Resonant nearly degenerate backward four-wave mixing in open and closed systems

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This paper presents perturbation calculations using the density matrix to describe the nearly degenerate four-wave-mixing spectral response in resonant systems subject to state-specific reservoir coupling. The calculations provide physical insight into the origin of narrow resonances observed in recent experimental work in atomic sodium and ultranarrow resonances in crystals. The calculations are for systems which are homogeneously broadened as well as systems which are inhomogeneously broadened due to velocity effects or random crystal fields. The calculations show that it is possible to eliminate the effects of either kind of broadening and measure the decay rate of the dipole coherence as well as the decay rates of both states of the transition. Furthermore, the calculations indicate that the method of cross-correlated optical fields which was used to eliminate the effects of laser jitter in longitudinal relaxation rate measurements could be extended to the measurements of slow dephasing rates in crystals.

INTRODUCTION

The study of line shapes in nearly degenerate backward four-wave mixing (NDFWM) can provide important spectroscopic information about the relaxation of states or coherent superposition states due to reservoir coupling. A common example of this is spontaneous emission due to coupling to the vacuum radiation field. Spontaneous emission causes decay of a state as well as decay of coherence between the states of the radiating transition. There are also other important forms of coupling to a reservoir. In gas-phase systems, examples of reservoir coupling include state-changing, velocity-changing, or phase-interrupting collisions. In solids in addition to spontaneous emission, examples of reservoir coupling include phonon and impurity scattering. Decay of coherence can also be caused by fluctuating fields in a crystal.

Furthermore, NDFWM is of great practical importance. The NDFWM spectral response is related to the reflectivity bandwidth associated with optical phase conjugate mirrors produced in backward four-wave mixing. Such mirrors are of potential importance to real-time aberration correction in optical systems.

This paper describes the spectral response of backward NDFWM in a two-level system in the presence of state-specific reservoir coupling. The NDFWM response is defined as the line shape associated with the signal as a function of frequency of any of the three input beams. A number of line shapes are discussed for different cases of state-specific reservoir coupling. The model provides a simple physical explanation of the origin of collision-induced subnatural narrow resonances in Doppler-broadened gases[1,2] and the ultranarrow resonances in solids[3] observed in earlier experiments. The physics is shown to be similar to the origin of pressure-induced extra resonances in FWM (PIER4) first discussed by Bloembergen[4–8] (see also review by Rothberg[9]) and the narrow spectral holes and antiholes observed in modulation spectroscopy discussed in detail by Boyd.[10–14] These effects arise due to an incomplete cancellation of quantum-mechanical amplitudes.[15–17] We also extend the calculation to include the NDFWM spectral response in a medium inhomogeneously broadened by random crystal fields. We show that in some cases, it is possible to eliminate the effects of both inhomogeneous broadening and laser jitter in the measurement of the effective transverse and longitudinal relaxation rate.

MODEL

Nearly degenerate four-wave mixing is described by a third-order nonlinear optical susceptibility which can be evaluated using third-order perturbation theory and double-sided Feynman diagrams.[18–21] General expressions for all 48 terms of the third-order susceptibility have been given by many authors.[4,22,23] In this calculation, we rederive the third-order nonlinear optical susceptibility for a two-level system for backward NDFWM in order to obtain a physical understanding of the origin of NDFWM spectral profiles. The calculation takes into account spontaneous emission into the ground state along with decays of both states to the reservoir and pure dephasing of the dipole. Because of its generality to multilevel systems and its extension to the treatment of nonexponential decay coupling to the reservoir, we use the density-matrix approach first pioneered by Bloembergen and Shen[24] with a classical description of the radiation fields. While this calculation is based on assuming exponential decays for the different matrix elements, the density-matrix equations are particularly powerful since they can be generalized to a more complete quantum-mechanical transport equation.[25,26]

The specific form of the density-matrix equation is given as[27,28]

$$i\hbar\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right)\rho=[H_0,\rho]+[V,\rho]-\frac{i\hbar}{2}\{\Gamma,\rho\}_+ +i\hbar\frac{d\rho}{dt}\bigg|_{\rm sp}+i\hbar\frac{d\rho}{dt}\bigg|_{\rm ph}+i\hbar\Lambda \quad (1)$$

where the $\mathbf{v}\cdot\nabla$ term accounts for motion and $\mathbf{v}$ is the classical velocity associated with the center of mass, H_0 is the Hamiltonian for the unperturbed system, V is the classical electromagnetic interaction of the form $-\boldsymbol{\mu}\cdot\mathbf{E}$, where $\mathbf{E}=\frac{1}{2}\sum\mathbf{E}_a e^{i\mathbf{k}_\alpha x-i\omega_\alpha t}+\text{c.c.}$ is summed over all electromagnetic fields. Γ is the decay operator; Λ is the source term to account for incoherent pumping. The other two terms, $(d\rho/dt)\,|_{\rm sp}$ and $(d\rho/dt)\,|_{\rm ph}$, account for decay into a state due to spontaneous emission from a higher state and decay of coherence due to dephasing, respectively.

