

Nonlinear Optical Response in Higher Fullerenes

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Nonlinear optical properties of extracted higher fullerenes – C_{70} , C_{76} , C_{78} , and C_{84} – are theoretically investigated. Magnitudes of off-resonant third-harmonic generation are calculated using 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

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It has been found that C_{60} thin films show large optical nonlinearities¹⁻⁴⁾ which is attracting from the viewpoint of scientific interest as well as technological applications. The magnitude of the third-order nonlinear susceptibility, $\chi_{\text{THG}}^{(3)}(\omega) = \chi^{(3)}(3\omega; \omega, \omega, \omega)$, for third-harmonic generation (THG) is of the order of 10^{-12} esu to 10^{-11} esu. This large response is comparable to the responses measured for polydiacetylenes. The optical spectra of C_{70} ⁴⁾ and higher fullerenes (C_{76} , C_{78} , C_{84} , etc.)^{5,6)} have been obtained. In order to explain the results of several interesting experiments, theoretical investigations⁷⁻¹¹⁾ have been performed. We have applied a tight binding model⁷⁾ to C_{60} , and have analyzed the nonlinear optical properties of C_{60} . Coulomb interaction effects on the absorption spectra and the optical nonlinearity of C_{60} have also been studied.¹⁰⁾ We have found that the linear absorption spectra of C_{60} and C_{70} are well explained by the Frenkel exciton picture¹¹⁾ except for the charge transfer exciton feature around the excitation energy of 2.8 eV of the C_{60} solids.¹²⁾ Coulomb interaction effects reduce the magnitude of the optical nonlinearity of C_{60} compared with that determined using the free electron calculation,¹⁰⁾ and we have discussed the possibility that the local field enhancement might be effective in solids.

In a previous study,¹³⁾ we investigated geometric effects on optical properties of higher fullerenes. We obtained optical absorption spectra at a certain combination of the pentagonal carbons, by using wavefunctions projected 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 found that the optical excitations in the energy region lower than about 4 eV have most of their amplitudes at the pentagonal carbons. The oscillator strengths of absorption projected onto these carbons are almost the same as those of the total absorption. We 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 study is to investigate further the nonlinear optical properties of higher fullerenes. The THG calculation method has been used for C_{60} in a previous work.¹⁰⁾ Recently, a THG calculation for isomers of C_{78} using a free electron model has been reported.¹⁴⁾ However, the Coulomb interaction effects, whose importance we have obtained for C_{60} , have not been discussed for higher fullerenes. The results of the present study give rise to a new contribution to this subject. We focus on the off-resonant THG in order to estimate the magnitudes of the nonlinear optical responses 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 study, 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 a distance $r = 0$, V is the strength of

the long range part, and r_0 is 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 the study the results of which are reported in ref. 7. For calculating the expectation values of the dipole moment, the lattice coordinates contained in the geometry package of higher fullerenes¹⁵⁾ are used. The coordinates can be obtained from the World-Wide Web at the URL: <http://cochem2.tutkie.tut.ac.jp:8000/~yoshida/fuller/Fuller.html>, too. We will discuss the properties of the THG for seven types of the extracted fullerene isomers, C_{70} , C_{76} , C_{78} , and C_{84} . Based on our results for the optical properties of C_{60} and C_{70} ,^{10,11)} we can assume $V = U/2$. The onsite Coulomb strength is varied within the range $0 \leq U \leq 4t$.

Figure 1 shows the absolute value of the off-resonant THG $|\chi_{\text{THG}}^{(3)}(0)|$ plotted against the Coulomb interaction strength U . The different plots indicate different types of isomers. The four isomers – C_{70} , D_2 - C_{76} , D_3 - C_{78} , and one type of C_{2v} - C_{78} isomer [C_{2v} by Kikuchi et al's notation (ref. 16)] – exhibit similar magnitudes of optical nonlinearities. On the other hand, the other three isomers – another type of C_{2v} - C_{78} isomer [C'_{2v} by Kikuchi et al's notation (ref. 16)], D_{2d} - C_{84} , and D_2 - C_{84} – show larger optical nonlinearities than those of the first four 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 in THG between the free electron model ($U = 0$) and the case in which $U = 4t$ is by a factor of approximately 0.1 for all the isomers. A similar finding was obtained in the calculation for C_{60} ¹⁰⁾ indicating that this is a general property of 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 $|\chi_{\text{THG}}^{(3)}(0)|$ 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, in other words, the optical gap. For each Coulomb interaction, the seven plots (squares, circles, or triangles) 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 in the energy gap of higher fullerenes is one origin of the larger optical nonlinearities of the systems. The actual magnitudes of nonlinearities would also be influenced by the detailed electronic structures of isomers.

In the calculations for C_{60} reported previously, the magnitudes of the THG at the energy zero are approximately 1×10^{-12} esu in the free electron model (ref. 7), and approximately 2×10^{-13} esu for $U = 4t$ and $V = 2t$ (ref. 10). In the present calculations for higher fullerenes, the magnitudes are a few times larger than those of C_{60} . Thus, the author predicts that nonlinear

optical responses in higher fullerenes are generally larger than in C_{60} . In our previous paper,¹⁰⁾ we discussed the fact that the local field correction factor is of the order of 10 for C_{60} solids. Since the distance between the surfaces of neighboring fullerene molecules in C_{70} and C_{76} solids is nearly the same as in C_{60} solids, we expect that local field enhancement in thin films of higher fullerenes is of a magnitude similar to that in C_{60} systems.

In summary, we have investigated the nonlinear optical properties of higher fullerenes. Theoretical off-resonant THG has been calculated using the intermediate exciton theory. We have found optical nonlinearities of higher fullerenes which are larger than those of C_{60} . The magnitude of THG tends to increase as the optical gap decreases in higher fullerenes.

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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 represent results for C_{70} and D_2-C_{76} , respectively. The closed circles represent results for D_3-C_{78} , and the open and crossed circles represent results for two types of $C_{2v}-C_{78}$. The closed and open triangles represent results for $D_{2d}-C_{84}$ and D_2-C_{84} , respectively.

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