Electric-field-induced optical second-harmonic generation and nonlinear optical rectification in semiconducting carbon nanotubes

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Received 23 February 2000; received in revised form 30 June 2000; accepted 10 July 2000

Abstract

We have calculated the nonlinear susceptibility for the optical second-harmonic generation (SHG) from a bundle of aligned single-walled carbon nanotubes (SWCNs) of the ‘zig-zag’ type subjected to a constant electric field $E_0$, parallel to their axis. The breakdown of inversion symmetry caused by the electric field is accompanied by the occurrence of the parity-forbidden two-photon transitions between the valence- and conduction-band edges. As a result, the third-order nonlinear-susceptibility $\chi^{(3)}$ spectrum for SHG clearly demonstrates two peaks strongly distinguished in intensity: one is the two-photon resonance exactly at the pump photon energy $h\omega$ equal to one half of the band gap $\Delta_e$; the other – small peak – sits at $h\omega = \Delta_e$, which corresponds to the one-photon interband transitions. It is found that the intensity of both peaks grows sharply with an increase of the SWCN radius. The susceptibility $\chi^{(3)}$ relevant to the effect of nonlinear optical rectification in SWCNs has also been calculated. It is shown that near the fundamental absorption edge, the electric voltage appearing on the ends of SWCNs due to the optical rectification effect sharply changes its polarity. For a bundle of identical 4y125,000 SWCNs, 3 μm in length and placed in an electric field $E_0 \approx 10^4$ V cm$^{-1}$, the optical rectification voltage is found to be about 0.35 μV under excitation of the sample by a continuous laser with a radiation intensity of 30 mW cm$^{-2}$, which may be of practical importance for mid-IR signal processing. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years there has been a growing interest in the physical properties of carbon nanotubes (CNs) – structures made of graphite sheets rolled up in a cylindrical form (for a review see [1–5]). Two kinds of CNs are now experimentally available: multi-walled nanotubes and single-walled (SW) ones. The latter can be synthesized through laser ablation of a carbon target [6–8] or by the electric-arc technique [9,10]. These tubes typically have diameters from 1.2 to 1.5 nm, while their length is greater than 1 μm. The SWCNs, produced by using either of the above mentioned methods, are normally forming ropes (bundles of tubes) which consist of closely-packed arrays of a few hundred nanotubes nearly uniform in diameter and chirality [11,12] (but with regard to the latter point there still exists some ambiguity [13–15]). There have also been reports on the preparation of
aligned SWCN thin films on various substrates [16] and on the synthesis of mono-sized and well-aligned SWCNs in the 1-nm sized channels of zeolite AlPO$_4$-5 crystals [17,18]. There is a lot of interesting physics in these systems which are very promising from the practical standpoint and are awaiting thorough investigation.

In this paper which continues our series of studies [19–22] we report new theoretical results on the nonlinear-optical properties of nonchiral SWCNs with a ‘zig-zag’ wrapping. Among the various kinds of CNs, these tubes have the most simplified structure possessing an inversion centre. Besides, they have a band gap and hence, should exhibit semiconducting behaviour. Within a simple two-band model of the electronic structure of the SWCNs we calculate the optical susceptibility for the second-harmonic generation (SHG) from an array of such CNs that have their axes parallel to each other. Since in the electric dipole approximation even-order nonlinear susceptibilities vanish in materials with inversion symmetry, the SHG process becomes possible only if the inversion symmetry of the system under consideration is broken by some kind of external perturbation, e.g., by an external DC electric field. In this case the cubic susceptibility $\chi^{(3)}$ is the lowest-order nonvanishing susceptibility which is responsible for the SHG of light. We also investigate one more third-order nonlinear optical effect associated with symmetry breaking produced by an applied electric field, namely, the nonlinear optical rectification (NOR) effect in SWCNs. This effect can be observed experimentally as a constant electric voltage appearing on the ends of CNs irradiated by a continuous laser.

