200 and 3400 cm^{-1} , observed in condensed water are absent,

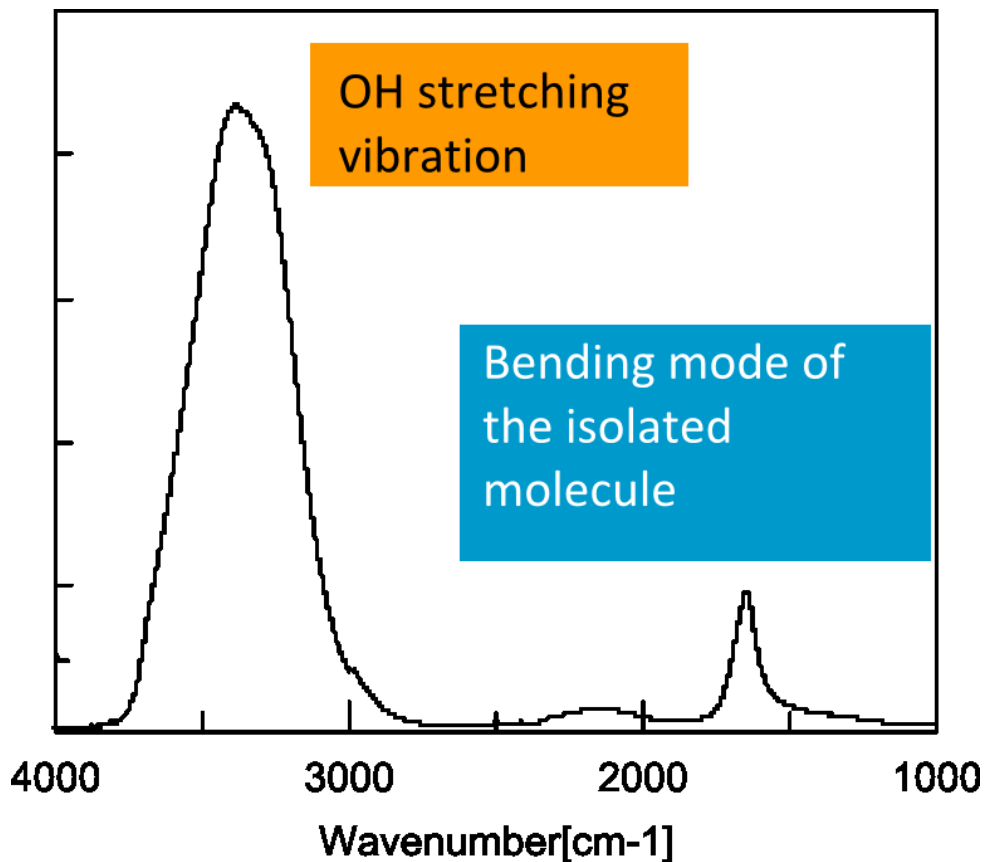


Figure 1. IR spectrum of liquid water at room temperature

whereas we can observe a number of peaks whose position is slightly higher than 3600 cm^{-1} . On the contrary in ice the dominant feature is the peak at 3200 cm^{-1} while the other features fade away by decreasing temperature. Since we know that component molecules in ice are mutually correlated we can assume that the peak at 3200 cm^{-1} is produced by the sub ensemble of molecules which are mutually correlated. In liquid, where we can observe three peaks, we should assume the simultaneous presence of a fraction of correlated molecules, a fraction of uncorrelated molecules and an intermediate fraction (responsible of the peak at $\sim 3400\text{ cm}^{-1}$) made up of water molecules that are connected with other molecules, but are unable to develop the full connections of the previous network.

