Optical third-harmonic generation from an array of aligned carbon nanotubes with randomly distributed diameters

Vl.A. Margulis\textsuperscript{a,*}, E.A. Gaiduk\textsuperscript{b}, E.N. Zhidkin\textsuperscript{a}

\textsuperscript{a}Department of Physics, N.P. Ogarev Mordovian State University, Saransk 430000, Russia
\textsuperscript{b}Department of Chemistry, N.P. Ogarev Mordovian State University, Saransk 430000, Russia

Received 8 April 2000; accepted 21 August 2000

Abstract

The optical susceptibility for third-harmonic generation (THG) from an array of aligned carbon nanotubes (CNs) is theoretically studied, taking into account the diameter distribution of CNs. The average THG susceptibility is calculated for three different types of distribution of CNs: Gaussian, rectangular and triangular ones. The results clearly demonstrate a strong broadening, intensity decrease, and red shift of the main three-photon resonant peak in the THG spectrum. It is shown that, in spite of the overall suppression of the average THG intensity, the amplitude of the peak strongly enhances with an increase of the average radius $R$ of CNs in a sample achieving record values up to $\sim 10^{-4}$ e.s.u. at $R_{av} = 5.2$ nm for a typically occurring normal distribution of CNs. The enhancement of the height of the peak is accompanied by the shift of the top of the peak towards lower frequencies. Both the resonance frequency and magnitude of enhancement are found to be dependent on the type of distribution of CNs. Our results thus indicate the possibility of using THG measurement as an experimental tool to extract information about the prevailing type of CN distribution in a sample. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Band structure; Graphite; Carbon nanotubes; Optoelectronic properties

1. Introduction

Carbon nanotubes (CNs) display a number of properties typical of the realms of one-dimensional physics (for recent reviews of the field, see, e.g. [1–5]). In particular, theoretical calculations show that the quantum one-dimensional confinement of the electrons in CNs leads to enhanced non-linear optical effects [6–11]. However, to our knowledge, no measurement of non-linear optical coefficients has yet been reported for CN materials, probably because, until recently, it has been difficult to obtain aligned CN arrays suitable to meet the phase-matching requirements in frequency mixing experiments, with collinear and polarized parallel to the tube axes pump and probe pulses. Meanwhile, considerable progress has recently been made in the synthesis of good-quality samples of well-aligned CNs with a rather narrow diameter distribution [12–19]. This important advance opens up the possibility of exploring the non-linear optical properties of CNs and of thereby obtaining reliable results. In this connection, the question arises as to how the diameter distribution of CNs, which is inevitable in many experiments, affects the nonlinear optical characteristics of realistic CN samples. Based on qualitative considerations, a particularly strong influence of the dispersion of the CN circumference length on the resonant structures in non-linear optical spectra would be expected. The aim of this paper is to quantitatively investigate the effect...
of randomly distributed diameters of CNs on the optical susceptibility of the third-harmonic generation (THG) process, that is, the production of light of frequency 3\omega from incident radiation of frequency \omega. The calculated spectrum of optical THG from an array of mono-sized and aligned single-wall CNs has been provided in our earlier works [6,8].

The paper is organized as follows. In the next section we describe the theoretical formulation, followed by analytical results for average THG susceptibility. The numerical results are given and discussed in Section 3 and the conclusions are summarized in the final section.

