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TITLE

OPTICAL LIMITING WITH C60 AND OTHER FULLERENES

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Optical limiting with C_{60} and other fullerenes

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In view of a possible application in optical limiting devices for protection against laser radiation, at the Defence Research Establishment Valcartier we have studied the nonlinear transmission properties of fullerenes. The study involved C_{60}, C_{70}, C_{76}, C_{84}, several derivatives of C_{60}, and a variety of solvents. The nonlinear measurements were made with 7-ns pulses at 532 nm from a Nd:YAG laser. For optical limiting applications, solutions of C_{60} yielded better results than the other fullerenes, with a solution of C_{60} in chlorobenzene being marginally the best. © 1997 Optical Society of America

Key words: Optical limiting, nonlinear optics, fullerenes, Nd:YAG.

1. Introduction

From the list of materials that have shown potential as optical limiters,[1–3] a liquid suspension of fine carbon particles (CBS) and a liquid solution of C_{60} have demonstrated good performance. In particular, studies of different fullerenes in suitable solvents have been undertaken[4–8] to find the best combination. The research that we present here deals precisely with the measurement of nonlinear transmission of solutions of C_{60} and other fullerenes with pulsed laser radiation at a 532-nm wavelength. Measurements were made with C_{60} in different solvents, with different fullerenes (C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}) in chlorobenzene, and with derivatives of C_{60} (grafts) in appropriate solvents.

One parameter used to compare optical limiters is the clamping level. The clamping level of an optical limiter is defined as the output energy level in a small solid angle when the device attenuates strongly the input energy. The small solid angle used is comparable to the laser beam divergence after the optical system when there is no nonlinear attenuation. The clamped output energy is quite independent of input energy. In fact, in this regime, the nonlinear transmission is inversely proportional to the input energy. Figure 1 shows the clamping levels of CBS [Defence Research Establishment Valcartier (DREV's recipe CBS-200)] and C_{60} in toluene relative to an arbitrary level as a function of the linear transmission at the laser wavelength. The measurement setup used and the additional data points in Fig. 1 are described below. The question remains if there exists a fullerene, a modified fullerene, or a combination fullerene solvent that would present a clamping level below the value obtained with CBS.

2. Materials Studied

Carbon 60 was procured from SES Research Inc. (Houston, Texas) and PyroGenesis Inc. (Montréal, Québec). PyroGenesis Inc. also provided C_{70}, C_{76}, C_{78}, and C_{84} extracted from the soot produced in their plasma reactor. An external contractor did the extraction of C_{76}, C_{78}, and C_{84}. Finally, the C_{60} derivatives were procured through PyroGenesis from Materials and Electrochemical Research Corporation (Tucson, Arizona). A general review of the chemistry of C_{60} derivatives is given in Refs. 9 and 10. More specific information on some of the derivatives used in this research appears in Refs. 11 and 12. The purity was 99.9% for C_{60} and 90% for C_{70}. The purity of the other fullerenes used is unknown.

The linear and nonlinear properties of all materials were studied in standard spectrometer cells made from fused silica and having a 2-mm path length. By the proper material/solvent ratio, the cells' transmission at 532 nm was adjusted to near 0.4 or, if not possible because of poor solubility, to the lowest value possible. Table 1 summarizes the observations on the cells. Apart from hydrogenated mixed fullerenes that precipitated slowly, the other derivatives were stable. A solution of C_{60} in tetra-hydronaphthalene (THN) is magenta whereas all the stable derivatives remained yellow or yellow-orange. Figure 2 shows the structures of three of the C_{60} derivatives.

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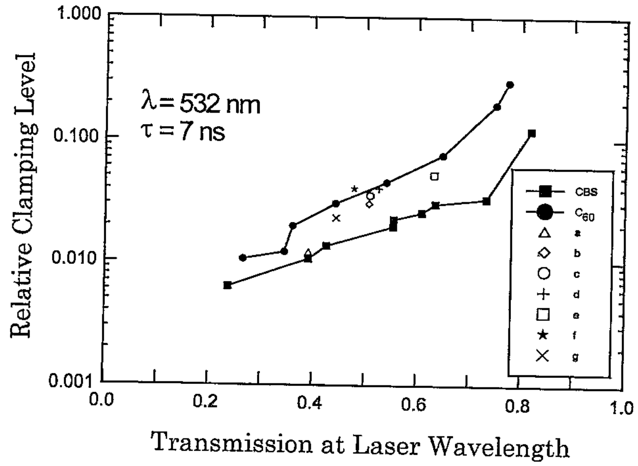

Fig. 1. Comparison of the clamping levels of CBS and C_{60}; the curve labeled C_{60} was with toluene used as the solvent. The other points are for C_{60} in the solvents: a, chlorobenzene; b, toluene; c, 1,2,4,trichlorobenzene; d, cumene; e, tetrachloroethylene; f, 1,2,3,5,tetramethylbenzene; g, 1,methylnaphthalene.

