PHYSICAL REVIEW A VOLUME 49, NUMBER 3 MARCH 1994

Transient four-wave-mixing line shapes: Effects of excitation-induced dephasing

H. Wang, K. B. Ferrio, and D. G. Steel
H. M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan 48109

P. R. Berman*
Physics Department, New York University, New York, New York 10003

Y. Z. Hu, R. Binder, and S. W. Koch
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

(Received 30 July 1993)

We describe the transient four-wave-mixing (FWM) response in systems where decay of the optically induced coherence depends on the excitation level of the system. Using modified optical Bloch equations, we show that excitation-induced dephasing due to phase-interrupting excited-state interactions qualitatively modifies the temporal behavior and polarization dependence of the FWM signal.

PACS number(s): 42.50.Md, 78.47.+p, 71.35.+z, 42.65.−k

Transient four wave mixing (FWM) has provided a powerful tool for studying electronic relaxation produced by optical excitations. The underlying physics for FWM spectroscopy in noninteracting atomic systems is well understood on the basis of the optical Bloch equations (OBE) [1]. The FWM line shapes not only provide information on decay of the excited-state population and the optically induced coherence but also distinguish the inhomogeneously broadened from homogeneously broadened systems. In self-diffracted FWM, two pulses arriving at times t_1 and t_2 and propagating with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ interact in a sample, producing a diffracted signal in the direction of $2\mathbf{k}_2-\mathbf{k}_1$. For homogeneously broadened systems, the FWM signal comes out promptly after the second pulse, leading to free polarization decay, whereas for inhomogeneously broadened systems, the signal is delayed and peaks at a later time $2t_2-t_1$ leading to a photon echo.

The above analysis of FWM line shapes needs to be modified when the simple OBE no longer provide an adequate description of the system. It has been pointed out in the early stages of nonlinear optics that in dense media the Lorentz local-field correction has to be included in the nonlinear susceptibility [2]. In FWM, local fields can lead to a delayed signal even in a homogeneously broadened system and a signal at negative time delay ($t_2-t_1<0$) [3]. The effects of local fields on nonlinear optical measurements have been studied extensively in dense atomic vapors [4], doped crystals [5], and semiconductors [6–8].

The inadequacy of the OBE is also rooted in the description of relaxation in these equations. A rigorous treatment of electronic relaxation has always been difficult except for a few simple cases such as spontaneous emission. Although discussions of the relaxation of optical excitation are often based on the OBE, the failure of the simple decay-parameter model used in the Bloch equations is revealed in the early work of magnetic resonance [9]. More recent studies of free induction decay in impurity-ion crystals [10] and velocity changing collisions in atomic vapors [11] further demonstrated the inadequacy of the Bloch equations in the optical regime. In impurity-ion crystals, dephasing due to frequency shifts induced by local-field fluctuations is quenched at a high field strength. Theoretical analysis has extended the OBE in an attempt to describe these processes [12].

In dense media the interaction between optical excitations further complicates relaxation of the system. For example, in semiconductors such as GaAs, exciton-exciton scattering increases the decay rate of the optically induced coherence, i.e., the dephasing rate depends on the excitation level of the system [13]. This excitation-induced dephasing (EID) provides an alternative origin for the nonlinear response and modifies the temporal behavior of the response. It was shown earlier that EID has to be included to account for differential transmission of excitons in $GaAs/Al_xGa_{1-x}As$ quantum wells at room temperature [14]. More recent measurements demonstrate that EID is one of the leading contributions to the excitonic nonlinear response in GaAs [15]. Interpretation of transient FWM in these systems can be complex since, as we discuss below, EID leads to qualitative changes in transient FWM line shapes similar to that induced by local-field effects.

In this paper we describe effects of EID on the transient FWM response. We are interested in EID induced by *phase-interrupting excited-state interactions* such as exciton-exciton scattering in semiconductors. We note that the most appropriate theoretical approach to analyzing coherent optical phenomena in semiconductors is based on the semiconductor Bloch equations (SBE) [16,17]. These equations are the Hartree-Fock equations for the optical interband polarization and the population probabilities of electron and hole states. Many-body Coulomb effects in these equations can lead to a renor-

*Present address: H. M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, MI 48109.

malized transition energy and to a renormalized electric field [16,17]. In a simplified version, this field renormalization can be regarded as a form of local-field effects [3]. Since it is our goal in the present paper to obtain simple analytical results and to present a model study of the influence of EID, we follow the simplified approach of Ref. [3] and ignore the exact form of SBE. We use the OBE for an atomic system and include local-field effects and EID phenomenologically. Even though this approach presents a drastic simplification of the theoretical problem for semiconductors, it should still allow us to obtain important insight into the different effects caused by EID and local-field effects.