Unlike our earlier work, we do not include any source terms from the reservoir. For example, if we are describing a gas-phase system with collisions, the reservoir decay terms account for loss of an atom at velocity v due to a velocity-changing collision. However, we do not allow for the possibility of an atom in a given state at velocity v' to undergo a velocity-changing collision and have its velocity changed to v. This means we will fail to describe such important behavior as collision-induced velocity hole filling.

The polarization is given by $P=\text{Tr}(\mu\rho)$. If the system is a gas, then ρ is a function of velocity, and the polarization must be integrated over the velocity distribution. If the system is a solid and inhomogeneously broadened due to random crystal fields, the $\mathbf{v}\cdot\nabla$ does not contribute to the density-matrix equation, but the polarization must be integrated over the distribution describing the energy levels. This integration is a very important part of the problem and can greatly effect the results and physical interpretation.

To illustrate the physics observed in the experiments, we consider a simple two-level system shown in Fig. 1. The λ_i represent incoherent pumping into level i, and the corresponding operator in the Eq. (1) has the form $\langle i\,|\,\Lambda\,|\,j\rangle=\lambda_i\delta_{ij}$. The Γ are exponential decays to the reservoir due to spontaneous emission, inelastic collisions, or other nonradiative-type transitions. The operator has the form $\langle i\,|\,\Gamma\,|\,j\rangle=\gamma_{ij}\delta_{ij}$. Note that these decays contribute to the dephasing of the dipole. This is seen by noting that these terms contribute to the decay of the off-diagonal matrix element, the optical coherence ρ_{12}. In addition to this contribution, to the decay of the dipole coherence, there is additional dephasing. This term in the general equation is given by $\langle i\,|\,(\partial\rho/\partial t)\,|_{\rm ph}\,|\,j\rangle=-\gamma_{\rm ph}(1-\delta_{ij})$. This term represents so-called pure dephasing because the physical origin for this term does not contribute to any other decays. (It should be noted that in the earlier work,[1,2] velocity changing collisions and dephasing collisions arise from the same scattering event. Hence, the effects of velocity-changing collisions on the diagonal matrix elements, causing loss or generation of a state in a specific velocity group, and collision-induced dephasing, causing loss of dipole coherence and frequency shift of the resonance, is handled by a single operator. However, physically, the origin of the resonant response does not depend on these details.[29]) Finally, state 2 can decay by spontaneous emission back to 1. This is accounted for by a source term for state 1 given by

$$\left\langle 1\left|\frac{\partial\rho}{\partial t}\right|_{\rm sp}\right|1\right\rangle=\gamma_{\rm sp}\rho_{22}\ .$$

In the rotating-wave approximation (and noting $\rho_{ij}=\rho_{ji}^*$), the equations for the matrix elements become

$$i\hbar\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right)\rho_{11}=[V_{12}\rho_{21}-\text{c.c.}]-i\hbar\gamma_1\rho_{11}+i\hbar\gamma_{\rm sp}\rho_{22}+i\hbar\lambda_1\ , \quad (2)$$

$$i\hbar\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right)\rho_{22}=-[V_{12}\rho_{21}-\text{c.c.}]-i\hbar\gamma_2^T\rho_{22}+i\hbar\lambda_2\ , \quad (3)$$

$$i\hbar\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right)\rho_{12}=-\hbar\omega_0\rho_{12}+[V_{12}\rho_{22}-\rho_{11}V_{12}]-i\hbar\gamma_{\rm ph}^T\rho_{12}\ , \quad (4)$$

where $\gamma_2^T=\gamma_2+\gamma_{\rm sp}$ and $\gamma_{\rm ph}^T=\frac{1}{2}(\gamma_2^T+\gamma_1)+\gamma_{\rm ph}$. For level degeneracies, one must be more careful about correctly including the effects of source terms on coherences between degenerate states and correctly accounting for the vector nature of the interaction term $-\boldsymbol{\mu}\cdot\mathbf{E}$.

Figure 1 also shows the optical beam configuration for backward NDFWM. There are three input fields, designated E_a, where $a=f$, b, or p for forward pump, backward pump, or probe, respectively. The nonlinear optical interaction of interest follows from a third-order nonlinear optical polarization of the form $P^{(3)}=\chi^{(3)}E_fE_bE_p^*$. The phase-matching conditions for the wave vectors result in the signal field, E_s, counterpropagating with respect to the probe beam, provided that the two pump beams are exactly counterpropagating. By energy conservation, if the pump beams are at frequency ω and the probe beam is at frequency

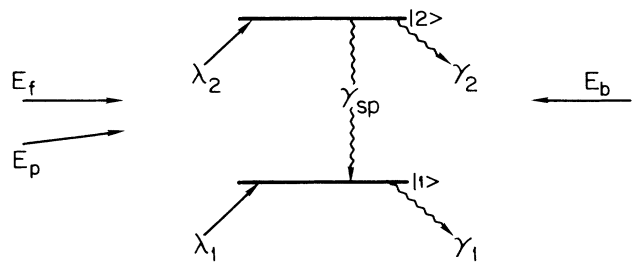

FIG. 1. Energy-level diagram for a general two-level system. For these calculations, the assumed experimental configuration is for backward NDFWM. Figure 1 shows the appropriate arrangement of incoming optical beams.

