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Gypsum Crystallization Water: Comparing a Laser Excited Raman Spectrum with a Mercury Resonance Radiation Excited Spectrum (Rasetti Technique)

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Abstract: Here we consider the gypsum mineral to investigate its broad scan Raman spectrum. The presence of water of crystallization is detected and its OH-stretching spectral region deconvoluted in q-Gaussian functions. That is, we follow the same approach that we used recently for minerals of the natrolite and vivianite groups. In the case of gypsum, we consider the Raman data from Rappal Sangameswaran Krishnan, 1945, and compare the bands given in his work with the components that we can obtain from the spectra provided by RRUFF database. We find a remarkable agreement between R. S. Krishnan's data and the decompositions in q-Gaussian functions. We will describe also the experimental method used by Krishnan, based on the Franco Rasetti technique with mercury resonance radiation excitation. In the RRUFF database, we can also find an infrared spectrum; we considered it and decomposed in q-Gaussian and q-BWF functions.

Keywords: Raman Spectroscopy, q-Gaussian Functions, Tsallis Statistics, Hydroxyl-Stretching Raman Region, OH-Stretching Raman Region, History of Raman Spectroscopy

Introduction

Recently, we have considered the detection of water by Raman spectroscopy in the cases of minerals of vivianite and barite groups. Using RRUFF database and broad scans available therein, we analyzed the OH-stretching region, decomposing it in bands with q-Gaussian profiles (see Appendix). These two studies about vivianite and barite groups followed the analysis of OH-stretching bands in the case of water and ice, where we proposed specifically the decomposition in components by means of q-Gaussian functions and stressed the use of q-parameter to characterize the local environments of O-H bonds and their symmetric and antisymmetric vibrations. After the minerals of the vivianite group and zeolites of barite group, here we pass to examine the gypsum mineral, with the same aim, that is the investigation of the Raman bands of its water of crystallization. However, we have another purpose in our study: it is that of comparing the broad scans obtained by means of a laser excitation with the spectra acquired with a mercury resonance radiation exciter as in the work by Rappal Sangameswaran Krishnan, 1945. There is an amazing agreement. We will stress that the Raman spectroscopy which is based on the mercury resonance radiation was developed by Franco Rasetti in 1929.

Gypsum

Gypsum belongs to the gypsum supergroup of mineral, composed by gypsum $CaSO_4.2H_2O$ (that is, calcium sulfate dihydrate), brushite $CaHPO_4.2H_2O$, churchite-(Nd) enriched churchite-(Y) $(Y,Nd)(PO_4).2H_2O$, churchite-(Y) $YPO_4.2H_2O$ and pharmacolite $CaHAsO_4.2H_2O$. In the RRUFF database, we can find also ardealite $Ca_2(PO_3OH)(SO_4)\cdot 4H_2O$, probably because "commonly intermixed with brushite and gypsum".

Gypsum is an ionic crystal, which has its unit cell containing four molecules of $CaSO_4.2H_2O$. It was a mineral investigated as soon as the Raman effect had been discovered (in Saksena, 1941, we can find the previous literature on the subject). In Table III [by Saksena], "the frequency shifts of Raman lines reported by these authors are listed along with those observed in the various spectrograms obtained in the [Saksena's] investigation. The numbers given within brackets against v_1, v_2, v_3 and v_4 are the Raman frequencies of the free SO_4 ion" (see Saksena, 1941, and Table III therein). "The presence of two water-bands at 3406 and 3493 [cm^{-1}] is well established. [Saksena] has been unable to confirm neither the presence of a third band at 3240 reported by Krishnan (1929) nor the splitting observed by Rasetti (1932) for the band 3406". Here the Table as given by Saksena, 1941 (see please references therein). Kariamanikkam Srinivasa Krishnan's paper is "The Raman spectra of crystals", Indian J. Phys. 4, 131-138(1929). This was the last article by K. S. Krishnan on Raman spectroscopy.

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Gypsum Raman shift (cm^{-1}), from Saksena, 1941, and references therein.

