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Optical limiting and excited-state absorption in fullerene solutions and doped glasses

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ABSTRACT

We report the ground-state and excited-state optical absorption spectra in the visible and near infrared for several substituted fullerenes and higher fullerenes in toluene solutions. Based on these measurements, broadband predictions of the optical limiting performance of these molecules can be deduced. These predictions are then tested in the wavelength range from 532 nm to 700 nm in intensity-dependent transmission measurements. We observe optical limiting in all fullerenes measured; higher fullerenes show the greatest potential for limiting in the near infrared (650-1000 nm), while substituted C_{60} shows optimal limiting in the visible (450-700 nm). We observe dramatically reduced limiting for solid forms of C_{60} (thin films and C_{60} -doped porous glasses), indicating that efficient optical limiting in fullerenes requires true molecular solutions.

1 INTRODUCTION

Fullerenes have attracted much recent interest for their potential to act as optical limiters of high fluence pulsed lasers.¹⁻⁷ The excited-state absorption cross-section for C_{60} is much larger than that in the ground-state, both in the singlet and triplet manifolds.⁸⁻¹⁰ This property results in significant additional absorption in the visible and near infrared spectral region, developing on a picosecond timescale, after photoexcitation into the lowest singlet state.⁴ This reverse saturable absorption (RSA), or optical limiting, phenomenon may be very useful for eye and sensor protection from pulsed laser light.

Previous studies have measured optical limiting only in a limited selection of fullerenes (C_{60} and C_{70}) and only

at 532 nm.¹⁻⁷ In this work, we report a survey of the optical limiting performance for several substituted fullerenes and higher fullerenes in toluene solution in the visible to near-infrared spectral regions (500-1000 nm). Excited-state absorption spectra are measured with picosecond resolution using time-resolved pump-probe absorption. This allows broadband predictions of the optical limiting performance. These predictions are then tested at selected wavelengths from 532-700 nm by measuring intensity-dependent transmission. We find that C₆₀ and substituted derivatives of C₆₀ display optical limiting from 532-700 nm, with the limiting performance increasing to the infrared, constrained by the vanishing ground-state absorption below 700 nm. Higher fullerenes (C₇₈, C₈₄) also show optical limiting in this range, with further potential for limiting out to 1000 nm. Comparisons of optical limiting and excited-state absorption in solid forms of C₆₀ (thin films and doped porous glasses) show that the much faster relaxation dynamics in the solid reduces the limiting effectiveness for nanosecond pulses. Hence, optimal use of fullerenes for optical limiting in a solid form will require that the fullerenes be microscopically dispersed in a solid host matrix.^{2,7,11}

2 EXPERIMENTAL

Toluene solutions of C₆₀, substituted derivatives of C₆₀ [C₆₀-C₂H₅N, 2[(η^2 - C_p)₂Fe]C₆₀ (Ferrocene-C₆₀), and phenyl-C₆₁-butyric acid cholesteryl ester (PCBCR)] and higher fullerenes (C₇₀, C₇₈, and C₈₄) were prepared in 2 mm path length optical cells. PCBCR was synthesized by a method which will be published elsewhere.¹² Other materials were provided by MER Corp. Concentrations for C₆₀, Ferrocene-C₆₀, PCBCR, and C₇₀ were 0.15 wt%, 0.15 wt%, 0.21 wt%, and .04 wt%, respectively. These concentrations were chosen to yield transmissions in the range of 20%-80% in the visible and near-infrared. The other materials (C₇₈, C₈₄ and C₆₀-C₂H₅N) were prepared as saturated solutions of uncalibrated concentration, due to limited solubility. Thin films of C₆₀ were prepared by sublimation in vacuum (10⁻⁶ Torr). C₆₀-doped porous SiO₂ glasses with 28% porosity and an average pore size of 4-6 nm (Corning Vycor brand¹³) were prepared by dipping in saturated C₆₀-toluene solution, followed by vacuum drying, to form a solid-state matrix with C₆₀ deposited along the insides of the glass pores.¹⁴

