Large non-resonant third-order optical nonlinearities in small C_{60}-derived nanotubes

RUI-HUA XIE (*)
Chemical Physics Theory Group, Department of Chemistry, University of Toronto Toronto, Ontario M5S 3H6, Canada

(ricevuto il 22 Ottobre 1997; approvato il 19 novembre 1977)

Summary. — In this paper, we have theoretically shown that large non-resonant third-order optical nonlinearities could be obtained in small C_{60}-derived nanotubes, which are important in photonic applications.

PACS 42.65.An – Optical susceptibility, hyperpolarizability.
PACS 42.70.Nq – Other nonlinear optical materials; photorefractive and semiconductor materials.
PACS 78.66.Tr – Fullerenes and related materials.
PACS 81.05.Tp – Fullerenes and related materials; diamonds, graphite.

Molecules with large non-resonant third-order optical nonlinearities, characterized by large second-order hyperpolarizability γ, are required for photonic applications [1]. But, the γ magnitudes of most materials needed for third-order effects are usually small. In contrast to the second-order materials for which the basic structure property relations are both relatively well understood and well explored, a comparable level of understanding the third-order ones is only just emerging. Theoretical and experimental studies have shown that polymeric materials are characterized by large third-order optical nonlinearities [1] due to their delocalized π electrons. However, these materials possess hydrogen atoms and are therefore characterized by a residual infrared absorption due to overtones of C-H stretching vibrations, which clearly limits their applications in the infrared (telecommunication window). Fullerenes [2], on the other hand, possess a large number of conjugated π electrons, but are uniquely composed of carbon atoms and therefore do not have any residual infrared absorption that the polymeric materials have. Naturally, these properties will make fullerenes become very exciting nonlinear optical materials for photonic applications. Hence, over these years, the third-order optical nonlinearities of C_{60} and C_{70} have been extensively studied, both theoretically and experimentally [2,3,4,5]. It is found that the non-resonant γ magnitudes for C_{60} or C_{70} are around 10^{-33} esu.

(*) E-mail: rhxie@tikva.chem.utoronto.ca

It is known that the lattice and electronic structures of carbon nanotubes derived from C_{60} greatly change with the increase of their carbon number [2]. So it is interesting to investigate theoretically this effect on the nonlinear optical properties of C_{60}-derived nanotubes. Based on this, in this note, we report our numerical calculation of the non-resonant γ magnitudes of C_{60}-derived nanotubes. Because of the numerical complexity for large tube, we only consider the small tube, which can be described very well by the following Hamiltonian:

$$(1) \qquad H = \sum_{\langle ij\rangle, s} (-t - \alpha y_{ij})(c^{\dagger}_{i,s} c_{j,s} + h.c) + \frac{K}{2} \sum_{\langle ij\rangle} y^2_{i,j} + \\ + U \sum_i c^{\dagger}_{i,\uparrow} c_{i,\uparrow} c^{\dagger}_{i,\downarrow} c_{i,\downarrow} + V \sum_{\langle ij\rangle s, s'} \sum c^{\dagger}_{i,s} c_{i,s} c^{\dagger}_{j,s'} c_{j,s'} ,$$

where t is the hopping integral of the undimerized system; α is the electron-phonon coupling constant; y_{ij} is the change of the bond length between the i-th and j-th atoms; the operator $c_{i,s}$ ($c^{\dagger}_{i,s}$) annihilates (creates) a π electron at the i-th carbon atom with spin s ($s = \uparrow, \downarrow$); K is the spring constant between the adjacent units; U is the usual on-site Coulomb repulsion strength for carbon atom; V is the Coulomb interaction between the nearest and next-nearest carbon atoms; and the sum $\langle ij\rangle$ is taken over the nearest-neighbor pairs.

Within the independent electron approximation and the sum-over-states (SOS) approach, the third-order nonlinear polarizability $\gamma(-3\omega; \omega, \omega, \omega)$ can be expressed by eq.(4) in the work of Shuai and Bredas [5]. Since the ratios between the different components of γ are not known, a spatial average of γ is given by

$$(2) \qquad \gamma_{\mathrm{av}} = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})/5 .$$

In this note, we consider the non-resonant case from the viewpoint of practical applications [1], and only report the static γ magnitudes of small C_{60}-derived nanotubes since these results can reflect our main conclusions.

In the actual calculation, for $C_{60+i\times 10}$ (armchair nanotube [2]), z-axis is taken along the direction from the pentagon at the bottom of this molecule to the pentagon at its top; and for $C_{60+i\times 18}$ (zigzag nanotube [2]), z-axis is taken along the direction from the hexagon at the bottom of this molecule to the hexagon at its top. If the length of every bond is given, the coordinates of every atom will be obtained. However, we find that the γ magnitudes are not sensitive to the small changes of the coordinates of atoms. So, for simplicity, we take the same bond length 1.4225 Å for all molecules, which is the average bond length of C_{70} given by the experiment [6]. In this note, the Coulomb interaction is taken to be $U = 2V = t$, which is not strong. Thus, the effective hopping integral may be taken the same value as that in the free-electron case. Our numerical results have shown that the parameters, t, α and K in eq. (1) do not sensibly depend on the shapes and size of the molecule. So here we take the same parameters as those in C_{60} and C_{70}: $t = 2.5$ eV, $\alpha = 6.31$ eV/Å, and $K = 49.7$ eV/Å^2.