2. Model and calculation

We shall consider an array of aligned CNs with randomly distributed diameters. As is well known, the structure of CNs depends on their size. According to experimental observations, very small CNs (with a radius \(R < 10 \text{ Å}\)) are single-walled and are formed from a graphene sheet that is rolled up into a long cylinder. Each CN of this type is characterized by a pair of integers \((n_1, n_2)\), which specify the tubule radius \(R = (a_0 / 2 \pi \kappa n_1^2 + n_2^2 - n_1 n_2)^{1/2}\) and the chiral angle \(0 = \tan^{-1}[\sqrt{3} n_2 / (2 n_1 - n_2)]\), where \(a_0 = \sqrt{3} d_0\) is the graphite lattice constant, \(d_0 = 1.42 \text{ Å}\) being the near-neighbour carbon atom separation on the graphite plane. The CNs larger than 10 Å in radius have a multiwall structure, resembling either a scroll or a ‘Russian doll’. Since the interaction between the adjacent layers in multiwall CNs is weak, such tubes can be simulated by an ensemble of diameter-distributed single-wall CNs. Then the system we consider here may be characterized by the statistical distribution function over the CN radii \(f(R)\), and we can compute the average THG susceptibility of interest, \(\chi^{(3)}_{abγδ}^{\text{THG}}\) (in this case, a fourth-rank susceptibility tensor), as:

\[
\langle \chi^{(3)}_{abγδ} (-3ω; ω, ω, ω) \rangle = \int \chi^{(3)}_{abγδ} (-3ω; ω, ω, ω) f(R) dR
\]

where the integration extends over all accessible values of radius \(R\).

The explicit form of the function \(f(R)\) depends on the conditions of the synthesis of CN arrays, and therefore it is not known a priori. As a first approach to exploring the effect of random distribution ofCNs, we consider three types of distribution, which involve most plausible experimental situations [19,20]. The first is the Gaussian distribution of width \(σ\) around the average radius \(R_{av}\). In this case, which corresponds to the usually well-justified assumption that physical variables in complex systems are normally distributed, we have:

\[
f(R) = \frac{1}{\sqrt{2\pi}σ} \exp\left\{ -\frac{(R - R_{av})^2}{2σ^2} \right\}
\]

(2)

The second is the rectangular distribution realized in experimental situations where the average number of layers in multiwall CNs does not depend on \(R\) and single-wall CNs are uniformly distributed over the interval \([R_{\text{min}}, R_{\text{max}}]\), \(R_{\text{min}}\) and \(R_{\text{max}}\) being the minimum and maximum radii of CNs in a sample, respectively. Then:

\[
f(R) = \begin{cases} 
\left(\frac{R_{\text{max}} - R_{\text{min}}}{\sqrt{3}}\right)^{-1}, & R_{\text{min}} \leq R \leq R_{\text{max}} \\
0, & R < R_{\text{min}}, R > R_{\text{max}}
\end{cases}
\]

(3)

with \(R_{av} = (R_{\text{min}} + R_{\text{max}}) / 2\).

Finally, the third type of distribution occurs when the average number of layers in multiwall CNs increases with the increasing radius of the outermost shell of the CNs. It implies that the number of tubes for which the radius is smaller than \(R_{av}\) prevails in a sample. In this case the distribution \(f(R)\) differs from normal and is asymmetric with respect to \(R_{av}\). The probability density corresponding to an extreme case of such a distribution has a triangular form:

\[
f(R) = \begin{cases} 
\frac{2(R_{\text{max}} - R_{\text{min}})}{\sqrt{3}}^2, & R_{\text{min}} \leq R \leq R_{\text{max}} \\
\times (R_{\text{max}} - R), & R < R_{\text{min}}, R > R_{\text{max}}
\end{cases}
\]

(4)

This formula is based on the additional assumption that, irrespective of the number of layers in a multiwall CN, the radius of its innermost shell is always equal to \(R_{\text{min}}\). It is easy to show that in this case \(R_{av} = (2R_{\text{min}} + R_{\text{max}}) / 3\).

