

Third-Order Nonlinear Optical Properties of C₆₀ CT Complexes with Aromatic Amines

Masao Ichida,* Takamitsu Sohda, and Arao Nakamura

*Center for Integrated Research in Science and Engineering, and Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464-8603 Japan**Received: March 13, 2000*

We have investigated third-order nonlinear optical properties of charge-transfer (CT) complexes of C₆₀ with various aromatic amines with different ionization potentials. The third-order nonlinear optical susceptibility $|\chi^{(3)}|$ measured by degenerate four-wave mixing shows a resonant enhancement at the absorption band due to the CT transition. We have found that the second hyperpolarizability γ of CT complexes increases with an increase of the oscillator strength, which depends on the ionization potential. The highest hyperpolarizability among CT complexes studied here is 5.2×10^{-28} esu for C₆₀/aniline CT complex.

Introduction

Since the discovery and establishment of the bulk preparation of fullerenes, in particular C₆₀, a great deal of experimental and theoretical work has been done. From a viewpoint of nonlinear optics in clusters, a fullerene is a fascinating molecule because it is a nanometer-sized cluster and has a large number of conjugated double bonds. These characteristics lead us to expect large nonlinear polarizabilities. Many works of nonlinear optical properties in fullerenes have been both experimentally and theoretically done.^{1–8} Although the second harmonic generation is forbidden for C₆₀ and C₇₀ due to their centrosymmetric structures, their center of symmetry is broken by forming charge-transfer (CT) complexes with appropriate donors, and a second harmonic may be generated.^{9–11} The charge separation in the CT complex may also lead to enhancement of third-order nonlinearity because of its large dipole moment. A C₆₀ molecule as an electron acceptor forms a CT complex with various aromatic amines, and optical and electronic properties of C₆₀ CT complexes have been studied by several groups.^{12–16} In a previous paper, we have reported an increase in oscillator strength of CT transition with increasing ionization potential of amines.¹⁶

In this paper, we studied third-order nonlinear optical properties of CT complexes of C₆₀ with various aromatic amines by using a degenerate four-wave mixing technique. We obtained second hyperpolarizabilities γ as a function of ionization potential. The highest γ value among the CT complexes studied here is $\sim 5.2 \times 10^{-28}$ esu. The large nonlinearity results from the oscillator strength dependence on the ionization potential and the permanent dipole in the ground and excited states due to complexation.

Experimental Section

Pure C₆₀ (>99.9%) powders and commercially purchased amines that were purified by distillation were used for all measurements. We prepared C₆₀ CT complexes with different amines: aniline (ANI), *o*-toluidine (*o*-TOL), *N,N*-dimethylaniline (DMA), and *N,N*-diethylaniline (DEA). The ionization potentials of isolated ANI, *o*-TOL, DMA, and DEA are 7.72, 7.44, 7.12, and 6.95 eV, respectively.¹⁷ Spectroscopic grade toluene was used as a solvent of C₆₀/amines. Absorption spectra

were taken using a Hitachi U-3500 spectrometer. All spectra were run in matched quartz cuvettes against the corresponding amine blank in order to cancel out amine absorbance and to correct for variations in dielectric constant of the solutions. A third-order nonlinear susceptibility $|\chi^{(3)}|$ was measured by degenerate four-wave mixing (DFWM) with a two-beam configuration. We used an excimer-laser pumped dye laser with a pulse duration of 20 ns operating at a repetition rate of 10 Hz. The two laser beams with a crossing angle of about 1° were focused onto the sample, and the power density was in the range 160–4700 kW/cm². The polarization of two incident beams was parallel. The spatially separated diffraction signal was collected by a photomultiplier tube and averaged by a boxcar integrator. An absolute value of $|\chi^{(3)}|$ in esu was calculated using the formula

$$|\chi^{(3)}| = \frac{n^2 c}{32\pi^2 (1 - T)\sqrt{T}} \sqrt{\frac{\eta}{I_0}} \quad (1)$$

where c is the light velocity in a vacuum and n is the refractive index of sample. α and T are the absorption coefficient and transmittance at wavelength λ , respectively, and I_0 is the intensity of the laser beam incident on the sample surface. The diffraction efficiency η is defined as a ratio of the diffraction signal intensity to I_0 . The detail of derivation of $|\chi^{(3)}|$ values from experimental data is described in ref 18.