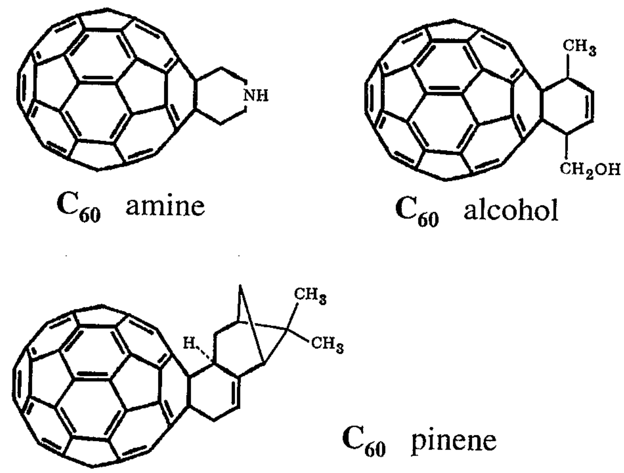

Fig. 2. Structures and commercial names provided by MER Corporation for the C_{60} derivatives.

As we show below, there seems to be no direct relationship between the color appearance and the nonlinear performance. However, magenta solutions usually perform more favorably.

3. Measurement System

We measured the nonlinear transmission of the prepared cells using the arrangement shown in Fig. 3. The output beam of a *Q*-switched doubled-Nd:YAG laser, emitting 7-ns pulses at 532 nm, passes through a series of variable attenuators (half-wave plates and polarizing prisms) and a Galilean beam expander before being apertured and focused by lens L1 into the sample cell. The focused spot then has a shape similar to an Airy pattern. The arrangement L1–L2 makes an $f/5$ afocal system with an output pupil diameter of 8 mm. Lens L3 has a 1-m focal length and images the laser spot in the cell onto the iris with a linear magnification of 25×. The angular diameter of the iris (1.5 mrad) equals approximately ten times the angular diameter of the central lobe of the diffraction pattern. The ratio $E_t/(T_{\text{lin}}E_i)$ was taken as a basis to compare the nonlinear transmission of the cells and is referred to here as the nonlinear transmission. T_{lin} is the linear transmission at 532 nm in Table 1, E_i is the incident energy, and E_t is the energy transmitted through the iris. We used the same arrangement without the cell to measure the input energy density at the focal plane of L1 by using a 0.1-mm-diameter iris and taking into account the magnification that was due to L2–L3. With this iris, the energy density measured is slightly less than the peak input energy density as it is an average over approximately half the central lobe of the diffracted

Table 1. Observations of the Cells

Material	Solvent	$T_{532\ \text{nm}}$	Color (Laboratory Illumination)
C_{60}	Chlorobenzene	0.39	Magenta
	Toluene	0.51	Magenta
	1,2,4,Trichlorobenzene	0.51	Magenta
	Cumene	0.53	Pink
	Tetrachloroethylene	0.63	Light orange
	1,2,3,5,Tetramethylbenzene	0.48	Orange
	1,methylnaphthalene	0.44	Dark orange
C_{70}	Chlorobenzene	0.37	Orange-yellow
C_{76}	Chlorobenzene	0.39	Orange
C_{78}	Chlorobenzene	0.40	Orange
C_{84}	Chlorobenzene	0.39	Orange
C_{60} OH_{22-26} fullerol	Water	0.42	Orange-yellow
Hydrogenated mixed fullerenes	1,2,3,4,Tetrahydronaphthalene (THN)	0.87	Pale yellow (precipitates)
C_{60} amine[a]	1,2,3,4,THN	0.60	Light yellow
C_{60} alcohol	1,2,3,4,THN	0.50	Yellow-orange
C_{60} pinene[b]	1,2,3,4,THN	0.44	Orange

[a]Ref. 11.
[b]Ref. 12.

