Non-degenerate optical four-wave mixing in single-walled carbon nanotubes

Vl.A. Margulis a,*, O.V. Boyarkina b, E.A. Gaiduk b

a Department of Physics, N.P. Ogarev Mordovian State University, Saransk 430000, Russian Federation
b Department of Chemistry, N.P. Ogarev Mordovian State University, Saransk 430000, Russian Federation

Received 14 September 2004; received in revised form 14 January 2005; accepted 20 January 2005

Abstract

A theory is presented that describes the generation of radiation at the anti-Stokes frequency \(2\omega_1 - \omega_2\) created by two coherent light beams, with a difference in frequency \(\omega_1 - \omega_2\), injected into an array of uniformly sized and closely packed semiconducting single-walled carbon nanotubes (SWCNTs), which are oriented along the polarization vector of all involved optical waves. Both the real and imaginary parts of the third-order nonlinear susceptibility \(\chi^{(3)}\), responsible for such an optical-frequency mixing, are calculated within a simple model based on the two-band approximation of the electronic structure of SWCNTs. It is shown that one can maximize the nonlinear optical response by tuning independently the frequencies \(\omega_1\) and \(\omega_2\) in resonance with the lowest interband transitions of the semiconducting SWCNTs. The highest peak value of \(|\chi^{(3)}|\) under such a resonance excitation is found to be about \(10^{-2}\) esu, which may be important for nonlinear optical applications of SWCNTs.

© 2005 Elsevier B.V. All rights reserved.

PACS: 42.65.An; 42.65.Hw; 61.46.+w

Keywords: Nonlinear optics; Third-order susceptibility; Optical mixing; Carbon nanotubes

1. Introduction

In the last few years there has been an upsurge of research activity in the area of nonlinear optics of carbon nanotubes, which are believed to be among the most promising materials to impact future nanotechnology (for a review see [1,2]), and now there is extensive literature on the subject [3–57]. Most of the interest has focused on the third-order nonlinear optical (NLO) properties of these materials. The
NLO coefficient relevant to such properties, the third-order susceptibility $\chi^{(3)}$, is proportional to the fourth power of the dipole transition matrix element (which is of the order of electron charge $-e$ times the nanotube radius $R$), and is expected to be large, even in nonresonant conditions [3]. Various calculations of $\chi^{(3)}$ for ensembles of parallel-arranged carbon nanotubes [4–10] and of the second-order hyperpolarizability of individual nanotubes of finite length [11–18], have indicated that strong enhancement of the NLO response is quite possible, especially under a resonant excitation. Until recently, experimental efforts have mainly been concentrated on the study of the optical nonlinearity and nonlinear time-resolved spectroscopy of carbon nanotubes imbedded in solids (nanocomposites), as well as of carbon nanotubes solutions and suspensions [22–46]. The values of $\chi^{(3)}$ on the order of $10^{-10}$–$10^{-12}$ esu obtained for such systems under off-resonant conditions by using different methods such as the optical Kerr effect, degenerate four-wave mixing and optical limiting, and simultaneously the fast response time (on the order of 1 ps) observed in time-resolved investigations indicate that the above-mentioned systems are very promising for potential applications in near-infrared signal processing. From those experiments with solutions of carbon nanotubes, the $\chi^{(3)}$ values measured for single-walled carbon nanotubes (SWCNTs) are much larger than those for multi-walled ones, which is in good agreement with the theoretical prediction of an overall suppression of the third-order NLO signal intensity from ensembles of SWCNTs with a broad diameter distribution of the tubes [8,9].

