

Brief Reports

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Time-resolved optical Kerr response of C_{84} in CS_2

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The large optical response of C_{84} is demonstrated by means of the optical Kerr effect. Using 150-fs laser pulses with a wavelength of 647 nm, we got a transient response that was primarily pulse limited. By comparing nonlinear responses with that of the CS_2 reference, we acquired large second-order hyperpolarizability for C_{84} and C_{70} with γ_{1111} of 5.2×10^{-31} and 4.7×10^{-31} esu, respectively. The different optical responses of C_{84} and C_{70} were interpreted using a pure- π -conjugated-electrons model and the influence of ground-state structures of C_{84} isomers. Our results further confirmed the postulated $D_{2d}(22)$ and $D_{2d}(23)$ structures as the ground-state structure of C_{84} .

INTRODUCTION

Organic materials possessing unusually large third-order nonlinear optical susceptibility have long been the focus of physicists^{1,2} and chemists³ over the past two decades for their potential applications in all-optical devices.⁴ The recent exciting discovery of fullerenes⁵ has attracted much attention. Like other organic materials, fullerenes have highly delocalized π -conjugated electrons, which is the main origin of their large nonlinear optical responses.⁶ After the breakthrough in the synthesis and the separation of the two most abundant fullerenes C_{60} and C_{70} ,⁷ a lot of systematic researches concerning their third-order optical nonlinearities were performed in different time scales, spanning from nanosecond⁸ to picosecond⁹⁻¹² to femtosecond¹³⁻¹⁵ with various experimental techniques.

However, owing to the infinitesimal quantity produced in graphite discharge and the difficulty in isolating and purification, C_{84} is still less studied than C_{60} and C_{70} . C_{84} is of particular attraction to us because of delocalization of π -conjugated electrons, which are less abundant in C_{60} and C_{70} and are considered to be the main source of large nonlinear optical responses. In this paper, we report the initial studies of optical nonlinearity of C_{84} in CS_2 , using the time-resolved optical Kerr effect (OKE). By using a femtosecond laser, we are able to probe pure electronic responses in fullerenes. Our observations show the large instantaneous nonlinear optical response of C_{84} . A comparison of second-order hyperpolarizability of C_{84} with that of C_{70} and C_{60} was given and the reason for their distinction was interpreted. C_{84} was dissolved in CS_2 solvent to avoid the uncertainties appearing in toluene and benzene solution.

EXPERIMENT

C_{84} was obtained from fullerite soot. The separation and purification were carried out by means of liquid phase chromatography combined with a recrystallization technique. NMR spectra showed a purity greater than 85% for C_{84} with no C_{60} or C_{70} left; the main impurities include C_{78} , C_{82} , C_{86} , and C_{90} .

The OKE experimental arrangement is shown in Fig. 1. The laser source was an ultrafast dye laser (Coherent, SATORI Model 774) synchronously pumped by a cw mode-locked Nd:YAG laser (Coherent, Antares 76-S) operating at 76 MHz. The average power of the output was about 200 MW with a pulse duration of about 150 fs and the working wavelength was 647 nm. A variable atten-

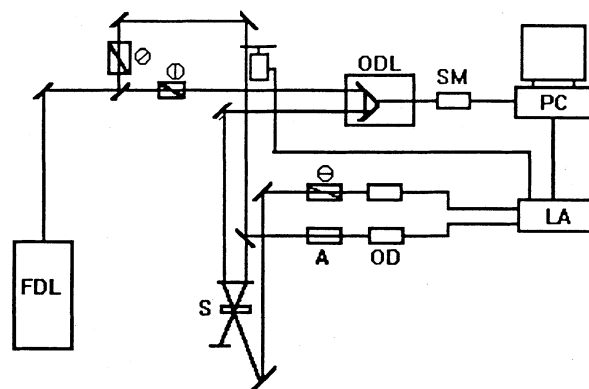


FIG. 1. The femtosecond optical Kerr effect experiment apparatus arrangement: FDL, femtosecond dye laser; S, sample; A, optical attenuator; OD, optical detector; LA, lock-in amplifier; PC, personal computer; SM, step motor; ODL, optical delay line.