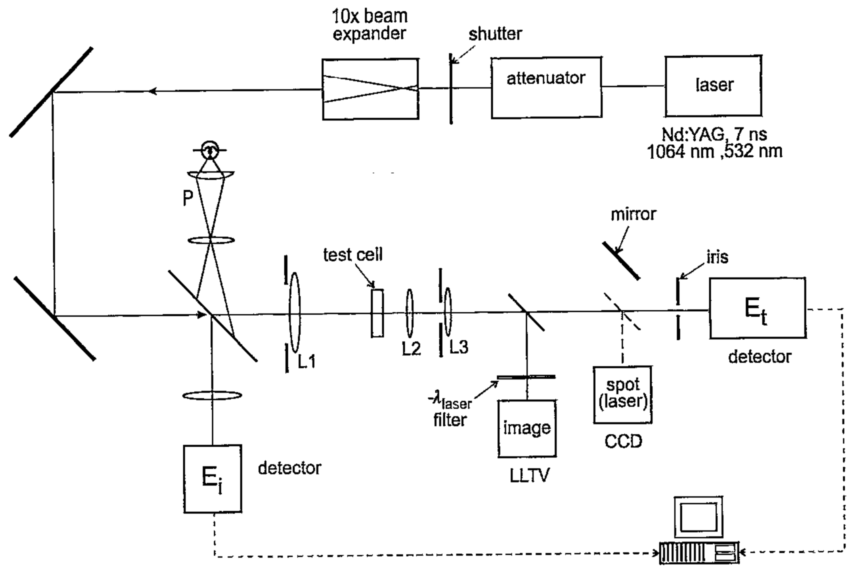

Fig. 3. Laser measurement system.

spot. Of course, with a cell present and acting as a limiter, this energy density cannot be attained at the focal plane.

The projector P and the low-light-level TV (LLTV) camera enable the observation of the cell during laser irradiation (a notch filter at 532 nm being in front of the LLTV camera) to verify for any possible degradation, bubbles in the liquid, or damage to the input window. A CCD laser beam analyzer also permits the observation of the laser spot at the focal plane of L3 (the analysis plane). Typically, the lens arrangement produces a focused spot diameter in the analysis plane that is within 1.5 times the calculated diffraction limit.

All nonlinear transmission measurements on the cells were taken in single-pulse mode. If irradiation-induced damage occurred or was suspected to occur in the cell, the cell was laterally displaced to change the irradiation site.

4. Results

Figure 4 shows the effect of various solvents on the nonlinear transmission of cells filled with a solution of C_{60}. The solution in chlorobenzene gives a slightly lower transmission and tetrachloroethylene gives the highest transmission for input energy as high as 100 J/cm^2, but it becomes similar to the other solvents above that energy. For all these solvents, the threshold for the nonlinear response is around 0.1 J/cm^2. That value agrees with that reported in Refs. 5, 8, and 13, but it is not clear if the definition of energy density is always consistent.

The solvents employed here were selected partly from Ref. 14 and partly from private communications. Some of the good solvents from Ref. 14 were not used because their freezing point was too high for a practical limiter.

It appears clearly from Fig. 4 that solvent effects are small (as shown in Ref. 5), but since the solution in chlorobenzene gave slightly better results and

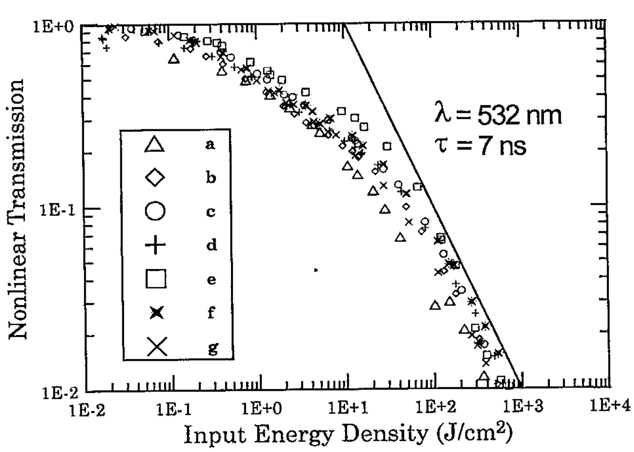

Fig. 4. Limiting by C_{60} in various solvents: a, chlorobenzene; b, toluene; c, 1,2,4,trichlorobenzene; d, cumene; e, tetrachloroethylene; f, 1,2,3,5,tetramethylbenzene; g, 1,methylnaphthalene.

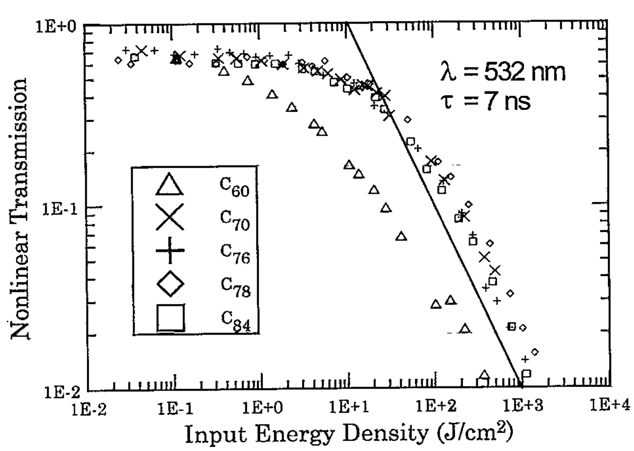

Fig. 5. Limiting by various fullerenes in chlorobenzene.

