Dispersion of Third-Harmonic-Generation Optical Susceptibility in C_{70} Thin Films

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We report wave dispersed optical third harmonic generation (THG) studied in the fundamental wavelength range of 0.8–1.9 μm in thin films of C_{70}. The THG spectrum shows a broad resonance enhancement in cubic susceptibility $\chi^{(3)}$ with a maximum value of $\chi^{(3)}(-3\omega; \omega, \omega, \omega) = (0.9 \pm 0.1) \times 10^{-10}$ esu located at 1.42 μm, and a dramatic decrease at higher energies. We interpret the data in terms of a three-level model consisting of a totally symmetric ground state, along with two excited states: a one-photon state and a two-photon state. We predict the presence of a low-lying dipole-forbidden electronic level in close proximity to a dipole-allowed level.

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The large nonlinear optical response of organic molecules and their fast time response make these materials interesting and potential candidates for applications in optoelectronics and for all-optical switching devices. The large optical hyperpolarizability of organic molecules is due to delocalized π electrons [1]. Quasi-one-dimensional conjugated polymers such as polydiacetylenes, polyacetylenes, and polythiophenes are indeed characterized by a large nonlinear optical response and fast time response [1].

All these materials possess hydrogen atoms and therefore are characterized by a residual absorption in the near IR due to overtones of C-H stretching vibrations. This constitutes an important limitation for their applications in the infrared (i.e., telecommunication window). Fullerenes, on the other hand, possess a large number of conjugated π electrons but are uniquely composed of carbon atoms and therefore do not have any residual IR absorption due to overtones of C-H stretches. Both these properties make these novel compounds very exciting materials for applications in photonics devices.

The nonlinear optical (NLO) properties of C_{60} have been already extensively studied in the literature [2–11].

The C_{70} mojety belong to the dihedral D_{5h} symmetry group which does not contain inversion symmetry. Yet the irreducible representations for dipole allowed (one-photon transition) and dipole forbidden (two-photon transition) are still mutually excluded. In the condensed phase, C_{70} crystallizes in the fcc system at room temperature [12–15].

The nonlinear optical response of C_{70} has already been studied using third harmonic generation (THG) [16], electric field induced second harmonic generation (EFISH) [7], and degenerate four-wave mixing (DFWM) techniques [17,18]. However, these measurements have been performed at discrete wavelengths only: 1.064, 1.2, and 2 μm in the case of THG, 1.907 μm for EFISH, and 1.064 μm in the case of DFWM.

In this paper we report a systematic study of NLO properties of C_{70} thin films using the third harmonic generation spectroscopy (THGS) technique, accounting for the dispersion of the purely electronic cubic susceptibility $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ and therefore contributing to the understanding of the location of the low-lying excited electronic levels of C_{70}.

Fullerenes were prepared by the arc method. The soot was extracted with benzene, and then C_{70} was chromatographically separated from C_{60} and higher fullerenes. C_{70} thin films were obtained by sublimation of pure C_{70} in high vacuum on calibrated fused silica substrates. Typical thicknesses, measured by a surface profilometer, were in the range of 50 nm. The thin film optical absorption spectrum at room temperature is shown in Fig. 1. The THGS measurement experimental setup has been described elsewhere [3].

THG measurements were performed in a vacuum chamber in order to avoid environmental effects [19] and the THG signal was calibrated versus the THG of the graded silica thin plate substrate considering the value of $\chi^{(3)}(-3\omega; \omega, \omega, \omega) = 2.8 \times 10^{-14}$ esu as given by Buchalter and Meredith [20] at 1.907 μm. The absence of THG in s-p and p-s polarization configurations shows that the film is isotropic. For an isotropic thin film $\chi^{(3)}_{xxxx} = \chi^{(3)}_{yyyy} = \chi^{(3)}_{zzzz}$, and $\chi^{(3)}_{xxyy} = \chi^{(3)}_{xxzz} = \chi^{(3)}_{yyzz} = \chi^{(3)}_{xxxx}/3$. In the THG experiment, with analyzer and polarizer set parallel, only diagonal components of the $\chi^{(3)}$ tensor are measured. Choosing the z axis parallel to the substrate and incident and harmonic electric fields parallel to the rotation axis we measure the $\chi^{(3)}_{zzzz}$ tensor component. For the sake of simplicity we omit hereafter the tensor component denomination.

