

# Formamide Raman Spectrum and q-Gaussian Tsallis Lines

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## Abstract

q-Gaussians are the probability distributions which are maximizing the Tsallis entropy in the canonical ensemble. A continuous real parameter  $q$  is characterizing them so that, in the range  $1 < q < 3$ , the  $q$ -functions pass from the usual Gaussian form, for  $q$  close to 1, to that of a heavy tailed distribution, at  $q$  close to 3. The value  $q=2$  corresponds to the Cauchy-Lorentzian distribution. This behavior of the Tsallis  $q$ -Gaussian functions, which is producing a line profile intermediate between the Lorentzian and Gaussian profiles, can be useful for fitting the Raman spectral bands as recently shown by Sparavigna, 2023. Here we consider the  $q$ -Gaussians in the analysis of formamide Raman spectrum, the deconvolution of which had been proposed by V. Kirillov, 2004, by means of the Egelstaff-Schofield line shapes. The  $q$ -Gaussians are successfully fitting the formamide spectrum, and therefore can be perfect substitutes of Egelstaff-Schofield functions, which are rather complex to handle in numerical calculations, being based on the modified Bessel functions of second kind.

**Keywords:**  $q$ -Gaussian distribution,  $q$ -Gaussian line shape, Gaussian distribution, Cauchy distribution, Lorentzian distribution, Egelstaff-Schofield line shape.

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In his article of 2004, about a new approach in spectroscopy analysis, Sviatoslav Kirillov stressed that Gaussian and Lorentzian line profiles were generally used for the spectral deconvolution, according to a theoretical background already proposed in the first comprehensive review on the subject, published by Seshadri and Jones, in 1963. However - Kirillov notes -, the "real vibrational lines seldom follow these limiting cases", being "intermediate between Gaussian and Lorentzian" functions. For such a behavior, the Voigt function has been used as a better representation of experimental data. Today, after twenty years from Kirillov's article, we can easily find that Gaussian, Lorentzian and Voigt profiles remain the most used line shapes in fitting the Raman spectra.

The best-known model for intermediate line profiles, that is the Voigt function (Meier, 2005), has a non-analytical expression (Kirillov, 2004). Sviatoslav Kirillov proposed a new fitting method based on a profile which is, like the Voigt one, intermediate between Lorentzian and Gaussian line profiles, but it is made of an analytical function which is also possessing an analytical counterpart in the time domain. The line shape proposed by Kirillov, applied by the researcher to the analysis of formamide Raman spectrum, is obtained from an analytical Fourier transform of the time-correlation function of vibrational dephasing. The line is known as the Egelstaff-Schofield profile, after the research by P. A. Egelstaff and P. Schofield (1962).

The Egelstaff-Schofield line shape is based on the modified Bessel function of the second kind  $K_1$  (see please Equations 5 and 6 in Kirillov, 2004). Abramowitz-Stegun Handbook, 1988, and Numerical Recipes allow us to calculate numerically this modified Bessel function. In Sparavigna, 2023b, using the numerical method, we have compared Egelstaff-Schofield line shapes with the  $q$ -Gaussian functions. The  $q$ -Gaussian is a generalization of the Gaussian function, that is a distribution which is

maximizing the Tsallis  $q$ -entropy in the canonical ensemble (Tsallis, 1988, Hanel et al., 2009, Sparavigna, 2022). The  $q$ -Gaussian is based on a generalized form of the exponential function (see Appendix), where a continuous real parameter  $q$  is characterizing the function. When  $q$  is going to 1, the  $q$ -exponential becomes the usual exponential function. In the range of  $q$ -parameter from 1 to 3, we pass from the Gaussian to a heavy tailed distribution. The value  $q=2$ , (Naudts, 2009), corresponds to the Cauchy-Lorentzian distribution. The change of  $q$ -parameter is therefore allowing the  $q$ -Gaussian function to pass from the Gaussian to the Lorentzian distribution.

In recent research (Sparavigna, 2023a, 2023c), the application of  $q$ -Gaussians has been considered for Raman spectroscopy. In Sparavigna, 2023c, many successful examples of fitting Raman spectra had been given. Here we consider the deconvolution in  $q$ -Gaussians of formamide<sup>1</sup> Raman spectrum, for comparison with the deconvolution proposed by V. Kirillov, 2004, and made by means of Egelstaff-Schofield line shapes. The  $q$ -Gaussians are successfully fitting the spectrum, and therefore can be the perfect simple substitutes of Egelstaff-Schofield functions. For the deconvolution of formamide spectrum, let us use data from the John Wiley & Sons SpectraBase Spectrum ID=7rkzy4YtXDy, available at <https://spectrabase.com/spectrum/7rkzy4YtXDy> (accessed 14/5/2023). Here in the following figures, fit and deconvolution of the same spectral range of wavenumbers proposed by Kirillov, 2004, are given.

