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ATOMS, SPECTRA, RADIATION

Second- and Third-Harmonic Generation by Carbon Nanotubes Irradiated with Femtosecond Laser Pulses

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Abstract—Femtosecond pulses of a Cr:forsterite laser are used to study second- and third-harmonic generation in a layer of single-wall carbon nanotubes produced by low-velocity spraying. The harmonic amplitude in our experiments scales as $(I_p)^n$ as a function of the pump intensity I_p, with $n = 2$ and 3 for the second and third harmonics, respectively. This scaling law holds up to pump intensities on the order of 10^{12} W/cm^2. The ratio of the maximum signal to the averaged background in the spectra of the second and third harmonics is estimated as 50 and 30, respectively. The second and third harmonics produced by a linearly polarized pump field are also linearly polarized, with their polarization vectors oriented along the polarization direction of the pump field. The capabilities of nonlinear-optical methods for structural and morphological analysis of carbon nanotubes are discussed, as well as ways to create solid-state carbon-nanotube generators of optical harmonic. © *2004 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

The nonlinear optics of carbon nanotubes (CNTs) is a new growing field of research that integrates advances in solid-state physics, laser science, photonics, physics of low-dimensional structures, nanoscale optics, and nanotechnologies. Research in this field is strongly motivated by the rapid progress in CNT technologies, opening ways of creating new materials with unique properties, including ultrahigh strength and broadly tunable electric conductivity [1–4]. Theoretical studies predict strong optical nonlinearities of CNTs [5–7], suggesting the possibility of using these nanoscale systems for the generation of optical harmonics, including harmonics of high orders [9, 10]. Results of experiments devoted to the investigation of nonlinear-optical phenomena in CNT systems and analysis of nonlinear-optical properties of CNTs are briefly summarized in the table. Until recently experimental efforts were mainly focused on optical limiting in CNT suspensions and CNT–polymer composite materials [11–16]. Experiments on degenerate four-wave mixing [17, 18] show that CNTs offer much promise for the creation of new nonlinear-optical materials and the development of switching and limiting photonic devices. Experiments performed in the past few years have demonstrated (see table) a high potential of CNTs as a nonlinear material for ultrafast optics and photonics. Investigation of the optical Kerr effect on the femtosecond time scale in CNT solutions [19] has revealed strong fast-response optical nonlinearities of CNTs. Chen *et al.* [20] have demonstrated ultrafast optical switching in CNT–polymer composite materials. Stanciu *et al.* [21] report third-harmonic generation (THG) in reflection of femtosecond Cr:forsterite-laser pulses from a CNT sample. The third-harmonic signal displayed saturation under conditions of experiments [21] with sufficiently low pump intensities on the order of 10^{10} W/cm^2.

In this work, we experimentally study generation of the second and third harmonics by femtosecond pulses of a Cr:forsterite laser in a layer of single-wall carbon nanotubes produced by low-velocity spraying. Based on the results of these experiments, we will discuss new possibilities of structural and topological analysis of CNTs using optical harmonic generation.

2. PREPARATION OF CARBON-NANOTUBE SAMPLES

Carbon-nanotube samples were produced with the use of the recently developed technique of low-velocity spraying [22, 23]. One of the main advantages of this technique is that carbon nanoparticles produced by

Catalog of nonlinear-optical phenomena experimentally demonstrated in CNT materials

Process	Nonlinear susceptibility	CNT samples	Laser	Pulse duration	References
Optical limiting	$\chi^{(3)}(\omega; \omega, -\omega, \omega)$	suspensions and polymer composites	mostly Nd:YAG laser	nano- and picosecond pulses	[11–16]
Degenerate four-wave mixing	$\chi^{(3)}(\omega; \omega, -\omega, \omega)$	suspension	Nd:YAG laser	8 ns, 30 ps	[17]
		solid-state sample	Nd:YAG laser	nanosecond pulses	[18]
Optical Kerr effect	$\chi^{(3)}(\omega; \omega, -\omega, \omega)$	solution	Ti:sapphire laser	120 fs	[19]
Optical switching	$\chi^{(3)}(\omega; \omega, -\omega, \omega)$ $\chi^{(3)}(\omega_2; \omega_2, -\omega_1, \omega_1)$	polymer composites	Fiber laser	150 fs	[20]
Third-harmonic generation	$\chi^{(3)}(3\omega; \omega, \omega, \omega)$	solid-state sample	Cr:forsterite	160 fs	[21]
				75 fs	this work
Second-harmonic generation	$\chi^{(3)}(2\omega; \omega, \omega)$	solid-state sample	Cr:forsterite	75 fs	this work

laser-induced pyrolysis at the first stage of this process are then used as a solid precursor for CNT growth with no metal catalysts, which are usually employed in standard CNT technologies [24, 25]. No additional purification is required for CNT samples produced with the use of this technique.

