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Wave-dispersed two-photon absorption of C_{60}

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We report the two-photon absorption (TPA) spectrum of C_{60} in the wavelength range $\lambda=0.7-1.5$ μm. The TPA coefficient β of the polycrystalline film shows a broad peak, with $\beta\approx25$ cm/GW, around 0.95 μm and drops below 3 cm/GW at $\lambda>1.2$ μm. We find that the nonlinear absorption, and also the sign of the nonlinear refraction above and below the TPA maximum, are satisfactorily accounted for by modeling the response with a two-photon state positioned at 2.58 eV. [S0163-1829(97)50940-4]

A considerable effort has been devoted in recent years to characterize and predict the nonlinear optical properties of fullerene.[1–12] A relevant quantity is the value of $\chi^{(3)}$, the third-order susceptibility, and in particular of $\chi(3)(-3\omega;\omega,\omega,\omega)$, the degenerate one, whose real and imaginary parts are related to the nonlinear refraction and two-photon absorption (TPA), respectively. In spite of the progresses made, our understanding of the electronic structure of C_{60} (or C_{70}) is still unsatisfactory and nonlinear optical spectroscopy can provide valuable information about states that cannot be excited through electric dipole transitions. A more practical motivation for these studies was due to the expected large nonlinear optical response of fullerenes and to their potential use in nonlinear optical devices. A large and fast third-order nonlinearity is typical of organic molecules possessing conjugated π electrons such as polydiacetylenes or polyacetylenes. With respect to the latter, fullerenes have the advantage to avoid the absorption in the near IR which is associated to the C-H vibration.

Values and dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of fullerenes were reported from third-harmonic generation (THG),[2,3] and $\mathrm{Im}\chi^{(3)}(-\omega;\omega,0,0)$ from electroabsorption measurements.[6] Data on the degenerate $\chi^{(3)}$, derived from four-wave mixing (DFWM) or nonlinear transmission, were produced at $\lambda=1.064$ μm (Ref. 1) and around 0.77 μm.[4,5] Efforts to reconcile $\chi^{(3)}$ from different techniques have recently been presented.[7] Theoretical calculations have been performed to predict the molecular hyperpolarizability and the $\chi^{(3)}$ values of the fullerenes.[9–12] An important point is the localization of the two-photon states and the relevance of the related transitions. Suggestions to this regard can be obtained from the THG spectrum, but the direct evidence of the two-photon states is given by the TPA spectrum. Two-photon excitation (TPE) measurements were performed in C_{60} at $2\hbar\omega=1.7-2$ eV.[8] TPE is quite sensitive; it gives the wavelength dependence of TPA, but does not provide the magnitude of β, the TPA coefficient, and it relies on the assumption that the fluorescence quantum yield does not change with the excitation wavelength. There are no such limitations when β is derived directly from nonlinear transmission. In this case, however, one must face the problems of two-step processes and of the absorption of radiation by the charge excited by TPA. The latter problem is more severe with thin samples, which is the case of solid C_{60} since samples of good optical quality are only available as thin films.

We report here the TPA coefficient of a polycrystalline film of solid C_{60} in the wavelength range 0.7–1.5 μm. The TPA spectrum is characterized by a maximum at $2\hbar\omega=2.58$ eV, and is well accounted for by a model based on a two-photon state at this energy. Dominance of this state on the third-order degenerate susceptibility is consistent with the magnitude and phase of $\chi^{(3)}$ at $\lambda=0.77$ μm,[4] and at $\lambda=1.06$ μm, the latter obtained here from nearly degenerate frequency-mixing measurements. We could obtain β from the nonlinear transmission of a 5.2-μm-thick film by employing tunable femtosecond pulses whose short-time duration minimizes the accumulation of the excitations generated by TPA.

The films were grown on a glass substrate by C_{60} thermal sublimation. The commercial high-purity C_{60} powder (Hoechst AG) was degassed for 6 h before deposition. The linear-optical properties of the films were characterized by ellipsometry,[13] while their thickness was measured by optical spectroscopy and scanning electron microscopy.