To proceed further, we need an explicit expression for the susceptibility tensor appearing in the right-hand side of Eq. (1). We assume that all the light waves involved are polarized in the direction of the CN axes (we choose it as the x-axis). In this case we ask for the completely diagonal component of the above mentioned tensor \(\chi^{(3)}_{XXHH}(−3ω; ω, ω, ω)\), which we shall designate further as \(\chi^{(3)}_{\text{THG}}(ω)\). In our previous paper [8] the closed-form expression for \(\chi^{(3)}_{\text{THG}}(ω)\) has already been found, and making use of this, it is easy to obtain the following results for the average susceptibility in the low-frequency limit (\(ω \rightarrow 0\)):

(a) For the Gaussian distribution,

\[
\langle \chi^{(3)}(0) \rangle_{\text{Gauss}} = \chi^{(3)}(0)
\times \left[ 1 + 6\left(\frac{σ}{R_{av}}\right)^2 + 3\left(\frac{σ}{R_{av}}\right)^4 \right]
\]

(5)
(b) For the rectangular distribution,  
\[
\left\langle \chi^{(3)}(0) \right\rangle_{\text{rect}} = \frac{1}{5} \chi^{(3)}_{\text{av}}(0)
\times \left[ \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^4 + 3 \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^3 \frac{R_{\text{min}}}{R_{\text{av}}} \right]
\times \left[ \frac{R_{\text{max}}}{R_{\text{av}}} \right]^2 \left( \frac{R_{\text{min}}}{R_{\text{av}}} \right)^2
\times \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^3 \frac{R_{\text{min}}}{R_{\text{av}}} \right]^3
\times \left( \frac{R_{\text{min}}}{R_{\text{av}}} \right)^4 \right)
\]

(c) For the triangular distribution,  
\[
\left\langle \chi^{(3)}(0) \right\rangle_{\text{triang}} \left[ \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^4 + 3 \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^3 \frac{R_{\text{min}}}{R_{\text{av}}} \right]
\times \left[ \frac{R_{\text{max}}}{R_{\text{av}}} \right]^2 \left( \frac{R_{\text{min}}}{R_{\text{av}}} \right)^2
\times \left( \frac{R_{\text{max}}}{R_{\text{av}}} \right)^3 \frac{R_{\text{min}}}{R_{\text{av}}} \right]^3
\times \left( \frac{R_{\text{min}}}{R_{\text{av}}} \right)^4 \right]
\]

where we have introduced the quantity  
\[
\chi^{(3)}_{\text{av}}(0) = \frac{4}{5} \frac{(3eR_{\text{av}})^4}{\pi^2 \gamma^3}
\]

by analogy with the expression obtained in [6–8] for the low-frequency third-order susceptibility of an ensemble of mono-sized single-wall CNs. In Eq. (8), \( \gamma \) is the electron charge, and \( \gamma \) is the \( \mathbf{k} \mathbf{p} \) interaction parameter linked with the resonance integral \( t_0 = -3.03 \text{ eV} \) [21–24] of the tight-binding method via the relation \( \gamma = \sqrt{3}|t_0|d_{0}/2 \). For estimate we set \( \sigma = 0.3R_{\text{av}} \), \( R_{\text{min}} = 0.5R_{\text{av}} \), and \( R_{\text{max}} = 1.5R_{\text{av}} \) (for the rectangular distribution) and \( R_{\text{max}} = 2R_{\text{av}} \) (for the triangular distribution). Eqs. (5)–(7) then yield:  
\[
\left\langle \chi^{(3)}(0) \right\rangle_{\text{Gauss}} = 1.56 \chi^{(3)}_{\text{av}}(0),
\left\langle \chi^{(3)}(0) \right\rangle_{\text{rect}} = 1.51 \chi^{(3)}_{\text{av}}(0),
\left\langle \chi^{(3)}(0) \right\rangle_{\text{triang}} = 1.89 \chi^{(3)}_{\text{av}}(0)
\]

Hence, for the distributions given above, the following hierarchy of the non-resonant susceptibility values takes place:  
\[
\left\langle \chi^{(3)}(0) \right\rangle_{\text{triang}} > \left\langle \chi^{(3)}(0) \right\rangle_{\text{Gauss}} > \left\langle \chi^{(3)}(0) \right\rangle_{\text{rect}}
\]