Krishnan (1929)	3240	3397		3493
Nisi (1931)		3404		3497
Cabannes (1932, 1938)		3404		3495
Rasetti (1932)		3399	3426	
Saksena (1941)		3406		3493

Note that three bands are present in the spectrum of water for sure, therefore the data from K. S. Krishnan, 1929, are very interesting.

Crystallization water

Rappal Sangameswaran Krishnan, in 1945, proposed a new study on gypsum. He used the mercury resonance radiation λ2536.5 for exciting the Raman spectrum. R. S. Krishnan selected a transparent crystal of gypsum from Sir C. V. Raman's personal collection. In Krishnan's article, 1945, which is relevant for the history of Raman spectroscopy too, we can find an interesting comparison regarding the spectrum of the crystallization water ("water of crystallisation is water that is chemically bonded into a crystal structure", BBC). "On comparing the Raman bands of water in gypsum as observed in the investigation [by R. S. Krishnan] with those of ordinary water and of ice (summarized in Hibben's book), we find that the number and distribution of the bands are common to all the three" (Krishnan, 1945).

Raman shift (cm^{-1}) as in R. S. Krishnan, 1945.

Gypsum	3258 3334	3406 3495	3606 3680
Water	3231	3436	3605
Ice at 0°C	3193	3391	3549

"The correspondence follows as a natural consequence of the fact that in gypsum the water molecules are concentrated in separate sheets which are only loosely bound with other sheets of ions and as such the oscillations of the water molecules are not appreciably modified in the crystalline state" (Krishnan, 1945). The gypsum crystal structure is shown in Yu et al., 2016, according to Chen, 2006.

"The bands in gypsum are very much sharper than those observed with ordinary water and consequently their maxima could be measured with a high degree of accuracy. The spectrum of gypsum shows another interesting feature. *The three principal water bands are split into six fairly narrow bands.* They form three pairs as shown [here in the previously given table]. The difference in the frequency shifts of the two components of each pair is approximately constant for the three pairs, … Results obtained by Cabannes (1938), Saksena (1941) and Rao (1941) from polarisation studies indicate that the band at 3406 belongs to the symmetric class, while the one at 3495 to antisymmetric class. Similar behavior should be exhibited by the other two pairs of bands also. Because of the antisymmetric nature of the band at 3495 cm^{-1} Cabannes (1938) had suggested that this band should correspond to the Raman inactive valence vibration of the H_2O molecule, which was rendered active in the crystalline environment" (Krishnan, 1945, and references therein). "The Raman bands of water in several crystalline hydrates have been the subject of study by numerous investigators" (see references in Krishnan, 1945). Regarding the experiment, we find that the spectrum of the water of crystallization in gypsum, as obtained by Roop Kishore and Krishnan, "shows far greater detail than any recorded by others not only in gypsum but in other crystalline hydrates as well. The success is due to the use of the intense *mercury resonance radiation* for exciting the Raman spectrum" (Krishnan, 1945). We will further discuss the Raman spectrum after the following section, which is stressing the importance of the gypsum crystallization water in biology.

Water source for microorganisms and plants

The crystallization water has received recent interest as a source of water for plants. "Some minerals, like gypsum, hold water in their crystalline structure. Although still unexplored, the use of such crystallization water by organisms would point to a completely new water source for life, critical under dry conditions" (Palacio et al., 2014). Palacio and coworkers have shown that the crystallization water is a "significant water source for organisms growing on gypsum, especially during summer". Due to the widespread occurrence of gypsum on Earth and also on Mars, Palacio and coworkers' results "may have important implications for arid land reclamation and exobiology". In Palacio et al., 2015, the researchers said that their findings of 2014, "open up exciting questions about the mechanisms used by plants to access gypsum crystallization water". Palacio and coworkers "suggest two complementary mechanisms": a passive uptake by soil and an active extraction. "In the second case, plants and/or their associated microorganisms could actively force the release of water molecules from the crystalline structure of gypsum by excreting organic acids or electrolytes". In de la Puente et al., 2022, we can find "analysed the principal water sources used by 20 species living in a gypsum hilltop, the effect of rooting depth and gypsum affinity, and the interaction of the plants with the soil beneath them".

