RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Resonant nonlinear optical response of the fullerenes C_{60} and C_{70}

S. R. Flom, R. G. S. Pong, F. J. Bartoli, and Z. H. Kafafi*

Naval Research Laboratory, Washington, D.C. 20375

(Received 2 September 1992)

Time-resolved degenerate four-wave mixing experiments were conducted on films of pure C_{60} and C_{70} using a picosecond tunable dye laser. The fullerenes exhibit a large third-order optical response, and their dynamics show wavelength and fluence dependence. The temporal response is characterized by a long-lived component attributed to the triplet excited state and an early decay associated with population of the singlet excited state. This fast response is considerably shortened at higher laser fluences and an excitonic singlet-singlet annihilation mechanism is proposed.

C_{60} and C_{70}, initially detected by mass spectroscopy,[1] and recently synthesized,[2] have been the subject of many recent nonlinear optical (NLO) studies.[3–15] These materials represent new forms of carbon with high symmetry and unique structures. The molecular clusters have the shapes of hollow soccer and rugby balls and consist of 12 five-membered rings separated by 20 (C_{60}) and 25 (C_{70}) benzenoid six-membered rings with alternating C—C single and C=C double bonds. This structure results in a three-dimensional delocalization of π electrons, a property often associated with enhanced NLO properties in organic materials.[16]

The majority of the NLO measurements reported to date have been carried out in the near-infrared spectral region, away from any one-photon resonance.[3–11] Meth, Vanherzeele, and Wang[9] measured the dispersion of the third-order NLO response of a C_{60} film by third-harmonic generation (THG) over the fundamental wavelength range 1.1–2.4 μm. Their study showed a three-photon resonance centered at 1.32 μm. The first degenerate four-wave mixing (DFWM) study of solid C_{60} was reported by Kafafi *et al.*[3] A predominantly pulse-limited NLO response was measured using 35-ps pulses at 1.064 μm. The third-order optical susceptibility, $\chi^{(3)}_{xxxx}=7\times10^{-12}$ esu, is similar to the value of 4×10^{-12} esu determined by THG, away from the three-photon resonance. These values obtained for solid C_{60} are in disagreement with that reported by Blau *et al.*[5] based on a DFWM study on solutions of C_{60} at 1.064 μm. Two comments[6,7] have recently appeared that specifically address the problems with the data and interpretation of this work.[5] Two independent DFWM studies[14,15] on solutions of fullerenes in the visible have recently been reported, but do not appear to be entirely consistent with each other. In this paper, we investigate the NLO properties of C_{60} and C_{70} films by time-resolved degenerate four-wave mixing, at 597 and 675 nm. These two wavelengths were chosen to study the dynamics of the third-order optical response of the fullerenes in a spectral region where resonant interactions are expected to play an important role. Special attention is given to the dynamics of the early NLO response for both fullerenes.

Cheville and Halas[17] have conducted pump-probe experiments on C_{60} films at 605 nm and have shown that the relaxation process follows a nonexponential decay. Excited-state absorption spectra of C_{60} and C_{70} have also been reported[18–26] with special focus on solutions at and below room temperature. Visible transient absorption spectra of C_{60} in solution yielded an excited-state singlet S_1 lifetime on the order of 650 ps.[23] This value is smaller than the 1.2-ns lifetime reported by Ebbesen, Tanigaki, and Kuroshima,[22] but much longer than the 43-ps decay time reported for solid C_{60}.[17] A lifetime close to 670 ps has been measured for C_{70} in solution.[22] In general, the measured S_1 lifetime of these fullerenes is shorter than that found for many planar aromatic hydrocarbons. Since the triplet quantum yield is close to unity,[19,23,25] this result implies a faster singlet-triplet (S_1-T_1) intersystem crossing rate for the fullerenes. The measured T_1 lifetimes, in the gas phase[20] and in solution,[18,19,21,22,24–26] vary between 42 and 410 μs, and 41 μs and 51 ms, for C_{60} and C_{70}, respectively. The decay of the T_1 state does not follow first-order kinetics and its lifetime depends upon the laser fluence, i.e., the population density of the excited states.[22] In solution at room temperature, the T_1 lifetime shows a concentration dependence and is shortened due to ground-state quenching and triplet-triplet annihilation.[22,24,26]

