Nonlinear optical response in higher fullerenes

Kikuo Harigaya

Physical Science Division, Electrotechnical Laboratory,
Umezono 1-1-4, Tsukuba 305, Japan

Abstract

Nonlinear optical properties of extracted higher fullerenes – \( C_{70}, \ C_{76}, \ C_{78}, \ \text{and} \ C_{84} \) – are theoretically investigated. Magnitudes of off-resonant third-harmonic-generation are calculated by the intermediate exciton theory. We find that optical nonlinearities of higher fullerenes are a few times larger than those of \( C_{60} \). The magnitudes of nonlinearity tend to increase as the optical gap decreases in higher fullerenes.

Keywords: excitons, nonlinear optical response, third harmonic generation, higher fullerenes, \( C_{70}, \ C_{76}, \ C_{78}, \ C_{84} \), electron-electron interactions, theory
It has been found that C\textsubscript{60} thin films show large optical nonlinearities\cite{1-4}. The observation is attractive in view of scientific interests as well as technological applications. The magnitude of the third-order nonlinear susceptibility, \( \chi^{(3)}(\omega) = \chi^{(3)}(3\omega; \omega, \omega, \omega) \), for third harmonic generation (THG) is of the order of \( 10^{-12} \) esu to \( 10^{-11} \) esu. This large response is comparable to the values measured in polydiacetylenes. The optical spectra of C\textsubscript{70}\cite{4} and higher fullerenes (C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{84}, etc.)\cite{5,6} have also been obtained. In order to explain the interesting experiments, several theoretical investigations\cite{7-11} have been performed. We have applied a tight binding model\cite{7} to C\textsubscript{60}, and have analyzed the nonlinear optical properties. Coulomb interaction effects on the absorption spectra and the optical nonlinearity have been also studied\cite{10}. We have found that the linear absorption spectra of C\textsubscript{60} and C\textsubscript{70} are well explained by the Frenkel exciton picture\cite{11} except for the charge transfer exciton feature around the excitation energy 2.8 eV of the C\textsubscript{60} solids\cite{12}. Coulomb interaction effects reduce the magnitude of the optical nonlinearity from that of the free electron calculation\cite{10}, and we have discussed that the local field enhancement might be effective in solids.

In the previous paper\cite{13}, we have investigated geometric effects on optical properties in higher fullerenes. We have obtained the optical absorption spectra at a certain combination of the pentagonal carbons, by using projected wavefunctions onto selected pentagons in order to calculate dipole moments. The contributions from a part of the fullerene to the optical spectra have been extracted. We have found that the optical excitations in the energy region smaller than about 4 eV have most of their amplitudes at the pentagonal carbons. The oscillator strengths of absorption projected onto these carbons almost accord with those of the total absorption. We have also found that the spectral shapes of the total absorption are mainly determined by the geometrical distributions of the pentagons in the fullerene structures.

The main purpose of this paper is to investigate nonlinear optical properties in higher fullerenes, further. The calculation method of the THG has been used for C\textsubscript{60} in the previous work\cite{10}. Recently, a calculation of the THG in isomers of C\textsubscript{78} by a free electron model has been reported\cite{14}. However, the Coulomb interaction effects, whose importance we have found in C\textsubscript{60}, have not been discussed for higher fullerenes. The present paper gives rise to a new contribution to this subject. We focus on the off-resonant THG in order to estimate possible magnitudes of the nonlinearities of each isomer. The Coulomb interaction strengths are also changed in a reasonable range, because realistic strengths are not well known in higher fullerenes.

In the present paper, the carbon network of the fullerene surface is taken into account by the hopping integral \( t \) between nearest neighbor sites. The Coulomb interactions are taken into account by the parametrized Ohno
potential, \( W(r) = 1/\sqrt{(1/U)^2 + (r/r_0V)^2} \), between two electrons with distance \( r \). Here, \( U \) is the interaction strength at the distance \( r = 0 \), \( V \) is the strength of the long range part, and \( r_0 \) the mean bond length. The Coulomb interaction is treated by the restricted Hartree-Fock approximation and the intermediate treatment of excitons.\(^{11}\) The THG is calculated by the sum-over-states method which has been used in ref. 7. In calculating the expectation values of the dipole moment, the lattice coordinates contained in the geometry package of higher fullerenes\(^{15}\) are used. We will discuss properties of the THG in seven kinds of the extracted fullerene isomers: C\(_{70}\), C\(_{76}\), C\(_{78}\), and C\(_{84}\). From our experiences of investigation on optical properties,\(^{10,11}\) we can assume \( V = U/2 \) in the following. The onsite Coulomb strength is varied within \( 0 \leq U \leq 4t \).

Figure 1 shows the absolute value of the off-resonant THG \( |\chi^{(3)}(0)|_T \) plotted against the Coulomb interaction strength \( U \). The different plots indicate different kinds of isomers. The four isomers – \( C_{70}, D_2-C_{76}, D_3-C_{78}, \) and one kind of \( C_{2v}-C_{78} \) (\( C_{2v} \) by Kikuchi’s notation (ref. 16)) – exhibit similar magnitudes of optical nonlinearities. On the other hand, the other three isomers – one kind of \( C_{2v}-C_{78} \) (\( C_{2v}' \) by Kikuchi’s notation (ref. 16)), \( D_{2d}-C_{84}, \) and \( D_2-C_{84} \) – show larger optical nonlinearities than those of the former isomers. This is mainly due to the smaller energy gap of the latter isomers, even though the negative correlation between the THG and the energy gap is not so complete through all the isomers. The decrease of THG from the free electron model (\( U = 0 \)) to the case with \( U = 4t \) is by the factor about 0.1 for all the isomers. The similar fact has been found in the calculation of C\(_{60}\).\(^{10}\) This would be a general property in various kinds of higher fullerenes. The overall magnitudes of the THG are around \( 10^{-12} \) esu for most of the Coulomb interactions considered.

