LA-UR-97-3520

Title:

ULTRAFAST AND NONLINEAR OPTICAL CHARACTERIZATION OF OPTICAL LIMITING PROCESSES IN FULLERENES

CONF-970706--

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SPIE Conference Proceeding, 7/29-8/4/97, San Diego, CA

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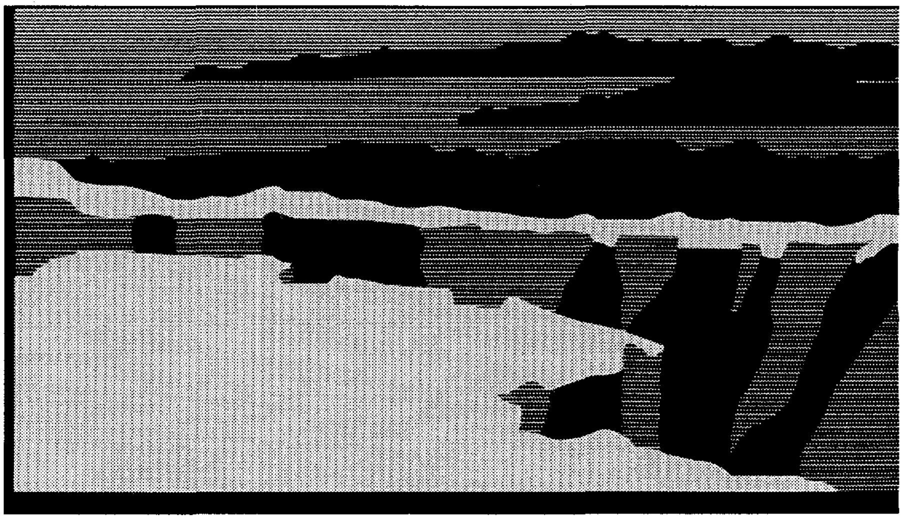

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Ultrafast and Nonlinear Optical Characterization of Optical Limiting Processes in Fullerenes

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ABSTRACT

We present recent results of broadband femtosecond (fs) transient absorption (TA) and broadband nanosecond (ns) optical limiting (OL) studies of C_{60} and derivatized C_{60}. Improvements in measurement techniques for fs TA spectra provide sensitivity to 10^{-5} in differential transmission, allowing detailed comparison of excited-state spectra with established energy level diagrams, as well as comparison of the ratio of triplet to singlet excited-state absorption cross sections from TA spectra with those obtained by modeling time transients at different wavelengths. For derivatized fullerenes, which provide enhanced solubility and a ground-state absorption extended into the infrared compared with C_{60} there is no spectral region where the triplet absorption cross section dominates the singlet as strongly as in C_{60}. Wavelength-dependent studies show that the OL response improves monotonically at longer wavelengths, demonstrating broadband limiting in all 6,6 mono-adducts and neat C_{60}. We report new approaches to processing sol-gel encapsulated fullerenes to improve the OL performance of solid-state materials to approach the response of solution limiters.

Key Words: fullerenes, C_{60}, transient absorption, optical limiting, sol-gel glasses

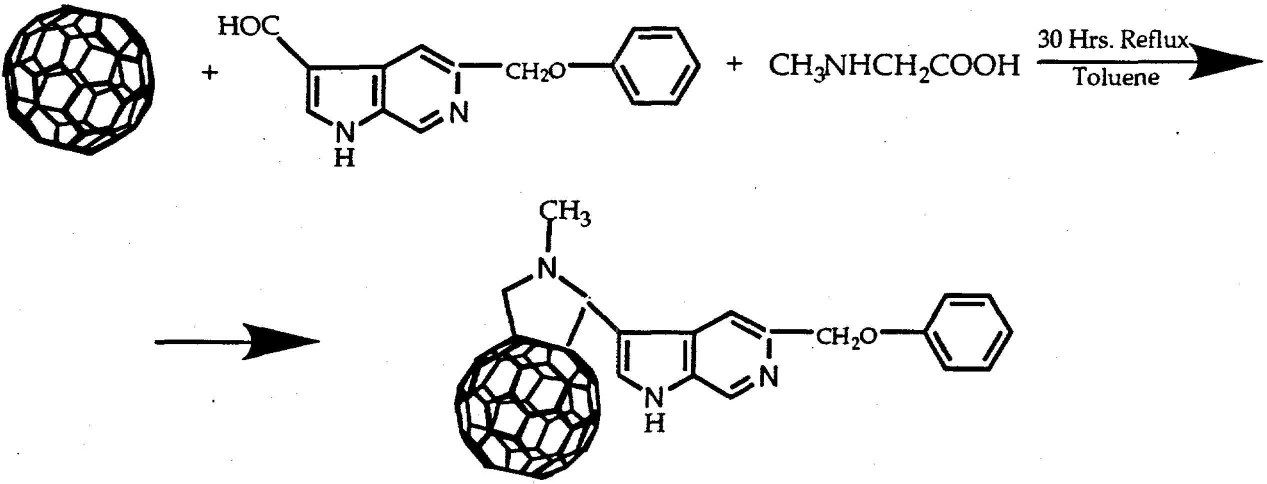
1. INTRODUCTION

Optical power limiting (OL) occurs when the optical transmission of a material decreases with increasing laser fluence.[1] This property is desirable for providing protection to optical sensors (such as human eyes) from the high fluence output of modern pulsed lasers. One mechanism for obtaining OL is reverse saturable absorption (RSA), which occurs when excited states formed through optical pumping of the ground state have a higher absorption cross-section than the ground state.[1,2] RSA has been described using five-level models in which the excited-state absorption cross section (σ^*) is larger than the ground-state absorption cross section [σ_0]. Upon ground-state pumping, broad singlet and triplet excited-state absorptions are induced in fullerenes such as C_{60} that extend throughout the visible and near infrared, in regions where σ_0 is small.[3–7] Therefore, C_{60} and other fullerenes have been studied in detail as a useful class of materials for OL with a potentially broadband response.[2,3,8–10] The possibility of selective derivatization across a bond joining two hexagons in the C_{60} molecule (to form a 6,6 fullerene adduct) allows these materials to be optimized for solubility and consequent ease of processing.[11,12] Earlier studies[3] have also demonstrated the possibility of extending the OL further into the infrared as a consequence of additional ground-state absorption at long wavelengths in derivatized fullerenes. Therefore, fullerenes form a rich family of materials within which to study OL.

