Size and helical symmetry effects on the nonlinear optical properties of chiral carbon nanotubes

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The electronic structures in chiral carbon nanotubes are obtained by using the Su-Schrieffer-Heeger model with the Coulomb interaction included. The periodic boundary condition is applied for the direction of the tubular axis. The third-order polarizabilities of chiral carbon nanotubes are calculated by using the electronic structures obtained. The results indicate that the narrower tube and the tube with higher helical degree have larger polarizability. Also, the metallic tube has larger polarizability than the semiconducting tube. [S0163-1829(99)12815-7]

Recently, a new form of carbon, carbon nanotube, has been synthesized,[1,2] which has a structure like a cylinder made from a graphite sheet. Carbon nanotube not only possesses a very high strength-to-weight ratio but also has fascinating electromagnetic properties.[3,4] Theoretical studies and experimental results have shown that a carbon nanotube can be a good conductor, a semiconductor, or an insulator, depending on its geometric parameters.[5,6]

Polymeric materials are characterized by large optical polarizabilities due to the delocalized π electrons.[7] However, the quasi-one-dimensional conjugated polymers have residual infrared (IR) absorption due to overtones of C-H streching vibrations which limits their applications in the optical communication. Carbon nanotubes, on the other hand, possess a large number of conjugated π electrons but are uniquely composed of carbon atoms, which makes them promising materials applied in photonic devices. Very recently, we calculated the third-order polarizability (γ) spectra of C_{60}-derived nanotubes.[8] We found that the γ value increases with the increase of carbon atom number N. We also found that in the case with similar N, an armchair tube has a larger γ value than a zigzag one. On the other hand, observed carbon nanotubes have various sizes and a majority of them have screw axes and chirality. Therefore, it is interesting to study the size and helical symmetry effects on their nonlinear optical properties in view of their practical application.

The structure of a tube can be described by reference to the graphite sheet in Fig. 1. The lattice point O and the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are the origin and the unit-cell basis vectors of the two-dimensional (2D) graphite sheet, respectively. The real lattice vector $\mathbf{C_h}$ can be expressed by a pair of integers $[n_1,n_2]$ such that $\mathbf{C_h}=n_1\mathbf{a}_1+n_2\mathbf{a}_2$, which defines a different way of rolling up the sheet into a tube, and so each tube can be labeled by the pair of integers $[n_1,n_2]$.

The coordinates of carbon atoms in a chiral carbon nanotube can be obtained by using the corresponding rotational and helical symmetry operators.[9,10] This is done by first introducing a cylinder with a radius $r=|\mathbf{C_h}|/2\pi$. The atoms 1 and 2 in Fig. 1, which locate at $\mathbf{d}=(\mathbf{a_1}+\mathbf{a_2})/3$ and $2\mathbf{d}$, re-

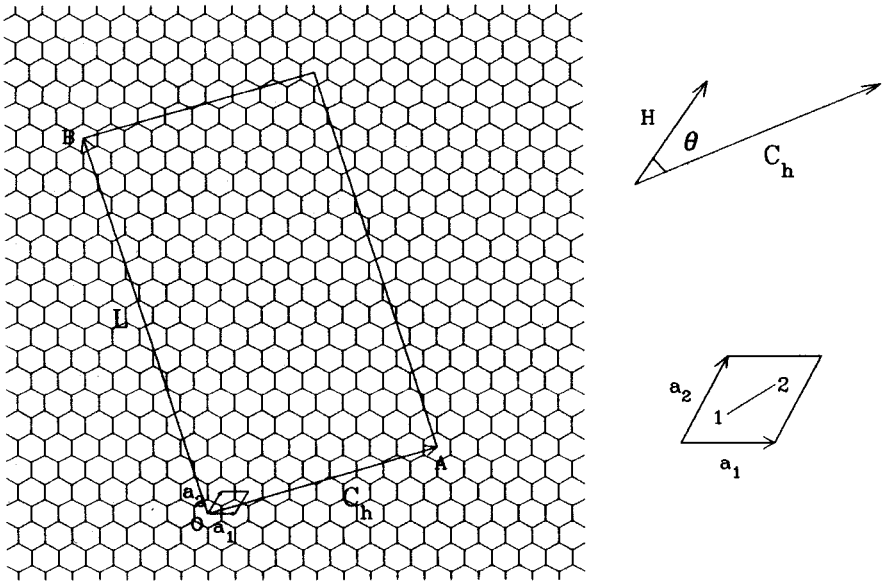

FIG. 1. Carbon nanotube is made by rolling a graphite sheet. The helical degree is described by θ.

