Nonlinear optical properties of the fullerenes C_{60} and C_{70} at 1.064 μm

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Time-resolved degenerate-four-wave-mixing experiments were conducted on films of pure C_{60} and C_{70} using a 35-ps laser at 1.064 μm. The fullerenes exhibit a two-photon resonantly enhanced third-order optical response that is primarily laser-pulse-limited. At high laser intensities, a fifth-order component to the nonlinear optical signal is observed and is attributed to a two-photon excited-state transient grating. The large two-photon absorption coefficients measured for C_{60} and C_{70} at 1.064 μm by nonlinear transmittance are consistent with this assignment.

Organic molecular systems with delocalized π electrons have been long recognized and identified as superior nonlinear optical (NLO) materials .[1] For these molecular solids, it is generally accepted that the NLO response originates from the microscopic properties of the molecules. C_{60} and C_{70}, initially detected by mass spectroscopy[2] and recently synthesized,[3] represent a unique organic molecular system where delocalization of π electrons is three dimensional. This third form of carbon, of which C_{60} and C_{70} represent the first two stable molecules in the series, offers high symmetry due to its spheroidal structure. C_{60} and C_{70} have the shape of hollow spheroids that consist of 12 five-membered rings separated by $20(C_{60})/25(C_{70})$ benzenoid six-membered rings with alternative C—C single and C=C double bonds. The three-dimensional π-electronic configuration and its influence on the NLO properties of the fullerenes have been the subject of several recent experimental[4–17] and theoretical studies.[18–23]

Table I gives a summary of the reported third-order optical susceptibility $\chi_{xxxx}^{(3)}$ of C_{60} at a few selected wavelengths in the near-infrared region, measured by degenerate four-wave mixing (DFWM), third-harmonic generation (THG) and electric-field-induced second-harmonic generation (EFISH). In general, there is reasonable agreement between the values of $\chi_{xxxx}^{(3)}$ of C_{60} measured by THG and EFISH, although some variation in the magnitudes of $\chi_{xxxx}^{(3)}$ is apparent. The large discrepancies reported for DFWM studies on solutions of C_{60} at 1.064 μm (Refs. 6 and 13) were recently addressed in two comments[7,8] and a review article.[15] The dispersion of the third-order NLO response of C_{60} over the fundamental wavelength range 0.85–2.4 μm was investigated by several THG studies on films[10–12] and solutions[16] of C_{60}. A three-photon resonance centered at 1.32 μm was observed by Meth, Vanherzeele, and Wang[11] and Kajzar *et al.*[12] The smallest response was recorded in the 2-μm region away from any resonant processes. The largest value for $\chi_{xxxx}^{(3)}$ of C_{60} in the near-infrared (NIR) region was reported at 1.064 μm.[10,12,16] The enhancement in the third-order optical susceptibility was attributed to a three-photon resonance with the T_{1u} electronic state. In the present study, DFWM and nonlinear transmission experiments were conducted on films of C_{60} and C_{70} at 1.064 μm. The goal of this investigation is to fully characterize the NLO properties of the fullerenes and identify the mechanism of their NLO response.

TABLE I. Third-order optical susceptibilities of C_{60} measured in the near-infrared region.

Wavelength (μm)	$\chi_{xxxx}^{(3)}$ (esu)	Technique	Reference
0.85	1.5×10^{-11}	THG	12
1.06	7×10^{-12}	DFWM	4
	6×10^{-8}	DFWM	6
	3.3×10^{-9}	DFWM	13
	1.4×10^{-11}	THG	11
	2×10^{-10}	THG	10
	8.2×10^{-11}	THG	12
	7.2×10^{-11}	THG	16
1.32	3×10^{-11}	THG	11
	6.1×10^{-11}	THG	12
1.50	3×10^{-11}	THG	16
1.91	1.6×10^{-11}	EFISH	5
	9×10^{-12}	THG	11
	3.2×10^{-11}	THG	12
2.00	3.7×10^{-11}	THG	16
2.37	4×10^{-12}	THG	11

C_{60} (99.99% pure) and C_{70} (99+% pure) were obtained from Strem and Texas Fullerenes, respectively, and were

