Rayleigh-Type Nondegenerate Four-Wave Mixing: Ultrafast Measurement and Field Correlation

Panming Fu, Qiang Jiang, Xin Mi, and Zuhe Yu

Laboratory of Optical Physics, Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, China

(Received 22 May 2001; revised manuscript received 16 October 2001; published 5 March 2002)

We report on an ultrafast longitudinal time measurement by a nonresonant Rayleigh-type nondegenerate four-wave mixing (NFWM). We investigated the field-correlation effects on Rayleigh-type NFWM by examining the time-delayed dependence of the NFWM spectra. Based on the field-correlation effects, a time-delayed method is proposed to suppress the thermal effect, and ultrafast relaxation time can be measured even in an absorbing medium.

DOI: 10.1103/PhysRevLett.88.113902 PACS numbers: 42.65.Hw, 42.50.Ar, 42.65.Es, 42.65.Re

Ultrashort-pulse nonlinear optical spectroscopy has proved to be a valuable technique for investigating the dynamics of a wealth of mechanisms in condensed matters. Using femtosecond time-resolved four-wave mixing (FWM), valuable information on the dephasing dynamics in semiconductors and molecular materials has been obtained [1,2]. The time resolution of this method is limited by the pulse width. The ultrafast dephasing phenomena can also be studied by time-delayed FWM with incoherent light [3]. This technique is intrinsically related to the optical coherent transient spectroscopy with an advantage that the time resolution is determined by the correlation time τ_c of the light source. While the dephasing time T_2 has been measured by many groups under the condition that $T_2 > \tau_c$, the measurement of longitudinal time T_1 has proved much more difficult and seemed to be limited at least by the condition $T_1 > \tau_c$ [4].

In this Letter, we report on Rayleigh-type nondegenerated four-wave mixing (NFWM). In contrast to the resonance-enhanced NFWM where the dephasing time can be measured [5], Rayleigh-type NFWM is a nonresonant process and can be employed to measure the longitudinal time. We employed Rayleigh-type NFWM to study the ultrafast molecular dynamics in CS_2. Previously, ultrafast molecular dynamics in liquid has been studied either in the time domain by time-resolved optical Kerr effect or in the frequency domain by light scattering measurement [6]. The time resolution of optical Kerr effect is limited by the laser pulse width. On the other hand, the frequency resolution of light scattering is determined by the resolution of the monochromator. Rayleigh-type NFWM is a frequency-domain nonlinear laser spectroscopy with high frequency resolution, which is determined by the laser linewidth. Since the relaxation time is deduced from the NFWM spectrum, the measurement is not limited by the laser pulse width or the laser correlation time.

We also investigated the field-correlation effects on Rayleigh-type NFWM. The outcome of these studies suggests a novel method for the suppression of thermal effect. Thermally induced phase grating in an absorbing sample can be quite efficient; contributions from a thermal grating may dominate the NFWM spectrum and obscure the valuable information of the spectrum. The difficulty of the problem of thermal grating suppression is that both the strength of the grating which we are interested in and the thermal-grating strength depend similarly on nearly all of the various experimental conditions. Based on the field-correlation effects, here we propose a time-delayed method for the thermal-grating suppression. Therefore, ultrafast longitudinal relaxation time can be measured even in an absorbing medium.

Rayleigh-type NFWM is a third-order nonlinear phenomenon which involves three incident beams (see Fig. 1). Beams 1 and 2 have the same frequency ω_1 and a small angle θ exists between them. Beam 3 with frequency ω_3 is propagating along the opposite direction of beam 1. The NFWM signal (beam 4) was propagated along a direction almost opposite that of beam 2. There are two mechanisms involved. First, the nonlinear interaction of beams 1 and 2 with the medium gives rise to a static molecular-reorientational grating. The NFWM signal is the result of the diffraction of beam 3 by the grating. Second, beams 2 and 3 with different frequencies build up a moving grating. If the grating lifetime $1/\gamma$ is larger than the time it needs to move over one spatial period (which is of order $1/|\omega_1 - \omega_3|$), then destructive interference occurs during