3. The two-phase model of liquid water

On the basis of the above experimental observations, let's assume that the spectral intensity $I(\omega, T)$ can be decoupled in two components: correlated water (1) and non-correlated water (2), the latter being the sum of what we call intermediate and free molecules, whose fractions has been observed to depend on the temperature T [5, 7]:

$$I(\omega, T) = I_1(\omega, T) + I_2(\omega, T) \quad (1)$$

In a two components system (in which the two components are in chemical equilibrium) an isobestic point exists, which is a point of equal absorption, invariant with respect to the relative concentrations of the two components. This is a very basic property of the system in equilibrium and it has been discussed widely in literature [8, 9, 10]. A van 't Hoff plot can be

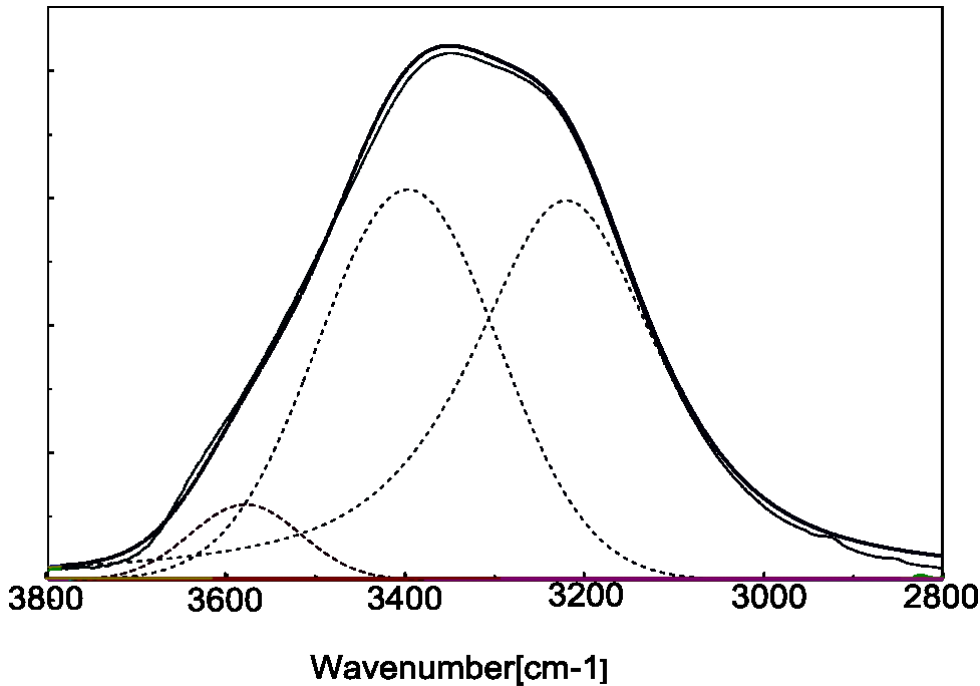


Figure 2. Deconvolution in sub-bands of the stretching peak in fig. 1.

done by bisecting the spectrum at the isosbestic point and plotting the natural logarithm of the ratio of the areas above and below that point versus $1/T$. The slope of that curve gives the energy difference between the two vibrational states 1 and 2:

$$\ln \frac{I_1(\omega, T)}{I_2(\omega, T)} = \frac{E_2 - E_1}{RT} + c \quad (2)$$

We have measured the IR spectrum of water in a range 25-60 C° . Fig. 3 shows the Van't Hoff plot we obtained for the model of the two populations, namely correlated and non correlated (including the intermediate population). The picture shows a perfect linearity thus confirming that the difference of energy of the two phases does not depend on temperature in the range under investigation. The slope of the curve $\Delta E/R$ (R is the ideal gas constant) gives an enthalpy difference between the two states

$$\Delta E = 2.9 \pm 0.6 \text{ Kcal/mol} \quad (3)$$

which is in reasonable agreement with various estimates in the literature $\Delta E = 2.5 \pm 0.6$ Kcal/mol [9] and 2.8 ± 0.4 Kcal/mol [17]; this value is usually associated to the enthalpy change in the hydrogen-bond rupture for water. However, this value is quite lower than 4.5 Kcal/mol the value for the rupture of the H-bond estimated by Linus Pauling from the enthalpy of sublimation of ice. The intercept of the curve is equal to molar entropy change $\Delta S/R$ between the two populations, from our data we found

$$T\Delta S = 2.7 \pm 0.2 \text{ Kcal/mol} \quad (4)$$

per particle at $T=300\text{K}$, which almost coincides with the above estimate for ΔE showing that the decrease of energy of the coherent fraction with respect to the non coherent comes from

