q-Gaussian and q-BWF functions for the deconvolution of Raman and infrared spectra of Calcite

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Abstract: Here we consider calcite and its spectra (Raman and infrared) that we can find in the RRUFF database. We apply q-Gaussian and q-BWF functions to decompose the spectra. The q-Gaussian functions had been derived in the framework of Tsallis analysis of entropy. Their use for Raman spectroscopy has been proposed by Sparavigna, 2023. The q-BWF functions have been defined by Sparavigna, 2023, to generalize the BWF (Breit-Wigner-Fano) functions, and proposed for fitting to asymmetric peaks in Raman spectroscopy. Besides examples of decompositions of RRUFF spectra, a review of literature about calcite is given. We will also add an appendix about the Raman spectra of calcite recorded by R. S. Krishnan (1945), by means of the F. Rasetti technique (1932) which was using the λ2536.5 mercury resonance radiation. As we can see, Krishnan succeeded to record the second order components of the spectrum.

Keywords: Raman spectroscopy, Infrared spectroscopy, q-Gaussian functions, q-BWF functions, History of Raman spectroscopy.

Introduction

In this work, we consider the calcite and its spectra (Raman and infrared) that we can find in the RRUFF database (Lafuente, 2015). This database is useful for testing new approaches to the deconvolution of spectra by means of functions which are not included among the line shapes commonly available in curve fitting software (that is, Gaussian, Lorentzian, Voigt, pseudo-Voigt functions). Here we apply q-Gaussian and q-BWF functions to decompose the spectra of calcite. The q-Gaussian functions had been derived in the framework of Tsallis analysis of entropy (Hanel et al., 2009). Their use for Raman spectroscopy has been proposed for the first time by Sparavigna, 2023. The q-BWF functions have been defined by Sparavigna, 2023, to generalize the BWF (Breit-Wigner-Fano) functions, and proposed as fitting functions of asymmetric peaks in Raman spectroscopy. Here we show that this generalization of BWF functions can be suitable for the decomposition of infrared spectra too.

The Raman and infrared spectra of calcite have been discussed in several publications. For instance, in Adler and Kerr, 1962, aragonite and calcite have been the subject of an infrared spectroscopy investigation. In Gunasekaran et al., 2006, we can find the study of Raman and mid-range infrared spectra, that the researchers have been measured on natural limestone and dolomite minerals. Four prominent absorption bands have been identified. Moreover, the "positions of the wavenumbers are unique for each carbonate mineral and are thus diagnostic of their mineralogy". Previously, in Andersen and Brecevic, 1991, the infrared spectrum of an amorphous form of calcium carbonate had been obtained and proposed with the spectra of crystalline polymorphs (vaterite, aragonite and calcite). Behrens et al., 1995, proposed the Raman spectra of vateritic calcium carbonate. Ultra-fine calcite samples, possessing similar particle size in different agglomeration states, have been synthesized and studied by Yue et al., 2001, with SEM-TEM measurements, infrared and Raman spectroscopy. Gillet et al., 1993, by means of Raman spectroscopy, investigated carbonates, that is the "high-pressure and high-temperature behaviour of calcite, magnesite, dolomite and aragonite". Previously, Fong and Nicol, 1971, studied the Raman spectrum of calcium carbonate at high pressures.

Sun and coworkers, 2014, proposed a "Raman spectroscopic comparison of calcite and dolomite". Dufresne et al., 2018, used the Raman spectroscopy on the eight natural carbonate minerals of calcite structure (that is, calcite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), smithsonite ($ZnCO3$), rhodochrosite ($MnCO_3$), otavite ($CdCO_3$), spherocobaltite ($CoCO_3$), and gaspeite ($NiCO_3$)). The data provided by Dufresne and coworkers "show that the carbonate E_g (T) phonon shifts are due to influences from the nearest neighbor distance" of lattice sites. De La Pierre et al., 2014, proposed the Raman spectra of calcite and aragonite, in a combination of experimental and computational studies. Anatolievich and Victorovich, 2018, proposed an "ab initio modeling of Raman and infrared spectra of calcite". In the study by Zhu et al., 2020, a natural carbonate rock was highlighted and investigated using mineralogical and IR spectroscopy methods.

