# Enhancements of third-order nonlinear optical response in excited state of the fullerenes $C_{60}$ and $C_{70}$

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Dynamic third-order nonlinear polarizabilities of three optical processes of third-harmonic generation, electric-field-induced second-harmonic generation, and degenerate four-wave mixing have been calculated at the both ground and excited states in $C_{60}$ and $C_{70}$ fullerenes in terms of the sum-over-states formula. The transition moment elements and the transition energies in this formula are obtained using the intermediate neglect of differential overlap and single- and double-excitation configuration interaction method. The calculated third-order polarizabilities show a dispersion behavior with different from ground state and a strong enhancement of third-order nonlinear optical response in the first excited singlet state. The calculated nonresonant susceptibilities $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ of this excited state reach the magnitude of $10^{-10}$ esu for $C_{60}$ and $C_{70}$ films.

## I. INTRODUCTION

The realization of all-optical switching, modulating and computing devices is an important goal in modern optical technology. Nonlinear optical (NLO) materials with large third-order nonlinear susceptibilities are indispensable for such devices, because the magnitude of this quantity strongly influences on the instrument performance. In order to reach the bistable region, for instance, very large NLO susceptibilities of materials are required in optical bistable devices. A strategy in the development of materials with large NLO susceptibilities is the exploration of fullerene systems, as these systems have exceptional optical, physical, and chemical properties, such as thermal and oxidative stability. These and the other exhibiting unique properties have warranted the vast amount of basic and applied research concerning fullerenes and fullerene derivatives.[1–4] In this paper, we expect third-order NLO polarizabilities of the first excited singlet state and explain the origin of dramatic enhancements of excited states for $C_{60}$ and $C_{70}$ fullerenes. We believe that they will be good candidates for use in optical devices due to the facts that the $C_{60}$ and $C_{70}$ films have large third-order NLO susceptibilities and unique thermal and oxidative stability.

## II. SIMPLE DESCRIPTIONS OF COMPUTATIONAL PROCEDURES

The tensor components of the frequency-dependent third-order polarizability $\gamma$ of molecule are obtained by the conventional sum-over-states (SOS) method[5] and an average value of $\gamma$ is calculated from

$$\langle \gamma \rangle = 1/5(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyxx} + \gamma_{yyzz}$$
$$+ \gamma_{zzxx} + \gamma_{zzyy}).$$

Hereafter the mark $\gamma(3\omega)$, $\gamma(2\omega)$, and $\gamma(\omega)$ symbolizes the third-order polarizability of third-harmonic generation (THG) of $\gamma(-3\omega;\omega,\omega,\omega)$, electric-field-induced second-harmonic generation (EFISHG) of $\gamma(-2\omega;\omega,\omega,0)$, and de-

generate four-wave mixing (DFWM) of $\gamma(-\omega;\omega,\omega,-\omega)$, individually. The prefactor $K(-\omega_p;\omega_1,\omega_2,\omega_3)$ in SOS method[5,6] must be taken as the same value in the THG, EFISHG, and DFWM for the static case of an input photon energy (i.e., input frequency) of zero, and it is the relative magnitudes of the ground and excited state nonlinear polarizabilities for each optical process at nonzero frequency.[6] This is due to the fact of that the prefactor $K$ $(-\omega_p;\omega_1,\omega_2,\omega_3)$ depends on distinguishable permutations of the input frequencies and factors arising from the definition of the electric field amplitudes.[5] In the following calculations, we use the same prefactor $K$ in order to make the remark to justify plotting curves for the three types of nonlinear polarizability against common axes. In SOS formula[6] the first summation involves the two-photon allowed states, referred to type-II terms, and the second summation involves four photon volleys between the reference and one-photon-allowed states, referring to type-I terms. In order to obtain a reliable value of $\gamma_{abcd}$, the INDO-SDCI method is employed to calculate the transition energies and dipole moments that are taken as input values. The geometrical structures of $C_{60}$ and $C_{70}$ fullerenes are optimized based on the HF/3-21G level of the *ab initio* method in the program GAUSSIAN 98.[7] The optimized geometrical parameters and atomic parameters listed in Ref. 8 are used to compute the electronic structures. The electron excited states of $C_{60}$ and $C_{70}$ fullerenes are obtained by configuration interactions of all single- and double-excited configurations from the six highest occupied molecular orbitals to the six lowest unoccupied orbitals. This leads to a total of more than 700 calculated states. For the calculation of $\gamma$, we generally truncate the infinite SOS expansion to a finite one over about 120 states after an apparent convergence of $\gamma$ has been reached.