By using Eqs. (1)–(4) and the formula for \( \chi^{(3)}_{\text{THG}}(\omega) \) given in [8], we can evaluate the spectral behaviour of the average THG susceptibility. The calculation is straightforward, but tedious, and we simply quote the result:  
\[
\left\langle \chi^{(3)}_{\text{THG}}(\omega) \right\rangle = \frac{45}{25} \chi^{(3)}_{\text{av}}(0) \left[ \delta_{r,1} - (1 - \delta_{r,1}) \frac{h \Gamma}{(\Delta_g)^{2\chi}} \right]
\]

where the subscript \( r = 1,2 \) indexes the real \( (r = 1) \) and imaginary \( (r = 2) \) parts of the susceptibility, \( \delta_{r,1} \) is the Kronecker delta symbol, \( \Gamma \) is the phenomenological damping constant of the excited electron states introduced to avoid artificial divergence of the susceptibility, \( (\Delta_g)^{2\chi} = |t_0|d_0/R_{\text{av}} \) is the magnitude of the band gap in the \( \pi \)-electron spectrum of CNs at \( R = R_{\text{av}} \), and the function \( \Phi_r(\delta, z) \) describing the frequency-dependence of the THG is expressed as:  
\[
\Phi_r(\delta, z) = F_r(\delta, z) + F_r(\delta, -z)
\]

with  
\[
F_r(\delta, z) = \frac{1}{16} \left[ Q_r(\delta, z) - 9Q_r(\delta, 3z) \right]
\]

\[
= \frac{1}{9} \left[ 23Q_r(\delta, z) - 512Q_r(\delta, 3z) \right]
\]

\[
+ 405Q_r(\delta, 3z)
\]

\[
- r \left[ \frac{1}{3} Q_r(\delta, z) - 63s_r(\delta, 3z) \right]
\]

where the functions \( Q_r(\delta, pz) \) at different values of \( r \) and \( p = 1,2,3 \) are given by:  
\[
Q_1(\delta, pz) = I_{1042}(\delta, pz);  
Q_2(\delta, pz) = I_{1043}(\delta, pz)  
Q_3(\delta, pz) = I_{1044}(\delta, pz);  
Q_4(\delta, pz) = I_{1044}(\delta, pz)  
Q_5(\delta, pz) = I_{1238}(\delta, pz) - 51I_{1032}(\delta, pz)  
Q_6(\delta, pz) = I_{1131}(\delta, pz)
\]

and the function \( I_{klmn}^{st}(\delta, pz) \) is defined as  
\[
I_{klmn}^{st}(\delta, pz) = \int_0^{+\infty} \left[ x^2 + y^2 \right]^k A^k(pz; x, y) \times B^{l+l}(\delta, pz; x, y) C^{m+m}(x) D^{n+n}(x)
\times f(y)dy
\]
Here the dimensionless variable of integration \( y = R/R_{av} \), and the following notations are used:

\[
A(p_z;x,y) = 1 + p_2y + (1 - p_2)y x^2
\]  
\[B(\delta,p_z;x,y) = [A^2(p_z;x,y) + \delta^2 y^2 D^2(x)]^{-1}
\]  
\[C(x) = (1 + x^2)^{-1}; \quad D(x) = 1 - x^2
\]

Formally, the above mentioned expressions for \( \langle \chi^{(3)}(\omega) \rangle \) are valid only for an array of CNs fully aligned with each other and with the polarization vector of the light waves. Experimentally, such a situation can be realized, for example in CN thin films investigated in [12]. However, it should be expected that the results obtained above will also be applicable (at least by the order of magnitude) in the case of weak disorientation of the CN symmetry axes. This statement is supported by the calculation of the static polarizability of CNs in a randomly oriented electric field [25]. The results obtained in [25] show that the electric field-induced dipole moment of an individual CN is directed mainly along its symmetry axis.

