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## Effects of Coulomb interaction on the nonlinear optical response in C<sub>60</sub>, C<sub>70</sub>, and higher fullerenes

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**Abstract.** Nonlinear optical properties of the fullerene C<sub>60</sub> and extracted higher fullerenes—C<sub>70</sub>, C<sub>76</sub>, C<sub>78</sub>, and C<sub>84</sub>—are theoretically investigated by using the exciton formalism and the sum-over-states method. We find that the off-resonant third-order susceptibilities of higher fullerenes are a few times larger than those of C<sub>60</sub>. The magnitude of the nonlinearity increases as the optical gap decreases for higher fullerenes. The nonlinearity is nearly proportional to the fourth power of the carbon number when the on-site Coulomb repulsion is  $2t$  or  $4t$ ,  $t$  being the nearest-neighbour hopping integral. This result, indicating important roles of Coulomb interactions, agrees with quantum chemical calculations for higher fullerenes.

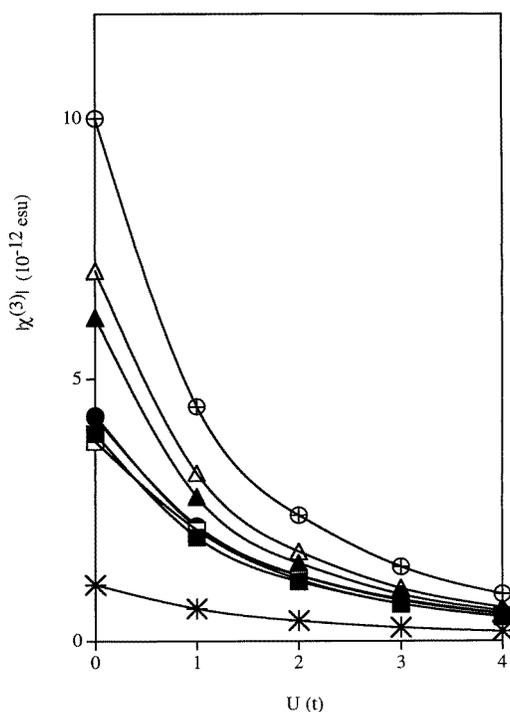
It has been found that C<sub>60</sub> thin films show large optical nonlinearities [1–4] which are attractive from the viewpoint of scientific interest as well as in view of the technological applications. The magnitude of the third-order nonlinear susceptibility,  $\chi_{\text{THG}}^{(3)}(\omega) = \chi^{(3)}(3\omega; \omega, \omega, \omega)$ , 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<sub>70</sub> [4] and higher fullerenes (C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, 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<sub>60</sub>, and have analysed the nonlinear optical properties of C<sub>60</sub>. The effects of Coulomb interaction on the absorption spectra and the optical nonlinearity of C<sub>60</sub> have also been studied [10]. We have found that the linear absorption spectra of C<sub>60</sub> and C<sub>70</sub> are well explained by the Frenkel exciton picture [11], except the charge-transfer exciton feature found at around the excitation energy of 2.8 eV of the C<sub>60</sub> solids [12]. The effects of Coulomb interaction reduce the magnitude of the optical nonlinearity of C<sub>60</sub> 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 for a certain combination of the pentagonal carbons, by using wavefunctions projected onto selected pentagons in order to calculate dipole moments. The contributions from the various parts of the fullerene to the optical spectra have been extracted. We found that the optical excitations in the energy region below about 4 eV have most of their amplitudes arising from the pentagonal carbons. The oscillator strengths of the absorption projected onto these carbons are almost the same as

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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 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 established for  $C_{60}$ , have not been discussed for higher fullerenes. The results of the present study represent 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 of the isomers. The Coulomb interaction strengths are also changed over a reasonable range, because realistic strengths are not well known for higher fullerenes.



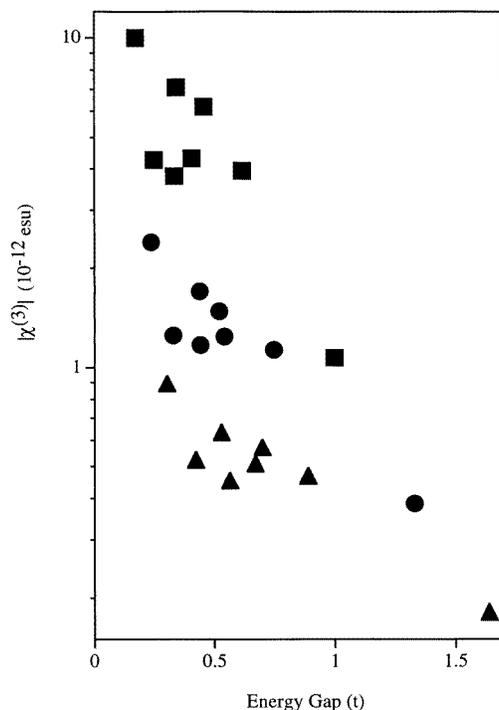
**Figure 1.** The absolute value of the off-resonant susceptibility  $|\chi^{(3)}(0)|$  plotted against the Coulomb interaction strength  $U$ . The stars represent numerical results for  $C_{60}$ . The closed and open squares represent results for  $C_{70}$  and  $D_2-C_{76}$ , respectively. The closed 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.

