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Water, q-Gaussians and Raman Spectroscopy

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Abstract: A large literature exists about the Raman spectroscopy of water. Here we present some articles regarding the spectral region between 2800 and 3800 cm^{-1}, that is the O-H stretching Raman band, and the proposed decomposition obtained by means of Gaussian profiles. We will also approach the decomposition of this region with three q-Gaussian functions, instead of the five Gaussians usually considered. Being the q-parameter of q-Gaussians related to the correlation time of stochastic Kubo modelling of fluctuations, we propose the use of this parameter to characterize the local environments of O-H bonds.

Keywords: Raman Spectroscopy, Q-Gaussian Tsallis Lines, Hydrogen Bonds, O-H Stretching Band

Introduction

Let us decide to investigate the liquid water by means of Raman spectroscopy. This inorganic compound is made of simple molecules, so we could imagine a simple spectroscopic investigation too, but it is not so. Even a review of literature about the subject is rather challenging. To simplify our task, let us start from a question posed by Brewer et al., 2019: "How much H_2O is there in the ocean?". "The question is surprisingly hard to answer because a large fraction of the water [is made of] molecules [which] are hydrogen bonded together forming molecular clusters. Rather little of the liquid water exists as the singlet H_2O molecule". So the water is depicted "as a bimolecular fluid in which the hydrogen bonded clusters and nonhydrogen bonded forms are in a temperature-controlled dynamic equilibrium" (Brewer et al., 2019).

Brewer and coworkers propose a brief review of literature, and report spectroscopic experiments "to test how well the knowledge of hydrogen bonding in pure water can be translated into the medium of sea water". Starting from the discussion provided by Brewer et al., we consider the Raman region between 2800 and 3800 cm^{-1}, that is the region of the O-H stretching Raman band. We will provide some further literature, and some decompositions of this Raman band, by means of q-Gaussian functions. In fact, Brewer and coworkers are giving decomposition - they call it "deconvolution" - in five Gaussian components. But other literature is giving different approaches, so we feel confident in the proposal of using q-Gaussian functions for the analysis of water Raman spectra too. Actually, for the Raman spectra previously considered (Sparavigna, 2023, 2024), the fitted q-Gaussian functions were successfully in several cases, for instance graphite, ChemRxiv1, SERS spectra, ChemRxiv2, and so on, SSRN.

The q-Gaussians, also known as "Tsallis functions", are probability distributions derived from the Tsallis statistics (Tsallis, 1988, 1995, Hanel et al., 2009). The q-Gaussians are based on a generalized form of the exponential function (see discussion in Sparavigna, 2022), characterized by a continuous parameter q in the range $1 < q < 3$. As given by Umarov et al., 2008, the q-Gaussian is based on function $f(x) = Ce_q(-\beta x^2)$, where $e_q(.)$ is the q-exponential function and C a constant. The q-exponential has expression:

$$exp_q(u) = [1 + (1 - q)u]^{1/(1-q)}$$

The function $f(x)$ possesses a bell-shaped profile. In the case that we have the peak at position x_o, the q-Gaussian is:

$$\text{q-Gaussian} = Cexp_q(-\beta(x - x_o)^2) =$$

$$C[1 - (1 - q)\beta(x - x_o)^2]^{1/(1-q)}$$

For q equal to 2, the q-Gaussian is the Cauchy-Lorentzian distribution (Naudts, 2009). The lineshape is that corresponding to a homogeneous broadening of the lineshape. For q close to 1, the q-Gaussian is a Gaussian. The lineshape corresponds to an inhomogeneous line broadening. For the q-parameter between 1 and 2, the shape of the q-Gaussian function is intermediate between the Gaussian and the Lorentzian profiles.

In the discussion of literature, we will consider the decomposition of the O-H stretching band with three q-Gaussian functions for some of the available spectra. Being the q-parameter of q-Gaussians related to the correlation time of stochastic Kubo approach to fluctuations, we propose its use to characterize the local environments of O-H bonds.