## III. RESULTS AND DISCUSSIONS

Before we investigate excited state enhancements of optical nonlinearities in fullerenes $C_{60}$ and $C_{70}$, we first discuss the third-order nonlinear optical properties based on the cal-
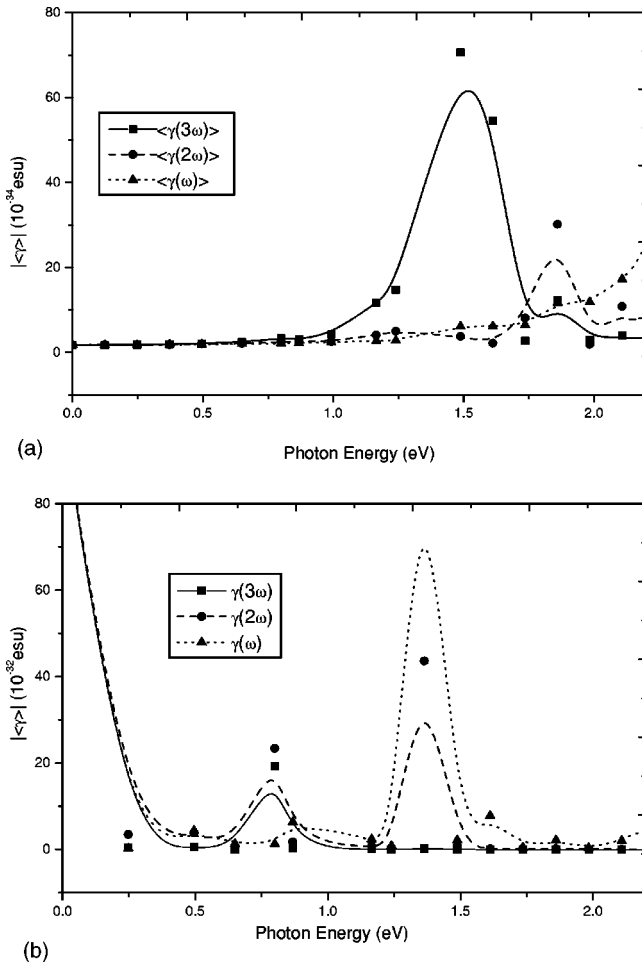
(a)

(b)

FIG. 1. (a) The dynamic third-order polarizabilities at the ground state of $C_{60}$ for different optical processes. (b) The dynamic third-order polarizabilities at the excited state of $C_{60}$ for different optical processes.
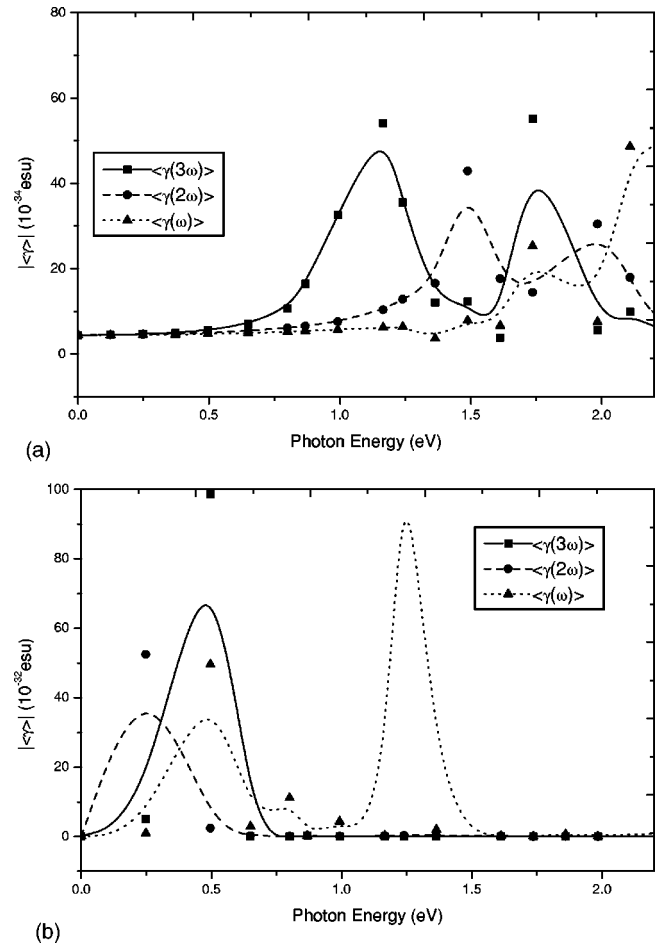