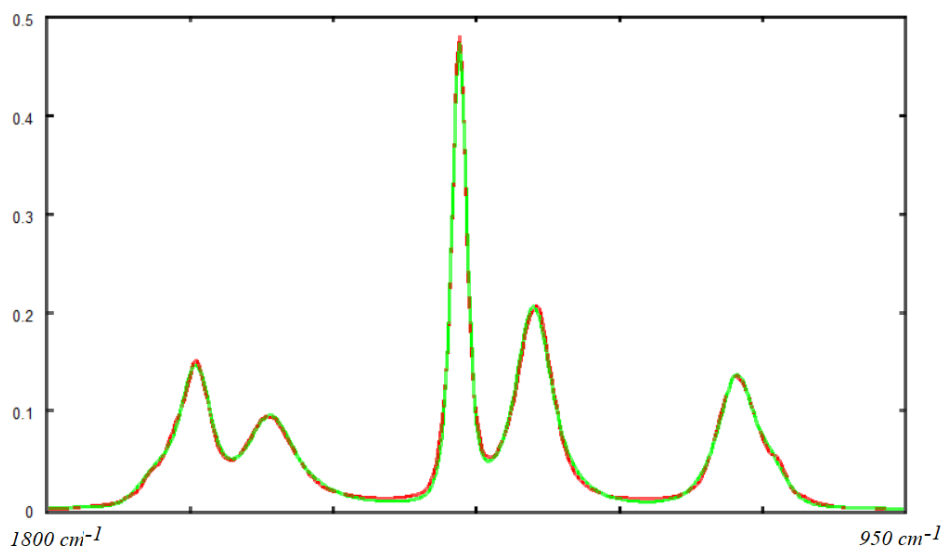


Figure 1: In red the data of formamide Raman spectrum (John Wiley & Sons, Inc. SpectraBase; SpectraBase Compound ID=1dRdojfNRZ1 SpectraBase Spectrum ID=7rkzy4YtXDy, link <https://spectrabase.com/spectrum/7rkzy4YtXDy> (accessed 14/5/2023). In green, the best fit obtained by means of the  $q$ -Gaussians.

<sup>1</sup> Formamide is a compound derived from formic acid. The liquid is miscible with water. It is also a solvent for many ionic compounds. The formamide can dissolve many electrolytes since it has a relatively large dielectric constant (Ohtaki et al., 1983). In the crystal state, the molecules form large ring structures due to the hydrogen bonds (Ohtaki et al., 1983). The hydrogen bonding in liquid formamide has been considered also with low frequency Raman studies (Faurkov Nielsen et al., 1982). Raman spectra of liquid formamide, in the region of C = O stretching vibration band, were investigated with experiments and quantum-chemical simulations by Hushvaktov et al., 2022, to clarify the shape of the C = O stretching Raman band.