HB and nHB

As described by Brewer and coworkers, "the structure of water is the result of the balance between

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the thermal forces pulling water clusters apart and the chemical forces holding these clusters together. The dominant chemical force holding water molecules together is the hydrogen bond, … water is in a state of temperature-controlled equilibrium between the hydrogen bonded (HB) and the nonhydrogen bonded (nHB) forms. The nHB form is simply the free H_2O molecule, and the various (HB) forms exist in a rapidly exchanging continuum of configurations of which the dominant form is the tetrahedral pentamer $(H_2O)_5$" (Brewer et al., 2019). This pentamer with tetrahedral form is known as the Walrafen pentamer; the "phenomenon of dominant end members represented by the H_2O and $(H_2O)_5$ forms connected by a continuum of rapidly exchanging intermediate forms (dimers, trimers, and tetramers) is essential for understanding the properties of water and sea water" (Brewer et al., 2019).

According to Brewer and coworkers, Walrafen, in 1964, investigated by means of the Raman spectroscopy the water structure determining it as dominated by a five-molecule hydrogen bonded tetrahedral structure: "the degree of association of water at 0°C obtained [was] 89.5%" (Brewer et al., mentioning Walrafen, 1964). "Strong evidence exists for the $(H_2O)_5$ species to exist in continuum with the presence of a population of rapidly exchanging other (dimer, trimer, tetramer, etc.) transient forms (Brewer et al., 2019, mentioning Keutsch & Saykally, 2001) with the tetrahedral form [which is] dominant (Smith et al., 2005)".

Deconvolution

Brewer and coworkers explain that the "Raman spectrum of liquid water is dominated by the stretching mode band complex in the region 2800–3800 cm^{-1}". The complex "can be *deconvolved into five Gaussians* (Furić et al., 2000; Walrafen et al., 1986) each with a specific spectral assignment. Walrafen (1964) was the first to attempt this and he identified *three bands* between 2800 and 3800 cm^{-1}. In subsequent papers he reported *four bands* (Walrafen, 1967) and *five bands* (Walrafen et al., 1986). More recently Carey and Korenowski (1998) and Furić et al., (2000) have identified five Gaussian peaks" (Brewer et al., 2019, and the references mentioned therein).

About one of these bands, that centered at 3052 cm^{-1}, Brewer and coworkers report that it is "attributable to the $2\nu_2$ overtone of the bending vibration of the singlet water molecule (Furić et al., 2000) … The remaining four bands reflect the population of the HB and nHB forms of water." (Brewer et al., 2019).

Brewer and coworkers observe that for pure water, the Raman band at 3220 cm^{-1} "shows a decrease in area with rising temperature indicating association with an HB form [see please the Figure 4A in Brewster et al., 2019]; the bands centered at 3390 cm^{-1} and 3485 cm^{-1} both increase in area with rising [temperature] showing their association with the nHB form. The remaining band centered at 3624 cm^{-1} shows a small decrease in area with rising [temperature]" (Brewer et al., 2019).

Other approaches

Let us consider the article by Hu et al., 2013. In it we can find told that, "though there are only covalence bonding and hydrogen bonding interactions, structure of water is rather complex due to the many-body and cooperative effects related to hydrogen bonds" (Hu et al., mentioning Ludwig, 2001). Some models have been proposed "to describe the molecular structure of liquid water, among which the two most representative are the *continuum models* characterized by water molecules with different hydrogen bonding configurations … , and the *mixture (cluster) models* describing liquid water as a mixture of distinguishing well defined species … . However, *controversy still exists* and none of the models proposed is sufficiently satisfactory for interpreting the structure of water" (Hu et al., 2013).

Raman spectroscopy is suitable for the study of water, being able of providing signals coming from the intramolecular O-H valence bonds. As tressed by Hu and coworkers, "Raman is sensitive to *molecular environment*, so intermolecular hydrogen bonding interaction could be analyzed. The Raman scattering of O-H stretching vibration at 2800–3800 cm^{-1} is most informative about structure of water" (Hu et al., mentioning Maeda & Kitano, 1995). "This broad band is usually deconvoluted into several components for analysis, commonly less than six, such as those Gaussian fit with *five center frequencies* by Carey and Korenowski. *Nevertheless, controversy on the quantity and assignment of components still remains*" (Hu et al., 2013).

