Extra resonances in time-domain four-wave mixing

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Received December 9, 1992

We show that extra resonances, such as those caused in frequency-domain nonlinear wave mixing by pure dephasing or laser fluctuations, can also be induced by operation in the time domain. These pulse-length-induced extra resonances arise in transient-grating experiments when the laser pulses are short enough that a steady state cannot be achieved during the excitation process. We show theoretically that these resonances increase in strength with decreasing excitation pulse length until the pulse length becomes shorter than the dephasing time of the medium and quote an experimental example to support this interpretation.

Although frequency- and time-domain four-wave-mixing techniques have long been mainstays of optical physics, the basic physics of nonlinear wave mixing (NWM) is replete with subtleties that have not been fully appreciated. For instance, more than a decade passed between the proper treatment of the effects of damping in frequency-domain NWM and the realization that dephasing can partially remove destructive interferences between different wave-mixing pathways, thus yielding resonance signals that would otherwise not exist. An example of these extra resonances is a resonance between two unpopulated excited states that is only observed in the presence of pure dephasing. Extra resonances have been studied extensively, both experimentally[1] and theoretically,[1] and appear in all orders of NWM.[2] Collision-induced dephasing,[3] stochastic laser fluctuations,[4] and strong[5] and transient[6] laser fields have all been shown to cause extra resonances. All these studies assumed operation in the frequency domain. Here we demonstrate that extra resonances can instead result simply from performing time-domain NWM experiments.

It is widely believed that the frequency-domain nonlinear susceptibility and the time-domain nonlinear response of techniques that share NWM pathways are related by a Fourier transform. Nearly degenerate four-wave-mixing (NDFWM) and transient-grating (TG) experiments are considered to form such a pair,[7] and thus it might be expected that if an extra resonance does not occur in a (frequency-domain) NDFWM experiment, the associated transient would be absent in the corresponding (time-domain) TG experiment. This assumption is belied by experiment. For example, Bogdan *et al.* performed NDFWM experiments on the D_1 line of Na vapor[3] at pressures sufficiently low that no significant dephasing takes place on the experimental time scale. They observed no resonances between initially unpopulated excited states and weak resonances between equally populated ground states. The corresponding TG experiment was first performed by Rose *et al.*,[8] and Fig. 1 shows TG data taken under similar conditions (at a pressure of approximately 10^{-7} Torr). Despite negligible dephasing, these data show strong resonances at both the ground-state (fast oscillations) and excited-state (slow oscillations) hyperfine-splitting frequencies. (A similar phenomenon is observed in quantum-beat experiments.[9]) Insofar as the same experimental conditions do not yield frequency-domain resonances, the time-domain resonances can be considered extra.

Thus there is a fundamental difference between the behavior of extra resonances in the frequency domain and in the time domain.[10] We show theoretically that, although frequency-domain extra resonances increase in strength as the pure dephasing rate in-

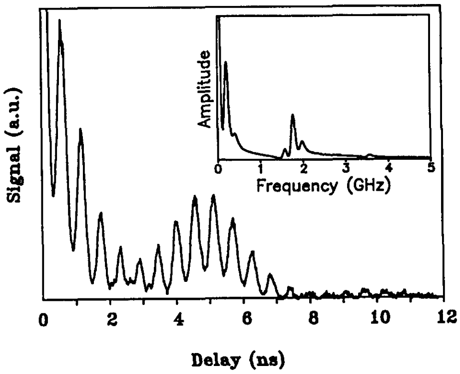

Fig. 1. TG data taken in a low-pressure Na cell by exciting and probing the D_1 line. The inset power spectrum shows frequency components at 1.77 GHz (ground-state hyperfine splitting) and 189 MHz (excited-state hyperfine splitting), as well as cross terms that arise in $|\mathcal{P}^{(3)}|^2$.

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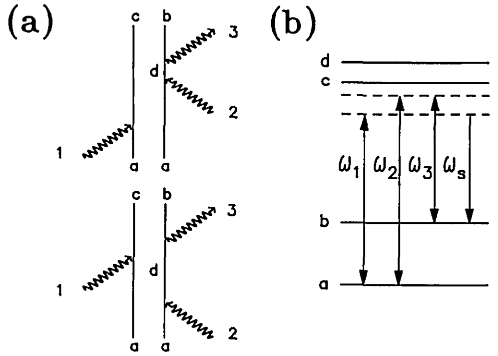

Fig. 2. (a) Feynman diagrams for extra resonances between initially unpopulated excited states. (b) Energy-level diagram and laser frequencies used in the calculations. (The dashed lines represent virtual energy levels split by E_{cd}.)

creases, the analogous time-domain extra resonances increase in strength as the pure dephasing rate decreases. These resonances occur naturally in TG experiments, and the resonance strength increases greatly as the laser pulse length decreases toward the relevant material dephasing time. We term this effect pulse-length-induced extra resonances (PLIERS).