The experimental setup is similar to the one previously used to measure TPA in semiconductor doped glasses.[14] The tunable ultrashort pulses ($\tau_p\approx150$ fs, with τ_p the pulse duration) were obtained from a traveling-wave optical parametric generator, based on β-barium borate in type-II phase matching, and pumped by the 1-kHz repetition-rate, femtosecond pulses at 0.8 μm from a regenerative Ti-sapphire laser system. Signal (1.2–1.6 μm), idler (1.6–2.4 μm), and their second harmonics allowed us to cover all the wavelength ranges of interest. Typically, a maximum energy of 5 μJ was gently focused to a 0.3–0.5 mm spot on the sample. A variable attenuator, made by two crossed polarizers and a Babinet compensator, allowed us to span the intensity range $0-20$ GW/cm^2. Transmitted and impinging energy were re-

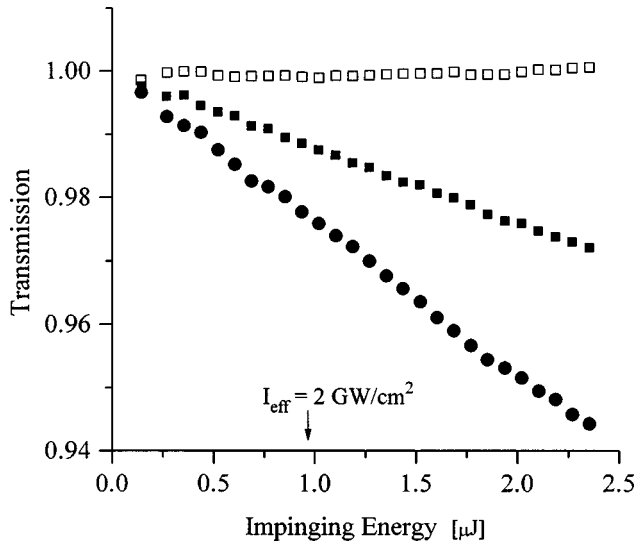

FIG. 1. Energy transmission of a 5.2-μm-thick C_{60} film (●); of the 150-μm-thick BBO calibrator phase-matched for SH generation (■) and out-of-phase matching (□). Wavelength: 935 nm.

corded at each shot; we denote by T their ratio. To calculate the optical intensity within the material we took into account only Fresnel losses and neglected multiple reflections. We note that, in the regime of small attenuation of the incoming beam, neglecting diffraction, time broadening of the pulses, and absorption from excited charge, T can be approximated as $T \approx 1-\beta L I_{\text{eff}}$, where I_{eff} is an appropriate spatial and temporal average of the impinging intensity $I(x,y,t)$ with x,y the transversal coordinates. A 150-μm-thick BBO crystal was used as TPA reference to calibrate the setup at each wavelength. Our method of calibration is based on the fact that a second-order crystal, when phase matched for second-harmonic (SH) generation, mimics a TPA absorber. In fact, its nonlinear transmission in the low-depletion regime, is given by $T \approx 1-(\beta L)_{\text{eq}} I_{\text{eff}}$, where $(\beta L)_{\text{eq}} = 2\omega^2 d_{\text{eff}}^2 (\varepsilon_0 n^3 c^3)^{-1} L^2$ and d_{eff} is the effective second-order coefficient. For the BBO calibrator we used $d_{11} = 2$ pm/V. We show in Fig. 1 an example of measurement: at 935 nm, the wavelength of the figure, we calculate $(\beta L)_{\text{eq}} = 5.9 \times 10^{-3}$ cm^2/GW, and, by comparing the slopes of the transmission curves, we derive $\beta L = 11.8 \times 10^{-3}$ cm^2/GW for the C_{60} film and hence $\beta = 22.7$ cm/GW. We could recover β with an error smaller than 25% even when the nonlinear absorption $A = 1-T$ was kept as small as 0.02. For $\beta = 10$ cm/GW, $A = 0.02$ implies, for our film thickness, to operate at $I_{\text{eff}} \approx 3.85$ GW/cm^2 and to produce, at 1 kHz repetition rate, $\approx 10^{-5}$ W of absorbed power and then a negligible increase of the temperature.