spectively, can be mapped to the surface of this cylinder. In the case where n_1 and n_2 have no common divisor, the other atoms of the tube can be obtained by repeating operation of a single screw operation $S(h,\alpha)$ on points $1'$ and $2'$ obtained from the mapping of the atom 1 and 2, where $S(h,\alpha)$ is determined by a real lattice vector $\mathbf{H}=p_1\mathbf{a_1}+p_2\mathbf{a_2}$ in the honeycomb lattice. The pair of integers $[p_1,p_2]$ is the solution of $p_2n_1-p_1n_2=1$ with $p_1\geqslant 0$, which yields the minimum value of $|\mathbf{H}|$. After finding $\mathbf{H}$, one gets $\alpha=2\pi(\mathbf{H}\cdot\mathbf{C_h})/|\mathbf{C_h}|^2$ and $h=|\mathbf{H}\times\mathbf{C_h}|/|\mathbf{C_h}|$. The helical degree is described by $\theta=\arccos(\mathbf{H}\cdot\mathbf{C_h}/|\mathbf{H}||\mathbf{C_h}|)$. It is easy to see that in the case where n_1 and n_2 have no common divisor, a carbon nanotube can be approximately modeled as a structure where all carbon atoms are situated along a base helix wrapped around the surface of a cylinder with a wrapping angle θ. In the case where n_1 and n_2 have the largest common divisor m, a tube (n_1,n_2) can be approximately modeled as a structure where atoms are situated along m base helices wrapped around the surface of a cylinder.

In this paper, we study tubes with finite atom numbers. In such a case, the tube edge effects cannot be neglected. A finite tube with one or several unit cells is open with a row of dangling bonds at each end. So an atom at an edge site may have fewer than three neighbors. On the other hand, for the most real tubes, the tube length is long enough to neglect the edge effects. Taking these into account, we apply periodic boundary condition for the tube axis, and each carbon atom at the end of finite tube can still find its three neighbors by imagining that the two ends of the tube are connected. Before we do so, we should define a unit cell along the tube axis. In Fig. 1, $\mathbf{C_h}$ and $\mathbf{L}$ construct the basis vectors of the unit cell, where $\mathbf{L}=\mathbf{OB}$ and B is the first lattice point of the 2D graphitic sheet through which a line through O and perpendicular to $\mathbf{C_h}$ passes. The length of $\mathbf{L}$ is $\sqrt{3}|\mathbf{C_h}|/m$ if (n_1-n_2) is not a multiple of $3m$ and it is $|\mathbf{C_h}|/m$ if (n_1-n_2) is a multiple of $3m$.[10] The atom number per unit cell of a chiral tube $[n_1,n_2]$ is then equal to $4(n_1^2+n_2^2+n_1n_2)/m$ if (n_1-n_2) is not a multiple of $3m$ and $4(n_1^2+n_2^2+n_1n_2)/3m$ if (n_1-n_2) is a multiple of $3m$.[10]

The Su-Schrieffer-Heeger (SSH) model has been successfully applied to describe conducting polymer, C_{60}, C_{70}, and tubes.[11–13] By including the Coulomb interaction, the SSH model can well describe the optical properties of C_{70}.[8] In this paper, we further use it to study the γ spectra of the chiral carbon nanotube. The SSH model including the Coulomb interaction can be written as[8,11]

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

where $c_{i,s}$ is an annihilation operator of a π electron, t is the hopping integral of the ideal undimerized system, α is the electron-phonon couping, and y_{ij} is the change of the bond length between the ith and jth atoms. The second term is the elastic energy of the lattice and the quantity K is the spring constant. The sum $\langle ij\rangle$ is taken over the nearest-neighbor pairs. The third and fourth terms are the on-site and the nearest-neighbor site Coulomb interaction, respectively. After Hartree-Fock decoupling, Eq. (1) is transformed into