In Kim et al., 2021, the "identification and composition of carbonate minerals of the calcite structure" has been proposed as gettable by means of portable devices. "A portable Raman device with a 532 nm excitation laser and a portable infrared spectrometer with ATR (Attenuated Total Reflection) mode were used to analyse the spectral features associated with the identification and compositional variation of Ca-Mg-Fe-Mn natural carbonate minerals with a calcite structure (calcite, ankerite, dolomite, siderite, rhodochrosite, and magnesite)" (Kin et al., 2021). Calcite has been also investigated in a very recent study by Tsuboi et al., 2024, who are proposing "attenuated total reflection infrared and far-infrared, and Raman spectroscopy studies of minerals, rocks, and biogenic minerals". Beck et al., proposed a "quantification of crystal chemistry of Fe-Mg carbonates" by Raman and near-infrared spectroscopy, for remote sensing. The researchers "discuss the framework of applicability of these calibrations and apply them to a typical CRISM [Compact Reconnaissance Imaging Spectrometer for Mars] spectrum of carbonates from the Nilli Fossae region of Mars". Besides investigations on Mars, the Raman study of calcite is relevant for biology too. Niessink et al., 2024, stressed the "discovery of calcite as a new pro-inflammatory calcium-containing crystal in human osteoarthritic synovial fluid".

In fact, we can find also very old articles regarding the Raman spectra of calcite, that is articles published just after the Raman effect had been discovered. We will discuss one of then to show that these articles are relevant for the history of spectroscopy (Appendix A).

The bands

In Gunasekaran et al., 2006, in their Table III, we can find data about limestone provided by the authors, and Raman data from White, 1974, and infrared data from Gaffey, 1986. The table is also reporting the assignments. In the following table we give the centers of the bands as published by Gunasekaran et al., 2006.

Raman bands (cm^{-1})

Gunasekaran et al.	89	162	288	716	1092	1437	1754
White	86	155	281	711	1085	1433	1748

Infrared bands (cm^{-1})

Gunasekaran et al.	712	874	1425	1798	2514	
Gaffey	712	876	1435	1812	2545	2873

In Andersen and Brecevic, 1991, where an investigation of the infrared spectra of calcium carbonate is given, we can find a discussion "of the strong broad absorption in the 1600-1400 cm^{-1} region at normal temperature and at low temperature". The "careful examination" of this band "indicates that this absorption originates from several overlapping bands". In the case of aragonite, bands are estimated by Andersen and Brecevic at 1570, 1525, 1488, 1473 and 1440 cm^{-1}. No information is available about the line shapes used for decomposition and the relative role of the components.

In the case of broad bands, it is common to use several Gaussian (or Lorentzian) functions to fit both Raman and infrared spectra. Here we use q-Gaussian and q-BWF functions. It is also suitable to repeat the observation made by Ferrari and Robertson, 2000: to compare different fitting parameters of a Raman spectrum [and of other spectra], it is fundamental the knowledge of the used fitting procedures. Once we have decided the number of components and their line shapes, we can compare parameters obtained from a set of measurements. Moreover, there is no a priori reason to choose a particular function to fit the spectrum. For instance, Ferrari and Robertson suggested the BWF line shape for the G band in carbonaceous materials.