In Fig. 2 we plotted the imaginary part of the third-order degenerate susceptibility, which—by adopting for $\chi^{(3)}$ the convention of Ref. 15—we calculated from β through $\text{Im}\chi^{(3)} = \frac{2}{3}\varepsilon_0 c^2 n^2 \beta/\omega$. In the transformation we assumed $n = 2$ at all the wavelengths.[13] From Fig. 2, one can recover the measured values of β's by applying $\beta(\text{cm/GW}) = 3.57 \times 10^{19} (2\hbar\omega) \text{Im}\chi^{(3)}$, with the last two quantities in the same units of the figure.

We notice that at 0.7 μm the linear absorption becomes appreciable and then, for the data point at $2\hbar\omega = 3.5$ eV, the quadratic absorption could be due not only to TPA, but also

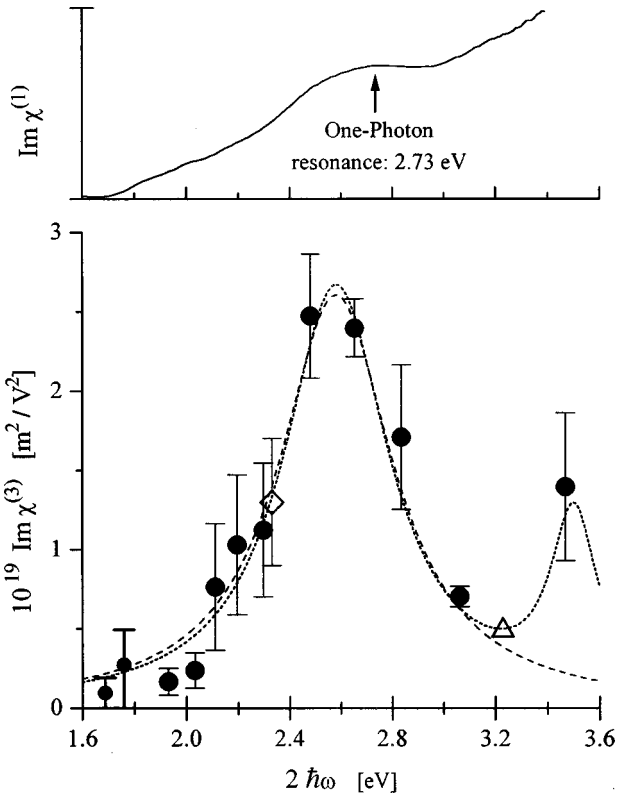

FIG. 2. Bottom. Im$\chi^{(3)}$ of C_{60} vs two-photon energy: ●, from nonlinear transmission; ◇, from nearly-degenerate frequency mixing; △, from Ref. 4. We remark that at $2\hbar\omega = 1.7$ and 1.8 eV we can only assess the upper boundary (1 and 2 GW/cm^2, respectively). The dashed line is a fit with model No. 1 (one-pole) while the dotted line is a fit with model No. 2 (two-pole). Top. Im$\chi^{(1)}$ of C_{60} vs one-photon energy.

