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Raman scattering measurements on floating water-bridge

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Abstract

It was observed that, when polarized by an intense electric field, water is able to self-arrange into macroscopic cylindrical wires that can hang up and remain floating against gravity. This phenomenon is now known as “water-bridge”. Several attempts have been made to give an explanation of this apparently unusual behavior of water. A number of experiments have been performed with the aim of probing any possible structural change of bulk water, after application of the electric field. None of the available findings looks at the moment conclusive.

Here we report the results of the first Raman scattering experiment on floating water-bridges. The intermolecular OH-stretching band has been investigated and the results have been compared with those from bulk water. Some changes in the scattering profiles after application of the electric field are shown to have a structural origin. The bridges have been obtained, for the first time, in a vertical geometry and under application of an alternating field. The adopted geometry has allowed to reveal a clear asymmetry between opposite d.c. biasing, that can be related with the nature of the charge carriers.

1. Introduction.

During the last few years, some papers have been appearing in the literature dealing with the so called water-bridge [1-5]. This locution indicates a *wire* of deionized water, which forms and stays suspended between two braces, when a sufficiently high voltage is applied between its ends. The first observation of this phenomenon was already reported in a pioneering paper in 1893 [6], together with a detailed description of the peculiar behavior of the water-bridge. After the bridge formation, a transport of water between the two reservoirs is observed. After the establishment of a difference between the water levels inside the two reservoirs, an equilibrium situation is reached and the levels remain stationary under compensating actions of two opposite currents.

The interaction between water and an electric field has been the subject of many investigations as in the cases related with electrospray ionization [7] or in the studies of the field induced

deformation of the internal hydrogen bonds of water clusters [8]. In spite of a huge number of research activities performed on water, the mechanisms driving the water-bridge formation remain obscure.

Different possible explanations have been proposed on the basis both of experimental and the theoretical studies. Schlieren imaging technique have put into evidence some inhomogeneity in the refractive index within the bridge [1] that can be related with the establishment of some local arrangement of the water molecules. This new arrangement should result in a change of the density of the water within the floating structure. The idea is that the bridge forms due to electrostatic charges on the water surface and it remains stable due to the high electric field and to the high dielectric constant of pure water. Within such a framework, the electric field is supposed to induce the building up an ordered structure of water. In particular, a high electric field could be able to enforce smaller intermolecular distances leading to a density change in the microstructure of water [9]. It was also proposed that the external electric field can completely destroy the local tridimensional arrangement of the water network, giving rise to the formation of linear chain-like structures of dipolar water molecules aligned along the field axis [8,10]. In the framework of a quantum field theory approach, it has been proposed that, when embedded in an electric field, water molecules can be in a state of coherence with the field itself [11]. An increase of the field strength can result in the formation of super-domains and in turns can induce a phase transition that could account for many of the features observed in water-bridge [12]. Very recently [13] an attempt has been made to model the tension that sustains the water against the downward force of gravity in terms of the Maxwell pressure tensor in a dielectric fluid. The frictionless Bernoulli flow is claimed to play a role in the bridge formation process and some analogy is proposed with similar phenomena occurring in super-fluids [13]. The results of a recent small angle neutron experiment on heavy water-bridge [3] seems to give evidence for the absence of any significant difference in the density of water after application of the electric field, in some contrast with previously reported findings [9]. Further results from a similar experiment performed on a wider q range [14], both on light and heavy water, seem to suggest for a partial breaking of the original H-bond connectivity. In addition, the presence of micro bubbles within the bridge has been detected and it was suggested that these micro bubbles can arrange into coherent domains [3,14].

It is worth to note that all the experiments on the water-bridge performed so far concerned the behavior of a horizontal structure (orthogonal with respect to the gravity) under application of a constant potential difference. Some studies of water droplets on insulators in outdoor high-voltage equipment [15,16] indicate changes in water behavior when exposed to an alternating field. In this situation, the geometry of the insulator imposed the vertical alignment of the electric field, parallel with respect to the direction of gravity.

Although the number of studies on floating water-bridge is increasing, none of the proposed explanations looks to be conclusive. One of the points that urge to be addressed is related to the restructuring effect of the hydrogen bond network of bulk water, under application of a high electric field. Such a task calls for the adoption of an experimental probe sensitive to any microscopic change of the local environment of water molecules. The shape of the intermolecular OH stretching band of bulk water is highly sensitive to any microscopic changes of the local symmetry [17-21].

In this paper, we report the first Raman investigation of the OH stretching spectral distribution from a floating water-bridge. The influence of the electric field geometry and its frequency on the behavior of the structure of the bridge is also discussed.

2. Experimental.

Double distilled and deionized water ($10\text{M}\Omega\cdot\text{cm}^{-1}$) has been used through all the experiments here reported. Platinum sheets ($25\times 25\text{mm}^2$ and 0.25mm thick), purchased by Goodfellow (UK) have been used as the electrodes.

A 664 TREK generator has been adopted as the power supply. This instrument is able to furnish a continuous output voltage up to 10 kV .

As a first step, an attempt has been made to reproduce the water-bridge formation following the procedure reported in the literature [1-4]. Two 50 ml beakers were mounted on a platform allowing for accurate adjusting of the gap between their edges. Both beakers have been filled with pure water up to about 1mm below their edges. After application of a 8 kV d.c. voltage, the formation of a horizontal water-bridge between beakers immediately took place, as previously reported [1-4].

After the bridge formation, the initial gap between beakers was increased up to 15mm and the voltage between electrodes has been reduced. It was found that a stable bridge forms when the voltage is higher than 4 kV . In such a condition, the current monitored through the bridge was about 3 mA and was not changing during 30 minutes of continuous working. The temperature of the bridge, monitored by means of a PM575 thermo camera (FLIR Systems), never rose above 36°C . In Fig. 1 we report a picture of the bridge obtained under the described experimental conditions.

An increase of the biasing voltage immediately produces an increase of the current through the bridge. The section of the bridge noticeably enlarges and the temperature rapidly reaches higher values. In such conditions, the bridge looks much less stable and after few minutes of working it breaks.

In order to perform a light scattering measurement on the water-bridge under different electric fields, while controlling the temperature of the bridge itself, a cell for vertically oriented bridges has been designed. The choice of this geometry has been suggested by the geometry of our Raman spectrometer, whose scattering plane is horizontal.