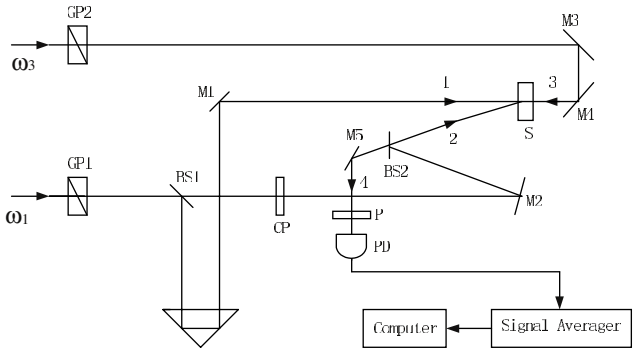

FIG. 1. Experimental setup. BS's, beam splitters; M's, mirrors; GP's, Glan prisms; CP, Soleil-Babinet compensator; P, Polarizer; PD, photodiode; S, sample.

engraving and erases the grating. In other words, the signal originates from the spectral region $|\omega_1 - \omega_3| < \gamma$.

The complex incident laser fields can be written as $E_i(\mathbf{r},t) = A_i(\mathbf{r},t)\exp(-i\omega_i t) = \varepsilon_i u_i(t)\exp[i(\mathbf{k}_i\cdot\mathbf{r} - \omega_i t)]$, $(i = 1,2,3)$. ε_i and $\mathbf{k}_i$ are the constant field magnitude and the wave vector of the ith beam, respectively; $u_i(t)$ is a dimensionless statistical factor that contains the phase and the amplitude fluctuations. We assume that beams 1 and 2 come from a single laser source, then $u_1(t) = u(t)$, $u_2(t) = u(t-\tau)$. Here τ is the time delay of beam 2 with respect to beam 1. The nonlinear polarization responsible for the Rayleigh-type NFWM is $P(\mathbf{r},t) = P_1(\mathbf{r},t) + P_3(\mathbf{r},t)$ with $P_1(\mathbf{r},t) = Q_1(\mathbf{r},t)E_3(\mathbf{r},t)$ and $P_3(\mathbf{r},t) = Q_3(\mathbf{r},t)E_1(\mathbf{r},t)$. Here $Q_1(\mathbf{r},t)$ and $Q_3(\mathbf{r},t)$ are order parameters of the gratings induced by beams 1 and 2 and beams 2 and 3, respectively, which satisfy

$$\frac{\partial Q_1}{\partial t} + \gamma Q_1 = \gamma\chi A_1 A_2^* \exp i[(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}],$$

$$\frac{\partial Q_3}{\partial t} + \gamma Q_3 = \gamma\chi A_3 A_2^* \exp i[(\mathbf{k}_3 - \mathbf{k}_2)\cdot\mathbf{r} - \Delta t]. \quad (1)$$

Here $\Delta = \omega_3 - \omega_1$; χ and γ are the nonlinear susceptibility and relaxation rate of the gratings. Equation (1) can be solved formally, from which we obtain

$$P_1(\mathbf{r},t) = S(\mathbf{r},t)\left[\chi\gamma A_3(t)\int_0^\infty dt' A_1(t-t')A_2^*(t-t')\exp(-\gamma t')\right],$$

$$P_3(\mathbf{r},t) = S(\mathbf{r},t)\left\{\chi\gamma A_1(t)\int_0^\infty dt' A_2^*(t-t')A_3(t-t')\exp[-(\gamma - i\Delta)t']\right\}. \quad (2)$$

Here $S(\mathbf{r},t) = \exp\{i[(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3)\cdot\mathbf{r} - \omega_3 t]\}$. The NFWM signal intensity is proportional to the average of the absolute square of the polarization over the random variable of the stochastic process, i.e., $I \propto \langle|P|^2\rangle$. We assume that the pump laser is a multimode thermal source. In this case, $u(t)$ has Gaussian statistics with its fourth-order coherence function satisfying $\langle u(t_1)u(t_2)u^*(t_3)u^*(t_4)\rangle = \langle u(t_1)u^*(t_3)\rangle\langle u(t_2)u^*(t_4)\rangle + \langle u(t_1)u^*(t_4)\rangle\langle u(t_2)u^*(t_3)\rangle$. If the laser sources have Lorentzian line shape, we have the second-order coherence function $\langle u(t)u^*(t-\tau)\rangle = \exp(-\alpha|\tau|)$ and $\langle u_3(t)u_3^*(t-\tau)\rangle = \exp(-\alpha_3|\tau|)$. Here $\alpha = \delta\omega_1/2$, $\alpha_3 = \delta\omega_3/2$ with $\delta\omega_1$ and $\delta\omega_3$ the laser linewidth (full width at half maximum) of beams 1 and 3. Following the process given in Ref. [7], an analytic closed form for the NFWM signal intensity can be obtained.