RRUFF calcite

The deconvolutions in the following figures are obtained by means of software Fityk (Wojdyr, 2010), after defining in it the q-Gaussian and q-BWF functions (see Appendix B for further details). We will show only the details of the spectra, which are better evidencing the role of q-Gaussian and q-BWF functions. Here four examples for samples proposed by RRUFF.
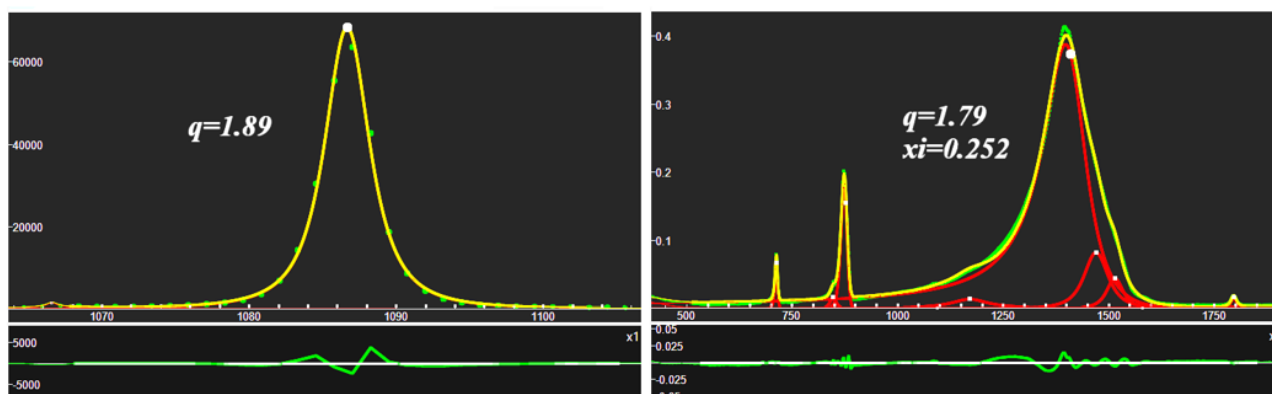

Fig.1: Deconvolution of calcite RRUFF R040070 Raman spectrum, depolarized (left, main peak, 1087 cm^{-1}) and infrared spectrum (right). On the left, the peak is symmetric, and we used a q-Gaussian function with q=1.9; on the right, we used three q-BWF functions for the asymmetric peaks (v_3, v_2, v_4). The asymmetry parameter ξ of the largest q-BWF component is given close to the curve, such as the q-parameter. Further q-Gaussian components have been added to improve the fit. The lower part of the images is showing the misfit, that is the difference between data (green) and the sum of components (yellow curve).
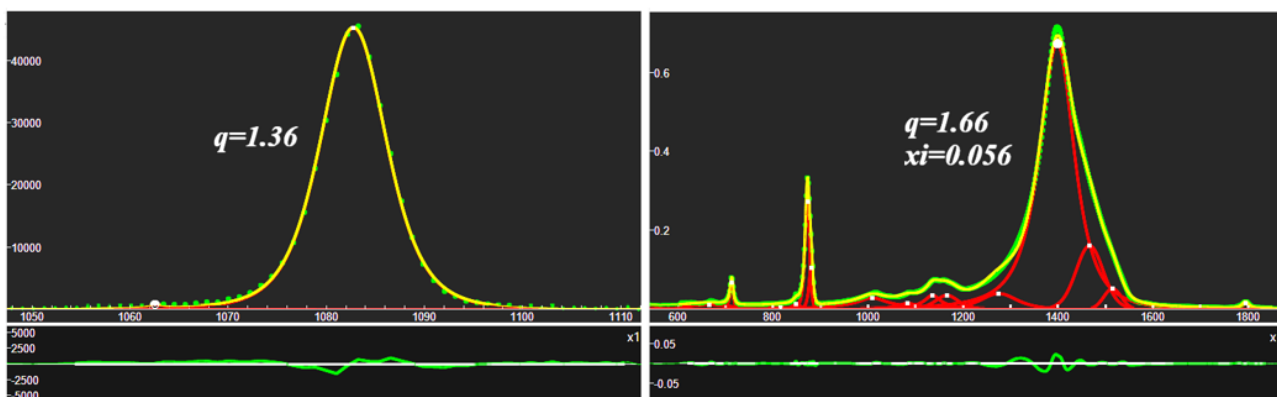
Fig.2: Deconvolution of calcite RRUFF R040170 Raman spectrum, depolarized (left, main peak, 1083 cm^{-1}) and infrared spectrum (right, data regarding the main peak).
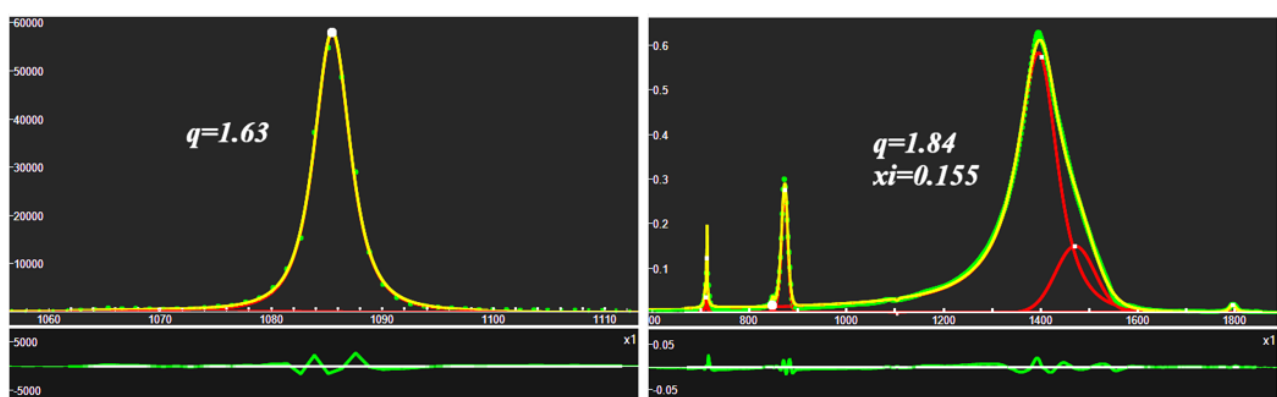