To characterize the RSA response, it is essential to understand the excited states induced by optical pumping, and their dynamics. For OL protection against nanosecond (ns) pulses, the lifetime of the excited state which provides the RSA response is important. Previous transient absorption (TA) studies have demonstrated triplet absorptions near 750 nm in C_{60}[3-6,13] which have lifetimes of order $\sim$ μs[6]-ms.[5] Also singlet transitions have been identified from TA spectra near 975 nm and 500 nm.[5,13] An intersystem crossing time from the singlet to the triplet manifold of 600 ps was determined from a multispectral analysis of the decay dynamics.[13] The previous spectra were obtained using a charge-coupled device (CCD) camera, giving a sensitivity of $\sim 10^{-3}$ in differential transition.[13] Recent improvements in instrumentation for kHz repetition rate fs TA spectrometers have resulted in a sensitivity of $\sim 10^{-5}$ and a simple means of chirp correction,[14] allowing detailed comparison of TA spectra with energy level diagrams obtained from theory and linear absorption.[15] We find a quantitatively good agreement with predictions of excited-state transition energies, based on results from linear absorption. Due to the improved signal to noise, the ratio of spectra at long delays ($\sim$1 ns) to that at short delays ($\sim$3 ps) can now be used for a quick quantitative prediction of the triplet to singlet excited-state absorption cross section ratio (σ_T/σ_S), which closely matches σ_T/σ_S obtained from multispectral analysis of the decay dynamics in both C_{60} and 6,6 derivatives. These σ_T/σ_S spectra provide predictions of where effective OL occurs for ps or ns pulses, based on where singlet or triplet transitions dominate the excited-state absorption spectra.

The ability to functionalize fullerenes with organic groups which enhance solubility provides a means of increasing the oscillator strength in the near-infrared for transitions from the ground state. This enhanced linear absorption in the near IR allows OL to be initiated at longer wavelengths, making the OL more broadband than for neat C_{60}.[3] We present TA spectra for these functionalized fullerenes which demonstrate that the essential dynamics are similar to those of C_{60}, but with a broadening of the singlet and triplet states. The predicted σ_T/σ_S for various 6,6 derivatives is not significantly greater than one in any wavelength range, unlike neat C_{60}. OL spectra measured at multiple wavelengths for these derivatized fullerenes confirm the broadband nature of the limiting predicted from the dynamics. Using five-level model fits to the OL response, we provide estimates of σ^*/σ_0 at multiple wavelengths, which are compared with predictions from the TA spectra. σ^*/σ_0 increases at long wavelengths, demonstrating optimal OL for fullerenes in the red. Earlier studies showed that the optical limiting response of C_{60} incorporated into sol-gel glasses was weaker than for C_{60} in solution, and showed faster decay kinetics. This same response is shown for derivatized C_{60}. However, by careful processing of post-doped sol-gel glasses, we demonstrate that the OL response of 6,6 mono-adducts in a sol-gel matrix can approach that of the fullerene derivatives in solution.

2. EXPERIMENTAL



Scheme 1. Synthesis of CPBPP.

Synthesis of C_{60}-pyrrolidine(3)-5-benzyloxy-1H-pyrrolo[2,3-C]-pyridine (CPBPP) was performed as depicted in Scheme 1 (a pyrrolidine linkage has also recently been described to form water-soluble fullerene derivatives[16]). To 400 ml of fresh distilled toluene solution were added 0.2 mmol (144 mg) C_{60} (purchased from South Chemical Group, 99.5+% purity, used without further purification), 0.2 mmol (17.9 mg) N-methylglacine, and 0.2 mmol 5-Benzyloxy -1H-pyrrole[2,3-c]pyridine-3-carboxaldehyde. The reaction solution was degassed for 20 minutes using N_2, then, refluxed for 30 hours under an N_2 atmosphere. Upon completion of the reaction, toluene was removed via vacuum evaporation. 5% methanol/ benzene on a silica gel column gave 0.11 mmol (110 mg) of mono-adduct CPBPP (55% yield). The ^{1}H NMR spectrum and electrochemistry measurements confirmed the mono-adduct structure. The 6,6 derivative 1-(3-methoxycarbonyl)propyl)-1-phenyl-[6,6]-C_{61} (PCBM) was synthesized as published previously.[11]

Silica gels containing C_{60}, CPBPP, and PCBM were prepared by mixing into a precursor sol, using either o-dichlorobenzene (DCB), tetrahydrofuran (THF), or toluene as co-solvents, as previously described.[17] These gels are termed "pre-doped" gels. "Post-doped" sol-gel samples were prepared using porous glass (GELTECH) with 75 Å nominal pore size produced by their proprietary process. Treated porous glass samples were placed in a solution containing the fullerene derivatives in various concentrations, and the solvent was dried to trap the fullerenes within the porous matrix.