The experimental setup is shown in Fig. 1. The second harmonic of a Quanta-Ray YAG laser was used to pump two dye lasers. The first dye laser had wavelength 585 nm, linewidth 0.007 nm, and pulse width 5 ns. It was split into beams 1 and 2 after passing through a beam splitter, and the two beams intersect in the sample with a small angle (1.3°) between them. Beam 3, which originated from the second dye laser, had linewidth 0.007 nm. The wavelength of beam 3 could be scanned by a computer-controlled stepping motor. Our sample was CS_2 which was contained in a cell with thickness 2 mm. In this experiment the incident fields had the following polarization configuration: $\mathbf{E}^{(1)} \parallel \mathbf{E}^{(3)} \parallel \mathbf{x}$ and $\mathbf{E}^{(2)} \parallel \mathbf{y}$, and the signal was polarized along $\mathbf{y}$. Figure 2(a) presents the Rayleigh-type NFWM spectrum when $\tau = 0$. The spectrum exhibits a symmetric resonant line added on a constant nonresonant background. Moreover, the resonant signal is larger than the nonresonant background by a factor of about 3. As is well known, the optical Kerr effect for the liquid CS_2 has at least two components, i.e., a relatively long "Debye" component and a shorter "interaction-induced" component. To fit our experimental data, we extend our theory to include two relaxation components with relaxation times γ_f and γ_s. The ratio between these two components is η, so that for the monochromatic incident lights, the nonlinear polarization $P \propto \eta[1 + \gamma_s/(\gamma_s - i\Delta)] + (1-\eta)[1 + \gamma_f/(\gamma_f - i\Delta)]$. The solid curves are the theoretical curves with the following parameters: $\tau = 0$ ps, $\eta = 0.3$, $\gamma_s = 3.0\times10^{11}$ sec^{-1}, $\gamma_f = 2.3\times10^{12}$ sec^{-1}, and $\alpha = \alpha_3 = 3.8\times10^{10}$ sec^{-1}. Considering the uncertainty of the measurement, the corresponding relaxation times are 1.7 ± 0.2 ps and 220 ± 30 fs. In our experiment two relaxation constants are obtained by assuming that the nonlinear polarization consists of a sum of two Lorentzians. This is consistent with the empirical formula used to fit the time-resolved optical Kerr effect data [8] that the signal decay consists of a sum of two exponentials.

The above experiment was performed in the condition that beams 1 and 2 were fully correlated. We now consider the case when the relative time delay between beams 1 and 2 is much larger than the laser correlation time so that no correlation exists between beams 1 and 2. Figure 2(b) presents the Rayleigh-type NFWM spectrum when $\tau = 2800$ ps. It shows that field correlation has little effect on the NFWM spectrum. The solid curve is the theoretical curve with $\tau = 2800$ ps, while all the other parameters are the same as that used in Fig. 2(a). Field correlation has a profound influence on the Rayleigh-type NFWM spectrum when $\alpha \gg \gamma$. To demonstrate this, we study Rayleigh-type NFWM mediated by thermal effects. Our sample was oxazine dye dissolved in ethanol (2×10^{-4} mol). All the laser beams were vertically polarized. Figures 3(a) and 3(b) present the Rayleigh-type NFWM spectra when $\tau = 0$ and 2800 ps, respectively. The Rayleigh-type NFWM spectrum exhibits a large nonresonant background which obscures the resonant signal almost completely when beams 1 and 2 are fully correlated [Fig. 3(a)]. In contrast, the intensity of the resonant signal and the nonresonant background are about the same when beams 1 and 2 are uncorrelated [Fig. 3(b)]. The solid curves in Fig. 3 are the theoretical curves. Thermal grating has long relaxation time (in the microsecond region), which is larger than