The THG process occurs in every media and, consequently, the harmonic intensity is a result of the superposition of harmonic fields generated in the separate media. In our case only the harmonic fields generated in the

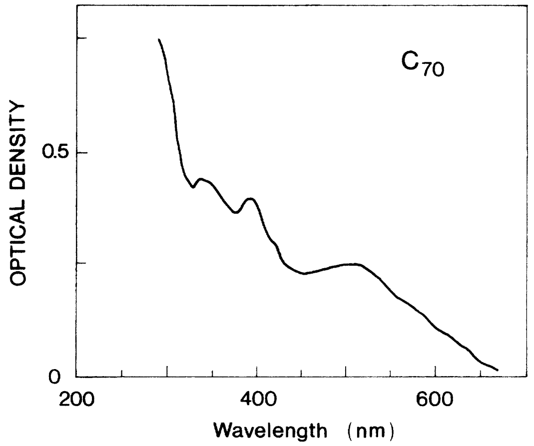

FIG. 1. Room temperature optical absorption spectrum of a 530 nm thick film of C_{70}.

substrate and in the C_{70} thin film contribute to the overall signal. If both fields have comparable intensities, and thickness and refractive indices are well known, it is possible to determine both the modulus and the phase (Φ) of the cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega) = |\chi^{(3)}|e^{i\Phi}$ [9]. Otherwise one may determine only the modulus. In the present study we could determine the phase of $\chi^{(3)}$ at 1.907 μm to be $\Phi = 0.9$ rad.

The incident angle dependent THG intensity was fitted by the formula derived by Kajzar, Messier, and Rosilio [21] and given by

$$\begin{aligned} I_{3\omega}(\theta) = & \left[64\pi^4/c^2(\chi^{(3)}/\Delta\varepsilon)_s^2\right] \\ & \times \left| e^{i\left(\psi_{3\omega}^f + \psi_{3\omega}^s\right)}\left[T_1\left(e^{-i\Delta\psi^s} - 1\right)\right.\right. \\ & \left.\left. + \rho T_2 e^{i\Delta\psi^s}\left(e^{i\Delta\psi^f} - 1\right)\right]\right|^2 I_\omega^{(3)}, \qquad (1) \end{aligned}$$

where

$$\rho = (\chi^{(3)}/\Delta\varepsilon)_f / (\chi^{(3)}/\Delta\varepsilon)_s^{-1}, \qquad (2)$$

I_ω is the incident light intensity, $\Delta\varepsilon = \varepsilon_\omega - \varepsilon_{3\omega}$ is the dielectric constant dispersion, and T_1 and T_2 are factors arising from transmission boundary conditions [19,21]. The superscripts or subscripts f and s refer to the C_{70} film and silica substrate, respectively. $\Delta\psi$ in Eq. (1) represents phase mismatches between fundamental (ω) and harmonic (3ω) frequencies:

$$\Delta\psi = \psi_\omega - \psi_{3\omega} = 3\omega l(n_\omega \cos\theta_\omega - n_{3\omega}\cos\theta_{3\omega})/c, \qquad (3)$$

where θ_ω and $\theta_{3\omega}$ are propagation angles at ω and 3ω (for details see Ref. [21]).

By introducing in Eq. (1) the complex refractive index $\tilde{n} = n + iK$, it is possible to account for thin film absorption. The imaginary part of the refractive index was determined from the thin film optical absorption spectrum whereas for the real part we took the values obtained by ellipsometry [22]. Equation (1) holds for any thickness, but in the case of absorbing films the thickness should be sufficiently small in order to assure a nonextinction of the free wave; the optical density should therefore not exceed the value of 1.5 at harmonic wavelength.

The dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is shown in Fig. 2 as a function of the fundamental wavelength. The relative precision in the measured values of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ falls in the range of 2%–3% within the same dye laser emission range.

The absolute precision depends on the thin film homogeneity and on the reliability of the standard. Dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the silica reference standard has been determined using Miller's rule obtaining 3.0×10^{-14}, 3.1×10^{-14}, and 3.2×10^{-14} esu at 1.3, 1.06, and 0.85 μm, respectively. An intense and broad resonance of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, with a maximum of $(0.9 \pm 0.1) \times 10^{-10}$ esu, is observed at 1.42 μm (FWHM $\sim$ 3000 cm^{-1}) while at higher energies $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ decrease dramatically.