Time-resolved excited-state absorption spectra were measured using a femtosecond (fs) pump-probe technique. The samples were photoexcited at 400 nm by 100 fs pulses from a frequency-doubled regeneratively-amplified mode-locked Ti:sapphire laser (Clark-MXR CPA-1000). The repetition rate of the pulsed output was $f = 1$ kHz, with pump pulse energies up to 5 μJ, corresponding to an excitation density of 10 mJ/cm^2. The pump beam was modulated synchronously at $f/2$ with a mechanical chopper. A fs broadband continuum (450-1000 nm) probe pulse was generated in a 1 mm sapphire plate in the single-filament regime.[14] The probe beam was split into a reference channel (directed through the sample) and a sample channel (focused with reflecting optics through the center of the photo-excited spot on the sample). The pump beam was delayed with respect to the probe beam via a mechanical translation stage (up to 1.5 ns total delay). The reference and the signal channels were sent via a two-leg fiber bundle through a scanning imaging monochrometer. The dispersed reference and signal channels were detected with matched large-area p-i-n Si photodiodes coupled to current preamplifiers, sent to a differential amplifier, and then to a digital lock-in amplifier synchronized to $f/2$. This method can be used for recording chirp-free TA spectra by scanning the monochrometer and simultaneously adjusting the relative pump-probe delay time according to the calibrated chirp.[14] In addition, time transients at a fixed wavelength can be recorded by scanning the delay line at a fixed wavelength. This technique provides an accuracy of up to 10^{-5} in differential transmission, an improvement of order 100 over similar single-shot CCD camera measurements.[14] For TA measurements, 6,6 mono-adducts and neat C_{60} were prepared as solutions in 2 mm path length cuvettes, with concentration adjusted to yield optical densities near unity at 400 nm.

Broadband optical limiting was measured using the output of an optical parametric oscillator (CASIX OPO BBO-3B with 6 ns pulses from 400-2200 nm) which was pumped by the frequency-tripled output (355 nm) of a Nd:YAG laser (Quanta Ray GCR-3). Intensity control of the laser beam was obtained by passing the beam through a combination half-waveplate and polarizing beam splitting cube. The beam was split into a reference arm, a sample arm, and an intensity measurement arm. Intensity-dependent transmission was measured by placing the sample at the focus of a 120 mm focal length lens, which focused the beam down to a gaussian spot with beam waist of roughly 47 μm. The transmitted energy in the reference and sample arms was measured using 13 mm^2 Si photodiodes followed by gated integration. Each point represents the average of 20 - 100 laser shots. Fullerene samples were prepared as solutions in 2 mm path length cuvettes, with concentration adjusted to yield a linear transmission in the range of 50%.

3. RESULTS AND DISCUSSION

Previously, we reported fs transient absorption spectra for C_{60} in solution in the wavelength range from 450–1000 nm.[13] These measurements showed excited-state absorption peaks attributed to the lowest excited singlet state at ~975 nm and ~500 nm (prominent in the ~10 ps spectrum) as well as absorption attributed to the lowest excited triplet state at ~750 nm and ~530 nm (prominent in the 1 ns spectrum). The singlet decay and triplet growth showed complimentary dynamics with an intersystem crossing time ranging in the literature from 650 ps[4] - 1.2 ns.[5] Our analysis of the dynamics at eleven separate wavelengths extending from 450 - 920 nm using a simple model with singlet decay and unit intersystem crossing to a triplet yielded an intersystem crossing time of ~600 ps.[13] In the present paper, we report fs transient absorption spectra measured using chirp-free scanning transient spectroscopy rather than the single shot CCD technique. The two order of magnitude improvement in the signal to noise allows a more accurate comparison of the TA spectrum with energy level predictions from theory and linear absorption experiments.[15]

