Reprint from:
Spectral Line Shapes · Editor: B. Wende

UNIFIED THEORY OF PRESSURE BROADENED ABSORPTION SPECTRA IN STRONG RADIATION FIELDS

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We consider a two-level molecular system ($|a\rangle$ and $|b\rangle$) which interacts with a strong monochromatic radiation field and with a bath of foreign perturbers in the low pressure gas phase. We assume that the perturbers do not induce relaxation of population (T_1) but have only diagonal interactions with the two-level system. The total hamiltonian within the rotating wave approximation is

$$H = H_0 + V \tag{1}$$

where

$$H_0 = \frac{1}{2}\Delta(|a\rangle\langle a| - |b\rangle\langle b|) + |a\rangle F_a(Q_B)\langle a| + |b\rangle F_b(Q_B)\langle b|, \tag{1a}$$

and

$$V = \mu(|a\rangle\langle b| + |b\rangle\langle a|) \tag{1b}$$

Here $\Delta = \omega_L - \omega_{ba}$ is the detuning of the radiation frequency (ω_L) from the two-level frequency ω_{ba}, and μ is the Rabi frequency (transition dipole times the field amplitude). The second term in H_o describes the two-level system interacting with the bath. Within the binary collision approximation we assume additive interactions of our system with the ν'th bath particle i.e.

$$F_i(Q_B) = \sum_\nu F_{i\nu}(Q_{B\nu}) \quad , \quad i = a,b \tag{2}$$

The eigenstates of F_a and F_b (normalized in a box with volume Ω) are therefore

$$|a\alpha\rangle = |a\rangle \prod_\nu |\alpha_\nu\rangle \tag{3a}$$

and

$$|b\beta\rangle = |b\rangle \prod_\nu |\beta_\nu\rangle \tag{3b}$$

with eigenvalues E_α and E_β respectively.

The time evolution of the density matrix for the entire system + bath + the radiation field is given by the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho - i\tilde{L}\rho \tag{4}$$

where $L \equiv [H, \ ]$ is the Liouville operator (commutator) corresponding to H. (Similarly we define $L_o \equiv [H_o, \ ]$ and $V \equiv [V, \ ]$). $\tilde{L}$ is a T_1 relaxation matrix $\tilde{L}_{aa,aa} = -\tilde{L}_{bb,aa} = -i\gamma_a$, $\tilde{L}_{bb,bb} = -\tilde{L}_{aa,bb} = -i\gamma_b$ and $\tilde{L}_{ab,ab} = \tilde{L}_{ba,ba} = -\frac{1}{2}\gamma$, where $\gamma = \gamma_a + \gamma_b$. $\tilde{L}$ guarantees the relaxation of the two-level system (in the absence of driving, $\mu = 0$) to thermal equilibrium where $\rho^{eq}_{aa} = \gamma_b/\gamma$ and $\rho^{eq}_{bb} = \gamma_a/\gamma$.

The absorption line shape $I(\Delta)$ for the system described by the Liouville equation (4) may be solved making use of the tetradic scattering formalism [1-7]. The final result is

$$I(\Delta) = (\rho_{aa}^{eq} - \rho_{bb}^{eq})S(\Delta) \tag{5}$$

where

$$S(\Delta) = \frac{R(\Delta)}{1+\frac{2}{\gamma} R(\Delta)} \tag{6}$$

and

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) - \mu^4 R^{(4)}(\Delta) + \mu^6 R^{(6)}(\Delta)..... \tag{7}$$

The n'th term in equation (7) is given by

$$R^{(2n)}(\Delta) = 2^{n-1} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \cdots \int_0^\infty d\tau_{2n-1}\, K^{(2n)}(\tau_1,\ldots,\tau_{2n-1})$$
$$\exp\left[- \tfrac{\gamma}{2} (\tau_1+2\tau_2+\tau_3+2\tau_4+....)\right] , \tag{8}$$

where $K^{(2n)}$ is a 2n'th order cumulant given formally by

$$K^{(2n)}(\tau_1,\tau_2,\ldots,\tau_{2n-1}) = \frac{1}{\mu^{2n}} \operatorname{Tr}_{bath} \langle\langle aa| \nu(t_1)\nu(t_2)\, D\nu(t_3)\nu(t_4) D \ldots$$
$$\ldots D\nu(t_{2n-1})\nu(0)|aa\rangle\rangle \rho_B^o, \tag{9}$$

