Signal to Noise Improvement in Simple Spectroscopic Line Shape Studies

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Often in spectroscopic line shape experiments one is interested in the line width of a Gaussian or Lorentzian profile. We want to call attention to a simple numerical procedure which allows a significant signal to noise improvement in such studies.

In this communication we want to call attention to a rather simple numerical method to improve the signal to noise ratio in spectroscopic line shape experiments, which to our knowledge has not been used in the present context. As is well known, under certain limiting conditions, e. g. central limit or live time broadening [1], the line shape becomes Gaussian or Lorentzian. These situations are frequently observed in wide line nuclear magnetic resonance experiments [1] or in Raman band studies [2]. A common procedure to improve the signal to noise ratio in such studies is to superimpose the signals of subsequent scans, which results in an improvement of this ratio with the square root of the number of scans. The physical basis of the signal to noise improvement is the correlation of signals of different scans. Since the noise is uncorrelated from scan to scan the resulting noise is the square root of the sum of the squared single-scan noise intensities, whereas the signal amplitude improves linearly.

A more efficient averaging of the noise can be achieved if the line shape is known in advance. In this case one obtains a meaningful result not only by pointwhise correlating the spectra but also by correlating the full spectra with each other. The cross-correlation function $\hat{I}(\omega)$ of two spectra $I_1(\omega)$ and $I_2(\omega)$ of different scans is defined as [3]:

$$\hat{I}(\omega) = \int_{-\infty}^{+\infty} I_1(\omega_1) \cdot I_2(\omega_1 + \omega)\,\mathrm{d}\omega_1 . \tag{1}$$

It will be assumed that the two spectra consist of a true spectrum $I(\omega)$ plus certain noise spectra $N_1(\omega)$ and $N_2(\omega)$ (detector noise):

$$I_1(\omega) = I(\omega) + N_1(\omega), \; I_2(\omega) = I(\omega) + N_2(\omega). \tag{2}$$

The correlation function now contains four contributions:

$$\begin{aligned} \hat{I}(\omega) &= \int_{-\infty}^{+\infty} I(\omega_1) I(\omega_1 + \omega)\,\mathrm{d}\omega_1 \\ &+ \int_{-\infty}^{+\infty} I(\omega_1) N_2(\omega_1 + \omega)\,\mathrm{d}\omega_1 \\ &+ \int_{-\infty}^{+\infty} N_1(\omega_1) I(\omega_1 + \omega)\,\mathrm{d}\omega_1 \\ &+ \int_{-\infty}^{+\infty} N_1(\omega_1) N_2(\omega_1 + \omega)\,\mathrm{d}\omega_1 . \end{aligned} \tag{3}$$

The first term is the autocorrelation function of the spectrum. The next two terms present cross-correlation functions of the noise with the spectrum. Here, fast fluctuating noise components average to zero, only slow fluctuations (of the order of the line width of $I(\omega)$ and larger) may survive. Further, a certain cancellation of the slow fluctuations occurs due to the statistical independence of the second and third term. The fourth contribution vanishes since $N_1(\omega)$ and $N_2(\omega)$ are statistically independent.

For Gaussian and Lorentzian line shapes $I(\omega)$ we have $I(\omega) = I(-\omega)$ and, therefore, the first term of Eq. (3) can be rewritten as:

$$\begin{aligned} \hat{I}_1(\omega) &= \int_{-\infty}^{+\infty} I(\omega_1) I(\omega_1 + \omega)\,\mathrm{d}\omega_1 \\ &= \int_{-\infty}^{+\infty} I(-\omega_1) \cdot I(\omega_1 + \omega)\,\mathrm{d}\omega_1 \\ &= \int_{-\infty}^{+\infty} I(\omega_1') \cdot I(\omega - \omega_1')\,\mathrm{d}\omega_1' , \end{aligned} \tag{4}$$

where in the last step ω_1 has been replaced by $-\omega_1'$. The last form of Eq. (4) is the convolution of $I(\omega)$ with itself [3]. Now it is well known [3], that the convolution of a Gaussian with itself results in a Gaussian with $\sqrt{2}$ times the half width of the original Gaussian and, similarly, convolution of a Lorentzian with itself leads to a Lorentzian with twice the original half width. This enables us to interpret the cross correlated spectra $\hat{I}(\omega)$ for these simple line shapes.