Time-resolved excited-state absorption spectra were measured using a femtosecond (fs) pump-probe technique. The samples were excited at 397 nm (3.12 eV) by 200 fs pulses from a regeneratively amplified modelocked Ti:Sapphire laser. The pump pulse energy was 5 μ J, corresponding to an excitation density of 12 mJ/cm², and the repetition rate was 1 kHz. Femtosecond white light pulses were generated in a 1 cm water cell. The transmission at the sample was measured using a .15 m spectrometer and CCD array with the pump beam on (T_{on}) and off (T_{off}). The differential transmission $\Delta T/T$ was determined from the expression $\Delta T/T = (T_{on} - T_{off})/T_{off}$. Each spectrum was the average of 500-1000 pulses.

Optical limiting (intensity-dependent transmission) measurements were made using a frequency-doubled Nd:YAG laser (Quanta Ray GCR-3) at 532 nm, and pulsed dye laser (Quanta Ray PDL-3) from 560-700 nm. The 6 ns pulses were split into reference and signal beams, and the signal beam was focused with a 150 mm lens onto the sample, to a radius of $\approx 10 \mu$ m (measured by scanning a knife edge across the beam). The transmitted light was collimated and sent onto a large area silicon photodiode. The signal and reference photodiodes were connected to a Stanford Research boxcar averager and computer for signal averaging. Each data point was an average of 20-50 individual laser pulses, and the beam spot was kept fixed through each data set. The incident energy was measured directly, and the input fluences were calibrated by measuring the two-photon absorption response of a ZnSe reference.¹⁵ This calibration yielded an effective beam area at 575 nm of 4.2×10^{-6} cm², consistent with the knife edge measurement; separate calibrations were performed at each wavelength measured. The laser fluence was ramped up first, and then an identical data set taken while ramping the fluence back down, to check for optical damage and slow thermal effects. Open aperture Z-scans were performed by fixing the incident fluence and scanning the sample through the focus.¹⁶ This allowed a direct determination of the effective two-photon absorption coefficient β relative to ZnSe at fluences well below the damage threshold.

3 RESULTS AND DISCUSSION

Figure 1(a) shows the ground-state optical absorption spectra for C_{60} and higher fullerenes from 400-750 nm. The absorption feature in C_{60} in this range corresponds to the lowest optical transition, a dipole-forbidden even parity transition which is weakly allowed by Herzberg-Teller coupling to the vibrational modes of the molecule.¹⁷ This symmetry specific feature is one factor governing the optical limiting efficiency in fullerenes. As the icosohedral symmetry of C_{60} is altered in going to higher fullerenes, this lowest transition is no longer symmetry forbidden, and significant absorption can be observed if the symmetry breaking mixes in strong transition moments. For example, the ground-state absorption cross section for C_{70} in this region is up to ten times higher than that of C_{60} (the concentration of the C_{70} solution is 0.25 $\times$ that of the C_{60} solution). Consequently, the limiting effectiveness for wavelengths shorter than ≈ 600 nm (the wavelength below which the ground-state absorption increases sharply) is expected to decrease in the higher fullerenes, as observed in C_{70} at 532 nm.¹ For wavelengths longer than ≈ 600 nm in C_{78} and C_{84} , there is a broad absorption tail extending to beyond 1000 nm. Figure 1(b) shows the ground-state optical absorption spectra for substituted derivatives of C_{60} . The Ferrocene- C_{60} derivative has a spectrum nearly identical to that of C_{60} , indicating that the weakly bound coordinative complex does not influence the symmetry of the π -electrons on the C_{60} . Both PCBCR and C_{60} - C_2H_5N consist of a single substitution across a double bond joining two hexagons in the C_{60} , resulting in the loss of two π -electrons and a corresponding loss of icosohedral symmetry. However, the primary result of the single substitution is that the spectrum is shifted and broadened, with the appearance of a new vibronic-coupled band in the region of 650-720 nm. The magnitude of the transition dipole moment remains small in the region 450-700 nm, despite the symmetry breaking; the excited-state wavefunction retains most of the character found in pure C_{60} .

