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Four-wave mixing in optically dense media

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We show that four-wave mixing in optically dense media is very different than in an optically thin medium. In time-resolved degenerate four-wave mixing we experimentally observe "negative" time delay response, fast decay rates at short delay times, and broad shoulders at long delays. The observations are explained very well in terms of pulse propagation effects, and a theoretical framework is presented for the analysis of the nonlinear interaction. We treat both the incident and generated fields self-consistently, and solve for the interaction of short pulses with a resonantly absorbing medium. The implications for the extraction of relaxation rates from four-wave-mixing experiments involving ultrashort pulses in optically dense matter are discussed.

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Nonlinear optical interactions are used routinely for the experimental determination of many material properties. The measurement of fast relaxation processes and decay rates is an important, difficult task for which many nonlinear optical techniques have been developed. Short and ultrashort (picosecond and femtosecond) pulses are normally used for this purpose, and of the many methods employed, time-resolved degenerate four-wave mixing (FWM) [1] is a very powerful and much used technique. The most elementary FWM experiment involves an ensemble of homogeneously broadened two-level systems, having a polarization dephasing time T_2, interacting with two short laser pulses of the same frequency and time duration to generate a coherent response in the phase-matched direction. This nonlinear process can also be considered as the diffraction of a "probe" pulse from a polarization grating formed by two "pump" pulses. In many gaseous samples the total optical absorption in the sample is negligibly small, even for resonant interaction on line center, and the sample is optically thin. In this case, the time-resolved four-wave-mixing signal follows the time dependence derived by Yajima and Taira [2]: the signal is zero for negative time delays (the probe pulse arrives before the pump pulses), increases with the pulse rise time near zero time delay, and falls exponentially for positive delays with a decay time $\propto T_2$. This classical analysis has been used often to derive the relaxation rates in various experimental situations.

The situation may be very different for condensed matter, where strong absorption may be present. Here, the standard treatment of thin optical samples is no longer valid, and a more general treatment of the nonlinear interaction is required. Propagation of short pulses in an absorbing medium had been studied in the context of self-induced transparency [3], and the area theorem was derived. The limit of small area pulse propagation was discussed theoretically by Crisp [4], and experimentally by Rothenberg and Grischkowsky [5] and shown to result in the formation of "zero area" pulses. These authors have shown that for short pulses propagating in an optically thick medium, the pulse energy is hardly attenuated while the pulse area (total integrated envelope) goes to zero. Significant pulse envelope reshaping occurs, resulting from the interplay between the pulse and the polarization induced by it in the medium. The reshaped pulse envelope may have several lobes, or even periodic oscillations, depending on the relaxation rate and total absorption in the length of the sample, and to a lesser extent on the pulse parameters. This pulse reshaping is pronounced for a pulse length which is shorter than or equal to the dephasing time T_2 of the material. Laenen and Laubrereau [6], and Aaviksoo *et al.* [7] used the pulse reshaping to estimate material dephasing times in homogeneously and inhomogeneously broadened spectral lines, and related optical density effects were discussed [8,9] for three-pulse photon echo decay. Recently, Belov *et al.* [10] published theoretical calculations of FWM in optically thick samples, predicting the appearance of negative time delay response and signal decay times shorter than T_2. Their calculations are limited to samples whose physical length is small compared with the spatial extent of the optical pulse ($L<ct_p$). The experimental observation of negative time delay response in FWM in quantum wells was reported by Leo *et al.* [11], and explained by the authors in terms of higher-order susceptibilities interfering with the third-order FWM process [12].

In this Rapid Communication we present experimental measurements of time-resolved FWM signals induced by short pulses in optically thick samples, and provide the theoretical framework for describing the interaction. We show, both experimentally and numerically from the modified equations of motion, that pulse reshaping due to propagation leads to the formation of negative time delay signals and to apparent decay rates which are not simply given by the dephasing or population decay rates in the sample. The deviations from the optically thin case appear even for moderate line center absorption ($\alpha_0 L \sim 1$), which implies a very minor total absorption (a few percent) for ultrashort pulses whose spectral width exceeds the absorption profile.

Accounting for propagation effects in nonlinear optical interactions necessitates solving the coupled Maxwell-Bloch equations. We treat the nonlinear interaction perturbatively, in the standard way introduced by Yajima and Taira [2], solving for the third-order induced polarization. Propagation is introduced into the calculation by using the self-consistent, reshaped pulse envelopes, as given by Crisp [4]. The nonlinear interaction and the propagation are decoupled by assuming small area pulses; i.e., changes to the ground-state population are negligible. Finally, the FWM amplitude cor-

responds to the total energy of the generated field in the phase-matched direction, arrived at by dividing the sample into optically thin slices and adding the propagated contributions from all slices.