Hu and coworkers remember some literature. For example, Zhelyaskov et al., 1989, decompose the O-H stretching spectral region "into four isotropic components and three anisotropic components applying Fourier deconvolution. Some other researchers decomposed the contour into four components" (Hu et al., 2013, mentioning Li et al., 2003). Li et al., 2004, fitted the band with five Gaussian components, which have been assigned to molecules with are fully or partly hydrogen bonded.

Hu et al. are also stressing that Qiang Sun, 2009, 2010, "classified the local hydrogen bonding of water molecule as DDAA (double donor–double acceptor), DDA (double donor–single acceptor), DAA (single donor–double acceptor) and DA (single donor–single acceptor) and free OH, which correspond *to five deconvoluted Gaussian sub-bands* of O–H stretching vibrational band of water" (Hu et al., 2013). Đuričković et al., 2011, "held that it was unnecessary to fit the spectrum and they directly analyzed the raw spectra without any deconvolution. *In practice, the method applied in treating the spectra can be an art depending on the hypothesis on the identification of possible species or conformations in water*" (Hu et al., 2013). Very interesting this sentence regarding the Raman band decomposition.

Models and overtones

In Brewer et al. we find mentioned an overtone. To understand the nature of this overtone, let us consider the article by Maeda and Kitano, 1995.

"Since the 1930s many kinds of models of the structure of liquid water have been proposed to account for its properties". As previously told, two main models exist and are usually designated as continuum model and mixture model. Continuum models "assume that all water molecules in the liquid continue to be hydrogen bonded to neighboring water molecules, but that the intermolecular links can be bent and stretched to produce irregular and varied networks [see the Fig. l(b) in Maeda and Kitano]" (Maeda & Kitano, 1995). The mixture models, as told by their name, are based on "a mixture of several distinct molecular species called water clusters ($(H_2O)_n$). All mixture models require the existence of broken hydrogen bonds: … One of the simplest models included in the mixture models is the two-structure model. Such a model has recently been proposed by Benson and Siebert …" (Maeda & Kitano. 1995).

In Maeda and Kitano, we can find described all the bands of the water Raman spectrum. "Raman scattering from liquid H_2O consists of the O-H *stretching vibration band* (2800-3400 cm^{-1}), the v_2 *bending band* near 1645 cm^{-1}, the combination of *bending and libration bands* (v_2+v_L) near 2100 cm^{-1}, and *intermolecular fluctuation bands* in the low-frequency regions which are due to the interaction between water molecules through the hydrogen bonds" (Maeda & Kitano, 1995). For what is regarding the low frequency region, Faurskov Nielsen, 2001, is mentioning that "Raman spectroscopy is a very fast technique, so the water molecules can be considered to be in specific sites during the time it takes to obtain a Raman spectrum. It means that in this Raman picture, we can talk about a fixed water structure", that is, "a hydrogen-bonded network with a continuous breaking and making of hydrogen bonds". Faurskov Nielsen is also mentioning the works by Walrafen, where we can find the water "five-mer". "It means a water molecule forming hydrogen bonds to four other molecules." (Faurskov Nielsen, 2001).

Let us continue the discussion by Maeda and Kitano. It is told that the O-H stretching region "have been studied more extensively than any other Raman bands of water. … The O-H stretching Raman band of liquid water is very broad and consists of several overlapping components, and i*nterpretation of the band itself is the subject of considerable discussion*. These components were considered to have arisen from the unperturbed O-H stretching band by intra- and intermolecular vibrational coupling of O-H oscillators and/or Fermi resonance with the first *overtone* of the bending motion of the H_2O molecule. However, the influence of Fermi resonance has recently been shown to be weak or absent, and today this idea seems obsolete" [Maeda and Kitano, mentioning Hare and Sorensen, 1992]. This is the overtone mentioned by Brewer et al., 2019, centered at 3052 cm^{-1}. Following Maeda and Kitano, it can be neglected.