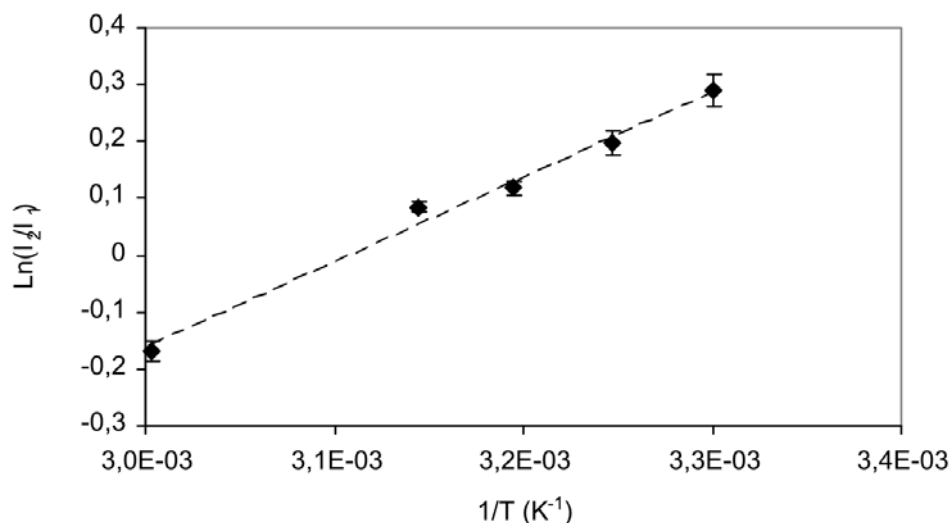


Figure 3. Van't Hoff plot

the vanishing of the entropic component¹

Since the beginning of the last century, it has been widely accepted that the attractive forces acting between two neutral atoms or molecules separated by a distance large in comparison with their dimensions (Van der Waals Forces) are electromagnetic in origin. A theory of long-range attractive forces in condensed matter was first proposed in 1961 by Dzyaloshinskii, Lifshitz and Pitaevskii, using Quantum Field Theory [11]. They proposed that “the interaction between bodies is considered to take place through a fluctuating electromagnetic field”. However this interaction does not induce a phase correlation among components.

The existence of water in two different populations made up by molecules having different degree of mutual correlation has been demonstrated in the framework of Quantum Electrodynamics (QED). According to general principles of Quantum Field Theory, an ensemble of electrically charged atoms or molecules (nuclei, electrons) is coupled with the quantum electromagnetic fluctuation of the vacuum. It can be proved that when the temperature T is lower than a certain critical temperature $T \leq T_{crit}$ and the density is greater than a critical density $N \geq N_{crit}$ the ensemble is subjected to a collective coherent oscillation between a couple of internal levels of its components, in tune with the electromagnetic field [12, 13, 14, 15]. These fields induce long-range forces which account for the actual existence of the condensed state. The short-range static attractions come into play only after the molecules have been brought sufficiently close together by the attraction of the long-range force. Liquid water is peculiar because of its electronic configuration. In the ground state all electrons are tightly bound, whereas in the excited configuration $E = 12.06$ eV electrons are only 0.54 eV below the ionization threshold $E_{exc} = 12.6$ eV, thus they can be considered as “quasi-free” or very loosely