Because in the cases in which we are interested the laser pulse duration cannot be assumed to be much longer than the material response of interest, we employ double-sided Feynman diagrams with the integral form of perturbation theory[11] to do our modeling. The TG and NDFWM are processes of the form $\omega_s = \omega_1 - \omega_2 + \omega_3$, so each term in the third-order polarization $\mathcal{P}^{(3)}$ follows the relation

$$\mathcal{P}^{(3)} \propto \int_{-\infty}^{t_{\mathrm{ob}}} \mathbf{E}_l(t_3)\exp[-i\Omega_3(t_{\mathrm{ob}} - t_3)]\mathrm{d}t_3 \times \int_{-\infty}^{t_3} \mathbf{E}_k^*(t_2)\exp[-i\Omega_2(t_3 - t_2)]\mathrm{d}t_2 \times \int_{-\infty}^{t_2} \mathbf{E}_j(t_1)\exp[-i\Omega_1(t_2 - t_1)]\mathrm{d}t_1\,, \quad (1)$$

where t_n and Ω_n are the time and complex material Bohr frequency of the nth field intervention, $\mathbf{E}_m$ is the electric field associated with ω_m, and j, k, and l depend on the four-wave-mixing pathway.

We consider resonances between initially unpopulated excited states, for which the Feynman diagrams are shown in Fig. 2(a). States $|c\rangle$ and $|d\rangle$ are closely spaced relative to the electronic transition energy, whereas ground states $|a\rangle$ and $|b\rangle$ can have an arbitrary spacing. Frequencies ω_1 and ω_2 are approximately resonant with ω_{ca} and ω_{da}, and ω_3 is approximately resonant with ω_{cb} and ω_{db}, where $\omega_{mn} = (E_{|m\rangle} - E_{|n\rangle})/\hbar$. In the frequency domain, we assume that $\mathbf{E}_m = E_m \exp(-i\omega_m t)$. Thus the NDFWM diagrams can be evaluated by using relation (1) to give[12]

$$\mathcal{P}^{(3)} \propto \frac{1 + i[(\Gamma_v - 2\Gamma_e)/(\omega_{cd} - \omega_1 + \omega_2 - i\Gamma_v)]}{(\omega_{ad} + \omega_2 - i\Gamma_e)(\omega_{ca} - \omega_1 - i\Gamma_e)}\,, \quad (2)$$

where Γ_v is the vibrational damping constant for coherences between states $|c\rangle$ and $|d\rangle$, and Γ_e is the electronic damping constant (which we assume is the same for all vibronic coherences). At two-photon resonance ($\omega_1 - \omega_2 = \omega_{cd}$), the relative contributions of the two diagrams to $\mathcal{P}^{(3)}$ are[12] $(i\Gamma_e + \Delta)/[\Gamma_v(\Delta^2 + \Gamma_e^2)]$ and $(i\Gamma_e - \Delta)/[\Gamma_v(\Delta^2 + \Gamma_e^2)]$, where Δ is the one-photon detuning. These relations illustrate two important effects that occur at two-photon resonance. First, in the absence of pure dephasing ($\Gamma_v = 2\Gamma_e$), there is no extra-resonance signal. Second, the real portions of the expressions for the two pathways exhibit complete destructive interference; only the imaginary part of these relations contributes to the signal. Under the conditions in which NDFWM is usually performed ($\Delta \gg \Gamma$), the extra-resonance strength is then proportional to Γ_e/Γ_v.

We now turn to the TG. So that the pulse duration and coherence time need not be considered separately, we use transform-limited model pulses of constant area. (The probe pulse is assumed to be a δ function, since its shape does not affect the extra-resonance strength at suitably long delays.) Here we present calculations for square pulses of duration d and amplitude E/d and for pulses given by one period of $(E/2d)[1 + \cos(\pi t/d)]$. Whereas the former shape gives simpler analytical expressions, the latter is more realistic and provides a way to check that results are not pulse-shape specific.

We can now evaluate relation (1) in the time domain. The relative contributions of the two diagrams (at two-photon resonance) to the portion of $\mathcal{P}^{(3)}$ that oscillates at ω_{cd} still take the form $A(iB + C)$ and $A(iB - C)$. We find for square pulses

$$A \propto \exp[-\Gamma_v(\tau - d/2)]/[d^2(\Delta^2 + \Gamma_e^2)], \quad (3a)$$

$$B = (\Gamma_e/\Gamma_v)k_1 + (k_2/k_3)[\exp(-\Gamma_v d) - \cos(\Delta d)\exp(-\Gamma_e d)] - (k_4/k_3)\sin(\Delta d)\exp(-\Gamma_e d)\,, \quad (3b)$$

$$C = -(\Delta/\Gamma_v)k_1 + (k_2/k_3)\sin(\Delta d)\exp(-\Gamma_v d) + (k_4/k_3)[\exp(-\Gamma_v d) - \cos(\Delta d)\exp(-\Gamma_e d)], \quad (3c)$$

where $k_1 = 1 - \exp(-\Gamma_v d)$, $k_2 = \Delta^2 - \Gamma_e^2 + \Gamma_e\Gamma_v$, $k_3 = \Delta^2 + (\Gamma_e - \Gamma_v)^2$, $k_4 = \Delta(2\Gamma_e - \Gamma_v)$, and τ is the experimental delay time.