In the present study, the carbon network of the fullerene surface is taken into account by the integral  $t$  for hopping between nearest-neighbour 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 separated by a 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 a study whose results are reported in reference [7]. For calculating the expectation values of the dipole moment, the lattice coordinates contained in a geometry package for 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 extracted fullerene isomer,  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$ . On the basis of our results for the optical properties of  $C_{60}$  and  $C_{70}$  [10, 11], we can assume that  $V = U/2$ . The on-site Coulomb strength is varied within the range  $0 \leq U \leq 4t$ .

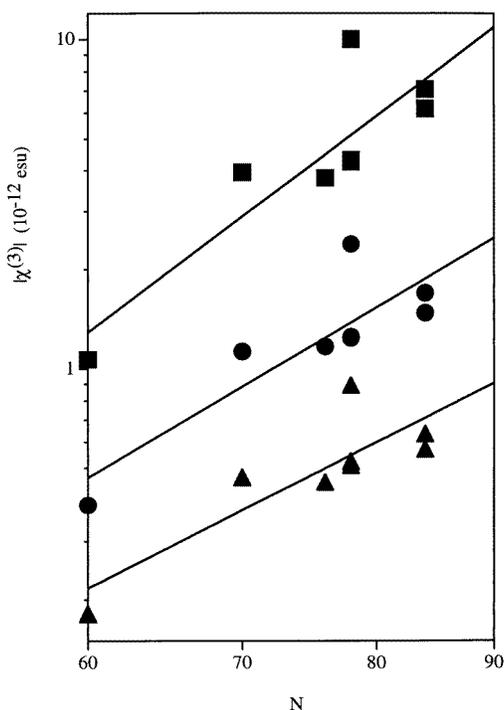


**Figure 2.** The absolute value of the off-resonant susceptibility  $|\chi^{(3)}(0)|$  for  $C_{60}$  and seven isomers of higher fullerenes, plotted against the energy gap (shown in units of  $t$ ). The squares, circles, and triangles represent results for  $U = 0t$ ,  $2t$ , and  $4t$ , respectively. The left-hand axis has a logarithmic scale.

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 isomer. The four isomers— $C_{70}$ ,  $D_2$ - $C_{76}$ ,  $D_3$ - $C_{78}$ , and one type of  $C_{2v}$ - $C_{78}$  isomer ( $C_{2v}$  in the notation of Kikuchi *et al* (reference [16]))—exhibit similar magnitudes of optical nonlinearities which are larger than those for  $C_{60}$ . On the other hand, the other three isomers—another type of  $C_{2v}$ - $C_{78}$  isomer ( $C'_{2v}$  in the notation of Kikuchi *et al* (reference [16])),  $D_{2d}$ - $C_{84}$ , and  $D_2$ - $C_{84}$ —show optical nonlinearities larger 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 of 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 of the isomers, indicating that this is a general property of various kinds of higher fullerene. The overall magnitudes of the susceptibility are around  $10^{-12}$  esu for most of the Coulomb interactions considered.

In figure 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 the nonlinearities would also be influenced by the detailed electronic structures of isomers.



**Figure 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-hand and bottom axes have logarithmic scales. The solid lines are the results of the linear fitting on a logarithmic scale:  $|\chi^{(3)}| \sim AN^\alpha$ .

In the calculations for  $C_{60}$  reported previously, the magnitudes of the THG at the energy zero are approximately  $1 \times 10^{-12}$  esu in the free-electron model [7], and approximately  $2 \times 10^{-13}$  esu for  $U = 4t$  and  $V = 2t$  [10]. These results have been shown in figure 1, also. In the present calculations for higher fullerenes, the magnitudes are a few times larger than those for  $C_{60}$ . Thus, I predict that nonlinear optical responses in higher fullerenes will

be found to be generally larger than those 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 neighbouring fullerene molecules in  $C_{70}$  and  $C_{76}$  solids is nearly the same as that in  $C_{60}$  solids, we expect the local field enhancement in thin films of higher fullerenes to be of a magnitude similar to that in  $C_{60}$  systems.

**Table 1.** The Coulomb interaction dependence of the power  $\alpha$ , where  $|\chi^{(3)}(0)| \sim AN^\alpha$ .

$U$	$\alpha$
$0t$	5.253
$2t$	4.133
$4t$	3.536

It is of some interest to look at the 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 on the logarithmic scale:  $|\chi^{(3)}(0)| \sim AN^\alpha$ . The powers  $\alpha$  for the three Coulomb interaction strengths are summarized in table 1. When  $U = 0t$ , the power  $\alpha$  is about 5. As  $U$  increases,  $\alpha$  decreases. It is about 4, when  $U \sim 2t$  and  $4t$ . This magnitude of the power, 4, agrees with the result of the quantum chemical calculation for higher fullerenes up to  $C_{84}$  [17]. Therefore, we have shown the importance of Coulomb interactions in the 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 of obtaining samples with good quality and of making the measurements. However, the recent report of the degenerate four-wave-mixing measurement of  $C_{90}$  in solutions [18] indicates a 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 higher than 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 to scientists and technologists in the field of photophysics.

In summary, we have investigated the nonlinear optical properties of higher fullerenes. The 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 for higher fullerenes. The nonlinearity is nearly proportional to the fourth power of the carbon number when the on-site Coulomb repulsion is  $2t$  or  $4t$ . This result, indicating the importance of Coulomb interactions, agrees with quantum chemical calculations for higher fullerenes.

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