Results and Discussion

Solid curves in the inset of Figure 1 show the absorption spectra of C₆₀ in toluene with the addition of ANI. For a C₆₀ solution without ANI, the weak absorption band due to the HOMO–LUMO (S₀–S₁) forbidden transition is observed around 2 eV and the strong absorption bands due to the allowed S₀–S₂ transition are observed above 3.0 eV.

As shown by the broken curve in the inset of Figure 1, the absorption spectrum of pure ANI indicates a very weak absorption tail in this energy region. A new absorption band due to the formation of charge-transfer complexes in solution appears at ~ 2.8 eV and grows with increasing ANI concentration. In the solution, C₆₀, amine, and the CT complex coexist, and their concentrations are determined by the equilibrium

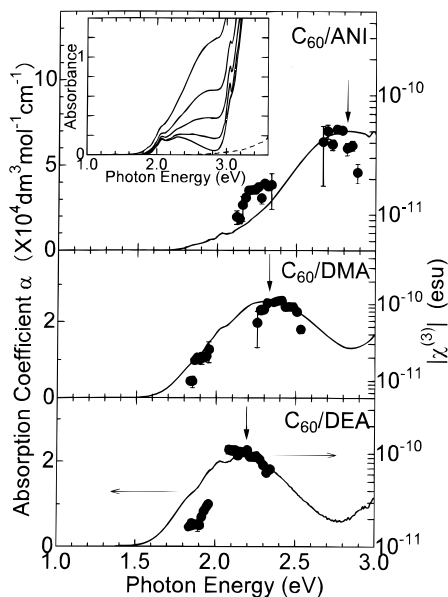


Figure 1. Absorption spectra for CT complexes of C₆₀ with various amines at room temperature. Closed circles show third-order nonlinear susceptibilities. The vertical arrows indicate the CT transition energy.¹⁶ Inset: Absorption spectra of C₆₀ in toluene with addition of ANI. The concentration of C₆₀ is 0.2 mM, and the ANI concentrations are 0, 1.10, 3.29, 6.57, and 11.0 M from bottom to top. The broken curve shows the absorption spectrum of pure ANI.

constant K . Analyzing the data by the Benesi–Hildebrand plot, we obtained the equilibrium constant of 0.02 for the C₆₀/ANI complex. K values of other CT complexes studied here were obtained as 0.04 for C₆₀/o-TOL, 0.09 for C₆₀/DMA, and 0.11 for C₆₀/DEA.¹⁶ The solid curves in Figure 1 display the absorption spectra of C₆₀ CT complexes with various amines.

The spectrum was obtained by subtracting the absorption component of C₆₀ molecules from the spectrum measured for the C₆₀/amine solution. Absorption bands due to the CT transition are observed in the visible region. The CT absorption band shifts to higher energy with increasing ionization potential. The molar absorption coefficient α is also dependent on donor species and increases with increasing ionization potential I_p : $\alpha = 2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for DMA ($I_p = 6.95 \text{ eV}$), and $\alpha = 7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for ANI ($I_p = 7.72 \text{ eV}$).

We measured absolute values of $|\chi^{(3)}|$ to investigate nonlinear optical properties of C₆₀/amine CT complexes using DFWM with the two-beam configuration. The DFWM signal of C₆₀/amine solution exhibits a cubic dependence on the excitation intensity in the range of 160–4700 kW/cm², which ensures that third-order nonlinearity is involved. Since no DFWM signal is detected for pure amine solvents, the contribution of amine solvent to the measured signal for C₆₀/amine CT complexes is negligible. Closed circles in Figure 1 show $|\chi^{(3)}|$ spectra for C₆₀/amine CT complexes. $|\chi^{(3)}|$ shows a resonant enhancement at the CT band for all CT complexes. For C₆₀/ANI, $|\chi^{(3)}|$ increases from 9.5×10^{-12} esu to 5.2×10^{-11} esu. The $|\chi^{(3)}|$ value measured for C₆₀/amine solution includes both contributions of C₆₀ molecules and CT complexes. We measured $|\chi^{(3)}|$ values by changing CT complex concentrations to evaluate a third-order susceptibility of the complex, i.e., second hyperpolarizability γ . Figure 2 shows the dependence of $|\chi^{(3)}|$ on the equilibrium C₆₀/o-TOL CT complex concentration. The $|\chi^{(3)}|$ value increases as the CT complex concentration increases. As the measured $|\chi^{(3)}|$ is a sum of the C₆₀ and CT complex