Fig.3: Deconvolution of calcite RRUFF R050048 Raman spectrum, depolarized (left, main peak, 1085 cm^{-1}) and infrared spectrum (right, data regarding the main peak).
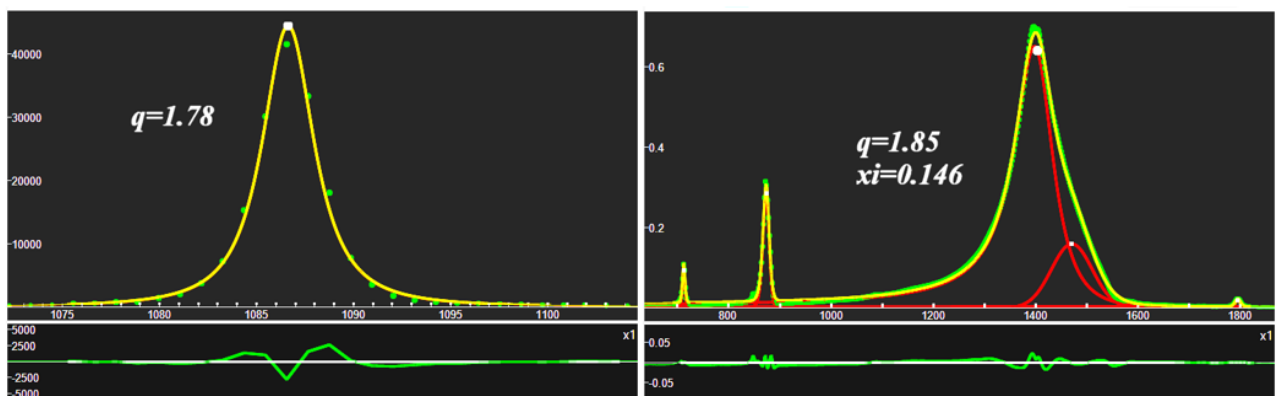

Fig.4: Deconvolution of calcite RRUFF R050009 Raman spectrum, depolarized (left, main peak, 1087 cm^{-1}) and infrared spectrum (right, data regarding the main peak).

In all the samples proposed by RRUFF, where an infrared spectrum is available, we can see that the main peak v_3 is well described by a q-BWF function, with one or two shoulders on the right. Regarding the Raman spectra, we can note that, in the figures given above, the q-parameter is ranging from 1.36 to 1.89 values, therefore we can conclude that the main Raman peak of calcte cannot be described by a Lorentzian function, a function which is characterized by q=2.

