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OPTICAL LIMITING MECHANISMS IN C_{60} SOLUTIONS.

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Abstract We report on optical limiting mechanisms in C_{60}/toluene solutions over a wide range of laser fluences. Nonlinear absorption in C_{60} can be modeled by reverse saturable absorption. However, our optical limiting experiments are sensitive to additional optical loss mechanisms. We observe thermally induced beam distortions, luminescence, and photo-decomposition. At high fluences many materials form plasmas and exhibit very strong optical limiting. However, C_{60}/toluene does not form a plasma even for incident energies 40 times the plasma threshold in pure toluene. At these high incident energies, 5 mJ, we do see a laser induced reaction of the solution with the Pyrex cuvette, etching of the Pyrex, and numerous organic products.

INTRODUCTION

Extensive effort has been directed toward developing a passive optical limiter for eye and sensor protection against high intensity light. Optical limiting materials must have a low limiting threshold, broad band response, excellent see through, high damage threshold, rapid response time, and high optical density. The specific requirements for a practical optical limiter are also highly dependent on the sensor to be protected as well as the level of protection required (glare, jamming, damage, cw or pulsed).

The optical limiting performance of C_{60} is competitive with current materials.[1,2] We report here on the optical limiting mechanisms in C_{60}/toluene solutions. Our research covers a wide range of incident laser fluences. Thermal effects at fluences near the optical limiting threshold are presented first. The lack of plasma formation in C_{60}/toluene solutions is next. Damage and degradation effects at high fluences conclude this report.

EXPERIMENT

Figure 1 illustrates the optical limiting and emission experiments. A 532 nm, 7 ns pulsed laser beam is spatially filtered to form an airy disk profile. After expanding the beam to 11.7 mm diameter ($1/e^2$), it is collimated before entering L1. Both L1 and L2 are f/# 1.8 Nikon camera lenses with a 50 mm focal length spaced in a confocal geometry. The effective f/# 4.3 of the system focuses the laser beam to a 7.2 μm

diameter spot centered in the C_{60}/toluene sample. For optical limiting, the incident and transmitted energies are measured for ten laser pulses at 10 Hz, and then repeated for increasing incident laser energies. Using a 100 mm focal length lens (L3), the transmitted beam is focused through a 50 μm pinhole.

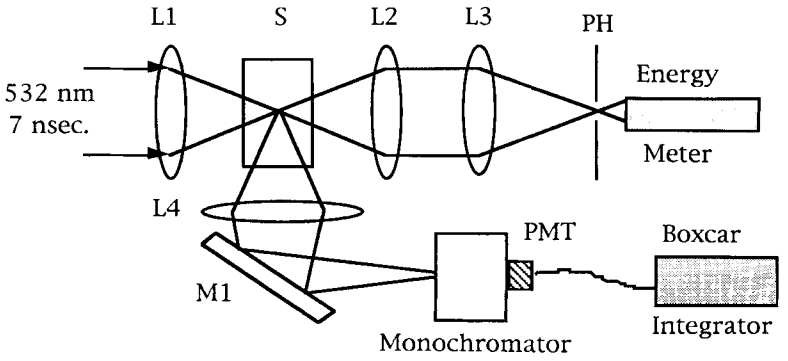

Figure 1. Optical limiting and emission experiments.

Optical limiting data for a 1 cm cuvette with 0.345 mM C_{60}/toluene are illustrated in figure 2. Only first pulse data are shown here because C_{60} limits all ten pulses equally well for the laser fluences shown. The incident laser fluence is calculated by dividing the measured incident energy by the measured beam waist area. The points labeled S and E indicate the incident laser fluences at which spatial beam profiles (S) and excited state emissions (E) were investigated.