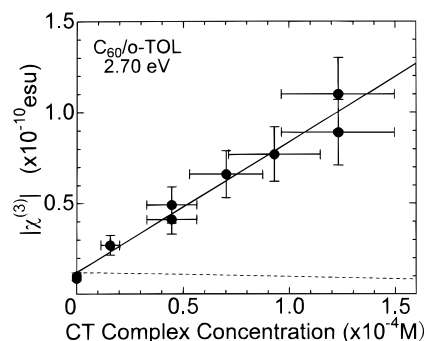


Figure 2. Third-order nonlinear susceptibility of the C₆₀/o-TOL solution as a function of molar concentration of the C₆₀/o-TOL CT complex. A solid line is the least-squares fitting of the data and a dotted line shows the contribution of C₆₀ molecules in solution.

components, the $|\chi^{(3)}|$ is given by second hyperpolarizabilities of both components,

$$\begin{aligned}
 |\chi^{(3)}| &= |\chi_{C_{60}}^{(3)}| + |\chi_{CT}^{(3)}| \\
 &= (\gamma_{C_{60}} L^4 N_{C_{60}} + \gamma_{CT} L^4 N_{CT}) N_A \times 10^{-3} \\
 &= N_A L^4 \{(\gamma_{CT} - \gamma_{C_{60}}) N_{CT} + \gamma_{C_{60}} N_0\} \times 10^{-3} \quad (2)
 \end{aligned}$$

where $L = (n^2 + 2)/3$ is a correction factor for the local field, n is the refractive index of the solution. N_A is the Avogadro number, $N_{C_{60}}$ and N_{CT} are molar concentrations of C₆₀ molecules and CT complexes in solution, respectively, and N_0 is the total concentration of C₆₀ and CT complex ($N_0 = N_{C_{60}} + N_{CT}$). $\gamma_{C_{60}}$ and γ_{CT} are the second hyperpolarizabilities of C₆₀ and the CT complex, respectively. A solid line in Figure 2 shows the result of least-squares analysis of the data, and we obtained a γ value of 2.9×10^{-28} esu for the C₆₀/o-TOL CT complex. A dotted line in Figure 2 is the $|\chi^{(3)}|$ component of the C₆₀ molecules in solution. The main contribution to the measured $|\chi^{(3)}|$ comes from the CT complex. The γ value of C₆₀/o-TOL is about 2 orders of magnitude larger than that of C₆₀ ($\sim 7 \times 10^{-30}$ esu for the S₀–S₁ transition), indicating that the third-order nonlinear optical response of C₆₀ in the fundamental absorption region is greatly enhanced by complexation with an electron donor such as ANI.

Using the same measurement and analysis, we obtained γ values for C₆₀ complexes with ANI, DMA, and DEA. The highest γ value among the CT complexes studied here is $\sim 5.2 \times 10^{-28}$ esu for the C₆₀/ANI CT complex.

Here we briefly discuss a thermal grating effect in $|\chi^{(3)}|$ measurements. In general, when we measured $|\chi^{(3)}|$ by DFWM, there are two contributions: electronic and thermal contributions. The thermal component depends on the laser power absorbed by the sample, i.e., the absorbance. The absorbance of C₆₀/ANI increases with increasing photon energy (see the inset of Figure 1) due to the CT transition and the S₀–S₂ allowed transition of C₆₀. However, the $|\chi^{(3)}|$ spectrum shows a maximum value at $\sim 2.8 \text{ eV}$ (see the top frame of Figure 1) corresponding to the CT transition energy ($2.82 \pm 0.01 \text{ eV}$),¹⁶ and the $|\chi^{(3)}|$ value drops in the higher absorbance region. This result indicates that the measured diffraction signal is not determined by the sample absorbance but determined by the species of the CT complex contained in the sample. Therefore, the contribution of the thermal grating effect to the $|\chi^{(3)}|$ value is negligible in our samples, and the measured value corresponds to the electronic contribution due to the CT complexes.