Maeda and Kitano refer about literature on analysis and interpretations of the O-H stretching Raman band. Among the early approaches, we can find those that "were carried out by the decomposition of the contour into *Gaussian or Lorentzian* components." We find again Walrafen, who investigated "pure water in the temperature range 10-95°C, and decomposed the band into four Gaussian components, pairs of which had opposite temperature dependencies, two lower-frequency components (3247, 3435 cm^{-1}) decreased in intensity with increasing temperature whilst two higher-frequency components (3535, 3622 cm^{-1}) increased in intensity" (Maeda and Kitano mentioning Walrafen, 1967, 1968). The work by Walrafen also "indicated the existence of an *isosbestic* point near 3460 cm^{-1} in the spectra. *The isosbestic behavior suggests that two distinct scattering components exist, the simplest probability being scattering from hydrogen-bonded and nonhydrogen-bonded O-H oscillators.* Walrafen interpreted the O-H stretching band as due to an equilibrium between the five-molecule, fully hydrogen-bonded structure having intermolecular C_{2v} symmetry, and nonhydrogen-bonded monomeric

water" (Maeda and Kitano, mentioning the Walrafen's work). The "isosbestic point" is the "wavelength, wavenumber or frequency at which the total absorbance of a sample does not change during a chemical reaction or a physical change of the sample" (IUPAC). Maeda and Kitano are also mentioning another interpretation. "Scherer et al. interpreted the O-H stretching band of water in terms of four Gaussian components, which were attributed to symmetric and antisymmetric O-H stretching vibrations of a symmetrically hydrogen-bonded and an asymmetrically hydrogen-bonded complex" (Maeda and Kitano, about Scherer et al.).

About the decomposition of the band, Maeda and Kitano remember the observation by Georgiev and coworkers, who stressed "a limitation of the decomposition method". The limitation is the "necessity of making a preliminary assumption concerning the number and the shape of the component" (Maeda and Kitano, 1996). Georgiev and coworkers used a Fourier deconvolution, dividing the O-H stretching region into "four components in the isotropic spectra and three in the anisotropic spectra" (Maeda and Kitano, mentioning Georgiev et al., 1983).

q-Gaussians decomposition

To start showing a decomposition obtained by means of q-Gaussian function, let us consider the article by Baschenko and Marchenko, 2011. These researchers tell that the water spectra can be approximated by four (or five) Gaussian-shaped peaks with positions at 3070, 3230, 3440, 3600 (and 3650) cm^{-1}. "The most intensive constituents were 3230 and 3440 cm^{-1} lines, their total contribution to the Raman spectrum of water is higher than 90%" (Baschenko & Marchenko, 2011). The investigated Raman spectra were those of distilled water, with the typical behavior as presented in Figs. 2 and 3 of Baschenko and Marchenko, 2011. In the Figure 2, we can find five Gaussian functions, whereas, in the Figure 3, the Gaussians are four. "It is clearly seen that with great precision the complex spectrum shape may be approximated by four or five Gaussian-shaped constituents: two main and two or three minor ones" (Baschenko and Marchenko, 2011).

Let us consider the left part of the Raman O-H stretching band, that at lower frequencies. In the Figure 2 in Baschenko and Marchenko, 2011, we can note that the component centered at 3070 cm^{-1} is within the tail of the component centered at 3230 cm^{-1}: this fact is suggesting that the use of a q-Gaussian function, which has a tail which is fatter than that of a Gaussian function, could be interesting for fitting this part of the band, instead of using two Gaussian components. In the following our Figure 1, this q-Gaussian turns out to be the blue profile with q=1.275.

In our Figure 1 we show the OH stretching band given by Baschenko and Marchenko, 2011, decomposed using three q-Gaussians, on the left, and four Gaussians on the right, for comparison.