C_{60} (99.99% pure) and C_{70} (99%+ pure) were obtained from Strem Chemicals, Inc. and Texas Fullerenes, respectively. The fullerene was placed inside a quartz cell and vaporized *in vacuo* by resistive heating at 400–500 °C. Pure C_{60} and C_{70} films were deposited onto various optical substrates for spectroscopic and NLO characterization. Optical spectra of C_{60} and C_{70} films were measured on a Perkin Elmer λ9 spectrometer to determine the film thickness and the linear absorption coefficients shown in Table I. At 597 nm, both fullerenes have moderate absorption coefficients with C_{70} being more absorbing than C_{60}. At 675 nm, both fullerenes are less absorbing. The absorption spectrum of C_{60} exhibits a broad band centered around 450 nm. The spectrum of C_{70} is qualitatively similar and extends from 450 to 700 nm. The similarity of the solid-state[27–30] spectra of the fullerenes to their solution or gas-phase spectra[31–34] at or below room temperature has been previously noted. These studies sug-

TABLE I. Linear and nonlinear optical properties of C_{60} and C_{70}.

Fullerene	λ (nm)	n^a	α (10^3 cm^{-1})	$\chi^{(3)}_{xxxx}$ (10^{-11} esu)	$\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}$
C_{60}	597	2.03	9.2±1.4	38±9	<0.011
	675	1.99	1.5±0.1	8.2±0.8	<0.070
C_{70}	597	2.12	48.2±0.3	210±10	<0.012
	675	2.04	8.5±3.0	64±20	<0.020

[a] Data are from Refs. 29 and 30 for C_{60} and C_{70}, respectively. $\chi^{(3)}_{xxxx} = 6.1$ and 5.3×10^{-13} esu at 597 and 675 nm are used for the reference CS_2 by interpolation from the reported values (Refs. 40 and 41).

gest that solid C_{60} and C_{70} should be viewed as molecular solids. This is further supported by the narrow peaks and fine structure observed in the photoemission and inverse photoemission spectra[35–39] of solid C_{60} and C_{70}.

The highest-occupied molecular-orbital (h_u) to lowest-unoccupied molecular-orbital (t_{1u}) excitation for C_{60} consists of fifteen transitions, all of which are orbitally forbidden and are predicted to lie to the red of the first optically allowed transition. Absorption bands observed between 410 and 620 nm have been assigned to these forbidden transitions from the singlet A_g ground state to excited singlet states with triple (T_{1g}, T_{2g}), quadruple (G_g), or quintuple (H_g) degeneracy.[37,38] The orbital forbiddenness is partially lifted by Herzberg-Teller interactions in which excitation of a vibration of a suitable symmetry results in intensity borrowing from an allowed transition. The degeneracy of the upper states may be removed by Jahn-Teller distortions. In solution, Leach *et al.*[32] have assigned the bands in the 560–620-nm region to vibronically allowed transitions between the A_g and quasidegenerate T_{1g} and T_{2g} states. The broad absorption band measured for solid C_{60} between 550 and 650 nm appears to be associated with these transitions. A series of very weak bands between 640 and 700 nm for C_{60} in solution[32] has been assigned to the spin and orbitally forbidden ${}^1A_g$-${}^3T_{1g}$ transition, the lowest singlet-triplet transitions. It is possible that the observed absorptions in the solid are due to similar transitions. For C_{70}, a detailed spectral assignment has not yet been reported.

Degenerate four-wave mixing experiments were performed on films of C_{60} and C_{70} using an amplified dye laser system. It consists of a dye laser (Coherent 702) that is synchronously pumped by the second harmonic of a mode-locked Nd:YAG (yttrium aluminum garnet) laser (Coherent Antares), and a three-stage dye amplifier (Continuum PTA60) that is pumped by the second harmonic of a 10-Hz regenerative Nd:YAG amplifier. A pulse width of 1.2 ps full width at half maximum was measured at both wavelengths. A phase conjugate geometry was adopted where the laser output is split into three beams, two counterpropagating pump beams and a weaker probe beam that interrogates the sample at 13.8° angle. The polarization of each of the temporally and spatially overlapped beams was adjusted by a half-wave plate or a Babinet-Soleil compensator. The NLO signal measured in the all parallel x polarization was several orders of magnitude larger than that measured when the pump-and-probe beams were cross-polarized. This NLO response showed the cubic laser intensity dependence expected for a third-order optical response. At high laser intensities, the NLO signal showed evidence of saturation. The magnitude of the tensor component $\chi^{(3)}_{xxxx}$ is derived using the expression