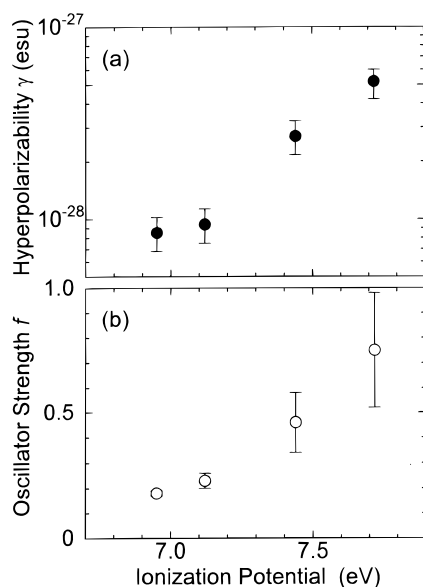


Figure 3. (a) Second hyperpolarizability of C_{60} /amine CT complex as a function of ionization potential. (b) Oscillator strength of the C_{60} /amine CT complex as a function of ionization potential.

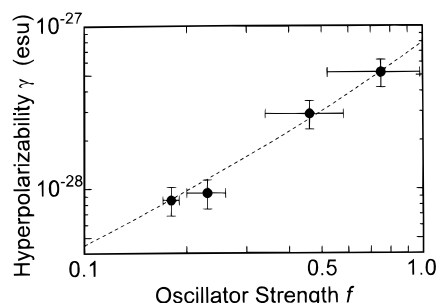


Figure 4. Second hyperpolarizability γ of the C_{60} /amine CT complex as a function of oscillator strength f . The broken curve is the dependence obtained by fitting the data to eq 5.

Let us discuss the origin of the large nonlinearity for C_{60} /amine CT complexes, plotting the γ value and the oscillator strength as a function of ionization potential. As shown in Figure 3a, the γ value increases with increasing ionization potential from 8.5×10^{-29} esu for C_{60} /DEA to 5.2×10^{-28} esu for C_{60} /ANI.

Figure 3b displays the oscillator strength of the CT transition as a function of ionization potential. The oscillator strength was determined by absorption spectrum analysis.¹⁶ The value of oscillator strength also increases from 0.18 for C_{60} /DEA to 0.75 for C_{60} /ANI with increasing ionization potential and shows a similar dependence of γ .

We plot the γ value as a function of oscillator strength in Figure 4. The γ value increases upon an increase of oscillator strength, which suggests that γ is expressed by the oscillator strength using a simple Mulliken two-state model.¹⁹ In this model, the ground (ψ_g) and excited (ψ_e) state wave functions of a CT complex are described by a linear combination of no-bond $\psi(D^0, A^0)$ and ionic $\psi(D^+, A^-)$ states

$$\psi_g = \sqrt{1 - \rho} \psi(D^0, A^0) + \sqrt{\rho} \psi(D^+, A^-) \quad (3)$$

$$\psi_e = \sqrt{1 - \rho} \psi(D^+, A^-) - \sqrt{\rho} \psi(D^0, A^0) \quad (4)$$

where ρ is the degree of charge transfer. $\psi(D^+, A^-)$ differs from $\psi(D^0, A^0)$ by the promotion of an electron from the donor to acceptor. Using perturbation theory, γ is given by