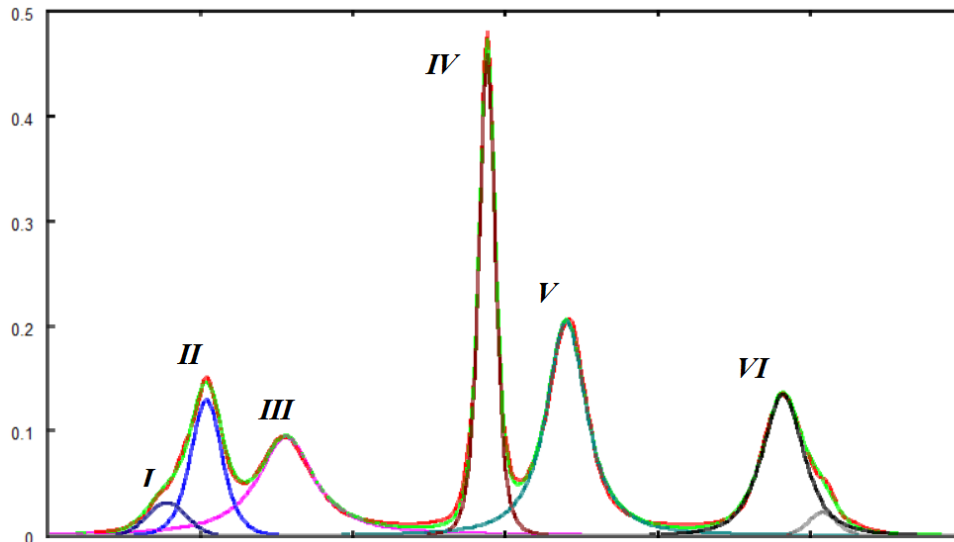


Figure 2: In red the data of formamide Raman spectrum and in green the best fit, as in the Fig.1. The other lines are showing the q-Gaussian components. The components are numbered from I to VII. The corresponding values of the q-parameter are: 1.01 (I), 1.31 (II), 1.93 (III), 1.43 (IV), 1.78 (V), 1.54 (VI), and 1.01 (VII). The positions of the peaks are (in  $\text{cm}^{-1}$ ) 1720 (I), 1670 (II), 1606 (III), 1393 (IV), 1310 (V), 1095 (VI), and 1055 (VII).

In the caption of the Fig. 2, we can find given the values of the q-parameter of q-Gaussians used for the deconvolution. Note please that the q-value 1.01 is giving a Gaussian, being this function numerically indistinguishable from the corresponding q-Gaussian function.

The best fit and the deconvolution given in the Figures 1 and 2 are in good agreement with the results shown by Kirillov (2004) (Kirillov used unpublished data obtained with O. Faurskov Nielsen, 1999). In his paper, Kirillov does not tell how the baseline has been determined. Notwithstanding the different baseline of the two plots (Kirillov-Faurslov Nielsen and Wiley SpectraBase), the shapes of the Raman bands are the same. This fact means that the q-parameter is a fundamental parameter for characterizing the Raman bands.

The deconvolution with q-Gaussian lines has two advantages with respect to that made by means of the Egelstaff-Schofield lines. I) The q-Gaussian function is simple (see Appendix) and it is requiring just a single instruction to define it, whereas the Egelstaff-Schofield line requires at least two subroutines to define the  $K_1$  modified Bessel function. Actually, the calculus of  $K_1$  requires the calculation of the  $I_1$  modified Bessel function too. II) The fitting by means of the q-Gaussians is giving a set of q-parameters. The q-parameter is providing a measure of the “intermediate profile”, between Lorentzian and Gaussian profiles, for each component of the deconvolution.

The formamide Raman spectrum given by the John Wiley & Sons, Inc. SpectraBase allows us to consider a further peak, and this is important for our research on q-Gaussians and Raman spectra. The result of the fit is given in the following figure.

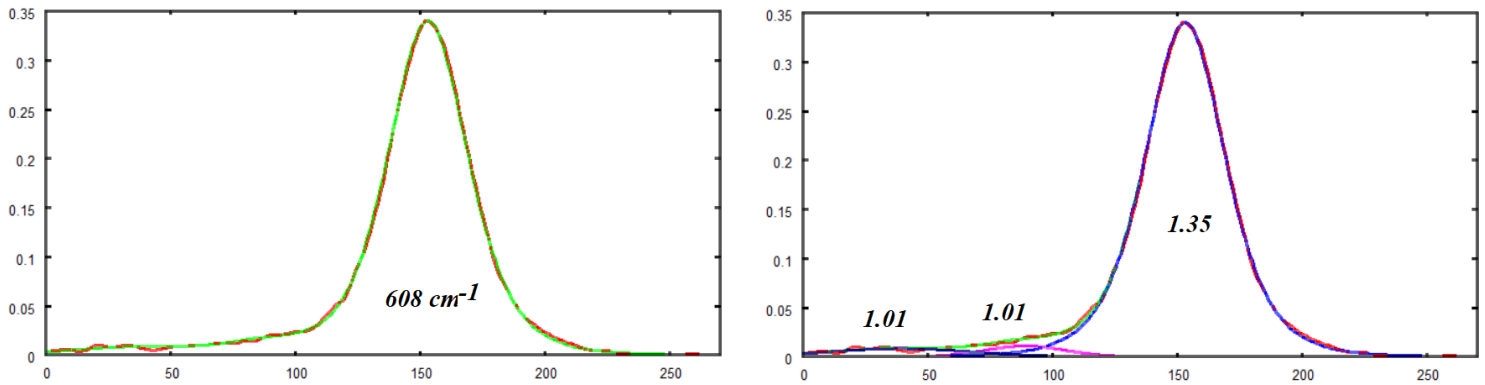


Figure 3: On the left, data (in red) of formamide Raman spectrum (John Wiley & Sons, Inc. SpectraBase; SpectraBase Compound ID=1dRdojfNRZ1 SpectraBase Spectrum ID=7rkzy4YtXDy, link <https://spectrabase.com/spectrum/7rkzy4YtXDy> (accessed 14/5/2023)). In green, the best fit obtained by means of  $q$ -Gaussians. On the right, the three components used for the deconvolution. The numbers are the values of the  $q$ -parameters. The main component has  $q$ -parameter equal to 1.35. On the  $x$ -axis, data are given as a function of integers  $n$  (270 data). A convenient scale is used for  $y$ -axis.