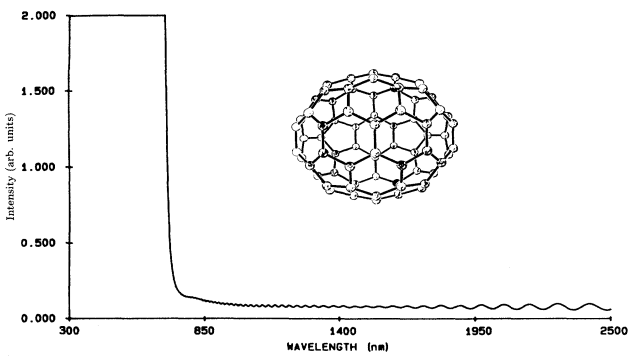

FIG. 1. Visible–near-infrared spectrum of a C_{70} film deposited on a CaF_2 substrate.

used without further purification. 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 obtained by vapor deposition onto various optical substrates for spectroscopic and NLO characterization. Fourier-transform infrared (FTIR) spectra of films, measured on a Nicolet 740 spectrometer, verified the identity and the purity of the material. Optical spectra of C_{60} and C_{70} films, measured on a Perkin Elmer λ9 spectrometer, were used to further characterize the materials. A spectrum of C_{70}, shown in Fig. 1, illustrates the transparent region in the NIR and the onset of absorption near ~750 nm, which is redshifted from that measured for C_{60}.[4] Film thickness of the fullerenes was derived from fringe patterns such as those depicted in Fig. 1 for C_{70}, based on the reported indices of refraction.[24,25] The measured absorption coefficient $\alpha=20.6\ \text{cm}^{-1}$ for C_{70} is 3.5 times larger than that of C_{60}; however, both fullerenes are quite transparent at the laser wavelength.

Degenerate-four-wave-mixing experiments on C_{60} and C_{70} films were carried out using 35-ps pulses of a passively mode-locked Nd:YAG laser and adopting the standard counterpropagating pump-beam configuration. The polarization of each of the temporally and spatially overlapped beams was adjusted using a half-wave plate. The data for C_{60} were previously reported[4] and will not be shown here. Figure 2 shows the phase conjugate signal of a C_{70} film plotted as a function of the laser-beam intensity. A cubic-power dependence characteristic of a third-order NLO process was observed below 1 GW/cm^2. A super-cubic-power dependence was noted above 1 GW/cm^2, giving evidence for a contribution from a fifth-order component possibly associated with a two-photon excited-state grating. The observed signal intensity was fit to a polynomial of the form $I_4=a_3I^3+a_5I^5$ from which the absolute value of the tensor component $\chi_{xxxx}^{(3)}$ was derived using the expression

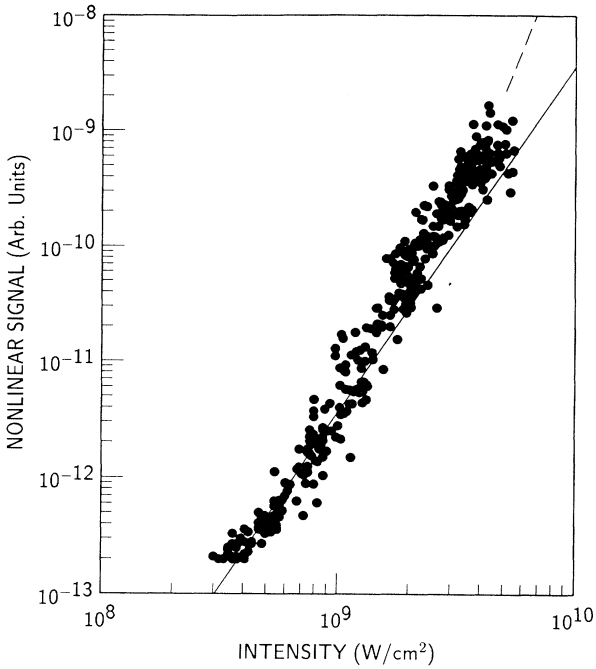

FIG. 2. Diffracted beam intensity I_4 in a 16.3-μm-thick C_{70} film as a function of the intensity of the three other beams $(I_1I_2I_3)^{1/3}$. All four beams I_1, I_2, I_3, and I_4 are polarized in the x direction. Solid and dashed lines refer to the cubic and fifth-order components of the signal intensity.

$$\chi_{xxxx}^{(3)}=[(a_3/a_{3\text{ref}})^{1/2}(l_{\text{ref}}/l)(n/n_{\text{ref}})^2(\alpha l e^{\alpha l/2})/(1-e^{-\alpha l})]\chi_{xxxx(\text{ref})}^{(3)},$$

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. Table II compares the measured third-order coefficients for both fullerenes. $\chi_{xxxx}^{(3)}$ for C_{70} is slightly larger than that of C_{60}. $\chi_{xyyx}^{(3)}$ of C_{60} and C_{70} was determined when the pump and probe beams were cross polarized. A value of 1×10^{-12} esu was measured for both fullerenes and, is $\frac{1}{7}$ and $\frac{1}{12}$ smaller than $\chi_{xxxx}^{(3)}$ for C_{60} and C_{70}, respectively.