(a)

(b)

FIG. 2. (a) The dynamic third-order polarizabilities at the ground state of $C_{70}$ for different optical processes. (b) The dynamic third-order polarizabilities at the excited state of $C_{70}$ for different optical processes.

culated results at the ground state. Figures 1(a) and 2(a) depict the calculated frequent dependence of absolute values $|\langle\gamma\rangle|$ with different optical physical processes at the ground state, respectively. In the static case where the input photon energy is zero, the absolute values $|\langle\gamma(0)\rangle|$ of the THG, EFISHG, and DFWM processes have the same numbers of $1.776\times10^{-34}$ and $4.441\times10^{-34}$ esu for $C_{60}$ and $C_{70}$, respectively. In the dynamic case, however, when the input energies of $\hbar\omega$ are 0.80, 1.165, and 1.165 eV, the calculated values of $|\langle\gamma(3\omega)\rangle|$, $|\langle\gamma(2\omega)\rangle|$, and $|\langle\gamma(\omega)\rangle|$ are individually 3.357 $\times10^{-34}$, 24.816$\times10^{-34}$, and 8.193$\times10^{-34}$ esu and 10.742 $\times10^{-34}$, 62.448$\times10^{-34}$, and 18.711$\times10^{-34}$ esu for $C_{60}$ and $C_{70}$. Table I lists the calculated $|\langle\gamma\rangle|$ values at three optical processes in typical values of input photon energies. It is shown that the $|\langle\gamma\rangle|$ value is larger for $C_{70}$ than for $C_{60}$ in the same optical process. This is due to the facts that $C_{70}$ with a rugbylike space structure has large dipole moments and $C_{60}$ with a football-like structure has small dipole moments at ground state. The observed values of $\gamma$ in one input frequency have been reported for $C_{60}$ and $C_{70}$[1,19] respectively, and are also listed in Table I. Note that different resonance enhancements take place in different optical processes. As

shown in Figs. 1(a) and 2(a), the first near resonant enhancement appears at about $\hbar\omega=0.70$ eV for the THG process and at about $\hbar\omega=1.05$ eV for the EFISHG or DFWM process. When $\omega_{\text{trans}}-3\omega=0$ or $\omega_{\text{trans}}-2\omega=0$, the first resonance will take place for the THG or DFWM process. Accordingly, from the dispersion curve we can make crude determination of the lowest ultraviolet-visible absorption region localized at about 2.1 eV ($3\times0.70$ or $2\times1.05$ eV) for the fullerenes $C_{60}$ and $C_{70}$. This estimated value is near to the observed value of 2.03 eV of $C_{60}$.[9,10]

To gain a better understanding of the origin of the third-order nonlinear optical response from the calculated results in $C_{60}$ and $C_{70}$ fullerenes, we consider two types of competing third-order virtual excitation processes in determining $\gamma$. The type-I processes are of the form $S_g\rightarrow S_m\rightarrow S_g\rightarrow S_m\rightarrow S_g$, where $S_g$ is the ground state and $S_m$ is a one-photon allowed excited state. The intermediate state is $S_g$ itself, and this process makes a negative contribution to $\gamma$ in the low-frequency region. For examples, the calculated $\langle\gamma(0)\rangle_{\text{I}}$ is $-6.981\times10^{-34}$ esu in the static case, and the calculated dynamic $\langle\gamma(3\omega)\rangle_{\text{I}}$, $\langle\gamma(2\omega)\rangle_{\text{I}}$, and $\langle\gamma(\omega)\rangle_{\text{I}}$ is $-20.139$ $\times10^{-34}$, $-62.931\times10^{-34}$, and $-26.586\times10^{-34}$ esu at an input photon energy of 0.80 eV for $C_{70}$, respectively. For the

TABLE I. The calculated third-order polarizabilities ($|\langle\gamma\rangle|/10^{-34}$ esu) in the different optical processes at ground state of $C_{60}$ and $C_{70}$ molecules.

| Energy (eV) | THG | | EFISHG | | DFWM | |
|---|---|---|---|---|---|---|
| | $C_{60}$ | $C_{70}$ | $C_{60}$ | $C_{70}$ | $C_{60}$ | $C_{70}$ |
| 0.00 | 1.78 | 4.44 | 1.78 | 4.44 | 1.78 | 4.44 |
| 0.65 | 2.52 | 7.04 | 13.19[a] | 32.89[a] | 6.11 | 14.90 |
| 1.165 | 11.78 | 54.16 | 24.82 | 62.45 | 8.19[b] | 18.71 |

[a]The observed values are $(7.5\pm2)\times10^{-34}$ esu and $(1.3\pm0.3)\times10^{-33}$ esu for $C_{60}$ and $C_{70}$ in toluene solution (Ref. 1) respectively.