The paper is organized as follows. In Section 2, we outline the theoretical framework that was used for calculating $\chi^{(3)}$. The results are presented and discussed in Section 3 and the conclusions are summarized in Section 4.

2. Theoretical framework

In order to investigate the influence of an external electric field on the optical nonlinearity of CN samples, we consider an idealized model of a bundle which is composed of (nominally) identical, very closely-packed and aligned SWCNs of the ‘zig-zag’ type. The DC electric field $E_0$ is assumed to be applied along the symmetry axis of SWCNs ($z$ axis). We shall confine ourselves to such an experimental situation where the incident light is polarized parallel to the $z$ axis too. In this case the total nonlinear-optical response of a SWCN bundle can be evaluated as just the sum of the responses of the individual SWCNs, that is, within the independent nanotube approximation [23,24]. This approach seems reasonable since the intertube separation in a bundle is much larger than the nearest-neighbour C–C distance $d_0 = 1.42$ Å. Within the same approximation, the results obtained below could then be generalized to the more complicated bundles that consist of SWCNs of different size and chirality [25].

In the model just described, the third-order nonlinear-optical response depends only on one component of the fourth-rank susceptibility tensor $\chi^{(3)} = \chi^{(3)}$. In order to calculate the electronic contribution to $\chi^{(3)}$, we need an explicit model of the band structure of individual SWCN. According to the theoretical predictions [26–31], recently confirmed experimentally [13–15], SWCNs can show metallic or semiconducting behaviours depending on their geometric structures. The latter is uniquely determined by the chiral vector $C = n_1a_z + n_2a_2$ which connects two crystallographically equivalent sites on a graphene sheet [27]. The pair of integers $(n_1, n_2)$ specifies the CN radius $R = (a_0/2\pi)(n_1^2 + n_2^2 - n_1n_2)^{1/2}$. $(a_0 = \sqrt{3}d_0$ is the in-plane lattice constant of the graphite) and the chiral angle $\theta = \tan^{-1}[\sqrt{3}n_2/(2n_1 - n_2)]$. The band-theory calculations [26–31] imply that the SWCNs are metallic when $|n_1 - n_2|$ is divisible by 3 and they are semiconducting otherwise. In the latter case the band-gap energy $\Delta_s$ in the $\pi$-electron spectrum of the SWCNs is expressed as follows [32–34]:

$$\Delta_s = \left(t_0d_0/R\right)\left[1 + (-1)^p\left(t_0/12R\right)\cos\theta\right]$$

(1)

with the integer $p = 1$ or 2 for the moderate-gap semiconducting SWCNs, where $t_0 = -3.03$ eV is the resonance integral of the tight-binding method [27,28,35]. The $\theta$-dependent term in Eq. (1) arises from the $\sigma$–$\pi$ hybridization effect which is due to the finite curvature of the graphene sheet bent to form the tubule. For SWCNs the radius of which is
not very small ($R > 4$ Å) this term is much smaller than the first term of Eq. (1) and hence, it can be neglected without sacrificing much accuracy.

Further we consider the high-symmetry type of SWCNs with a 'zig-zag' wrapping ($n,0$) which possess an inversion centre [36]. The electron energy dispersions of these nonchiral semiconducting SWCNs are easily obtained within the two-band $kp$ approximation scheme in the explicit form [37]:

$$
\epsilon_c(k) = -\epsilon_c(k) = \left[ (\Delta_e/2)^2 + \gamma^2 k^2 \right]^{1/2},
$$

(2)

where the subscript $c$ ($v$) refers to the conduction (valence) band, $k$ is the component of the electron wave vector along the $z$ axis, and $\gamma$ is the $kp$ interaction parameter connected with the resonance integral $t_0$ via the relation $\gamma = \sqrt{3} |t_0| a_0 / 2$.