The cell has an axial symmetry with one water reservoir, consisting in a brass cylinder with another Teflon cylindrical beaker fitted in it. The first platinum electrode is inserted close to the cylinder edge. A thermostatic glove, surrounding the beaker, has been built where a cooling fluid can circulate. The beaker and the glove are put on an Ertalon basis and centered on the axis of an outer glass cylinder. The whole cell is then closed at the top by an Ertalon cover where the second electrode was mounted at the center of the cover. The second (top) electrode consists of a cylindrical Ertalon rod, carrying a platinum disk (8 mm in diameter) on its end. A micro-translator allows for adjusting the gap between the upper electrode and the water-pool surface. A more detailed description of the cell is over the aim of this paper and it will be described elsewhere [22]. After polarization of the electrodes, the bridge forms vertically between the surface of the water pool and the electrode above it.

The adopted design allows for temperature stabilization of the water-bridge in inert atmosphere. In the Raman measurements herein reported, the water-bridges have been obtained in normal laboratory atmosphere. We made this choice because of the need to monitor the bridge

temperature by a thermo-camera. In such a case any glass window would filter the infrared radiation from the bridge. For these reasons the outer glass cylinder has been substituted by a brass spacer with apertures large enough to allow a large view angle around the bridge.

The cell in working condition, placed on the sample holder platform of our Raman spectrometer, is shown in Fig. 2 (a).

In Fig. 2 (b) a picture of the vertically oriented water-bridge is reported, where the gap between the upper electrode and the water-pool surface in absence of electric field is 10 mm. -

The temperature of the thermostatic liquid has been controlled by a RTE-740 D+ 230/50 refrigerator (Thermo NESLAB).

In Fig. 3 the scheme of the experimental power supply set-up is reported. A 664 TREK generator operates as a voltage amplifier. The signal from a wave generator (TG1010 - Thurlby Thandar Instruments) can be amplified up to a factor of 1000. The maximum amplitude allowed for the input signal, V_{in} , is 10 V and the maximum frequency allowed is 40 kHz.

The Raman measurements have been performed in a 90° scattering geometry, both in VV and VH polarization, by means of an U1000 Jobin-Yvon spectrometer. OH stretching Raman spectra have been recorded from 2800 cm^{-1} to 3800 cm^{-1} with a resolution of 5 cm^{-1} and an integration time of 2s. The 5145 \AA line from an Ar^+ laser, working at a mean power of 400mW, have been used as the probe. OH stretching profiles from bulk water, at different temperatures, have been recorded for comparison.

Taking into account the possibility of structural effects induced by the interaction with the coherent electromagnetic field of the probe, the OH-stretching spectra have been collected for different wavelengths (5145 \AA , 4880 \AA and 4579 \AA) and different power (50 and 400mW) of the laser beam. No probe dependent effect has been detected for vertically oriented water bridges. The same observation concerns the water and its solutions under normal (without external field) conditions. Also in these cases, never a probe dependent effect has been reported in the OH-stretching profile. In Fig. 4, two normalized OH stretching spectra of water bridges, recorded at different probe intensities and wavelengths, are reported as an example.

The conductivity of the water has been monitored during each measurement. When any increase of the conductivity has been detected, the measurement has been aborted, the cell has been accurately cleaned and refilled with freshly filtered water and then the measurement has been repeated.

3. Results and discussions.

From earlier experiments reported in literature it is known that a stable water-bridge forms after application of a constant electric field [1-6]. An increase of the applied potential difference results in a larger section of the water-bridge and in an increase of the load current value. To our knowledge, the observation of the water-bridge formation under alternating fields has never been reported in the literature. We want to remark that we were able to produce water-bridges, under the usual horizontal geometry reported in Fig. 1, also after the application of an oscillating (sinusoidal) electric field. We tried to apply fields of different frequencies, from few Hz to 10 kHz. The I_0 and V_0 signals have not revealed any phase difference in the explored frequency range. The bridge looks stable at frequencies as low as 50Hz. At lower frequencies the bridge starts to pulse following the field. The amplitude of the pulsing increases with the frequency lowering. Below 20 Hz, the pulsing starts to be chaotic and, in a short time, the bridge breaks.

Since no offset biasing has been applied, we are led to conclude that any possible relaxation of the water-bridge must be of the order of 50 ms. As a consequence, any polarization induced structure responsible for the bridge stability, if exists, must be macroscopic. Once the bridge has been established, it remains stable for very long times (typically 30 minutes) if the electric energy to be dissipated is controlled to be lower than 30 W. During this phase an equilibrium temperature of the bridge is reached, whose value depends on V_0 and I_0 . On longer times the current through the bridge starts to increase, the temperature rises and, finally, the bridge breaks. The bridge appears stable at the higher frequencies explored. However, when the frequency becomes higher than about 5 kHz the conductivity of the bridge appears to be slightly higher and the life time of the stable stationary phase is shortened.

When the cell for the vertically oriented water-bridge was adopted, the same behaviors are retrieved. Some advantages of our cell design concerns the thermal stability of the system. The cooling bath allows to dissipate more heat flux and the temperature is much better controlled. As an example, when a sinusoidal field with amplitude of 4.9kV (peak to peak) at a frequency of 100 Hz is applied to produce the vertical bridge reported in Fig. 2 (b), the current through the bridge is about 3mA, and its temperature stabilizes at about 23°C when the temperature of the refrigerator is fixed at 17°C. Without any refrigerating system, the temperature of the bridge, under the same experimental conditions, rapidly rises over 40°C.

The differences between the results obtained for horizontal and vertical bridges were observed when a constant biasing of the electrodes was adopted. For horizontal bridges, some dependence on the polarity of the biasing has been reported [1-5]. The differences were small, due to the obvious symmetry against the change of the polarity of biasing. In a vertical bridge, however, the gravity immediately breaks the original symmetry. The bridge appears definitely more stable if the positive electrode is the one located on the top of the cell. In such a situation the section of the bridge appears larger than that observed when the polarization is reversed (with the same absolute value of the potential difference). These observations could provide some useful hints about the nature of the charge carriers through the bridge. It should be mentioned that different phenomena occurring at the two electrodes have been already pointed out for low electric fields [23]. The formation of some dynamical structures was observed around the anode due to the high concentration of OH⁻ ions, being the proton current between anodes the generating process. When the electric field becomes as high as in the cases here examined, probably the situation can become more complicated and the formation of some ionized complex structures can take place. Some indication for the establishment of two opposite flows has been already reported [6,14]. It has been proposed that the main charge carriers are positive. It was also estimated that with each charge carrier a mass is transported, which corresponds to the volume of a sphere with a diameter of some tenth of nanometers [14]. The asymmetry between different polarizations seems to suggest that the positive carriers can be more massive, in consistence with the above reported indications. Another point that must be pointed out is that while in producing water-bridges under a constant field in horizontal configuration we recorded current values very close to those reported in literature [1,14], higher values are found when the vertical configuration is adopted (independently on the field polarization). As a result of higher current values, the vertical bridges look less stable than the horizontal ones, and this is particularly evident under d.c. polarization.

