Coulomb interaction effects on nonlinear optical response in $C_{60}$, $C_{70}$, and higher fullerenes

Kikuo Harigaya

Electrotechnical Laboratory, Tsukuba 305, Japan

Abstract

Nonlinear optical properties in the fullerene $C_{60}$ and the extracted higher fullerenes – $C_{70}$, $C_{76}$, $C_{78}$, and $C_{84}$ – 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 $C_{60}$. 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.

*E-mail address: harigaya@etl.go.jp; URL: http://www.etl.go.jp/~harigaya/
It has been found that C\textsubscript{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, $\chi^{(3)}_{\text{THG}}(\omega) = \chi^{(3)}(3\omega; \omega, \omega, \omega)$, 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\textsubscript{70} [4] and higher fullerenes (C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{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\textsubscript{60}, and have analyzed the nonlinear optical properties of C\textsubscript{60}. Coulomb interaction effects on the absorption spectra and the optical nonlinearity of C\textsubscript{60} have also been studied [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 [11] except for the charge transfer exciton feature around the excitation energy of 2.8 eV of the C\textsubscript{60} solids [12]. Coulomb interaction effects reduce the magnitude of the optical nonlinearity of C\textsubscript{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 this paper, we investigate nonlinear optical properties of higher fullerenes. We focus on the off-resonant third order 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. The Coulomb interactions are taken into account by the parametrized Ohno potential, $W(r) = 1/\sqrt{(1/U)^2 + (r/r_0 V)^2}$, 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. Based on our results for the optical properties of C\textsubscript{60} and C\textsubscript{70} [10,11], we can assume $V = U/2$. The onsite Coulomb strength is varied within the range $0 \leq U \leq 4t$, $t$ being the hopping integral between nearest neighbor carbon atoms.

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 \( [C_{2v} \text{ by Kikuchi et al’s notation (Ref. 13)}] \) – 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 \( [C'_{2v} \text{ by Kikuchi et al’s notation (Ref. 13)}], D_{2d}-C_{84}, \) 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 \( 1 \times 10^{-12} \) 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 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 $\alpha$ for the three Coulomb interaction strengths are summarized in TABLE I. When $U = 0t$, the power $\alpha$ is about 5. As $U$ increases, $\alpha$ 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$_{84}$ [14]. 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 [15] 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.
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. Lumin. 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. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho and Y. Achiba, Nature 357 (1992) 142.
[14] M. Fanti, G. Orlandi and F. Zerbetto, J. Am. Chem. Soc. 117 (1995) 6101.
[15] H. Huang, G. Gu, S. Yang, J. Fu, P. Yu, G. K. L. Wong and Y. Du, Chem. Phys. Lett. 272 (1997) 427.
TABLE I. Coulomb interaction dependence of the power $\alpha$ where $|\chi^{(3)}(0)| \sim A \cdot N^\alpha$.

| $U$ | $\alpha$ |
|-----|---------|
| 0$t$ | 5.253  |
| 2$t$ | 4.133  |
| 4$t$ | 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: $|\chi^{(3)}| \sim A \cdot N^\alpha$. 

$\chi^{(3)}$