Figure 1. Ground-state absorption spectra for a) C_{60} (solid line) and higher fullerenes (C_{70} , dotted line; C_{78} , dashed line; C_{84} , dash-dot line) and b) substituted C_{60} derivatives (Ferrocene- C_{60} , solid line; C_{60} - C_2H_5N , dotted line; PCBCR, dash-dot line).

The criterion for optical limiting due to RSA is simple: the ratio of the excited-state absorption cross section σ^* to the ground state absorption cross section σ_0 must be greater than one.¹⁸ In addition, the ground state absorption cross section must be finite in order to access the strong excited-state absorptions. For a transient absorption experiment (in the limit that the pump beam is absorbed in a thickness smaller than the pump/probe interaction

length), the differential transmission is directly proportional to the excited-state absorption cross section σ^* :

$$-\frac{\Delta T}{T} \approx \sigma^* N_{\text{pump}} \quad \left(-\frac{\Delta T}{T} \ll 1\right),$$

where N_{pump} is the pump beam photon flux. Hence the time-resolved excited-state transmission experiment provides a direct measure of σ^* . For our photon flux ($N_{\text{pump}} \approx 2.4 \times 10^{16} \text{ cm}^{-2}$) we obtain the conversion:

$$-\frac{\Delta T}{T} = 0.1 \iff \sigma^* = 4.2 \times 10^{-18} \text{ cm}^2.$$

This is a lower limit, assuming perfect geometric overlap of the pump and probe beams.

Figure 2. Excited-state absorption $-\Delta T/T$. C₆₀ (solid line) and higher fullerenes (C₇₀, dashed line; C₇₈, dotted line; C₈₄, dashed-dotted line) at a) 20 ps, and c) 500 ps. Substituted C₆₀ derivatives (Ferrocene-C₆₀, solid line; C₆₀-C₂H₅N, dashed line; PCBCR, dotted line) at b) 20 ps, and d) 500 ps.

Figure 2 shows the excited-state absorption spectra $-\Delta T/T$ for C₆₀, higher fullerenes, and substituted C₆₀, at short times (20 ps) following photoexcitation, and at longer times (500 ps). In Fig. 2(c) the triplet absorption peak in

C_{60} at 750 nm is clearly evident.⁸ The spectral features for both the substituted and higher fullerenes are broadened relative to C_{60} and the weakly bound complex Ferrocene- C_{60} . The excited-state absorption for the higher fullerenes gradually decreases at progressively longer wavelengths (> 600 nm), both at short and long times; the ground-state absorption cross section also gradually decreases over the same wavelength range. For C_{78} and C_{84} , there is a small but finite absorption throughout the range from 600-1000 nm. Hence, it is expected from this measurement that the optimal wavelength range for limiting in the higher fullerenes will be in the range from 600-1000 nm. The two substituted derivatives PCBCR and C_{60} - C_2H_5N show similar broad excited-state spectra at short and long times. For optical limiting applications, inhomogeneous broadening of spectral features can be an advantage, since uniform wavelength response is desirable. At both short and long times, σ^* increases over the wavelength range 500-700 nm in which the ground-state absorption is small but finite, and decreasing. Thus, as for pure C_{60} ,⁸ the ratio σ^*/σ_0 grows larger for wavelengths longer than 532 nm. These conclusions are consistent with independent measurements by Heflin *et al.*¹⁹

The signal magnitudes are not corrected for different absorption depths at the pump wavelength of 397 nm (3.12 eV). For direct comparison between compounds of the excited-state absorption in the more dilute solutions (especially C_{84} and C_{60} - C_2H_5N), this correction should be made. This requires detailed knowledge of the pump and probe beam overlap in the sample. From the measured 200 μ m pump beam spot size, and the 5° angle between pump and probe beams, we estimate an overlap region of ≈ 1 mm. The correction takes into account the percentage of the pump beam photons which are absorbed in this interaction volume. For C_{84} , the observed spectra should be multiplied by approximately 1.8, and for C_{60} - C_2H_5N the factor is 2.1. Hence, for all the fullerenes observed, there are large and broadband photoinduced absorption features which provide a mechanism for broadband RSA optical limiting.