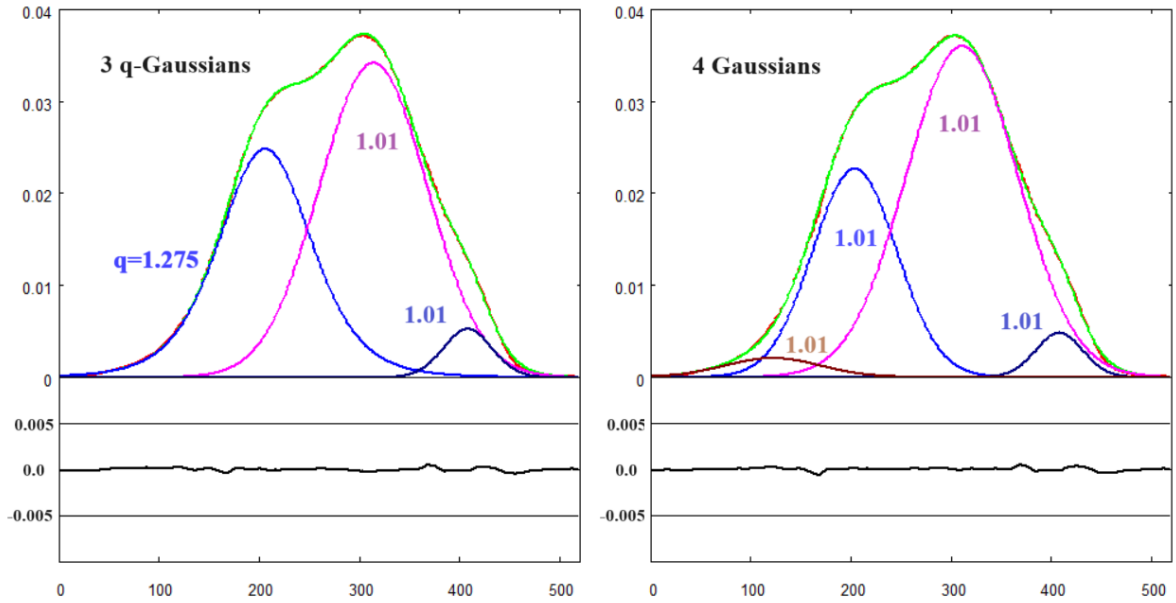

Fig.1: Left - The Raman spectrum, shown in the Figs. 2 and 3 of Baschenko and Marchenko, is here proposed with a red line. It is decomposed by three q-Gaussians (magenta and blue colors). The green line is representing the sum of these q-Gaussians. Their q-parameters are given in the figure. Value q=1.01 is giving a q-Gaussian function which is numerically indistinguishable from a Gaussian. In the lower part of the figure, the difference between data and the sum of q-Gaussian functions is given. Right - The same, obtained with four Gaussians (that is, four q-Gaussians with q=1.01).

In Fig.1, the magenta q-Gaussian on the left and the magenta Gaussian on the right are in very good agreement with the decomposition proposed by of Baschenko and Marchenko (in their Figs. 2 and 3 too, this is the main component). In the Figure 1, our "data" are the intensity values that we can obtain from the Figure 2 of Baschenko and Marchenko, interpolated to have the red line shown in the plot. Data and q-Gaussians are given as functions of integers n (equally spaced points used in fitting), for the x-axis which is representing the Raman shift. A convenient scale is used for the y-axis (intensity axis). The same we will do for our Figs. 2, 3 and 4. The fitting calculation is obtained by minimizing the sum of the squares of the deviations Σ (sum from n=1 to n=520 in Fig.1) of the green points from the red data. On the left, $\Sigma = 1.44 \times 10^{-5}$, on the right $\Sigma = 1.43 \times 10^{-5}$.

In the following Figure 2, another q-Gaussian decomposition is made for the plot by https://www.stellarnet.us/application-note-raman-spectrum-water/ .