This difference could be related with the bridge geometry. Probably, due to the occurrence that the force producing the bridge works against gravity, it is almost impossible to obtain the formation of a water column higher than 1 cm (which is about one half of the maximum bridge length that can be reached in horizontal geometry). If one imagines that the bridge acts as a resistor, the different sections and lengths obtained under the different geometries can be enough for explaining the differences in the load currents above reported. Also the lack of the second reservoir could play a role. This is a point that must be clarified by further examinations.

A first series of Raman spectra have been recorded from water-bridges under different field strengths and frequencies, at about 1 cm distance between the upper electrode and the water surface. The temperature of the cooling fluid was fixed at 17°C for the whole set of measurements. As a result, bridges at different biasing conditions equilibrate at different temperatures due to different intensity of current flowing through them.

In Fig. 5 we report the spectra obtained under the following experimental conditions: 4900V, d.c. (T=42°C); 4900V a.c., 100 Hz (T=23°C); 4900V a.c., 500Hz (26°C); 7000V a.c., 1KHz (45°C). It is quite evident that all spectra registered look very similar. In order to separate thermal effects from the polarization ones, Raman spectra of the pure water have been recorded as a function of the temperature. In Fig. 6 two spectra at 20°C and 50°C are reported as an example. The spectra reproduce the well known result of an increasing of the anisotropic contribution of the OH-stretching spectrum with temperature, while the isotropic vibrational modes behave in the opposite direction [19,21]. After appropriate normalization, all the spectra cross each other in an isosbestic point located at about 3350 cm.⁻¹. The more evident result is that all the spectra reported in Fig. 5 look very close to the spectrum of pure water at a temperature of about 35°C, with no respect of the actual temperature of the bridge. We have to imagine that two different contributions can affect the shape of the spectra, namely the temperature distortion of the H-bonded network and further distortions due to polarization effects. In order to find a tentative way for separating contributions from these two effects, we performed further measurements of water-bridges under the same polarization condition and trying to better control the bridge temperature by appropriate setting of the thermostatic bath. The measurements has been performed at fixed voltage, V=3900V, and at a frequency of 100Hz. At this particular frequency the intensity of current through the bridge turned out to be low enough to avoid unwanted heating effects. In addition, the stability of the bridge turned out the best, allowing averaging over several measurements from the same bridge in order to increase statistics. In Fig. 7 we report the obtained normalized spectra (I_{VV}) of bridges over the temperature range 5°C÷50°C.

In order to provide an interpretative framework able to rationalize both the observed differences between bulk water and water-bridge and the dependence of their spectral profiles on the temperature, a suitable analysis method must be individuated. An approach, widely adopted by the physical chemistry community, consists in the interpretation of the OH-stretching Raman profile as the superposition of the contributions corresponding to the normal modes that can be ascribed to the C_{2v} symmetry of the water molecule. Rigorously speaking, such a procedure implies some shortcomings in the analysis of liquid water. The difficulty arises from the occurrence that water molecules interact via H-bonding and this interaction lowers the original symmetry of individual molecule and removes the degeneracy of the total symmetric vibration. Such a difficulty is usually bypassed taking into account for the contemporary occurrence of H-

bonded and not H-bonded water molecules, which rises the original two normal modes to four. In addition, each water molecule can develop one or two H-bonds with neighboring molecules and the radiation collected from the macroscopic scattering volume carries only averaged information about vibrations with different symmetries. As a further point, H-bonding produces the establishment of large water clusters with a wide distribution of sizes and local topologies. This reflects in further averaging affecting the Raman spectral profile. Such a situation plays a significant role particularly in the temperature dependence of the shape of the OH-stretching band. Since the H-bonded network of liquid water is a dynamical structure (arising from the kinetic equilibrium between the thermally activated processes of breaking and reforming of hydrogen bond), a change of the temperature produces a change in the average local structure. As a consequence, performing Raman experiments on water volumes at different temperatures means to investigate different physical systems.

In any case, taking into account for the above difficulties, the analysis of the Raman spectra in terms of normal modes can be performed only if one assumes that the spectral contribution from each normal mode is hugely broadened due to the averaging process.

In Fig. 8, we report as an example the results of such a procedure for bulk water and for a water bridge at 20°C. A Voigt profile has been adopted to describe the spectral contribution from each normal mode. In both cases, the four detected spectral components are centered at the following frequencies and can be assigned as usual: 3241 cm⁻¹ (symmetrical stretching of H-bonded water), 3415 cm⁻¹ (anti-symmetrical stretching of H-bonded water), 3530 cm⁻¹ (symmetrical stretching of not bonded water), 3617 cm⁻¹ (anti-symmetrical stretching of not bonded water). The results of the fitting are in very good agreement with literature data. No frequency shift of the components is revealed with the temperature change, within the experimental uncertainty (5 cm⁻¹). The only effect of increasing temperature detected in bulk water is an increasing of the relative intensity of the band centered at 3415 cm⁻¹ with respect to the band centered at 3241 cm⁻¹. This agrees with the observation that the number density of H-bonds decreases with the temperature. When the OH-stretching bands from water-bridges are analyzed, the same four contributions, centered at the same frequencies, are resolved. Also in this case, increasing the temperature essentially reduces to the increase of the relative intensity of the band centered at 3415 cm⁻¹.

