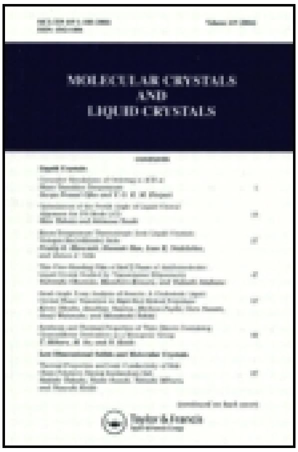

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Degenerate Four-Wave Mixing as a Nonlinear Optical Probe of the Fullerenes

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DEGENERATE FOUR-WAVE MIXING AS A NONLINEAR OPTICAL PROBE OF THE FULLERENES.

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Abstract Time-resolved degenerate four-wave mixing experiments were conducted on pure C_{60} and chemically modified C_{60} using a picosecond tunable dye laser. Photopolymerization, oxygen doping or formation of charge transfer complexes in the ground or excited states were used to alter the electronic and chemical structure of C_{60}. The third-order optical response for C_{60} was largely unaffected by photopolymerization or oxygen-doping whereas significant enhancements were observed for a C_{60}:phenylenediamine derivative charge transfer complex and for a C_{60}/substituted-polyphenylenevinylene composite. The chemical modification of C_{60} has a strong influence on the dynamics of the third-order response and gives rise to differing mechanisms.

INTRODUCTION

Since the discovery of methods to produce Buckminsterfullerenes[1] in bulk quantities, the technique of time-resolved degenerate four-wave mixing (DFWM) has been used to identify the nonlinear optical (NLO) properties[2-6] of this fascinating form of carbon. In some cases, the NLO mechanism may be inferred from the dynamics of the response. For instance, the third-order optical response measured by DFWM for films of C_{60} and C_{70} at 1.064 μm was attributed to a two-photon resonantly enhanced electronic process.[5] Other techniques have also been used[7,8] to identify the NLO properties of fullerenes. The technique of third harmonic generation (THG) has been used to probe the electronic NLO response of a C_{60} film.[8] Strong three-photon resonances have been identified at 1.3 and 1.064 μm using this technique. DFWM has been used to probe the large resonant NLO response in fullerene films.[3] The dynamics of the NLO response were both wavelength and fluence dependent, and were attributed to excited-state population.

This paper focusses on studies of chemically modified fullerenes using degenerate four-wave mixing (DFWM) as the nonlinear optical probe. These measurements have been undertaken to further understand and exploit the NLO response observed in the fullerenes. The chemical modifications of fullerenes include photopolymerization of thin films of C_{60}, oxygen doping of C_{60} thin films, formation of 1:1 charge transfer complexes of C_{60} with N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD) in 1-chloronaphthalene solutions and using C_{60} as a dopant, 1:1 by weight, in thin films of a polyphenylenevinylene derivative. These studies compare the NLO response of chemically modified fullerenes to that of C_{60} and demonstrate the degree to which the NLO response varies with these chemical and structural changes.

EXPERIMENTAL SECTION

C_{60} (99.99%) was obtained from Strem Chemicals or from Bluegrass Fullerenes (Lexington, KY 99+%) and used without further purification. Thin films were formed through vacuum vapor deposition (400° C) onto optical substrates held at ambient temperature. For the photopolymerized samples the newly formed film was exposed under vacuum to either the UV from a HeCd laser, or the light from a 300 W Hg arc lamp as described previously.[9] Oxygen doped samples were prepared[10] by a 25 hr exposure of the freshly prepared C_{60} film to 1 atm of room temperature O_2 with simultaneous irradiation of the sample with either the output of a 75 W Xe lamp or that of an Ar ion laser.