Discussion

In Campbell and Poduska, 2020, we can find a study of polycrystalline carbonate minerals and their infrared spectra. "A quick and easy way" to investigate carbonate materials is to use infrared spectroscopy, "which is one of the most widely used forms of vibrational spectroscopy". The mid-infrared (MIR) range is 400–4000 cm^{-1}, and it "corresponds to vibrations within single carbonate moieties. Even in crystalline calcite, MIR spectra show distinctive peak-broadening trends that are correlated with crystallinity differences arising from greater microstrain fluctuation values and smaller crystalline domain sizes" (Campbell and Poduska, mentioning Xu et al., 2015). "Earlier theoretical work demonstrated that analogous crystallinity differences do indeed trigger systematic peak broadening trends" (Campbell and Poduska, mentioning Gueta et al., 2007, Valenzano et al., 2007). In Xu et al., 2015, we find told that experimental studies of "calcite showed that v_4 peak is the mode that softens (broadens) the most at high temperatures" (Xu et al., mentioning Xu and Poduska, 2014). It is interesting the broadening of the peak v_4; however, in the RRUFF spectra given above, it is the v_3 band which is huge and broad.

In the [Figure 1 by Campbell and Poduska](#), we can find illustrated the bands in "mid-infrared (MIR) (2000–400 cm^{-1}) and far-infrared (FIR) (650–80 cm^{-1}) spectra for eight calcite-containing samples, … to demonstrate the extent and overlap of the spectral ranges. The intensity of each spectrum is normalized to either the ν_3 peak (MIR configuration) or the B_1 peak (FIR configuration)".
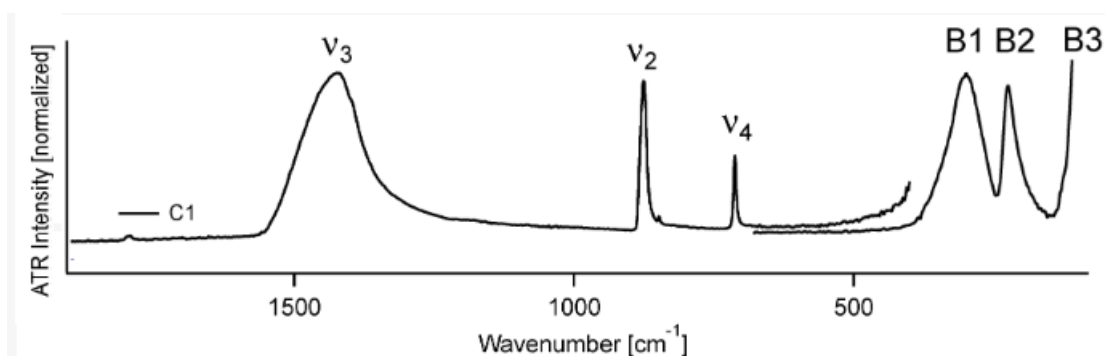

Fig. 5: IR spectrum of calcite, adapted from the Figure 1 in Campbel and Poduska, 2020, an article which is open access, under terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

In Xu and Poduska, 2014, we find told that, for analyses, the IR "spectra were baseline corrected", using software and, the position of peaks, such as their amplitude and full width at half maximum (FWHM) obtained from Lorentzian peak fits. "Lorentzian functions are widely utilized for peak fitting in IR and Raman spectra, and recent studies have demonstrated that the IR-active v_2 and v_4 modes in calcite are well matched by this function" (Xu and Poduska, mentioning Stolen et al., 1984, Gazit et al., 1996, Long et al., 2012). Actually, in our Figure 1-4, we used for v_2 and v_4 the q-BWF functions as line shapes.

In Stolen et al., 1984, the Lorentzian functions in mentioned regarding "the stimulated Raman threshold", [that] "was developed by assuming a Lorentzian gain profile". In Gazit et al., we find told that using "an iterative least squares routine and assuming either Voight or Lorentzian line shapes for the IR peaks, [a fit procedure] was performed in order to determine" some specific features.

"Although a Lorentzian line shape is widely used in IR curve fitting, [Gazit and coworkers] obtained better results with a Voight line shape". In Long et al., 2012, it is told that "Lorentzian-type multi-peak curve fitting was performed on the v_2 and v_4 vibration bands". Peak v_3 which is large and asymmetric is not considered in the given literature.