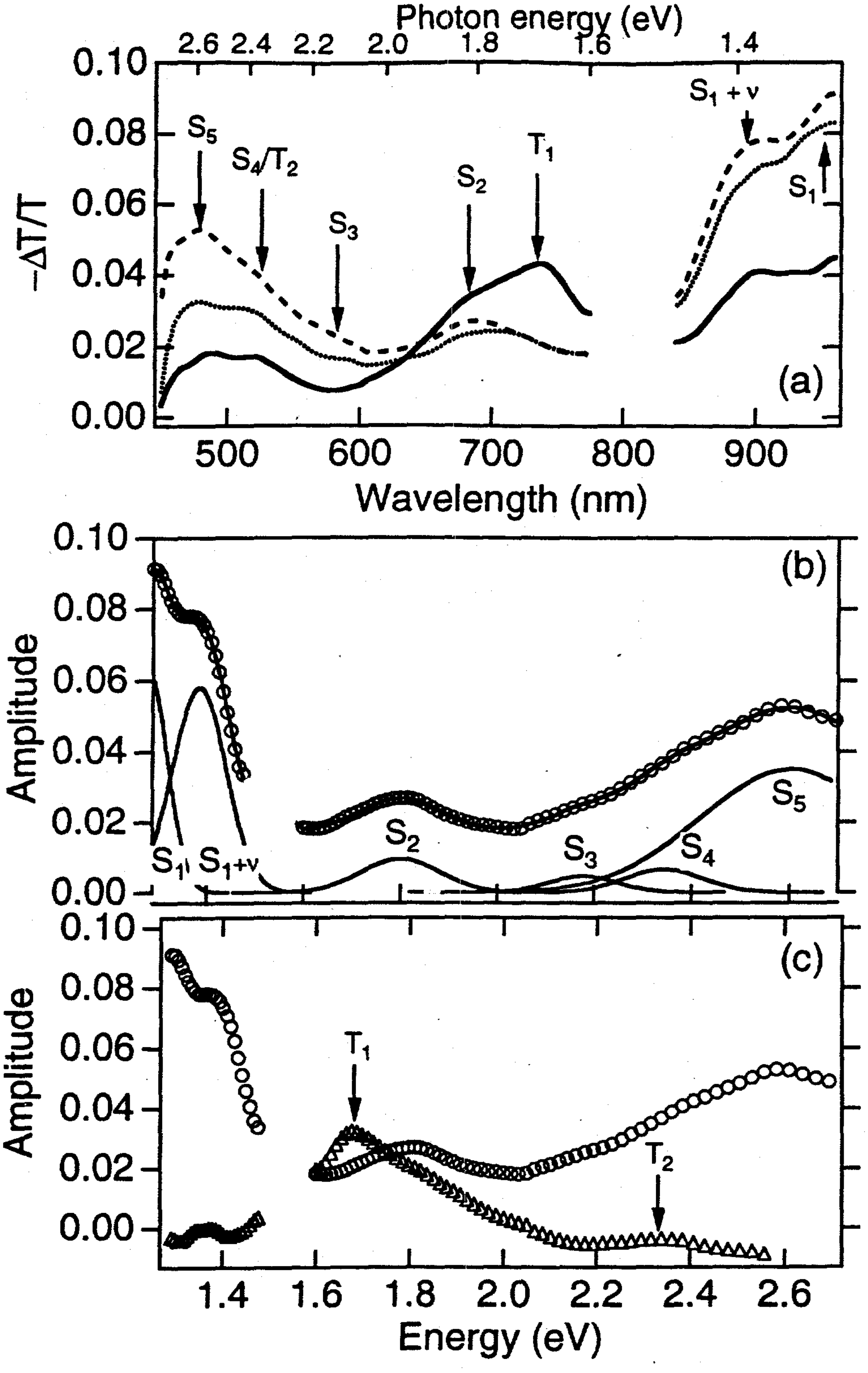


Figure 1. (a) -$\Delta T/T$ for C_{60} in toluene solution taken at three delay times: 3 ps (solid line, singlet excited state absorption), 100 ps (dashed line), and 1 ns (dot-dashed line, triplet excited state absorption). (b) Nonlinear least quares fit of 3 ps TA spectrum for C_{60} using six gaussians. (c) Spectrum for the triplet at 1 ns obtained by subtracting the time-decayed singlet spectrum.

Figure 1 shows the transient absorption for C_{60} in toluene at delay times of 3 ps, 100 ps, and 1 ns measured using chirp free TA spectroscopy. The spectra show the same qualitative features reported earlier,[3-6,13] including singlet absorptions at ~500 nm and ~900 nm at early times as well as a strong triplet transition near ~750 nm at 1 ns time delay. The spectrum at early times (3 ps) was modeled with a series of gaussian peaks representing different transitions from the lowest excited singlet state. Six gaussians labeled S_1, $S_1+\nu$, S_2–S_5 ($S_1+\nu$ designates a phonon sideband of S_1) were used for the fit, as shown in Fig. 1(b). The center energy and area (normalized to the area of the S_5 transition) of each of the six transitions are shown in Table 1. For comparison, we used the energy levels for C_{60} in toluene deduced from linear absorption measurements and theory.[15,18] Since the lowest excited singlet state (1^1T_{1g}) has the same parity as the ground state (1^1A_g), the energies of the excited-state transitions revealed in TA (upon photoexcitation to the 1^1T_{1g} state) should mirror those observed in the ground-state absorption spectra, but displaced by thedifference between the energies of the lowest singlet excited state and the ground state. The transition energies of various singlet transitions observed in Ref.[15] within the energy range of our TA experiment are also shown in Table 1. There is very good quantitative agreement between the excited-state transition energies determined from TA and those expected based on the linear absorption spectra. However, the different symmetry of the first excited singlet state would be expected to lead to modifications of the transition probabilities (oscillator strengths) relative to those observed in ground-state absorption. Indeed, the oscillator strength of the lowest excited-state singlet transition (S_1) is enhanced by a factor of approximately forty compared to the higher transition (S_5) which is the dominant transition in the ground-state spectrum. Calculations for the oscillator strength of the excited-state transitions S_1 - S_5 are still needed for comparison, and to our knowledge have not been reported. By subtracting the singlet (3 ps) spectrum, scaled for decay based on the measured 600 ps decay for the singlet state, from the 1 ns spectrum, the triplet spectrum shown in Figure 1 (c) is obtained. The triplet spectrum has transitions at ~740 nm and ~530 nm, in agreement with past reports.[5,13]

Due to the enhanced signal to noise obtained with scanning TA spectroscopy, the ratio of the TA spectrum at 1 ns to that at 3 ps becomes a useful tool to predict the ratio of triplet to singlet excited state absorption cross sections (σ_T/σ_S). In a previous study,[13] we used a simple model to fit the TA transients for C_{60} in toluene at multiple wavelengths to obtain the intersystem crossing time, as well as σ_T/σ_S at multiple wavelengths, which is reproduced in Figure 2. For comparison, we also show σ_T/σ_S determined from the ratio of TA spectra at 1 ns and 3 ps. Clearly, σ_T/σ_S estimated directly from the TA spectra closely resembles the more exact results obtained from modeling the decay dynamics *vs.* wavelength, but is obtained more easily. Figure 2 demonstrates that in the wavelength range from 620-810 nm, σ_T is larger than σ_S. In this wavelength range, OL is predicted to be more effective for ns pulses than for ps pulses, due to the long lifetime and large σ_T of the triplet state. In other parts of the spectrum OL should be stronger for ps pulses.

Figure 3 shows σ_0 for C_{60} in toluene; the absorption drops toward zero beyond 650 nm. This indicates an important limitation of OL using neat C_{60}. Since there is little or no ground state absorption to initiate population of the excited states in the range where the triplet excited states have their maximum absorption, we can not take advantage of the long-lived triplet for OL beyond ~650 nm. In addition, it is not possible to prepare more concentrated samples, due to limited solubility. Figure 3 also compares σ_0 of the derivatized fullerenes PCBM and CPBPP with C_{60}. For both of these 6,6 mono-adducts, the derivitization not only enhances the solubility of the fullerene but also activates new vibrationally-coupled optical transitions in the wavelength range 650 - 740 nm.[3] The presence of additional ground state absorption in this wavelength range can enhance the wavelength range of RSA response if the excited-state response is not drastically affected by the derivitization.

Figure 4 (a) shows the TA spectra measured for CPBPP. The spectral dynamics of CPBPP are very similar to those of C_{60}. There is a region of dominant singlet decay near ~500 nm and ~900 nm. Around 700 nm, the induced absorption has slow dynamics and no clear triplet peak growth, due to broadened overlapping singlets and triplets in this wavelength range. These results are similar to the spectral dynamics observed in PCBM and other 6,6 derivatives.[3,20] σ_T/σ_S obtained from the ratio of the 1 ns to 3 ps TA spectra for PCBM and CPBPP are compared with that of C_{60} in Fig. 4 (b). σ_T/σ_S obtained from fitting time transients for PCBM are shown as well to point out the generality of the agreement between these two techniques for obtaining $\sigma_T/\sigma_S(\lambda)$. For both PCBM and CPBPP, there is not a wavelength region where σ_T is much greater than σ_S, indicating that the RSA response should be more uniform in time at different wavelengths.