to two-step processes. The magnitude of the latter can be estimated as follows: propagating through the sample, the pulse intensity decreases according to $dI/dz = -\alpha I - \beta I^2 - \Sigma N I$, with N and Σ, respectively, the number density and the absorption cross section of the excited charge. For small depletion, neglecting decay, the charge density produced by linear absorption is $N \approx 0.5\alpha I \tau_p/(\hbar\omega)$ so that $\Sigma N I \approx \tilde{\beta} I^2$, with $\tilde{\beta} = 0.5\alpha\Sigma\tau_p/(\hbar\omega)$. At 0.7 μm we measured $\alpha \approx 0.5 \times 10^3$ cm^{-1}, and even for Σ as large as 10^{-16} cm^2 (quite unrealistic), we estimate $\tilde{\beta} \approx 1$ cm/GW. With $\tilde{\beta}$ being much smaller than the measured coefficient of quadratic absorption ($\approx$20 cm/GW), the latter can all be attributed to TPA. By employing 300-fs dye-laser pulses at 0.61 μm, the authors of Ref. 16 concluded $\beta \leqslant 30$ cm/GW, the indeterminacy being due to the incertitude on the role of two-step processes. Indeed, moving from 0.7 to 0.61 μm, all the rest being equal, $\tilde{\beta}$ increases by more than one order of magnitude due to the larger α, and assessing β becomes problematic. Ultrashort pulses decrease the role of two-step processes, but we used them—first of all—in order to neglect the absorption from the charge excited by TPA. Indeed, the condition to neglect this fifth-order process turns out $\beta L > \Sigma A \tau_p/(2\hbar\omega)$ which, for $A = 0.02$ is satisfied here for β as small as 2 cm/GW and Σ as large as 10^{-16} cm^2.

From Fig. 2 one notices that Im$\chi^{(3)}$ shows a maximum around 2.6 eV. To account for it we shall use a model with a single two-photon state tp, and denote by $\hbar\Omega_{tp}$ its energy

with respect to the ground state g. One can expect the degenerate $\chi^{(3)}$ to be dominated by this tp state in a range of frequency around $\Omega_{tp}/2$. In this case, the expression of the third-order susceptibility simplifies to[15]

$$\chi^{(3)}(-\omega;\omega,-\omega,\omega)=\frac{1}{6}\frac{N}{\varepsilon_0}\frac{1}{\hbar\Omega_{tp}-2\hbar\omega-i\Gamma_{tp}}|\delta|^2, \quad (1)$$

where $\delta=\Sigma_i 2\mu_{tp;1}\mu_{1;g}/(\hbar\Omega_i-\hbar\omega)$, μ being the dipole element and i running over all the one-photon intermediate states of energy $\hbar\Omega_i$ and connected by a dipole-allowed transition to both g and tp. In the transparency range, Ω_i is always larger than ω, the frequency of measurements, and we shall assume δ to be constant. The frequency dependence of $\mathrm{Im}\chi^{(3)}$ is then given by the Lorentzian $1/[(\hbar\Omega_{tp}-2\hbar\omega)^2+\Gamma_{tp}^2]$. The best fit of this Lorentzian to the data points at $2\hbar\omega\leqslant 3$ eV is obtained for $\hbar\Omega_{tp}=2.58$ eV and $\Gamma_{tp}=0.27$ eV and is represented in Fig. 2 by the dashed line. We shall call this one-pole model of $\chi^{(3)}$ No. 1.

Obviously, one could improve the model by also introducing two-photon states of higher energy. The dotted line in Fig. 2 is the prediction of such a conceivable model, hereafter denoted No. 2, where we added the contribution of a second two-photon state tp' whose energy $\hbar\Omega_{tp'}$ has been arbitrarily set at 3.5 eV (the fit of model No. 2 gave $\hbar\Omega_{tp}=2.58$, the same as model No. 1, and $\Gamma_{tp}=0.25$ eV). We notice that the position of tp turns out to be insensitive to the different reasonable assumptions one can make on tp'. Indeed, a two-photon state at higher energy is necessary to account for the growth of TPA observed at $2\hbar\omega=3.5$ eV, but its role is modest up to 3.2 eV.

