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LETTER TO THE EDITOR

Sum rules in testing non-linear susceptibility obtained using the maximum entropy model

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Abstract. The applicability of sum rules of non-linear optical constants is shown using the coherent anti-Stokes Raman spectrum of nitrogen Q-branch and the associated complex third-order non-linear susceptibility obtained by a procedure utilizing the maximum-entropy model.

About twenty years ago, Altarelli *et al* [1–2] derived sum rules for linear optical constants. Such sum rules are integral equations that can be considered as constraints for the frequency dependent complex refractive index or permittivity. Sum rules can provide information about the oscillator strengths or they can be simply exploited to test the validity of a measured spectrum of an optical constant or the validity of a spectrum obtained from the Kramers–Kronig dispersion relations [3–4].

Some years ago, Peiponen [5–8] derived a set of sum rules for non-linear susceptibilities under the assumption of an anharmonic oscillator model. Basically these sum rules resemble those of linear optical constants. It was recently pointed out that the assumption of the anharmonic oscillator model is not necessary in order to derive sum rules for non-linear optical constants [9]. Bassani and Scandolo [10] confirmed the existence of the previously derived sum rules in [5–8] and presented also new sum rules for non-linear optical constants. Furthermore, they investigated the role of sum rules of non-linear optical processes in the interpretation of atomic transitions and exciton transitions in solids using theoretical line models for the non-linear permittivity [11]. So far the applicability of the sum rules in [5–11] have not been verified for experimental data. Such evidence will be presented in this work.

In non-linear optics, it is common that, in experiments, one can obtain information only about the squared modulus of the non-linear susceptibility of the material. This is the case for instance when we measure coherent anti-Stokes Raman spectra (CARS). Now a problem arises if the sum rules in [5–11] are taken into consideration. They are useless unless the real and imaginary parts of the susceptibility can be resolved. One can imagine that, if the CARS signal takes a complicated function of frequency, the separation of the real and imaginary parts is difficult even if one uses the Lorentzian line fitting technique [12, 13]. This problem was one of the reasons why sum rules were derived for the modulus of the non-linear susceptibility itself [14].

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To overcome the above mentioned problem, Vartiainen [15] presented recently a novel method, which is based on the exploitation of a maximum entropy model [16] that makes it possible to resolve the real and imaginary parts from a complicated spectrum proportional to the squared modulus of the non-linear susceptibility. The method was applied to study the third-order non-linear susceptibility involved in CARS spectra. For details of the calculation procedure we only refer here to the ref. [15]. After the realization of this new method, the sum rules for the real and imaginary parts can be applied to test the calculated data.

Let us consider as an example the CARS spectrum which is proportional to $|\chi^{(3)}(\Delta = \omega_1 - \omega_2)|^2 = |\chi_N + \chi_R(\Delta)|^2$, where $\chi^{(3)}$ is the effective third-order non-linear susceptibility, χ_N is the non-resonant background, and χ_R is the Raman susceptibility. The variables ω_1 and ω_2 are the angular frequencies of the two pump lasers. Usually one of the frequencies is fixed while the other is scanned so that the difference $\Delta = \omega_1 - \omega_2$ sweeps over the desired Raman resonances. Since $\chi_R(\Delta)$ can be assumed to fall off faster than $\sim O(\Delta^{-1})$ at high frequencies where there are no Raman resonancies, and since the symmetry relation $\chi_R^*(\Delta) = \chi_R(-\Delta)$ now holds, we can write the following sum rules [6, 9] for the Raman susceptibility $\chi_R = \chi^{(3)} - \chi_N$:

$$\int_0^\infty [\mathrm{Re}\,\chi^{(3)}(\Delta) - \chi_N]\mathrm{d}\Delta = 0 \tag{1}$$

$$\int_0^\infty [\mathrm{Re}\,\chi^{(3)}(\Delta) - \chi_N]^2\mathrm{d}\Delta = \int_0^\infty [\mathrm{Im}\,\chi^{(3)}(\Delta)]^2\mathrm{d}\Delta \tag{2}$$

where χ_N is assumed to have a real value.