Table 1. Energies and oscillator strengths for transitions from the first excited singlet state.

Transition	Energy (eV) (Linear Abs)	Energy (eV) (-ΔT/T)	Osc. Strength (-ΔT/T) Normalized to S_5
2 $^1T_{1u}$ - 1 $^1T_{1g}$ (S_1)	1.29	1.28	0.38
2 $^1T_{1u}$ + ν - 1 $^1T_{1g}$ ($S_1 + \nu$)	1.36	1.38	0.5
3 $^1T_{1u}$ - 1 $^1T_{1g}$ (S_2)	1.78	1.8	0.12
4 $^1T_{1u}$ - 1 $^1T_{1g}$ (S_3)	2.06	2.18	0.05
5 $^1T_{1u}$ - 1 $^1T_{1g}$ (S_4)	2.35	2.34	0.08
6 $^1T_{1u}$ - 1 $^1T_{1g}$ (S_5)	2.82	2.6	1.0

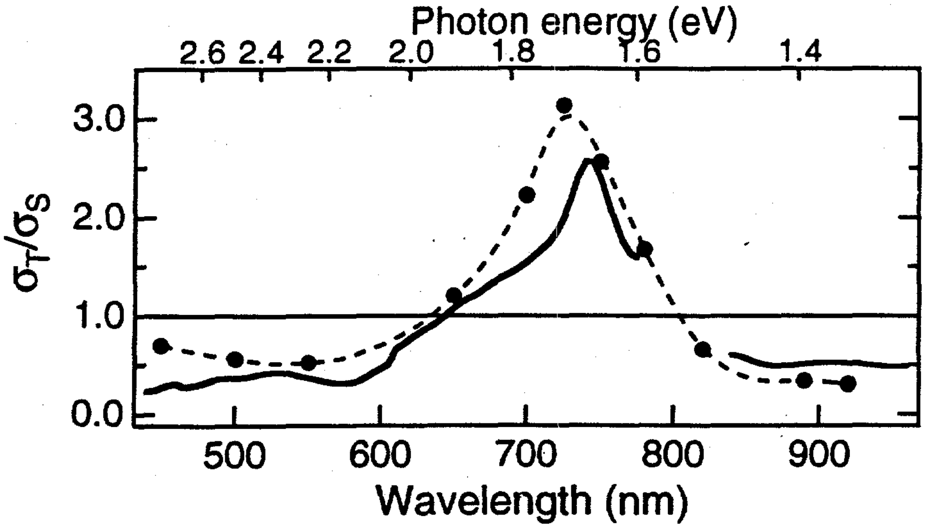


Figure 2. Comparison of σ_T/σ_S obtained from ratio of fs TA spectra at 1 ns and 3 ps (solid line) with ratio obtained from fitting time transients (solid circles, from references[17,19]).

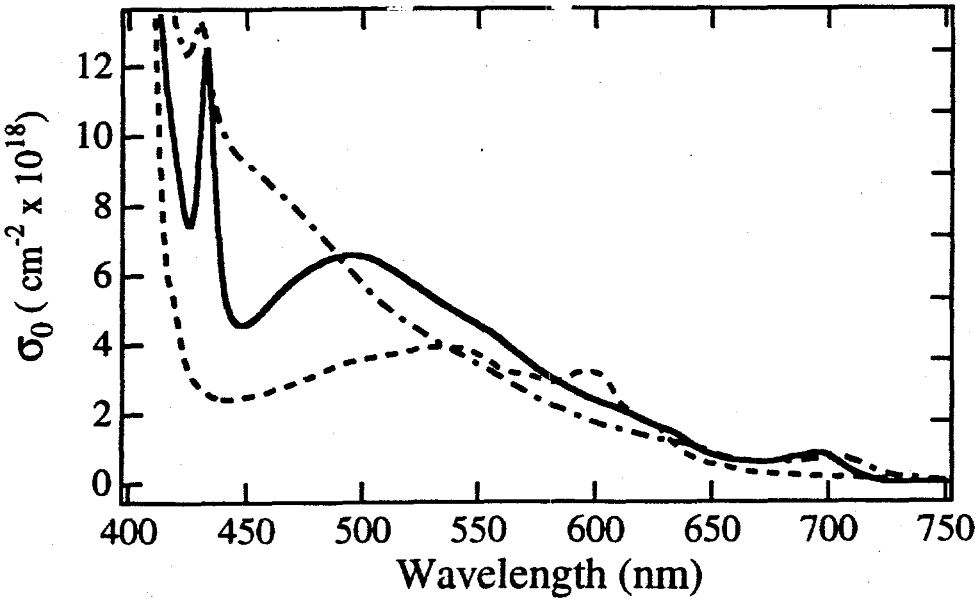


Figure 3. Ground state absorption for solutions of C_{60} (dashed), PCBM (solid), and CPBPP (dot-dash).