Assuming that the dephasing rate due to EID is proportional to the excited-state population [18], we have

$$i\hbar\frac{\partial}{\partial t}\rho_{eg}(\omega)=V_{eg}[\rho_{gg}(\omega)-\rho_{ee}(\omega)]+\hbar\omega\rho_{eg}(\omega) -i\hbar(\gamma+\sigma\rho_{ee})\rho_{eg}(\omega)\ . \quad (1)$$

The excited-state population is determined by

$$i\hbar\frac{\partial}{\partial t}\rho_{ee}(\omega)=-[V_{ge}\rho_{eg}(\omega)-\text{c.c.}]-i\hbar\gamma_e\rho_{ee}(\omega)\ , \quad (2)$$

where ρ_{ee} and ρ_{eg} are the standard population density matrix elements [19], and $V=-e\mathbf{r}\cdot\mathbf{E}_{\text{loc}}$ is the interaction Hamiltonian with $\mathbf{E}_{\text{loc}}=\mathbf{E}+L\mathbf{P}$, where L is the effective Lorentz local field factor and $\mathbf{P}=\text{Tr}(e\mathbf{r}\rho)$ is the polarization. For inhomogeneously broadened systems,

$$\mathbf{P}=\int d\omega\, g(\omega)\text{Tr}[e\mathbf{r}\rho(\omega)]\ , \quad (3)$$

where $g(\omega)$ is the inhomogeneous distribution [assuming $\rho_{ee}(\omega)+\rho_{gg}(\omega)=Ng(\omega)$ with N being the density of the two-level systems]. We also assume that the entire excited-state population contributes equally to the EID, that is, ρ_{ee} in Eq. (1) is the overall excited-state population [20]. Note that these equations do not describe the more complicated problem of resonant collisions.

The dephasing term due to EID in Eq. (1) not only affects decay of the polarization but also gives rise to *an additional FWM signal.* In self-diffracting FWM, the first and second pulses induce optical polarization propagating in the direction of $\mathbf{k}_1$ and $\mathbf{k}_2$, respectively. The two pulses also interfere in the sample, producing a population grating. For noninteracting systems, self-diffraction of the second pulse from the grating results in the conventional FWM signal in the direction of $2\mathbf{k}_2-\mathbf{k}_1$. In dense media, the optical polarization can induce large electric fields. Scattering of these electric fields from the grating leads to a FWM signal in the direction of $2\mathbf{k}_2-\mathbf{k}_1$. The population grating of the excited state, however, can also *modulate the optical polarization* through the EID term in Eq. (1), which results in an additional FWM signal in the direction of $2\mathbf{k}_2-\mathbf{k}_1$. Note that this discussion is valid only when the characteristic length scale of the excited-state interaction is small in comparison with the grating spacing.

For a homogeneously broadened system, the relevant nonlinear polarization can be obtained by solving the density matrix equation in perturbation theory. The applied optical fields can be described by

$$E=E_1f(t-t_1)\exp[i(\mathbf{k}_1\cdot\mathbf{r}-\Omega t] +E_2f(t-t_2)\exp[i(\mathbf{k}_2\cdot\mathbf{r}-\Omega t)]+\text{c.c.}\ , \quad (4)$$

where $f(t-t_i)$ $(i=1,2)$ is the normalized pulse shape centered at t_i and E_i is the pulse area. To obtain analytical solutions we assume the pulse duration to be much shorter than all the relevant time scales, except the inverse of the optical frequency. The nonlinear polarization propagating in the direction of $2\mathbf{k}_2-\mathbf{k}_1$ is then given by

$$P^{(\text{NL})}=\kappa\exp[i\delta(t-2t_2+t_1)]\left\{\Theta(t-t_2)\Theta(t_2-t_1)e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)} +\frac{N(\sigma+i\eta)}{\gamma_e}[\Theta(t-t_2)\Theta(t_2-t_1)(1-e^{-\gamma_e(t-t_2)})e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)} +\Theta(t-t_1)\Theta(t_1-t_2)(1-e^{-\gamma_e(t-t_1)})e^{-\Gamma_t(t-t_1)-2\Gamma_2(t_1-t_2)}]\right\}+\text{c.c.}\ , \quad (5)$$