Technologically, the procedure of CNT-sample preparation by low-velocity spraying consists of two steps. The first step involves the generation of carbon nanoparticles by laser-induced pyrolysis of an ethylene–acetylene mixture. This process, initiated by CO_2-laser radiation, yields carbon nanoparticles with a mean size of 50 ± 20 nm. At the second step, a beam of carbon nanoparticles passes through a nozzle in an argon gas jet, expanding to a vacuum chamber evacuated to a pressure of 10^{-6} atm. The gas flow rate was kept constant at a level of 30 m/s. In the vacuum chamber, carbon nanoparticles were deposited on a (100) surface of a silicon substrate. The substrate was then heated, which resulted in a self-organized growth of single-wall carbon nanotubes.

The morphology and the composition of CNT samples were analyzed with the use of a scanning electron microscope (Jeol 5400) with a spatial resolution of about 3 nm and by means of Raman scattering. The diameter of single-wall CNTs in the samples under study ranged from 0.9 up to 1.5 nm. The CNT length exceeded 1 μm. Analysis of scanning electron microscope images (Fig. 1) shows that CNTs tend to form bundles in our samples with a typical diameter of about 30 nm.

3. THE LASER SYSTEM

The laser system employed in our experiments (Fig. 2) consisted of a Cr^{4+}:forsterite master oscillator, a stretcher, an optical isolator, a regenerative amplifier, and a compressor. The master oscillator, pumped with a fiber ytterbium laser, generated 30–50-fs light pulses with a repetition rate of 120 MHz. The central wavelength of this laser radiation was 1250 nm with a bandwidth of 26 nm and the mean power of about 180 mW.

Horizontally polarized 30–50-fs pulses were then stretched up to 700 ps in a grating stretcher (Fig. 2). Upon passing through a Faraday isolator and a λ/4 plate, the light pulses became vertically polarized. These pulses were then transmitted through a broadband polarizer to be injected in the regenerative amplifier at the moment of time corresponding to maximum population inversion, created by pump pulses with a repetition rate of 1 kHz. A switch was used to set a horizontal polarization of pulses injected into the cavity of the amplifier. An amplified pulse with an energy of 100 μJ was coupled out of the amplifier through the switch, triggered at the moment of time corresponding to optimal amplification. Radiation coming out of the amplifier was vertically polarized again. The amplified pulse was returned to the isolator along the same optical path. Radiation passing through the isolator in the backward direction experienced no change in its polarization since polarization rotations introduced by the λ/4 plate and the Faraday isolator compensate for each other. The pulses coupled out of the isolator through the broadband polarizer were transmitted through a λ/2 plate and compressed to a 75-fs duration in a grating compressor. Approximately 50% of the pulse energy was lost at this stage. Radiation generated by the Cr:forsterite laser system was focused onto a CNT film deposited onto a glass substrate (Fig. 3).

4. INTERACTION OF LASER RADIATION WITH CARBON NANOTUBES

The quasi-one-dimensional structure of carbon nanotubes is the key to understanding the regimes of inter-