Next we show how these sum rules in equations (1) and (2) can be applied in practice, where the measurement is always limited to a finite frequency range $\Delta_1 \leqslant \Delta \leqslant \Delta_2$. According to equation (1) we can write

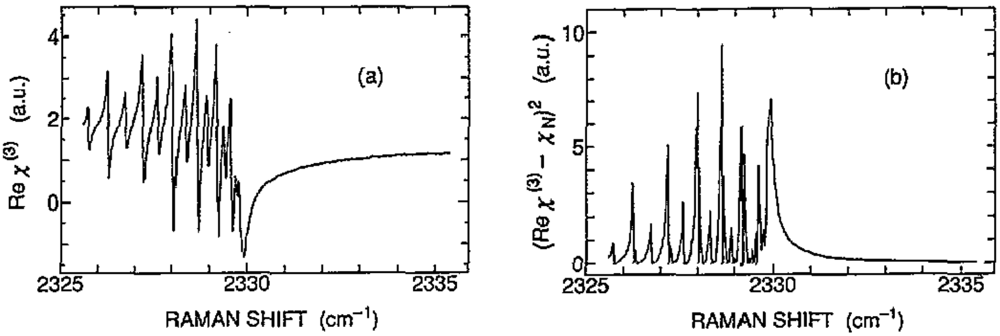
$$I_1(\Delta_{21}) = \Delta_{21}^{-1} \int_{\Delta_1}^{\Delta_2} \mathrm{Re}\,\chi^{(3)}(\Delta)\,\mathrm{d}\Delta = \chi_N \pm |\epsilon_{21}| \tag{3}$$

where $\Delta_{21} = \Delta_2 - \Delta_1$ and $\pm|\epsilon_{21}|$ is a deviation parameter whose value depends on Δ_{21}; consequently $|\epsilon_{21}| \to 0$ when $\Delta_{21} \to \infty$. Futhermore, we can assume that, when Δ is away from any resonances, Im $\chi^{(3)}(\Delta)$ falls off much faster than Re $\chi^{(3)}(\Delta) - \chi_N$. Thus, it follows from equation (2) that

$$I_2(\Delta_{21}) = \int_{\Delta_1}^{\Delta_2} [\mathrm{Re}\,\chi^{(3)}(\Delta) - \chi_N]^2\,\mathrm{d}\Delta \leqslant \int_{\Delta_1}^{\Delta_2} [\mathrm{Im}\,\chi^{(3)}(\Delta)]^2\,\mathrm{d}\Delta = I_3(\Delta_{21}). \tag{4}$$

Now, the above integrals $I_1(\Delta_{21})$ and $I_3(\Delta_{21})$ we can directly compute since their integrands are obtained by the maximum entropy procedure. The value of $I_2(\Delta_{21})$ usually remains unknown since the value of χ_N is not generally known nor can it be directly obtained from a CARS measurement. However, it follows from equation (3) that

$$\begin{aligned} I_4(\Delta_{21}) &= \int_{\Delta_1}^{\Delta_2} [\mathrm{Re}\,\chi^{(3)}(\Delta) - I_1(\Delta_{21})]^2\,\mathrm{d}\Delta = \int_{\Delta_1}^{\Delta_2} [\mathrm{Re}\,\chi^{(3)}(\Delta) - \chi_N]^2\,\mathrm{d}\Delta \\ &\quad \mp 2|\epsilon_{21}| \int_{\Delta_1}^{\Delta_2} [\mathrm{Re}\,\chi^{(3)}(\Delta) - \chi_N]\,\mathrm{d}\Delta + |\epsilon_{21}|^2 \int_{\Delta_1}^{\Delta_2} \mathrm{d}\Delta \\ &= I_2(\Delta_{21}) - |\epsilon_{21}|^2\Delta_{21} \end{aligned} \tag{5}$$