On top of Fig. 2 we reported $\mathrm{Im}\chi^{(1)}$, the imaginary part of the linear dielectric susceptibility ($\mathrm{Im}\chi^{(1)}\propto\alpha/\omega$). By fitting $\chi^{(1)}$ with the Lorentz oscillator form, one finds the position and the half width of the first one-photon state op to be $\hbar\Omega_{op}=2.73$ eV and $\Gamma_{op}=0.17$ eV, respectively.[13] The two-photon state appears then to be located at an energy 0.15 eV lower than the one-photon state. The difference is comparable to broadenings but cannot be attributed to experimental errors.

It is worthwhile to look for additional measurements that support the β's we have obtained, the energy of tp and, eventually, the fact that tp alone [and then Eq. (1)] can account for the whole nonlinear response (including refraction) in the range 0.8–1.5 μm. Of the complex quantity $\chi^{(3)}$, we shall compare with the experiments, beside $\mathrm{Im}\chi^{(3)}$, the value of the phase Φ. According to Eq. (1), one expects $\Phi<90°$ (and then $\mathrm{Re}\chi^{(3)}$ positive) for $\lambda>0.95$ μm ($2\hbar\omega<2.58$ eV), and $90°<\Phi<180°$ (and $\mathrm{Re}\chi^{(3)}$ negative) in the other case. We then tried to have one datum above and one datum below the wavelength of 0.95 μm. Values of $\chi^{(3)}$ at $\lambda=0.768$ μm have been reported very recently by the authors of Ref. 4. They find $\Phi=142°\pm5°$, in broad agreement with $\Phi=157°$ and 135° predicted by models No. 1 and No. 2, respectively. Furthermore, by converting their $|c_{1111}|$ to present notation, one obtains $|\chi^{(3)}|=7.93\times10^{-19}$ $\mathrm{m^2/V^2}$ and then a value of $\mathrm{Im}\chi^{(3)}$ which is in good agreement with our TPA results, as shown in Fig. 2. In Ref. 5, the same authors have reported $|\chi^{(3)}|$ to decrease on moving from 0.85 to 0.75 μm, a fact which is also consistent with the predictions of our models.

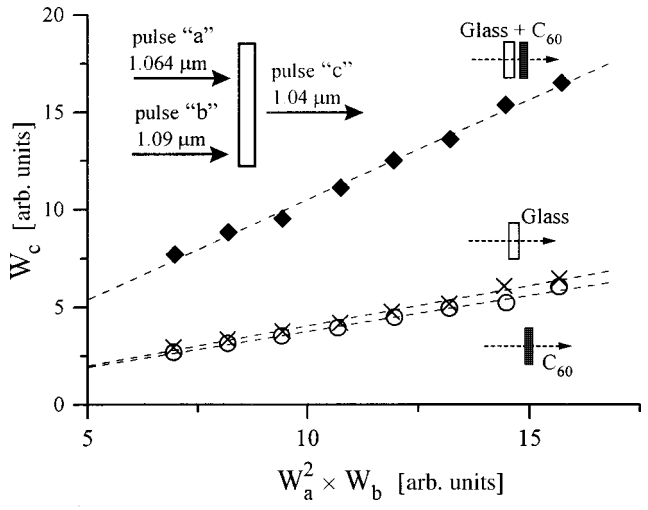

FIG. 3. Energy of the frequency-mixing signal W_c vs $W_a^2W_b$ for (○) 10.8-μm-thick C_{60} film on a 0.2-mm-thick borosilicate glass substrate; (×) 1-mm-thick SF6 glass platelet; (♦) the previous two stacked together. The inset shows the experimental scheme.