In Huang et al., 2020, it has been reported the analysis "of how microorganisms are able to survive in the world's driest non-polar place, the Atacama Desert, Chile". Microorganisms extract water from gypsum rocks, "enabling these colonizing microorganisms to sustain life in this extreme environment". The researchers illustrate how microorganisms "can obtain water under severe xeric conditions, but also provide insights into potential life" on Mars, and "offer strategies for advanced water storage methods". The microorganisms "can extract water of crystallization (i.e., structurally ordered) from the rock, inducing a phase transformation from gypsum ($CaSO_4 \cdot 2H_2O$) to anhydrite ($CaSO_4$)". In Huang et al., it is told that "Interestingly, anhydrite was observed in areas populated with microorganisms, while substrate areas without microorganisms consisted only of gypsum. Fourier transform-infrared spectroscopy (FTIR) maps were acquired in the areas with microorganisms to further verify the existence of anhydrite phase" (Huang et al., mentioning Bishop et al., 2014, Liu et al., 2009). "The resulting spectrum shows a reduction in the intensity of peaks representative of water of crystallization …, suggesting a transformation to anhydrite in that region. FTIR mapping … further validated the existence of an anhydrite phase around the gypsum phase" (Huang et al., 2020). Therefore, spectroscopy of gypsum crystallization water is relevant for biology too. Regarding gypsum "and other evaporites as a potential source for water extraction on Mars", we can find an "experimental update", provided by van Susante and coworkers, 2018. About the isotopic composition of hydration water in gypsum, see Sofer, 1978. Further literature about gypsum is mentioned in Appendix B.

Gypsum in RRUFF database

Let us return to the work by R. S. Krishana and its relevant importance in the history of Raman spectroscopy. As we are here showing, there is a remarkable agreement between the measurements made by Krishnan and the data from laser spectroscopy. Let us consider the spectra available in RRUFF database (Lafuente et al., 2015). We have two available scans, the R040029 and R060509 broad scans, with unoriented samples and instrument setting Thermo Almega XR 532nm at 100% of 150 mW. We use data in the range from 3000 to 4000 cm^{-1}. A spline baseline adjustment is applied.

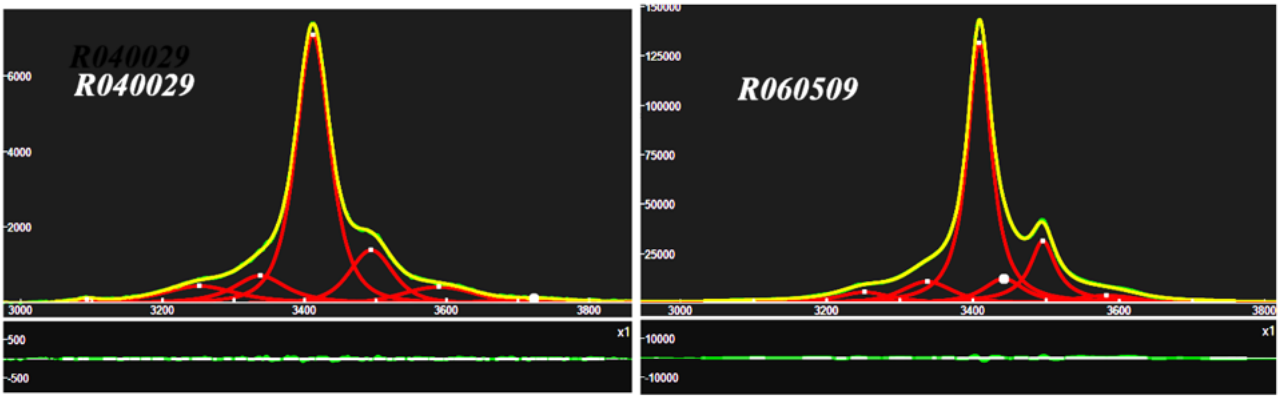

Fig.1: Deconvolution of gypsum RRUFF R040029 (left) and RRUFF R060509 (right) spectra. The region of the crystallization water is decomposed into seven and six q-Gaussian bands (red curves) respectively. The lower part of the images is showing the misfit, that is the difference between data (green) and the sum of components (yellow curve). R040029: the centers of components are at 3093, 3252, 3338, 3411, 3493, 3589, 3722 cm^{-1}. R060509: the centers of components are at 3252, 3337, 3409, 3496, 3583 cm^{-1}.