$$H=\sum_{\langle ij\rangle}\sum_{s}(-t-\alpha y_{ij})(c_{i,s}^{\dagger}c_{j,s}+\text{H.c.})+\frac{K}{2}\sum_{\langle ij\rangle}y_{ij}^2+U\sum_i\left(\sum_s\rho_{i,s}c_{i,s}^{\dagger}c_{i,s}-\rho_{i,\uparrow}\rho_{i,\downarrow}\right)+V\sum_{\langle ij\rangle,s}\left(\sum_{s'}\rho_{j,s'}c_{i,s}^{\dagger}c_{i,s}-\rho_{i,s}\sum_{s'}\rho_{j,s'}-\langle c_{i,s}^{\dagger}c_{j,s}\rangle c_{i,s}^{\dagger}c_{j,s}+\langle c_{i,s}^{\dagger}c_{j,s}\rangle^2\right), \tag{2}$$

where $\rho_{i,s}=\langle c_{i,s}^{\dagger}c_{i,s}\rangle$ is the electron density at the ith site with spin s. Equation (2) is solved by the adiabatic approximation for phonons. The Schrödinger equation for the π electron is

$$\epsilon_k Z_{k,s}(i)=\sum_j(-t-\alpha y_{ij}-V\langle c_{i,s}^{\dagger}c_{j,s}\rangle)Z_{k,s}(j)+\left(U\rho_{i,s}+V\sum_{j,s'}\rho_{j,s'}\right)Z_{k,s}(i), \tag{3}$$

where ϵ_k and $Z_{k,s}$ are the single-electron eigenvalue and eigenfunction, respectively. The self-consistency equation for the lattice is

$$y_{ij}=\left(\frac{2\alpha}{K}\right)\sum_{k,s}{}'Z_{k,s}(i)Z_{k,s}(j)-\frac{1}{N_b}\sum_{\langle mn\rangle}\sum_{k,s}{}'\left(\frac{2\alpha}{K}\right)Z_{k,s}(m)Z_{k,s}(n), \tag{4}$$

where the prime means the sum over the occupied states, the last term is due to the constraint $\Sigma_{\langle ij\rangle}y_{ij}=0$, and $N_b=3N/2$ is the number of π bonds. Through Eqs. (3) and (4), ϵ_k and $Z_{k,s}$ can be obtained self-consistently.

Within the sum-over-states method, the third-order polarizability $\gamma(-3\omega;\omega,\omega,\omega)$ has been expressed in Ref. 14. In the actual calculation, we include a lifetime broadening factor η in the denominator and is taken to be 1.6×10^{-2} eV. The spatial average of γ is taken as $\gamma_{\text{av}}=(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\gamma_{xxyy}+2\gamma_{yyzz}+2\gamma_{zzxx})/5$.

Based upon the electronic structures obtained, we calculate the third-order polarizabilities of chiral carbon nanotubes. In the actual calculation, the bond length of graphite sheet, a is taken as 0.142 nm, which is the experimental value for crystalline graphite. In our numerical calculation, the parameters in Eq. (1) are taken as $t=2.5$ eV, $\alpha=6.31$ eV/Å, $K=49.7$ eV/Å^2, and $U=2V=t$.

We take $(n_1,n_2)=(7,3)$ and $(n_1,n_2)=(14,6)$ to study the size effects on the γ spectrum. For both tubes, n_1-n_2 is not a multiple of 3. So they are semiconducting tubes. The diameter of the (7,3) tube is about 0.699 nm and that of the (14,6) tube is about 1.398 nm. The atom number per unit cell is 316 for the (7,3) tube and 632 for the (14,6) tube. We

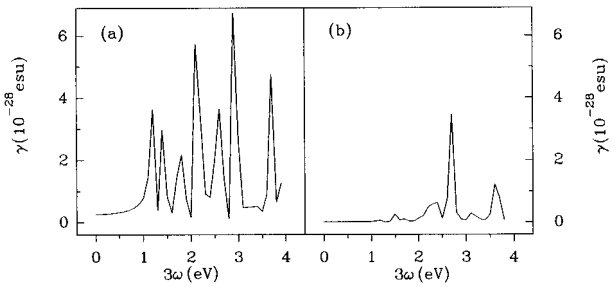

FIG. 2. The γ spectra for (a) (7,3) tube and (b) (14,6) tube. The atom numbers of the tubes are 632.

study tubes with $N=632$. It is equivalent to take two unit cells for the (7,3) tube and one unit cell for the (14,6) tube. The energy gaps of (7,3) and (14,6) tubes are about 1.0 eV and 0.5 eV, respectively. Because the energy gaps for both tubes saturate at $N\sim600$, the large gaps remain when $N\rightarrow\infty$. Obviously, the energy gap decreases with the diameter increasing, which is in agreement with the result of Ref. 9.