In table I, based upon the electronic structure obtained in the above model, we show the theoretical static γ magnitudes of several C_{60}-derived nanotubes. For C_{60}, it is known that there is a very slight difference between the z and x (or y) components since it is not strictly a sphere [5], whereas table I shows that this difference for C_{60}-derived nanotubes, which contain a large number of carbon atoms, is much

TABLE I. – *The theoretical static* γ (*in* 10^{-33} esu) *tensor components for* C_{70} (*armchair nanotube*), $C_{60+9\times10}$ (*armchair nanotube*), $C_{60+5\times18}$ (*zigzag nanotube*) *and* C_{144} (*uncapped zigzag nanotube*). *The mark # denotes the VEH-SOS theoretical results of* C_{70} *by Shuai and Bredas.*

γ	C_{70}	$C_{70}^{\#}$	$C_{60+9\times10}$	$C_{60+5\times18}$	C_{144}
γ_{xxxx}	0.51	0.5163	1.33	1.448	14.13
γ_{yyyy}	0.51	0.5163	1.33	1.48	14.13
γ_{zzzz}	0.63	0.8165	31.2	27.83	256.68
γ_{xxyy}	0.16	0.1411	0.46	0.5	4.47
γ_{yyzz}	0.31	0.5435	1.94	0.62	13.23
γ_{zzxx}	0.31	0.5435	1.94	0.62	13.23
γ_{av}	0.64	0.8623	8.5	6.86	69.76

pronounced because of their cylindrical shapes. In our numerical calculation, we found that when the carbon number of these nanotubes increases, the interval between the neighboring levels increases and the dipole matrix, at the same time, increases. Thus, their static γ_{av} magnitude may be enhanced by increasing their carbon number. Indeed, table I shows that γ_{av} of $C_{60+9\times10}$ is about 14 times larger than that of C_{70}.

Since π electrons in the fullerene C_n with higher symmetry are more delocalized [2], its static γ magnitude will be larger than that containing identical carbon number but with different symmetry. Now, we define a quantity $\Delta Q = (\sum_i Q_i^2/N - 1)^{1/2}$ to measure the degree of π electron distribution of fullerenes deviating from its homogeneous distribution, where Q_i is the π electron density at the i-th site. Our calculated results show that the corresponding ΔQ values of $C_{60+9\times10}$ and $C_{60+5\times18}$, which have D_{5h} and D_{3h} symmetries [2], respectively, are 0.12 and 0.18. These results mean that π electrons in $C_{60+9\times10}$ are more delocalized than those in $C_{60+5\times18}$. Thus, the static γ_{av} magnitude of $C_{60+9\times10}$, as shown in table I, is bigger than that of $C_{60+5\times18}$.

Experimental and theoretical studies [2] have shown that the caps of carbon nanotubes,in the synthesis of them, may be destroyed partially or completely, and such cap effects greatly influence their geometric and electronic structures, which will also have a large effect on their nonlinear optical properties. Therefore, in the following, we discuss the cap effect on the third-order optical nonlinearities of C_{60}-derived nanotubes. As an example, we study the static γ magnitude of uncapped zigzag nanotube containing 144 carbons. The results are shown in table I. We find that its static γ_{av} magnitude is about 10 times larger than that of capped zigzag nanotube (*i.e.* $C_{60+5\times18}$) containing almost identical carbons. Compared with the symmetry effect discussed above, the cap effect is more obvious. Such results may be explained as follows. It is known that the rather larger nonlinear optical response for C_{60} system [2] is mainly produced by delocalized π electrons as in conjugated polymer chain. However, the three-dimensional character of C_{60} causes severe limitations on its nonlinear optical properties and makes its γ magnitudes become about two orders of magnitude smaller than those of linear polymers containing a similar number of carbon atoms. For a C_{60}-derived nanotube with both caps, a π electron on a site can transfer to the site's three neighbors. Moreover, if both caps of this nanotube are cut, a π electron on the site at the edge of cylinder can only transfer to the site's two neighbors. Naturally, this kind of edge effect will reduce the effective space dimensions of π electrons and thus enhance the static γ magnitude of C_{60}-derived nanotubes.

Previous and present studies have shown that the non-resonant γ magnitude of C_{70} is about 10^{-33} esu, which is several orders of magnitude smaller than those needed in photonic applications [1]. According to above theoretical calculations, we see that the static γ_{av} values of C_{60}-derived nanotubes can be greatly enhanced by increasing their carbon number, *e.g.*, for uncapped zigzag tube containing 144 carbons, the static γ_{av} magnitude is about 10^{-31} esu, which is almost two orders of magnitude larger than that of C_{70}. These imply that C_{60}-derived nanotubes may have potential applications in optoelectronics, all optical-switching devices and integrated optics due to their large non-resonant third-order optical nonlinearities.

Wang and Cheng [3], and Neher *et al.* [4] have reported that the non-resonant γ magnitudes of C_{70} are $(1.3 \pm 0.3) \times 10^{-33}$ esu and $(3.8 \pm 1.1) \times 10^{-33}$ esu at the wavelength 1906 nm and 2000 nm, respectively. We see that our theoretical findings are in agreement with their experimental measurements. In table I, we list the theoretical VEH-SOS results of C_{70} obtained by Shuai and Bredas [5]. Our theoretical findings are also in consistent with theirs. Hence, the above-chosen parameters are reasonable.

In summary, we have theoretically shown that large non-resonant third-order optical nonlinearities could be obtained in small C_{60}-derived nanotubes, which are important in photonic applications.

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