with

$$t_1 = \tau_1 + \tau_2 + \ldots + \tau_{2n-1}, \tag{10}$$
$$t_2 = \tau_2 + \tau_3 + \ldots + \tau_{2n-1},$$

$$t_{2n-1} = \tau_{2n-1}$$

and

$$\nu(\tau) = \exp(i L_o \tau)\ \nu \exp(-i L_o \tau). \tag{11}$$

The projection operator D is defined by (see Appendix)

$$D \equiv |aa\rangle\rangle\langle\langle aa| \ (1-\rho_B^o \mathrm{Tr}_{bath}) \tag{12}$$

and ρ_B^o is the canonical equilibrium distribution function for the bath

$$\rho_B^o = \sum_\alpha |\alpha> P(\alpha) <\alpha| , \tag{13a}$$

and

$$P(\alpha) = \exp(-E\alpha/kT)/Tr\ \exp(-F_a/kT). \tag{13b}$$

We may further define 2n'th order moments $M^{(2n)}(\tau_1,\tau_2,\ldots,\tau_{2n-1})$ by an expression similar to (9) whereby each projection D is replaced by $D_a = |aa>><<aa|$. From these definitions we see that each cumulant $K^{(2n)}$ may be expressed in terms of the lower moments $M^{(j)}$, j = 2,4,..,2n, i.e.

$$K^{(2)}(\tau_1) = M^{(2)}(\tau_1), \tag{14a}$$

$$K^{(4)}(\tau_1,\tau_2,\tau_3) = M^{(4)}(\tau_1,\tau_2,\tau_3) - M^{(2)}(\tau_1)M^{(2)}(\tau_3), \tag{14b}$$

$$K^{(6)}(\tau_1,\ldots,\tau_5) = M^{(6)}(\tau_1,\ldots\tau_5) - M^{(4)}(\tau_1,\tau_2,\tau_3)M^{(2)}(\tau_5) - M^{(2)}(\tau_1)M^{(4)}(\tau_3,\tau_4,\tau_5) - M^{(2)}(\tau_1)M^{(2)}(\tau_3)M^{(2)}(\tau_5) \text{ etc.} \tag{14c}$$

The molecular information relevant for the absorption line shape in a strong field is thus expressed in terms of the hierarchy of moments $M^{(2n)}$ which are used to construct $R^{(2n)}$. This is a common feature to multiphoton processes in general [5-7]. The evaluation of $M^{(2)}$ is equivalent to the solution of the ordinary (weak field) line shape [8-10] so that we have

$$K^{(2)}(\tau) = M^{(2)}(\tau) = \exp[-i\Delta\tau - g(\tau)] + C.C \tag{15}$$

where

$$g(\tau) = \frac{N}{\Omega} \sum_{\alpha,\beta} P(\alpha)|<\alpha|\beta>|^2(1-\exp(i\omega_{\beta\alpha})), \tag{16}$$

and $\omega_{\beta\alpha} = E_\beta - E_\alpha$. Substitution of (16) in (8) results in

$$R^{(2)} = 2Re \int_0^\infty d\tau \exp[-i\Delta\tau - \tfrac{1}{2}\gamma\tau - g(\tau)]. \tag{17}$$

We note that $g(\tau)$ is a single-particle correlation function involving the Franck-Condon overlap factors $\langle\alpha|\beta\rangle$ of the F_a and F_b potential surfaces and is proportional to the number density of perturbers N/Ω (where N is the number of perturber molecules and Ω is the volume of the system).

All the moments $M^{(2n)}$ may be evaluated rigorously using a systematic density expansion [7] resulting in

$$R^{(4)} = 2\int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3$$
$$\left\{\exp\left[(-i\Delta - \tfrac{\gamma}{2})\tau_1 - g(\tau_1) + (-i\Delta - \tfrac{1}{2}\gamma)\tau_3 - g(\tau_3)\right]\right\} \exp\left[-\gamma\tau_2\right]$$
$$\left\{\exp\left[g(\tau_1+\tau_2) - g(\tau_2) + g(\tau_2+\tau_3) - g(\tau_1+\tau_2+\tau_3)\right] - 1\right\}$$
$$+ 2\int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3$$
$$\left\{\exp\left[(i\Delta - \tfrac{\gamma}{2})\tau_1 - g(\tau_1) + (-i\Delta - \tfrac{1}{2}\gamma)\tau_3 - g(\tau_3)\right]\right\} \exp\left[-\gamma\tau_2\right]$$
$$\left\{\exp\left[-g(\tau_1+\tau_2) + g(\tau_2) - g(\tau_2+\tau_3) + g(\tau_1+\tau_2+\tau_3)\right] - 1\right\} + C.C \qquad (18)$$