Following our recent papers [19,21,22], we can write the general expression for the susceptibility $\chi^{(3)}$ in the two-band model under consideration as follows:

$$
\chi^{(3)}(\Omega; \omega_1, \omega_2, \omega_3) = \chi^{(3)}_{\text{inter}}(\Omega; \omega_1, \omega_2, \omega_3) + \chi^{(3)}_{\text{comb}}(\Omega; \omega_1, \omega_2, \omega_3),
$$

(3)

$$
\chi^{(3)}_{\text{inter}}(\Omega; \omega_1, \omega_2, \omega_3) = -\frac{\epsilon^4}{12V_h^3} \sum_k \sum_p D(\omega_{cv} + \omega_1 + i \Gamma/2) \times D(\omega_{cv} - \Omega + i \Gamma/2) \left[ D(\omega_{cv} - \omega_3 + i \Gamma/2) + D(\omega_{cv} + \omega_3 + i \Gamma/2) \right] X_c(k),
$$

(4)

$$
\chi^{(3)}_{\text{comb}}(\Omega; \omega_1, \omega_2, \omega_3) = -\frac{\epsilon^4}{12V_h^3} \sum_k \sum_p D(\omega_{cv} + \omega_1 + \Omega + i \Gamma/2) \times D(\omega_{cv} + \omega_1 + i \Gamma/2) X_c(k) \times \frac{\partial}{\partial k} \left[ D(\omega_{cv} + \omega_1 + i \Gamma/2) X_c(k) \right],
$$

(5)

where

$$
\omega_{cv} \pm \omega + i \Gamma/2 = (\omega_{cv} \pm \omega + i \Gamma/2)^{-1},
$$

$$
\hbar \omega_{cv} = \epsilon_c(k) - \epsilon_c(k).
$$

(6)

$\omega_i (i = 1,2,3)$ and $\Omega = -(\omega_1 + \omega_2 + \omega_3)$ are the input and output frequencies, respectively, $V$ is the normalized volume of the system, $-e$ is the electron charge, $\Gamma$ is the damping constant which describes the population decay of the excited electronic states, the symbol $\Sigma_p$ designates the summation over all the permutations of the frequencies $\omega_1, \omega_2, \omega_3$ and $\Omega$, and, finally, $X_c(k)$ is the matrix element for the dipole interband transition, which in the model under consideration is given by

$$
X_c(k) = \gamma \Delta_e / \epsilon_c^2(k).
$$

(7)

The first and second terms in Eq. (3) represent, respectively, the contributions to $\chi^{(3)}$ from purely interband transitions and from combined intraband-interband ones. From formula (7) with regard to Eq. (2) it follows that the quantity $X_c(k)$ changes essentially with the change of $k$. Therefore one can expect that the contribution to $\chi^{(3)}$ from the combined electron transitions will be dominant, which has already been remarked in our earlier work [20].

The range of applicability of Eqs. (4) and (5) is restricted to the inequality $\Delta_v \gg T$, where $T$ is the temperature in energy units. The estimations based on Eq. (1) show that for the moderate-gap semiconducting SWCNs the above mentioned condition is always satisfied even at room temperature. It means that we can regard the valence band and the conduction band as being completely filled and quite empty, respectively. In this case virtual electron transitions are the basic source of optical nonlinearity of the SWCNs. Strictly speaking, it implies that the inequality $\hbar \omega_i \ll \Delta_v$ is fulfilled. It is necessary to remark, however, that actually Eqs. (4) and (5) remain valid (at least approximately) even at $\hbar \omega_i \sim \Delta_v$ if the intensity of pump radiation is such that the nonlinearity related to the effect of saturation of resonant transitions is negligible. As it has already been noted in our earlier work [22], in the presence of the DC electric field $E_0$ parallel to the symmetry axis of CNs, the saturation effect, that is, the equalization of the population of the valence- and conduction-band states is achieved at higher values of radiation power than in the zero-DC field case. The physical explanation why the saturation regime is destroyed by the strong DC electric field is as fol-
lows. When intense optical radiation pumps the electron from the \( n \)-band state to the \( c \)-band state of wave number \( k_n \), the excited charge carriers accelerating under the DC field \( E_0 \) set free the \( k_o \)-state, thus making possible an additional generation of carriers in this state. The criterion for destroying the saturation regime in SWCNs placed in an electric field can then be written as [22]