Very recently, several papers came out reporting experimental data on the third-order optical nonlinearities and femtosecond pump–probe spectroscopy of carbon nanotubes fabricated into solid-state forms such as thin films or layers deposited on various substrates (glass, silicon or quartz) [47–56], which are often required in device applications. Near-infrared saturable absorption observed by Tatsuura et al. [49] and Sakakibara et al. [50] in thin film samples of SWCNTs is of particularly great interest because of its possible applications in NLO devices such as all-optical switch in optical telecommunication systems. A very large enhancement of $\chi^{(3)}$ (by two orders of magnitude) over the previously reported $\chi^{(3)}$ values for carbon nanotubes in suspensions and nanocomposites has been observed by the Tatsuura [49] and Lauret [53] groups, and the imaginary part of $\chi^{(3)}$ in their measurements has been estimated as $10^{-7}$ esu under resonant conditions, which is in satisfactory agreement with the value of $\text{Im}\chi^{(3)}$ calculated for the degenerate four-wave mixing process in Ref. [4]. An appealing feature of SWCNT films explored in Refs. [49,50] in that they exhibit the very useful combinations of optical properties when studied in the infrared region: high NLO response, high linear absorption coefficient, and ultra-fast response time (on the order of 1 ps). The results obtained by Tatsuura et al. [49] also provide strong support to the simple one-electron model used in our previous analysis [3–9] of third-order NLO response of semiconducting SWCNTs, indicating that it contains a fair amount of the essential physics necessary to explain the data and the theoretical results thereof can form a reasonable basis to predict details of the frequency dispersion of the $\chi^{(3)}$ and to give the correct order of its magnitude.

A logical next step in the development of third-order nonlinear optics of SWCNTs with the prospects for their device application in new optical communication technologies is paying attention to investigating various four-frequency processes that may occur when several coherent light beams with, in general, different frequencies are incident on a SWCNT sample. In this paper, we consider non degenerate four-wave mixing (NDFWM), resulting in difference-frequency generation, as a typical process of this kind. The NDFWM is determined by a third-order nonlinear polarization of the form

$$P^{(3)}(\omega_s) = \chi^{(3)}(-\omega_s; \omega_1, \omega_1, -\omega_2)E^2(\omega_1)E^*(\omega_2),$$

where $\omega_s = 2\omega_1 - \omega_2$ is the frequency of a field that is generated as a result of the wave mixing, $\omega_1$ and $\omega_2$ are the frequencies of two incidental coherent light waves with $\omega_1 > \omega_2$, $E(\omega_1)$ and $E(\omega_2)$ are the amplitudes of the electric fields associated with those waves, and $\chi^{(3)}(-\omega_s; \omega_1, \omega_1, -\omega_2)$ is the third-order nonlinear susceptibility, responsible for the optical-frequency mixing. The effect we are concerned with here is closely related to the coherent anti-Stokes Raman scattering process, in which the two $\omega_1$ photons are converted...
2. Calculation of the third-order optical susceptibility

Our basic model and computational scheme remain the same as described before [4–9]. The model uses the simplified band structure of SWCNTs, based on an effective-mass approximation [58], and treats only the nonlinearities created by virtual excitations of \( \pi \)-electrons from the highest occupied valence band (v-band) to the lowest empty conduction band (c-band) in semiconducting SWCNTs with a “zig-zag” wrapping \((n, 0)\). This model gives an analytical description to those bands as follows:

\[
e_v(k) = -\varepsilon_c(k) = \left[ (\Delta_v/2)^2 + \gamma^2 k^2 \right]^{1/2},
\]

where \( k \) is the one-dimensional wave vector along the tube axis, \( \Delta_v = |t_0|d_0/R \) is the band gap energy in the \( \pi \)-electron spectrum at the point \( k = 0 \) (\( t_0 \) is the transfer integral between the \( \pi \)-orbitals of the nearest-neighbouring carbon atoms and \( d_0 \) is the distance between these atoms), and \( \gamma = 3|t_0|d_0/2 \) is the interaction parameter of the \( k \cdot p \) Hamiltonian in the two-band model. An application of a similar band structure model to the description of the linear optical properties of ensembles of diameter-distributed SWCNTs [59,60] shows that it reproduces successfully the relevant experimental results for thin films samples of SWCNTs [61].

