ON THE DENSITY EXPANSION OF SPECTRAL LINESHAPES

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We compare two types of expansions (in the density of perturbers) of collisionally broadened spectral lineshapes. The first is the more conventional frequency-domain expansion of Fano whereas the second is made in the time domain. In the impact limit they both predict a simple lorentzian line shape but otherwise they yield very different results upon truncation. Our calculations indicate that the time-domain expansion is more adequate and should be preferred.

We consider a two-level absorber (the "system") interacting with a radiation field with frequency ω and with a bath of perturbers which may be either different atoms (foreign broadening) or identical with the system atom (self broadening). The absorption lineshape is given by [1]

$$\hat{I}(\Delta) = -(1/\pi)\,\mathrm{Im}\,I(\Delta)\,, \tag{1}$$

where

$$I(\Delta) = -\mathrm{i}\int_0^\infty \mathrm{d}\tau\,\exp(\mathrm{i}\Delta\tau)\,I(\tau)\,. \tag{2}$$

Here Δ (eq. (7)) is the detuning of ω from the two-level frequency and $I(\tau)$ is the dipole correlation function $I(\tau) = \langle D(\tau)\,D(0)\rangle$. We wish to evaluate $I(\tau)$ microscopically using the potentials of interaction of the various atoms involved. Fano had shown how $I(\Delta)$ may be expanded in the density of perturbers $n = N/\Omega$ (N being the number of atoms and Ω is the volume). The expansion is based on the conventional reduced equations of motion used in statistical mechanics which are non-local in time, and assumes the form [2, 3]:

$$I^{\mathrm{COP}}(\Delta) = 1/[\Delta - \tilde{F}(\Delta)]\,, \tag{3}$$

where

$$\tilde{F}(\Delta) = \sum_{q=1}^{\infty} \frac{n^q}{q!}\,\tilde{F}_q(\Delta)\,. \tag{3a}$$

The various terms $\tilde{F}_q(\Delta)$ have closed formal expressions which are quite complicated to evaluate. The superscript "COP" (chronological time ordering prescription) indicates that $F(\Delta)$ exhibits an expansion which is completely time ordered [4]. An alternative expansion which was developed recently is based on a new type of reduced equations of motion which are local in time and reads [4,5]

$$I^{\mathrm{POP}}(\tau) = \exp[-F(\tau)]\,, \tag{4}$$

where

$$F(\tau) = \sum_{q=1}^{\infty} \frac{n^q}{q!}\,F_q(\tau)\,. \tag{4a}$$

The superscript "POP" (partial time ordering prescription) indicates that the expansion of $F(\tau)$ contains terms which are only partially time ordered [4]. Both expansions (3) and (4) are in principle exact but may yield different results upon truncation. The simplest way to get $\tilde{F}_q(\Delta)$ or $F_q(\tau)$ is to derive a naive density expansion of $I(\tau)$ [4,5]:

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$$I(\tau) = 1 + \sum_{q=1}^{\infty} \frac{n^q}{q!} \chi_q(\tau) , \tag{5}$$

where $\chi_q(\tau)$ are related to the spectrum of a system containing the absorber + q perturbers and are readily available for small q. $\tilde{F}_q(\Delta)$ or $F_q(\tau)$ may be then expressed in terms of $\chi_{q'}(\tau)$ $(q' \leqslant q)$ by expanding eqs. (3) and (4) in n and comparing term by term with eq. (5). A detailed analysis and comparison of both expansions was given recently [4]. We should note that if either of the expansions (3), (4) or (5) is truncated at the q'th order then the first q moments of the lineshape (1) will be exact and the difference between the various expansion will enter only in the higher moments. We shall consider here the expansions to first order in density. In this case both expansions are given in terms of $\chi_1(\tau)$, i.e. [4]

$$I^{\mathrm{COP}}(\Delta) = \left[\Delta - \mathrm{i}n \int_0^{\infty} \mathrm{d}\tau \exp(\mathrm{i}\Delta\tau)\, \ddot{\chi}_1(\tau)\right]^{-1} , \tag{6a}$$

and

$$I^{\mathrm{POP}}(\Delta) = -\mathrm{i} \int_0^{\infty} \mathrm{d}\tau \exp\left[\mathrm{i}\Delta\tau + n \int_0^{\tau} \mathrm{d}\tau_1 \, (\tau - \tau_1)\, \ddot{\chi}_1(\tau_1)\right] , \tag{6b}$$

where Δ is the detuning of the radiation field from the two-level frequency ω_{ba},

$$\Delta = \omega - \omega_{\mathrm{ba}} - n\mathrm{i}\dot{\chi}_1(0) . \tag{7}$$