3. Numerical results and discussion

We now present the frequency dependence of the average susceptibility \( \langle \chi^{(3)}_{THG}(\omega) \rangle \) numerically calculated on the basis of the above-mentioned equations. The calculations are performed for three types of ensembles of diameter-distributed CNs (see Eqs. (2)–(4)), and also for an ensemble of identical single-wall zigzag CNs (16,0) with the radius \( R_0 = 6.26 \) Å, the latter ensemble being described by the distribution \( f(R) \) in the form of the Dirac delta-function \( \delta(R - R_0) \). In order to make the comparison of the results for various distributions more clear, it is convenient to choose the value of \( R_{av} \) also to be equal to 6.26 Å. The double integrals (17) appearing in Eqs. (13)–(16) are calculated using the Simpson formula. For the time being, there are no experimental data available on the damping factor \( \Gamma \), and therefore we have used the broadening parameter \( h \Gamma = 0.01 \) eV, as set by the lattice relaxation processes theoretically studied by Jishi et al. [26].

The real and imaginary parts of the susceptibility \( \langle \chi^{(3)}_{THG}(\omega) \rangle \) averaged over CN radii are plotted in Fig. 1a,b as functions of the dimensionless photon energy \( h \omega/(\Delta_{g})_{av} \). In Fig. 2 we show the absolute magnitude of the average THG susceptibility vs. \( h \omega/(\Delta_{g})_{av} \).

The detailed analysis of the spectra of the above-mentioned quantities for an ensemble of identical CNs (see curves 4 in Figs. 1 and 2) is given in our previous papers [6,8], and therefore we do not repeat it here. We only point out that in this case a most prominent feature of the THG spectrum is the high and narrow peak located at one third of the bandgap energy. This peak is attributed to the three-photon resonant transitions from the top edge of the valence band to the bottom edge of the conduction band in the \( \pi \)-electron spectrum of CNs. From Fig. 3 we see that the height of the peak increases significantly with increasing CN radius. The enhancement of \( |\chi^{(3)}_{THG}(\omega)| \) at the resonance energy \( h \omega_{res} = \Delta_{g}/3 \) reaches one order of magnitude when the type of CNs changes from (10,0) to (22,0), the radius of the latter being approximately two times that of the former.

We now proceed to the discussion of the spectral curves of \( \chi^{(3)}_{THG}(\omega) \) for ensembles of diameter-distributed CNs. Because of the size-dependence of the bandgap energy \( \Delta_{g} \) in the \( \pi \)-electron spectrum of CNs \( (\Delta_{g} \propto R^{-1} [21–24]) \), both the resonance frequency \( \omega_{res} \)
Fig. 2. Absolute magnitude of average THG susceptibility as a function of dimensionless photon energy \( \frac{h \omega}{(\Delta_p)_{av}} \) for the same ensembles of CNs as in Fig. 1.

and magnitude of enhancement of \( |\chi^{(3)}_{THG}(\omega)| \) are functions of \( R \). In this case it in natural to expect that, as a result of the averaging over the CN radii in a sample, the position, width and amplitude of the resonant peaks in the spectra of \( \langle \chi^{(3)}(\omega) \rangle \) will change significantly in comparison with a case of an ensemble of mono-sized CNs with the same average radius. Such changes are clearly seen from the graphs plotted in Figs. 1 and 2. For example, the hump structure near one-half of the bandgap energy can be observed on curve 4 in Fig. 2. Since the two band-edge states in single-wall zigzag CNs under consideration possess reversed symmetries, the true two-photon absorption in the system is forbidden; the above-mentioned structure is rather the consequence of a small increase in the polarizability of the system near \( h \omega = \frac{\Delta_g}{2} \) (see curve 4 in Fig. 1a). However, after making the average, the corresponding feature on curves 1–3 in Fig. 2 disappears, which is quite reasonable in physics and can be accounted for by a random distribution of CN radii.