At the same time, it is evident that each water-bridge spectrum is definitely different from the corresponding spectrum of normal water, recorded at the same temperature. Fig. 8 clearly shows that the only difference between the spectrum of bulk water and that from a water bridge at the same temperature, is the relative increase of the weight of the contribution centered at 3415 cm⁻¹. Taking into account for the above discussion about the temperature dependence of the OH-stretching band of pure water, we can summarize our result asserting that the water-bridge spectrum recorded at a temperature T closely resembles the normal water spectrum recorded at a temperature $T_e > T$. In addition, the difference $T - T_e$ appears temperature dependent, approaching to zero for $T \sim 50^\circ\text{C}$. One can try to rationalize this result as follows: i) the polarization effect due to the external field acts on the original hydrogen bonded cage of bulk water distorting the inter-molecular bonds; ii) such a distortion produces a decreasing of the degree of association of water molecules moving the vibrational spectrum towards that corresponding to free water molecule; iii) since a similar effect is played by temperature, thermal and polarization effects act in the same direction producing the detected result; iv) at $T \geq 50^\circ\text{C}$ the effects due to the temperature

become so high that any manifestation of polarization effects becomes undetectable, at least within our experimental accuracy.

Summarizing, the fitting procedure of the OH-stretching profiles in terms of normal modes is enough to demonstrate that the application of an external electric field produces a change in the OH-stretching Raman spectrum.

However, we remain faced with the trouble of individuating the more appropriate way for disentangling temperature and polarization effects. As follows from the above discussion about the origin of the observed broad spectral feature of the OH-stretching vibration in liquid water, a more physical approach can be obtained from its interpretation in terms of a vibrational density of states [21,22,24]. When the collective character of the Raman scattering from water is recognized, the interpretation of the broad OH-stretching band, as originated by coexisting structures, becomes immediate. Such an approach turned out fruitful in many situations, e.g. in the interpretation of the Raman scattering from water pools within micelles in terms of *open* and *closed* structure of water [25-29] or in the interpretation of the effects of dissolving a solute able to coordinate itself with water [24,29,30] or, more recently, in the interpretation of the temperature evolution of the spectral profile of pure water in terms of the competition between different local arrangements [21].

On this basis, one can assume that the Raman spectrum of water-bridge is given by the superposition of two distinct spectral features, that can be ascribed to the structure of normal water and to the polarized structure induced by the applied electric field. Then, we can attempt to extract the spectral contribution of polarized water by the difference between the water-bridge spectrum, at a given temperature, and the normal water spectrum, at the same temperature. After suitable normalization of all the recorded spectra, this procedure reveals that in any case the difference reduces to the same, roughly Gaussian shaped, spectral contribution, centered at about 3500 cm^{-1} (see Fig. 9, right). When all the experimental and the calculated spectra have been normalized to the same integrated intensity, the water-bridge spectrum, I_{WB} , can be fitted with the linear combination of the pure H_2O spectrum, I_H , and the polarized H_2O spectrum, I_P , both obtained at the same temperature

$$I_{WB} = \alpha I_H + (1 - \alpha) I_P \quad (1)$$

In Fig. 9 (left) we report, as an example, the results of such a fitting procedure for a water-bridge at 20°C . In the reported fit the value of the fitting parameter was $\alpha=0.04$. The good agreement between the fitting and the experimental results makes us confident about the suitability of the proposed approach.

As pointed out above, a similar approach has been already proposed in the past to take into account the observed changes in the OH-stretching band profile of water after addition of salts of transition metals [21]. It was assumed that in an electrolytic solution, due to interaction with salt ions, large volumes of bulk water coexist with volumes where a different structure is established (hydration shell). Also in that case, the spectrum associated with polarized water molecules was found to consist in a band centered at a frequency of about 3500 cm^{-1} . Furthermore, it is known that due to a very high surface charge density of ions, the electric fields generated in their surroundings are much higher (about 10^9 V/m) than the external field applied in any water-bridge experiment. At these extreme conditions, the electrostriction pressure can induce a phase

transition in the water being close to the ion. As a result, the density of the water in the hydration shell can be two times higher than in a normal bulk environment [31].

This can be enough to conclude that also the OH-stretching profile from water-bridge can be assumed as having a structural origin. In water-bridge the bulk water coexists with volumes where polarized or ionized water molecules self-arrange in a different local structure.

4. Concluding remarks.

The comparison between the behaviors observed in horizontal and vertical water-bridges ensures that we are faced with the same phenomenon, in spite of the different geometry and of the occurrence that, in our experiment, the bridge is in direct contact with one of the electrodes. The only difference observed is related with the direction of the force of gravity, acting orthogonal to the bridge in the usual experiments and parallel in our case. In addition, the water-bridge formation under alternating field has been reported for the first time. The time required for switching on and off the bridge has been estimated to be of the order of 50 ms, which would suggest that we are faced with a macroscopic phenomenon. The results from the first Raman scattering measurements on water-bridges, here reported, revealed that the OH-stretching band of the floating structure can be fitted with the superimposition of the spectrum of pure water and the spectrum of a polarized water, consisting of a roughly Gaussian profile centered at about 3400 cm^{-1} .

The low value we have obtained for the parameter α (the weight of the polarized spectrum) indicates that only small volumes of polarized water exist within the bridge. This observation can justify why neutron scattering measurements turned out unable to clearly observe any significant structural modification [3,14]. Probably the structurally changed water is localized within the bridge-volumes where the flow of the charge carriers gives rise to the dynamic structure of the bridge, i.e. at the bridge surface [14]. Due to the above mentioned concomitant effect of the temperature, the value of the α parameter accounts for both the temperature and the polarization effects. At the moment, however, it is not safe to compare results at different temperatures in order to get information about the temperature evolution of the bridge structure.

In addition, we have to mention that a large variation of the current intensity with the temperature is observed. With reference to the data reported in Fig. 7, the current flux was about 2mA at 5°C and rose up to 9mA at 50°C . At the moment it is hard to understand if this effect is originated by the change in water viscosity or by other effects.

As a final comment, we wish to point out that the observation of a polarized structure of water does not imply that such a structure plays any direct role in the bridge formation, or that this structure is directly related with the applied electric field. If ion formation occurs at the electrodes, ions flowing through the bridge can induce a modification of the local coordination of the neighboring water molecules, which results in the observed Raman feature. In addition, the revealed structure is a microscopic one while, as above addressed, some behaviors of the water bridge are suggesting for a macroscopic phenomenon.

In summary, at the moment, we cannot confirm that this microscopic change in the local arrangement of water is related with the structure that sustains the bridge or represents just a secondary effect playing no fundamental role.

Within this perspective both experimental investigations and a theoretical studies are required to solve this point.