\[
\left( \frac{\Delta_g}{|\hbar \omega - \Delta_g|} \right)^{1/2} \left( \frac{\epsilon X_i}{\epsilon_0 (\epsilon E_0 d_0)} \right) \ll 1, \tag{8}
\]

where \( E_0 \) is the amplitude of the electric field strength of the light wave. Using this criterion, it is easy to show that we can neglect the band-filling optical nonlinearity even at a rather high intensity of the incident radiation (~10^5 W cm⁻²) if the electric field strength \( E_0 \) is large enough (~10^3 V cm⁻¹).

3. Results and discussion

Let us consider the constant electric field \( E_0 \) as a coherent superposition of photons of zero frequency. Using the above mentioned formulas, it is easy to obtain the following expression for the susceptibility \( \chi^{(3)}(-2\omega;\omega,\omega,0) \) determining the polarizability \( P^{(3)}(2\omega) \) at the SHG frequency:

\[
\chi^{(3)}(-2\omega;\omega,\omega,0) = \frac{15}{2^5} \chi^{(3)}(0) \left[ \delta_{r,1} - (1 - \delta_{r,1}) \frac{\hbar \Gamma}{\Delta_g} \right] \times F \left( \frac{\hbar \Gamma}{\Delta_g}, \frac{\hbar \omega}{\Delta_g} \right), \tag{9}
\]

where the subscript \( r = 1,2 \) refers to the real \( (r = 1) \) and imaginary \( (r = 2) \) parts of the susceptibility, \( \delta_{r,1} \) is the Kronecker delta symbol, the low-frequency susceptibility \( \chi^{(3)}(0) \) is given by

\[
\chi^{(3)}(0) = \frac{4}{5} \frac{(3\pi R)^3}{\pi^2 \gamma}, \tag{10}
\]

and the function \( F(\delta,z) \), describing the frequency dependence of \( \chi^{(3)} \) can be written as

\[
F(\delta,z) = S_z(\delta,z) - 4S_0(\delta,2z) + 7[J_r^{(\delta,2)}(\delta,z) + 16J_{r+1}^{(\delta,2)}(\delta,z) + 19J_{r+2}^{(\delta,2)}(\delta,z) + 32J_{r+3}^{(\delta,2)}(\delta,z)]. \tag{11}
\]

Here we use the notation

\[
S_z(\delta,z) = Q_z(\delta,z) + Q_{-z}(\delta,-z), \quad l = 1,2.
\]

where the functions \( Q_{\pm z}(\delta,z) \) at various values of the index \( r \) are defined as

\[
Q_{l}(\delta,z) = I_{02210}(\delta,z), \tag{13}
\]

\[
Q_{2}(\delta,z) = I_{03200}(\delta,z),
\]

\[
Q_{3}(\delta,z) = I_{02310}(\delta,z), \tag{14}
\]

\[
Q_{4}(\delta,z) = I_{21120}(\delta,z),
\]

\[
Q_{5}(\delta,z) = I_{20212}(\delta,z) - \delta^2 I_{22110}(\delta,z), \tag{15}
\]

\[
Q_{6}(\delta,z) = I_{21310}(\delta,z),
\]

\[
Q_{7}(\delta,z) = I_{20032}(\delta,z) - 3\delta^2 I_{22012}(\delta,z), \tag{16}
\]

\[
Q_{8}(\delta,z) = 3I_{21002}(\delta,z) - \delta^2 I_{33002}(\delta,z), \tag{17}
\]

and by means of \( I_{\text{nor}}(\delta,z) \) we designate the following integral:

\[
I_{\text{nor}}(\delta,z) = \int_0^1 x^{\lambda A^{\delta z}}(x) B^{\delta z}(x) C^{\delta z}(l;x) \times D^{\delta z}(l;x) dx \tag{18}
\]

where the integrands are defined as

\[
A(x) = 1 - x^2, \quad B(x) = (1 + x^2)^{-1}, \tag{19}
\]

\[
C(l;x) = 1 + l_z + (1 - l_z)x^2, \tag{20}
\]

\[
D(l,z;y) = \left[ \delta^2 A^2(x) + C^2(l;z;x) \right]^{-1}. \tag{21}
\]

