Single-atom versus coherent pressure-induced extra resonances in four-photon processes

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The spectrum of light emitted by a single atom in a thermal bath interacting with three electromagnetic fields is calculated using the dressed-atom picture. The emission spectrum consists of an elastic Raman-like component and dephasing-induced redistribution components that are inelastic in nature. In contrast to coherent four-wave mixing [as given by $\chi^{(3)}$], in which a pressure-induced elastic component (PIER 4) has been predicted and observed, the single-atom response does not contain any elastic pressure-induced components. We derive explicit expressions for the single atom and for the PIER 4 spectra that are not restricted to the impact limit.

There has been considerable interest in recent years in the appearance of new pressure-induced elastic-component (PIER 4) resonances in four-wave mixing (4WM) that are induced by proper dephasing.[1–5] In this Letter the dressed-atom picture together with the tetradic $\mathcal{T}$ matrix is used to calculate the response of a single absorber atom in a thermal bath interacting with four light waves, $S_{SA}(\omega_1, -\omega_2, \omega_3, -\omega_4)$. This enables us to explore recent conjectures[2,5] regarding the resemblance between the cooperative PIER 4 and the more-common collisional redistribution,[6] which exists in two-photon processes with a single absorber. We show that, despite some similarities, there are fundamental differences between the two phenomena. Moreover, making use of recently developed techniques for multiphoton processes,[7,8] we derive explicit expressions for the single atom and the 4WM spectra that are not restricted to the impact limit and allow us to use exact single-photon line-shape functions in the calculation of these nonlinear optical processes.

Consider the following seven states of an absorber atom interacting with four modes of the radiation field as shown in Fig. 1:

$$|a\rangle \equiv |\bar{a}, n_1, n_2, n_3, n_4\rangle, \qquad E_a = \epsilon_a, \tag{1a}$$

$$|b\rangle \equiv |\bar{b}, (n_1-1), n_2, n_3, n_4\rangle, \qquad E_b = \epsilon_b - \hbar\omega_1 \tag{1b}$$

$$|b'\rangle \equiv |\bar{b}', (n_1-1), n_2, n_3, n_4\rangle, \qquad E_{b'} = \epsilon_{b'} - \hbar\omega_1, \tag{1c}$$

$$|c\rangle \equiv |\bar{c}, (n_1-1), (n_2+1), n_3, n_4\rangle, \qquad E_c = \epsilon_c + \hbar(\omega_2 - \omega_1), \tag{1d}$$

$$|d\rangle \equiv |\bar{b}, (n_1-1), (n_2+1), (n_3-1), n_4\rangle, \qquad E_d = \epsilon_b + \hbar(\omega_2 - \omega_1 - \omega_3), \tag{1e}$$

$$|d'\rangle \equiv |\bar{b}', (n_1-1), (n_2+1), (n_3-1), n_4\rangle, \qquad E_{d'} = \epsilon_{b'} + \hbar(\omega_2 - \omega_1 - \omega_3), \tag{1f}$$

$$|e\rangle \equiv |\bar{a}, (n_1-1), (n_2+1), (n_3-1), (n_4+1)\rangle, \qquad E_e = \epsilon_a + \hbar(\omega_4 + \omega_2 - \omega_1 - \omega_3). \tag{1g}$$

Here ϵ_r is the energy of the bare molecular state $|\bar{r}\rangle$ and n_i is the photon occupation number of the ith mode.