However, upon ensemble averaging over CN radii, the most essential changes are suffered by the main parameters of the three-photon resonant peak in the THG spectrum. The results for \( |\chi^{(3)}_{THG}(\omega)| \) for ensembles of CNs with randomly distributed diameters, plotted in Fig. 2, show a strong broadening, intensity decrease, and spectral red shift of the peak in comparison with the corresponding peak in the THG spectrum of an ensemble of mono-sized CNs. Such behaviour results from superimposing the tops and tails of the resonant peaks originating from different CNs. As to the general trend of a shift in the peak position towards lower photon energy, we can easily understand this if we take into account that, as mentioned above, in the case of an ensemble of identical CNs, the height of the peak grows sharply with increasing \( R \) (see Fig. 3). This means that for an ensemble of diameter-distributed CNs, the main contribution to the peak comes from the CNs with the radius \( R > R_{av} \), and hence, with the bandgap energy \( \Delta_g < (\Delta_v)_{av} \). Accordingly, the position of the peak suffers a red shift, which increases with the growth of \( R_{av} \) (Fig. 4). In addition, as seen from Fig. 4, the magnitude of the shift varies for different distributions of CNs. Simultaneously, the height of the peak increases significantly with increasing \( R_{av} \), achieving record values up to \( \sim 10^{-4} \) e.s.u. at \( R_{av} = 52 \) Å for all the three above-mentioned distributions of CNs (Fig. 5). We believe that it is not difficult

Fig. 3. Intensity of the three-photon resonant peak in the THG spectrum for five ensembles of mono-sized single-wall CNs with indices (10,0), (13,0), (16,0), (19,0) and (22,0). The continuous line is drawn to guide the eyes.

Fig. 4. Variation in the three-photon resonant peak position in the THG spectrum due to a change in the average radius of CNs in a sample for three different CNs distributions. Circles correspond to the Gaussian distribution with \( \sigma = 0.3 R_{av} \); squares correspond to the rectangular distribution with \( R_{\text{min}} = 3.5 \) Å and \( R_{\text{max}} = 9.5, 22.5, 35.5, 48.5, 74.5 \) and 100.5 Å; and triangles correspond to the triangular distribution with \( R_{\text{min}} = 3.5 \) Å and \( R_{\text{max}} = 12.5, 32, 51.5, 71.5, 110 \) and 149 Å. The continuous lines are drawn to guide the eyes.
3. The position and intensity of the resonant peak in the THG spectrum has been made for three various diameter distributions of CNs randomly distributed diameters. The ensemble averaging calculation of the optical THG susceptibility with sufficient accuracy. Such an experimental measurement can therefore be used as a tool to extract information about the prevailing type of CN distribution in a sample. Note that up to now, information of this kind has been obtained by using either transmission electron microscopy or Raman scattering spectroscopy [19].

4. Conclusions

In this paper we have presented a theoretical study of the THG spectra of ensembles of aligned CNs with randomly distributed diameters. The ensemble averaging calculation of the optical THG susceptibility has been made for three various diameter distributions of CNs (Gaussian, rectangular and triangular) that are realized in CN samples, depending on the experimental conditions of their synthesis. The results obtained can be summarized as follows:

1. In all the cases considered, the diameter distribution of CNs leads to a strong broadening, intensity decrease, and red shift of the main three-photon resonant peak in the THG spectrum.

2. With an increase in the average radius $R_{av}$ of CNs in a sample, the position of the resonant peak suffers a spectral red shift, and the height of the peak grows sharply, achieving record values of the order of $10^{-4}$ e.s.u. at $R_{av} = 52$ Å for all the three distributions of CNs we have considered.

3. The position and intensity of the resonant peak in the THG spectrum depend on the type of the diameter distribution of CNs; this can be used in experiments in order to obtain information about the prevailing type of CN distribution in a sample.

Acknowledgements

We are deeply indebted to the anonymous reviewer of our previous paper in Diamond and Related Materials [8], who called our attention to the importance of ensemble averaging calculation of non-linear optical coefficients of realistic CN samples. We also are grateful to him for his remark in the form of a question as to whether the distribution of CNs in a sample could be inferred from optical measurements, which inspired the present paper. Finally, we would like to thank Professor Y. Saito of Mie University (Tsu, Japan) for providing the reprints of his papers [18,19].

References