¹ Several authors have interpreted the existence of the isobestic point as the result of changes in a continuous distribution of hydrogen bonding geometries and of the microscopic nature of the fluctuations of the (single state) thermal bath. They also stated that a single specie coupled to a Gaussian bath satisfies the Van't Hoff behaviour equation. However the demonstration always implies the existence of two species artificially dividing the spectrum at a cutoff frequency. In order to guarantee that the energy difference in eq. (2) depends weakly on temperature, it must be required that the fluctuations are dominated by a few bath modes. In such a way the origin of the effect is moved from the two-state picture of the liquid structure to the two-state fluctuations of the thermal bath whose energy are below and above the average.

bound. The coherent state is a superposition of the ground state and the excited state with weights 0.87 and 0.13 respectively. The size of the region where molecules are phase locked is the wavelength of the e.m. mode

$$\lambda = \frac{hc}{E_{excit}} = 0.1\mu \quad (5)$$

This region has been termed Coherence Domain (CD). At the border of the CD the thermal collisions extract molecules from the coherent phase thus the fractions of the coherent and non-coherent states is a function of T:

$$F_{coh}(T) + F_{non-coh}(T) = 1 \quad (6)$$

Calculations show [16] that the energy gap of the coherent water at T = 0K is

$$\Delta E = -0.17 \pm 0.05eV \quad (7)$$

This value is ~ 6.8 KT (T = 300K), this means that the gap is well protected against thermal collisions at room temperature. Accordingly, the lifetime of the coherent structure, i.e. the time each single molecule spend in the coherent phase is $\sim 2.3 \times 10^{-14}$ sec. The calculated gap must be compared to the energy gap measured by the Van't Hoff plot between correlated and non correlated fraction of dipoles in the FT-IR spectra, $\Delta E = 0.12 \pm 0.02eV$ per molecule (2.9Kcal/mol).² The fair agreement with the value calculated for the energy gap by the Preparata and Del Giudice theory allows us to identify the correlated population with the coherent fraction of water and the non-correlated population with the non-coherent fraction. In such a picture, even the so called intermediate population could find a rationale. The measured spectrum emerges from a dipole-dipole transition between two specific quantum states. We have seen that the first and third peak describe the transitions occurring within the coherent and non coherent fraction respectively. It is very natural to assign the second (intermediate) peak to the transitions where the initial state is in the coherent fraction and the final state is in the non-coherent fraction and vice versa.

On the basis of such assignment we can also evaluate the energy content of a solution. In fact we have previously shown [7] that when a solute is added to pure water the percentage of the two components is changed. In Fig. 4 we show the relative abundance of the correlated and non-correlated water upon the addition of NaCl to the solution. While the non-correlated plus intermediate fraction is almost unchanged, the correlated fraction is reduced .

In Fig. 5 the ratio between the non-coherent and coherent populations is shown. The addition of NaCl into water increases this ratio and affects the energy content of the system, in other words the energy content of a solution increases when the solute content is increased. This observations may be used qualitatively to control the lowering of the freezing point.

4. The mixed cluster model in biology

The structure of liquid water and of aqueous solutions of non polar and polar molecules it is argument of debate among the biologists because it influences the structure and the reactivity of protein molecules. Actually, in order to explain long range cohesion of liquid water we are compelled to consider clusters of structured H-bonded molecules, nevertheless, biologists describes hydration processes as interactions of independent water molecules with ions or non polar molecules. Therefore the explanation of two different properties of aqueous systems demands two different internal structures of liquid water. A model describing water as a rapidly

² The value in (7) has been calculated at T=0 K where the cross over (of the boundaries of CDs) is not allowed. At T \neq 0 the energy gap is decreased by the thermal collisions.