Figure 3. Intensity-dependent transmission for C_{60} (open triangles), C_{78} (closed circles), and PCBCR (open squares) at a) 575 nm, and b) 680 nm. The low fluence transmittances (corrected for reflection) for C_{60} , C_{78} , and PCBCR, respectively, are 50%, 44%, and 57% at 575 nm, and 91%, 67%, and 87% at 680 nm.

Given that all fullerenes measured satisfy the condition for optical limiting over some wavelength range, the primary practical considerations for using these materials revolve around two issues: 1) how broad and flat is the wavelength range over which these materials are effective; 2) how soluble are the materials. The two materials most promising from this standpoint are PCBCR, and C_{78} . PCBCR is approximately ten times more soluble than C_{60} in common organic solvents, with a small but finite ground-state absorption which extends past 700 nm. C_{78} , which is substantially more soluble than C_{84} , has broad (small) ground-state and (large) excited-state absorptions extending

from 600-1000 nm. In the following, we examine the predictions obtained from the excited-state transient absorption for these specific materials using intensity-dependent transmission measurements.

Figure 3 compares the intensity-dependent transmission curves for C_{60} , C_{78} , and PCBCR at 575 nm (Fig. 3(a)), and 680 nm (Fig. 3(b)). As expected for an RSA mechanism, the curves display a shoulder with a transition from a linear intensity dependence of the transmission at lower fluences, to linear dependence at higher fluence with smaller slope, corresponding to the higher excited-state absorption. At 575 nm, the low fluence linear transmission of all three samples is similar (50%, 44%, and 57% for C_{60} , C_{78} , and PCBCR, respectively). Inspection of the excited-state absorption spectra in Fig. 2 indicates that σ^* increases at this wavelength going from C_{78} to C_{60} to PCBCR. This same result is observed in the optical limiting comparison in Fig. 3(a). By contrast, at 680 nm, the linear absorption of C_{60} is very small, so that the excited-state is not sufficiently populated to activate the RSA, despite the large σ^* . For C_{78} and PCBCR, substantially better limiting effectiveness is observed, as expected. For wavelengths longer than 700 nm, the PCBCR does not absorb sufficiently, and C_{78} should be a better limiting material.

Figure 4. Open aperture Z-scan measurement of the intensity-dependent transmission at 575 nm for C_{60} (solid triangles) and PCBCR (solid squares). The solid lines are fits (see text).

Figure 4 shows the open aperture Z-scan data obtained by scanning the samples through the beam focus at a fixed intensity,¹⁶ for C_{60} and PCBCR at 575 nm. The solid lines are fits, using an expression $\alpha(I) = \alpha_0 + \beta_{eff} \cdot I$, where $\alpha(I)$ is the intensity-dependent absorption coefficient, α_0 is the low fluence absorption coefficient, and β_{eff} is the effective two-photon absorption coefficient. In these fits, the intensity as a function of beam position is determined by fitting the data obtained for a reference ZnSe window, with β_{eff} fixed at the known value (5.8 cm/GW at 532 nm).¹⁵ β_{eff} for the fullerenes is then determined by holding $I(z)$ fixed at the calibrated value. For the case of a single transition with negligible relaxation within the laser pulsewidth, β_{eff} can be related to an excited-state cross section using the expression $\beta_{eff} = \sigma_0 \sigma^* \eta \tau / 2 \hbar \omega$, where η is the concentration of molecules, τ is the laser pulsewidth, and $\hbar \omega$ is the photon energy at the wavelength of interest.¹⁵ Table 1 shows the values of β_{eff} , α_0 , σ^* , and the ratio σ^* / α_0 , (a measure of the relative optical limiting effectiveness), obtained for C_{60} , C_{78} , and PCBCR at several wavelengths. While the magnitudes deduced for σ^* are smaller than those obtained from the high-intensity transmission and excited-state absorption, the trends with wavelength are similar. For C_{60} and PCBCR, σ^* / α_0 grows larger with longer wavelength beyond 532 nm, consistent with the observation of increasing excited-state absorption, and decreasing ground-state absorption, in this range. For C_{78} , σ^* / α_0 is approximately constant, but increasing slightly, consistent with the observation that both the ground-state and excited-state absorption cross

sections decrease gradually in this range.