$$|\chi^{(3)}_{xxxx}| = |\chi^{(3)}_{xxxx(\mathrm{ref})}| (a_3/a_{3\mathrm{ref}})^{1/2} (l_{\mathrm{ref}}/l)(n/n_{\mathrm{ref}})^2 \times (\alpha l)/[(1-e^{-\alpha l})e^{-\alpha l/2}] \, ,$$

where a_3 is the coefficient of the cubic term in the least-squares fit of the phase conjugate signal, l is the path length, n is the refractive index, and α is the linear absorption coefficient of the sample. CS_2 was used as the reference.[40,41] Table I lists the values of $|\chi^{(3)}_{xxxx}|$ measured for both fullerenes at 597 and 675 nm. At 597 nm, C_{60} has a $\chi^{(3)}_{xxxx} = 3.8 \times 10^{-10}$ esu 5 and 50 times larger than those determined at 675 nm and 1.064 μm,[3] respectively. Its third-order nonlinear response increases monotonically as the wavelength shifts to the blue, approaching resonance with the symmetry-forbidden transition. A similar wavelength dependence was observed for the third-order optical coefficient of C_{70}. The largest measured $\chi^{(3)}_{xxxx}$ of 2×10^{-9} esu for C_{70} at 597 nm is more than 5 times larger than that of C_{60} at the same wavelength. There appears to be a direct correlation between the measured $\chi^{(3)}_{xxxx}$ and α. These results suggest that resonant interactions contribute significantly to the large nonlinear optical response of the fullerenes.

The temporal response of the phase conjugate signal was measured as a function of the delay time of the back pump at different laser intensities. This is illustrated for C_{70} at 597 nm in Fig. 1. The response exhibits a rapidly decaying component and a slower component that persists much longer than the nanosecond time scale of the experiment. These dynamics yield direct evidence for participation of excited states in the nonlinear process. The fast component, shown below in more detail in Fig.

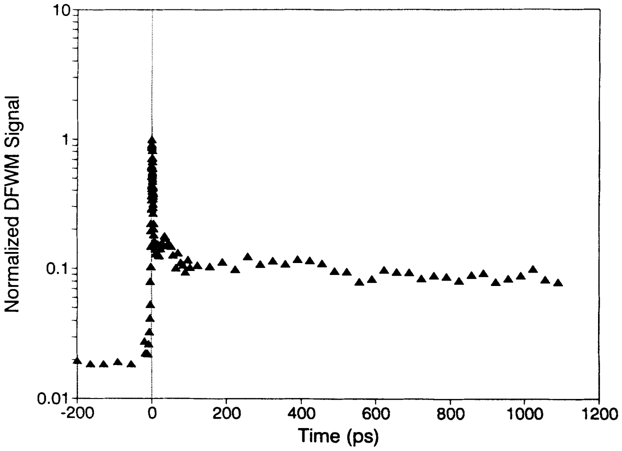

FIG. 1. Time dependence of the degenerate four-wave signal measured at 597 nm and a laser fluence of 6.8 mJ/cm^2 for a 150-nm-thick C_{70} film deposited on a CaF_2 substrate. All four beams I_1–I_4 are polarized in the x direction.

3, appears to be associated with population of the S_1 singlet excited state. The slow component seems to be related to population of the T_1 triplet state reached via intersystem crossing. The ratio of $\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}<0.01$ obtained for C_{60} and C_{70} at 597 nm is inconsistent with a nonresonant electronic nonlinearity but supports a mechanism that involves excited-state population. Excited-state contributions to the $\chi^{(3)}_{xyyx}$ tensor component are associated with the orientation correlation function of the transition dipoles.[42,43] The correlation decays rapidly to zero on the time scale of the picosecond NLO measurements for the triply degenerate excited states of C_{60}. An upper limit of the nonresonant electronic $\chi^{(3)}_{xxxx}$ of C_{60} may be estimated from the experimentally measured $\chi^{(3)}_{xyyx}<4.2\times10^{-12}$ esu at 597 nm. Considering the ratio $\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}=1/3$ expected for an instantaneous electronic nonlinearity in an isotropic medium, the nonresonant electronic component of $\chi^{(3)}_{xxxx}$ for C_{60} must be smaller than 1.3×10^{-11} esu. This value is close to $\chi^{(3)}_{xxxx}=7\times10^{-12}$ esu measured at 1.064 μm,[3] away from any one-photon resonance.