[b]The observed $\gamma$ value of $2\times10^{-34}$ esu from a third-order susceptibility value of $7\times10^{-12}$ esu for $C_{60}$ at the DFWM optical process (Ref. 19).

type-II processes, $S_g\rightarrow S_m\rightarrow S_n\rightarrow S_m\rightarrow S_g$, the intermediate state $S_n$ is a two-photon-allowed excited state. The obtained results illustrate the positive type-II contributing term in $\gamma$. For instances, the calculated $\langle\gamma(0)\rangle_{II}$ is $3.433\times10^{-34}$ esu in the static case, and the calculated $\langle\gamma(3\omega)\rangle_{II}$, $\langle\gamma(2\omega)\rangle_{II}$, and $\langle\gamma(\omega)\rangle_{II}$ is $9.397\times10^{-34}$, $26.029\times10^{-34}$ and $10.815\times10^{-34}$ esu at an input photon energy of 0.80 eV in $C_{70}$, respectively. Comparing these two processes, we can find that the type-I process makes a larger, negative contribution to $\gamma$ and therefore determines the overall sign of $\gamma$ to be negative. This situation tell us that one-photon allowed excited states make major contributions to the third-order nonlinear polarizabilities in ground state of $C_{60}$ and $C_{70}$ fullerenes.

In the following, we present a theoretical enhancement mechanism for third-order nonlinear processes originating from real population of electronic excited states in $C_{60}$ and $C_{70}$ fullerenes. In experiments, an electron excited state can be generated to use laser pulse at certain wavelength and then populated for times long enough to permit nonresonant measurements.[11–15] Excited-state optical nonlinearities of the $C_{60}$ fullerene and its derivative have been investigated in terms of the pump-probe technique.[16–18] Therefore, when an excited state is populated prior to a measurement, we can define this state as a reference state. In the calculation of the SOS, we select this excited state, usually, the first excited singlet state as the reference state, and the beginning of summation is from this reference state. Figures 1(b) and 2(b) show the frequent dependence of $|\langle\gamma\rangle|$ with different optical

physical processes at the first excited singlet state for $C_{60}$ and $C_{70}$ fullerenes, respectively. Comparing with the obtained results of the ground state shown in Figs. 1(a) and 2(a), we can see that the calculated third-order optical polarizabilities $|\langle\gamma\rangle|$ at the first ($S_1$) excited singlet state of $C_{60}$ and $C_{70}$ are enhanced throughout the considering frequency region. For examples, the calculated $|\langle\gamma(3\omega)\rangle|$, $|\langle\gamma(2\omega)\rangle|$, and $|\langle\gamma(\omega)\rangle|$ at the $S_1$ excited state are $1.927\times10^{-31}$, $1.406\times10^{-30}$, and $3.9251\times10^{-32}$ esu for $C_{60}$ at an input energy of 0.80 eV, respectively. The absolute value $|\langle\gamma\rangle|$ of the $S_1$ excited state is compared with $|\langle\gamma\rangle|$ of the $S_0$ ground state. Throughout the entire calculated frequency range, as shown in Figs. 1 and 2, the $|\langle\gamma\rangle|$ of $S_1$ is significantly larger than that of $S_0$, reaching enhancements as high as a factor of more than 100 for $C_{60}$ and more than 50 for $C_{70}$. Table II gives the calculated $|\langle\gamma(\omega)\rangle|$ values at the DFWM process in an input energy of 1.165 eV for ground and excited states. By comparisons of the calculated results between the $C_{60}$ and $C_{70}$, we can see that there is a small enhancement of the first excited singlet state and a large third-order optical polarizability at the ground state. However, there is a large enhancement of the excited state and a small third-order optical polarizability at the ground state. The dispersion behavior of $|\langle\gamma\rangle|$ at $S_1$ is different from that at $S_0$, and the nonresonant frequent region is smaller at the $S_1$ than at the $S_0$ in the THG, EFISHG, and DFWM processes. Enhancements of excited state of optical nonlinearly in linear conjugate molecule and bacteriochlorophylls[11,12,14] have been observed and the third-order optical susceptibility $\chi^{(3)}$ can be enhanced by more than two orders of magnitude. In terms of an analysis of the obtained results, we can introduce the three principal origins in the enhanced magnitude of nonlinear optical polarizability $|\langle\gamma\rangle|$ of the $S_1$ excited state. First, the transition energies of $\hbar\omega_{mS1}$ between the $S_1$ and intermediate virtual $m$ ($m<120$ in this study) states are all smaller than the transition energies of the $S_0$ ground state excitation processes. Second, many excited states with large transition dipole moments are accessible through the populated $S_1$ state and the $S_m$ excited states. As we know, the smaller transition energies of $\hbar\omega_{mn}$ and larger transition dipole moments of $\mu_{mn}$ cause the individual virtual excitation processes that make up $\gamma$ at the $S_1$ state to be larger than those of $\gamma$ at the $S_0$ state. Third, in contrast to $\gamma$ at $S_0$, which is primarily determined by the type-I terms as mentioned above, $\gamma$ at $S_1$ is composed of a great number of terms that are not only individually larger than those of $\gamma$ at $S_0$ but also have a reduced degree of