The plot in the Fig.1 is obtained by means of software Fityk (Wojdyr, 2010), after defining in it the q-Gaussian functions (see Appendix A for further details). By means of the data obtained from q-Gaussian deconvolution, we can compare the Raman shift (cm^{-1}) of the centers of components given in the Figure 1, with the results given in Krishnan, 1945. It is admirable the agreement. The main peak is at 3406-3411 cm^{-1}, according to Krishnan, 1945. Here in the following table, the comparison is shown (centers of components given in cm^{-1}).

Gypsum (Krishnan)		3258	3334	3406	3495	3606	3680
R040029	3093	3252	3338	3411	3493	3589	3722
R060509		3252	3337	3409	3496	3583	

Infrared

In RRUFF, regarding R040039, we can find and infrared spectrum. Let us try a deconvolution of it by means of q-Gaussians. After trying with all q-Gaussian, we observed that a better fit can be obtained using q-BWF functions too (the function is asymmetric).

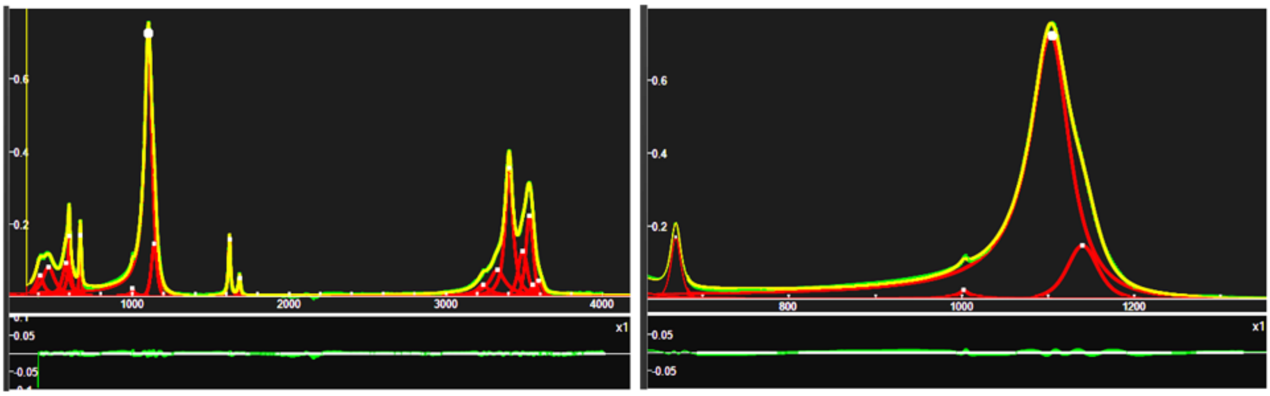

Fig. 2: Deconvolution of the infrared spectrum by means of q-BWF functions. On the right, the two q-BWF functions of the main peak are shown in detail.

It seems that q-BWF functions can be useful for deconvolution of infrared spectra too. Further investigations are necessary.

The discovery of the Raman effect

Previously, we have mentioned an article of 1929 by Kariamanikkam Srinivasa Krishnan, who discovered with Chandrasekhara Venkata Raman the Raman effect. For his life and research see please K. S. Krishnan (Man behind the first Asian Nobel in Science); here we refer to this text as "Man behind". During January 1928, "Mr. Venkateswaran, a part-time worker at the laboratory [University of Calcutta], was studying the phenomenon of light scattering in highly viscous organic liquids. While experimenting with glycerine, he made the curious observation that the color of sunlight scattered in a highly purified sample of the liquid was green instead of the customary blue. … Raman prevailed upon Krishnan to undertake a thorough investigation of the episode. The liability of carrying on the experiments fell upon Krishnan's shoulders. The Raman effect was discovered on 28th February 1928" (Man behind). The first paper on Raman effect was published in Nature, with title "A new type of secondary radiation". Raman became Nobel laureate in 1930 for the study about scattering of light. "It was a resolute quest of four to five weeks and eventually it happens to be a great experimental discovery. Krishnan kept a record of the events in the form of a diary. The diary contains the detailed description of the pursuit that conclusively led to this great discovery" (Man behind). "Being a co-discoverer of Raman effect", the phenomenon would have been termed as "Raman-Krishnan effect" (Man behind).