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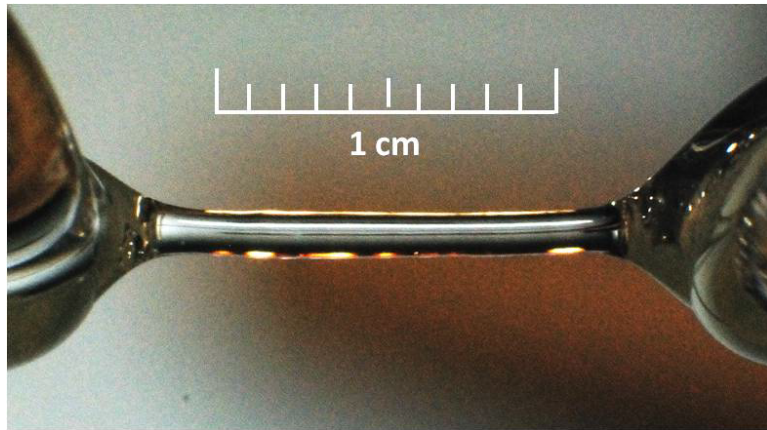


Fig. 1 Picture of a water-bridge between two beakers (see text for details).

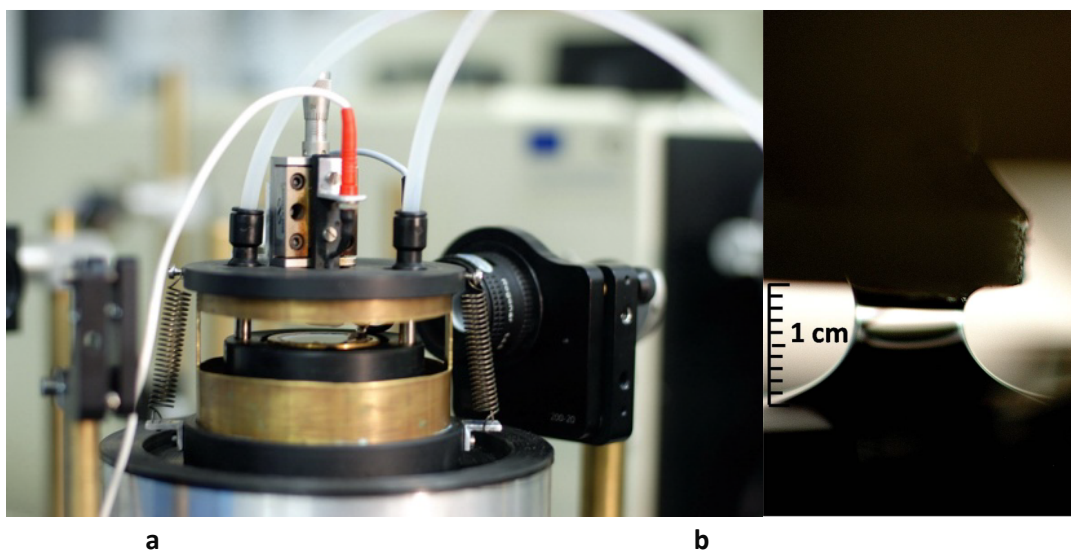


Fig. 2 (a) The cell for vertically oriented water-bridges in working position on the sample-holder platform of our monochromator. (b) Picture of a vertically oriented bridge.

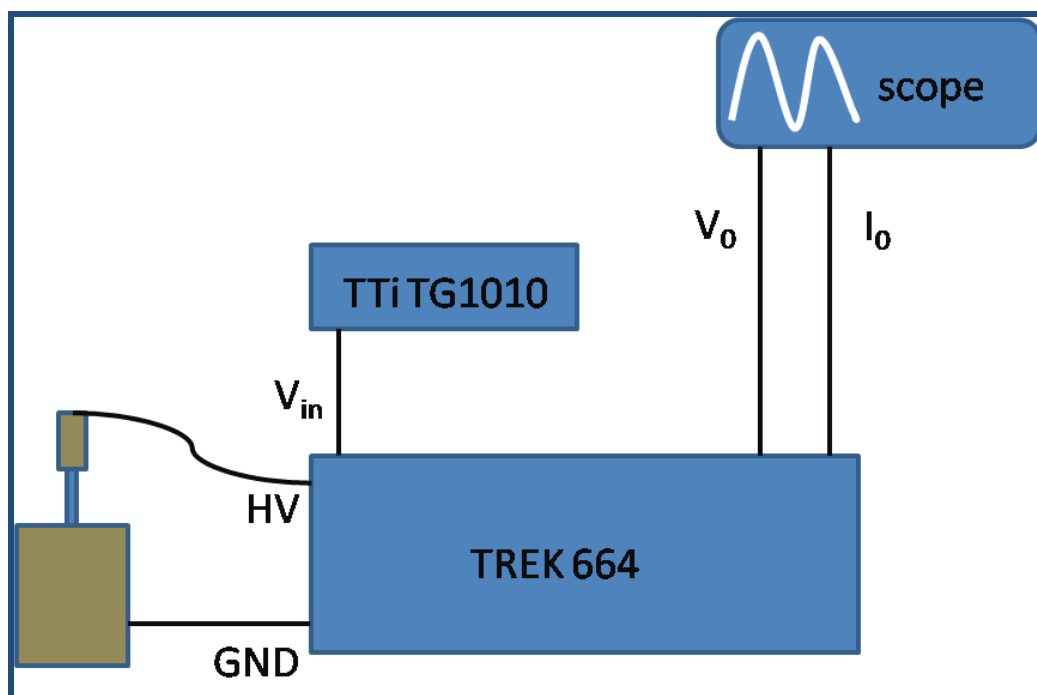


Fig. 3 Scheme of the experimental set up for driving the formation of water-bridges. TREK 664 amplifies the signal from a pulse generator, biasing the electrodes of the cell. V_0 and I_0 are low voltage signals for monitoring biasing of the bridge and the current through it.