There are several notable points about relations (3). First, as in the frequency domain, the real terms (C) exhibit complete destructive interference. Second, there are imaginary terms (B) for which the signal is not proportional to Γ_e/Γ_v when $\Delta \gg \Gamma_e$, as well as terms that do not go to zero when $\Gamma_v = 2\Gamma_e$. Finally, B increases with decreasing d. As a consequence of these properties, resonances that would not exist in NDFWM can appear in TG experiments.

This behavior can be understood in terms of the Feynman diagrams in Fig. 2(a). In the frequency domain, a steady state is reached between excitation and relaxation processes, and the two diagrams are exactly out of phase. Pure dephasing acts to break the direct relationship between vibronic and vibrational dephasing, allowing extra resonances to appear. However, given short enough pulses in the time domain, a steady state is never reached, and the resonances appear naturally.

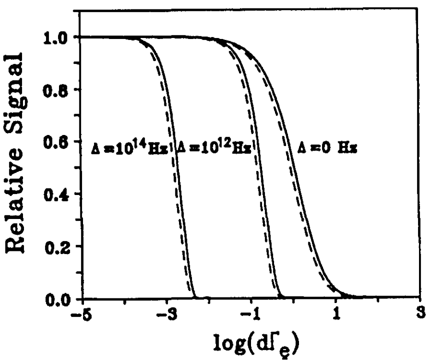

Fig. 3. PLIERS strength versus $d\Gamma_e$ for square pulses (solid curves) and 1 + cos pulse (dashed curves) for various values of Δ; Γ_e is 10^{11}/s.

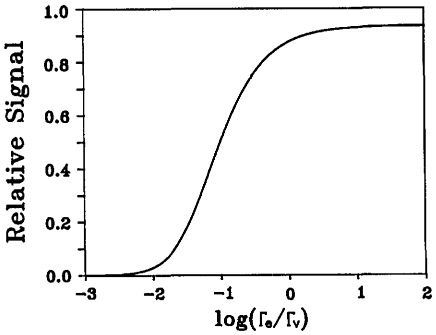

Fig. 4. Square-pulse PLIERS strength versus Γ_e/Γ_v for $d\Gamma_e = 0.1$.

In Fig. 3, the square of the terms in $\mathcal{P}^{(3)}$ that oscillate at ω_{cd} is plotted versus the ratio of the pulse length to the dephasing time $d\Gamma_e$ for square pulses (solid curves) and 1 + cos pulses (dashed curves), given $\Gamma_e = 10^{11}$/s and various values of Δ. At $\Delta = 0$, the signal is essentially constant when $d \ll 1/\Gamma_e$ but drops precipitously when d reaches a critical value (d_c) of approximately $1/\Gamma_e$. The same sort of behavior occurs for $\Delta \neq 0$, except that d_c decreases as Δ increases. Thus PLIERS occur when $d\Delta \lesssim 1$ (i.e., near or on electronic resonance).

Plotted in Fig. 4 is the square of the extra-resonance portion of the square pulse $\mathcal{P}^{(3)}$ as a function of Γ_e/Γ_v (for $d\Gamma_e = 0.1$). The signal increases monotonically with Γ_e/Γ_v and displays no special feature when $\Gamma_v = 2\Gamma_e$. Behavior similar to that in Fig. 3 is seen for all values of Γ_v, although varying Γ_v does change d_c.

It is interesting to contrast our results to those of Kumar and Agarwal, who investigated the effects of performing NDFWM experiments with short laser pulses[6] and showed that extra resonances can be caused by transient terms in $\mathcal{P}^{(3)}$ that are negligible in the steady state. PLIERS come about naturally through time-domain operation, although they arise similarly through terms that are neglected in the steady state. In contrast, the use of short pulses to operate in the frequency domain poses potentially severe frequency resolution problems.

In summary, the behavior of extra resonances in the time domain provides a stark contrast to those in the frequency domain. Time-domain extra resonances increase in strength with decreasing electronic dephasing, whereas the frequency-domain extra resonances decrease with decreasing electronic dephasing. Furthermore, in the absence of pure dephasing, PLIERS exist even though frequency-domain extra resonances disappear. Although the PLIERS strength is dependent on detuning and the electronic and vibrational dephasing rates, the maximum PLIERS signal that is attainable, given short enough constant-area pulses, is independent of all these parameters. These results underscore the fact that it is desirable in some instances to use a time-domain NWM technique rather than its Fourier-transform frequency-domain technique when probing phenomena that involve extra resonances.

This Letter is based on research supported by the National Science Foundation (grant CHE-9203603). Rick Trebino is supported by the Chemical Sciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy. This research was also supported by the Office of Naval Research, Physics Division (grant N000014-89-J1119). Computing equipment was provided by the National Science Foundation (grant CHE-88-21737). We thank Tim Brewer for assistance in obtaining the Na TG data.

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