Figures 2(a) and 2(b) show γ spectra for (7,3) and (14,6) tubes, respectively. The static γ values for (7,3) and (14,6) tubes are 2.60×10^{-29} esu and 5.85×10^{-31} esu, respectively. The static γ value of the (7,3) tube is about 44 times larger than that of the (14,6) tube. The first peak in Fig. 2(a) is located at about 1.2 eV and the corresponding value is about 3.62×10^{-28} esu. The first peak in Fig. 2(b) is located at about 0.7 eV and the corresponding value is about 2.17×10^{-30} esu. The first peaks in Fig. 2 are caused by a three-photon resonance between two energy levels with one in the conduction band and the other in the valence band. The highest peak in Fig. 2(a) is located at $3\omega\sim2.9$ eV and its value is about 6.74×10^{-28} esu. In Fig. 2(b) it is located at $3\omega\sim2.7$ eV and its value is about 3.46×10^{-28} esu. Comparing Fig. 2(a) with 2(b), it is seen that Fig. 2(a) possesses more larger peaks.

The diameter of the (14,6) tube is two times larger than that of the (7,3) tube. With the increase of diameter the 1D tube will gradually become a 2D graphite sheet. On the other hand, the nonlinearity will decrease with the increasing of space dimension. For an example, 3D C_{60} possesses smaller γ values than 1D conducting polymer with the same atom number. From the (7,3) tube to the (14,6) tube, the space dimension increases. So the (14,6) tube possesses smaller γ values than the (7,3) tube. It is natural to expect that the narrower the carbon tube, the larger the γ value.

The helical symmetry effects on the optical properties of chiral tubes can be seen by comparing the γ spectra of the (6,5) tube with that of the (9,1) tube. Both of the (6,5) and (9,1) tubes have the same diameter, which is about 0.750 nm. They also have the same atom number per unit cell, which is 364. Moreover, both of them are semiconducting tubes. The difference between them is that the helical degree of the (6,5) tube is $\theta\approx3°$ and that of the (9,1) tube is $\theta\approx0.6°$. (6,5) and (9,1) tubes can be approximately modeled as Figs. 3(a) and 3(b), respectively. It is seen that the atoms of the (6,5) tube situate along a more straight line. This can also be seen by the following facts. In the case with the same N, (6,5) and (9,1) tubes have the same height but the length of the base helix of the (6,5) tube is shorter than that of the (9,1) tube. For example, in the present case with $N=364$, the height of

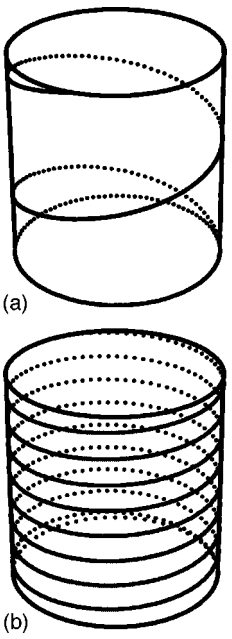

FIG. 3. Schematic of the geometry for (a) (6,5) tube and (b) (9,1) tube.

both (6,5) and (9,1) tubes is about 4.1 nm but the length of the base helix of the (6,5) tube is about 77.8 nm and that of the (9,1) tube is about 384.0 nm. The fact that the atoms of the (6,5) tube situate along a more straight line indicates that the (6,5) tube has lower space dimension. So one may expect that the (6,5) tube possesses a larger γ value. Indeed, this can be seen by comparing Figs. 4(a) with 4(b). Figures 4(a) and 4(b) are the γ spectra of (6,5) and (9,1) tubes, respectively. Although the two tubes have almost the same values for the highest peaks, the (6,5) tube has larger static and main peak values. The static γ values for (6,5) and (9,1) tubes are 2.31×10^{-30} esu and 0.52×10^{-30} esu, respectively.

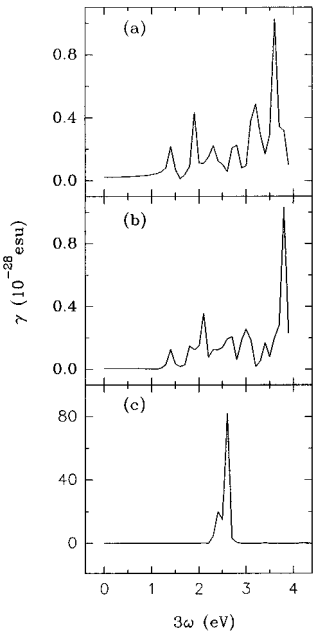

FIG. 4. The γ spectra for (a) (6,5) tube, (b) (9,1) tube, and (c) (7,4) tube.