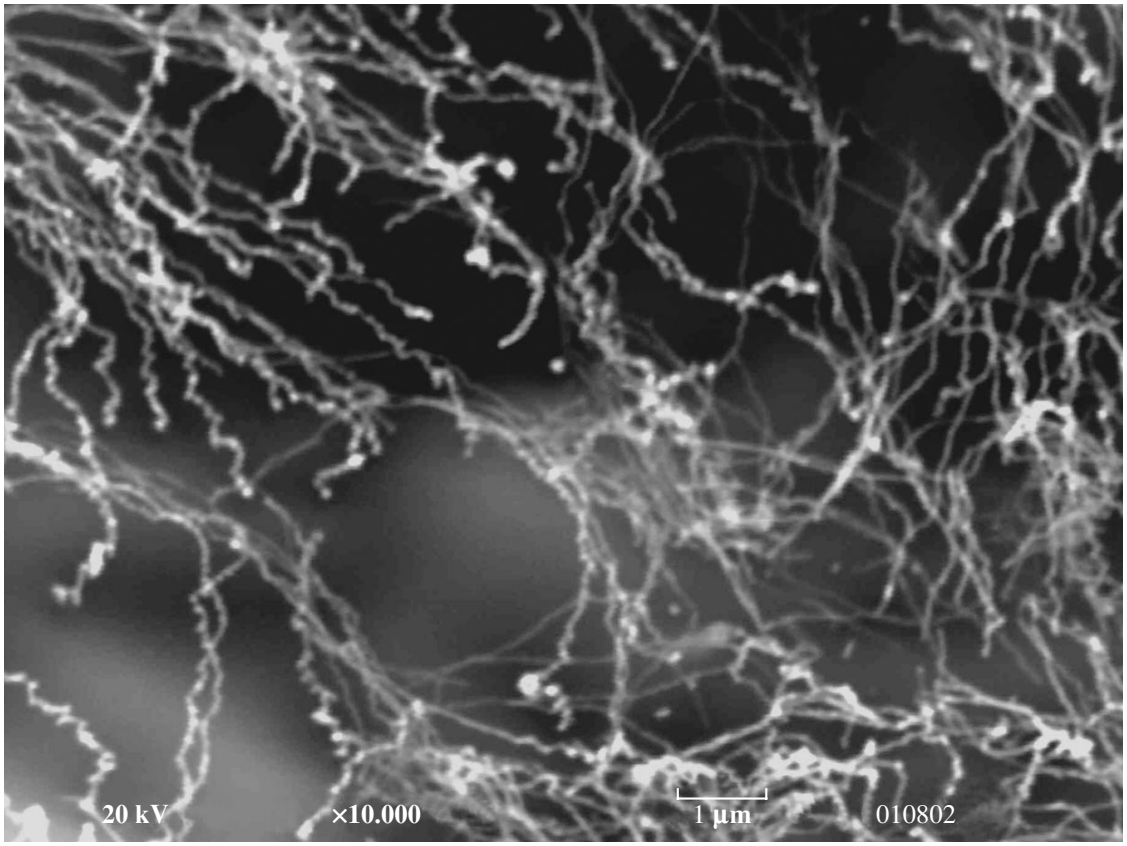

Fig. 1. Scanning electron microscope image of a carbon-nanotube sample. The spatial scale marker corresponds to 1 μm.

action of laser radiation with CNT systems. Quantum confinement of electrons in directions perpendicular to the nanotube axis is manifested in the density spectrum of electron states [26], displaying van Hove singularities (Fig. 4). Fluorescence and Raman studies [26, 27] indicate a strongly resonant character of the interaction of laser radiation with CNTs, revealing the significance of optical van Hove transitions between electron states in the valence and conduction bands (Fig. 4).

The use of strong optical nonlinearities of CNT systems for the generation of reliably detectable harmonic signals, resulting from the nonlinear coherent scattering of pump radiation from CNTs and carrying information on the structure and physical properties of CNTs, is at the heart of our harmonic-generation experiments. Optical harmonics were generated in our experiments using pump radiation with a wavelength of 1.25–1.27 μm produced by a femtosecond Cr:forsterite laser. Within this wavelength range, scattering of radiation by CNT systems can be enhanced due to a series of one-photon resonances corresponding to $v_1 \longrightarrow c_1$ transitions between the electron states in the valence and conduction bands (Fig. 4) with CNT indices (10, 3), (10, 5), (11, 1), (8, 7), (13, 2), and (9, 5), as well as two-photon resonances corresponding to $v_2 \longrightarrow c_2$ transitions (Fig. 4) with CNT indices (10, 3), (7, 5), (11, 1), and others.

Absorption spectra of CNT samples employed in our experiments display clearly resolved peaks at 1.28 and 2.2 eV (Figs. 5a, 5b). These peaks are attributed to optical van Hove transitions. Pump radiation used in our experiments is thus red-detuned from both one- and two-photon resonances with the frequency of optical transitions characteristic of the predominant type of CNTs in the samples. However, the optical density of our CNT systems at the energy of 2 eV, corresponding to the exact two-photon resonance under conditions of our experiments (Fig. 5b), is only a few percent lower than the optical density at the maximum of the absorption spectrum. Our samples are, therefore, characterized by a sufficiently high content of CNTs with electron-state spectra meeting conditions of a two-photon resonance with the frequency of a Cr:forsterite laser (Figs. 4, 5).