For the calculation of \( \chi^{(3)} \) one also needs the momentum matrix element \( X_{cv}(k) \) for the interband transitions. As shown in [3,4], the \( X_{cv}(k) \) is linked to the parameters of the model by the following simple relation:

\[
X_{cv}(k) = \gamma \Delta_v/\varepsilon_c(k).
\]

According to the third-order NLO response theory [3,4], the expression for \( \chi^{(3)} \), which provides the starting point for the calculations to be described in this paper, can be partitioned as

\[
\chi^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) = \chi_1^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) + \chi_2^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2),
\]

where the first term, \( \chi_1^{(3)} \), is defined as that originating from purely interband transitions of \( \pi \)-electrons, while the second one, \( \chi_2^{(3)} \), is defined as that arising from the combination of interband transitions and intraband motion of \( \pi \)-electrons in the unoccupied c-band. The relevant formulae for both the above-mentioned contributions to \( \chi^{(3)} \) are given by

\[
\chi_1^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) = -\frac{e^4}{12\hbar^3 V} \sum_k \sum_p \left[ \frac{1}{\omega_{cv}(k)+\omega_1} - \frac{1}{\omega_{cv}(k) - \omega_1} \right] \frac{X_{cv}^4(k)}{[\omega_{cv}(k)+\omega_1][\omega_{cv}(k)-\omega_2]}, \tag{5}
\]

\[
\chi_2^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) = \frac{e^4}{6\hbar^3 V} \sum_k \sum_p \left[ \frac{1}{\omega_{cv}(k)+\omega_1+\omega_2} \frac{\partial}{\partial k} \left[ \frac{X_{cv}^4(k)}{\omega_{cv}(k)+\omega_1} \right] \right] \frac{\partial}{\partial k} \left[ \frac{X_{cv}^4(k)}{\omega_{cv}+\omega_1} \right], \tag{6}
\]
where $\sum_P$ stands for the summation over all the different permutations of the frequencies $\omega_1$, $\omega_2$ and $\omega_3$, resulting in 12 terms, $\hbar \omega_{cv}(k) = \varepsilon_{c}(k) - \varepsilon_{v}(k)$ is the energy difference of electronic states connected by a single-photon transition, $V (= L/\sigma)$ is the volume of the system, $L$ is the normalized length of the tubes which are assumed to be oriented along the polarization vector of all involved optical waves, and $\sigma$ is the surface concentration of SWCNTs in the plane perpendicular to the longitudinal axis of nanotubes. For the ensemble of closely-packed SWCNTs we are concerned with here, the $\sigma$ is given by

$$\sigma = \frac{1}{S},$$

(7)

where $S = \pi R^2$ is the cross-sectional area of a SWCNT. Note that for the same SWCNTs packed into a two-dimensional triangular lattice (a crystalline bundle of SWCNTs) with the lattice constant $d (= 3.15 \, \text{Å})$ [62,63] the concentration $\sigma$ is

$$\sigma = \frac{2}{\sqrt{3}(2R + d)^2}. \quad \text{(8)}$$

It is worth mentioning that $X_{cv}(k)$ and $\hbar \omega_{cv}(k)$ in Eqs. (5) and (6) also depend parametrically on the nanotube radius $R$. However, to simplify the notation this dependence will not be indicated explicitly.

After performing the $P$ summation in Eqs. (5) and (6) and introducing dimensionless photon energies as follows:

$$z_i = \frac{\hbar \omega_i}{A_g} \quad (i = 1, 2), \quad z_r = \frac{\hbar \omega_r}{A_g},$$

(9)

the expressions for $\chi^{(3)}_1$ and $\chi^{(3)}_2$ take the form

$$\chi^{(3)}_1(-\omega_i, \omega_1, -\omega_2) = \frac{(\gamma e)^3}{3 V A_g^2 z_{12}} \sum_k \frac{1}{u^8} \left[ 2 \left( \frac{1}{u-z_1} + \frac{1}{u+z_1} \right) - \frac{z_2}{z_1} \left( \frac{1}{u-z_2} + \frac{1}{u+z_2} \right) - \frac{z_r}{z_1} \left( \frac{1}{u-z_r} + \frac{1}{u+z_r} \right) \right],$$