$\omega_p = \omega + \delta$, then the signal frequency is at $\omega - \delta$.

The equation of motion for the density operator is solved to third order in the electric field. Using Fig. 1, we can associate a simple physical interpretation for the origin of the signal wave. For a simple system such as this (in the absence of two-photon resonances), there are two important contributions to the signal. In the first case, the forward pump and probe interact to form an effective interference pattern which spatially modulates the ground-state and excited-state population. This spatial modulation of the population results in a spatial modulation of the absorption and dispersion. The "grating" spacing is $\lambda/[2\sin(\theta/2)]$, where θ is the angle between the forward pump and probe. If the backward pump is counterpropagating with respect to the forward pump, then it Bragg scatters off the grating in the direction counterpropagating with respect to the incoming probe. The second case is similar, except that the backward pump and probe interfere with a grating space of $\lambda/[2\cos(\theta/2)]$. In this case, the forward pump scatters from the spatially modulated population.

DISCUSSION

Initially, we consider a very simple homogeneously broadened system of two-level atoms with no motion. For a two-level system, we can ignore field polarization effects. The nonlinear polarization for the case of frequency degenerate pump beams at frequency ω, and probe beam at frequency $\omega_p = \omega + \delta$ is given by

$$P^{(3)} = -2N_0 \frac{\mu_{12}}{8} \chi_f \chi_b \chi_p^* e^{-i[(\omega-\delta)t + \vec{k}_p \cdot \vec{r}]} \{(\Delta + i\gamma_{\rm ph}^T)^{-1} + [(-\Delta-\delta) + i\gamma_{\rm ph}^T]^{-1}\}[(-\Delta+\delta) - i\gamma_{\rm ph}^T]^{-1}$$
$$\times \left[\left[1 - \frac{\gamma_{\rm sp}}{\gamma_2^T - \gamma_1} \right] (\delta - i\gamma_1)^{-1} + \left[1 + \frac{\gamma_{\rm sp}}{\gamma_2^T - \gamma_1} \right] (\delta - i\gamma_2^T)^{-1} \right] + \text{c.c.} \tag{5}$$

where Δ is the pump resonance detuning $\Delta = \omega - \omega_0$. χ_a is the Rabi flopping frequency $\mu_{12}E_a/\hbar$ associated with optical field E_a. N_0 is the equilibrium population difference:

$$(\rho_{11} - \rho_{22})_{\rm eq} = \frac{\lambda_1}{\gamma_1} - \frac{\lambda_2}{\gamma_2^T} \left[1 - \frac{\gamma_{\rm sp}}{\gamma_1} \right] .$$

In the limit of weak coupling (no pump depletion and no coupling of energy to the probe beam) the field equations decouple and the frequency dependence (as a function of δ) of the signal intensity is obtained by looking at the absolute value squared of the polarization. Equation (5) shows a number of denominators with resonances as a function of δ. In general, there are resonances at $\delta = 0$ and $\pm\Delta$ with widths and amplitudes determined by the various state decays and dephasing.

In the first case, we examine Eq. (5) in the limit that the system is absolutely closed; i.e., $\gamma_1 = \gamma_2 = 0$ and there is no additional dephasing, $\gamma_{\rm ph} = 0$ and $\gamma_{\rm ph}^T = \gamma_{\rm sp}/2$. In this case state $|1\rangle$ is the ground state, and we take $\lambda_1 = \lambda_2 = 0$ and $N_0 = (\rho_{11})_{\rm eq}$. Figure 2(a) shows the NDFWM spectrum as a function of pump-probe detuning, δ. (In this discussion, all parameters are put in dimensionless form by normalizing with respect to the spontaneous emission rate.) There are two resonances. The first occurs when the probe frequency is coincident with the resonant frequency ω_0 at $\delta = -\Delta$. The second at $\delta = \Delta$ corresponds to the signal frequency being resonant with ω_0. The resonances are associated with the dipole coherence and the width of the resonances are determined by $\gamma_{\rm ph}^T$. The resonances are expected at these values of δ because they correspond to the frequency of the probe where either the probe resonates with the dipole in absorption, or the signal resonates with the dipole in emission.

The individual time-ordered perturbation sequences are characterized by a resonance at $\delta = 0$ associated with population dynamics (seen in the second-order contribution to the perturbation sequence), though from Fig. 2(a) there is obviously no such resonance. The nonlinear response in the vicinity of $\delta = 0$ is determined in part by the dynamics of both the ground state and the excited state. The dynamics are determined by the rate at which a specific state decays. In this paper, we have restricted the discussion to a simple two-level system and are not considering excited-state or ground-state coherences. Hence, the tuning of δ can be interpreted as a temporal modulation of the populations. We first consider the origin of the resonance for each of the states separately