$\chi_1(\tau)$ depends on the dynamics of a pair of atoms (absorber + a single perturber) and the dot in $\dot{\chi}_1$ denotes derivative with respect to time $\dot{\chi}_1 = \mathrm{d}\chi_1/\mathrm{d}\tau$ etc. $\mathrm{i}\dot{\chi}_1(0)$ is a real number and is a static level shift. In order to write $\chi_1(\tau)$ explicitly let us denote the potential of interaction between the absorber in the $|\mathrm{a}\rangle$ ($|\mathrm{b}\rangle$) state and the perturber by $V_{\mathrm{a}}(Q)$ ($V_{\mathrm{b}}(Q)$), Q being their relative separation. We further introduce the box normalized states $\{|\alpha\rangle\}$ and $\{|\beta\rangle\}$ defined as follows:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2} + V_{\mathrm{a}}(Q)\right]|\alpha\rangle = E_\alpha |\alpha\rangle , \tag{8a}$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2} + V_{\mathrm{b}}(Q)\right]|\beta\rangle = E_\beta |\beta\rangle . \tag{8b}$$

$\chi_1(\tau)$ then assumes the form:

$$\chi_1(\tau) = \Omega \sum_{\alpha\beta} P(\alpha) |\langle\alpha|D|\beta\rangle|^2 \times [\exp(\mathrm{i}\omega_{\alpha\beta}\tau) - 1]/\langle D^2\rangle , \tag{9a}$$

so that

$$\dot{\chi}_1(0) = \mathrm{i}\Omega \sum_{\alpha\beta} P(\alpha) |\langle\alpha|D|\beta\rangle|^2 \omega_{\alpha\beta}/\langle D^2\rangle , \tag{9b}$$

$$\ddot{\chi}_1(\tau) = -\Omega \sum_{\alpha\beta} P(\alpha) |\langle\alpha|D|\beta\rangle|^2 \times \omega_{\alpha\beta}^2 \exp(\mathrm{i}\omega_{\alpha\beta}\tau)/\langle D^2\rangle , \tag{9c}$$

and

$$\langle D^2\rangle = \sum_{\alpha\beta} P(\alpha) |\langle\alpha|D|\beta\rangle|^2 . \tag{9d}$$

$P(\alpha)$ is the equilibrium population of $|\alpha\rangle$ i.e.

$$P(\alpha) = \exp(-E_\alpha/kT) \Big/ \sum_{\alpha} \exp(-E_\alpha/kT) . \tag{9e}$$

We have recently calculated $\chi_1(\tau)$ for a collinear model system with exponential repulsive interactions [6], i.e.

$$V_{\mathrm{a}}(Q) = A_{\mathrm{a}} \exp(-Q/L) , \tag{10a}$$

$$V_{\mathrm{b}}(Q) = A_{\mathrm{b}} \exp(-Q/L) , \tag{10b}$$

and

$$D = |b\rangle\langle a| + |a\rangle\langle b| . \tag{10c}$$

Here L is the range of the interaction and we have taken the dipole D to be independent on Q. The line broadening arises in this case from the difference $V_{\mathrm{a}} - V_{\mathrm{b}}$. We shall therefore introduce the dimensionless parameter C which measures the strength of the line broadening interaction

$$C = A_{\mathrm{b}}/A_{\mathrm{a}} - 1 . \tag{11}$$

Since our calculation is collinear, we shall introduce an effective collision rate f defined as

$$f = n\sigma\bar{v} , \tag{12}$$

where σ and $\bar{v}$ are an effective cross section and the relative velocity, respectively. We then write

$$n \int_0^{\infty} \mathrm{d}\tau\, \ddot{\chi}_1 \exp(\mathrm{i}\Delta\tau) \equiv f R(\Delta) , \tag{13}$$