We turn now to the nonlinear susceptibility \( \chi^{(3)}_{\text{nor}}(\omega) = -\Re \chi^{(3)}(0;0,\omega, -\omega) \) describing the NOR effect in CNs in the presence of the constant electric field \( E_0 \). On the basis of the general expressions (3)-(5), we obtain

\[
\chi^{(3)}_{\text{nor}}(\omega) = -\frac{15}{32} \chi^{(3)}(0) \Phi \left( \frac{\hbar \Gamma}{\Delta_g}, \frac{\hbar \omega}{\Delta_g} \right), \tag{22}
\]
where

\[
\Phi(\delta,z) = 22P_1(\delta,z) + 18P_2(\delta,z) + 10P_3(\delta,z) \\
+ 4P_4(\delta,z) + P_5(\delta,z),
\]

\[
P_1(\delta,z) = H_1(\delta,z) + H_2(\delta,-z),
\]

and the functions \(H_i(\delta,z)\) are defined as

\[
H_1(\delta,z) = J_{0410}(\delta,z),
\]

\[
H_2(\delta,z) = J_{0321}(\delta,z) - \delta^2 J_{3101}(\delta,z),
\]

\[
H_3(\delta,z) = J_{0232}(\delta,z) - 3\delta^2 J_{2212}(\delta,z),
\]

\[
H_4(\delta,z) = J_{0143}(\delta,z) - 6\delta^2 J_{1213}(\delta,z) \\
+ \delta^4 J_{4103}(\delta,z),
\]

\[
H_5(\delta,z) = J_{0054}(\delta,z) - 10\delta^2 J_{2034}(\delta,z) \\
+ 5\delta^4 J_{4014}(\delta,z).
\]

Here we use the notation

\[
J_{mnpq}(\delta,z) = \int_0^1 A^{m+2}(x) B^{n+2}(x) C^p(z;x) \\
\times D^{q+2}(\delta,z;x) \left[1 - A^2(x) B^2(z)\right] dx.
\]

Strictly speaking, the above mentioned expressions for the susceptibility \(\chi^{(3)}\) are valid only for a set of SWCNs with the symmetry axes parallel to each other and to the vector of polarization of the light waves. As has already been noted, experimentally such a situation can be realized, for example, in SWCN thin films fabricated by using the techniques developed in Ref. [16]. It should be expected, however, that the obtained results will be applicable (at least by the order of magnitude) in case of weak disorientation of the tube axes as well. This statement is supported by the calculations of the static polarizability of SWCNs in a randomly oriented electric field carried out by Benedict et al. [38]. Their results show that the electric-field induced dipole moment of a SWCN is directed mainly along its symmetry axis.

Using Eqs. (9)–(29), we have calculated the dependence of the susceptibilities \(\chi^{(3)}(-2\omega;\omega,\omega,0)\) and \(\chi^{(3)}_{\text{Re}}(\omega)\) on the magnitude \(\hbar \omega/\Delta_{e}\) for three uniform ensembles of SWCNs consisting of the tubes (13,0), (19,0) and (25,0), respectively. The integration in Eqs. (18) and (29) has been carried out numerically by using the Simpson formula. Since there are no available experimental data on the broadening parameter \(\hbar \Gamma\), we have accepted the value \(\hbar \Gamma = 0.01\) eV, as it follows from the theoretical estimation given in Ref. [39]. The results of our calculations are presented in Figs. 1–4, to the discussion of which we proceed now.