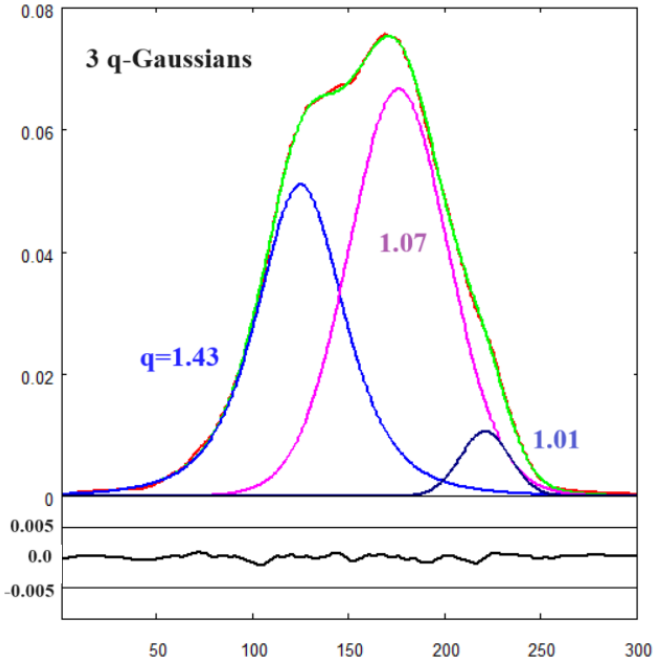

Fig.2: The Raman spectrum from stellarnet.us is here proposed with red points, decomposed by three q-Gaussians (magenta and blue colors). The green line is representing the sum of these q-Gaussians.

The web site (archived) is talking about the Raman scattering spectrum of pure water in the following manner. "The shoulder at ~3250 cm^{-1} [here in the Fig.2, the blue component on the left] corresponds to the asymmetric OH stretch, and the most intense feature at ~3410 cm^{-1} [magenta] corresponds to the symmetric OH stretch. Even more intriguing, there is a small shoulder at ~3630 cm^{-1} [the blue component on the right] which corresponds to the OH stretch of a water molecule which is only partially involved in hydrogen bonding – a particularly rare event." So let us remember that Maeda and Kitano mentioned the interpretation of the spectrum by Scherer et al., with symmetric and antisymmetric O-H stretching vibrations.

Carey's interpretation

Google Scholar, for the article "Carey, David M., and Gerald M. Korenowski. Measurement of the Raman spectrum of liquid water. The Journal of chemical physics 108.7 (1998): 2669-2675" is proposing a pdf document of August 1996, by Carey as Senior Scientist at Lockheed Martin Corporation, Schenectady, New York. In this work, we can find explained by Carey the following.

The OH stretching vibrational region is decomposed into four bands, with two bands coming from "a fully hydrogen bonded system and two from a partially bonded system". Carey considers these bands corresponding to four modes due to "the splitting of the v_1 symmetrical stretching vibration into four distinct vibrations". The lowest band, at ~3240 cm^{-1}, "corresponds to a fully symmetric 4-hydrogen bonded tetrahedral water molecule where all neighboring water molecules are vibrating together in phase. This is analogous with that observed in ice" (Carey, 1996). The next vibration at ~3385 cm^{-1} is

due to "the loss of vibrational harmony between neighboring molecules. Although still fully tetrahedrally bound, this vibration is the result of neighboring water molecules stretching; but no longer in phase with each other" (Carey, 1996). The two further vibrations at ~3490 and ~3620 cm^{-1} are representing "the loss of a hydrogen bond, leaving one hydrogen atom "dangling" while the other is fully hydrogen bonded". Carey proposes to view "the two OH bonds as nonequivalent local mode oscillators", and then the ~3490 cm^{-1} band is due to the OH bond vibration "where the hydrogen atom is hydrogen bonded, while the ~3620 cm^{-1} peak represents the vibration of the dangling OH bond" (Carey, 1996). When the temperature increases, a new vibration appears at ~3670 cm^{-1}. This is the vibration of a free OH stretching, "unhindered by neighboring hydrogen bonds, as observed in the vapor state" (Carey, 1996). As we can see in the Figure 3, we have consequently five Gaussian components. However, we can obtain a good fit also with three q-Gaussians.