where $\kappa=-iN\mu^4\hbar^{-3}E_2^2E_1^*\exp[-i\Omega t+i(2\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{r}]$, $\Theta(t)$ is the Heavyside function, μ is the dipole moment between the ground and excited states (assumed to be real), $\eta=2\mu^2L/\hbar$, and $\delta=\Omega-\omega-\varepsilon$ with $\varepsilon=N\mu^2L/\hbar$ being the static Lorentz shift. In the limit of the third-order nonlinear susceptibility, decay rates Γ_t, Γ_1, and Γ_2 are all determined by the intrinsic dephasing rate γ. As the excitation level increases, decay of the nonlinear polarization becomes dependent on field intensities. In the limit $\gamma_e(t-t_1)\ll1$ and $\gamma_e(t-t_2)\ll1$, we have $\Gamma_1=\gamma+\sigma N_1$, $\Gamma_2=\gamma+\sigma N_2$, and $\Gamma_t=\gamma+\sigma N_1+\sigma N_2$ where N_i $(i=1,2)$ are the excited-state population densities due to the first and second pulses, respectively. Other higher-order nonlinear optical processes will also start to contribute to the nonlinear polarization. Inclusion of all the higher-order corrections is straightforward but is not given here for the clarity of the presentation. These higher-order processes can give rise to additional signals in directions other than $2\mathbf{k}_2-\mathbf{k}_1$.

The first term in the large parentheses of Eq. (5) is identical to the *prompt* free polarization decay term for a simple noninteracting two-level system, except that decay of this polarization can depend linearly on the excitation level: Decay of the time-integrated signal as a function of t_2-t_1 is determined by $2\Gamma_1$, while decay of the time-resolved signal as a function of $t-t_2$ is determined by $2\Gamma_t$. The second term in Eq. (5) describes the additional FWM signals due to the local-field correction (propor-

tional to η) and EID (proportional to σ). Scattering of the polarization-induced by $\mathbf{E}_2$ leads to a signal that is *delayed* with respect to the prompt signal when $t_2-t_1>0$ and to a signal occurring at $t_2-t_1<0$ (*negative* time delay), as shown in [3]. Similarly, modulating the polarization induced by $\mathbf{E}_2$ through the EID also results in a *delayed* signal when $t_2-t_1>0$ and a signal at *negative* time delay. However, the dephasing-induced signal is 90° out of phase with the signal induced by the local fields. In addition, FWM signals induced by the EID or the local fields have a rise time (as a function of $t-t_2$) on the order of the total dephasing time, as is evident in Eq. (5). Figures 1(a) and 1(b) show FWM responses induced by the EID and illustrate both the delayed signal and the signal at negative time delays.

We now consider systems with inhomogeneous broadening. The nonlinear polarization, including contributions from both saturation and EID, is given by

$$P^{(\mathrm{NL})}=\kappa\exp[i\delta_0(t-2t_2+t_1)]\times\left\{\Theta(t-t_2)\Theta(t_2-t_1)e^{-[w(t-2t_2+t_1)]^2/2}e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)}+\frac{N\sigma}{\gamma_e}e^{-[w(t_2-t_1)]^2/2}\left[\Theta(t-t_2)\Theta(t_2-t_1)e^{-[w(t-t_2)]^2/2}(1-e^{-\gamma_e(t-t_2)})e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)}+\Theta(t-t_1)\Theta(t_1-t_2)e^{-[w(t-t_1)]^2/2}(1-e^{-\gamma_e(t-t_1)})\times e^{-\Gamma_t(t-t_1)-2\Gamma_2(t_1-t_2)}\right]\right\}+\text{c.c.}\,, \tag{6}$$