Pfaltz and Bauer were the suppliers of 1-chloronaphthalene (95%) while N,N,N',N'-tetramethyl-1,4-phenylenediamine and chlorobenzene were obtained from Aldrich. Poly-[2-methoxy, 5-(2'-ethylhexyloxy)-p-phenylenevinylene], MEH-PPV, was purchased from Uniax (Santa Barbara, CA) in a chlorobenzene solution (3.3 mg/ml). Films of C_{60}/ MEH-PPV were prepared by adding 3.3 mg of C_{60} to one ml solution of MEH-PPV which was then spin coated onto CaF_2 substrates.

Absorption spectra were taken using a Perkin-Elmer Lamda 9 spectrophotometer. The laser system used for the DFWM measurements consists of a dye laser (Coherent model 702) that is synchronously pumped by the second harmonic of a CW mode-locked Nd:YAG laser (Coherent, Antares). The output of the dye laser is amplified by a three stage dye amplifier (Continuum, PTA 60) that is pumped by the second harmonic of the output of a regenerative Nd:YAG amplifier (Continuum, RGA60). The laser system provides 1.2 ps (FWHM) pulses with energies up to 1 mJ.

DFWM measurements are performed using the phase conjugate geometry. Intensity is varied by rotating a half wave plate between crossed polarizers. The dependence of the signal on the incident intensity is fit by least squares to a cubic expression, and the cubic coefficient, a_3, is compared to the cubic coefficient, a_{3ref}, extracted from an identical experiment using CS_2 as a standard reference. The effective third-order optical susceptibility is determined by means of the expression,

$$|\chi^{(3)eff}_{ijkl}| = |\chi^{(3)ref}_{ijkl}| \left(\frac{a_3}{a_{3ref}}\right)^{\frac{1}{2}} \left(\frac{n}{n_{ref}}\right)^2 \left(\frac{l_{ref}}{l}\right) \left(\frac{\alpha l}{e^{-\alpha l/2}(1 - e^{-\alpha l})}\right) \qquad (1)$$

where n is the refractive index, l is the path length, α is the linear absorption coefficient of the sample and $\chi^{(3)}$ is denoted effective $\chi^{(3)eff}$ to encompass processes whose lifetimes are longer than the laser pulse width. Time resolved measurements are accomplished by delaying the arrival of the back pump beam.

RESULTS AND DISCUSSION

Poly-C_{60} and C_{60}-O_2

The measured absorption spectra of C_{60} photopolymer and C_{60}-O_2 are quite similar to that of C_{60} with slightly broader spectral features in the visible region. Table I summarizes the measured NLO properties of these chemically modified fullerenes in comparison to C_{60} at different wavelengths. The variation of the $\chi^{(3)eff}$ from sample to sample is small, and indicates that structural changes through oxygen doping or polymerization does not radically affect the magnitude of the NLO response. Further, the ratio of $\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}$ remains unusually small. This small ratio was observed earlier[3] for the fullerenes and was explained in terms of an ultrafast loss of the orientational correlation of the transition dipole moments of

TABLE I. Linear and Nonlinear Optical Properties of C_{60}, Poly-C_{60} and C_{60}-O_2

Fullerene	λ	α	$\chi^{(3)}_{xxxx}$	$\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}$
	nm	cm^{-1}	10^{-11} esu	
C_{60}	590.5	9800	52	<0.006
Poly-C_{60}	590.5	16,600	84	<0.005
C_{60}-O_2	590.5	14,000	43	<0.007
C_{60}	675	1500	8.2	<0.07
Poly-C_{60}	675	4800	8.7	<0.03
C_{60}-O_2	675	4600	9.5	<0.03

the multiply degenerate excited states of C_{60}. Apparently, the structural change of the molecule, disrupting its symmetry, does not change the degeneracy of the electronic excited states that participate in the NLO mechanism at these resonant wavelengths.