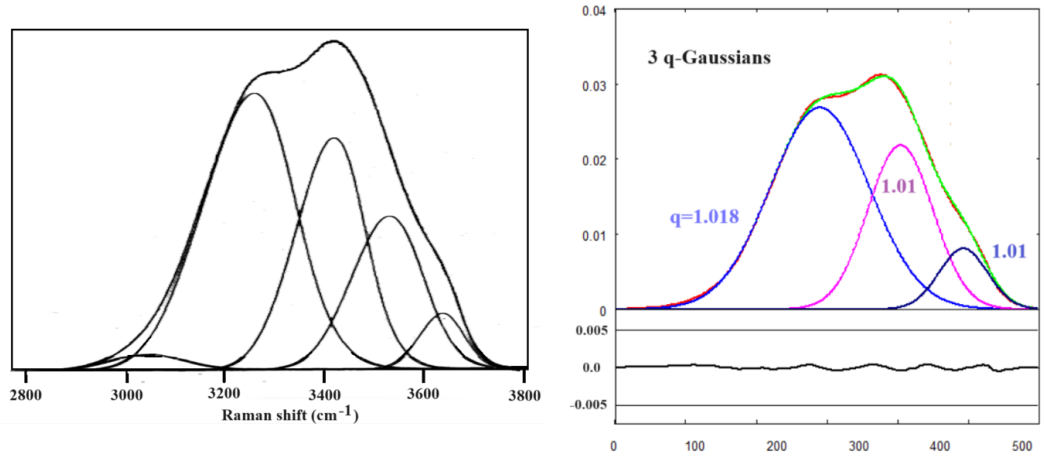

Fig. 3: Left - Sketch adapted from the Figure 9 by Carey, 1996, giving the "Gaussian deconvoluted vibrational Raman spectrum of liquid water at 24°C and 128 Bar pressure". In the caption, Carey is mentioning five Gaussian peaks, postulated as a Fermi resonance at 3050 cm^{-1} and four v_1 symmetrical stretching vibrations at ~3240, ~3390, ~3490, and ~3627 cm^{-1}. For what is regarding the Fermi resonance, see please again Maeda and Kitano, mentioning Hare and Sorensen, 1992. Right - Decomposition with three q-Gaussians.

In the Figure 3 we compare the decomposition in five Gaussians given by Carey in the Figure 9 of his work, and a decomposition with three q-Gaussians. The blue q-Gaussian (q=1.018) substitutes the Fermi resonance and the band at ~3240 cm^{-1}. The other three Gaussians, at ~3390, ~3490, and ~3627 cm^{-1}, become two q-Gaussians (q=1.01), that is practically two Gaussians.

Discussion

In the Figures 1-3 we have, in the lower frequency part of the O-H stretching band, blue q-Gaussians with q values ranging from 1.018 to 1.43; they represent the "fully symmetric 4-hydrogen bonded tetrahedral water molecule where all neighboring water molecules are vibrating together in phase" (Carey, 1996). With a q-Gaussian, we do not need to postulate the presence of a further component, as the Fermi resonance in Carey, 1996. The other main component, the magenta q-Gaussian, can correspond to "the loss of a hydrogen bond". The last blue component on the right of the band is due to the free OH stretching as in the vapor state.

In previous works (ijsciences1, ijsciences2), we considered that the q-Gaussians can be used to represent the stochastic Kubo lineshapes, which are characterized by the time scale of fluctuations. As discussed by Tokmakoff, "a fluctuating environment influences measurements of an experimentally observed internal variable". Tokmakoff explains that, in condensed matter, "time-dependent interactions with the surroundings can lead to time-dependent frequency shifts, known as spectral diffusion. How these dynamics influence the line width and lineshape of absorption features depends on the distribution of frequencies available to your system Δ and the time scale of sampling varying environments (τ_c)" (Tokmakoff, 2014). According to the values of these two parameters, three cases of line broadening exist. We have the homogeneous and the inhomogeneous broadening, and a more general case of "spectral diffusion", with the system positioned between the homogeneous and inhomogeneous cases (see Tokmakoff for further discussion). For what is regarding the resulting lineshape according to a stochastic theory of fluctuation, in the framework of Kubo approach, a detailed discussion is available in LibreTexts-Chemistry. The homogeneous broadening

is giving a lineshape which is close to a Lorentzian profile, whereas the inhomogeneous case is like a Gaussian profile, with differences in the far wing region, as we have shown in ijsciences1, ijsciences2. The q-Gaussians can be used to mimic the Kubo lineshapes, so that the q-parameters can be linked to the local environments of the oscillating dipoles. The value of the q-parameter turns out to the related to the time scale of dynamics (fast q=2, mid q=1.4 and slow q=1). Returning to the O-H stretching band, we could therefore consider that the blue q-Gaussian at about 3250 cm^{-1} is characterized by a modulation which is "faster" than that of the magenta component. It means that the local environments of the O-H bond, in the blue and magenta cases, are different. Further investigation is therefore interesting in the framework of a q-Gaussian approach.