The temporal response of the NLO signal was measured as a function of the delay time of the back pump. Figure 3 depicts the time dependence of the NLO response of a C_{70} film measured at two different power densities. The NLO response is largely laser-pulse-limited. A slowly decaying component that persists much longer than the 450-ps time scale of the experiment

TABLE II. Linear and nonlinear optical properties of C_{60} and C_{70} at 1.064 μm.

Fullerene	α (cm^{-1})	β[a] (cm/GW)	γ_{xxxx} (esu)	$\chi_{xxxx}^{(3)}$ (esu)	$\chi_{xyyx}^{(3)}/\chi_{xxxx}^{(3)}$
C_{60}	6	40	3×10^{-34}	7×10^{-12}	$\frac{1}{7}$
C_{70}	20.6	75	5×10^{-34}	12×10^{-12}	$\frac{1}{12}$

[a]The values of the nonlinear absorption coefficient were calculated based on two-photon absorption and do not include contributions from higher excited states.

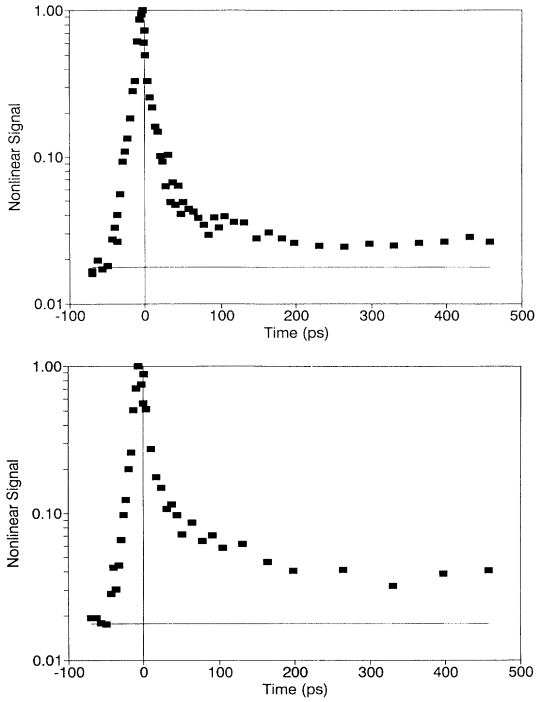

FIG. 3. Time dependence of the NLO signal of a 16.3-μm-thick C_{70} film measured at a power density of (a) 1.3 and (b) 2.2 GW/cm^2. All four beams I_1, I_2, I_3, and I_4 are polarized in the x direction.

is also present. It becomes more prevalent at a higher laser intensity as depicted in Fig. 3(b). This component must be associated with population of a long-lived excited state. A similar long-lived electronic excited state was detected in the dynamics of the NLO response[28] observed upon excitation at 0.6 μm. Since there are allowed two-photon transitions at 1.064 μm, it is possible that this same long-lived state is accessed at 1.064 μm via a two-photon process.

In order to find direct evidence for two-photon absorption, the nonlinear transmissions of C_{60} and C_{70} films were measured at 1.064 μm. Figure 4 shows the nonlinear transmittance of these fullerenes as a function of laser intensity. The transmittance of both fullerenes decreases with increasing laser intensity as would be expected for two-photon absorption. Assuming that the absorption coefficient $\alpha(I)$ varies linearly with the laser intensity, the nonlinear transmittance may be expressed[26] as

$$T=[2(1-R)^2e^{-\alpha l}/(\pi)^{1/2}Q]\int_0^{\infty}\ln[1+Qe^{-x^2}]dx\ ,$$

where α is the linear absorption coefficient, l is the path length, and x is the normalized time, i.e., t/τ, where τ is the pulse width. Q is a dimensionless parameter defined as