Let us consider at first the curves of the frequency dependence of the real and imaginary parts of the susceptibility \(\chi^{(3)}(-2\omega;\omega,\omega,0)\), displayed in Figs. 1 and 2. The spectral behaviour of these quantities is easy to understand on the basis of the following arguments. In the nonchiral \((n,0)\) SWCNs the two-photon transitions between \(e\)- and \(c\)-band-edge states are forbidden in the electric dipole approximation because these states possess opposite parity. However, the transitions will be allowed if there is perturbation which violates the parity. In the case under consideration the external electric field \(E_0\) plays the role of such a perturbation. As the result, in the spectrum of \(\text{Im} \chi^{(3)}(-2\omega;\omega,\omega,0)\) there appear two resonant peaks (Fig. 2a) located in the vicinity of the energy of the two-photon resonant transition \(\hbar \omega_{\text{res}} = \Delta_e/2\) between the band edges. At small detuning of the resonant frequency \(\Delta \omega = \omega - \omega_{\text{res}} < 0\) in the spectrum of \(\text{Im} \chi^{(3)}(-2\omega;\omega,\omega,0)\) we can see a peak of negative absorption, to which there corresponds a resonant amplification of the polarizability \(P^{(3)}(2\omega)\), the latter being proportional to the intensity \(I_0\) of the pump radiation at the frequency \(\omega\). At small positive values of the detuning frequency \(\Delta \omega\) this peak is transformed into a smaller on intensity resonant peak of positive absorption. As to the real part of the susceptibility \(\chi^{(3)}(-2\omega;\omega,\omega,0)\), it tells us how an optical field changes the dielectric constant of SWCN samples at the SHG frequency. According to the graphs plotted in Fig. 1a, \(\text{Re} \chi^{(3)}(-2\omega;\omega,\omega,0)\) vanishes at the resonant energy \(\hbar \omega_{\text{res}} = \Delta_e/2\), its magnitude and sign changing sharply in the vicinity of the resonance.

This kind of nonmonotonic behaviour of the curves of the real and imaginary parts of \(\chi^{(3)}(-2\omega;\omega,\omega,0)\) accounts for the appearance of a narrow and high peak which sits at \(\hbar \omega = \Delta_e/2\) (Fig. 3a) in the spectrum of the magnitude...
Fig. 1. Spectral dependence of the real part of the susceptibility $\chi^{(2)}(\omega; 0, \omega, 0, 0)$ for three different uniform arrays consisting of the SWCNs (13,0), (19,0) and (25,0), respectively.

Fig. 2. Spectral dependence of the imaginary part of the susceptibility $\chi^{(2)}(\omega; 0, \omega, 0, 0)$ for the same arrays of SWCNs as in Fig. 1.
Fig. 3. Theoretical SHG spectrum for the same arrays of SWCNs as in Fig. 1.

\[ |\chi^{(3)}(-2\omega;\omega,\omega,0)| \text{ determining the SHG signal intensity} \]

\[ I_{2\omega} \propto |\chi^{(3)}(-2\omega;\omega,\omega,0)|^2 I_\omega E_0^2. \]  

(30)

We see from Fig. 3a that the height of this peak grows approximately by one order of magnitude at substituting the type of SWCNs (13,0) by (25,0), the radius of the latter being approximately twice as large. The increase of the SHG signal with the growth of \( R \) is explained by the fast scaling of the off resonant susceptibility \( \chi^{(3)}(0) \) with the size of SWCNs (\( \alpha R^4 \)), which originates from the one-dimensional nature of the energy band structure of SWCNs [20]. As it is seen from Fig. 3a, for SWCNs with the index (25,0) the magnitude \( |\chi^{(3)}(-2\omega;\omega,\omega,0)| \) under resonant conditions achieves values of the order of \( 10^{-7} \) e.s.u. The SHG signal enhancement predicted above represents a significant interest from the point of view of applications, since the experimental realization of the SHG process in the presence of a constant electric field is possible at much lower intensity of incident radiation than the third harmonic generation process studied earlier in our works [19,21].