About the assignment of the band, it is given in Andersen and Brecevic, 1991; we find told that v_1, v_2, v_3 and v_4 modes are the normal vibrations of the carbonate ion; v_1 is the symmetric C-O stretching mode, v_2 is the CO_3 out-of-plane deformation mode, v_3 is the asymmetric C-O stretching mode and v4 is the OCO bending, in-plane, deformation. In the articles mentioned above, we do not find any deconvolution in components of the v_3 band. Moreover, in Andersen and Brecevic, it is told that this band can be split in v_{3a} and v_{3b} components. In the decompositions of our Figures 1-4, we have used two or three components, with rather good results. Further studies of the other carbonate minerals are necessary to test the use of q-BWF functions for IR spectra and the splitting of v_3 band.

Appendix A – Calcite Raman data obtained by means of F. Rasetti technique

As previously told in the introduction, we can find articles about calcite Raman spectra as soon as the effect had been discovered. To find remarkable results, however, we must wait until 1942 and 1945, when Rappal Sangameswaran Krishnan obtained his Raman spectra of calcite and gypsum. Regarding the experiment, we find that the spectra, as obtained by Roop Kishore, 1942, and then by Krishnan, 1945, show "far greater detail than any [spectrum] 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). In fact, if we consider the region of Raman spectrum regarding the gypsum crystallization water, we find an excellent agreement between the Krishnan's data and the decomposition we can obtain by means of q-Gaussian functions of RRUFF spectra (Sparavigna, Zenodo).

The Raman effect had been discovered by Chandrasekhara Venkata Raman and Kariamanikkam Srinivasa Krishnan on 28th February 1928. Raman and K. S. Krishnan illustrated the phenomenon, besides with natural light and complementary filters, with the 4358 A.U. line of mercury as exciting line. In 1945, for calcite and gypsum, R. S. Krishnan used the Rasetti technique. Franco Rasetti was a physicist that, with Enrico Fermi, discovered the key processes to obtain fission. In 1930, he was appointed to the chair in spectroscopy at the University of Rome. It was in 1929, that Rasetti proposed a 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" (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. … 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, measuring on calcite). Passing to 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. 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).

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 can be easily absorbed by a filter of mercury vapor.

As we have seen, Rasetti technique was fundamental for obtaining good spectra for studying Raman broad scans of crystals. Let us consider the peaks of the calcite Raman spectrum as given in the Figure 1, by Krishnan, 1945, available Indian Academy of Science. The peaks are at (in cm^{-1}): *−1085.6, −711.8, −283.8, −155.5, **λ2536.5 A.u.,** 155.5, 221, 283.8, 711.8, 864, 1065, 1085.6, 1360, 1433.8, 1583, 1750, 2147, 2172.5, 2220, 2310 and 2500.* We can compare with the data provided by Gunasekaran et al., 2006, and White, 1974. In Krishnan, 1945, we can find also data from Rasetti.

Krishnan			155.5	221	283.8	711.8	864	1065	1085.6	1360	1433.8	1583	1750
Gunasekaran et al.	89	162			288	716			1092		1437		1754
White		86	155		281	711			1085		1433		1748
Rasetti			155.7		283	713.8			1087.6		1436.7		

Data coming from Gunasekaran et al., White and Rasetti are the peaks of the first order Raman spectrum. In Krishnan we can find the second order spectrum: a "heavily exposed spectrogram taken with the E$_3$ spectrograph" is evidencing the peaks. Krishnan is also proposing assignations.

Appendix B – 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: $e_q(u) = [1 + (1-q)u]^{1/(1-q)}$.

To have an asymmetric form of the q-Gaussian function, let us write it in the following manner (the center of the band is at x_o):

$$q\text{-}Gaussian = Cexp_q(-\beta(x - x_o)^2) = C\,[1 + (q-1)\beta(x - x_o)^2]^{1/(1-q)}$$

We have generalized the Breit-Wigner-Fano into a [q-Breit-Wigner-Fano](#).

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))

q=1.5 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. 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.

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