where

$$R(\Delta) = R_1(\Delta) + \mathrm{i}R_2(\Delta) , \tag{14}$$

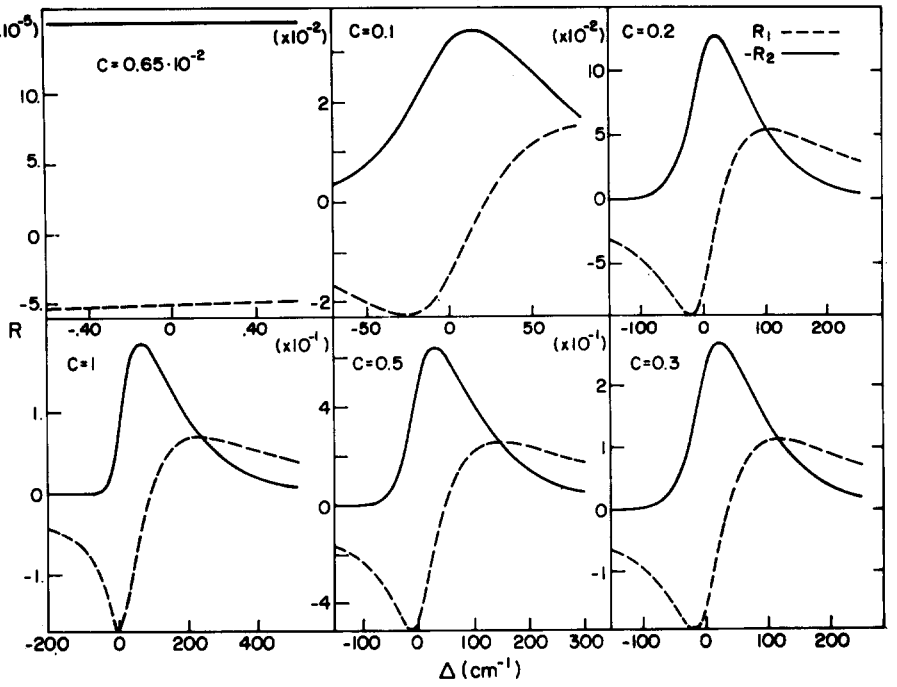

Fig. 1. The dimensionless line broadening function $R(\Delta)$ eq. (15) for various values of the interaction strength C. $T = 77$ K, the reduced mass of the absorber-perturber $m = 14$, $f = 0.8 \times 10^{13}$ Hz (typical collision frequency in a liquid), $L = 0.2$ Å, details of the calculation are given in ref. [6]

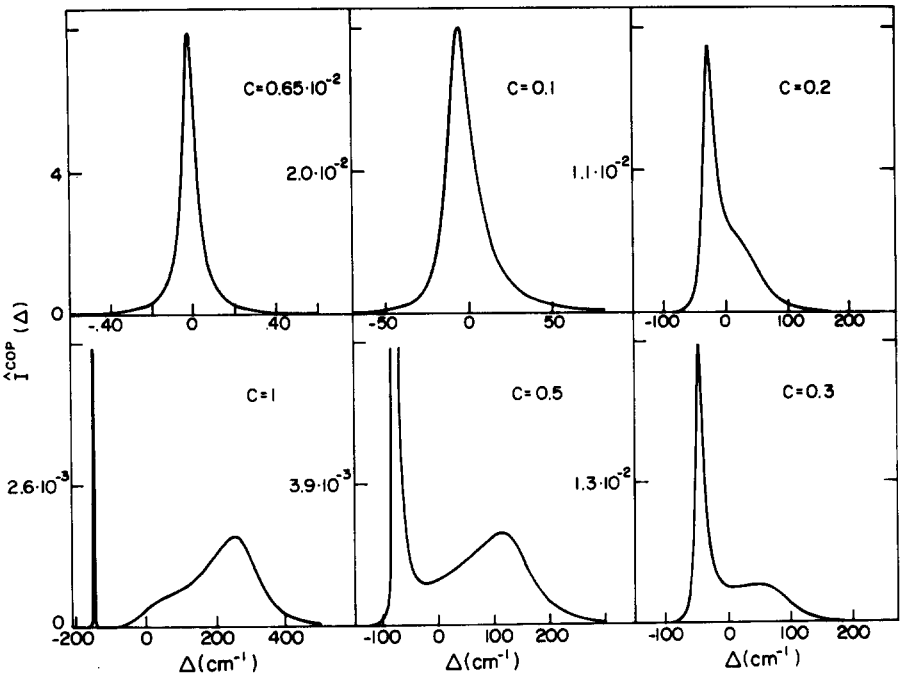

Fig. 2. The COP lineshapes (eq. (6a)) using the same parameters as in fig. 1.