The dynamics of the early NLO response and the photophysics of the associated excited states are displayed in some detail in Figs. 2–4. Figure 2 illustrates the first 40 ps of the NLO response of C_{60} measured at 597 nm at different laser fluences. A nonexponential decay is observed and at low laser fluences the decay is consistent with the results of the pump-probe study conducted at 605 nm.[17] The dynamics exhibit a strong dependence on the laser fluence with the decay becoming much faster as the fluence increases. In contrast, the decay displayed in Fig. 3 for C_{70} at 597 nm is much faster and shows very little dependence on the laser fluence. Since the linear absorption coefficient of C_{70} is six times larger than that of C_{60} at this wavelength, this difference may be simply related to differences in population densities of the excited states of the two molecular clusters. Indeed, when the laser was tuned to a wavelength where the absorption of C_{70} was comparable to that of C_{60} at 597 nm, similar dynamics were observed for the two fullerenes. This result is shown in Fig. 4 where the dynamics of the early NLO response of C_{70} at 675 nm exhibit a strong dependence on the fluence. Similar dynamics were observed for C_{60} at 675 nm with varying laser fluences.

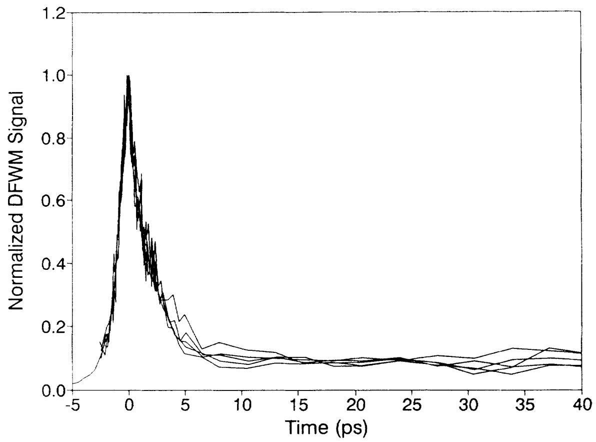

FIG. 3. The early temporal response measured as a function of laser fluence for a 150-nm-thick C_{70} film at a fluence of *a*, 0.73; *b*, 1.5; *c*, 2.4; *d*, 4.5; and *e*, 6.8 mJ/cm^2 at 597 nm.

The above NLO results indicate that, on a picosecond time scale, excitation of solid C_{60} and C_{70} at either wavelength lead to population of excited states primarily in the singlet manifold. This conclusion is supported by recent nonlinear transmission measurements[44] which showed that C_{60} and C_{70} behave as reverse saturable absorbers (i.e., the absorption cross section for the singlet excited state is larger than that of the ground state) at these same wavelengths. As previously observed in solutions,[19,23,25] the lifetime of the excited singlet state seems to be governed by the S_1-T_1 intersystem crossing. These S_1 lifetimes are expected to be even shorter for solid C_{60} and C_{70} than their solution counterparts[22,23] due to intermolecular interactions. Our dynamics results have also shown that the lifetime of the S_1 state is strongly dependent on the excited-state population density. At the highest fluence levels where the S_1 population density

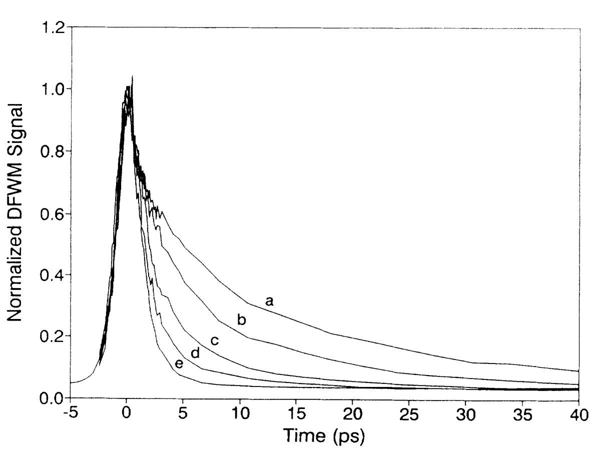

FIG. 2. The early temporal response measured as a function of laser fluence for a 1.2-μm-thick C_{60} film at a fluence of *a*, 0.91; *b*, 1.4; *c*, 2.4, *d*, 4.1; and *e*, 11 mJ/cm^2 at 597 nm.