The general expression for the 2n'th moment is (for real $g(\tau)$)

$$M^{(2n)}(\tau_1, \tau_2 \ldots, \tau_{2n-1}) =$$
$$= \sum_{v_1=\pm 1} \sum_{v_2=\pm 1} \cdots \sum_{v_n=\pm 1} \left\{\exp\left[\sum_{k=1,3}^{2n-1} \phi_k(v_k)\right]\right.$$
$$\left.\exp\left[\sum_{k=1,3}^{2n-1} \sum_{\ell=k+2,k+4}^{2n-1} \xi_{k\ell}(v_k, v_\ell)\right]\right\}, \quad n \geq 2 \qquad (19)$$

where

$$\phi_k(+1) = -i\Delta\tau_k + g(\tau_k),$$
$$\phi_k(-1) = \phi_k^*(+1) = i\Delta\tau_k + g(\tau_k), \qquad (20)$$

and

$$\xi_{k,\ell}(+1,+1) = \xi_{k,\ell}(-1,-1) = -\xi_{k,\ell}(-1,+1) = -\xi_{k,\ell}(+1,-1) = g(t_k - t_\ell)$$
$$- g(t_k - t_{\ell-1}) - g(t_{k-1} - t_\ell) + g(t_{k-1} - t_{\ell-1}). \qquad (21)$$

In conclusion we note the following:

1. We have presented a general solution for the absorption line shape in a strong field in the presence of dephasing collisions of arbitrary nature. The only molecular information required for the evaluation of the line shape (6) is contained in the line broadening function $g(\tau)$ which appears in ordinary (weak field) line shapes. All moments $M^{(2n)}$ may be expressed in terms of $g(\tau)$.

2. In the weak radiation field limit we may expand $S(\Delta)$ to lowest order in μ resulting in

$$S(\Delta) = \mu^2 R^{(2)}(\Delta), \tag{22}$$

where $R^{(2)}$ is given by Eq. (17). This is the well-known expression of the linear unified theory of line shapes [10].

3. In the impact (Markovian) limit of fast collisions (relative to the line broadening) we take $g(\tau)$ (on a coarse-grained time scale) to be linear in τ, i.e. [10,7]

$$g(\tau) \equiv \int_0^\tau d\tau_1 (\tau - \tau_1) g''(\tau_1) \cong \tau \int_0^\infty d\tau_1 g''(\tau_1) = \hat{\Gamma}\tau \quad , \tag{23}$$

where $g''(\tau_1)$ is the second derivative of g. From Eq. (21) we note that in this case all $\xi(\upsilon_k, \upsilon_\ell)=0$ so that the moments factorize

$$M^{(2n)}(\tau_1, \ldots \tau_{2n-1}) = M^{(2)}(\tau_1) M^{(2)}(\tau_3) \ldots M^{(2)}(\tau_{2n-1}) \tag{24}$$

(such a factorization was assumed recently for other multiphoton processes [5,6] without a rigorous proof).

Using (24) we immediately get

$$K^{(4)} = K^{(6)} = \ldots = 0 \tag{25}$$

so that

$$R(\Delta) = \mu^2 R^{(2)}(\Delta) = \frac{2\mu^2 \Gamma}{\Delta^2 + \Gamma^2} \quad , \tag{26}$$

where

$$\Gamma = \frac{1}{2}\gamma + \hat{\Gamma} \quad . \tag{27}$$

Upon substitution of (26) in (6) we recover the Karplus-Schwinger [11] formula

$$S(\Delta) = \frac{2\mu^2 \Gamma}{\Delta^2 + \Gamma^2 + 4\mu^2 \frac{\Gamma}{\gamma}} \quad . \tag{28}$$

It should be noted that Lisitsa and Yakovlenko [12] have suggested an expansion for $S(\Delta)$ based on Eq. (28), by taking Γ to depend on the Rabi frequency and the detuning i.e. $\Gamma = \Gamma(\mu,\Delta)$. Such an expansion is convenient near the impact limit but becomes very tedious in the quasistatic limit even for weak fields.