$$Q=[\beta(1-R)I(1-e^{-\alpha l})]/\alpha\ ,$$

where R is the sample reflectivity, I is the intensity of incident beam (Gaussian in space and time), and β is the nonlinear absorption coefficient. A least-squares fit to the intensity dependent transmittance is shown as a solid curve in Fig. 4. Table II lists the nonlinear absorption coefficients for the two fullerenes. The value of β determined for C_{60} is roughly twice as large as that of C_{70}. These values are quite large and lie in the same range as the two-photon absorption coefficients of the polydiacetylenes PTS and P-4-BCMU.[29,30] However, in addition to two-photon absorption, reverse saturable absorption can also account for a linear increase in α with laser intensity. A very large excited-state cross section on the order of 10^{-16} cm^2 would be needed to account for the large measured nonlinear absorption coefficients. Since a cross section of this magnitude would seem surprisingly large for excitation at 1.064 μm, we propose that nonlinear absorption is dominated by a two-photon process at this wavelength. This real two-photon excitation gives rise to the fifth-order component measured in the NLO signal at high laser intensities.

In addition, two-photon absorption also contributes to the third-order optical process. The two-photon absorption contribution to the imaginary part of the $\chi_{xxxx}^{(3)}$ tensor component may be calculated from the measured two-photon absorption coefficient β (cm/GW) using the expression[26]

$$\mathrm{Im}(\chi_{xxxx}^{(3)})=(10^{-16}n^2c^2/96\pi^2\omega)\beta\ ,$$

where c (cm/sec) is the speed of light, n is the index of refraction, and ω is the frequency. $\mathrm{Im}(\chi_{xxxx}^{(3)})=8.6\times10^{-12}$ and 1.6×10^{-11} esu have been estimated for C_{60} and C_{70}, respectively. These estimated values are of the same order of magnitude as those measured by DFWM and are consistent with two-photon resonance at 1.064 μm. A more detailed analysis of nonlinear transmittance for the fullerenes is in progress and will be the subject of a future publication.

The measured ratio $\chi_{xyyx}^{(3)}/\chi_{xxxx}^{(3)}$ for C_{60} and C_{70} is smaller than the value of $\frac{1}{3}$ expected for a nonresonant electronic NLO process. Since the measured $\chi_{xyyx}^{(3)}$ for the fullerenes yields an upper limit to a nonresonant electronic NLO response for this tensor component, one may also obtain an upper limit of the nonresonant $\chi_{xxxx}^{(3)}$. Using the expected ratio $\chi_{xxxx}^{(3)}/\chi_{xyyx}^{(3)}$ of $\frac{1}{3}$, an upper limit on the value of the nonresonant $\chi_{xxxx}^{(3)}=3\times10^{-12}$ esu is estimated for both C_{60} and C_{70} at 1.064 μm. This estimate is in reasonable agreement with that measured for C_{60} by THG (Ref. 11) in the 2-μm region away from any one-, two-, or three-photon resonance.

In comparing $\chi_{xxxx}^{(3)}$ of C_{60} and C_{70} measured at 1.064 μm by DFWM and THG, one must recall that $\chi_{xxxx}^{(3)}$ measured by THG is enhanced by a three-photon resonance which is not operative in DFWM. The value of 7×10^{-12} esu measured by DFWM for C_{60} is much smaller than the values reported by THG.[10,12,16] The same conclusion is valid for C_{70} as reflected in Table III. Thus it appears that the third-order optical susceptibility of both C_{60} and C_{70} measured by DFWM and THG is respectively two- and three-photon resonantly enhanced. Shuai and Bredas have also predicted that in C_{60} and C_{70}