TABLE II. The calculated third-order NLO susceptibilities at energy of 1.165 eV in the DFWM process for both ground and first excited singlet states of fullerenes.

| state | N($10^{21}$ cm$^{-3}$) | $f_\omega$ | $|\langle\gamma\rangle|$($10^{-34}$ esu) | $\chi^{(3)}_{cal.}$($10^{-12}$ esu) | $\chi^{(3)}_{obs}$($10^{-12}$ esu) |
|---|---|---|---|---|---|
| $C_{60}$ | | | | | |
| Ground | 1.4416 | 1.4700 | 8.1939 | 5.5158 | 7 (Ref. 19) |
| $S_1$ state | 1.4416 | 1.4700 | 724.08 | 487.42 | |
| $C_{70}$ | | | | | |
| Ground | 1.3989 | 1.9103 | 18.712 | 34.863 | |
| $S_1$ state | 1.3989 | 1.9103 | 82.945 | 154.54 | |

cancellation, or even the same sign between the type-I and -II terms. For example, the calculated $\langle\gamma(\omega)\rangle_\text{I}$ and $\langle\gamma(\omega)\rangle_\text{II}$ values at the first excited singlet state are $0.678\times10^{-32}$ and $6.562\times10^{-32}$ esu at an input energy of 1.165 eV for $C_{60}$, respectively.

In order to compare the calculated values with the available observed values,[19] we calculate the third-order nonlinear optical susceptibility of $C_{60}$ and $C_{70}$ films at the DFWM by the formula

$$\chi^{(3)}(-\omega;\omega,\omega,-\omega)=Nf_\omega^4\langle\gamma(-\omega;\omega,\omega,-\omega)\rangle. \quad (1)$$

Here $N$ is the molecular density number and $f_\omega$ is the local-field correction factor at radiation frequency $\omega$. We note here that the molecular number density $N$ in Eq. (1) is defined as the product of mass density and Avogadro's constant divided by the molar mass. The $N$ values of $C_{60}$ and $C_{70}$ films calculated from the mass density[20,21] and formula mass are listed in Table II. With the assumption of a Lorentz-Lorenz local field,[22] $f_\omega=[n_\omega^2+2]/3=1/[1-(4\pi/3)N\alpha_\omega]$, in which $n_\omega$ and $\alpha_\omega$ are separately the refractive index and the polarizability. Accordingly, the local-field factor $f_\omega$ can be obtained by the calculating first-order microscopic polarizability and described as the interaction between a selected molecule and the surrounding molecules in the film.[23] At an input energy of 1.165 eV, the calculated $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ values at ground and first excited singlet states of $C_{60}$ and $C_{70}$ films are listed in Table II, respectively. It is shown that the excited

state NLO susceptibilities can be enhanced by about two orders of magnitude and that the values reach $10^{-10}$ esu.

## IV. SUMMARY

In this study, we have presented the calculated third-order optical polarizabilities $\gamma$ in the three optical processes at the both ground state and first excited singlet states for the $C_{60}$ and $C_{70}$ fullerenes. We found that the $\gamma$ at an excited state is much larger than that at a ground state and that the nonresonant region of the $\gamma$ at the excited state are all smaller than those at ground state in the THG, EFISHG, and DFWM optical processes. We describe the principal origins in the enhancements of NLO polarizability at excited states. The calculated nonresonance susceptibilities $\chi^{(3)}$ at DFWM process show that the third-order NLO responses have a strong enhancement in excited states and are about $4.87\times10^{-10}$ and $1.54\times10^{-10}$ esu in the first excited singlet state of $C_{60}$ and $C_{70}$ films, respectively.

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