Let us consider the article by Raman and K. S. Krishnan, 1928. "The new type of light scattering discovered by us [Raman and Krishnan] naturally requires very powerful illumination for its observation. In our [Raman and Krishnan] experiments, a beam of sunlight was converged successively by a telescope … and by a second lens … At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation in vacuo) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, *completely extinguished the track of the light through the liquid* or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available" (Raman & Krishnan, 1928). Then, in 1928, Raman and Krishnan used natural light.

In Raman and Krishnan, 1929, we can find told that, in two preliminary papers, the authors "recorded the discovery that when monochromatic light is scattered in a transparent medium (be it gas, vapour, liquid, amorphous solid or crystal), the diffused radiation ceases to be monochromatic, and several new lines or sometimes bands (associated in many cases with a continuous spectrum) appear in the spectrograms of the diffused radiation. Further, the new radiations are, in general, strongly polarized". Raman and Krishnan illustrated the phenomenon with the case of "transparent crystalline quartz in which the effect is very well shown with the 4358 A.U. line of mercury as the exciting line, the new lines also appearing in the indigo-blue region of the spectrum". In the 1929 article, we can find measurements on liquids. "The spectrum of the scattered light was taken with a Hilger quartz spectrograph (E_2), *using very rapid photographic plates* (Ilford Iso-zenith, II. & D. 700). In the case of the single line pictures of benzene and toluene an exposure of about 40 hours was necessary, while for carbon tetrachloride, for which the complete mercury arc was incident, an exposure of only 25 hours was given" (Raman and Krishnan, 1929).

"After leaving Calcutta, the scientific collaboration between [K. S. Krishnan] and Raman came to an end. After 1928, Krishnan did not work on Raman scattering" (Man behind). The last article on Raman effect was published in 1929.

Rasetti technique with the mercury resonance radiation

In 1945, we can find evidenced by the Raman spectroscopy on calcite and gypsum a strong enhancement of the technique. In fact, Rappal Sangameswaran Krishnan improved his Raman spectroscopy by using the "Rasetti technique". Franco Rasetti was a physicist that, with Enrico Fermi, discovered the key processes to obtain fission (he refused to work on the Manhattan Project). In 1930, he was appointed to the chair in spectroscopy at the University of Rome. It was in 1929, that Rasetti proposed his new approach to Raman spectroscopy. "We owe to Rasetti (1929, 1930) the development of a remarkably useful technique for the study of the Raman effect, the value of which has been demonstrated by the resounding success with which he himself applied it in several cases of fundamental interest. In this field of research generally, and especially in investigating substances such as gases or vapours which scatter light only feebly, or crystals which exhibit only feeble Raman spectra, it is essential to employ a light source which emits the most intense possible and highly monochromatic radiation, and that there should be no unwanted radiations and especially no continuous spectrum accompanying the same. Further, it is highly desirable that the exciting radiation (but not the excited ones) should be removed from the light scattered by the medium before its entry into the spectrograph, as otherwise the photographic plates would be fogged by its general diffusion within the instrument. Rasetti secured all these advantages and in addition the enormously increased scattering power of short wavelength radiations" (Krishnan, 1943). Rasetti proposed to use "the 2537 A.U. monochromatic radiations of mercury vapour under special conditions which ensured that only this radiation and none other would give an observable Raman effect. The technique consists in using a low-pressure quartz mercury arc in which the mercury vapour is prevented from reaching any considerable density, and from absorbing the 2537 radiation emitted by itself. This is accomplished firstly by very effective water-cooling, and secondly by squeezing the discharge against the walls of the quartz tube by the field of a specially designed electromagnet. A filter of mercury vapour at room temperature is placed in the path of the scattered light emerging from the substance under study to absorb the 2537 radiation. This filter works so effectively that some of the feeble mercury lines which have intensities negligibly small in comparison with the 2537 radiations and which therefore give no observable Raman effect nevertheless appear stronger than the 2537 line in the recorded spectra" (Krishnan, 1943).