The other suitable wavelength is 1.06 μm of the Nd-YAG (yttrium aluminum garnet) laser. Reference 1 reports values of $|\chi^{(3)}|$ and of β at 1.06 μm (obtained from nonlinear transmission and DFWM), but no information on the sign of $\mathrm{Re}\chi^{(3)}$. Furthermore, these measurements certainly established the correct order of magnitude of the nonlinearities, but, in our opinion, due to the relatively long pulses (30 ps) used there, the values of the nonlinear susceptibilities could still be somehow affected by absorption/refraction of the charges excited by TPA. To avoid this problem when using the same pulses, we adopted a nearly degenerate frequency-mixing technique: as shown in the inset of Fig. 3, pulse a (of frequency ω_a) is mixed in the sample with pulse b (frequency $\omega_b=\omega_a-\Delta$) to yield pulse c at the new frequency $\omega_c=2\omega_a-\omega_b$. The large contrast provided by frequency discrimination allowed us to detect c employing moderate intensities ($I_a\approx400$ MW/cm^2, $I_b\approx I_a/10$) and then with negligible nonlinear absorption. Provided that the wave-vector mismatch for the process $2\mathbf{k}_a\Rightarrow\mathbf{k}_b+\mathbf{k}_c$, the depletion of a, and the gain of b are all negligible, one has $W_c=A|\chi^{(3)}|^2L^2W_a^2W_b$, with W denoting the pulse energy, and the constant A accounting for refractive indices and overlapping of the pulses. Examples of measurements are shown in Fig. 3. By comparing the slope of the sample with that of the reference glass (we take as a final reference the $BK7$ glass and assume $\chi^{(3)}_{BK7}=3\times10^{-22}$ $\mathrm{m^2/V^2}$) we derive $|\chi^{(3)}_{C_{60}}|=(2.6\pm0.3)\times10^{-19}$ $\mathrm{m^2/V^2}$. The additional data, which are necessary to obtain the phase Φ, have been taken by stacking the sample with platelets of glass of known $\chi^{(3)}$ (real and positive). From repeated measurements we found $\Phi=(37^{+12}_{-10})°$ in fair agreement with $\Phi=47°$ and 44°, which are predicted by models No. 1 and No. 2, respectively. As evident from Fig. 2, the value of $\mathrm{Im}\chi^{(3)}$ we obtain agrees with those measured through nonlinear transmission at nearby wavelengths. This agreement and the steady decrease of T with I of Fig. 1 suggest that TPA saturation is not relevant for C_{60} at the intensities used here.

Concerning theory, we notice that, by adopting a valence-

effective Hamiltonian approach, Shuai and Bredas predicted a two-photon state at 2.45 eV.[9] The good agreement of this prediction with our finding is even surprising, when one considers the complexity of the system. Reference 10 predicts the first H_g level at 2.56 eV (or at $\approx$2.3 eV, should one apply a systematic empirical correction as mentioned by the authors) and we are tempted to identify it with the tp state of our model. We notice that states of representation H_g are two-photon allowed also in the molecule and are then expected to produce a strong TPA.

A two-photon level of lower energy, hereafter denoted tp^* with $\hbar\Omega_{tp^*}=1.87$ eV, was suggested from THG measurement performed between 0.8 and 1.5 μm,[3] and also by TPE which, in the range $2\hbar\omega=1.7-2$ eV, show the onset of fluorescence above 1.8 eV.[8] tp^* was identified with the lower T_{1g} level which is TPA forbidden in the isolated molecule but becomes partially allowed in the solid (crystal-field effect). At $2\hbar\omega=1.92$ eV, and then close to $\hbar\Omega_{tp^*}$, we measured $\mathrm{Im}\chi^{(3)}=(0.25\pm0.1)\times10^{-19}$ $\mathrm{m}^2/\mathrm{V}^2$, an order of magnitude smaller than at the peak. Our data are not in contradiction with the existence of the state tp^*, but they show that its role in the nonlinear response must be modest compared to tp. Indeed, estimations have predicted TPA of the T_{1g} level to be $\approx10^{-2}-10^{-1}$ that of the H_g level.[11]

After this work was completed, it came to our knowledge that Strokendl *et al.* extended the DFWM measurements to the IR.[17] They find the two-photon resonance at $2\hbar\omega=2.67$ eV with $\beta\approx20$ cm/GW (converting to β, we took into account that, due to the different conventions used, $\chi^{(3)}$ of Strokendl *et al.* is four times smaller than ours). It is a remarkable agreement, especially considering that two completely different techniques have been used.