The theoretical formulation starts with two incident pulses which enter the sample as plane waves at $z=0$, having identical polarizations and arrival times delayed by τ. The propagation equation for each one is solved independently of the other pulse (linear regime) by the method outlined in [4], solving in the frequency domain for each frequency component of the input pulses, $\mathscr{E}_{1,2}(\nu,z)$. The linear material response is taken to be a homogeneous line with peak absorption at line center α_0 and width $1/T_2$, $A(\nu)=i\alpha_0/[(\imath/T_2)+\nu]$. The propagated pulses in frequency and space are

$$\mathscr{E}_{1,2}(\nu,z)=\mathscr{E}_{1,2}(\nu,0)\exp[(i/c)\nu z-A(\nu)z]. \tag{1}$$

The reshaped pulses are Fourier transformed back to the time domain and used to obtain the time- and space-dependent third-order polarization in the $2k_2-k_1$ direction. For zero detuning from resonance and for no population decay $(1/T_1\equiv 0)$, this polarization is given by [2]

$$\rho^{(-1,2)}(t,z)\propto\exp(-t/T_2)\int_{-\infty}^{t}\int_{-\infty}^{t'}\int_{-\infty}^{t''}\{\mathscr{E}_2(t',z)\mathscr{E}_2(t'',z)\mathscr{E}_1^*(t''',z)+\mathscr{E}_2(t',z)\mathscr{E}_1^*(t'',z)\mathscr{E}_2(t''',z)\}$$
$$\times\exp[T_2^{-1}(t'-t''+t''')]dt'dt''dt'''. \tag{2}$$

For the propagation of the generated wave we use the same small area treatment, but now in addition to the linear propagator of absorption and dispersion, the wave equation has an added source term given by the third-order induced polarization. The solution for the generated wave becomes

$$\mathscr{E}_3(\nu,L)=\exp[(i/c)\nu L-A(\nu)L]\int_0^L\exp[-(i/c)\nu z$$
$$+A(\nu)z]P^{(-1,2)}(\nu,z)dz\ , \tag{3}$$

where $P^{(-1,2)}\equiv N\rho^{(-1,2)}$ and we use the Fourier transform to go from the time to frequency domains. Extension of the analysis to nonresonant interaction is straightforward [13].

The measured integrated FWM signal corresponds to the total energy

$$S(\tau)=\int_{-\infty}^{+\infty}|\mathscr{E}_3(\nu,L)|^2d\nu \tag{4}$$

for each time delay τ between the two pulses. Both the reshaping of the generated wave and the oscillatory time dependence developed in the pulse envelopes are manifested in the behavior of the FWM signal as a function of the delay between the input pulses. Thus, the decay rate of the FWM amplitude is not necessarily a simple exponential decay with rate proportional to $1/T_2$. At high optical density, the measured decay rate is governed mostly by the effects of the linear absorption and dispersion, and not by the actual dephasing. In addition, the "long tails" developed by the pulse are manifested as "negative" time delay response.

In order to experimentally separate the effects of absorption and of pure dephasing, we used an atomic vapor system. The experiments were performed using potassium vapor in a 2-mm-thick quartz cell, on the D_2 line at 767 nm. Separate control of temperature and buffer-gas (He) pressure in the cell allowed the independent variation of the absorption α_0 and the polarization dephasing time T_2. The laser system consists of a Coherent 702 double jet dye laser pumped by a frequency-doubled coherent mode-locked Antares neodymium doped yttrium aluminum garnet (Nd:YAG) laser. The dye laser was optimized for $\sim$ 2 ps pulses with stable spectrum and clean autocorrelation. The pulse energy used in these experiments was $\sim$ 1 nJ/pulse, which is translated to a pulse area of <0.05, so that the experiments conform to the range of validity of the small area theoretical treatment. We used the three-dimensional [14] phase-matching geometry, where all beams propagate forward almost collinearly in the sample. All three input beams had the same polarization, were focused into the interaction zone by a 25-cm lens and chopped at two different frequencies, and the signal was detected by a phase-sensitive detector. Two of the beams were set for temporal coincidence while the third was variably delayed. Zero time delay was determined independently by the observation of interference fringes between any two incident beams. The inaccuracy in the zero time determination is estimated at less than ± 0.15 ps. The pulses were nearly transform limited, as was ascertained by comparing the intensity autocorrelation to the spectrum observed on an optical multichannel analyzer (OMA). The spectrum for a single picosecond pulse compared to that for a train of pulses showed some spectral jitter, estimated at less than the pulse spectral width. The time-resolved FWM intensity was measured for a set of buffer-gas pressures and temperatures.