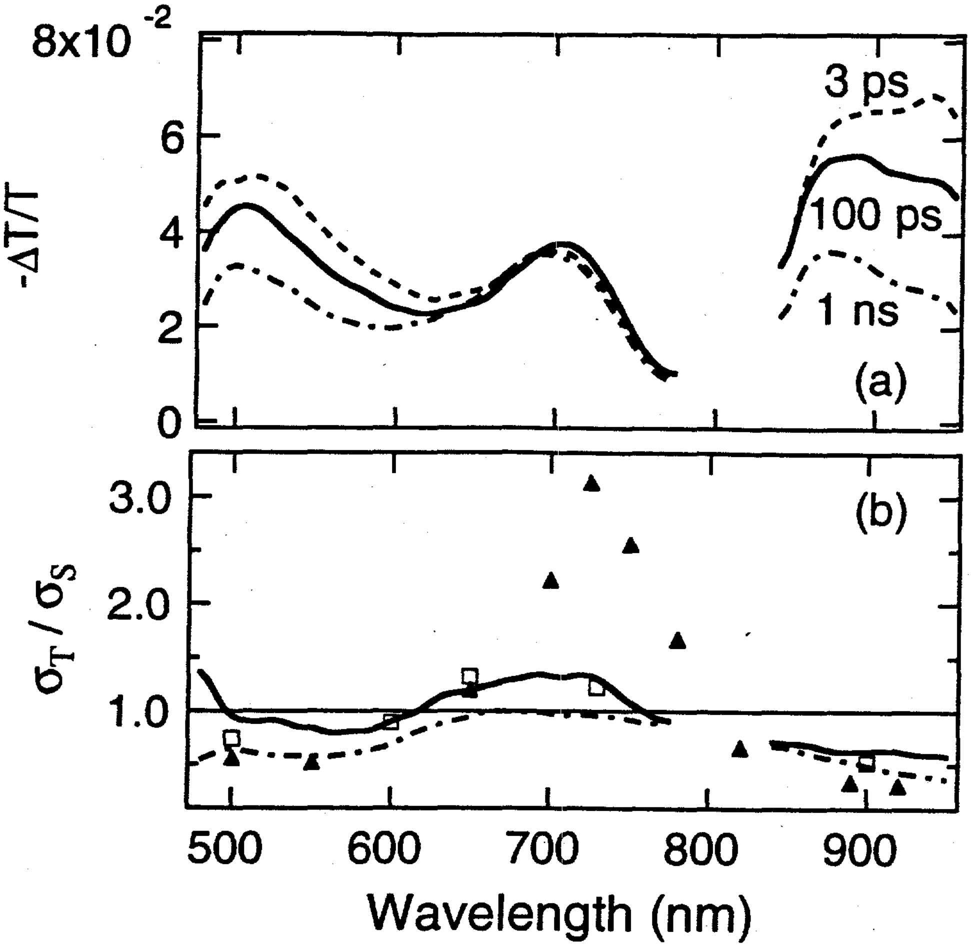


Figure 4. (a) Fs TA spectra for CPBPP at 3 ps (dashed line), 100 ps (solid line) ,and 1 ns (dot-dashed line). (b) σ_T/σ_S from TA for PCBM (solid line) and CPBPP (dot-dashed line line). σ_T/σ_S from time transient modeling for C_{60} (solid triangles) and PCBM (solid circles) are also shown for comparison.

For PCBM and CPBPP, strong excited-state absorption and weak ground-state absorption extend throughout the visible and near-infrared, indicating that both materials should be broadband optical limiters. Figure 5 shows the wavelength-dependent optical limiting measured with 6 ns pulses for solutions of PCBM and CPBPP, adjusted to have a linear transmission of 50%. Both compounds show strongly increasing OL with increasing wavelength between 532 nm and 650 nm, as reported previously for neat C_{60} and another 6,6 mono-adduct,[3] confirming that all 6,6 mono-adducts exhibit similar broadband optical limiting. In addition, CPBPP at 720 nm (where the initial transmission was 80%) also shows strong OL. The clamping level decreases monotonically with increasing wavelength, consistent with the broad singlet and triplet induced absorption and the decreasing linear absorption at long wavelengths. The solid lines in Fig. 5 (b) are five-level fitting results for each of the wavelengths. In solution, the deviation from the fits for high input energies is due to additional limiting due to thermal mechanisms such as thermal lensing.[10,21]

The resulting ratio of the excited state absorption cross section σ^* ($= \nu_S\sigma_S + \nu_T\sigma_T$, where ν_x and σ_x are the population fraction and absorption cross section respectively for the excited singlet and triplet) divided by the ground state absorption cross section (σ_0) for CPBPP is shown in Fig. 5 (c). For comparison, the ratio σ^*/σ_0 evaluated from the TA spectra at 1 ns and the ground state absorption is shown also in Fig. 5 (c). $\sigma^*/\sigma_0 \sim 3$ is obtained at 532 nm, in agreement with past reports.[21] At longer wavelengths, σ^*/σ_0 increases monotonically up to ~10 at 720 nm. This behavior is in qualitative agreement with the predicted σ^*/σ_0 from TA spectra. This figure demonstrates that fullerenes are broadband optical limiters which are optimal for red and near IR applications. The σ^*/σ_0 obtained from five-level model fits do not grow as quickly as predicted from the TA and ground state absorption spectra. This