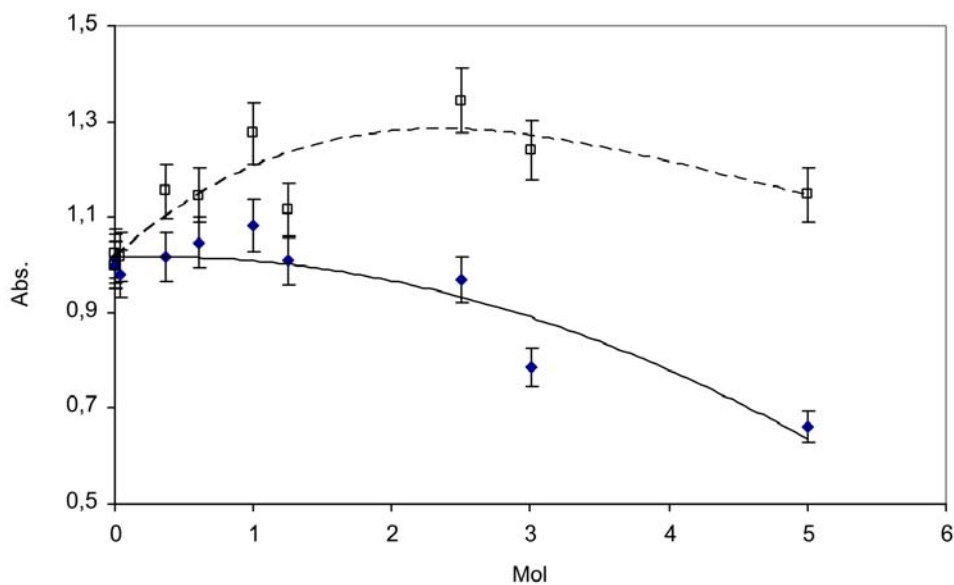


Figure 4. Relative abundance of the two populations of water in NaCl solution vs molarity. Open squares: non-correlated plus intermediate fractions; black diamonds: correlated fraction.

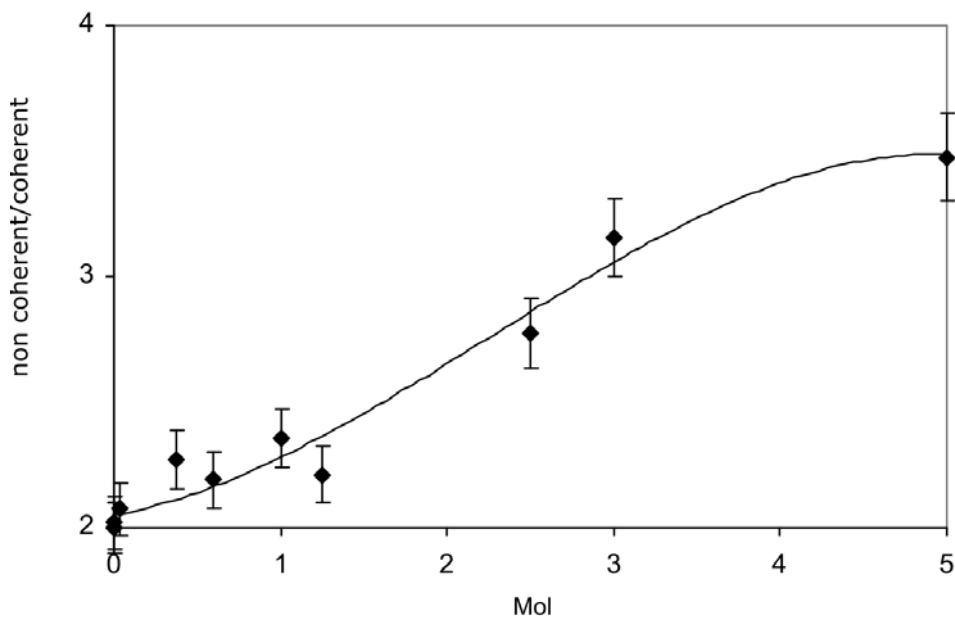


Figure 5. Ratio between the non-coherent to coherent fractions of water in NaCl solution vs molarity. This ratio is directly related to the energy content of the solution (see text).