R.S. Krishnan, in his article about calcite, 1945, is adding that for Raman measurements "it is essential to employ a monochromatic light source which is very intense for recording the second order Raman frequency shifts. It is also of great importance that there should be no continuous spectrum accompanying the same. This is secured by using the 2536.5 A.U. mercury resonance radiation from a water-cooled magnet-controlled quartz arc". "The 2536.5 A.U. radiation from the light scattered by the medium is effectively suppressed before its entry into the spectrograph by absorption in a column of mercury vapour, … This makes it possible to record faint Raman lines with small frequency shifts on a clear background. Rasetti (1929) was the first to use this technique for the study of the Raman effect in gases and crystals" (Krishnan, 1945, on calcite).

In Krishnan's study of gypsum, we find told that the used technique is that based on the *mercury resonance radiation* λ 2536.5 for exciting the Raman spectrum of the crystal. "The flat faces [of the crystal] were parallel to the cleavage plane. In all the experiments the specimen was illuminated with unpolarised light through one of its flat faces and the scattered light was photographed through one of its edges. As in the case of calcite, two different instruments were used for recording the Raman spectra: (1) A Hilger E_1 quartz spectrograph and (2) a Hilger E_3 quartz spectrograph". The high dispersion instrument was used to record the spectrum in all detail, and to measure the frequency shifts and the line widths very accurately. "For this purpose, an iron arc comparison spectrum was taken on the same negative partially overlapping the Raman spectrum. Using a slit width of 0.04 mm exposures of the order of three days were given in order to get a spectrogram showing the lines with reasonable intensity. The E_3 quartz spectrograph was used to get intense photographs of the complete Raman spectrum of gypsum. With a slit width of 0.03 mm, exposures of the order of two days were given to record intense spectrograms" (Krishnan, 1945).

Again, in his study on gypsum, Krishnan is mentioning Rasetti for his technique. "Rasetti (1932) using the 2536.5 *mercury resonance radiation* as exciter recorded as many as nine lattice fines, while those who employed the 4046 and 4358 radiations recorded only a couple of lines instead. Roop Kishore (1942) using *the Rasetti technique* and giving long exposures reported for the first time the existence of a weak line at 1622 cm^{-1}, a weak band at about 2249

cm^{-1} and three more weak water bands with mean frequency shifts 3244, 3309 and 3584 cm^{-1} in the neighborhood of the two principal water bands" (Krishnan, 1945). Then, let us add Kishore's results to our previous table for comparison.

Gypsum (Krishnan)		3258	3334	3406	3495	3606	3680
R040029	3093	3252	3338	3411	3493	3589	3722
R060509		3252	3337	3409	3496	3583	
Gypsum (Kishore)		3244	3309	3410	3480	3584	

Also in Kishore, 1942, we find given details about Rasetti method. "Most of the investigations so far published on the Raman spectra of crystals have been made with 4047 and 4358 radiations of the mercury arc. As early as 1931, however, Rasetti developed a technique which enabled the 2537 radiations in the ultra-violet to be used with signal success in this field of research" (Kishore, 1942). Kishore continues describing the experimental set-up. "Rasetti worked with several crystals, … used a Hilger E. 315 Quartz spectrograph giving a dispersion of 130 wave numbers per mm. The exposures necessary ranged from 10 minutes in the case of calcite to 5 hours for rocksalt. Rasetti's technique is, of course, applicable only with crystals which are transparent to the 2537 radiations. But for such crystals it is convenient and extremely efficient. … The high intensity and large scattering power of the 2537 radiations coupled with their elimination from the scattered light enable even small crystals to be successfully employed" (Kishore, 1942). Kishore is referring to Rasetti, 1932.