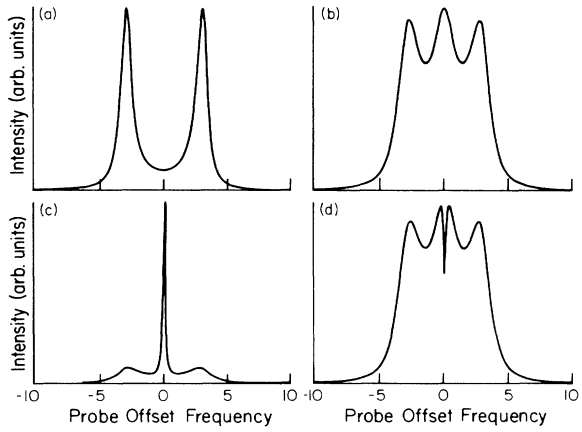

FIG. 2. NDFWM spectrum for $\Delta = 3$ for various decays. All frequencies and decays are normalized to the spontaneous emission rate. (a) The system is closed and there is no additional dephasing ($\gamma_1 = \gamma_2 = \gamma_{\rm ph} = 0$). (b) Same as (a), except additional dephasing has been added, $\gamma_{\rm ph} = 0.5$. (c) $\gamma_1 = 0.1$, $\gamma_2 = 1$, $\gamma_{\rm ph} = 0$. (d) $\gamma_{\rm ph} = 0.5$, $\gamma_1 = 0.1$, and $\gamma_2 = 0.05$. (See text for discussion.)

and then examine why in some cases, the resonance is not observed.

The perturbation of state $|2\rangle$ caused by the optical field exciting atoms from state $|1\rangle$ decays at a rate determined by the total decay rate out of state $|2\rangle$. The perturbation of state $|1\rangle$ caused by the optical field exciting atoms to state $|2\rangle$ decays with a rate determined by the net decay rate of state $|2\rangle$ back down to state $|1\rangle$ due to spontaneous emission (a "filling in" of state $|1\rangle$) plus the decay rate out of state $|1\rangle$. However, for $\gamma_1=\gamma_2$ (for a closed system, population is conserved and $\gamma_1=\gamma_2=0$,) the perturbation of state $|1\rangle$ decays at exactly the same rate as state $|2\rangle$; hence, there is no relaxation of the ground state determined by just γ_1: The resonance width determined by γ_1 is multiplied by an overall factor of zero [determined by $1-\gamma_{sp}/(\gamma_2^T-\gamma_1)$]. For a closed system, this result is physically expected since $\rho_{11}+\rho_{22}=N_0$ for all time. (The case for different state decays is discussed below.)

For the excited state, the perturbation of state $|2\rangle$ is described by a resonant denominator with a width determined by the relaxation rate of state $|2\rangle$. The overall multiplier of this factor is not zero $[1+\gamma_{sp}/(\gamma_2^T-\gamma_1)]$. The resonance occurs at second order in the perturbation and is due to the fact that at second order the response of the system is determined by the dynamics of the diagonal matrix elements or population, in this case state $|2\rangle$. To understand, however, why this resonance is not observed under the conditions of Fig. 2(a), we note that formally, the numerator obtained by combining the two terms in the first set of square brackets is $-(\delta-2i\gamma_{ph}^T)$, and for a closed system, with no additional dephasing, $\gamma_{ph}^T=\gamma_{sp}/2$. In addition, $\gamma_2^T=\gamma_{sp}$, and the numerator exactly cancels the resonant denominator, thus accounting for the lack of resonance at $\delta=0$. This represents an interference of two different time-ordered perturbation sequences for the density matrix operator such as the type represented by Gustafson-Yee diagrams.

However, the strength of this interference is reduced in the presence of additional dephasing, γ_{ph}, or nonzero state decays. Hence, in a closed system, a third resonance at $\delta=0$ will be observed in the presence of additional dephasing. This behavior is shown in Fig. 2(b), and can be seen in the original equations of Bloembergen.[4] When these resonances are caused by the presence of pure dephasing, they are called dephasing-induced coherent emission resonances and have been discussed by Andrews and Hochstrasser.[30] However, the above description shows that these resonances can also be caused by state decay as well as "pure dephasing" and as the discussion below will show, the spectral response can be extremely narrow if $\gamma_1 \ll \gamma_2$. Finally, for a closed system in the presence of additional dephasing, the amplitude of the $\delta=0$ resonance is determined by γ_{ph} and the width is determined by the spontaneous emission lifetime.

We now consider the two-level system with state coupling to the reservoir; i.e., γ_1 and γ_2 are nonzero. For small γ_i and for $\gamma_1=\gamma_2$ there is little difference in the NDFWM line shape with Fig. 2(a) except for some slight additional broadening because of the additional dephasing due to the state decay, and some slight filling in around $\delta=0$ due to the fact that the interference between the first-order pump and probe interactions is no longer complete. However, Fig. 2(c) shows the NDFWM response when $\gamma_1<\gamma_2$. A very narrow resonance is observed with a width determined by γ_1. To understand the origin of this behavior, we note that as before, when the decays are equal, the resonant enhancement at $\delta=0$ due to the response of the upper-state dynamics is reduced by the interference between the two dispersive contributions. In addition, the ground-state dynamics are determined by the decay of the excited state back to the ground state in addition to the net decay out of the ground state. Hence, as before, there is no contribution from the dynamics associated with the pure decay of the ground state (the factor multiplying the ground state $\delta=0$ resonance is still zero). However, when $\gamma_1<\gamma_2$, the ground-state perturbation does not decay as fast as the upper state. Hence, there is a residual nonlinear contribution remaining due to the ground state. The dynamics of this nonlinear response is determined by γ_1, and we obtain a resonance at $\delta=0$ with a width given by γ_1. In the case of an experiment where the presence and magnitudes of the state-specific reservoir coupling rates is controllable from zero to some finite value, it would appear to be an extra resonance, of a type similar to PIER4 resonances referenced earlier.