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. Figure

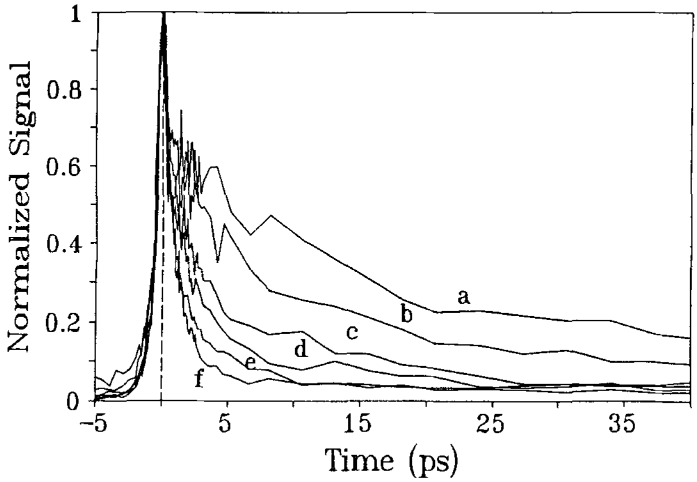

FIGURE 1A. The early temporal response of the NLO signal of poly-C_{60} measured at 590.5 nm as a function of laser fluence (a) 0.36, (b) 0.55, (c) 0.82, (d) 1.4, (e) 2.7 and (f) 6.8 mJ/cm^2.

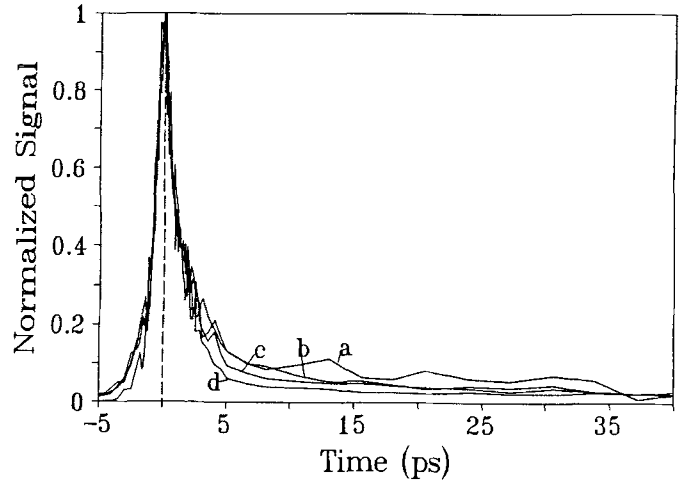

FIGURE 1B. The early temporal response of the NLO signal of C_{60}-O_2 measured at 590.5 nm as a function of laser fluence (a) 0.76, (b) 1.5, (c) 3.3 and (d) 7.1 mJ/cm^2.

1 shows the early temporal response of the DFWM signal observed for films of C_{60} photopolymer and C_{60}-O_2 at 590.5 nm. The response exhibits rapidly decaying components and a slower component (not shown in Fig. 1) that persists for more than a nanosecond. These dynamics are quite similar to those exhibited by pristine films of fullerenes.[3] The fast component was previously attributed to the decay of singlet excitons. For the photopolymer, a strong fluence dependence is observed with the decay becoming much faster at higher fluences. Fluence dependence arises from bimolecular exciton-exciton annihilation which competes with unimolecular decay processes. At the lowest fluence, the decay seems to be slower than that observed for pristine films at the same fluence and suggests that exciton migration may occur at a slower rate in the photopolymerized film. In contrast, the decay displayed in Fig. 1B for the oxygen-doped fullerene shows a much weaker dependence on the fluence. It is possible that oxygen doping shortens the lifetime of the singlet exciton through enhanced intersystem crossing while photopolymerization may slow the apparent response through disruption of exciton migration.