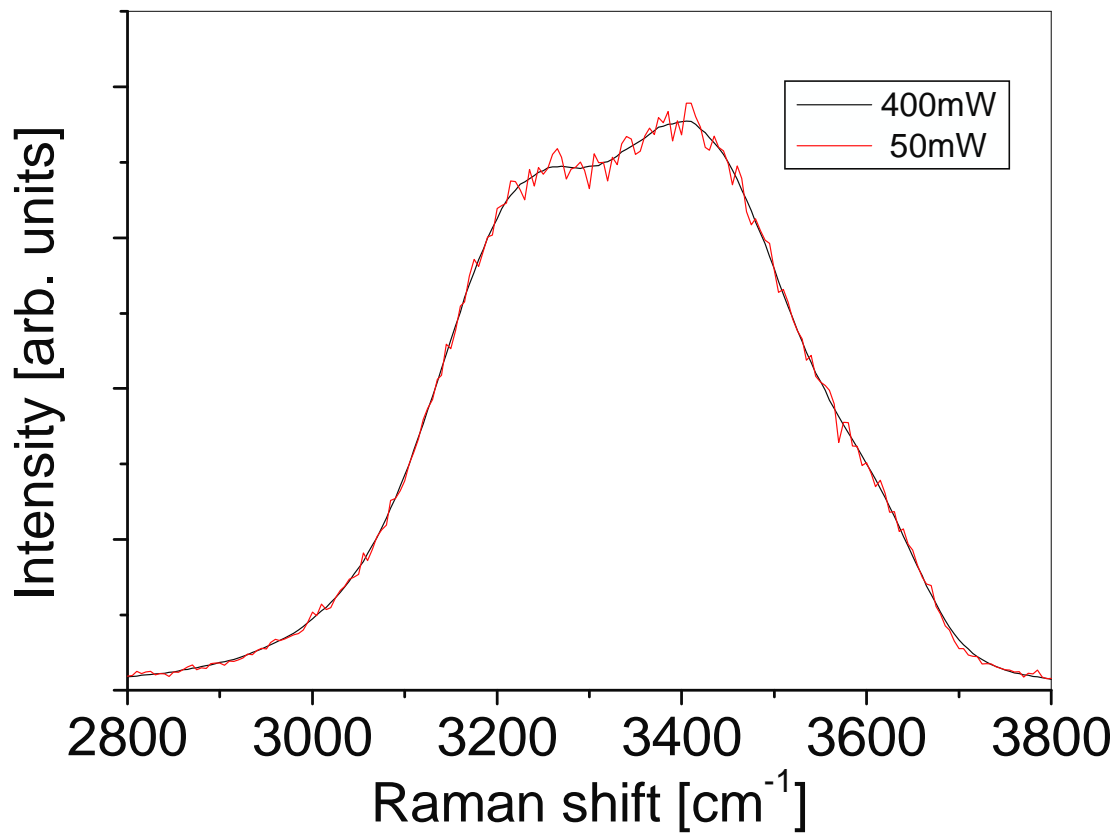


Fig. 4 OH stretching spectra of water-bridges obtained at 20°C and at different probe wavelengths. The spectrum at 50mW has been excited by the 4880 Å line, while the spectrum recorded at 400mW has been excited by the 5145 Å line

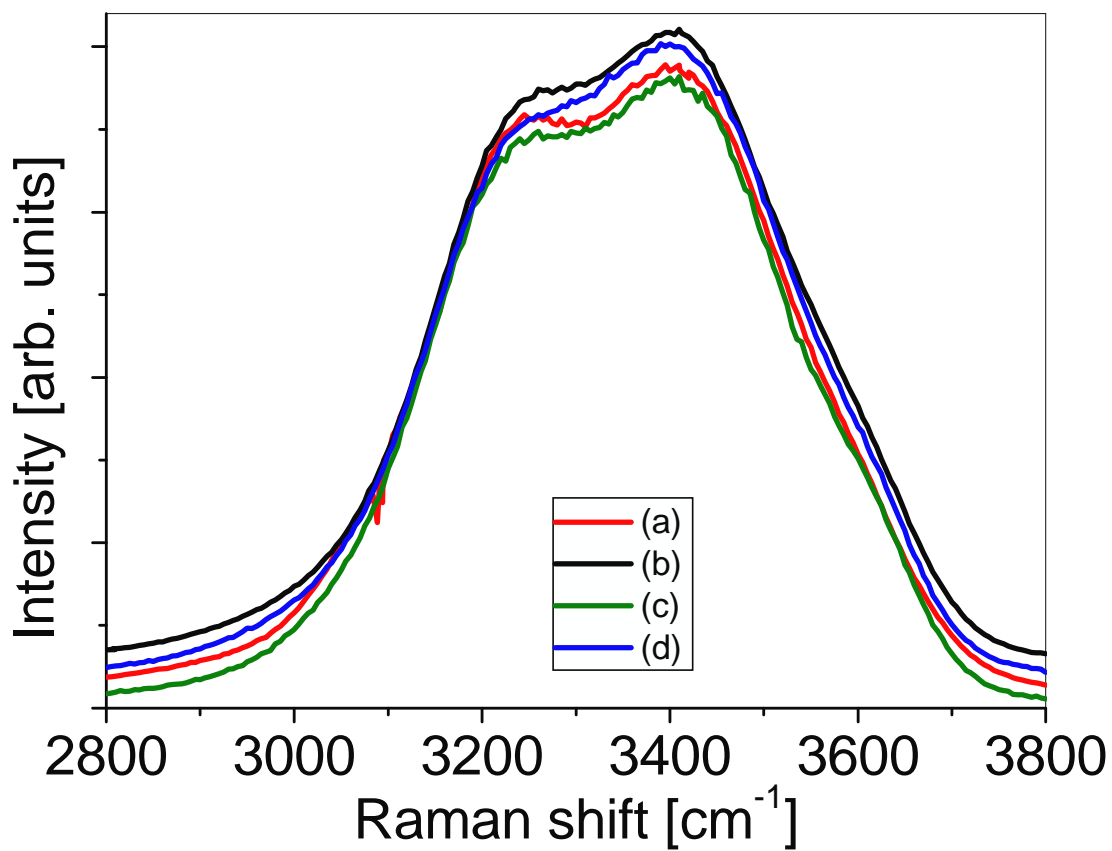


Fig. 5 OH stretching spectra of water-bridges under different conditions. (a): 4900V, d.c., T=42°C; (b): 4900 V, a.c.100Hz, T=23°C; (c): 4900 V, a.c. 500Hz, T=26°C; 7000V, a.c. 1000Hz, T=45°C. The gap between electrodes was about 1 cm. A different background is summed to each spectrum in order to provide curve separation.