The efficiency of nonlinear-optical processes, including second-harmonic generation (SHG) and THG, increases with the growth in the pump radiation intensity. Optical breakdown, however, imposes a limitation on the pump intensity. In the case of shorter pulses, the efficiency of nonlinear-optical interactions in solids can often be increased due to higher intensities corresponding to laser fluences at the threshold of optical breakdown. To illustrate this possibility, we use the following qualitative arguments.

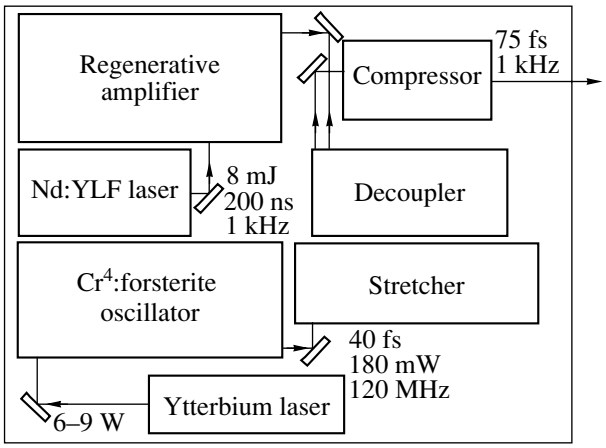

Fig. 2. Diagram of a Cr:forsterite femtosecond laser system with a regenerative amplifier.

Let us represent the intensities of the second and third harmonics, I_{SH} and I_{TH}, perturbatively generated by a pump pulse with an intensity right below the breakdown threshold as

$$I_{SH} \propto |\chi^{(2)}|^2 [F_{\text{th}}(\tau)/\tau]^2, \quad I_{TH} \propto |\chi^{(3)}|^2 [F_{\text{th}}(\tau)/\tau]^3,$$

where $\chi^{(n)}$ is the nth-order nonlinear-optical susceptibility, $n = 2, 3$; $F_{\text{th}}(\tau)$ is the breakdown threshold fluence; and τ is the pump pulse duration. With the scaling law

$$F_{\text{th}} \propto \tau^{1/2},$$

which is typical of a broad class of optical materials irradiated with pulses having durations $\tau > 10$ ps [28–30], the intensities of the second and third harmonics scale as

$$I_{SH} \propto 1/\tau \quad \text{for} \quad \text{SHG}$$

and

$$I_{TH} \propto 1/\tau^{3/2} \quad \text{for} \quad \text{THG}.$$

For shorter pulses, including pulses in the femtosecond range of durations, the dependence of the threshold fluence on the pulse duration becomes even slower than $F_{\text{th}} \propto \tau^{1/2}$ [29], allowing even higher intensities of the second and third harmonics to be achieved around the breakdown threshold [31]. The use of femtosecond pulses in our experiments thus provides a substantial increase in the yield of optical harmonics relative to the picosecond regime. This argument agrees well with the results of earlier experiments on four-wave mixing in CNTs [32], performed with the use of nanosecond pump pulses.

5. RESULTS AND DISCUSSION

Amplified Cr:forsterite-laser pulses were focused on a CNT film to generate the second and third harmonics. Harmonic signals were detected in our experiments in transmission geometry (Fig. 3). We investigated the spectral and polarization properties of optical harmonics and measured the harmonic yields as functions of the pump radiation intensity. The second- and third-harmonic yields scaled (Figs. 6, 7) as $(I_p)^n$, where I_p is the pump intensity and n is the harmonic number, within the range of pump intensities up to at least 10^{12} W/cm^2, indicating the perturbative regime of nonlinear-optical interactions and suggesting a convenient calibration for the second and third harmonics employed as spectroscopic probes:

$$I_n \propto |\chi^{(n)}|^2 I_p^n.$$

THG in reflection from multiwall CNTs, as demonstrated by Stanciu *et al.* [21], is saturated at pump intensities on the order of 10^{10} W/cm^2, resulting in a scaling law of $(I_p)^q$, $q < 3$, for the third-harmonic yield. The results of our measurements show that the intensity range of unsaturated increase in the harmonic yield can be extended under certain conditions up to 10^{12} W/cm^2.