C_{60}:TMPD Charge Transfer Complex

Figure 2 shows the absorption spectrum obtained from a chloronaphthalene solution with equilibrium concentrations of 1.1 M TMPD, 5.3 mM C_{60} and 2.8 mM of the C_{60}:TMPD charge transfer (CT) complex. Also shown in the figure are spectra of the fullerene and the electron donor compound adjusted to the approximate height of their contribution to the mixed solution. A new absorption

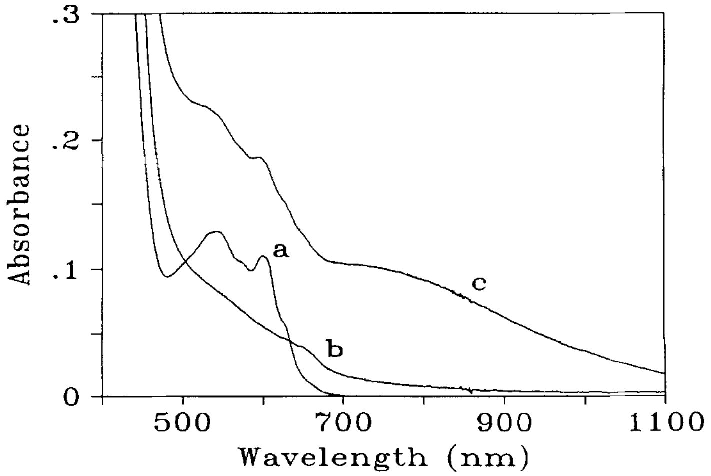

FIGURE 2. The absorption spectra of 1-chloronaphthalene solutions of (a) C_{60}, (b) TMPD and (c) C_{60}/TMPD.

band that is dependent on the concentrations of both C_{60} and TMPD appears at 725 nm and has been assigned to the charge transfer complex between C_{60} and TMPD. An equilibrium constant of 0.51 was calculated for the charge transfer complex which has an extinction coefficient of 1400 l/mole-cm at 675 nm.

DFWM experiments at 675 nm were carried out on five solutions of C_{60} and TMPD with varying concentrations. Neither C_{60} nor TMPD solutions exhibited a DFWM signal that was distinguishable from that of the solvent. Hence, only an upper limit to $|\chi^{(3)}|$ of solutions of pure C_{60} or TMPD may be obtained. Solutions containing both molecules gave a strong NLO signal that changed with concentration. The DFWM signal exhibited a cubic power dependence characteristic of a third-order effect, and increased with the concentration of the C_{60}:TMPD CT complex. Figure 3 shows the dependence of the solution $\chi^{(3)}$ on equilibrium CT complex concentration. Least squares analysis of the data yields an effective second hyperpolarizability of $7.1\text{x}10^{-33}$ esu for the charge transfer complex. Extrapolation to the pure C_{60}:TMPD complex yields $\chi^{(3)}=1.2\text{x}10^{-10}$ esu. Comparing this value with the upper-limit value of $7.1\text{x}10^{-12}$ esu (extrapolated for the fullerene in the solid state), one concludes that the third-order optical response of C_{60} has been greatly enhanced by complexation with a good electron donor such as TMPD.

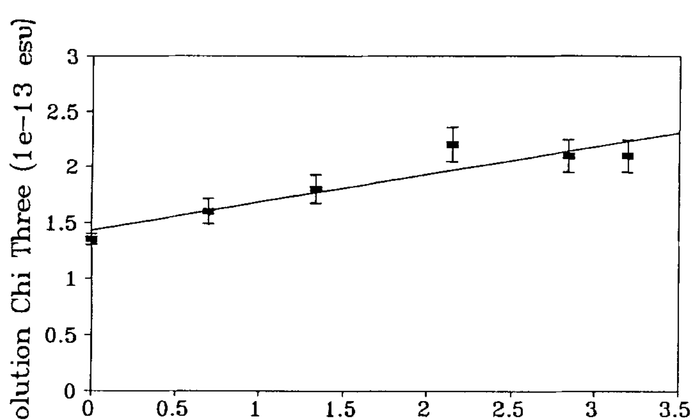

FIGURE 3. The third-order optical susceptibility of 1-chloronaphthalene solutions of C_{60}/ TMPD as a function of molar concentration of the C_{60}:TMPD charge transfer complex.