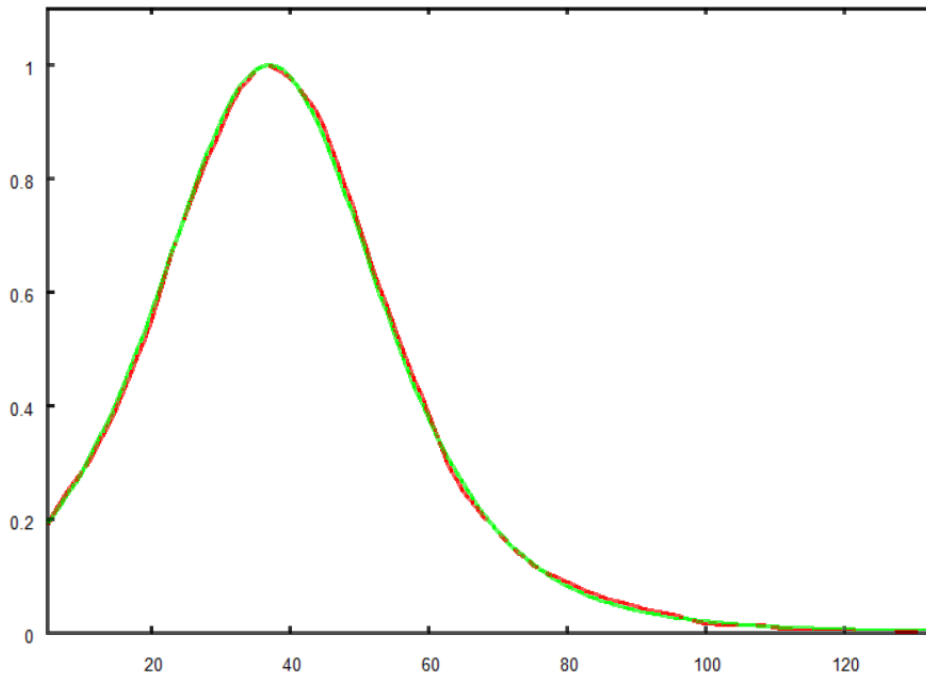


Figure 4: Let us assume just a part of the band given in Fig.3, to enhance the role of the peak. We can fit (green) the data (red) with a  $q$ -Gaussian (best  $q$ -parameter  $q=1.36$ ). The agreement is perfect. Please consider that data are given as a function of integers  $n$  (150 data, here proposed from 5 to 135,  $x$ -axis). A convenient scale is used for  $y$ -axis. The best position of the  $q$ -Gaussian center is  $n=38$ . The following Figure 5 is illustrating the role of the center position.