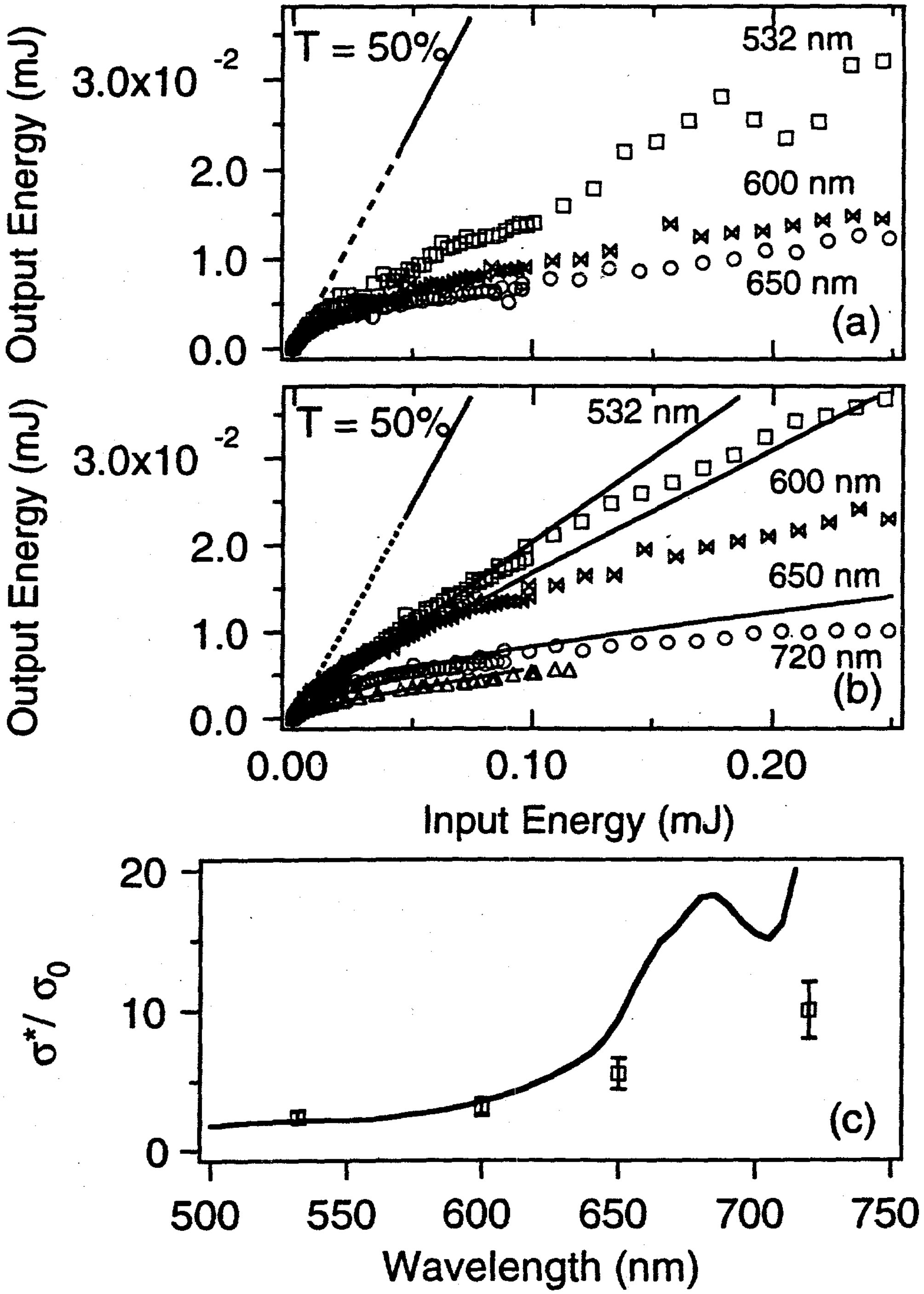


Figure 5. Optical limiting curves for PCBM (a) and CPBPP (b) as a function of wavelength. (c) Comparison of σ^*/σ_0 for CPBPP obtained from five-level fits to OL in (b) [open squares] and from TA spectra at 1 ns and ground state absorption [solid line].

may be due to particular aspects of the modeling: the beam is propagated as a top hat beam profile that saturates the excited states more rapidly than typical of a more realistic gaussian beam profile; and in practice saturation fluence is always harder to attain than in simple models.[22] Therefore, we should take the σ^*/σ_0 obtained from fits to a five-level model as a *lower limit* to the actual values.

To take advantage of the broadband optical limiting of fullerenes for most applications, a solid-state dispersion is required. Due to enhanced solubility, the concentration of 6,6 fullerene derivatives such as PCBM in pre-doped sol-gels can be varied to achieve a wide range of linear transmissions.[7,17,23] Compared with thin films of C_{60}, in which there is rapid quenching of the singlet (on ps or sub-ps time scales), C_{60} pre-doped sol-gels have much slower dynamics, indicating molecular dispersions of the C_{60}.[7,24] However, the dynamics of the C_{60} pre-doped sol-gels indicate some quenching or competing pathways to the triplet, as there is no clear growth of the triplet state as seen for C_{60} in solution.[17,13] Similar results are shown for PCBM at 600 nm in pre-doped sol-gels compared with solutions in Figure 6. The dynamics are clearly more rapid in the pre-doped sol-gel glass than in the solvents. The DCB solutions also show clearly faster relaxation kinetics than those in solution, indicative perhaps of aggregation or solvent interactions, which can lead to new relaxation pathways which compete with the triplet state. Since PCBM gels were most commonly prepared using DCB as a co-solvent to take advantage of the rapid gelation times, this may also explain some of the observed more rapid kinetics in the pre-doped gels.

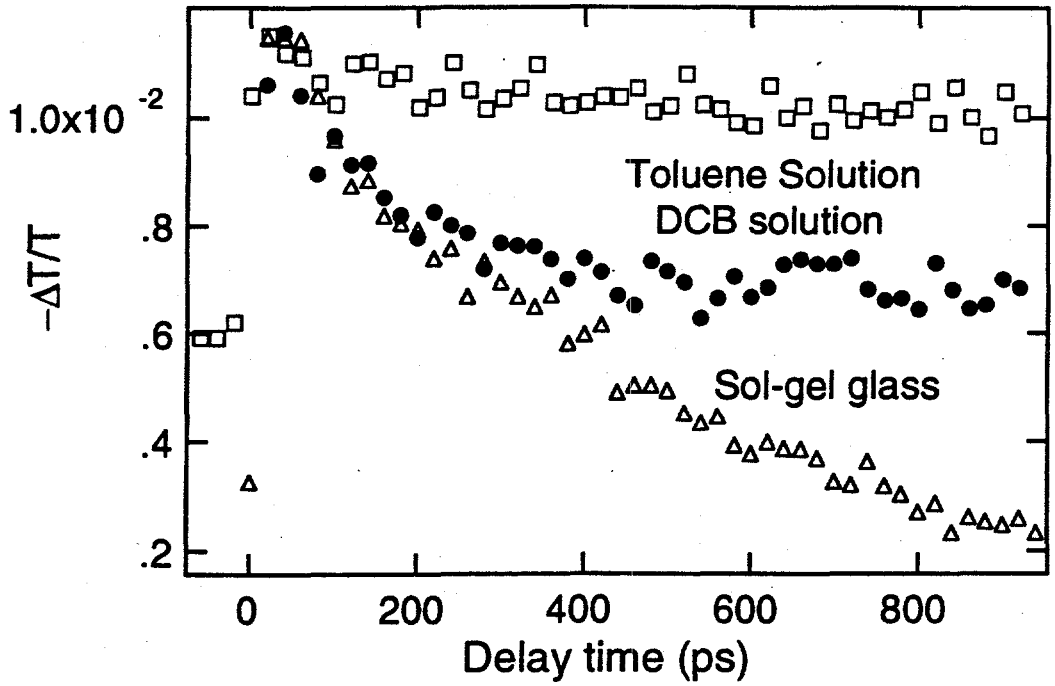


Figure 6. Dynamics at 600 nm of PCBM in toluene and DCB compared with pre-doped sol-gel.