In conclusion, we have reported the full TPA spectrum of C_{60}, relying to this end on nonlinear transmission measurements with ultrashort pulses. TPA shows a broad peak at a fundamental wavelength around 0.95 μm, with $\beta\approx25$ cm/GW. We clearly identify a two-photon state positioned at 2.58 eV. The nonlinear response at wavelength longer than 0.8 μm is dominated by this two-photon state, and, despite the complexity of the structure of C_{60}, is well accounted for by a simple single-resonance model.

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[1] Z. H. Kafafi, J. R. Linde, R. G. S. Pong, F. J. Bartoli, L. J. Lingg, and J. Milliken, Chem. Phys. Lett. **188**, 492 (1992); J. R. Linde, R. G. S. Pong, F. J. Bartoli, and Z. H. Kafafi, Phys. Rev. B **48**, 9447 (1993).

[2] J. S. Meth, H. Vanherzeele, and Y. Wang, Chem. Phys. Lett. **197**, 26 (1992).

[3] F. Kajzar, C. Taliani, R. Danieli, S. Rossini, and R. Zamboni, Chem. Phys. Lett. **217**, 418 (1994). See also Phys. Rev. Lett. **73**, 1617 (1994).

[4] F. P. Strohkendl, R. L. Dalton, R. W. Hellwarth, H. Sarkas, and Z. H. Kafafi, J. Opt. Soc. Am. B **14**, 92 (1997).

[5] F. P. Strohkendl, R. L. Larsen, T. Axenson, R. L. Dalton, R. W. Hellwarth, H. Sarkas, and Z. H. Kafafi, Proc. SPIE **2530**, 165 (1995).

[6] B. C. Hess, D. V. Bowersox, S. H. Mardirosian, and L. D. Unterberger, Chem. Phys. Lett. **248**, 141 (1996).

[7] B. C. Hess, D. V. Bowersox, S. H. Mardirosian, and L. D. Unterberger, Proc. SPIE **2854**, 63 (1996).

[8] M. Muccini, R. Danieli, R. Zamboni, C. Taliani, H. Mohn, W. Muller, and H. U. ter Meer, Chem. Phys. Lett. **245**, 107 (1995).

[9] Z. Shuai and J. L. Bredas, Phys. Rev. B **46**, 16 135 (1992).

[10] M. Fanti, G. Orlandi, and F. Zerbetto, J. Am. Chem. Soc. **117**, 6101 (1995).

[11] R. Eder, A. M. Janner, and G. A. Swatzky, Phys. Rev. B **53**, 12 786 (1996).

[12] T. Hara, Y. Nomura, S. Narita, and T. Shibuya, Chem. Phys. Lett. **240**, 610 (1995).

[13] S. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. Wang, W. Lee, H. F. Ni, J. Selegue, and P. C. Eklund, Appl. Phys. Lett. **59**, 2678 (1991); M. Manfredini, C. Castoldi, G. Casamassima, and P. Milani, Mater. Sci. Eng. B **39**, 62 (1996).

[14] G. P. Banfi, V. Degiorgio, D. Fortusini, and M. Bellini, Opt. Lett. **21**, 1490 (1996).

[15] P. N. Butcher and D. Cotter, *The Elements of Nonlinear Optics* (Cambridge University Press, Cambridge, 1990).

[16] I. V. Bezel, S. V. Chekalin, Yu. A. Matveets, A. G . Stepanov, A. P. Yartsev, and V. S. Letokhov, Chem. Phys. Lett. **218**, 475 (1994).

[17] F. P. Strohkendl, R. L. Larsen, T. Axenson, R. L. Dalton, R. W. Hellwarth, H. Sarkas, and Z. H. Kafafi, Proc. SPIE **2854**, 191 (1996).