$$\chi^{(3)}_2(-\omega_i, \omega_1, -\omega_2) = \frac{4(\gamma e)^3}{3 V A_g^2 z_{12}} \sum_k \left\{ \frac{u^2 - 1}{u^8(u+z_1)} \left[ \frac{3u + 2z_1}{(u+z_1)^2} + \frac{3u + 2z_2}{(u+z_2)^2} \right] \right. $$

$$+ \left. \frac{u^2 - 1}{u^8(u+z_{12})} \left[ \frac{3u + 2z_1}{(u+z_1)^2} + \frac{3u + 2z_2}{(u+z_2)^2} \right] \right\} - \frac{3u - 2z_1}{(u-z_1)^2} - \frac{3u + 2z_1}{(u+z_1)^2} - \frac{3u - 2z_2}{(u-z_2)^2} - \frac{3u + 2z_2}{(u+z_2)^2} \right\},$$

(10)

$$+ \{z_i \rightarrow -z_i\},$$

(11)

where

$$u = \frac{2\varepsilon_c(k)}{A_g}, \quad z_{12} = z_1 - z_2.$$  

(12)

Based on Eqs. (10) and (11), one expects $\chi^{(3)}$ to exhibit a resonant behaviour not only when either the laser frequencies $\omega_1$ and $\omega_2$, or the generated frequency $\omega_r$, or all, approach the band gap energy $A_g$, but also when twice the frequency $\omega_1$ or the difference frequency $\omega_1 - \omega_2$ are near such a resonance.

The mathematical procedure used in the further evaluation of $\chi^{(3)}_1$ and $\chi^{(3)}_2$ follows essentially the same lines as those described in the Appendix of our previous work [9]. In particular, the damping of excited electronic states must be included into Eqs. (10) and (11) to avoid divergences. It can be made by introducing a phenomenological damping constant $\Gamma$, which suppresses the height of the resonant peaks, and replacing $u$ by $u + i\delta$ with $\delta = \hbar \Gamma/A_g$ in the denominators of the above-mentioned equations. The result is that $\chi^{(3)}_1$ and $\chi^{(3)}_2$ in Eqs. (10) and (11) become complex and need to be separated into real and imaginary parts. The
relevant formulae for these parts are rather complicated, but their derivation is straightforward in principle and details will not be given here. We only quote the results which are as follows:

\[
\text{Re} \chi_{1,2}^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) = \frac{15}{2\pi} \chi^{(3)}(0) F_{1,2}(\delta, z_{12}|z_s),
\]

\[
\text{Im} \chi_{1,2}^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_2) = -\frac{15\delta}{2\pi} \chi^{(3)}(0) \Phi_{1,2}(\delta, z_{12}|z_s),
\]

where the low-frequency third-order susceptibility \( \chi^{(3)}(0) \) is given by [4]

\[
\chi^{(3)}(0) = \frac{4}{45\pi} e^{4x^3} (A_3/2)^6,
\]

or, taking into account in Eq. (7),

\[
\chi^{(3)}(0) = \frac{4}{5} \frac{(3eR)^4}{\pi^2 x^3},
\]

and where the functions \( F_{1,2}(\delta, z_{12}|z_s) \) and \( \Phi_{1,2}(\delta, z_{12}|z_s) \) are defined as

\[
F_1(\delta, z_{12}|z_s) = \left\{ \frac{1}{z_1} \left[ 2I_{0112}(\delta, 0|z_s) - \frac{z_2}{z_1} I_{1102}(\delta, 2z_{12}|z_s) - \frac{z}{z_1} I_{1120}(\delta, z_{12}|z_s) \right] \right\} + \{z_1 \to -z_1, z_2 \to -z_2\},
\]

\[
F_2(\delta, z_{12}|z_s) = \left\{ A_1 J(z_{12}) + A_2 I_{1102}(\delta, 2z_{12}|z_s) + A_3 I_{1102}(\delta, 0, z_s) + A_4 I_{1102}(\delta, z_{12}|z_s) + A_5 I_{1102}(\delta, 2z_{12}|z_s) + A_6 I_{2212}(\delta, 0, z_s) - \delta^2 I_{2232}(\delta, 0|z_s) + A_7 I_{2212}(\delta, z_{12}|z_s) - \delta^2 I_{2232}(\delta, z_{12}|z_s) \right\} + \{z_1 \to -z_1, z_2 \to -z_2\},
\]