The Hamiltonian for the combined system, bath, and radiation field is

$$H = H_S + H_B + H_{SB} + V \equiv H_0 + V. \tag{2}$$

H_S is the system Hamiltonian, given by

$$H_S = \sum_{j=a,b,c\ldots e} |j\rangle \left(E_j - \frac{i\gamma_j}{2}\right) \langle j|, \tag{2a}$$

and V is the interaction with the radiation field, written as

$$V = \mu_{ab}(|a\rangle\langle b| + |e\rangle\langle d|) + \mu_{ab'}(|a\rangle\langle b'| + |e\rangle\langle d'|) + \mu_{cb}(|c\rangle\langle b| + |e\rangle\langle d|) + \mu_{cb'}(|c\rangle\langle b'| + |c\rangle\langle d'|) + \text{c.c.}, \tag{2b}$$

where $(2\pi\gamma_r)^{-1}$ is the lifetime of level $|r\rangle$ and μ is the radiative coupling moment. The bath Hamiltonian H_B and the system–bath interaction H_{SB} are not written explicitly here. Suffice it to say that the bath causes dephasing and does not change the system states (adiabatic interaction).[7,8]

To calculate the cross section for a four-photon process, we introduce the tetradic $\mathcal{T}$ matrix[7,9]

$$\mathcal{T}(\omega) = \mathcal{V} + \mathcal{V}\frac{1}{\omega - L + i\epsilon}\mathcal{V}, \tag{3}$$

where $\mathcal{V} = [V, \quad]$ and $L = [H, \quad]$ is the Liouville operator. In this formalism the cross section for scattering into mode 4 by a single system atom is

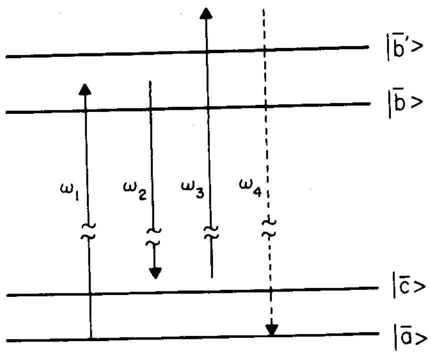

Fig. 1. Energy-level scheme and mode frequencies for the dephasing-induced resonances in four-wave mixing.

$$S_{SA}(-\omega_4, \omega_1, -\omega_2, \omega_3) = -i\langle \mathcal{T}(0)_{ee,aa}\rangle, \tag{4}$$

where $\langle\ \ \rangle$ denotes a thermal average over the bath degrees of freedom and the expression gives the cross section up to a normalizing constant in the incident photon flux. $\mathcal{T}$ can be expanded in powers of $\mathcal{V}$, and for the four-photon processes of interest we consider only the term to eighth order in $\mathcal{V}$, i.e.,

$$S_{SA}(-\omega_4, \omega_1, -\omega_2, \omega_3) = -i\{\mathcal{V}[\langle G_0(0)\rangle \mathcal{V}]^7\}_{ee,aa}, \tag{5}$$

where $G_0 = (\omega - L_0 + i\epsilon)^{-1}$ and $L_0 = [H_0,\ \ ]$. Note that the factorization approximation[7,8] has been introduced, that is, each G_0 is averaged separately. This approximation is exact in the impact limit.

A pictorial representation of Eq. (5) is given in Fig. 2. Each bond corresponds to a radiative coupling $\mathcal{V}$, and each point to a Green function. Since the process is eighth order in $\mathcal{V}$, one must sum over all the eight bond pathways that lead from $|aa\gg$ to $|ee\gg$. Each pathway contributes a term proportional to the product of the seven complex line-shape functions corresponding to the seven Green functions per path.[7,8] Just as in the well-known case of two-photon collisional redistribution,[6,7] the spectrum of the scattered light contains a sharp Raman-like transition and broad collision-induced components. We note that the Green function corresponding to the point ae is

$$\langle G(0)\rangle_{ae,ae} = PP\left(\frac{1}{\omega_2 + \omega_4 - \omega_1 - \omega_3}\right) - i\pi\delta(\omega_2 + \omega_4 - \omega_1 - \omega_3). \tag{6}$$

Consequently, the pathways that pass via ae (or ea) will contain a δ-function Raman-like component, whereas no other pathways include such a δ function. The coherent PIER 4 signal[2] occurs when $\omega_2 - \omega_3 = \omega_{b'b}$, and we now look for contributions to the scattering that are resonant at $\omega_2 - \omega_3 = \omega_{b'b}$. They can come only from those pathways that pass through point $b'd$ or db'. The opposite resonance at $\omega_2 - \omega_3 = \omega_{bb'}$, also dephasing induced, comes from bd' or $d'b$, whereas the contribution equivalent to the degenerate[3] PIER 4 comes from bd and $b'd'$ or db and $d'b'$. These can be treated by direct analogy to what follows.