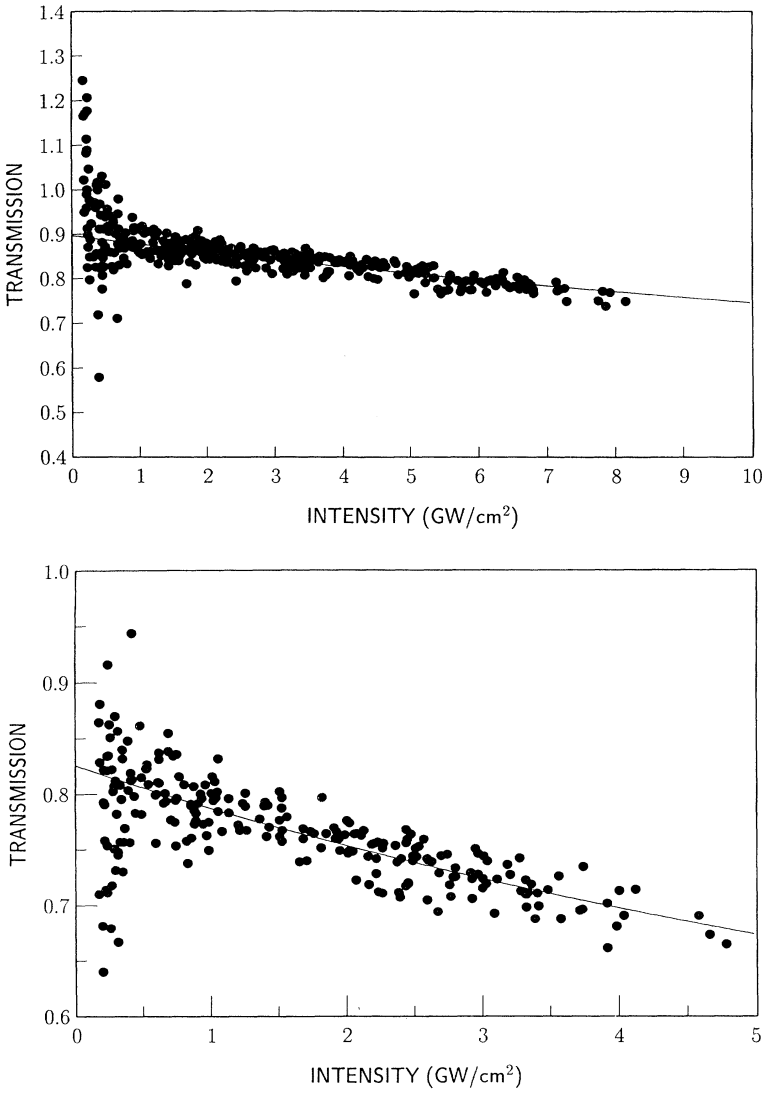

FIG. 4. Nonlinear transmittance of films of (a) C_{60} and (b) C_{70}. Film thickness is 17.9 μm for C_{60} and 16.3 μm for C_{70}. The solid line is a theoretical fit to the experimental data assuming two-photon absorption.

two-photon resonance occurs at almost the same frequency (1.22 vs 1.17 eV).[23] These theoretical findings support the above interpretation of our present DFWM studies and explain the differences in the magnitude of the third-order optical susceptibility measured by DFWM and THG at 1.064 μm.

The delocalization of π electrons has been often cited as a major contributor to large off-resonant third-order optical susceptibility.[27] C_{60} and C_{70} possess a delocalized π-conjugated electron system with a large polarizability arising mainly from $\pi \rightarrow \pi^*$ virtual transitions. Such an instantaneous electronic process would give rise to a fast NLO response, as was measured for both fullerenes. This is consistent with recent calculations using the valence effective Hamiltonian[23] (VEH) predicting that the large NLO response of the fullerenes arise from electron delocalization. Comparing the second hyperpolarizability of C_{60} to that of benzene, it appears that C_{60} has a γ that is 75 times larger than that of benzene. However, the γ–carbon-carbon bond for C_{60} is only 4.7 larger. This difference is less pronounced than what would be expected for a C_{60} one-dimensionally delocalized π-conjugated system and is due to σ-π electron mixing which occurs in the spherical molecule.

The present DFWM results indicate that, on a picosecond time scale, virtual ($\chi^{(3)}$) and real ($\chi^{(5)}$) two-photon excitation of solid C_{60} and C_{70} does occur at 1.064 μm with partial population of the singlet excited state.

TABLE III. Third-order optical susceptibilities of C_{70} measured in the near-infrared region.

Wavelength (μm)	$\chi_{xxxx}^{(3)}$ (esu)	Technique	Reference
1.06	1.2×10^{-11}	DFWM	present work
	2.5×10^{-8}	DFWM	14
	1.4×10^{-9}	THG	16
1.50	5.4×10^{-10}	THG	16
1.91	4.4×10^{-11}	EFISH	5
2.00	9.1×10^{-11}	THG	16

This short-lived singlet S_1 state[28] decays to the triplet T_1 state by intersystem crossing, which is very efficient for the fullerenes. Dynamics studies[28] of the NLO response of the fullerene in the visible have shown the presence of a fast and a long-decaying component, the latter giving direct evidence for a long-lived excited state. This conclusion is also supported by the nonlinear transmission measurements which showed that two-photon absorption is the dominant mechanism at 1.064 μm with some contribution from population of higher excited states. This also accounts for the fifth-order NLO response measured at higher laser intensities, which we attribute to a two-photon excited-state grating. In conclusion, the third-order optical response measured by DFWM for C_{60} and C_{70} at 1.064 μm is attributed to a two-photon resonantly enhanced electronic process.

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