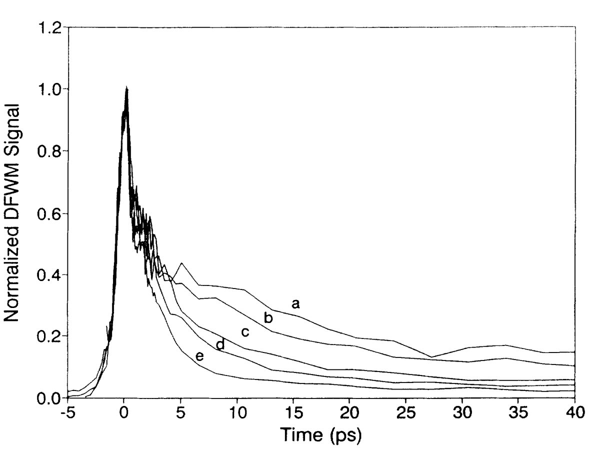

FIG. 4. The early temporal response measured as a function of laser fluence for a 0.97-μm-thick C_{70} film at a fluence of *a*, 0.22; *b*, 0.33; *c*, 0.90; *d*, 1.3; and *e*, 2.5 mJ/cm^2 at 675 nm.

may exceed one-tenth of the ground-state density, decay times of a few picoseconds are observed. Longer decay times were measured at lower laser fluences. At the lowest excitation densities, the decay of the NLO signal of C_{60} is consistent with the 43-ps lifetime previously measured, also at low fluence, by transient absorption at 605 nm.[17] The shortening of the lifetime of the electronic excited state, observed at high laser fluence, is attributed to an excitonic singlet-singlet annihilation mechanism. This fast decay appears to follow second-order kinetics and will be treated in more detail in a future publication.

In summary, the fullerenes C_{60} and C_{70} exhibit large third-order NLO response at 597 and 675 nm, arising from excited-state population. The early temporal response is dominated by the decay of the short-lived S_1 singlet excited state whose lifetime is strongly dependent on the population density. Exciton-exciton annihilation is suggested as the contributing mechanism for the fast decay rates measured at high laser fluences. A long-lived component observed in the temporal response is attributed to the triplet T_1 excited state. The dynamic model proposed in this study is consistent with conclusions of the nonlinear transmission measurements[44] on C_{60} and C_{70}, performed at the same wavelengths.

We thank P. C. Eklung, Y. Wang, F. Kajzar, and J. M. Nunzi for communication of their group's results in advance of publication, and J. R. Lindle and J. S. Shirk for valuable discussions. S.R.F. acknowledges ONT for financial support.

---

[*] Author to whom correspondence should be addressed.