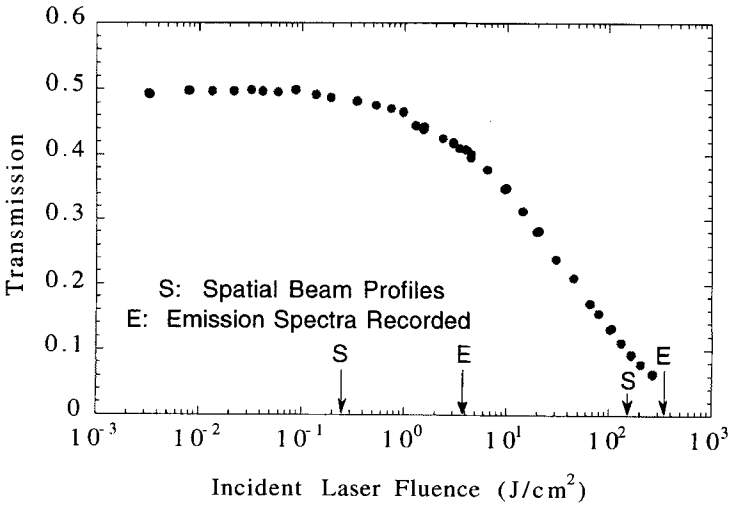

Figure 2. Optical limiting in 0.345 mM C_{60}/toluene.

THERMAL BEAM DISTORTIONS

We reported previously on our five level model of nonlinear absorption in C_{60}/toluene solutions.[3] Reverse saturable absorption accurately models nonlinear absorption data when all the transmitted light is collected and measured. However, the pinhole in the optical limiting experiment restricts the transmitted light to near axial rays. This geometry enhances the sensitivity of our measurements to optical losses from aberrations in the transmitted laser beam (figure 3).

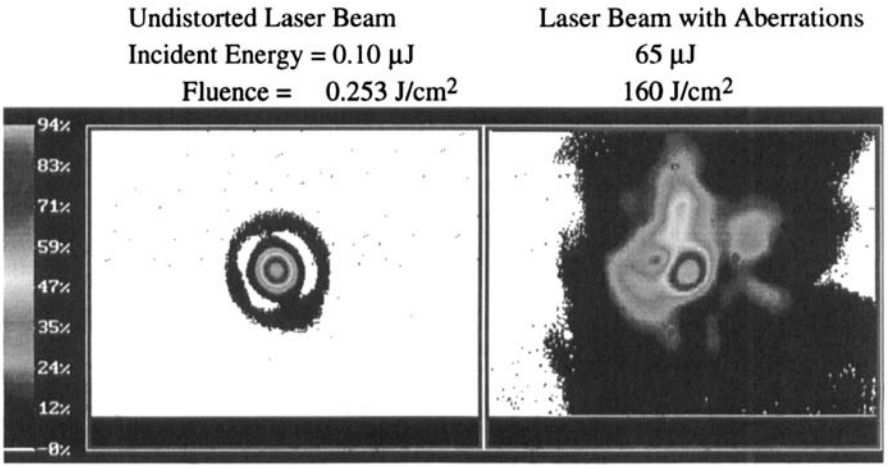

Figure 3. Single pulse, laser beam spatial profiles transmitted through a 1 cm, 0.345 mM C_{60}/toluene sample.

Single pulse, laser beam spatial profiles were captured by removing the pinhole and focusing the transmitted laser pulse onto a CCD camera. The transmitted laser beam was attenuated to avoid saturation of the CCD camera. The left spatial beam profile was captured at an incident laser fluence below the optical limiting threshold. This image represents the linearly transmitted beam without distortions. Beam distortions are observed at incident laser fluences as low as 1.4 J/cm^2. The right image was captured at an incident laser fluence above the optical limiting threshold. There is extensive aberration of the transmitted laser beam. With the pinhole inserted, 31% of this aberrated beam is blocked. Thus the optical limiting performance is enhanced by blocking off axis light rays of an aberrated beam.

The aberrated single pulse image agrees with published reports that this beam distortion is thermally induced and occurs within the 7 ns pulse time.[4] The high intensity laser beam thermally induces refractive index changes in the solution. These changes act like an imperfect thermal lens with aberrations. The rate at which these changes occur depends on density changes emanating from the beam waist at the speed of sound.[5] A sound wave in toluene traverses the beam waist, 3.6 μm radius, in 2.7 ns. This occurs within the 7 ns laser pulse time, and distorts the laser beam.

EMISSION SPECTRA AND PLASMA FORMATION

At higher fluences, we not only observe laser beam distortion but also visible emission from the focal volume. In the emission experiment, 532 nm laser radiation at 10 Hz excites C_{60} from the ground state. Relaxation from these excited states produce visible radiation. This emission is collected and focused into a Digikrom 240 monochromator. A Corning GS 3-67 filter is used to attenuate scattered 532 nm radiation and prevent saturation of the Hamamatzu, R928 PMT. The monochromator is slowly scanned over the visible spectrum while the laser is held at a constant fluence.