uator was placed in the beam path to ensure the measurements of cubic dependence of the OKE signal versus input laser. The pump and probe beams polarized 45° to each other were split from the laser source with a pump-probe ratio of 7:1 and then focused tightly on the sample with the common spot size of about $20 \mu\text{m}$ via a convex lens ($f=10 \text{ cm}$). The time delay of the probe beam relative to the pump beam was fulfilled by a submicrometer-resolved slide linked with a computer-activated step motor. Changing the time delay, the transmitted signal was sent through a polarizer with polarization perpendicular to that of the probe beam and then detected by a photomultiplier connected with a lock-in amplifier and stored in computer. The zero delay time was determined by the maximum of the instantaneous optical Kerr response signal exhibited by a standard reference sample, which in our case is the CS_2 solution.

The $\chi^{(3)}$ of C_{84} was deduced from the formula¹⁶

$$\chi_s^{(3)} = \left(\frac{I_s}{I_r}\right)^{\frac{1}{2}} \frac{L_r}{L_s} \left(\frac{I_{r,\text{pump}}}{I_{s,\text{pump}}}\right)^{\frac{3}{2}} \left(\frac{n_s}{n_r}\right)^2 \times \frac{\alpha_s L_s}{e^{-\frac{\alpha_s L_s}{2}} (1 - e^{-\alpha_s L_s})} \chi_r^{(3)},$$

where subscripts s and r denote samples and CS_2 , respectively, α is the linear absorption coefficient, n is the refractive index, and L is the interaction length. Following the standard procedure, the OKE intensity for the C_{84} solution is measured relative to that for CS_2 under identical experimental conditions. By comparing the measured intensities from a reference CS_2 with samples of the same concentration, we retrieved the $\chi^{(3)}$ value of fullerenes in the CS_2 solution.

RESULTS AND DISCUSSIONS

According to the studies of the optical nonlinearities of C_{60} and C_{70} in toluene¹⁰ and benzene,¹¹ the contribution from the solvent cannot be ignored. Recent research by Liu *et al.*¹² showed that the anomalous periodic laser induced phonon signal appeared from fullerenes in toluene solution. Both of these phenomena made the $\chi^{(3)}$ measured in toluene and benzene untenable. Here we tried to adopt CS_2 as a solvent to avoid the uncertainties arising from the toluene solution.

In Fig. 2 we show transient responses of C_{84} and C_{70} in the same molar concentration. In molecular systems, the optical nonlinearity is often normalized to one molecule, which yields second-order hyperpolarizability following the relation¹⁷ $\chi^{(3)} = NL^4\gamma_{1111}$, in which L is the local field correction factor and N is the number density. By comparing the magnitude of the OKE signal from the samples and the reference (the value of $\chi_{1111}^{(3)}$ for CS_2 is¹⁸ 1×10^{-13} esu), we derive γ_{1111} for C_{84} and C_{70} to be 5.2×10^{-31} esu and 4.7×10^{-31} esu, respectively. We also obtained $\gamma_{1111} = 1.6 \times 10^{-31}$ esu for C_{60} , which is approximately one-third that of C_{70} . Our results for C_{60} and C_{70} are compatible with previous studies by Gong *et al.*¹⁴ Additionally, we could estimate the values of $\chi^{(3)}$ for the solid compounds of C_{84} and C_{70} , assuming that their