For two tubes with the same diameter, atom number, helical degree, and the largest common divisor between n_1 and n_2, the only difference between them is that one is a semiconducting tube and the other is a metallic one. What about the difference between their γ spectra? For a semiconducting tube a large energy gap remains when $N \rightarrow \infty$, whereas the energy gap approaches zero for a metallic tube when $N \rightarrow \infty$. Therefore, we expect that if the other conditions are the same, a metallic tube should possess a larger γ value than a semiconducting one. This can be seen by comparing the γ spectrum of the (9,1) tube with that of the (7,4) one. The two tubes have almost the same diameter, which is about 0.750 nm. The helical degree of the (9,1) tube is about $\theta \sim 0.6°$ and that of the (7,4) tube is about $\theta \sim 0.7°$. So, they have almost the same helical degree. The atom number per unit cell of the (9,1) tube is 364 and that of the (7,4) tube is 374. In this paper, we studied both tubes with one unit cell. So, the atom numbers between them are also almost the same. However, the (7,4) tube is metallic and the (9,1) tube is semiconducting. The γ spectra for them are shown in Figs. 4(b) and 4(c), respectively. From them, it is seen that the (7,4) tube possesses higher peak γ values than that of the (9,1) tube. Actually, the static γ value of the (7,4) tube is 2.30×10^{-30} esu, i.e., about four times larger than that of the (9,1) tube. The largest γ value of the (7,4) tube is about 82 times larger than that of the (9,1) tube.

In summary, we study the diameter and helical symmetry effects on the nonlinear optical properties of chiral carbon nanotubes. In detail, we find that the narrower the tube and the higher the helical degree, the larger the nonlinearity of the tube. Also, the metallic tube favors larger γ values. From our numerical results, it is clear that the γ value of the carbon nanotube can reach the corresponding value of the conducting polymer, and so the nanotube is a promising nonlinear optical material with no additional residual infrared absorption due to overtones of C-H streching vibrations.

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[1] T. W. Ebbesen, Annu. Rev. Mater. Sci. **24**, 235 (1994); Phys. Today **49** (6), 26 (1996); M. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996); A. Maiti, C. J. Brabec, and J. Berbholc, Phys. Rev. B **55**, R6097 (1997).

[2] S. Iijima and T. Ichihashi, Nature (London) **363**, 603 (1993); D. S. Bethune *et al.*, *ibid.* **363**, 605 (1993); S. Seraphin and D. Zhou, Appl. Phys. Lett. **64**, 181 (1994); J. M. Lambert *et al.*, Chem. Phys. Lett. **226**, 364 (1994); Y. Saito *et al.*, *ibid.* **236**, 419 (1995); A. Thess *et al.*, Science **273**, 483 (1996).

[3] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature (London) **381**, 678 (1996).

[4] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **78**, 1932 (1997); S. N. Song *et al.*, *ibid.* **72**, 697 (1994).

[5] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. **68**, 631 (1992); X. Blase, L. X. Benedict, E. L. Shirley, and S. G. Louie, *ibid.* **72**, 1878 (1994).

[6] T. W. Ebbesen, H. J. Lezee, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, Nature (London) **382**, 54 (1996).

[7] J. Messier, F. Kajzar, and P. N. Prasad, *Organic Molecule for Nonlinear Optics and Photonics* (Kluwer Academic, Dordrecht, 1991).

[8] J. Jiang, Jinming Dong, X. Wan, and D. Y. Xing, J. Phys. B **31**, 3079 (1998).

[9] C. T. White, D. H. Robertson, and J. W. Mintmire, Phys. Rev. B **47**, 5485 (1993).

[10] R. A. Jishi, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **47**, 16 671 (1993); R. A. Jishi, L. Venkataraman, M. Dresselhaus, and G. Dresselhaus, *ibid.* **51**, 11 176 (1995).

[11] K. Harigaya, J. Phys.: Condens. Matter **3**, 8855 (1991).

[12] K. Harigaya and S. Abe, Phys. Rev. B **49**, 16 746 (1994).

[13] K. Harigaya and M. Fujita, Phys. Rev. B **47**, 16 563 (1992).

[14] J. Dong *et al.*, Phys. Rev. B **52**, 9066 (1995).