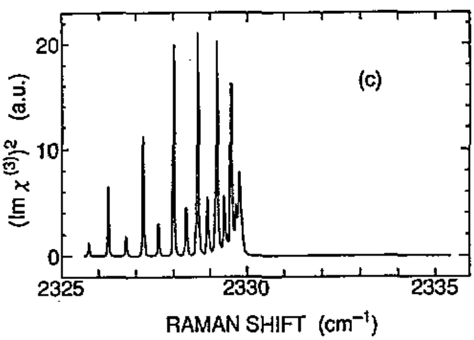


Figure 1. Maximum entropy estimates of CARS spectrum $|\chi^{(3)}|^2$ of the nitrogen Q-branch: (a) Re $\chi^{(3)}$, (b) (Re $\chi^{(3)} - \chi_N)^2$ and (c) (Im $\chi^{(3)})^2$.

and further from equations (4) and (5) that

$$I_2(\Delta_{21}) = I_4(\Delta_{21}) + |\epsilon_{21}|^2\Delta_{21} \leqslant I_3(\Delta_{21}) \tag{6}$$

or

$$|\epsilon_{21}|^2 \leqslant \Delta_{21}^{-1}[I_3(\Delta_{21}) - I_4(\Delta_{21})] = |\delta_{21}|^2 \,. \tag{7}$$

Thus, by using the inequality $-|\delta_{21}| \leqslant \pm|\epsilon_{21}| \leqslant |\delta_{21}|$ and equation (3), the upper and lower limits of the non-resonant susceptibility can be estimated as

$$I_1(\Delta_{21}) - |\delta_{21}| \leqslant \chi_N \leqslant I_1(\Delta_{21}) + |\delta_{21}| \,. \tag{8}$$

We applied the present analysis for the calculated data of [15] in the case of the nitrogen Q-branch (lines $Q(0)$–$Q(15)$). The corresponding CARS spectrum, measured by Farrow and Rahn [12], shows the presence of a relatively strong background susceptibility of argon owing to the fact that the spectrum was obtained from a 1% nitrogen-in-argon mixture. After measuring the Raman broadening *coefficients (for nitrogen broadened by argon), i.e. the linewidths, using the high-*resolution inverse-Raman spectroscopy (IRS) technique [17], Farrow and Rahn were able to compare their measurements with theoretical spectra and obtained the value $\chi_N = 9.6 \times 10^{-18}\text{cm}^3\ \text{erg}^{-1} \pm 10\%$ for the background susceptibility. This was 17% smaller than the value $\chi_N = 11.63 \times 10^{-18}\text{cm}^3\ \text{erg}^{-1}$ initially proposed by Rado [18] and rescaled by Hall and Eckbreth [19]. In figure 1(a), (b) and (c) we show the curves of Re $\chi^{(3)}$, (Re $\chi^{(3)} - \chi_N)^2$ and (Im $\chi^{(3)})^2$, respectively. These were obtained as explained in [15]. The curves are shown in the same arbitrary units corresponding to the original CARS spectrum in [12]. In this arbitrary scale the correct value of χ_N is 1.33. After evaluating the integrals $I_1(\Delta_{21})$, $I_3(\Delta_{21})$ and $I_4(\Delta_{21})$ numerically, with $\Delta_1 = 2325.6\ \text{cm}^{-1}$ and $\Delta_2 = 2335.4\ \text{cm}^{-1}$, we obtained the limits to χ_N (transformed into true units) as $6.1 \times 10^{-18}\text{cm}^3\ \text{erg}^{-1} \leqslant \chi_N \leqslant 10.9 \times 10^{-18}\text{cm}^3\ \text{erg}^{-1}$.

Although the above range of possible values for χ_N given by the present analysis is rather wide due to the low value of $\Delta_{21} = 9.8\ \text{cm}^{-1}$, it is nevertheless tight enough to rule out the possibility of the intially proposed value for χ_N being correct. It should be further pointed out that the present result was obtained without using any specific theoretical fits nor using any additional information (about linewidths, Raman cross section or amplitudes etc) apart from the measured CARS spectrum and its maximum entropy estimates. As a conclusion, we may state that sum rules for non-linear susceptibilities can be used to estimate the value of the background susceptibility when applied to CARS measurements. This is important in theoretical modelling or in order to obtain information about the bulk properties of the material under investigation.

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