In side-by-side comparisons, PCBM pre-doped sol-gels have demonstrated less effective limiting than solutions.[17] In Figure 7, we show the optical limiting at 650 nm of PCBM in toluene (2 mm path length), in a pre-doped sol-gel (1.4 mm thick), and in a post-doped sol-gel (2 mm thick) all prepared to have a linear absorption ~50%. The transmission (OL) for high input energy of PCBM in toluene decreases four times that of PCBM in a typical pre-doped sol-gel. Based on values deduced from five-level model fits to the OL response, the effective excited-state absorption cross section σ^* in the gel (2.0×10^{-18} cm^2) is less than half that of PCBM in toluene (5.5×10^{-18} cm^2). Comparing the behavior of a post-doped PCBM sol-gel in Figure 7, the OL response is improved such that $\sigma^* \sim 4.0\times10^{-18}$ cm^2 for the post-doped sol-gel. Other post-doped PCBM sol-gels showed values as high as $\sigma^* \sim 4.8\times10^{-18}$ cm^2, indicating that ~90% of the OL response of PCBM in toluene can be observed in post-doped sol-gels.

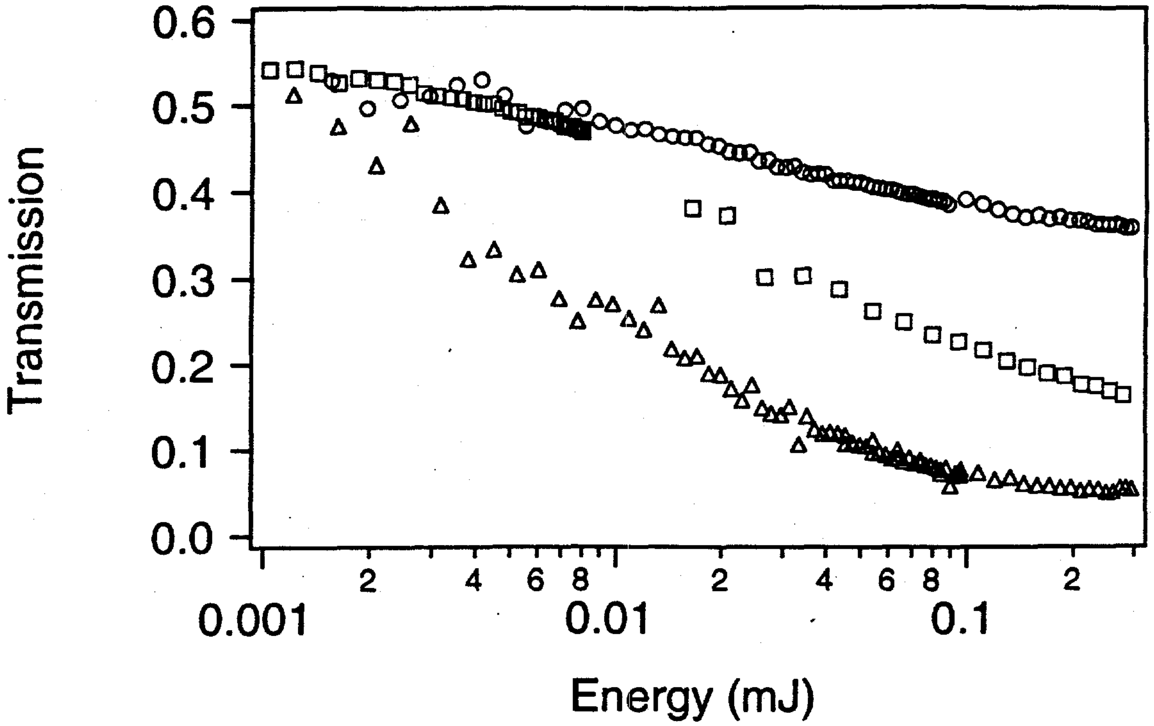


Figure 7. Optical limiting at 650 nm for PCBM in toluene, pre-doped sol-gel, and post-doped sol-gel.

4. CONCLUSIONS

Improvements in measurement techniques for fs TA spectra provide sensitivity to 10^{-5} in differential absorption and have allowed us to make a detailed comparison of excited state spectra with established energy level diagrams for C_{60} with excellent quantitative agreement between the energy levels of the two. In addition, we demonstrated that σ_T/σ_S from modeling time transients at different wavelengths for C_{60} can be predicted well from TA spectra. For 6,6 fullerene derivatives, which exhibit an infrared-extended ground-state absorption compared with C_{60}, there is no spectral region where the σ_T dominates σ_S as strongly as is observed in C_{60}. Wavelength-dependent studies show that the OL response improves monotonically at longer wavelengths for all 6,6 mono-adducts and for neat C_{60}, demonstrating broadband limiting with $\sigma^*/\sigma_0 \geq 10$ at 720 nm, and confirming predictions from the TA spectra. New approaches to processing sol-gel encapsulated fullerenes demonstrate that the OL performance of solid-state dispersed fullerenes can be engineered to approach the response of solution limiters.

5. ACKNOWLEDGMENTS

This work was supported in part by Los Alamos National Laboratory Directed Research and Development funds and Collaborative University of California/ Los Alamos Research funds, under the auspices of the U.S. Department of Energy. Additional funding was provided by the U.S. Army Small Business Technology Transfer program, under contract DAAH04-96-C-0077.

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