In 1931, Rasetti told that he had been "investigating the Raman effect in a number of crystals, using the same method of excitation which proved to be particularly successful with gases" (Rasetti, mentioning his work on gases, 1929). "The primary source consists of a powerful water-cooled mercury arc, which gives an extremely intense and sharp resonance line λ2537". He mentioned advantages such as a short exposure (10 minutes to three hours), a wide range of frequency shift (about 20,000 cm^{-1}), and the exciting radiation that can be easily absorbed by a filter of mercury vapor.

To conclude, we report a passage of Rasetti's article, 1932: "L'uso della riga di risonanza del mercurio λ 2537 per l'eccitazione degli spettri Raman, già applicato e descritto più volte per lo studio dei gas, presenta notevoli vantaggi anche nel caso dei cristalli. Usando una lampada a mercurio raffreddata, si può riassorbire la radiazione di risonanza mediante vapore di mercurio, ciò che permette l'osservazione di righe Raman nell'immediata vicinanza della riga eccitatrice; e inoltre si ottiene una grande intensità. Per darne un'idea, basterà dire che per es., con la calcite, si può fotografare lo spettro Raman con lo spettrografo di media luminosità Hilger E 315 con una posa di cinque minuti" (Rasetti, 1932). As we have seen, Rasetti technique was fundamental for obtaining good spectra for studying Raman broad scans on crystals, including the second-order effects. Using Rasetti method, in 1945 Krishnan recorded a very interesting spectrum of water of crystallization in gypsum; in fact, his results are in excellent agreement with contemporary Raman spectra.

Appendix A: q-Gaussian and q-BWF functions

Sparavigna, 2023, proposed for the first time the use of q-Gaussian function in Raman spectroscopy. She defined also the q-BWF functions which are generalizing the Breit-Wigner-Fano (asymmetric) line shape in the framework of the q-exponential function. Here we show how to apply, by means of Fityk software, the q-Gaussian and the q-BWF functions in spectroscopy.

The q-Gaussian functions are probability distributions proper of the Tsallis statistics (Tsallis, 1988, Hanel et al., 2009). These functions are based on a generalized form of the exponential function, characterized by a continuous real parameter q. When q is going to 1, the q-exponential becomes the usual exponential function. The value q=2 corresponds to the Cauchy distribution, also known as the Lorentzian distribution; the q-Gaussian function is therefore a generalization of the Lorentzian distribution too. The change of q-parameter is allowing the q-Gaussian function to pass from the Gaussian to the Lorentzian distribution.

The q-Gaussian function is: $f(x) = Ce_q(-\beta x^2)$, where $e_q(.)$ is the q-exponential function and C a scale constant (in the exponent, $\beta = 1/(2\sigma^2)$). The q-exponential has expression: $e_q(u) = [1 + (1-q)u]^{1/(1-q)}$. For spectroscopy, we can write the q-Gaussian function in the following manner (with the center of the band at x_o): $q\text{-}Gaussian = Cexp_q(-\beta(x-x_o)^2) = C\,[1 + (q-1)\beta(x - x_o)^2]^{1/(1-q)}$.

In Fityk, a q-Gaussian function can be defined in the following manner: define Qgau(height, center, hwhm, q=1.5) = height*(1+(q-1)*((x-center)/hwhm)^2)^(1/(1-q)), where q=1.5 is the initial guessed value of the q-parameter. Parameter hwhm is the half width at half maximum of the component. When q=2, the q-Gaussian is a

Lorentzian function, that we can find defined in Fityk as: Lorentzian(height, center, hwhm) = height/(1+((x-center)/hwhm)^2). When q is close to 1, the q-Gaussian becomes a Gaussian function.