In a recent study,[6] nonlinear transmittance has been undertaken to determine the absorptive contribution of the third-order optical coefficient of the C_{60}:TMPD CT complex. At 675 nm, it was found that solutions of the charge transfer complex act as "reverse saturable absorbers" in that their transmittance decreases with increasing incident laser intensity. An $\mathrm{Im}\chi^{(3)}=3.9\times10^{-11}$ esu was obtained for a bulk C_{60}:TMPD CT complex as compared to $|\chi^{(3)}|=1.2\times10^{-10}$ esu deduced from the DFWM measurements at 675 nm. This comparison shows that absorptive contributions to the third-order optical response of the CT complex are quite significant. Direct optical excitation into the CT band accesses higher excited states with larger absorption cross-sections than that of the ground state and contributes to the enhanced NLO response observed for the complex.

C_{60}/MEH-PPV Composite

Figure 4 shows absorption spectra of the C_{60}/MEH-PPV composite film and the separate components. The spectrum of the composite material is quite similar to a composite of the spectra of C_{60} and MEH-PPV. The significant difference is that the peak near 340 nm for the composite material is narrower and blue shifted relative to that observed in the pure C_{60} film. On the other hand, this peak is strikingly similar in position and width to that measured for solutions of C_{60}. This resemblance between liquid solutions of C_{60} and C_{60}/MEH-PPV solid film is an indication that C_{60} is dispersed in the composite film.

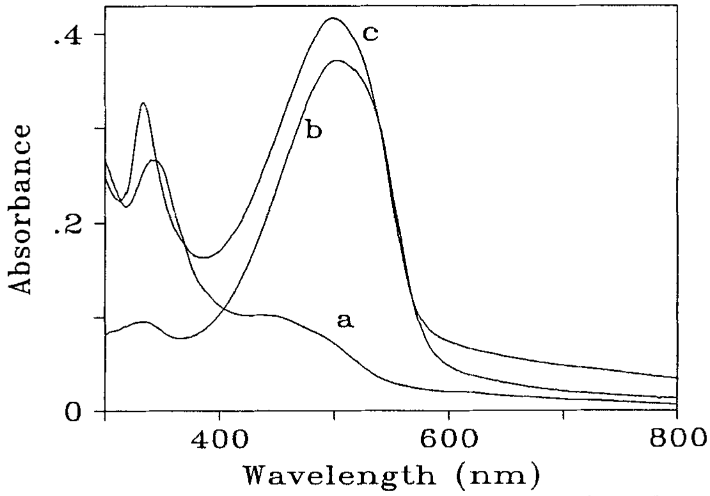

FIGURE 4. The absorption spectra of films of (a) C_{60}, (b) MEH-PPV and (c) C_{60}/MEH-PPV.

DFWM experiments were conducted on films of C_{60}, MEH-PPV and C_{60}/MEH-PPV at 590.5 nm. The DFWM signal of MEH-PPV film exhibits a small third-order response and its intensity dependence is dominated by a fifth-order component. Nevertheless, a $\chi^{(3)}_{xxxx}$ on the order of 3×10^{-10} esu was deduced for MEH-PPV, consistent with previously reported values[11] for PPV. This value is also quite similar to that measured for C_{60} at 590.5 nm and shown in table I. A much larger NLO signal than that exhibited by the separate components was measured for the C_{60}/MEH-PPV composite film. It shows a cubic power dependence, similar to that observed for films of pure C_{60}, at moderate laser intensities. The NLO signal becomes markedly subcubic at higher intensities with no obvious contribution from a fifth-order component.