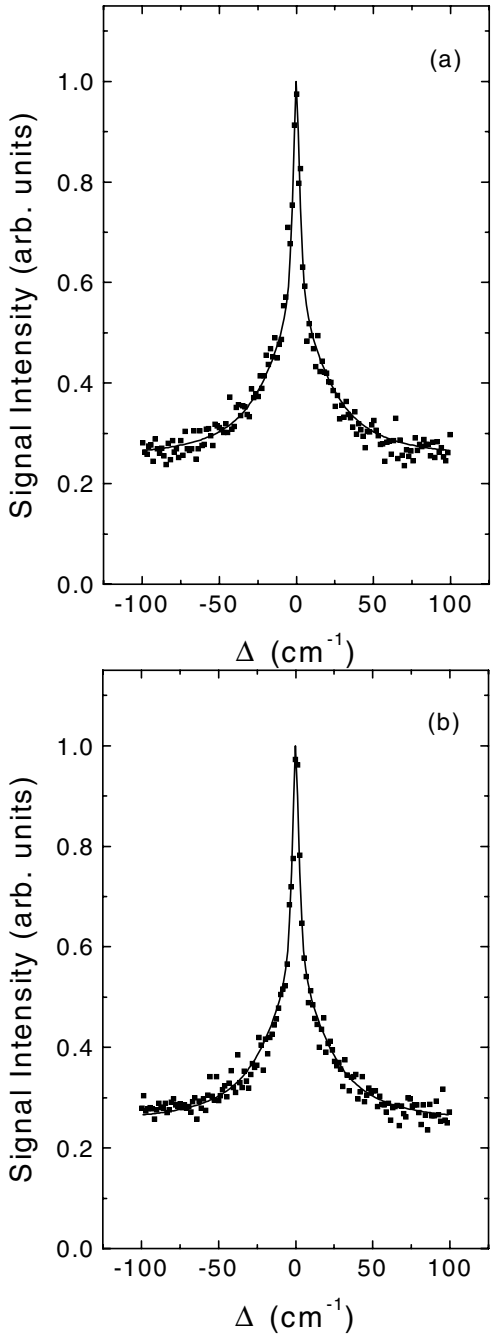

FIG. 2. Rayleigh-type NFWM spectra in CS_2 when (a) $\tau = 0$ ps and (b) $\tau = 2800$ ps. Solid curves are theoretical curves with $\gamma_s = 3.0 \times 10^{11}$ sec^{-1}, $\gamma_f = 2.3 \times 10^{12}$ sec^{-1}, $\alpha = \alpha_3 = 3.8 \times 10^{10}$ sec^{-1}, and $\eta = 0.3$.

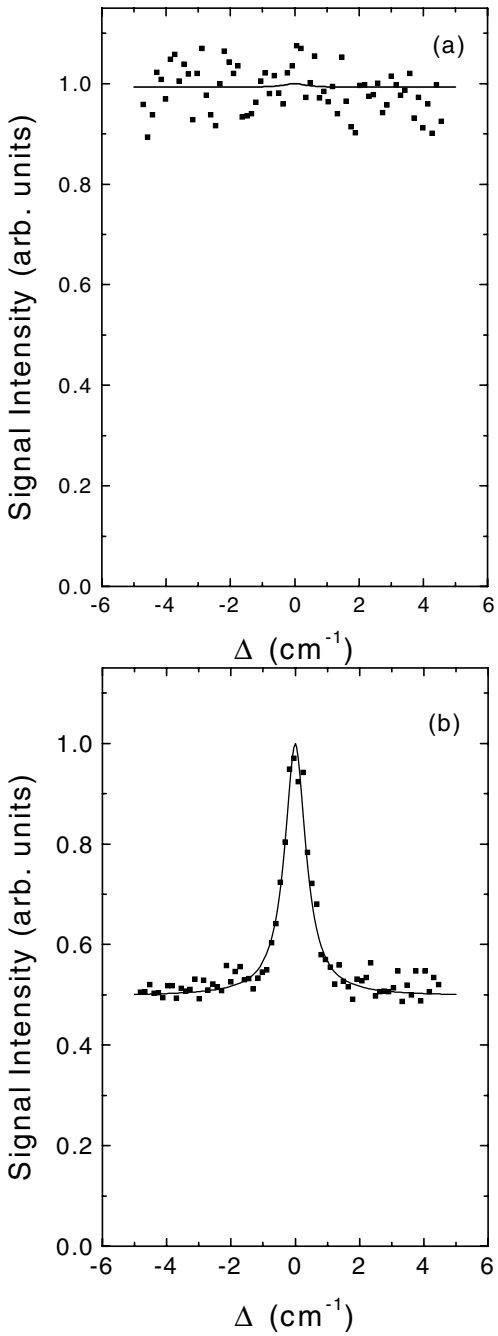

FIG. 3. Rayleigh-type NFWM spectra in oxazine dye when (a) $\tau = 0$ ps and (b) $\tau = 2800$ ps. Solid curves are theoretical curves with $\gamma_1 = \gamma_3 = 2 \times 10^8$ sec^{-1} and $\alpha = \alpha_3 = 3.8 \times 10^{10}$ sec^{-1}.