We have proposed an asymmetric form of the q-Gaussian function, generalizing the Breit-Wigner-Fano into a q-Breit-Wigner-Fano. The q-BWF can be defined as: Qbreit(height, center, hwhm, q=1.5, xi=0.1) = (1-xi*(q-1)*(x-center)/hwhm)^2 * height*(1+(q-1)^0.5 *((x-center)/hwhm)^2)^(1/(1-q)). And the BWF can be defined as: Breit(height, center, hwhm, xi=0.1) = (1-xi*(x-center)/hwhm)^2 * height/(1+((x-center)/hwhm)^2). Using +xi instead of -xi does not change the fitting results in Fityk.

Appendix B: Literature on Gypsum

In the text, we have given a short review about the gypsum crystallization water and its interaction with plants and microorganisms. Here we mention some further literature about gypsum. In Charola et al., the deterioration of buildings and monuments by gypsum is reviewed. The researchers propose “the relevant information that will serve to explain the deterioration observed on building materials by the crystallization of gypsum and thus allows developing improved conservation methods". In Kuttah and Sato, 2015, we find a review which "captures the current state of the art in the field of sulfate bearing soils used as construction materials through a detailed discussion of different studies that pave the way to the possible treatment of such soils to be used in road construction”. The researchers discussed also how to recycle waste gypsum components.

Another important feature of gypsum addressed by literature is its role in soil. In Porta, 1998, we can find a review of "the main methodologies and techniques that have been used to characterize gypsum in soils, especially in gypsiferous soils of semiarid and arid regions”, “from the identification of gypsum in soil surveys in the field to the study of gypsum in the laboratory". As told by Shainberg et al., 1989, gypsum “is a relatively common mineral that is widely available in agricultural areas and has a number of specialized agronomic uses, principally as a Ca source on legumes and as a soil conditioner on sodic soils”. At the time, 1989, the review suggested “that the utility of gypsum may extend to a greater range of soils and crops”. And in fact, Prakash et al., 2024, consider gypsum as “a valuable resource for farmers, supplying essential calcium and sulfur for plant growth. It serves as a crucial soil amendment, particularly in reclaiming alkali and sodic soils”. Moreover, “gypsum promotes improved root development in crops, exerting a multifaceted impact on soil physicochemical properties, ultimately bolstering crop productivity” and therefore its sustainability. Moreover, according to Prakash and coworkers, “gypsum contributes to mitigating greenhouse gas emissions in acidic soils, particularly in reducing methane emissions”.

Bello and coworkers, 2021, discuss the mitigation of soil salinity stress by means of gypsum and bio-organic amendments. “Salinity impedes soil and crop productivity in over 900 million ha of arable lands worldwide due to the excessive accumulation of salt (NaCl). To utilize saline soils in agriculture, halophytes (salt-tolerant plants) are commonly cultivated. However, most food crops are glycophytes (salt-sensitive). Thus, to enhance the productivity of saline soils, gypsum ($CaSO_4 \cdot 2H_2O$) as well as bio-organic (combined use of organic materials, such as compost and straw with the inoculation of beneficial microbes) amendments have been continuously recognized to improve the biological, physical and chemical properties of saline soils”. Gypsum is regulating the exchange of sodium ion for calcium ion on the clay surface, and therefore it is increasing the ratio of Ca ions in the soil solution. “Simultaneously, gypsum furnishes crops with sulfur (S) for enhanced growth and yield through the increased production of phytohormones, amino acids, glutathione and osmoprotectants, which are vital elicitors in plants’ responses to salinity stress”.

Returning to plants and gypsum, in Escudero et al., 2015, we can find explained the adaptation of plants to gypsum. “Plants living on gypsum soils can be classified into three categories: (i) wide gypsophiles are specialists that can penetrate the physical soil crust during early life stages and have physiological adjustments to cope with the chemical limitations imposed by gypsum soils; (ii) narrow gypsophiles are refugee plants which successfully deal with the physical soil crust and can tolerate these chemical limitations but do not show specific adaptations for this type of soils; and (iii) gypsovags are non-specialist gypsum plants that can only thrive in gypsum soils when the physical crust is absent or reduced”. The researchers investigated the biological soil crusts (BSCs), stressing that “climate change and habitat fragmentation negatively affect both plants and BSCs in gypsum habitats, and are among the major threats to these ecosystems” (Escudero et al., 2015).

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