\[
\Phi_1(\delta, z_{12}|z_s) = \left\{ \frac{1}{z_1} \left[ 2I_{0130}(\delta, 0|z_s) - \frac{z_2}{z_1} I_{0130}(\delta, 2z_{12}|z_s) - \frac{z}{z_1} I_{0130}(\delta, z_{12}|z_s) \right] \right\} + \{z_1 \to -z_1, z_2 \to -z_2\},
\]

\[
\Phi_2(\delta, z_{12}|z_s) = \left\{ A_2 I_{0112}(\delta, 2z_{12}|z_s) + A_3 I_{0112}(\delta, 0|z_s) + A_4 I_{0112}(\delta, z_{12}|z_s) + A_5 I_{0112}(\delta, 2z_{12}|z_s) + A_6 I_{2222}(\delta, 0|z_s) + A_7 I_{2222}(\delta, z_{12}|z_s) + A_8 I_{2222}(\delta, 2z_{12}|z_s) \right\} + \{z_1 \to -z_1, z_2 \to -z_2\}.
\]

Here, the following shorthand notations are used:

\[
J(z_{12}) = \int_0^1 (1 + x^2)^{-8} (1 - x^2)^5 \times [1 + z_{12}(1 + x^2)^{-1}(1 - x^2)]^{-1} x^2 \mathrm{d}x,
\]

\[
I_{\alpha\beta\mu}(\delta, l_{z_{12}}|mz_s) = \int_0^1 (1 + x^2)^{-7}(1 - x^2)^{\nu+5} \times K^2(l_{z_{12}}, mz_s|x) P^\beta(\delta, l_{z_{12}}, mz_s|x) x^\alpha \mathrm{d}x
\]

with

\[
K(l_{z_{12}}, mz_s|x) = 1 - l_{z_{12}} + mz_s + (1 + l_{z_{12}} - mz_s)x^2,
\]

\[
P(\delta, l_{z_{12}}, mz_s|x) = \left[ K^2(l_{z_{12}}, mz_s|\delta) + \delta^2(1 - x^2) \right]^{-1}
\]

and with the indices \( \alpha, \beta, \mu \) and \( \nu \) running from 0 to 3. The frequency-dependent coefficients \( A_i \) (\( i = 1 \sim 8 \)) in Eqs. (18) and (20) are given by
Note that according to Eq. (16) the off-resonant NLO susceptibility $\chi^{(3)}(0)$ increases with increasing $R$ as a power function with the exponent equal to 4, or as $R^6/\left(2R + d\right)^2$ in the case when Eq. (8) is satisfied, but does not obey the law $R^6$, as it is claimed in Ref. [10]. The experimental verification of this theoretical prediction is of great interest, but, to our knowledge, it has not been performed yet.

The explicit analytical formulae derived above for the real and imaginary parts of $\chi^{(3)}_1$ and $\chi^{(3)}_2$ enable numerical results to be readily obtained, and these are shown in the next section.