where $g(\Delta)=1/(\sqrt{2\pi}w)\exp[-\Delta^2/(2w^2)]$ is the inhomogeneous distribution (assumed to be Gaussian), $\delta_0=\Omega-\omega_0$, with ω_0 being the center of the distribution. It is well known that, for noninteracting two-level atoms, nonlinear polarization from atoms with different transition energies can constructively interfere at a later time $t=2t_2-t_1$, generating a photon echo. Integration of the first term in Eq. (5) over the inhomogeneous distribution gives rise to the conventional photon echo. The EID-induced signal now arises from modulating the optical polarization through the spatial grating of the *frequency-integrated* excited-state population. The amplitude of this grating is proportional to $\int d\Delta g(\Delta)\exp(i\Delta\tau)=\exp[-(\tau w)^2/2]$ with $\tau=t_2-t_1$. Different frequency components of the induced signal always interfere destructively (no echo) because the above integration in the *population* averages out the phase information necessary for generating an echo. The dephasing-induced signal can become significant when $|t_2-t_1|<1/w$, or when Γ_t approaches the inhomogeneous width. Figure 2 shows a FWM response due to both saturation and EID in an inhomogeneous system.

The result for contributions from the local-field correction is more complicated but the physical behavior of the induced FWM signal is easy to describe: The *total* local-field correction is determined by the *frequency-integrated* optical polarization not by polarization at a particular frequency ω, in contrast to the approach used in [3]. The integrated polarization is proportional to

$$\int d\Delta g(\Delta)\exp(i\Delta t)\theta(t)=\exp[-(tw)^2/2]\theta(t)\,.$$

The signal due to scattering of the polarization induced by $\mathbf{E}_2$ will give rise to a photon echo when $t_2-t_1>0$ since the frequency integration in calculating the total local fields does not affect the phase information necessary

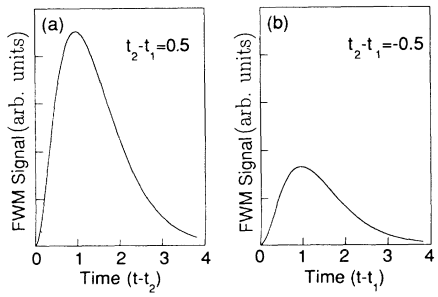

FIG. 1. Time-resolved transient FWM response induced by excitation-induced dephasing in a homogeneous system (all time scales are normalized to the intrinsic dephasing time $1/\gamma$). (a) Delayed signal with $t_2-t_1=0.5$. (b) Signal at negative delay, $t_2-t_1=-0.5$.

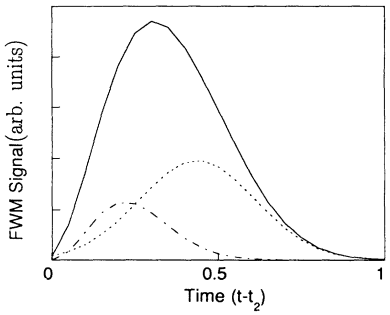

FIG. 2. Time-resolved transient FWM signals for an inhomogeneous system. The dot-dashed line is the signal due to excitation-induced dephasing and the dashed line is the echo due to saturation. Parameters used are $N\sigma=30$, $w=4$, and $t_2-t_1=0.5$.

for generating an echo. The dephasing-induced signal at negative time delay will not lead to an echo (no rephasing) since $t_2-t_1<0$. This signal is negligible when $|t_1-t_2|\gg 1/w$.

Finally we emphasize that the EID-induced signal depends on the relative polarization of the incident pulses. To illustrate this magnetic substates have to be included in the calculation. Here we take as an example the energy structure of heavy-hole transitions in GaAs (see Fig. 3). The transition is characterized by independent σ_+ and σ_- transitions. When $\mathbf{E}_1\perp\mathbf{E}_2$, the grating produced by the σ_+ transition is out of phase with that produced by the σ_- transition. If we take the dephasing rate to depend on the *total* exciton density as shown in [15], the EID-induced signal vanishes because there exists no spatial modulation in the dephasing rate. The time-integrated FWM signal intensity for a homogeneously broadened system (without including local-field effects) is given by

$$I(\phi)/I(90^\circ)=1+\left[\frac{N\sigma}{\Gamma_t}+\frac{1}{2}\left[\frac{N\sigma}{\Gamma_t}\right]^2\right]\cos^2(\phi)\ , \quad (7)$$

where ϕ is the angle between $\mathbf{E}_1$ and $\mathbf{E}_2$ and we assume $t_2-t_1>0$ and $\gamma_e(t-t_1)\ll 1$. The ratio also depends on the total dephasing rate. These EID effects are very important in understanding the polarization dependence of the nonlinear optical response in semiconductors [15].