This spectral behavior of C_{70} is somewhat different from that of C_{60} [3]. The decrease at higher energies is most likely due to cancellation effects between resonant terms with different excited electronic states. The values of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of C_{70} are indeed quite large and comparable with the values observed in conjugated polymers. The slight increase of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ compared to C_{60} [3] may be due to larger numbers of delocalized π electrons [23,24]. Larger values of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ have also been observed by Neher *et al.* [16] through THG in solution at three wavelengths: 1.0642, 1.5, and 2.0 μm. Significantly larger values have been observed by DFWM in the tail of C_{70} optical absorption [17,18]. Obviously, these values

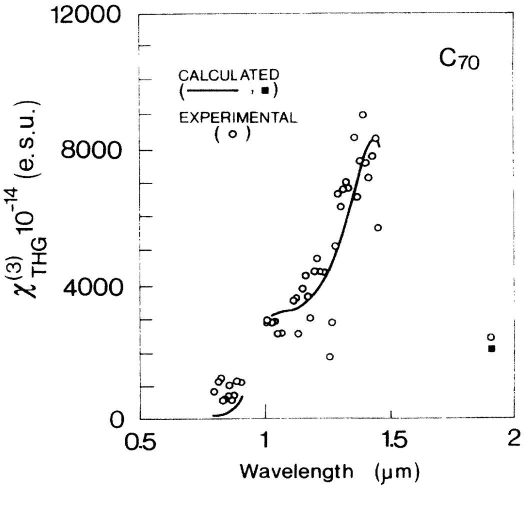

FIG. 2. Fundamental wavelength variation of the optical cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ measured for a 530 nm thick C_{70} film at room temperature. The solid line plots the calculated $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ spectrum derived by a three-level model.

are one-photon resonantly enhanced, and are expected to be larger in C_{70} than in C_{60} because of the redshift of the absorption tail in C_{70}. A smaller value has been obtained by Wang and Cheng from EFISH measurements in toluene solutions of charge transfer complexes of C_{70} at 1.91 μm $[\gamma(-2\omega;\omega,\omega,0) = (1.3 \pm 0.3) \times 10^{-33}$ esu]. These are most likely nonresonant values, since the harmonic frequency lies within the gap of C_{70}.

In order to describe the dispersion of cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ we make use of a three-level quantum model. In fact, theoretical calculations of Shuai and Bredas [24] show that the low energy spectrum of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in C_{70} is dominated by two excited states, of which one is one-photon and one is two-photon allowed. On the other hand, a simple two-level model will give rise to a negative static value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in disagreement with our finding of a positive sign at 1.907 μm. Similarly, and for the same reason, we should include at least one two-photon level when considering higher level models. Thus the lowest acceptable level model is a three-level model. Inclusion of a larger number of levels may improve the fitting by introducing more free parameters but will lead to a loss of physical meaning. According to Orr and Ward [25] and in the framework of a three-level model, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is given by

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = (2\pi^3 Nf\,|\mu_{01}|^2/h^3) \times \Big[|\mu_{12}|^2 F(\omega_1,\omega_2,\Gamma_1,\Gamma_2) - |\mu_{01}|^2 G(\omega_1,\omega_2,\Gamma_1,\Gamma_2)\Big], \tag{4}$$

where N is the density of molecules, f is the local field factor, ω_i are transition energies between fundamental and first dipole-allowed ($i = 1$) and -forbidden ($i = 2$) levels, respectively, Γ_i are the corresponding damping terms, and μ_{01} and μ_{12} are the dipole transition moments between the ground (0) and the first allowed excited state (1) and between states 1 and 2, respectively. The transition between states 0 and 2 is forbidden by symmetry. The functions $F(\omega_1,\omega_2,\Gamma_1,\Gamma_2)$ and $G(\omega_1,\omega_2,\Gamma_1,\Gamma_2)$ describe the dispersion of cubic susceptibility and their exact form is given elsewhere [26].