$$\gamma = af^2 + b(\Delta\mu)^2 f \quad (5)$$

where a and b are constants for a given acceptor and donor, and $\Delta\mu$ is the difference of dipole moment between the excited and ground states of the CT complex. The value of $\Delta\mu$ can be estimated by $|1 - 2\rho|ed$, where d is the distance between donor and acceptor molecules. As ρ is much smaller than unity ($\rho = 0.04-0.07$) and d can be regarded as a constant value for all the C_{60} /amine CT complexes studied here,¹⁶ $\Delta\mu$ is approximately constant. The broken curve in Figure 4 shows the dependence expected from eq 5 assuming that a , b , and $\Delta\mu$ are constant for all the CT complexes studied here. The observed dependence is well reproduced by eq 5 taking a as 3.9×10^{-28} esu and $b(\Delta\mu)^2$ as 4.1×10^{-28} esu. This result indicates that the enhancement of third-order optical nonlinearity originates from an increase in oscillator strength and the contribution of the permanent dipole in the ground and excited states due to complexation.

Summary

We have studied third-order nonlinear optical properties of CT complexes of C_{60} with various aromatic amines. We have obtained second hyperpolarizabilities γ of CT complexes by measuring $\chi^{(3)}$ values by means of degenerate four-wave mixing. The highest γ value among the CT complexes studied here is $\sim 5.2 \times 10^{-28}$ esu. The γ value increases with increasing ionization potential in the range 6.95–7.72 eV. The dependence of γ on the oscillator strength obtained from the absorption spectra is well explained by the Mulliken two-level model.

Acknowledgment. We greatly thank to Dr. K. Ishiguro for useful discussion and the sample preparation. This work was supported by the Grant-in-Aid for General Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan, and Aichi Science and Technology Foundation.

References and Notes

- (1) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Phys. Rev. Lett.* **1991**, *67*, 1423.
- (2) Kafafi, Z. H.; Bartoli, E. J.; Lindle, J. R.; Pong, R. G. S. *Phys. Rev. Lett.* **1992**, *68*, 2705.
- (3) Kajzar, F.; Taliani, C.; Zamboni, R.; Rosini, S.; Danieli, R. *Synth. Met.* **1993**, *54*, 21.
- (4) Meth, J. S.; Vanherzeele, H.; Wang, Y. *Chem. Phys. Lett.* **1992**, *197*, 26.
- (5) Hoshi, H.; Nakamura, N.; Maruyama, Y.; Nakagawa, T.; Suzuki, S.; Shiromaru, H.; Achiba, Y. *Jpn. J. Appl. Phys.* **1991**, *30*, L1397.
- (6) Lindle, J. R.; Pong, R. G. S.; Bartoli, E. J.; Kafafi, Z. H. *Phys. Rev. B* **1993**, *48*, 9447.
- (7) Flom, S. R.; Pong, R. G. S.; Bartoli, F. J.; Kafafi, Z. H. *Nonlinear Optics* **1995**, *10*, 183.
- (8) Harigaya, K.; Abe, S. *Jpn. J. Appl. Phys.* **1992**, *31*, L887.
- (9) Okada-Shudo, Y.; Kajzar, F.; Merritt, C. D.; Kafafi, Z. H. *Proc. SPIE* **1996**, *2854*, 52.
- (10) Okada-Shudo, Y.; Kajzar, F.; Merritt, C. D.; Kafafi, Z. H. *Synth. Met.* **1998**, *94*, 91.
- (11) Kajzar, F.; Okada-Shudo, Y.; Merritt, C. D.; Kafafi, Z. H. *Proc. SPIE* **1998**, *3142*, 128.
- (12) Wang, Y. J. *Phys. Chem.* **1992**, *96*, 764.
- (13) Wang, Y.; Cheng, L.-T. *J. Phys. Chem.* **1992**, *96*, 1530.
- (14) Seshadri, R.; Rao, C. N. R.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett.* **1993**, *205*, 395.
- (15) Sibley, S. P.; Campbell, R. L.; Silber, H. B. *J. Phys. Chem.* **1995**, *99*, 5274.
- (16) Ichida, M.; Sohda, T.; Nakamura, A. *Chem. Phys. Lett.* **1999**, *310*, 373.
- (17) Seki, K. *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 255.
- (18) Li, Y.; Takata, M.; Nakamura, A. *Phys. Rev. B* **1998**, *57*, 9193.
- (19) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; 1969; p 419.