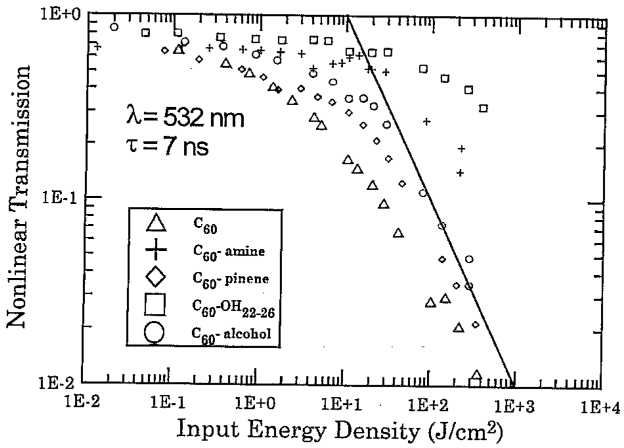

Fig. 6. Limiting by C_{60} derivatives.

chlorobenzene is a relatively good solvent for many fullerenes, we continued our investigation with this solvent.

The solid line in Fig. 4 has a slope of −1. It demonstrates that the output energy in the analysis aperture is really clamped to a constant value for input energy density above 20 J/cm^2 (in chlorobenzene). Above 100 J/cm^2, we observed bubble and carbon particle formation. At this energy level, limiting seems to arise from the effects of the liquid being heated by the energy absorbed by the C_{60} molecules (see Refs. 15 and 16 for similar comments).

Figure 1 shows these clamping levels relative to an arbitrary reference as a function of linear transmission at the laser wavelength. The seven cells studied are compared with eight toluene solutions of C_{60} in different concentrations studied previously at DREV. The general behavior as a function of transmission is the same.

The nonlinear transmission of various fullerenes is shown in Fig. 5. It appears clearly that C_{60} is a much better limiter at 532 nm than the other fullerenes. This is consistent with the results presented in Ref. 15 in which the solvent was tetrahydronaphthalene for C_{76}, C_{78}, and C_{84} and in Refs. 6 and 13 for C_{70} in toluene. The threshold for C_{70}, C_{76}, C_{78}, and C_{84} occurs around 2 J/cm^2, and they clamp at an input energy density above 100 J/cm^2.

Finally, in Fig. 6 we present the nonlinear transmission of the C_{60} derivatives. Two of them offer a performance approaching that of C_{60}: C_{60} pinene and C_{60} alcohol. This may be an indication that an unknown or untried derivative could possibly surpass the performance of C_{60}.

5. Conclusion

From this study and similar ones, CBS and C_{60} are still our choices for use as optical limiters. A survey of solvents for C_{60} of different fullerenes and of derivatives of C_{60} has not led to a material better than C_{60} in chlorobenzene. The measurements were taken at 532 nm with 7-ns pulses.

From the results shown in Figs. 1, 4, 5, and 6, it appears that CBS still surpasses fullerenes for single-pulse limiting at 532 nm in cells with comparable linear transmission. Some possibility exists for improved nonlinear properties with C_{60} derivatives but further investigation is hampered by the fact that many of these materials are not available in a large enough quantity commercially and that DREV does not have the capability to synthesize them.

Similar measurements at other wavelengths and other pulse lengths[5] have shown that CBS is also better than C_{60} in the red (for comparable linear transmission in the center of the visible spectrum) and that C_{60} seems to offer a performance better than CBS against pulses a few microseconds long in the green.

Although CBS showed the best limiting characteristics, it is well known that CBS performance degrades at high laser repetition rates, whereas the C_{60} solution still offers good limiting. DREV is presently experimenting with a carbon suspension that offers reasonable performance as high as 15 pulses/s.

The color of C_{60} cells changes from magenta to orange when exposed to daylight for extended periods (e.g., several days), even when in a sealed cell. In fact, the solution remains magenta (albeit clearer), but a yellow film deposits on the window. This removal of C_{60} from the solution increases its linear transmission and the value of the clamping level. With a UV blocker such as polycarbonate, the time required for degradation can be extended. In reduced illumination conditions, as would be found in an optical sight not turned continuously toward the Sun, the time required for degradation can be very long (perhaps years). At high laser energy density, carbon particles are also created in the cell, but this is of little consequence, as a limiting device is not intended for continuous operation. Degradation can also occur in a CBS cell under sustained exposure to intense light. However, the times involved were found to be several times longer than for C_{60}.

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