3. Numerical results and discussion

Here, we give examples of NLO susceptibility spectra obtained for three highly-ordered arrays of aligned SWCNTs with indices (13,0), (16,0) and (19,0). The $\chi^{(3)}$ values are calculated as a function of $\hbar\omega_1A_g$ instead of the true frequency $\omega_x = 2\omega_1 - \omega_2$ of the NDFWM signal. In the numerical evaluations the following values of the parameters are used: $t_0 = -2.84$ eV, $d_0 = 1.41$ Å, $h\Gamma = 0.55$ meV. The latter corresponds to the relaxation time of excited electrons of about 1 ps [49]. Our recent calculations of the linear optical spectra of thin film samples of SWCNTs [59,60] have shown that the above value of $h\Gamma$ provides a surprisingly accurate description of the experimental data [61]. For lack of more information $h\Gamma$ is taken to be independent of electron energy. The range of variation of the difference frequency $\Delta\omega = \omega_1 - \omega_2$ is chosen as 0.5–1.5 meV (or 4–12 cm$^{-1}$, which is just the same), so that the regime close to degenerate is assumed to be realized. In this regime, the NDFWM process is of particular interest because it is readily phase matched for collinear input beams, and the coherence length $l_{coh}$ is large, since $l_{coh} \propto (\Delta\omega)^{-2}$ when $\Delta\omega$ is small compared to $\omega_1$ [64]. In this connection, it is worthwhile to note that the NDFWM experiments on bulk narrow gap semiconductors such as InSb, HgTe and HgCdTe, which were performed in the 1980s (for a review, see [65]), revealed that the largest $\chi^{(3)}$ values, as well as
the most pronounced dispersion of $\chi^{(3)}$, can be observed just for small frequency differences $\Delta \omega \lesssim 1 \text{ cm}^{-1}$.

The typical behaviour of the real and imaginary parts of $\chi^{(3)}$ for a fixed value of $\hbar \Delta \omega = 0.5 \text{ meV}$ is illustrated in Figs. 1 and 2. It can be seen that the magnitude of $\text{Re} \chi^{(3)}$ strongly depends on the frequency $\omega_s$, increasing monotonically by more than four orders as $\hbar \omega_s / \Delta_g$ approaches 1 and reaching its maximum positive (negative) value slightly below (above) the band gap. One may also see an enhancement of $|\text{Re} \chi^{(3)}|$ with increasing nanotube radius $R$. The enhancement achieves a value of about two near the resonance frequency while changing $R$ from 5.09 Å (tube (13, 0)) to 7.44 Å (tube (19, 0)). Larger enhancement of $\text{Re} \chi^{(3)}$, in proportion to $R^4$, can be observed throughout the off-resonant frequency range (Fig. 1(a)), in good agreement with Eq. (16).

The significance of $\text{Im} \chi^{(3)}(\omega_s)$, plotted in Fig. 2, is in that it is proportional to the differential change in the optical transmission or in the absorption coefficient. The positive peaks situated slightly above the band gap (Fig. 2(b)) correspond to strong absorption, while the negative peaks at the energies just below $\Delta_g$ (Fig. 2(b)), as well just above $\Delta_g/2$ (Fig. 2(a)), correspond to the spectral regions of strong transmission. Again, one may see the enhancement effect with increasing tube radius, the enhancement factor being about two in the near-resonant region (Fig. 2(b)) while passing from tube (13, 0) to tube (19, 0).

In Fig. 3, we plot the output NDFWM spectra which show a resonant structure at $\hbar \omega_s / \Delta_g = 1$. The intensity of the peaks as a function of $\hbar \Delta \omega$ is shown in Fig. 4. We can see that the peak values of $|\chi^{(3)}|$ are on the order of $10^{-2}$ esu. Such an enormous enhancement of $|\chi^{(3)}|$ near the resonance may be crucial to the optimal design of a variety of all-optical devices based on SWCNTs.

Note that the efficiency of resonance enhancement of $\chi^{(3)}$ near the band gap of SWCNTs can be still more strengthened by detecting the effect of real (rather than virtual) excitation of carries. Describing interband recombination by a time $T_1$ and intraband scattering by a dephasing lifetime $T_2$, one can state that

![Fig. 1](image1.png)

Fig. 1. The real part of $\chi^{(3)}(\omega_s, \omega_1, \omega_2, \omega_2)$ as a function of $\hbar \omega_s / \Delta_g$ at fixed $\hbar \Delta \omega = 0.5 \text{ meV}$ for three different arrays of aligned SWCNTs with indices (13, 0), (16, 0) and (19, 0), respectively.
Fig. 2. The imaginary part of $\chi^{(3)}(-\omega_s, \omega_1, -\omega_2)$ as a function of $h\omega/\Delta_g$ at fixed $\hbar\Delta \omega = 0.5$ meV for the same arrays of SWCNTs as in Fig. 1.