At all but the lowest pressures these pathways are dominated by those that pass through points $b'b'$ and dd (or, in the degenerate case, through bb and dd or $b'b'$ and $d'd'$) because $b'b'$ and dd are always resonant. Hence we consider only these eight pathways, indicated by heavy lines in Fig. 2. The sum of these eight pathways and the two Raman-like pathways that pass via ae and ea is given by

$$S_{SA}(-\omega_4, \omega_1, -\omega_2, \omega_3)\, a = \sum_{j,k=b,b'} |\mu_{aj}\mu_{jc}\mu_{ck}\mu_{ka}|^2 \times [A(\omega_1, -\omega_2, \omega_3)\delta(\omega_4 + \omega_2 - \omega_1 - \omega_3) + B(\omega_1, -\omega_2, \omega_3) I''_{ak}(\omega_4 - \omega_{ka})], \tag{7}$$

where

$$A(\omega_1, -\omega_2, \omega_3) = 2\pi|I_{aj}(\omega_{ja} - \omega_1) I_{ac}(\omega_{ca} + \omega_2 - \omega_1) \times I_{ak}(\omega_{ka} + \omega_2 - \omega_1 - \omega_3)|^2 \tag{7a}$$

and

$$B(\omega_1, -\omega_2, \omega_3) = \frac{8}{\gamma_k\gamma_j} I''_{aj}(\omega_1 - \omega_{ja}) \times \mathrm{Im}[I_{jc}(\omega_{jc} - \omega_2) \times I_{jk}(\omega_{jk} - \omega_2 + \omega_3) I_{ck}(\omega_3 - \omega_{kc})]. \tag{7b}$$

Here $\omega_{\nu\mu} \equiv \epsilon_\nu - \epsilon_\mu$ and $I_{\nu\mu}[(E_\nu - E_\mu)/\hbar] \equiv \langle G_{\nu\mu}(0)\rangle$ is the complex line-shape function for the ν–μ transition, i.e.,

$$I_{\nu\mu}(\omega) = -i\int_0^\infty d\tau \exp\left[i\omega\tau - \frac{1}{2}(\gamma_\nu + \gamma_\mu)\tau - g_{\nu\mu}(\tau)\right], \tag{8}$$

where $g_{\nu\mu}(\tau)$ is the term responsible for the line broadening.[7,8] The real and imaginary parts of $I_{\nu\mu}$ ($I_{\nu\mu} = I'_{\nu\mu} - iI''_{\nu\mu}$) satisfy the Kramers–Kronig relations, i.e.,

$$I'_{\nu\mu}(\omega) = \frac{1}{\pi} PP \int \frac{I''_{\nu\mu}(\omega')}{\omega - \omega'} d\omega'. \tag{9a}$$