However, when the dephasing is large, the sidebands associated with resonances at $\delta=\pm\Delta$ broaden and disappear altogether, leaving a single Lorentzian profile with a width given by γ_1. In the limit of very large dephasing ($\gamma_{ph} \gg \gamma_1,\gamma_2,\gamma_{sp}$), this response is very similar to the work in Cr: $YA1O_3$.[3] In that work, the model was a three-level system; however, the physical result of decay to a metastable state was to create a long-lived perturbation in the ground state with the ground-state dynamics determined by the decay of the metastable. We see, however, that these interactions are also viewed in terms of temporal modulations of the populations at frequency δ and, hence, are closely related to the population pulsation effects which give rise to spectral holes in the nonlinear absorption spectrum of homogeneously broadened material.[10,12]

In the discussion below, we will generalize the calculation to include the effects of velocity-induced inhomogeneous broadening; however, the physics of linewidth effects of reservoir coupling are not effected by this addition. In the earlier experiment,[1,2] we observed collision-induced line narrowing. For these experiments, we described the observations for $\Delta=0$ because of improved signal-to-noise ratio (the effects were also observed for finite Δ.) For $\Delta=0$, Eq. (5) predicts a single resonance, corresponding to the merging of the two resonances in Fig. 2(a), with the width determined by the spontaneous emission decay rate ($\gamma_1=\gamma_2=0$). In the presence of state-specific decay, however, where $\gamma_1<\gamma_2$, the line narrows to a linewidth given by γ_1 which would have been anticipated from Fig. 2 in the limit $\Delta\rightarrow 0$. (The physical origin of γ_i for these experiments is either velocity-changing or state-changing collisions.) We see from the analysis, however, that this resonance is the result of a

finite contribution from the ground-state dynamics. Hence, though this resonance appears as a narrowing of the spectral response, the physical origin is more correctly understood as arising from a resonance which is observed only in the presence of state specific reservoir coupling. This behavior is similar to the pressure-induced resonances mentioned earlier[4–8] if the physical origin of γ_1 and γ_2 is due to collisions. We note, however, that there is really no fundamental difference between this kind of resonance and the kind of resonance seen in solids such as Cr:YA$1O_3$.

It should be noted that in many experiments, one decay is significant compared to other decays resulting in line shapes which are often nearly Lorentzian. This is not seen in the figures shown because for the sake of illustration, the different decay rates were chosen to be comparable though different. A Lorentzian line shape is unusual for nonlinear spectroscopy signatures in homogeneously broadened systems, but was seen experimentally in the Cr:YA$1O_3$ measurements.[3] This is in contrast to the fully degenerate four-wave mixing response where the spectral profile (in the limit of weak pumps) is given by the cube of a Lorentzian.[31]

Finally, we consider the case where $\gamma_2 < \gamma_1$. In this case, we note that as a result of interference between ground-state and excited-state dynamics it is possible to produce a NDFWM spectra with a dip in the middle as shown in Fig. 2(d). The figure shows a NDFWM spectrum but with $\gamma_1 = 0.1$, $\gamma_2 = 0.05$, and $\gamma_{\rm ph} = 0.5$.

We now consider the case where the atoms are moving, and we must consider Doppler effects and thermal washout described by $\mathbf{v}\cdot\nabla$. In this case, after velocity integration, we find that in the extreme Doppler limit[32] the polarization is given by (assuming a fully collinear geometry and a thermal velocity distribution)

$$P^{(3)} = \frac{N_0}{8ku_0}\mu_{12}\chi_f\chi_b\chi_p^* e^{-i[(\omega-\delta)t+\mathbf{k}_p\cdot\mathbf{r}]}\frac{2i\pi^{1/2}}{\delta-2\Delta-2i(\gamma_{12}+\gamma_{\rm sp}/2+\gamma_{\rm ph})} \times\left[\left[1-\frac{\gamma_{\rm sp}}{\gamma_2^T-\gamma_1}\right]\frac{1}{\delta-i\gamma_1}+\left[1+\frac{\gamma_{\rm sp}}{\gamma_2^T-\gamma_1}\right]\frac{1}{\delta-i\gamma_2^T}\right]+\text{c.c.} \tag{6}$$

In the Doppler limit, we have ignored the interference term between the backward pump and probe (small spacing grating) because this term is extremely small due to washout by thermal motion. In the limit that $\delta=0$, the back grating effects are discussed very thoroughly by Lam and Abrams.[33] Physically, the thermal motion washout results when the transit time between fringes is small compared to the effective longitudinal relaxation rate. This motion has the effect of lowering the contrast ratio between the fringes that result between the backward pump and probe that spatially modulate the population difference, resulting in a reduced scattering efficiency for the forward pump.