The SHG spectrum distinctly demonstrates a second resonant peak which sits at \( h\omega = \Delta_s \) (Fig. 3b). This peak cannot be simply attributed to the one-photon resonant transition between the two band-edges involved, since such a transition is symmetry-forbidden in the presence of the electric field \( E_0 \). But the other transitions from the states inside the \( v \)-band to the states inside the \( c \)-band are all possible. From the expression (9) for the SHG susceptibility we can easily see that it is these transitions between inside-band states which induce the one-photon resonance at \( h\omega = \Delta_s \). Actually, the profile of the second peak in the SHG spectrum is the envelope curve of the many peaks each of which is produced by the one-photon transitions between the inside-band states, which are close to the top edge of the \( v \)-band and to the bottom edge of the \( c \)-band. Based on quantitative arguments, one can expect that the height of the second peak in the SHG spectrum will be lower than that of the two-photon resonant peak. The reason is that the probability of electron transitions is proportional to the density of electronic states which is divergent only at the band edges for a one-dimensional system. This is in good agreement.
with the SHG spectrum calculated theoretically which shows that the main peak is about two orders of magnitude higher than the second one (compare the graphs in Fig. 3a and Fig. 3b). But the common feature observed in Fig. 3a and Fig. 3b is that the heights of both peaks increase almost by one order of magnitude with lowering the resonant interband transition energy from 0.85 to 0.44 eV when the type of SWCNs changes from (13,0) to (25,0).

We next turn to a discussion of the dispersion curves of the susceptibility $\chi^{(3)}_{\text{NOR}}(\omega)$ (Fig. 4) which is responsible for the optical rectification effect, i.e., the occurrence of the nonlinear polarizability $P^{(3)}(0)$ of CNs at zero frequency:

$$P^{(3)}(0) = \frac{8\pi}{\varepsilon_0 c} \chi^{(3)}_{\text{NOR}}(\omega) I_m E_0,$$  \hspace{1cm} (31)

where $\varepsilon_0$ is the real part of the linear refractive index and $c$ is the speed of light.

As seen from Fig. 4a, in the region far from the one-photon resonance the susceptibility $\chi^{(3)}_{\text{NOR}}(\omega)$, being negative, grows monotonously in its absolute magnitude with the increase of frequency. But quite a different behaviour of $\chi^{(3)}_{\text{NOR}}(\omega)$ can be observed in the spectral region near the fundamental absorption edge. The graphs in Fig. 4b show that $\chi^{(3)}_{\text{NOR}}(\omega)$ changes essentially nonmonotonously: in the beginning it achieves large positive values ($\sim 5 \times 10^{-4}$ e.s.u.), then passes through zero and, at last, accepts large negative values ($\sim 10^{-3}$ e.s.u.). Such behaviour of $\chi^{(3)}_{\text{NOR}}(\omega)$ is potentially very important from a practical viewpoint because it means that by slightly shifting the radiation frequency, which is adjusted to the resonance frequency of the interband transition, it is possible ‘to switch on’ and ‘to switch off’ the electric voltage on the CN ends induced by a light wave.

The optical rectification voltage appearing on the CN ends is given by

$$V = \frac{4\pi}{\varepsilon_0} P^{(3)}(0) L,$$ \hspace{1cm} (32)

where $L$ is the CN length. Using Eqs. (31) and (32), we shall estimate the magnitude $V$ for a bundle of aligned (25,0) SWCNs, 3 $\mu$m in length and placed in

![Fig. 4. Spectral dependence of the susceptibility $\chi^{(3)}_{\text{NOR}}(\omega)$ determining the optical rectification effect for the same arrays of SWCNs as in Fig. 1.](image-url)
an external electric field \( E_0 = 10^4 \text{ V cm}^{-1} \). Then, setting \( \chi^{(3)}_{\text{NOR}}(\omega) = 10^{-1} \text{ e.s.u.} \), \( h\omega = \Delta_g = 0.44 \text{ eV} \) and \( n_0 = 3 \) we get \( V = 0.35 \mu\text{V} \) under excitation of the CN bundle by a continuous laser with the radiation intensity \( I_r = 30 \text{ mW cm}^{-2} \). Thus the optical rectification voltage in the SWCNs can be large enough to be exploited in novel mid-IR signal detectors.