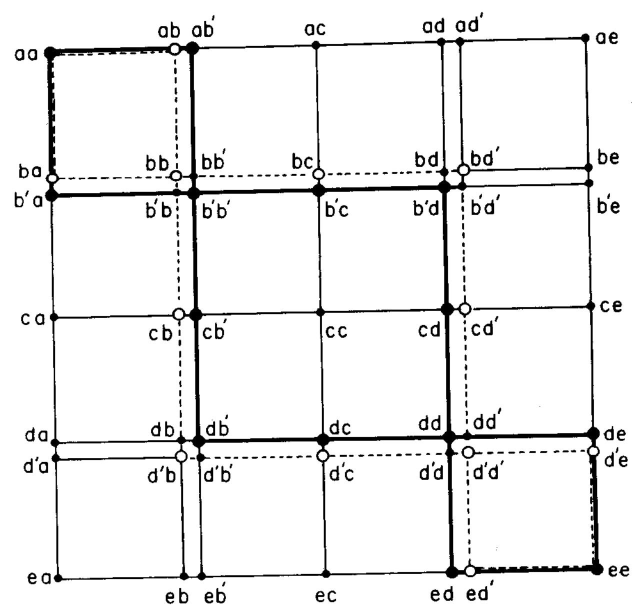

Fig. 2. Pictorial representation of the possible pathways for four-wave mixing in the dressed-atom picture. We need consider all the eight bond pathways leading from aa to ee. The heavy lines indicate the eight pathways responsible for the resonance at $\omega_{bb'} = \omega_2 - \omega_3$. The dashed lines correspond to the opposite resonance at $\omega_{bb'} = \omega_3 - \omega_2$.

$I''_{\nu\mu}$ is normalized such that

$$\int I''_{\nu\mu}(\omega)\mathrm{d}\omega = \pi. \qquad (9b)$$

In the *impact limit*, $g_{\nu\mu}(\tau) = \hat{\Gamma}_{\nu\mu}\tau$, and we have

$$I_{\nu\mu}(\omega) = \frac{1}{\omega + i(\hat{\Gamma}_{\nu\mu} + \gamma\nu/2 + \gamma_\mu/2)}. \qquad (10)$$

We now turn to the coherent pressure-induced four-wave mixing (PIER 4) experiment. The PIER 4 signal is usually calculated within the impact limit by using a third-order nonlinear susceptibility.[1] Using the same techniques utilized in the calculation of Eq. (7) and following Bloembergen's semiclassical procedure,[1] we derived the following expression for the 4WM signal:

$$S_{4\mathrm{WM}} = |\chi^{(3)}|^2\delta(\omega_4 + \omega_2 - \omega_1 - \omega_3), \qquad (11)$$

where

$$\chi^{(3)}(-\omega_4, \omega_1, -\omega_2, \omega_3) \propto \sum_{j,k=b',b} (\mu_{aj}\mu_{jc}\mu_{ck}\mu_{ka})\{I_{ca}(\omega_{ca} + \omega_1 - \omega_2)I_{ja}(\omega_{ja} - \omega_2)I^*_{ka}(\omega_{ka} - \omega_3)[1 + K_2]\} \qquad (12)$$

and where

$$K_2 = \frac{I^*_{kc}(\omega_{kc} - \omega_4)}{I_{ca}(\omega_{ca} + \omega_1 - \omega_2)}\bigg\{I_{ca}(\omega_{ca} + \omega_1 - \omega_2) \times \left[\frac{1}{I^*_{ka}(\omega_{ka} - \omega_3)} - \frac{1}{I^*_{kc}(\omega_{kc} - \omega_4)}\right] + I^*_{kj}(\omega_{kj} + \omega_2 - \omega_3)\left[\frac{1}{I_{ja}(\omega_{ja} - \omega_2)} - \frac{1}{I^*_{ka}(\omega_{ka} - \omega_3)}\right]\bigg\}. \qquad (13)$$

Equation (12) is a generalization of the conventional expression[1] for $\chi^{(3)}$, as it allows for nonimpact line shapes. In the impact limit [Eq. (10)], Eq. (12) reduces to the expression for $\chi^{(3)}$ that appears in App. 1 of Ref. 1. Equations (7) and (12) are the main results of this Letter. We are now in a position to compare S_{SA} and $S_{4\mathrm{WM}}$:

1. Both $S_{4\mathrm{WM}}$ and S_{SA} contain a pressure-induced component that is resonant at $\omega_2 - \omega_3 = \omega_{b'b}$. The resonance is in the $I_{jk}(\omega_{jk} - \omega_2 + \omega_3)$ term that appears in both. However, in $S_{4\mathrm{WM}}$ this is an elastic component $\sim\delta(\omega_4 + \omega_2 - \omega_1 - \omega_3)$, whereas in S_{SA} it is in the B inelastic component $\sim I''_{ak}(\omega_4 - \omega_{ka})$.
2. In both cases the resonance vanishes at zero pressure. This result is exact if all the eight bond pathways leading from *aa* to *ee* in Fig. 2 are added. This, in both cases, the dephasing process prevents a cancellation of terms that would otherwise be exact.
3. The coherent process is cooperative, parametric (i.e., $\omega_4 \equiv \omega_1 - \omega_2 + \omega_3$), highly nonisotropic, and subject to phase-matching conditions, whereas the inelastic emission in S_{SA} is centered around the atomic transition and is isotropic in space.
4. The pressure-induced components exhibit a different dependence on the detuning and on the pressure, with a much stronger dependence in the coherent case, as it is a delicate interference between several line-shape functions. Under typical impact conditions, as in Fig. 3, the integrated intensity grows like P (pressure) for S_{SA} and like P^2 for $S_{4\mathrm{WM}}$. Figure 3 displays the dependence of both signals on detuning of ω_1 and on pressure. The difference frequency is kept at the peak of the extra resonance, namely, $\omega_2 - \omega_3 = \omega_{b'b}$, and the scattering intensity is plotted for both cases.

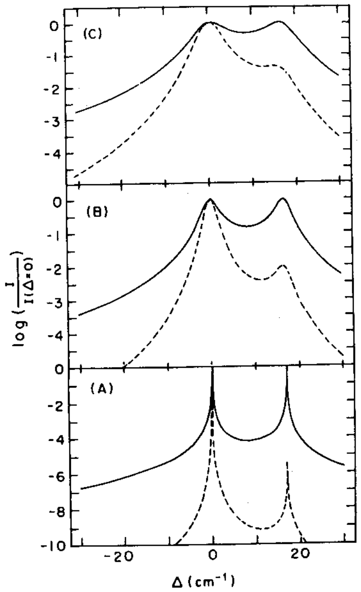

Fig. 3. Intensity versus detuning ($\Delta = \omega_1 - \omega_{ka}$) at the peak of the PIER 4 resonance in the impact limit, normalized to the value at zero detuning. The solid lines show $B(\omega_1, -\omega_2, \omega_3)$, which is the integrated intensity of the redistribution component of S_{SA} [Eq. (7)], whereas the dashed lines represent $|\chi^3|^2$, which is the integrated intensity of the 4WM signal $S_{4\mathrm{WM}}$ [Eq. (11)]. The parameters were taken to be typical for the Na–He experiment[2]: $\omega_1 - \omega_2 = \omega_{bb'} = 17\ \mathrm{cm}^{-1}$, $\omega_1 = \omega_3$, $\hat{\Gamma}_{bb'} = 0$, $\hat{\Gamma}_{ab} = \hat{\Gamma}_{ab'} = AP$, where $A = 10$ MHz/Torr, $\gamma_a = 0$, $\gamma_b = \gamma_{b'} = 10$ MHz. (A) $P = 100$ Torr, (B) $P = 5000$ Torr, (C) $P = 10{,}000$ Torr. (A), (B), and (C) were shifted vertically for clarity in presentation. At $\Delta = 5\ \mathrm{cm}^{-1}$, the ratios of the absolute magnitudes are $S_{\mathrm{SA}}(A){:}S_{\mathrm{SA}}(B){:}S_{\mathrm{SA}}(C) = 1{:}45{:}65$, $S_{4\mathrm{WM}}(A){:}S_{4\mathrm{WM}}(B){:}S_{4\mathrm{WM}}(C) = 1{:}2000{:}4500$.

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