In this case, we have considered the problem where the reservoir coupling may be due to velocity-changing or state-changing collisions. In the limit that we do not consider velocity-changing collisions into the resonant velocity group or consider collision-induced frequency shifts, we find that this equation follows directly from our earlier work.[1] The analytical description in the earlier analysis was more complete; however, the physical implications of state-changing collisions is not as easily seen. To illustrate the behavior, Fig. 3(a) shows the NDFWM spectral response as a function of pump-probe detuning for a system in the Doppler limit when $\gamma_1=\gamma_2$. When the pump beam is tuned off resonance (with respect to the zero velocity group), we see that two resonances are observed. The first resonance occurs at $\delta=0$ and has a width determined by the spontaneous emission rate. The second resonance occurs at $\delta=2\Delta$ and has a width determined by the total dephasing rate. In the absence of state-specific reservoir coupling, these results are similar to those of Yariv and Nilsen.[34] Again, as we examine the polarization, we see that the resonance at $\delta=0$ has a width given by γ_1 but does not contribute for the same reasons as given above. However, unlike the homogeneously broadened system, even when the system is closed, a resonance occurs at $\delta=0$.

The physical origin of the two resonances is seen by considering the motion of the holes in velocity space as a function of pump-probe detuning. Figure 4 shows the ground-state velocity distribution assuming the pumps are detuned from resonance by an amount Δ. Assuming the pumps are degenerate, we find that they burn holes in the velocity distribution at velocities given by $\Delta-\mathbf{k}\cdot\mathbf{v}=0$. Two holes are burned corresponding to velocities Doppler shifted into resonance for the backward and forward pump beams. The probe is detuned and burns a corresponding hole, according to the amount of detuning. If the probe is given by $\omega+\delta$, then by energy conservation, the signal is at frequency $\omega-\delta$. A corresponding hole is burned by the signal, but the signal **k**

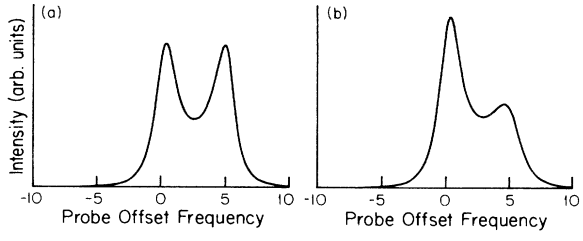

FIG. 3. NDFWM spectrum in a closed system inhomogeneously broadened by velocity effects at $\Delta=2.5$. (All frequencies and decays normalized to $\gamma_{\rm sp}$.) (a) Closed system with $\gamma_1=\gamma_2=\gamma_{\rm ph}=0$. (b) The same conditions as (a) except now $\gamma_{\rm ph}=0.25$. (See text for discussion.)

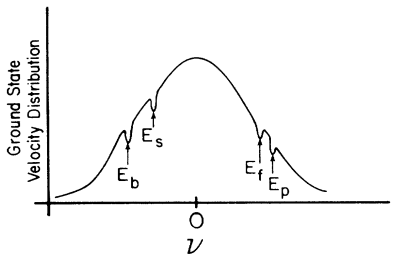

FIG. 4. A schematic of the origin of NDFWM resonances in Doppler-broadened material. This is a plot of the ground-state velocity distribution showing four velocity holes burned by the two frequency degenerate pumps, the probe beam, and the signal.

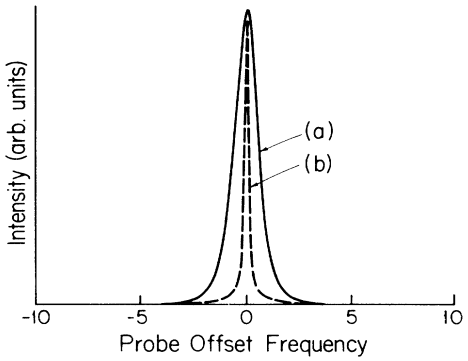

FIG. 5. (a) In order to show the apparent collisional narrowing observed in the atomic sodium experiments which were performed with $\Delta=0$, we show the predicted NDFWM spectrum under these conditions with no state-specific decay. (γ_i took on identical values corresponding to the transit time across the beam. The value is 0.001.) (b) In the presence of velocity or state-changing collisions, the γ_i become different ($\gamma_1=0.1$ and $\gamma_2=1$) resulting an apparent narrowing of the NDFWM spectrum. However, as shown from the analysis, this narrowing is really the appearance of a new resonance with a width due to the ground-state lifetime.

vector is shifted by a minus sign since the signal is propagating backward with respect to the probe (according to the phase-matching conditions). Resonances in the signal will then be observed when holes can be made to overlap. In this case, the probe hole can be adjusted. The two resonances described above are observed to occur when $\delta=0$ and $\delta=2\Delta$. The first corresponds to when the probe hole aligns with forward pump hole and the second corresponds to when the signal hole aligns with the forward pump hole. The remaining resonance at $\delta=-2\Delta$ corresponds to the probe hole aligning with backward pump hole, but is usually not observed inside the Doppler limit because of thermal washout described above. Hence, we see that the origin of the observed resonant structure can be interpreted in terms of velocity hole burning pictures.