the laser pulse width. Therefore, because of the finite interaction time between the laser and the material, the role of the relaxation time should be replaced by the laser pulse width. We have $\gamma = \tau_p^{-1}$, where $\tau_p = 5 \times 10^{-9}$ sec is the laser pulse width. Other parameters used are $\alpha = \alpha_3 = 3.8 \times 10^{10}$ sec^{-1}. We note that, previously, τ dependence of thermal grating has been used to measure the coherence time of picosecond pulses [9].

The resonant signal and the nonresonant background originate from the order parameters $Q_3(\mathbf{r}, t)$ and $Q_1(\mathbf{r}, t)$, respectively. According to Eq. (2), integration effects are involved in the establishment of order parameters of the gratings. Considering the broadband case (i.e., $\gamma \ll \alpha, \alpha_3$), the effect of integration is to wash out the gratings. At zero time delay no washout takes place in the establishment of $Q_1(\mathbf{r}, t)$ because the phase factor ϕ_1 of $A_1(t - t')A_2^*(t - t')$ is stationary. On the other hand, the phase factor ϕ_3 of $A_3(t - t')A_2^*(t - t')$ is a random variable which fluctuates with a characteristic time scale $(\alpha + \alpha_3)^{-1}$. Because of the integration effect, the fast random fluctuation of ϕ_3 leads to the reduction of the amplitude of Q_3. Therefore, the Rayleigh-type NFWM

spectrum is dominated by a large nonresonant background when $\tau = 0$. The Rayleigh-type NFWM spectrum in the limit of $\alpha|\tau| \gg 1$ is quite different. Similar to Q_3, Q_1 is now induced by mutually incoherent fields. If $\alpha_3 = \alpha$, then the influences of the integration effect on Q_1 and Q_3 are equal. In the case of $\Delta = 0$, the signals from Q_1 and Q_3 will be equal. Furthermore, the relative phase between $P_1(\mathbf{r}, t)$ and $P_3(\mathbf{r}, t)$ is a stochastic variable. Since there is no interference between them, we have $B = 1$, where B is the ratio between the intensity of the resonant signal at $\Delta = 0$ and the nonresonant background. We now consider the case when $\gamma \gg \alpha, \alpha_3$. In this case, the material gratings have very short relaxation times; therefore, they can respond to the phase fluctuations of the fields almost immediately. More specifically, $A_1(t - t')A_2^*(t - t')$ and $A_2^*(t - t')A_3(t - t')$ in Eq. (2) are slowly varying functions in comparison with $\exp(-\gamma t')$ which have a peak at $t' = 0$, and therefore can be approximated as $A_1(t)A_2^*(t)$ and $A_2^*(t)A_3(t)$, respectively. We have $P(\mathbf{r}, t) \propto \chi\gamma A_1(t)A_2^*(t)A_3(t) \int_0^\infty dt' \{\exp(-\gamma t') + \exp[-(\gamma - i\Delta)t']\}$. The above equation indicates that the Rayleigh-type NFWM spectrum is independent of τ. Although the phases of P_1 and P_3 fluctuate randomly, the relative phase between them is fixed; therefore, we have $B = 3$ instead of 1 due to the interference between P_1 and P_3.

Based on the field-correlation effects, here we propose a time-delayed method for the thermal-grating suppression. Consider a Rayleigh-type NFWM experiment in an absorbing sample. Because of the high efficiency of thermal effects, then similar to Fig. 3(a) the Rayleigh-type NFWM spectrum will exhibit a large nonresonant background when $\tau = 0$. The nonresonant background can be reduced if we increase the relative time delay between beams 1 and 2. A reduction factor of $2\alpha/\gamma$, which is about 4×10^2 in our case, can be achieved when beams 1 and 2 become uncorrelated. The residue thermal effects can be reduced further if we use pump beams with broader linewidth and/or longer pulse width. On the other hand, in contrast to the thermal grating, the field correlation has little influence on the Rayleigh-type NFWM spectrum when the grating has fast relaxation time. Therefore, ultrafast longitudinal relaxation time can be measured even in an absorbing medium. Using a similar idea, we have revealed the hidden Raman resonance from thermal background by a time-delayed method in Raman-enhanced NFWM experiments [10].