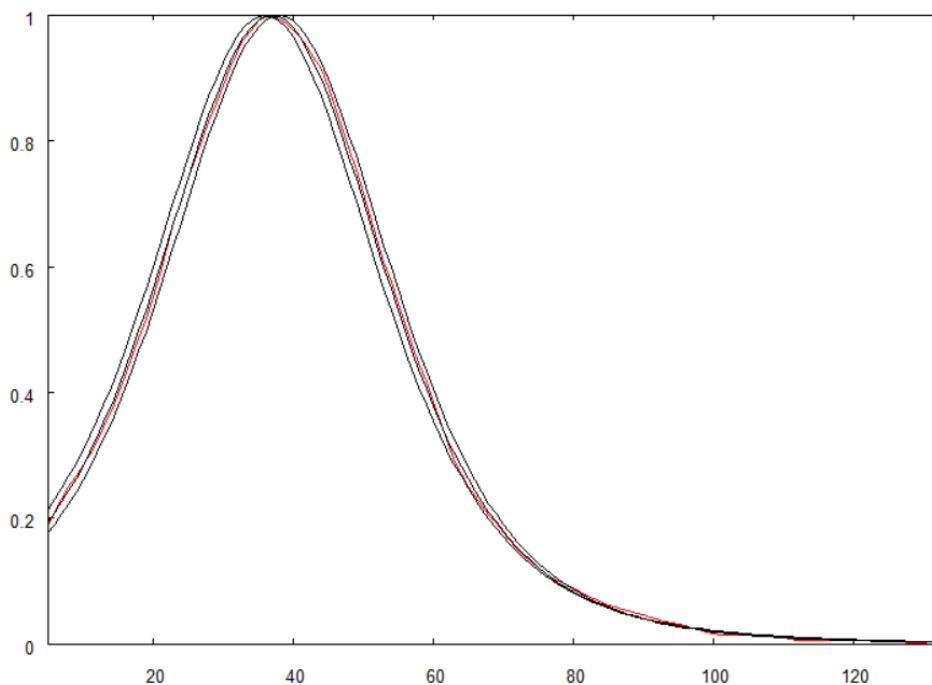


Figure 5: This plot is proposed to illustrate the role of the center position of  $q$ -Gaussian function. Data are given in red. The three black curves correspond to positions  $n=37$ ,  $n=38$  (as in the Figure 4) and  $n=39$ . As told in the caption of Fig.4, the  $q$ -Gaussian with center  $n=38$  is perfectly fitting the data.

In this research we have proposed the use of  $q$ -Gaussians to fit the formamide Raman spectrum. The results that we have obtained are showing that  $q$ -Gaussians are properly fitting the spectrum and are perfect substitutes of the Egelstaff-Schofield line shapes, proposed by Kirillov, 2004. Besides being simple, the  $q$ -Gaussian is possessing a parameter, the  $q$ -parameter, which is a measure of the “intermediation”, between Lorentzian and Gaussian profiles, of each band component.

### Appendix

As given by Umarov et al., 2008, the  $q$ -Gaussian function is:  $f(x) = C e_q(-\beta x^2)$ , where  $e_q(\cdot)$  is the  $q$ -exponential function and  $C$  a scale constant. In the exponent, we use  $\beta = 1/(2\sigma^2)$ . The  $q$ -exponential has the expression:

$$\exp_q(u) = [1 + (1 - q)u]^{1/(1-q)} \quad (2).$$

The plots in the Figures 1 and 2 are showing the behaviour of this exponential for different  $q$  values. Note that, for  $q$  less than one, the function is different from zero on a limited interval.

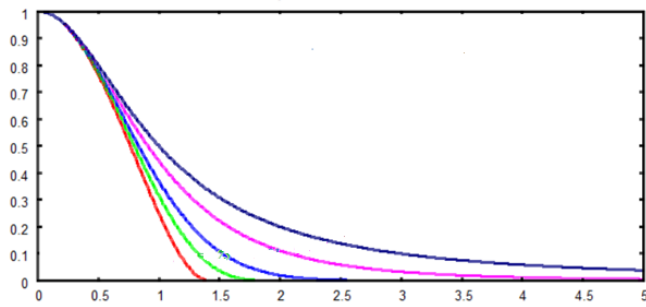


Fig.1:  $q$ - exponential functions, where the blue curve is representing a Lorentzian function ( $q=2$ ). The pink curve corresponds to  $q=1.5$  and light blue to  $q=1.01$ , practically a Gaussian function. The green curve is the  $q$ -Gaussian for  $q=0.75$  and red curve for  $q=0.5$ . For  $q < 1$ , the function is different from zero in a limited interval. Being the line symmetric, only the right part of it is given in the figure.

The Half Width at Half Maximum of  $q$  line shape is given by:  $\sqrt{2} \sigma \sqrt{(1 - (1/2)^{1-q}) / (1 - q)}$ .

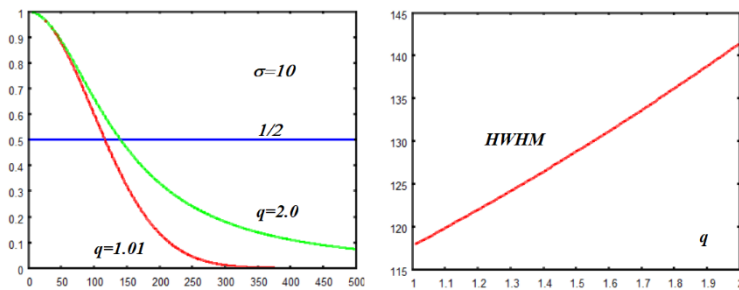


Fig.2:  $q$ - exponential functions for  $q=1.01$  and  $q=2$  on the left, on the right the Half Width at Half Maximum as a function of  $q$ .

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