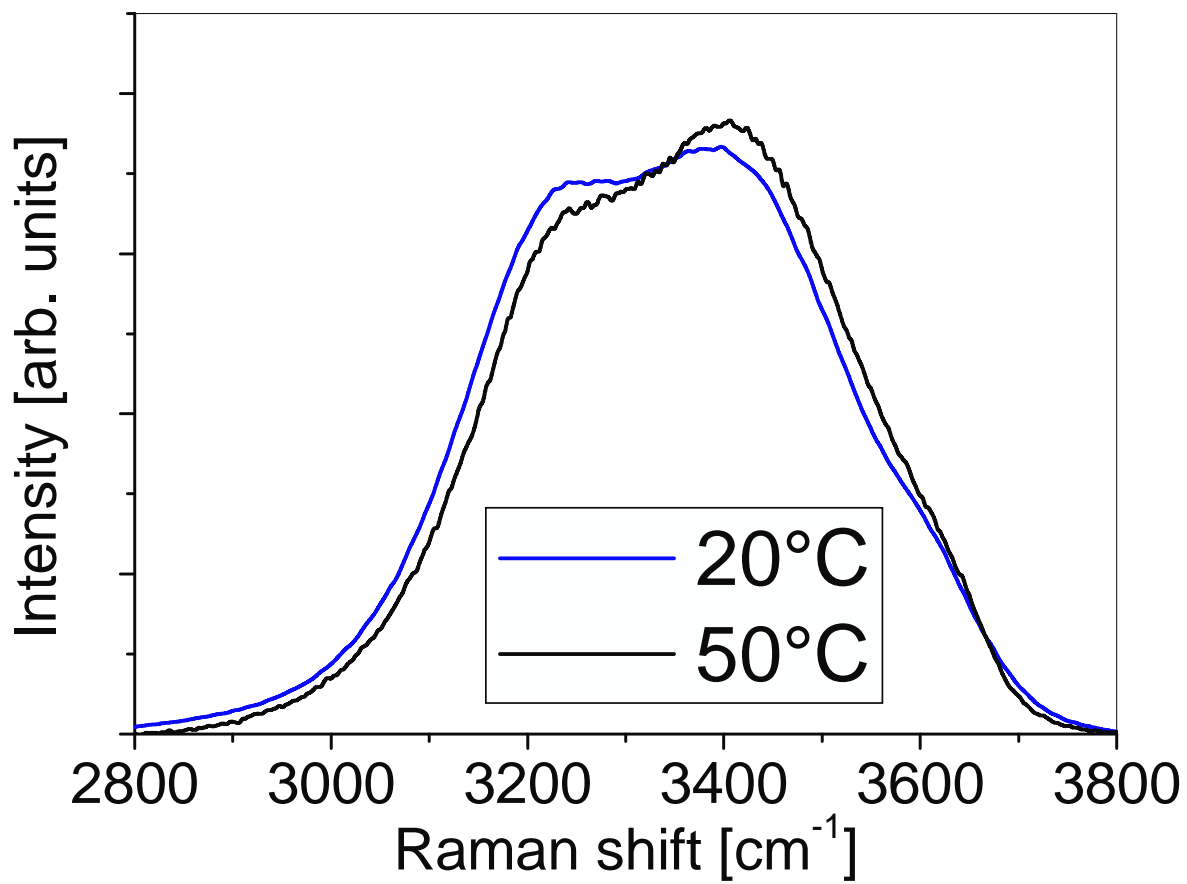


Fig. 6 OH-Stretching Raman spectra from pure water at two different temperatures.

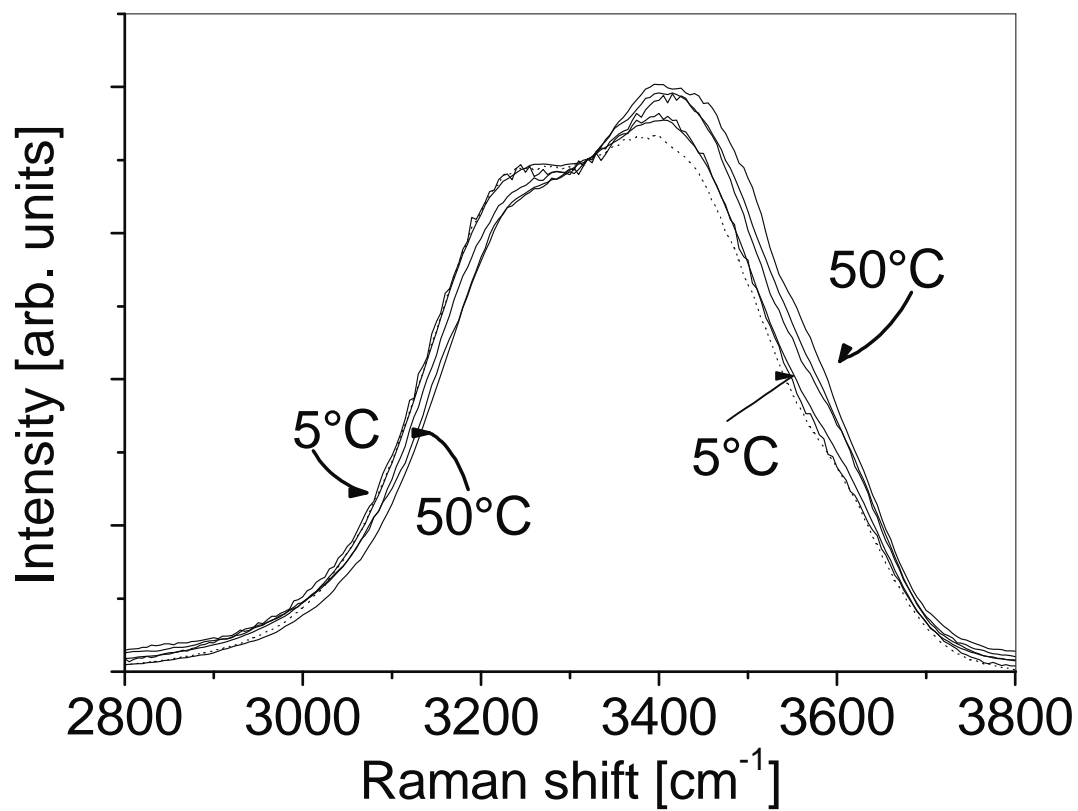


Fig. 7 Normalized I_v Raman spectra from water-bridges at different temperatures. The applied voltage was 3900 V a.c. (100Hz) for all the samples. The gap between electrodes was about 1cm.