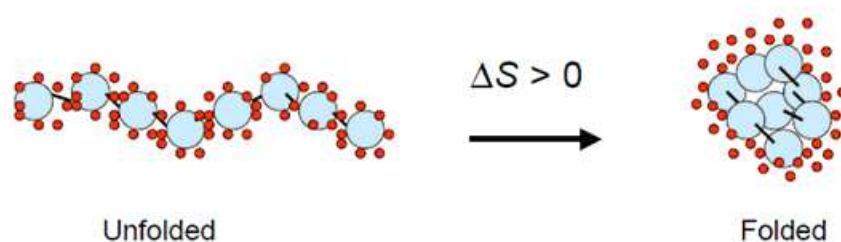


Figure 6. Formation of protein hydrophobic core in water.

fluctuating mixture of variously hydrogen bonded aggregates of molecules is known as “flickering cluster” model [18, 19]. It was assumed that liquid water consists of a mixture of monomers and clusters uniform in size. The size of the cluster, the relative numbers of cluster and monomers and their thermodynamic properties are assumed to be a function of the temperature. The “flickering clusters” models deals with this necessary double nature of liquid water. However, in order to calculate the partition function it uses several adjustable parameters. The Preparata-Del Giudice theory provides for the first time a theory for the water structure without adjustable parameters. In this picture the CDs and are responsible for the long range structure whereas isolated molecules belong to the non-coherent fraction, in fact, as explained above, solutes dissolve exclusively into the non-coherent fraction. Another key issue in the understanding of the living systems is the existence of what is called “vicinal water” [20]. It is well known that a water layer exists near the surface of an organic macro-molecule having peculiar properties: 1) the effective dielectric constant decreases dramatically to 10 (from 80 of bulk water); 2) the entropy content is lower than in bulk phase. Electrostatic interactions may justify the existence of a structured layer having a thickness of 0.1- 0.2 nm. However, in order for biological processes take place, the changes in the structure of water must extend over a zone large enough to accommodate the reaction species in a layer larger than the one obtained only via short-range forces. The coherent phase of water is compatible with all the peculiar properties observed by biologists at surfaces: the dielectric constant is decreased by the polarizability for deformation of the CDs³ and the entropy is lowered by the ordering. Also the folding process of biomolecules can be understood with a two phase system: in the formation of macromolecules the surface available for the interaction with water may decrease and water molecules are expelled (the simplest case is the formation of the peptidic bond). From a thermodynamic point of view this means a decrease of the entropy of the macromolecule, which becomes more structured and a decrease of the thickness of the surface water layer with a major increase of the entropy of water. As a result, the entropy of the whole system increases, therefore, these kind of processes may occur spontaneously and are called *entropy driven* (see fig. 6):

$$\Delta G = \Delta H_{system} - T\Delta S_{system} \quad (8)$$

We are able to estimate from (4) the contribution of water to the entropy change ~11.3 KJ/mol, however, it is not easy to evaluate the amount of water molecules expelled by the surface because of the side-chain rotations or movements of fragments of polypeptide chains, so that the quantitative evaluation of the ΔG of protein folding remains still hard to do.

³ A detailed description is out of the scope of the present paper but extensive descriptions can be found in the quoted literature, in particular in Ref.12.

5. Conclusions

The vibrational spectra of liquid water give a strong support to the picture of water as a two phase liquid. The value of the energy gap of the coherent water calculated by Preparata and co-workers is in good agreement with the energy gap measured by the van 't Hoff plot between correlated and non correlated fraction of dipoles in the FT-IR spectra. The two phase picture also allows to explain several features of the biologic systems such as the protein folding and the structured layer of water around cells and membranes. Details of the formation of such a layer require a detailed analysis of the electronic structure of the Coherence Domains. This appear to be a very stimulating challenge and will be the core of our research in the next future.

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