Figure 1 depicts the measured FWM signal at low potassium concentration, which is closest to the conditions of a thin optical sample ($T=390$ K, $P_{\mathrm{He}}=800$ Torr, $\alpha_0 L=0.1$). The FWM response exhibits the "normal" fast rise time and exponential decay, and the determination of T_2 by fitting the measured data to a simple exponential yields $T_2=29$ ps, very close to the value of 28.5 ps which is computed from the measured pressure and temperature. The dashed line is a theoretical calculation which coincides with the thin sample prediction, the only difference being a negative time delay response three orders of magnitude smaller than the peak response, not discernible in this linear plot. The inset to the figure depicts the pulse intensity autocorrelation measurement, which reveals a clean pulse with a full width at half maximum of 2 ps.

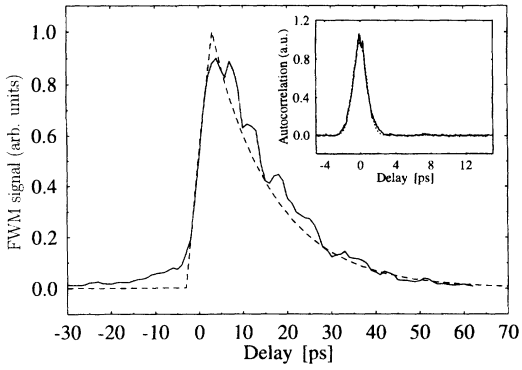

FIG. 1. Time-resolved four-wave mixing at low optical density ($T=390$ K, $P_{He}=800$ Torr, $\alpha_0 L=0.1$). The dashed line is the calculated theoretical curve (see text). The inset depicts the measured pulse intensity autocorrelation trace and a Gaussian envelope fit.

The theoretical curves (dashed lines) in all the figures were calculated by the method outlined in this Rapid Communication, without any fitting parameters. We measured the temperature and buffer-gas pressure, and for the collisional parameters we used published values for the potassium line broadening due to K-K and K-He collisions [15]. We used intensity autocorrelation measurements to derive the incident pulse spectral line shape, and the observed frequency jitter was accounted for by calculating the off-resonance response and allowing the pulse central frequency to be (on the average) 10% of the time detuned by 1/6 of the linewidth.The results are insensitive to variations of the averaging procedure. We have also included the corresponding thin sample prediction in each graph (dotted lines) for comparison.

Figure 2 depicts the measured and calculated FWM spectra at a constant buffer-gas pressure ($P_{He}=400$ Torr) and increasing potassium concentration (temperature $T=410$, 430, 450 K; partial potassium pressure $P_K=0.2$, 0.7, 2.1 mTorr; absorption $\alpha_0 L=0.5$, 2.0, 5.6). It should be noted that these absorption coefficients are for a narrow probe at line center, and the highest actual absorption of the short pulses was less than 5% in all cases. In Fig. 2(a) the general shape of a sharp increase followed by what appears to be an exponential decay (straight line on the semilog plot) is maintained, whereas in Figs. 2(b) and 2(c) the shape is distorted completely to the point where the curve appears almost symmetric, and the Yajima shape is completely lost. The theory (shown in dashed lines) quantitatively captures the features of the change as the absorption increases, both for negative, and for positive delay times. The buffer-gas pressure, which is the dominant contribution to the dephasing, is the same in all the graphs. Thus, the calculated dephasing times are similar as well (60, 63, 66 ps), but the observed signals are very different. Even when there seems to be exponential decay the apparent decay gives the wrong dephasing time (estimated $T_2=$ 47, 30, 16 ps), unless the full theory is applied to the analysis. As the absorption increases, the deviation from the thin sample prediction (dotted lines) becomes even more significant, and the extraction of any rates directly from the measurement is all but impossible.

In Figure 3 we present the FWM signal at two temperatures ($T=410$,450 K, $P_K=0.2$,2.1 mTorr), and two helium

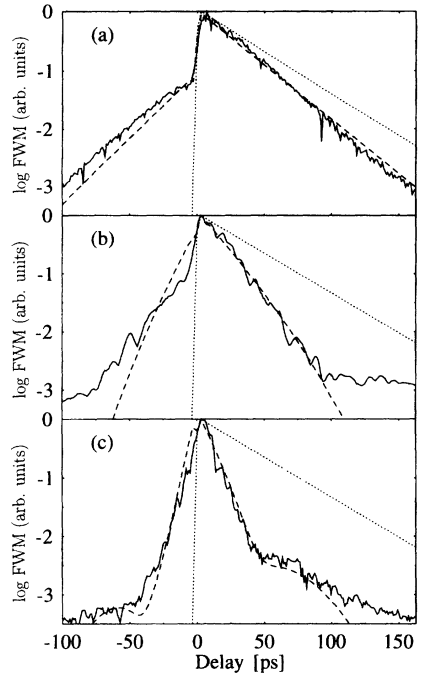

FIG. 2. Experimental measurements (solid), theoretical calculations (dashed), and thin sample predictions (dotted) of $\log_{10}$ FWM signal amplitudes vs time delay. The buffer-gas pressure is 400 Torr; the temperatures and peak absorption for each case are (a) $T=410$ K, $\alpha_0 L=0.5$; (b) $T=430$ K, $\alpha_0 L=2.0$; (c) $T=450$ K, $\alpha_0 L=5.6$.