Confined water

To conclude, let us consider a recent article by Malfait et al., 2022, where we can find Raman spectra of water confined in mesoporous silicas. Of mesosilica, we discussed in 2023. The reason for considering this confined water, is the following. "In most frequent situations, water is found as spatially confined or in an interfacial state rather than forming a bulk phase. Confining water in synthetic mesoporous solids is a well-suited method to mimic these natural environments" (Malfait et al., 2022). When the pore size of the silica is reduced, the structure of the liquid water is perturbed and the molecular arrangements involving a high connectivity becomes unfavorable (Malfait et al., 2022). Therefore, the researchers considered the O-H stretching region (2800−4000 cm^{-1}) "to probe the molecular structure and the intermolecular H-bonds" in confined water. Let us note that the Raman signal of the mesoporous silica matrix is "negligible compared to the signal of the confined water, as already observed for other molecules confined in the SBA-15 matrix" (see Malfait et al. and references therein).

Malfait and coworkers describe the O-H stretching Raman band in the following manner. "Spectra of bulk water and confined water exhibit qualitatively the same shape, composed of a broad triple hump extending over this selected spectral region" (Malfait et al., 2022). "The first component (~3200 cm^{-1}) is generally associated with the O−H stretching vibration of water molecules involved in a tetrahedral structure, while the second (~3400 cm^{-1}) corresponds to the distorted H-bond network [Malfait and coworkers mentioning D'Arrigo et al., 1981]. The third component (~3600 cm^{-1}) is related to the O−H stretching of water molecules that are not involved in intermolecular HB (named free water)" (Malfait et al., 2022). Accordingly, three Gaussian functions have been used, as in the case of Figure 3a of their publication and fitted to the experimental spectra.

In the Figure 2 by Malfait et al. we can find the Raman spectrum of the bulk water. As previously done, let us try to fit this spectral band using three q-Gaussians. The result is given in the following Figure 4.

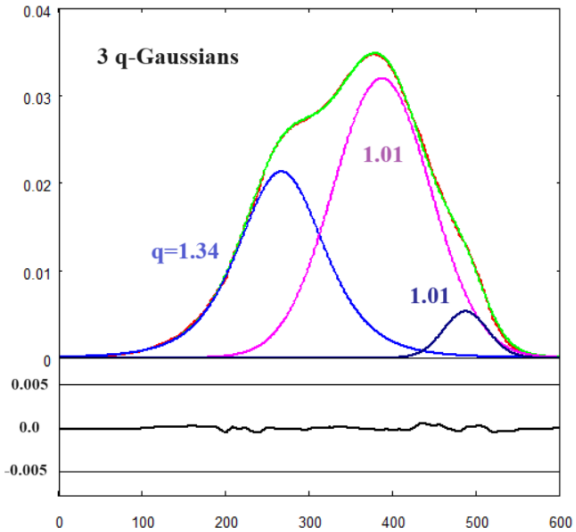

Fig.4: The Raman spectrum in the O-H stretching region from the data given in the Figure 2 by Malfait et al., 2022, for bulk water. The data recovered from the figure are here proposed with red points, decomposed by three q-Gaussians (magenta and blue colors). The green line is representing the sum of these q-Gaussians. In the lower part of the figure, the misfit is proposed.

In the case of saturated porosity, Malfait et al. tell that the spectra "are qualitatively similar to those of bulk water", so that a classical model with a "deconvolution into three populations (i.e., H-bonded water molecules in tetrahedral and distorted environments, and free hydroxyls)" can be used. "A very different situation is obtained for partially filled porous matrices (33% RH), where water is present as a layer adsorbed on the pore surface" (Malfait et al., 2022). Also in this case, a decomposition with q-Gaussians can be relevant. This will be done in a future research work.

Let us conclude stressing that the decomposition proposed in the Figure 4 agrees with the cases given in the Figures 1 and 2. In the case of the Figure 3, let us note that we have data from Carey, 1996, of water at a pressure of 128 Bar.

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