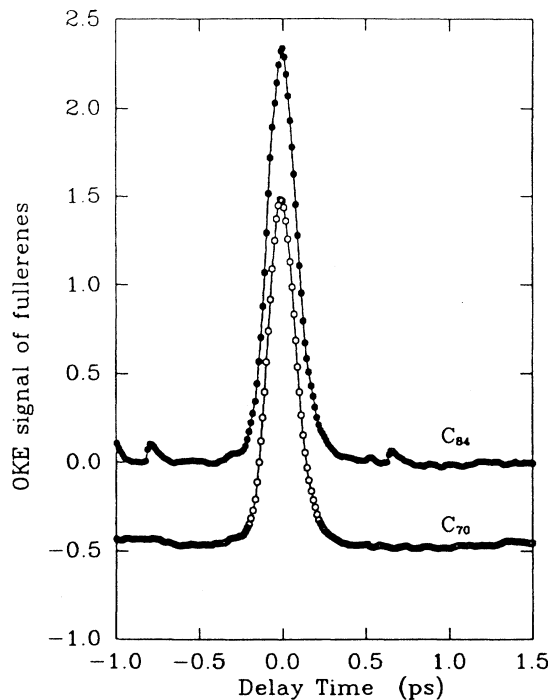


FIG. 2. Time-resolved transient optical Kerr signal of C_{84} (1.24 mM) and C_{70} (1.24 mM) in CS_2 at 647 nm.

index of refraction is 2. We obtain the values 8.0×10^{-9} esu and 8.7×10^{-9} esu for C_{84} and C_{70} , respectively. The OKE signal profile of C_{84} is similar to the original sech^2 line shape directly from the laser system, which indicates a primarily pulse width limited response. We did not observe the long time component observed by Rosker *et al.*; the reason might be attributed to the strong wavelength dependence of the long-lived component.¹³

It is commonly accepted that the large and fast optical response originates from transient motion of the π -conjugated-electron distribution occurring upon the excitation. In fullerenes, there are more polarized and delocalized π electron clouds over the spherical-like surface in C_{84} than in C_{70} , which is the main reason for C_{84} 's larger γ_{1111} . But, in contrast to the γ_{1111} increment of C_{70} to C_{60} , the small accretion of the optical Kerr response of C_{84} in comparison to C_{70} seems to be a puzzle unless appealing to the following reasons.

To further explore the origin of the unexpected discrepancy between hyperpolarizabilities of C_{84} and C_{70} , the influence of their symmetries should be considered. Although the ultimate structures of C_{84} have not been determined definitely due to the existence of 24 topologically distinct isomers,¹⁹ we prefer to assume a hypothesis based on the theoretical research by Wang *et al.*²⁰ and a comparison between experiments and calculations by Schneider *et al.*²¹ Various calculation techniques including tight-binding molecular dynamics,²² the first-principles local-density-functional method,²³ and the all-electron local-density-functional method²⁰ had predicted that $D_2(22)$ and $D_{2d}(23)$ with a ratio of 2:1 are the most energetically favorable structures.

The all-electron local-density-functional method of

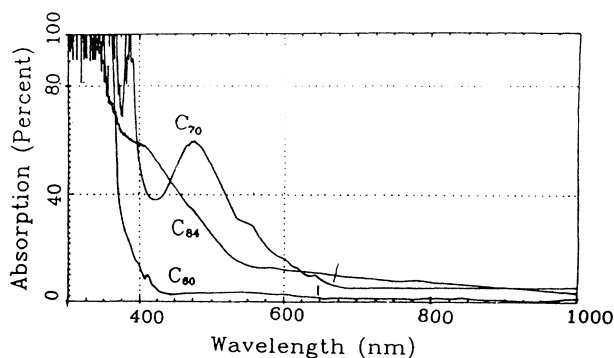


FIG. 3. Visible and infrared absorption spectra of the fullerenes in CS_2 solution. The vertical bar indicates excitation wavelength.

fers the lower binding energies and higher highest occupied and lowest unoccupied molecular orbital gaps of $D_2(22)$ and $D_{2d}(23)$ than those of the other three D_2 [$D_2(21)$, $D_2(5)$, and $D_2(1)$] isomers, which is consistent with the results of the ^{13}C NMR study^{24,25} of these isomers. It is beneficial to study the dimension parameters of four D_2 isomers and $D_{2d}(23)$ provided by Wang *et al.* (see Table I and Fig. 1. in Ref. 20) in detail.