We now consider the effect of reservoir coupling. First, as the system begins to experience additional pure dephasing, we see in Fig. 3(b) that, as expected, the second resonance begins to broaden. To examine the case of state specific reservoir coupling we consider the case for $\Delta=0$ (corresponding to experiments[1]). Curve (a) in Fig. 5 shows the NDFWM response, again with a width determined by the total dephasing for the case $\gamma_1=\gamma_2\simeq 0$ and $\gamma_{\rm ph}=0$. As the state decay rates increase in the presence of state-specific reservoir coupling (due say to state- or velocity-changing collisions), we see in curve (b) the line narrows (for $\gamma_1<\gamma_2$). Nearly identical behavior is observed off resonance ($\Delta\neq 0$) in both the theory and experiment; however, in the experiment, the signal to noise becomes poor due to collision-induced optical pumping. Agreement between theory and experiment is excellent at low pressures. At high pressures this theory becomes inadequate, and it is necessary to correctly account for collisional processes that thermalize the effects of velocity hole burning.[1,17,35]

Finally, we consider NDFWM in material inhomogeneously broadened by random crystal fields. In this case, we simply assume a normal distribution in ω_0 and integrate Eq. (5) over ω_0. In the limit of extreme broadening,[32] the result for the polarization is

$$P^{(3)}=-\frac{N_0}{8W}\mu_{12}\chi_f\chi_b\chi_p^*\,e^{-i[(\omega-\delta)t+\vec{k}_p\cdot\vec{r}]}\frac{2i\pi^{1/2}}{-2\delta_{pf}-\delta_{fb}+2i(\gamma_{12}+\gamma_{\rm sp}/2+\gamma_{\rm ph})}$$
$$\times\left[\left[1-\frac{\gamma_{\rm sp}}{\gamma_2^T-\gamma_1}\right]\left[\frac{1}{\delta_{pf}-i\gamma_1}+\frac{1}{\delta_{pf}+\delta_{fb}-i\gamma_1}\right]\right.$$
$$\left.+\left[1+\frac{\gamma_{\rm sp}}{\gamma_2^T-\gamma_1}\right]\left[\frac{1}{\delta_{pf}-i\gamma_2^T}+\frac{1}{\delta_{pf}+\delta_{fb}-i\gamma_2^T}\right]\right]+\text{c.c}\,, \tag{7}$$

where W is the inhomogeneous width, and δ_{ij}, is $\omega_i-\omega_j$. In this polarization, we can identify two terms as fp [$1/(\delta_{pf}-\gamma_1)$ and $1/(\delta_{pf}-1\gamma_2^T)$] and two terms as bp [$1/(\delta_{pf}+\delta_{fb}-i\gamma_1)$ and $1/(\delta_{pf}+\delta_{fb}-i\gamma_2^T)$]. These terms describe the dynamics associated with either the ground state (state 1) or the excited state (state 2) and are associated with linewidths γ_1 or γ_2^T, respectively. The terms identified by fp are due to the interaction by the forward pump and probe, and hence are associated with the large spacing grating (in a nearly collinear interaction). The terms identified by bp are due to the interaction by the backward pump and probe and hence are associated with the small spacing grating. In the line shape discussions which follow, we do not include contributions from the terms identified by bp since these terms are usually small even in solids because of excita-

tion diffusion. Many times, these terms can be further reduced experimentally, however, by rotating the polarization of the backward pump. The magnitude of the backward pump and probe interaction is then determined by the strength of the alignment term which is often small.

For this problem, we notice that there is no dependence on the absolute resonance frequency (except by way of a Gaussian factor with a width determined by W; the broadening is assumed to be large, and the value of the exponential is taken as 1). This is because the strength of the interaction for any given atom is the same for all three input optical fields, independent of the field propagation direction. The only frequency group that has a strong interaction with the optical fields is the group in exact resonance with the fields. Hence there is no dependence on ω_0 except through the overall probability factor which determines how many atoms are in the specific resonance group. These results are similar to those obtained earlier for polarization spectroscopy techniques in condensed phases.[36]

To appreciate the effects of NDFWM in material inhomogeneously broadened by random fields, we first note that in degenerate four-wave mixing, the DFWM response in Doppler-broadened media is Doppler free. The line width as a function Δ (for $\delta=0$) is determined by the natural linewidth. Again, the reason is because it is only for the optical frequency corresponding to resonance for the zero velocity group for which a signal is observed. The equal but opposite Doppler shift for counter propagating beams eliminates the signal when the laser interacts with any other velocity group. This is not the case if the material is inhomogeneously broadened by random fields. The spectral width of DFWM would be determined by the total inhomogeneous width. However, if one of the optical beams is detuned in frequency, while the other beams are held fixed, it becomes possible to measure linewidths associated with fundamental decay processes, rather than a linewidth associated with the inhomogeneous width. In a typical system the probe frequency is detuned with respect to the pumps, then the linewidth is determined by the relaxation rates of states 1 and 2 as shown in Fig. 6(a) ($\delta_{fb}=0$). However, if the backward pump beam is detuned, then the linewidth is given by twice the dipole coherence relaxation rate, as shown in Fig. 6(b) (note the scale change on the x axis.) This kind of spectroscopy is clearly closely related to hole burning spectroscopy.[37] It is interesting to note that these results suggest a very powerful aspect to this kind of spectroscopy. Namely, using correlated fields, it should be possible to eliminate the effects of laser jitter on both transverse and longitudinal relaxation rate measurements. In the earlier work, we demonstrated that the longitudinal relaxation rate was measured as a function of δ_{fp}. Hence, if ω_f and ω_p are correlated (come from the same laser), then they have the same jitter, and δ_{fp} should be free of jitter, as we demonstrated.[3] We see now in the current calculation that the transverse relaxation rate is measured as a function of δ_{bf}, which if we use correlated fields, would also be free of laser jitter. The absence of laser jitter in these measurements is because the nonlinear response is independent of the absolute resonance frequency. Hence, the system does not sense changes in the absolute laser frequency, and it should be possible to measure very long dephasing times without resorting to the development of ultrastable lasers.