A least squares fit of Eq. (2) to experimental data is plotted in Fig. 2 as a solid line. An overall good description of the dependence of the cubic susceptibility on the fundamental photon energy is obtained with the following reasonable parameters:

$$\omega_1 = 20\,700\ \text{cm}^{-1}, \quad \omega_2 = 20\,100\ \text{cm}^{-1},$$
$$\Gamma_1 = 1560\ \text{cm}^{-1}, \quad \Gamma_2 = 1650\ \text{cm}^{-1},$$
$$|\mu_{12}/\mu_{01}|^2 = 1.1\,.$$

Despite the complexity of the electronic structure of C_{70}, we think that the use of a three-level model is justified by its simplicity and capability to address the electronic excitations which are essential to describe the dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$. This procedure enables us to predict a dipole-forbidden level at an energy (2.49 eV) lower than the allowed level (2.57 eV). This is in good agreement with theoretical predictions [24,27]. As we have already mentioned, the calculated THG spectrum of C_{70} [24] is dominated by a two-photon resonance at 1.03 μm and a three-photon resonance at 1.68 μm fundamental wavelength, respectively, corresponding to $\omega_1 = 17\,900$ cm^{-1} and $\omega_2 = 19\,500$ cm^{-1}. We notice a good agreement between these calculations [24,27] and our findings. Significant two-photon contribution to γ was indeed predicted for noncentrosymmetric molecules with $\beta = 0$ (or very small) by Dirk, Cheng, and Kuzyk [28].

The large and complex value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ at 1.907 μm, with a phase of $\Phi = 0.9$ rad, most likely indicates a three-photon resonant contribution.

The C_{70} molecular hyperpolarizability may be derived from $\chi^{(3)}$ using the following relation:

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = Nf\langle\gamma(-3\omega;\omega,\omega,\omega)\rangle\,, \tag{5}$$

where N is the number of molecules per unit volume and f is the local field factor, and

$$\gamma = \tfrac{1}{5}\,[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]. \tag{6}$$

For a spherical molecule and at the given frequency the local field factor is given by

$$f = [(n_\omega^2 + 2)/3]^3\,(n_{3\omega}^2 + 2)/3\,. \tag{7}$$

Taking the refractive indices determined by Ren *et al.* [22] and the same density as C_{60} ($d = 1.65$ g/cm^3) we obtain, at 1.907 μm, $\gamma(-3\omega;\omega,\omega,\omega) = (1.1 \pm 0.1) \times 10^{-32}$ esu. This value is about twice as large as that reported in solution at 2 μm by Neher *et al.*, suggesting the presence of a three-photon resonance in this spectral range. We note that Neher *et al.* [16] reported a negative γ at 2 μm and a positive one at 1.5 μm; the origin of the reversal in sign [16] is not clear. We find a positive γ at 1.907 μm in agreement with EFISH determination [7] in C_{70}. Positive real part of γ has been found also in C_{60} at this wavelength [26].

At 1.907 μm we find that $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is complex with a small phase $\Phi = 0.9$ rad indicating that the real part of $\chi^{(3)}$ is positive. The three-level model used here gives also a positive real value of $\chi^{(3)}$ at this wavelength.

Contrary to the case of C_{60} [3,5], and despite the fact that C_{70} does not contain inversion symmetry, we did not observe any second order nonlinear optical response (SHG) in C_{70}. The absence of SHG in C_{70} thin films is in agreement with the room temperature centrosymmetric fcc crystal structure [12–15] and with the prediction [29] that molecules belonging to the dihedral D_{5h} group must have a vanishing second order polarizability β.

In conclusion, the wave dispersed THG of C_{70} thin films shows a large resonant enhancement at a fundamental wavelength of around 1.42 μm and a dramatic decrease at higher energy with a shoulder at 1 μm. A reasonably good description of the dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is obtained in the framework of a three-level model which locates a two-photon level at 2.49 eV and a one-photon level at 2.57 eV. A dramatic decrease in the cubic susceptibility observed at higher photon energies is accounted for, within the three-level model, as the result of a cancellation between two terms with different signs. The molecular second hyperpolarizability of C_{70} is $\gamma(-3\omega;\omega,\omega,\omega) = (1.1 \pm 0.1) \times 10^{-32}$ esu at 1.907 μm and it is still a resonant value.

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