Figure 4 illustrates spectra of both pure toluene and C_{60}/toluene at incident laser energies of 0.015 mJ and 0.14 mJ (37 J/cm^2 and 340 J/cm^2). Ten emission lines between 547 and 635 nm are observed in both toluene and C_{60} solutions. These lines correlate with published Raman spectra of toluene. In C_{60} solutions, an additional broad feature is observed with peaks at 692 nm and 732 nm. These features agree with published fluorescence spectra of C_{60}.[6]

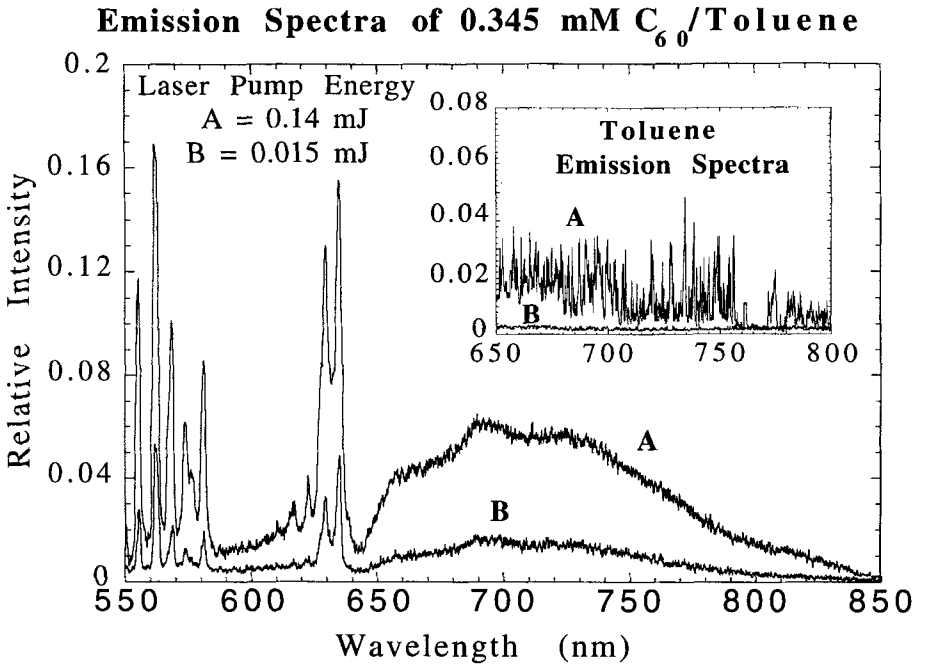

Figure 4. Emission spectra at two pump energies.

There is an interesting connection between these spectra and optical limiting mechanisms. In our optical set up, we observe plasma formation in pure toluene at 0.12 mJ (300 J/cm^2) and up. The plasma is accompanied by an audible pinging and a visible flash of light. In addition, we see evidence of a plasma in the emission spectra of toluene. The spectra of toluene taken below plasma threshold is a smooth flat line between 650 and 800 nm. While the spectra above threshold consists of a continuum of

spectral features consistent with plasma formation. From an optical limiting perspective, the plasma in toluene strongly attenuates the laser beam.

The point of interest is that we do not see any evidence of plasma formation in C_{60}/toluene. None of the spectral features observed in toluene plasmas occur in the C_{60}/toluene spectra. We have also increased the incident laser energy to 5 mJ or 40 times the plasma threshold of toluene. These high energy spectra of C_{60}/toluene show no signs of plasma formation. We only observe the same spectral features as at low energies, but with increased amplitude. This lack of plasma formation in C_{60}/toluene is unusual. At these high energies the C_{60}/toluene solution transmits more laser radiation than the pure toluene which forms a plasma.

We currently do not fully understand this behavior. But a plausible explanation is that the energy density within the C_{60}/toluene solution never reaches the plasma threshold, even for 5 mJ of incident energy. Two optical limiting mechanisms may prevent the plasma formation. Reverse saturable absorption reduces the energy, and beam distortions defocus the energy. CCD camera images at 5 mJ show a highly diffused transmitted laser beam. The diameter of the laser beam waist at 5 mJ is much larger than the 7.2 μm diameter measured at low incident energies. Due to this beam spreading, the laser fluence inside the C_{60}/toluene solution is much less than when the laser beam is tightly focused in pure toluene.