As a nonlinear spectroscopy, the most important question in Rayleigh-type NFWM is the "frequency bandwidth," or, equivalently, the avoidance of phase mismatch during wavelength tuning. The coherence length in Rayleigh-type NFWM is given by $l_c = 2c/[n(\omega_1/\omega_3)|\omega_1 - \omega_3|\theta^2]$, where n is the refractive index. To ensure that the phase mismatching does not affect the experimental results, it requires that the coherence length l_c is larger than the thickness L of the sample cell. Under our experimental conditions (i.e., $n \simeq 1.5$, $\theta \simeq 2.27 \times 10^{-2}$ rad, and $L = 2$ mm), the frequency bandwidth is about 3600 cm^{-1}. Frequency bandwidth can be increased further by reducing the angle between beams 1 and 2; therefore, in principle, relaxation time shorter than 10 fs can be measured. In the coherent Raman spectroscopy the spectrum usually exhibits an asymmetric line shape, because of the interference between the resonant signal and the nonresonant background [11]. In contrast, Rayleigh-type NFWM is a nonresonant process, and the line shape is symmetric even though interference between signals from two gratings exists. Finally, although several frequency-domain nonlinear laser spectroscopies have been suggested for the ultrafast measurement [12], Rayleigh-type NFWM possesses the following features. This involves three incident beams; therefore, different tensor components of the nonlinear susceptibility can be measured independently. The angle between beams 1 and 2 can be adjusted for individual experiments to optimize the tradeoff between better phase matching and larger interaction volume or better spatial resolution.

In conclusion, we report on an ultrafast longitudinal time measurement by a nonresonant Rayleigh-type NFWM. We also propose a time-delayed method to suppress the thermal effect, so that ultrafast relaxation time can be measured even in an absorbing medium.

This work is supported by the National Natural Science Foundation of China.

[1] D. S. Chemla, in *Nonlinear Optics in Semiconductors,* edited by R. K. Willardson and A. C. Beers (Academic Press, New York, 1999).
[2] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[3] N. Morita and T. Yajima, Phys. Rev. A **30**, 2525 (1984); R. Beach and S. R. Hartmann, Phys. Rev. Lett. **53**, 663 (1984).
[4] A. Débarre, J-L. Le Gouët, I. Lorgeré, and P. Tchénio, J. Phys. B **26**, 3435 (1993); M. Tomita and M. Matsuoka, J. Opt. Soc. Am. B **3**, 560 (1986).
[5] Z. Yu, H. Lu, P. Ye, and P. Fu, Opt. Commun. **61**, 287 (1987); X. Mi, Z. Yu, Q. Jiang, and P. Fu, Phys. Rev. A **48**, 3203 (1993).
[6] S. Kinoshita, Y. Kai, M. Yamaguchi, and T. Yagi, Phys. Rev. Lett. **75**, 148 (1995), and references therein.
[7] P. Fu, Z. Yu, X. Mi, Q. Jiang, and Z. Zhang, Phys. Rev. A **46**, 1530 (1992).
[8] B. I. Greene and R. C. Farrow, Chem. Phys. Lett. **98**, 273 (1983).
[9] H. J. Eichler, U. Klein, and D. Langhans, Appl. Phys. **21**, 215 (1980); R. Trebino, E. Gustafson, and A. E. Siegman, J. Opt. Soc. Am. B **3**, 1295 (1986).
[10] Z. Yu, X. Mi, Q. Jiang, P. Ye, and P. Fu, Opt. Lett. **13**, 117 (1988); Z. Yu, X. Mi, Q. Jiang, and P. Fu, Opt. Commun. **107**, 120 (1994).
[11] Y. R. Shen, *The Principles of Nonlinear Optics* (John Wiley & Sons, Inc., New York, 1984).
[12] T. Yajima, H. Souma, and Y. Ishida, Phys. Rev. A **17**, 324 (1978); J. J. Song, J. H. Lee, and M. D. Levenson, Phys. Rev. A **17**, 1439 (1978); R. Trebino, C. E. Barker, and A. E. Siegman, IEEE J. Quantum Electron. **QE-22**, 1413 (1986).