

Coulomb interaction effects on nonlinear optical response in C₆₀, C₇₀, and higher fullerenes

(Running head: *Nonlinear optical response in higher fullerenes*)

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Abstract

Nonlinear optical properties in the fullerene C₆₀ and the extracted higher fullerenes – C₇₀, C₇₆, C₇₈, and C₈₄ – are theoretically investigated by using the exciton formalism and the sum-over-states method. We find that off-resonant third order susceptibilities of higher fullerenes are a few times larger than those of C₆₀. The magnitude of nonlinearity increases as the optical gap decreases in higher fullerenes. The nonlinearity is nearly proportional to the fourth power of the carbon number when the onsite Coulomb repulsion is $2t$ or $4t$, t being the nearest neighbor hopping integral. This result, indicating important roles of Coulomb interactions, agrees with quantum chemical calculations of higher fullerenes.

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It has been found that C_{60} thin films show large optical nonlinearities [1-4] which are attractive 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 investigations [7-11] have been performed. We have applied a tight binding model [7] 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 picture [11] 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 susceptibility 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 optical susceptibility 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 fullerenes [15] 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 susceptibility, $\chi^{(3)}(0) = \chi^{(3)}(0; 0, 0, 0)$, 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 which are larger than those of C_{60} . 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 susceptibility and the energy gap is not so complete through all the isomers. The decrease in the susceptibility 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, indicating that this is a general property of various kinds of higher fullerenes. The overall magnitudes of the susceptibility 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 susceptibility 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 plots (squares, circles, or triangles) cluster in a bunch. When the energy gap becomes larger, the susceptibility tends to decrease. However, the correlation between the susceptibility 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 [7], and approximately 2×10^{-13} esu for $U = 4t$ and $V = 2t$ [10]. These results have been shown in Fig. 1, also. 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.

It is of some interests to look at carbon number dependence of the magnitude of the optical nonlinearity of the calculated isomers in higher fullerenes. Figure 3 shows $|\chi^{(3)}(0)|$ as functions

of the carbon number N for three Coulomb interaction strengths, $U = 0t$, $2t$, and $4t$. The solid lines indicate the linear fitting in the logarithmic scale: $|\chi^{(3)}(0)| \sim A \cdot N^\alpha$. The powers α for the three Coulomb interaction strengths are summarized in TABLE I. When $U = 0t$, the power α is about 5. As U increases, α decreases. It is among 4, when $U \sim 2t$ and $4t$. This magnitude of the power 4 agrees with the result of the quantum chemical calculation of higher fullerenes upto C_{84} [17]. Therefore, we have shown important roles of Coulomb interactions in nonlinear optical response of higher fullerenes.

Experimental measurements of optical nonlinearities in higher fullerenes whose carbon number is larger than 70 have not been reported so much, possibly because of the difficulty in obtaining samples with good quality and the difficult measurements. However, the recent report of the degenerate four-wave-mixing measurement of C_{90} in solutions [18] indicates the larger optical nonlinearity than that in C_{60} . The magnitude of $\chi^{(3)}$ is about eight times larger than in C_{60} , and is apparently enhanced from that of the theoretical predictions: $(90/60)^4 = 1.5^4 = 5.063$. Therefore, further experimental as well as theoretical investigations of nonlinear optical properties in higher fullerenes should be fascinating among scientists and technologists of the field of photophysics.

In summary, we have investigated the nonlinear optical properties of higher fullerenes. Theoretical off-resonant third order susceptibility has been calculated using the exciton theory. We have found optical nonlinearities of higher fullerenes which are larger than those of C_{60} . The magnitude of $\chi^{(3)}$ tends to increase as the optical gap decreases in higher fullerenes. The nonlinearity is nearly proportional to the fourth power of the carbon number when the onsite Coulomb repulsion is $2t$ or $4t$. This result, indicating important roles of Coulomb interactions, agrees with quantum chemical calculations of higher fullerenes.

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TABLE I. Coulomb interaction dependence of the power α where $|\chi^{(3)}(0)| \sim A \cdot N^\alpha$.

U	α
$0t$	5.253
$2t$	4.133
$4t$	3.536

Figure Captions

Fig. 1. The absolute value of the off-resonant susceptibility $|\chi^{(3)}(0)|$ plotted against the Coulomb interaction strength U . The stars represent numerical results for C_{60} . 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 susceptibility $|\chi^{(3)}(0)|$ for C_{60} and 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.

Fig. 3. The absolute value of the off-resonant susceptibility $|\chi^{(3)}(0)|$ for C_{60} and seven isomers of higher fullerenes, plotted against the carbon number N . The squares, circles, and triangles represent results for $U = 0t, 2t$, and $4t$, respectively. The left and bottom axes are in the logarithmic scale. The solid lines are the results of the linear fitting in the logarithmic scale: $|\chi^{(3)}| \sim A \cdot N^\alpha$.