How reverse saturable absorption inhibits plasma formation is rather subtle. We have observed that the location of the visible emission from C_{60}/toluene moves with increasing energies. For the spectra in figure 4, the emission emanates from near the laser beam waist. For increasing energies, the emission source moves toward the front surface of the cuvette. At the highest energy, 5 mJ, the emission is occurring near the glass/liquid interface. For the tight focus geometry (f/# 4.3) the beam diameter is about 1 mm at the glass/liquid interface. When the incident laser energy is 5 mJ, the energy density is about 1 J/cm^2 near the glass/liquid interface. This energy density is sufficient to produce both reverse saturable absorption and thermal beam distortions. This is consistent with our observation that at this high energy the visible emission occurs near the glass/liquid interface. Thus, both reverse saturable absorption and thermal beam distortions reduce the energy density within the C_{60}/toluene solution and prevent plasma formation.

PHOTO-DECOMPOSITION

At 5 mJ incident laser energy, visible emission occurs quite close to the glass/liquid interface. In a separate experiment, the C_{60} solution was exposed for 1.5 hours at 5 mJ laser energy at 10 Hz in the tight focus geometry of figure 1. After this prolonged laser exposure, the glass surface was damaged and a black precipitate formed.

We designed a different optical layout to study this damage and photo-decomposition. In the optical limiting experiment, the tight focus geometry made it difficult to determine the beam diameter at the glass/liquid interface. In order to know the laser fluence at the glass/liquid interface precisely, we used a collimated beam test geometry. A long focal length lens (f=2m) was used to reduce and collimate the 532

nm, 7 ns beam to a 0.840 mm diameter throughout the sample. A nitrogen purged, 2.371 mM C_{60}/toluene solution was loaded in a 1 mm path length Pyrex cuvette. For this optical geometry and solution concentration, the optical limiting threshold occurred at 0.17 mJ (30 mJ/cm^2) of incident laser energy. At 0.55 mJ (100 mJ/cm^2) incident laser energy no changes in the sample occurred, even after 3 hours at 10 Hz of laser exposure. However, at 5.5 mJ (1 J/cm^2) a visible emission and an audible pinging sound was apparent from the glass/liquid interface. The visible emission and pinging increased over the next several minutes. After 9 minutes, significant black precipitate formed and the experiment was stopped.

In addition to the precipitate, we observed a black damage spot on the cuvette at the point of laser entry at the glass/liquid interface. Also, the remaining solution had changed color from purple to pink. Scanning electron microscope images of the damage spot showed an etching pattern on the glass.[7] Proton NMR, with a silicon probe, of the pink solution revealed a Si-CH_x peak. HPLC also showed $C_{60}O$ in the pink solution. This indicates a laser induced reaction between the Pyrex and the C_{60}/toluene solution. GCMS of the solution also revealed numerous organic products from this reaction. When 1 J/cm^2 is incident at the glass/liquid interface, the glass is etched, a reaction with the solution occurs, and numerous organic products are formed.

SUMMARY AND CONCLUSIONS

Our research of optical limiting in C_{60}/toluene solutions has revealed a variety of mechanisms operating over a large range of laser fluences. Thermal beam distortions enhance optical limiting if apertures are used to block off axis light. Visible emission spectra confirmed our observations that C_{60}/toluene does not form a plasma even at incident laser energies 40 times the plasma threshold in pure toluene. A high incident laser energy of 5 mJ and a fluence of 1 J/cm^2 at the glass/liquid interface produces several damaging effects. The Pyrex cuvette reacts with the C_{60}/toluene, the cuvette is etched, and numerous organic products are formed.

REFERENCES

1. L.W. Tutt and A. Kost, Nature (London), 356, 225 (1992).
2. F. Henari, J. Callaghan, H. Stiel, W. Blau, and D. J. Cardin, Chem. Phys. Lett., 199, 144 (1992).
3. D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz, and T. Pottenger, Opt. Lett., 18, 11 (1993).
4. B. L. Justus, Z. H. Kafafi, and A. L. Huston, Opt. Lett., 18, 19 (1993).
5. J. N. Hayes, Appl. Opt., 11, 455 (1972).
6. D. Kim and M. Lee, J. Am. Chem. Soc., 114 (1992).
7. D. M. Brandelik, M. C. Brant, D. G. McLean, R. L. Sutherland, H. Jiana, and M. S. Meier, MRS Symposium, Abstract G3.29 (Fall,1993)