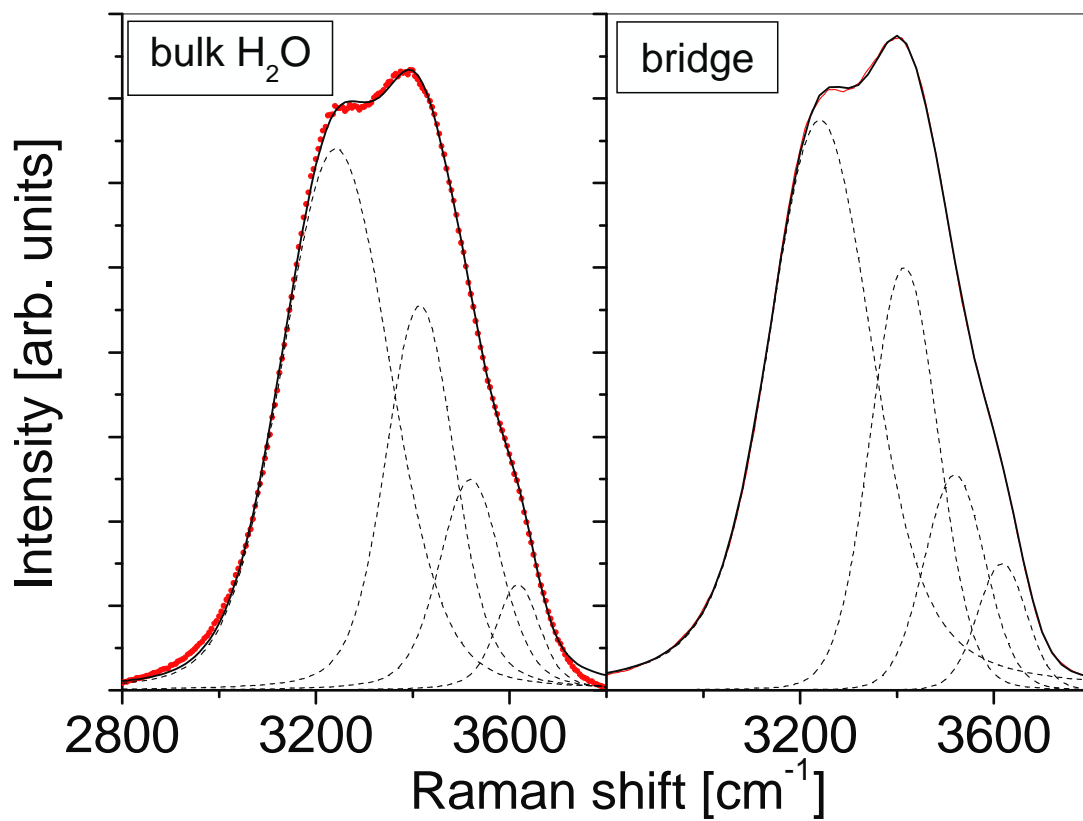


Fig. 8 Normalized I_w Raman spectra from bulk water and water-bridge at 20°C. Red lines are experimental data while the continuous black lines represent the result of the fitting with the sum of the contributions from the four normal modes. Dashed lines represent the contribution from each normal mode.

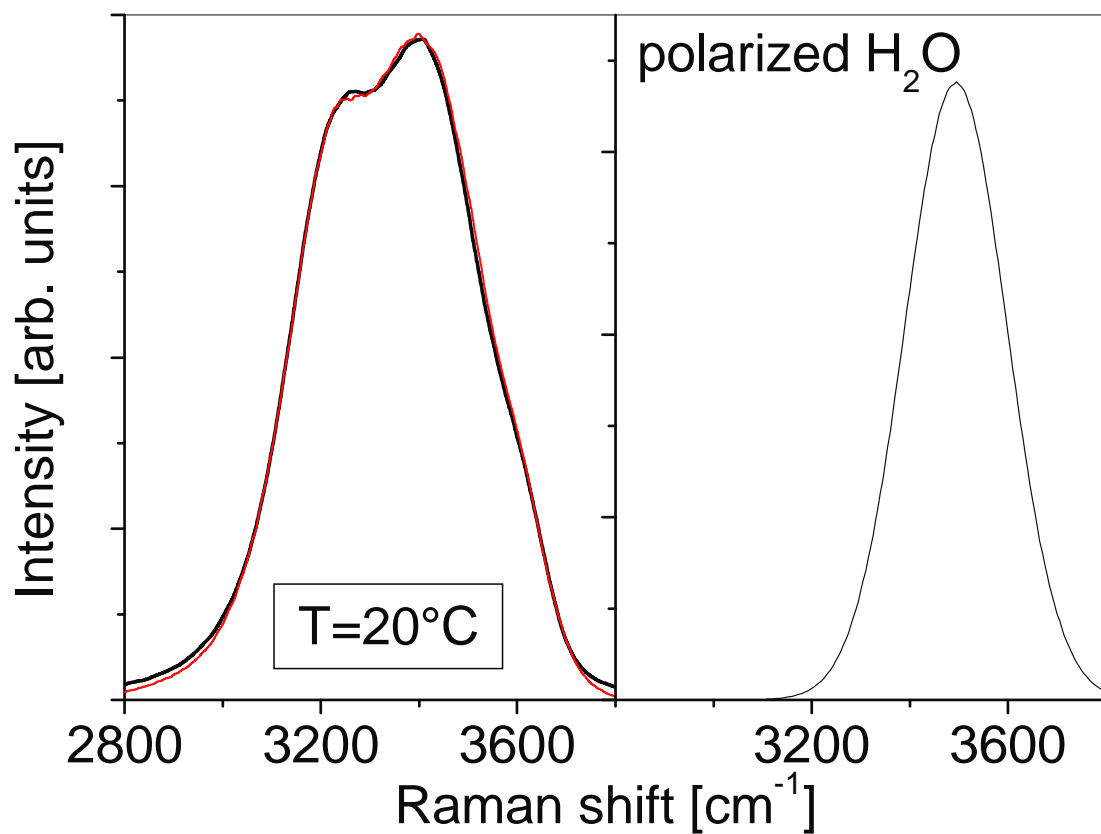


Fig. 9 Left, continuous black line: Raman spectrum of water-bridge; continuous red line: fit with eq. 1. The spectrum on the right represents the calculated contribution from water involved in a polarized structure (see text).