Table 1: Values of β_{eff} , α_0 , and σ^* obtained for C_{60} , C_{78} , and PCBCR at 561 nm, 575 nm, and 680 nm

Wavelength	Compound	β_{eff} (cm/GW)	α_0 (cm ⁻¹)	σ^* ($\times 10^{-18}$ cm ²)	σ^*/α_0 ($\times 10^{-18}$ cm ³)
561	C_{60}	9.6	3.4	0.39	0.11
575	C_{60}	18.5	3.4	0.72	0.21
680	C_{60}	1.8	0.45	0.45	1.00
561	C_{78}	1.9	4.7	0.05	0.011
575	C_{78}	3.2	4.1	0.11	0.027
680	C_{78}	1.3	2.0	0.07	0.035
561	PCBCR	14.8	3.8	0.53	0.14
575	PCBCR	21.7	2.8	1.0	0.36
680	PCBCR	16.2	0.70	2.61	3.71

Figure 5 shows a comparison of the relaxation dynamics of the observed transient photoinduced absorption in a C_{60} thin film (open squares) with that of C_{60} in toluene solution (solid circles). The data are normalized, and the entire photoinduced absorption spectrum for each material is integrated over the spectral range of the measurement. The fit to the thin film data (solid line) is a double exponential, with time constants $\tau_1 = 1.5$ ps and $\tau_2 = 20$ ps. The extremely rapid and nonlinear recombination dynamics for C_{60} thin films at high fluences has been attributed to bimolecular recombination due to exciton-exciton annihilation.^{20,21} The solution data, by contrast, show a very slow decay on this timescale; the integrated excited-state absorption is approximately constant, since the initial relaxation to the triplet state conserves excited-state oscillator strength. Hence, for ns pulses, the excited-state absorption remains large over a broad wavelength range for the duration of the pulse in solution, while the decay back to the ground-state in the solid form is much more rapid than the pulsewidth. In this case, the fact that the optical properties (energy positions and transition moments) of the solution and the solid are very similar (due to the inherently molecular nature of C_{60}) does not assure that the limiting performance will be similar also; determination of the recombination dynamics is also essential. Optical limiting measurements of thin films and doped porous glass confirmed this prediction: the optical limiting effectiveness of both was drastically reduced for ns pulses at all wavelengths measured. This phenomenon is independent of the additional triplet quenching in the presence of oxygen,³ and arises because of the proximity of adjacent fullerenes.²¹ Hence, we conclude that effective solid-state optical limiters using fullerenes must take the form of dispersed solid solutions in a host matrix.^{2,7,11}

Figure 5. Dynamics of the integrated transient absorption for C_{60} thin film (open squares) and toluene solution (solid circles). The solid line is a fit to a double exponential, with time constants $\tau_1 = 1.5$ ps and $\tau_2 = 20$ ps.

4 CONCLUSION

We have performed broadband picosecond transient absorption experiments, in conjunction with intensity-dependent transmission measurements, to compare the optical limiting performance of C_{60} with several higher fullerenes and substituted C_{60} derivatives. We find optical limiting in all of the fullerenes measured. The ratio of excited-state to ground-state absorption cross section increases in going from 532 nm to 700 nm. All of the fullerenes measured display large values of the excited-state cross section from 500-1000 nm. The limiting performance is constrained primarily by solubility and the range over which the ground-state absorption is small but finite (440-630 nm in C_{60}). Based on these considerations, monosubstituted C_{60} with a substituent chosen for maximum solubility, and C_{78} , are the most promising materials for broadband limiting from 450-1000 nm. Comparison of the optical limiting and excited-state absorption dynamics in solid forms of C_{60} (thin films and doped porous glass) shows a decreased effectiveness for limiting of ns pulses in the solid state, indicating that solid forms of C_{60} and derivatives for optical limiting must be dispersed in a host matrix.

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