[1] H. W. Kroto *et al.*, Nature **318**, 162 (1985).
[2] W. Kratschmer *et al.*, Nature **347**, 354 (1990).
[3] Z. H. Kafafi *et al.*, Chem. Phys. Lett. **188**, 492 (1992).
[4] Y. Wang and L-T. Cheng, J. Phys. Chem. **96**, 1530 (1992).
[5] W. J. Blau *et al.*, Phys. Rev. Lett. **67**, 1423 (1991).
[6] R. J. Knize and J. P. Partanen, Phys. Rev. Lett. **68**, 2704 (1992).
[7] Z. H. Kafafi *et al.*, Phys. Rev. Lett **68**, 2705 (1992).
[8] H. Hoshi *et al.*, Jpn. J. Appl. Phys. **30**, L1397 (1991).
[9] J. S. Meth, H. Vanherzeele, and Y. Wang, Chem. Phys. Lett. **197**, 26 (1992).
[10] F. Kajzar, C. Taliani, R. Zamboni, S. Rossini, and R. Danieli, in *Fullerenes: Status and Perspectives, First Italian Workshop on Fullerenes,* edited by C. Taliani and G. Ruani (World Scientific, Singapore, in press).
[11] X. K. Wang *et al.*, Appl. Phys. Lett. **60**, 810 (1992).
[12] Q. Gong *et al.*, J. Appl. Phys. **71**, 3025 (1992).
[13] L. W. Tutt and A. Kost, Nature **356**, 225 (1992).
[14] G. B. Talapatra *et al.*, J. Phys. Chem. **96**, 5206 (1992).
[15] Z. Zhang *et al.*, Opt. Lett. **17**, 973 (1992).
[16] *Nonlinear Optical Properties of Organic Molecules and Crystals,* edited by D. S. Chemla and J. Zyss (Academic, Orlando, 1987), Vols. 1 and 2; *Introduction to Nonlinear Optical Effects in Molecules and Polymers,* edited by P. N. Prasad and D. J. Williams (Wiley, New York, 1990); in *Nonlinear Optical Properties of Organic Materials III,* edited by G. Khanarian (SPIE, Bellingham, WA, 1990), Vol. 1337; G. Bjorklund, ed., *Polymeric Materials for Photonic and Optical Applications,* ACS Polymer Preprints **32**, 61 (1991).
[17] R. A. Cheville and N. J. Halas, Phys. Rev. B **45**, 4548 (1992).
[18] M. R. Wasielewski *et al.*, J. Am. Chem. Soc. **113**, 2774 (1991).
[19] J. W. Arbogast *et al.*, J. Phys. Chem. **95**, 11 (1991).
[20] R. E. Haufler *et al.*, Chem. Phys. Lett. **179**, 449 (1991).
[21] Y. Kajii *et al.*, Chem. Phys. Lett. **181**, 100 (1991).
[22] T. W. Ebbesen, K. Tanigaki, and S. Kuroshima, Chem. Phys. Lett. **181**, 501 (1991).
[23] R. J. Sension *et al.*, J. Phys. Chem. **95**, 6075 (1991).
[24] K. Tanigaki, T. W. Ebbesen, and S. Kurashima, Chem. Phys. Lett. **185**, 189 (1991).
[25] J. W. Arbogast and C. S. Foote, J. Am. Chem. Soc. **113**, 8886 (1991).
[26] N. M. Dimitrijevic and P. Kamat, J. Phys. Chem. **96**, 4811 (1992).
[27] C. Reber *et al.*, J. Phys. Chem **95**, 2127 (1991).
[28] A. Skumanich, Chem. Phys. Lett. **182**, 486 (1991).
[29] S. L. Ren *et al.*, Appl. Phys. Lett. **59**, 2678 (1991).
[30] S. L. Ren *et al.*, Appl. Phys. Lett. **61**, 124 (1992).
[31] J. P. Hare, H. W. Kroto, and R. Taylor, Chem. Phys. Lett. **177**, 394 (1991).
[32] S. Leach *et al.*, Chem. Phys. **160**, 451 (1992).
[33] R. L. Whetten, M. M. Alvarez, S. J. Anz, K. E. Schriver, R. D. Beck, F. N. Diederich, Y. Rubin, R. Ettl, C. S. Foote, A. P. Darmanyan, and J. W. Arbogast, in *Cluster and Cluster-Assembled Materials,* edited by R. S. Averback, J. Bernholc, and D. L. Nelson, MRS Symposia Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 639.
[34] R. E. Haufler *et al.*, J. Chem. Phys. **95**, 2197 (1991).
[35] J. H. Weaver *et al.*, Phys. Rev. Lett. **66**, 1741 (1991).
[36] J. L. Martins, N. Troullier, and J. H. Weaver, Chem. Phys. Lett. **180**, 457 (1991).
[37] M. B. Jost *et al.*, Phys. Rev. B **44**, 1966 (1991).
[38] M. B. Jost *et al.*, Chem. Phys. Lett. **184**, 423 (1991).
[39] J. W. Mintmire *et al.*, Phys. Rev. B **43**, 14 281 (1991).
[40] N. Phu Xuan *et al.*, Opt. Commun. **51**, 433 (1984).
[41] A. Yariv, *Quantum Electronics* (Wiley, New York, 1989); D. A. Pepper, Opt. Eng. **21**, 156 (1982).
[42] A. B. Meyers and R. M. Hochstrasser, IEEE J. Quantum Electron. **QE-22**, 1482 (1986).
[43] F. W. Deeg and M. D. Fayer, J. Chem. Phys. **91**, 2269 (1989).
[44] R. J. Lindle, S. R. Flom, R. G. S. Pong, F. J. Bartoli, and Z. H. Kafafi (unpublished).