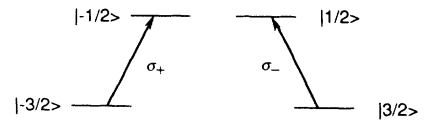

FIG. 3. The energy structure for the heavy-hole transition at zone center in GaAs.

Note that the local-field correction gives rise to an additional FWM response even in the cross-polarized geometry. In general, the different polarization dependence discussed above can be used to distinguish these effects experimentally.

In conclusion, although transient FWM provides a powerful method for studying electronic relaxation in materials, the interpretation of these measurements can be complex especially in dense interacting media. The temporal line shape and polarization dependence of the FWM signal can be used to study interactions between optical excitations.

The work performed at the University of Michigan is supported by AFOSR. The work performed at New York University is supported by NSF Grant No. PHY-9113590. The Arizona group acknowledges financial support through NSF, ARO/AFOSR(JSOP), and OCC.

[1] Tatsuo Yajima and Yoichi Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).

[2] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965); see also D. Bedeaux and N. Bloembergen, Physica **69**, 57 (1973).

[3] M. Wegener, D. S. Chemla, S. Schmitt-Rink, and W. Schafer, Phys. Rev. A **42**, 5675 (1990).

[4] See, for example, R. Frieberg, S. R. Hartmann, and J. T. Manassah, Phys. Rep. **7**, 101 (1973); Phys. Rev. A **42**, 5573 (1990); Jeffery J. Maki, Michelle S. Malcuit, J. E. Sipe, and Robert W. Boyd, Phys. Rev. Lett. **67**, 972 (1991).

[5] S. Saikan, H. Miyamoto, Y. Tosaki, and A. Fujiwara, Phys. Rev. B **36**, 5704 (1987).

[6] K. Leo, M. Wegener, J. Shah, D. S. Chemla, E. O. Gobel, T. C. Damen, S. Schmitt-Rink, and W. Schafer, Phys. Rev. Lett. **65**, 1340 (1990).

[7] D.-S. Kim, J. Shah, T. C. Damen, W. Schafer, F. Jahnke, S. Schmitt-Rink, and K. Kohler, Phys. Rev. Lett. **69**, 2725 (1992).

[8] S. Weiss, M.-A. Mycek, J.-Y. Bigot, S. Schmitt-Rink, and D. S. Chemla, Phys. Rev. Lett. **69**, 2685 (1992).

[9] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[10] R. G. Devoe and R. G. Brewer, Phys. Rev. Lett. **50**, 1269 (1983).

[11] A. G. Yodh, J. Golub, N. W. Carlson, and T. W. Mossberg, Phys. Rev. Lett. **53**, 659 (1984); see also P. R. Berman, Phys. Rep. **43**, 101 (1978).

[12] For a review, see, for example, P. R. Berman, J. Opt. Soc. Am. B **3**, 564 (1986).

[13] L. Schultheis, J. Kuhl, A. Honold, and C. W. Tu, Phys. Rev. Lett. **57**, 1635 (1986); A. Honold, L. Schutheis, J. Kuhl, and C. W. Tu, Phys. Rev. B **40**, 6442 (1989).

[14] D. S. Chemla, D. A. B. Miller, P. W. Smith, A. C. Gossard, and W. Wiegmann, IEEE J. Quantum Electron **QE-20**, 267 (1984).

[15] H. Wang, K. B. Ferrio, D. G. Steel, Y. Z. Hu, R. Binder, and S. W. Koch, Phys. Rev. Lett. **71**, 1261 (1993).

[16] For a text book discussion, see H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors*, 2nd ed. (World Scientific, Singapore, 1993); see also S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).

[17] See, for example, M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988); M. Lindberg, R. Binder, and S. W. Koch, Phys. Rev. A **45**, 1865 (1992); S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. **57**, 2752 (1986).

[18] The excited-state interaction can also lead to a shift in the transition energy. This energy shift can be included in Eq. (1) by making σ complex.

[19] M. Sargent, M. O. Scully, and W. E. Lamb, *Laser Physics* (Addison-Wesley, Reading, MA, 1974).

[20] In inhomogeneous systems such as strongly localized excitons [H. Wang *et al.*, Phys. Rev. Lett. **65**, 1255 (1990)], it is likely that only the excited-state population at ω contributes to the EID of $\rho_{eg}(\omega)$. In this limit EID will lead to an echo in the FWM signal, in contrast to the result presented in this paper.