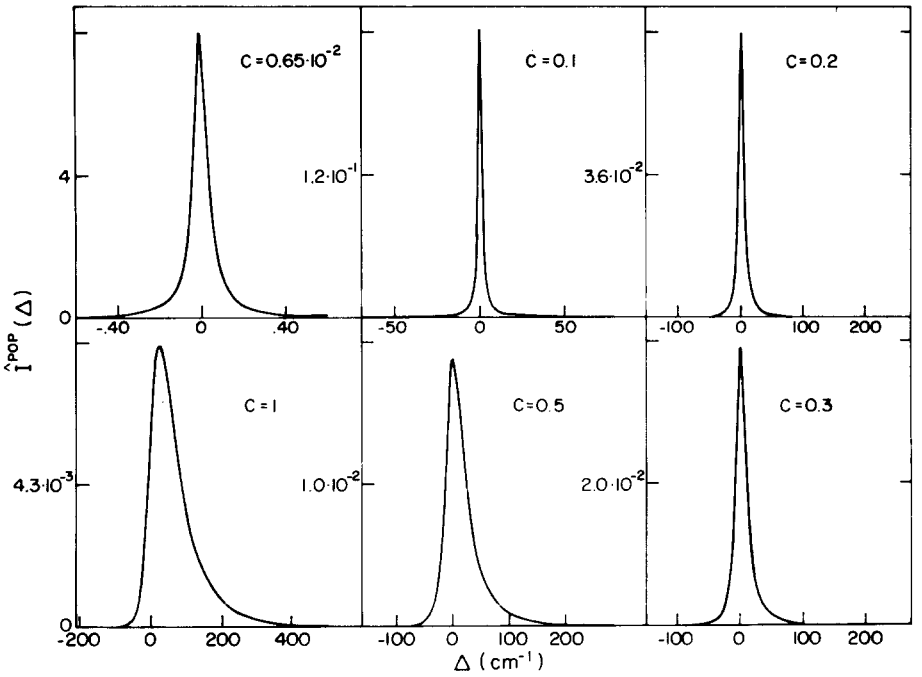

Fig. 3. The POP lineshapes (eq. (6b)) using the same parameters as in fig. 1.

is a dimensionless measure of the line broadening and where

$$R_2(\Delta) = \frac{-\pi n \Omega}{f} \sum_{\alpha,\beta} P(\alpha)\, \omega_{\alpha\beta}^2 |\langle\alpha|\beta\rangle|^2 \delta(\omega - \omega_{\alpha\beta}) , \tag{15a}$$

and

$$R_1(\Delta) = \frac{1}{\pi} \mathrm{PP} \int_{-\infty}^{\infty} \mathrm{d}\Delta' \frac{R_2(\Delta')}{\Delta' - \Delta} . \tag{15b}$$

The detailed evaluation of R is presented in ref. [6]. We present here a few calculations of $R(\Delta)$, $I^{\mathrm{COP}}(\Delta)$, and $I^{\mathrm{POP}}(\Delta)$ to lowest order in density for various values of the line broadening interaction strength C (eq. (11)). When C is small enough we are in the impact limit and both lines reduce to the simple lorentzian form:

$$I^{\mathrm{COP}}(\Delta) = I^{\mathrm{POP}}(\Delta) = \frac{1}{\pi} \frac{\Gamma}{\Delta^2 + \Gamma^2} , \tag{16}$$

where

$$\Gamma = -f R_2(0) . \tag{17}$$

Otherwise I^{POP} and I^{COP} may be very different. Fig. 1 shows $R_1(\Delta)$ and $R_2(\Delta)$ for various values of C whereas figs. 2 and 3 present $I^{\mathrm{COP}}(\Delta)$ and $I^{\mathrm{POP}}(\Delta)$ respectively calculated using $R(\Delta)$ of fig. 1. We note that the POP lineshapes are well behaved in all cases and are gradually broadened as C increases whereas the COP lines exhibit a very peculiar behaviour for large C and they are split into two components. For the simple potentials used eq. (10) which contain no resonances this is a very unphysical behaviour and is clearly an artifact of the usage of the COP scheme. We further note that the first order POP line (eq. (6b)) has a simple physical significance, it is the *exact* solution of the Anderson-Talman model [6,7] where the perturber atoms are assumed to interact with the absorber but not with each other. We thus conclude that the POP expansion scheme seems much more adequate for the density expansion of spectral lineshapes.

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