The comparison between the quasispherical structure of the two most probable C_{84} isomers [$D_2(22)$ and $D_{2d}(23)$] with the ellipsoidal structure characteristic of C_{70} (D_{5h}) was illuminating. The ellipsoid configuration of C_{70} makes it more prone to polarization than C_{84} and may be one of the major reasons for the small optical response distinction between C_{84} and C_{70} . Conversely, our measurements can be used as additional evidence for the postulated $D_2(22)$ and $D_{2d}(23)$ isomers as the ground-state structures of C_{84} instead of $D_2(5)$,²⁶ in view of the geometrical similarity between the other three D_2 isomers with C_{70} .

To get a full understanding of the differences between C_{84} and C_{70} , a comparison between their absorption spectra as well as that of C_{60} , which is illustrated in Fig. 3, is indispensable. Because the excitation wavelength was near their significant absorption, the optical Kerr responses of C_{84} and C_{70} , which are larger than that of C_{60} , could be partly accredited to various degrees of their resonant enhancement associated with their individual energy gaps.

In addition, we measured the OKE signal versus excitation laser intensity. At low laser intensity, a cubic dependence is observed, while at high laser intensity the OKE signal starts to saturate, as shown in Fig. 4.

We also compared the nonlinear optical responses for C_{70} and C_{60} from different groups. Our values strengthened former studies by Gong *et al.* in the femtosecond domain.

Before concluding this section, we would like to bring to the readers' attention that to get a comprehensive understanding of the origins of optical responses from fullerenes, the consideration of only ground-state characteristics is insufficient. A more accurate analysis should account for electron behaviors of the excited state of fullerenes, the symmetries of fullerenes will be lowered

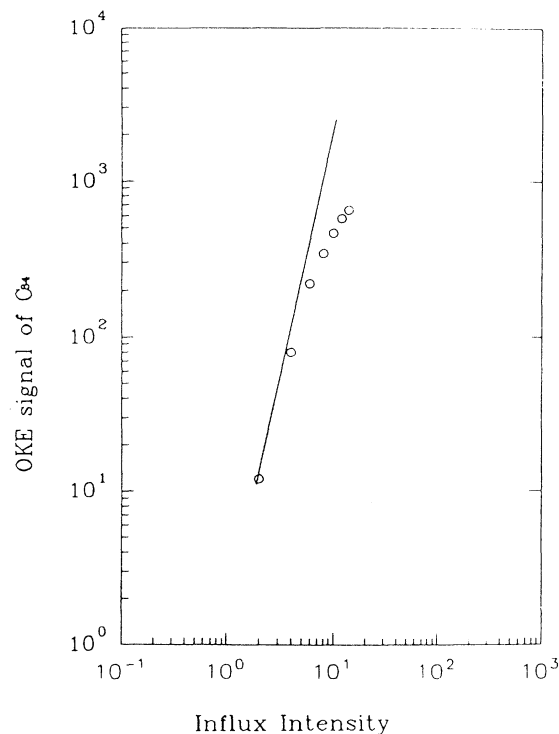


FIG. 4. Intensity dependence of the OKE signal of C_{84} in CS_2 at 647 nm. The straight line is fitted with a slope of 3.

and π electrons can itinerate more freely over the spherical surface. Our more penetrating investigations will be presented elsewhere. It is worth mentioning that the direct introduction of a one-dimensional box model to the three-dimensional spherical shell is irrational.²⁷

SUMMARY

We employed the time-resolved optical Kerr response to investigate the third-order nonlinearity of C_{84} in comparison with C_{70} ; an indistinctive increase of second-order hyperpolarizability was observed. Apart from purely electronic contributions, we take the influence of geometrical structures into consideration. The increase of second-order hyperpolarizability will be the trade-off between the number of π -conjugated electrons and the geometrical configuration; the $\chi^{(3)}$ enhancement will play an important role in the case of the excitation wavelength adjacent to the energy gap. This preliminary study demonstrates that C_{84} is a nonlinear optical material with an attractive second-order hyperpolarizability deserving further investigation.

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