In the cross-polarized configuration, both MEH-PPV and C_{60}/MEH-PPV films display a cubic intensity dependence. For MEH-PPV, a ratio of $\chi^{(3)}_{xyyx}/\chi^{(3)}_{xxxx}=1/3$ is measured, consistent with either an electronic or an excited state third-order optical process. For the composite film, the ratio is of the order of 0.07, much smaller than the ratio measured for the MEH-PPV film, and is inconsistent with a purely nonresonant electronic process. However, it is much larger than the upper-limit value given for C_{60} in table I. It is possible that the differences between the measured ratios for C_{60} and C_{60}/MEH-PPV arise from different NLO mechanisms. In summary, the third-order optical susceptibility of the composite material appears to be larger than the sum of the susceptibilities of the two components in the solid state. If one assumes that the fullerene in solid MEH-PPV behaves more like C_{60} in solution, one may speculate that the measured enhancement in the NLO response is even more pronounced since the measured $\chi^{(3)}_{xxxx}=5\text{x}10^{-10}$ esu for a film of the fullerene is at least 70 times larger than that deduced from solutions of C_{60}.

Figure 5 shows the dynamics of the NLO response for the film of the C_{60}/MEH-PPV composite. There are multiple decay processes contributing to the

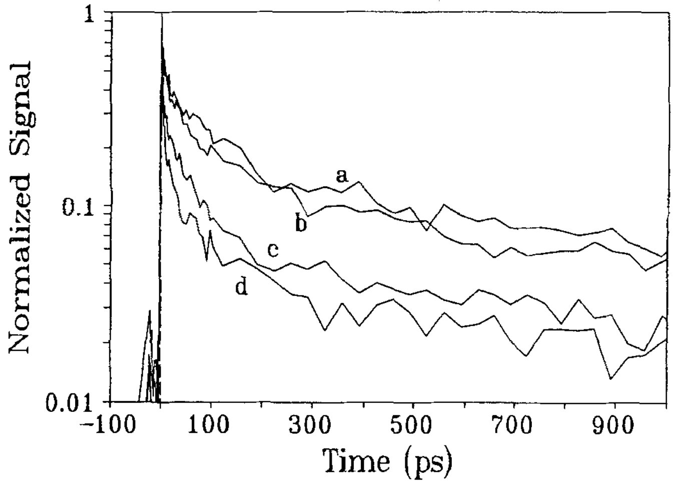

FIGURE 5. The temporal response of the degenerate four-wave signal of a film of C_{60}/MEH-PPV measured at 590.5 nm as a function of laser fluence (a) 0.45, (b) 1.1, (c) 3.2 and (d) 5.0 mJ/cm^2.

temporal response on the pico- and nanosecond time scale. The early temporal response is characterized by a fast component that shows a strong fluence dependence. This response is qualitatively similar to that measured for films of pure C_{60}[3] but quite different from that exhibited by MEH-PPV film whose signal is very nearly pulse-width (1.2ps) limited. However, quantitatively the response is more complex than that observed for films of pure C_{60}. The presence of a kinetic component that decays on the hundreds of picosecond time scale strongly suggests that a new process occurring that is unique to the composite film. Recently, a very rapid photo-induced electron transfer from the excited state of MEH-PPV onto C_{60} has been reported to occur on a picosecond time scale.[12] This charge-separated state in the composite films is metastable at low temperatures. Direct excitation into the tail of the π-π^* transition of MEH-PPV may access this state via fast electron transfer from the conducting polymer to C_{60}. The present NLO results are consistent with the formation of a charge transfer excited-state.

CONCLUSIONS

In summary, the present study demonstrates that chemical modification of C_{60} has varying effects on the NLO response as probed by degenerate four-wave mixing. The presence of oxygen in films of C_{60} has little effect if any on the magnitude of its third-order optical susceptibility. Photopolymerization of the fullerene enhances its physical properties without affecting its NLO response. In addition, altering the chemical and electronic structure by formation of charge transfer complexes with C_{60} in the ground or excited state, result in a greatly enhanced NLO response. The dynamics of the NLO response and its laser fluence dependence are greatly influenced by these chemical modifications.

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