In Fig. 1 and Fig. 2 we present one example each for a Gaussian and a Lorentzian band. In both cases the spectra (only one of which is shown) have been created numerically on a digital computer by superimposing normally distributed pseudo-random num-

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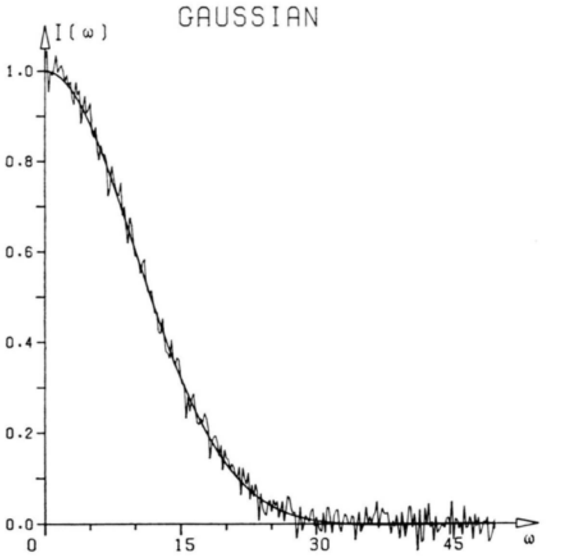

Fig. 1. Signal to noise improvement by cross-correlating two scans of a Gaussian spectrum. Details are given in the text.

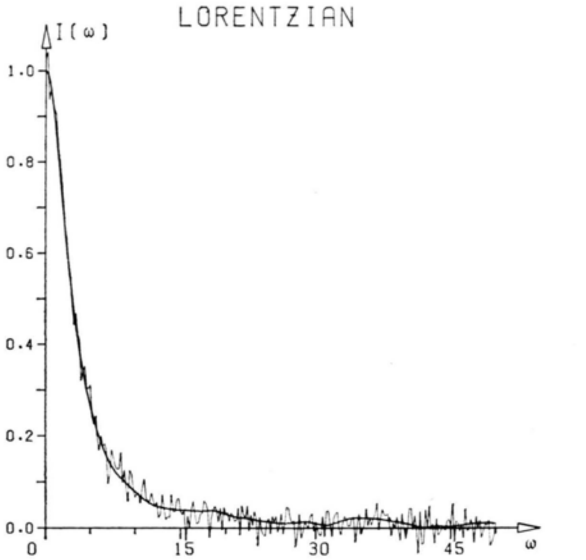

Fig. 2. Signal to noise improvement by cross-correlating two Lorentzian spectra.

bers on a Gaussian or Lorentzian, respectively. The solid lines give $\hat{I}(\omega)$ which has been calculated according to Equation (1). In order to facilitate the comparison the spectra have been normalized so that $I(0) = \hat{I}(0) = 1$ and the cross-correlation spectra have been scaled on the frequency axis by a factor of $\sqrt{2}$ and 2 in Fig. 1 and Fig. 2, respectively. In both cases a considerable improvement of the signal to noise ratio has been achieved. The slow fluctuations which occur especially in Fig. 2 can be understood in terms of the discussion given above.

We should point out that the considerable improvement of the signal to noise ratio is accompanied by a loss in spectral information and an interpretation of the result $\hat{I}(\omega)$ is possible only if the precise shape of $I(\omega)$ is known, as discussed for Gaussian or Lorentzian spectra.

In conclusion, we mention that one could attempt to correlate one single spectrum directly with itself. But then the noise terms would no longer be statistically independent and the resulting $\hat{I}(\omega)$ would be the sum of the autocorrelation functions of $I(\omega)$ and of the noise $N(\omega)$, which is no longer related in a simple manner to the spectrum $I(\omega)$ of interest.

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