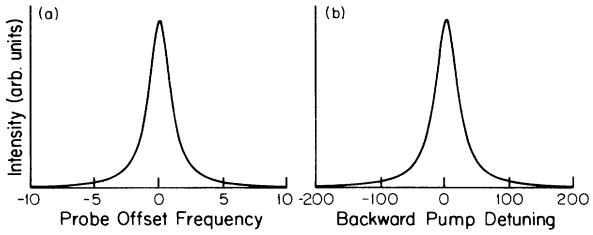

FIG. 6. NDFWM spectrum in a material which is inhomogeneously broadened by random crystal fields. In these curves, γ_{ph} was taken to be 10 times γ_{sp} and $\gamma_1=\gamma_2=0$. In these spectra, it is assumed that the grating formed by the backward pump and probe is small either because of excitation diffusion or because the polarization of the backward pump is rotated giving only a small alignment contribution. (a) The probe beam is scanned showing a width determined by γ_{sp}. (For both of these measurements, we took $\delta_{fb}=0$.) (b) The backward pump beam is scanned, showing a width determined by γ_{ph}.

SUMMARY

This paper describes the physical origin of many line shapes observed in frequency domain NDFWM. While there is considerable interest in using frequency domain four-wave mixing to study state specific reservoir coupling and ultrafast phenomena,[38] it is clear from this analysis that it may become difficult to interpret any given line shape without having considerable detailed information on the system from other experiments.

Note added in proof. Since this paper was first submitted, we have experimentally demonstrated the existence of narrow spikes and dips similar to Fig. 2 in collisionless systems. These narrow features are induced by radiative decay and are present when either population, alignment, or orientation is not conserved. Results for systems that do not conserve population are discussed in Ref. 39. Results and complete theory for systems that conserve population but not alignment and orientation will be discussed elsewhere.[40]

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[29]To more accurately account for collisions, a general collision term is added to the right-hand side of the equation. In the optical region of the spectrum, collisions change the velocity and cause a broadening and shift of the resonance. The general description used in our earlier work was of the form: *for populations*

$$\left.\frac{d\rho_{ii}(\mathbf{r},\mathbf{v},t)}{dt}\right|_{\text{collision}} = -\Gamma_i\rho_{ii}(\mathbf{r},\mathbf{v},t) + \int_{-\infty}^{\infty} d\mathbf{v}' W_i(\mathbf{v}'\rightarrow\mathbf{v})\rho_{ii}(\mathbf{r},\mathbf{v}'t) ,$$

where W_i is the collision kernel for state i and

$$\Gamma_i = \int dv' W_i(\mathbf{v}'\rightarrow\mathbf{v}) ,$$

and *for coherences*

$$\left.\frac{d\rho_{ij}(\mathbf{r},\mathbf{v},t)}{dt}\right|_{\text{collisions}} = -(\Gamma_{ij}+i\sigma_{ij})\rho_{ij}(\mathbf{r},\mathbf{v},t) .$$

For understanding the physical origins of the spectral response of NDFWM, including the above formalism helps to quantify agreement. Such behavior was discussed in the earlier work, and much more extensively, by G. Kitrova and P. Berman at the International Quantum Electronics Conference, San Francisco, 1986 (unpublished). However, the basic effect is to give rise to an apparent state specific reservoir coupling which, except for details of the frequency shift, and the velocity changing collision kernel, closely resembles the above discussion. It should be noted that one important difference between the current calculation and the more correct calculation for collision effects has been pointed out by Berman and Kitrova. Namely, that as the pressure increases, the magnitude of the γ's increase and the narrow resonance produced in the figures begins to broaden, without bound. However, when the correct collisional formulation is included, the linewidth is observed to broaden only to the natural linewidth. Physically, this appears to be due to the fact that at high pressure the system appears to be described by identical reservoir coupling for the excited state and the ground state.

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$$Z(a+ib)=(\pi)^{-1/2}\int_{-\infty}^{\infty} dx \frac{\exp(-x^2)}{[x-(a+ib)]}$$

and

$$(\pi)^{-1/2}\int_{-\infty}^{\infty} dx \frac{\exp(-x^2)}{[x-(a-ib)]} = -Z(-a+ib) .$$

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