Fig. 3. Absolute magnitude of the NDFWM susceptibility $|\chi^{(3)}(-\omega_s, \omega_1, -\omega_2)|$ as a function of $h\omega/\Delta_g$ at fixed $\hbar\Delta = 0.5$ meV for the same arrays of SWCNTs as in Figs. 1 and 2.
real (long-term) excitation becomes important for \(|A_{g} - \hbar \omega_{0}| \lesssim 1/T_{2}\) and, in optical mixing, for \(|\Delta \omega| \lesssim 1/T_{1}\) [66]. Then, by analogy with the theory developed by Wherrett [66], we arrive at the result

\[
\chi^{(3)} \approx \frac{T_{1}}{T_{2}} \chi_{\text{virtual}},
\]

where \(\chi_{\text{virtual}}^{(3)}\) is described by the above equations, which leads to an additional \((T_{1}/T_{2})\) enhancement factor in \(\chi^{(3)}\), as \(T_{1} > T_{2}\) in all cases (for example, from the pump–probe spectroscopy experiments on micelle-suspended SWCNTs [44], \(T_{1}\) is estimated as 5–20 ps, while \(T_{2}\) is approximately equal to 0.3–1.2 ps).

It should be stressed that the theory developed in this paper uses many simplifications. The approximations are made not only in the description of the electronic structure of SWCNTs, but at many other steps. For instance, the local-field effects are not included in the present treatment at all. The effects of electron–hole Coulomb interaction are also neglected as they are not expected to alter the results qualitatively (see, e.g., [67]). In addition, it is assumed in the theory that all nanotubes in a sample have the same radius. Of course, this assumption is a great oversimplification. Actual SWCNT samples fabricated into thin films are mixtures of diameter-distributed nanotubes, and both the resonance frequency and magnitude of enhancement are functions of the nanotube circumference. The results obtained above are readily extended to incorporate this feature by making a suitable weighted average over the nanotube radius \(R\), which is similar to that carried out in our previous papers [8,9] for optical third-order susceptibilities related to third-harmonic generation, nonlinear refraction and two-photon absorption. Based upon the calculations made in those papers, one can expect that in any case, with the introduction of a distribution of tube diameters, the sharp resonant structure in the NDFWM spectrum will be redshifted and broadened compared to that presented in Fig. 3(b). Simultaneously, the \(|\chi^{(3)}|\) values near the resonance will be about one or two orders of magnitude smaller than those predicted above for arrays of mono-sized SWCNTs. But even the reduced enhancement of \(|\chi^{(3)}|\) remains giant and is of great interest for practical applications in NLO devices.

**Fig. 4.** Peak changes of \(|\chi^{(3)}(-\omega_{0}, \omega_{1}, \omega_{1}, -\omega_{2})|\) at \(\hbar \omega_{0} = A_{g}\) versus \(\hbar \Delta \omega\) for the same arrays of SWCNTs as in Figs. 1–3.
4. Conclusion

We have investigated the NLO susceptibility $\chi^{(3)}(\omega_x, \omega_1, \omega_1, -\omega_2)$ which describes optical-frequency mixing of the form $\omega_x = 2\omega_1 - \omega_2$ for a number of arrays of uniformly sized, well-aligned and closely packed semiconducting SWCNTs. We have shown that in such systems a very sharp peak of $|\chi^{(3)}|$, reaching extremely high values $\sim 10^{-2}$ esu, arises when the excitation frequencies $\omega_1$ and $\omega_2$ are brought close to the band gap of the material. This effect may lead to useful applications in optical switching and other NLO devices, and can also be used as a tool to probe the relaxation mechanism of the corresponding nonlinear process in SWCNTs.

Acknowledgements

It is pleasure for Vl. A.M. to thank Dr. Satoshi Tatsuura of the Fuji Xerox Company (Kanagawa, Japan) for having sent the reprints of his papers [49,50] and Prof. J.-S. Lauret of École Normale Supérieure (Paris) for supplying an electronic copy of his article [53]. The authors are grateful to the referee for providing additional useful references.

References