buffer-gas pressures ($P_{He}=200$,800 Torr). A negative delay response is apparent in Fig. 3(a), but the positive time delay signal is described well by an exponential. The decay rate extracted directly from the plot corresponds to $T_2=26$ ps, while a thermodynamic estimate gives $T_2=30$ ps. The observed behavior is very different for Figs. 3(b), 3(c), and 3(d). The qualitative structure of a sharp increase at $\tau=0$

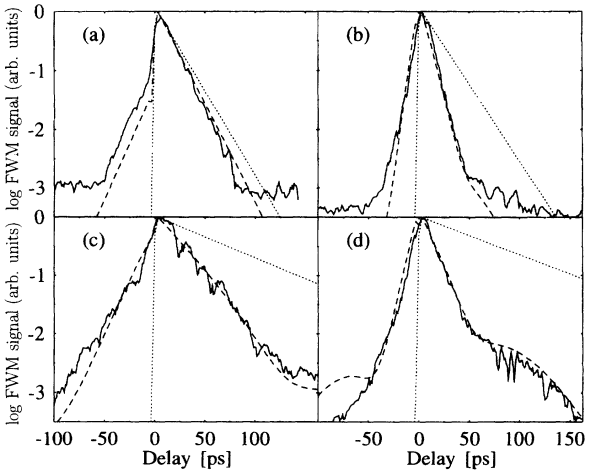

FIG. 3. Measured $\log_{10}$ FWM signal vs delay (solid) and respective full theory (dashed) and thin sample (dotted) calculations. (a) $P_{He}=800$ Torr, $T=410$ K, $\alpha_0 L=0.3$; (b) $P_{He}=800$ Torr, $T=450$ K, $\alpha_0 L=2.8$; (c) $P_{He}=200$ Torr, $T=410$ K, $\alpha_0 L=3.3$; (d) $P_{He}=200$ Torr, $T=450$ K, $\alpha_0 L=9.6$.

followed by an exponential decay for positive delays is not maintained and the signal is almost symmetric around zero delay, while at longer positive time delays the signal develops pronounced "shoulders." The qualitative change in decay rate for increasing concentration at a constant buffer-gas pressure is manifested in the comparison of Figs. 3(a) to 3(b), and 3(c) to 3(d). Any attempt to extract the dephasing time from measurements like Figs. 3(b), 3(c), and 3(d) would erroneously result in a rate much faster than the actual $1/T_2$. Directly extracted times by a simple exponential fit are 13, 44, and 22 ps for 3(b), 3(c), and 3(d), respectively, while the actual numbers from the known collision cross sections are 33, 126, and 132 ps.

In conclusion, the present paper is concerned with the analysis of four-wave mixing in optically dense media in general, and with the extraction of relaxation rates from such experiments in particular. A self-consistent methodology is presented for the calculation of the FWM response of optically thick samples, which is based on the proper handling of propagation of the incident as well as the generated pulses. We show that propagation effects should be included in the analysis, and present a formalism to do it in the small area limit, valid for many experiments involving picosecond pulses interacting with a resonant transition. The signature of optical density effects includes negative time delay response, deviation from purely exponential decays, and the appearance of broad "shoulders" for long time delays, and all of them are quantitatively explained by our generalized treatment. It is further shown that for ultrashort pulses, even moderate absorption significantly affects the apparent FWM decay rates, and care should be taken in inferring polarization dephasing times directly from the measurements. Extension of the theory to inhomogeneously broadened lines or to the interaction with several resonant transitions simply requires the incorporation of the appropriate line-shape function and summation over the different contributions. Moreover, the methodology presented here is not restricted to four-wave-mixing interactions. It is applicable, after the proper changes in the details of the equation describing the nonlinear interaction, to any experimental situation where short pulses nonlinearly interact with an optically thick medium. Utilizing the theoretical framework presented in this Rapid Communication, it is now possible to calculate the effect of optical density on measured nonlinear signals for specific experimental situations. Whenever propagation effects are suspected, a cross-correlation measurement of the propagated and incident pulses can determine the degree of pulse reshaping and whether the standard perturbative treatment should be replaced with the more general formulation presented in this paper.

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