4. In the non-Markovian case (when $g(\tau)$ is not linear in τ) we may use the expansion (7) to get the line shape. Simple arguments based on Eq. (8) show that $\frac{\mu^{2n} R(2n)}{\mu^2 R(2)} \tilde{=} \left(\frac{\mu^2 \tau_c}{\gamma}\right)^{n-1}$ where τ_c is the duration of a collision. To lowest order in τ_c we thus have the approximate relation:

$$S(\Delta) = \frac{\mu^2 R(2)(\Delta)}{1 + \frac{2}{\gamma}\mu^2 R(2)(\Delta)} \tag{29}$$

5. The present formalism may be easily extended [13] to other processes (Resonance Raman etc.) which also require the evaluation of cumulants similar in form to Eq. (9).

6. The authors are grateful to Prof. Ben-Reuven for pointing out that the above theory does not treat the problem of initial statistical correlations. The present theory is unified in the sense that it achieves the unification of the linear Franck-Condon treatment of Szudy and Baylis [10] with the non-linear impact theory of Karplus and Schwinger [11].

Appendix

The absorption line shape can be represented in terms of the matrix elements (in double-bracket notation) of the tetradic scattering matrix $\mathcal{T}$ [3,4],

$$I(\Delta) = i \sum_{\alpha,\alpha'} \langle\langle \begin{matrix} \alpha'\alpha' \\ aa \end{matrix} | \mathcal{T}(0) | \begin{matrix} \alpha\alpha \\ aa \end{matrix} \rangle\rangle P(\alpha) (\rho_{aa}^{eq} - \rho_{bb}^{eq}) \tag{A1}$$

where $P(\alpha)$ is defined by Eq. (13b).

The above matrix elements are now evaluated in the binary collision approximation. It can be shown [7] that this implies that the interaction (v) can either leave the bath state (α) unchanged or change it twice during the absorption process. Hence, $S(\Delta)$ can be expanded in the following manner:

$$S(\Delta) = R(\Delta) + R(\Delta)\, G R(\Delta) + \ldots = \frac{R(\Delta)}{1 - G\, R(\Delta)} \tag{A2}$$

where $R(\Delta)$ is the part of the scattering matrix containing only terms in which the state of the bath is changed twice by the interaction.

This separation is achieved by the use of the projection operators [14,16]

$$P = 1 - \gg\!\ll 1 \rho^{0}_{B} \quad \text{Tr}_{\text{bath}} \tag{A3a}$$

$$Q = 1 - P \tag{A3b}$$

where

$$1 - \gg\!\ll 1 = \frac{1}{2}\left[\eta\, |aa\rangle\!\gg\ll\!\langle aa| + (1-\eta)\, |bb\rangle\!\gg\ll\!\langle bb| - \right. \tag{A4}$$

$$\left. - \eta\, |bb\rangle\!\gg\ll\!\langle aa| - (1-\eta)\, |aa\rangle\!\gg\ll\!\langle bb|\right],$$

with $\eta = \rho^{eq}_{bb} = \frac{\gamma_a}{\gamma}$.

Using the methods of [15,4] to find G, one obtains

$$G = -i\frac{2}{\gamma} \tag{A5}$$

Also, quite generally [6],

$$R(\Delta) = -i \int_0^\infty d\tau P\, v\, e^{-iQ(L+\tilde{L})\tau} Q\, v\, P, \tag{A6}$$

and Eqs. (6)-(8) follow.

In the limit (characteristic of the spectra of low density gases at room temperature)

$$kT \gg \text{line width} \tag{A7}$$

$g(\tau)$ is real and one can show that the contributions of $|aa\rangle\!\gg\ll\!\langle aa|$ and $|bb\rangle\!\gg\ll\!\langle bb|$ are identical. Furthermore, their contribution is equal in magnitude and opposite in sign to that of $|aa\rangle\!\gg\ll\!\langle bb|$ and $|bb\rangle\!\gg\ll\!\langle aa|$. Hence the operator Q can be replaced by D (see Eq. (12)).

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