In Fig. 2, the relations between the absolute value of the off-resonant THG \( |\chi^{(3)}(0)|_T \) and the energy gap are shown for three Coulomb interaction strengths: \( U = 0t, 2t, \) and \( 4t \). Here, the energy gap is defined as the optical excitation energy of the lowest dipole allowed state. This is called the optical gap, in other words. For each Coulomb interaction, the seven plots cluster in a bunch. When the energy gap becomes larger, the THG tends to decrease. However, the correlation between the THG and the energy gap is far from that of a smooth function. The correlation is merely a kind of tendency. Therefore, the decrease of the energy gap in higher fullerenes is one of origins of the larger optical nonlinearities of the systems. The actual magnitudes would also be influenced by detailed electronic structures of isomers.

In the calculations of C\(_{60}\), the magnitudes of the THG at the energy zero are about \( 1 \times 10^{12} \) esu in the free electron model (ref. 7), and about \( 1 \times 10^{-13} \) esu for \( U = 4t \) and \( V = 2t \) (ref. 10). In the present calculations of higher fullerenes, the magnitudes are a few times larger than those of C\(_{60}\). Thus, this paper predicts that
nonlinear optical responses in higher fullerenes are generally larger than in C\textsubscript{60}. In the previous paper\textsuperscript{10}, we have discussed that the local field correction factor is of the order 10 in C\textsubscript{60} solids. As the distance between the surfaces of neighboring fullerene molecules in C\textsubscript{70} and C\textsubscript{76} solids is nearly the same as in C\textsubscript{60} solids, we expect that local field enhancement in thin films of higher fullerenes is of the similar magnitudes as in C\textsubscript{60} systems.

In summary, we have investigated nonlinear optical properties of higher fullerenes. Theoretical off-resonant THG has been calculated by using the intermediate exciton theory. We have found the optical nonlinearities of higher fullerenes which are larger than in C\textsubscript{60}. The magnitudes of THG tend to increase as the optical gap decreases in higher fullerenes.
References

1) J. S. Meth, H. Vanherzeele, and Y. Wang: Chem. Phys. Lett. 197 (1992) 26.
2) Z. H. Kafafi, J. R. Lindle, R. G. S. Pong, F. J. Bartoli, L. J. Lingg, and J. Milliken: Chem. Phys. Lett. 188 (1992) 492.
3) F. Kajzar, C. Taliani, R. Danieli, S. Rossini, and R. Zamboni: Chem. Phys. Lett. 217 (1994) 418.
4) B. C. Hess, D. V. Bowersox, S. H. Mardirosian, and L. D. Unterberger: Chem. Phys. Lett. 248 (1996) 141.
5) R. Ettl, I. Chao, F. Diederich, and R. L. Whetten: Nature 353 (1991) 149.
6) K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, H. Matsumiya, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto, and Y. Achiba: Chem. Phys. Lett. 188 (1992) 177.
7) K. Harigaya and S. Abe: Jpn. J. Appl. Phys. 31 (1992) L887.
8) E. Westin and A. Rosén: Int. J. Mod. Phys. B 23-24 (1992) 3893.
9) Z. Shuai and J. L. Brédas: Phys. Rev. B 46 (1992) 16135.
10) K. Harigaya and S. Abe: J. Limun. 60&61 (1994) 380.
11) K. Harigaya and S. Abe: Phys. Rev. B 49 (1994) 16746.
12) S. L. Ren, Y. Wang, A. M. Rao, E. McRae, J. M. Holden, T. Hager, K. A. Wang, W. T. Lee, H. F. Ni, J. Selegue and P. C. Eklund, Appl. Phys. Lett. 59 (1991) 2678.
13) K. Harigaya and S. Abe: J. Phys.: Condens. Matter 8 (1996) 8057.
14) X. Wan, J. Dong, and D. Y. Xing: J. Phys. B 30 (1997) in March issue.
15) M. Yoshida and E. Ōsawa: The Japan Chemistry Program Exchange, Program No. 74.
16) K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba: Nature 357 (1992) 142.
Figure Captions

Fig. 1. The absolute value of the off-resonant THG $|\chi_{\text{THG}}^{(3)}(0)|$ plotted against the Coulomb interaction strength $U$. The closed and open squares are for $C_{70}$ and $D_2$-$C_{76}$. The closed circles are for $D_3$-$C_{78}$, and the open and crossed circles are for two kinds of $C_{2v}$-$C_{78}$. The closed and open triangles are for $D_{2d}$-$C_{84}$ and $D_2$-$C_{84}$, respectively.

Fig. 2. The absolute value of the off-resonant THG $|\chi_{\text{THG}}^{(3)}(0)|$ in seven isomers of higher fullerenes, plotted against the energy gap (shown in units of $t$). The squares, circles, and triangles are for $U = 0t$, $2t$, and $4t$, respectively. The left axis is in the logarithmic scale.