4. Conclusions

We have calculated the third-order nonlinear optical susceptibility \( \chi^{(3)}(\omega) \) responsible for the SHG from a bundle of aligned and mono-sized semiconducting ‘zig-zag’ SWCNs where inversion symmetry has been broken by an applied electric field. The results of the calculations show that the spectrum of the SHG susceptibility has two peaks strongly distinguished on intensity. The first one is produced by the two-photon resonance between the valence- and conduction-band edges. The height of this peak grows sharply with an increase of the radius of CNs achieving values \( \Delta_g \) from 0.85 to 0.44 eV when the type of SWCNs with the index (25,0). The second peak, the height of which is about two orders of magnitude smaller than that of the first one, comes from the one-photon interband transitions and sits exactly at the fundamental absorption edge. The height of this peak also increases almost by one order of magnitude with the decrease of the band-gap energy \( \Delta_g \) from 0.85 to 0.44 eV when the type of SWCNs changes from (13,0) to (25,0).

We have investigated one more third-order nonlinear optical effect which is possible in the nonchiral \((n,0)\) SWCNs in the presence of an external electric field, namely, the occurrence of constant voltage on the CN ends induced by an AC electric field of a light wave. We have found that the optical rectification voltage in CNs sharply changes its polarity in the narrow spectral range near the fundamental absorption edge. It has been estimated that for a bundle of identical (25,0) SWCNs, 3 \( \mu\text{m} \) in length and placed in an electric field \( E_0 \sim 10^4 \text{ V cm}^{-1} \), the optical rectification voltage is about 0.35 \( \mu\text{V} \) at the pump photon energy \( h\omega = 0.44 \text{ eV} \).

In conclusion, we briefly discuss the effect of a distribution of CN diameters and chirality on the results obtained above. Based on qualitative considerations one can expect that the diameter distribution of SWCNs, which is inevitable in many experiments, will lead to a broadening and spectral ‘red’ shift of the peak positions in the SHG spectrum. It will also reduce the intensity of the peaks. Such behaviour results from superimposing the tops and tails of the resonant peaks originating from SWCNs with different diameters. The direction of the shift of the peak positions can easily be understood if we take into account that, as mentioned above, for an array of identical SWCNs the height of the peaks grows sharply with an increase of \( R \). It means that for a sample containing diameter-distributed SWCNs, the main contribution to the resonant peaks in the SHG spectrum comes from the SWCNs with the radius \( R \) larger than the average radius \( R_{av} \) of the tubes in a sample. According to Eq. (1), the bandgap energy \( \Delta_g \) in such tubes is smaller than that in tubes with the average radius \( R_{av} \), i.e., than \( (\Delta_g)_{av} = |\phi_0|d_0/R_{av} \). Consequently, the peak positions in the SHG spectrum for a bundle of SWCNs with different diameters should suffer a ‘red’ shift with respect to their positions for a bundle of identical SWCNs with the same average radius. As to the effect of a chirality distribution of the SWCNs in a bundle, one can expect that it will be insignificant as compared with a diameter distribution of the tubes, since the contribution of the chirality-dependent term to the bandgap energy \( \Delta_g \) (see Eq. (1)) is, as already mentioned, negligibly small. On the other hand, the NOR effect we predict in this paper is more sensitive to a distribution of CN diameters and chirality, and we believe that in order to investigate it experimentally one will need samples with mono-size and well-defined symmetry of SWCNs. In the light of the important recent progress in the synthesis of an array of well-aligned SWCNs with a very narrow size distribution, our above theoretical findings may be significant for photonic applications of SWCNs.

References