The spectra of the second and third harmonics generated by 75-fs pulses of a Cr:forsterite laser passing through a CNT sample are shown in the insets to Figs. 6 and 7, respectively. Under the conditions of the experiments reported in [21], THG signal was detected against intense nonresonant background. It is important that the ratio η of the harmonic signal at the center of harmonic spectral lines to the background is 30 for

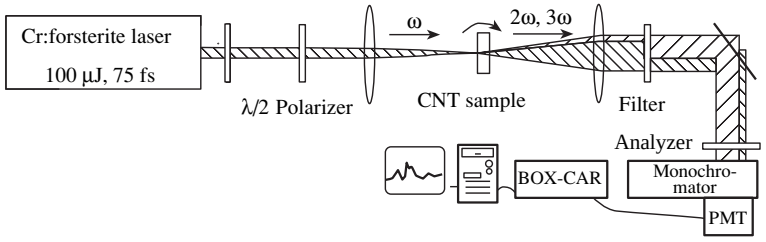

Fig. 3. Diagram of the experimental setup for second- and third-harmonic generation in carbon-nanotube samples using amplified 75-fs pulses of a Cr:forsterite laser.

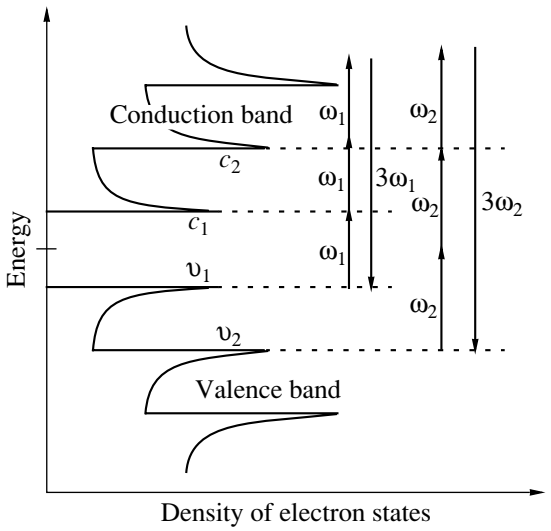

Fig. 4. Diagram of the density of electron states for a carbon nanotube, featuring van Hove singularities. Nonlinear-optical scattering, including harmonic generation, can be enhanced in a system of carbon nanotubes due to one- and two-photon resonances at the frequencies of the first ($\upsilon_1 \longrightarrow c_1$) and second ($\upsilon_2 \longrightarrow c_2$) optical van Hove transitions between the states in the valence and conduction bands.

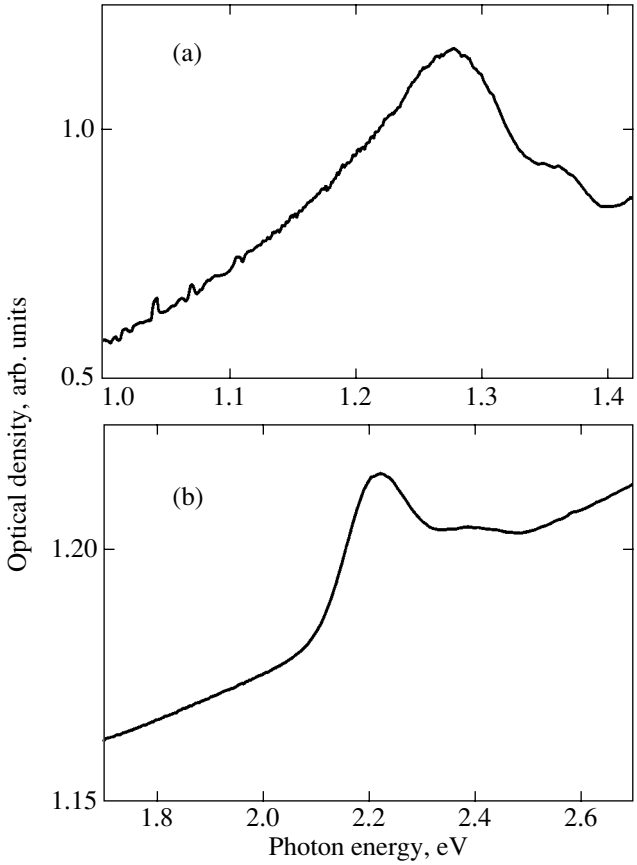

Fig. 5. Spectra of optical density measured for CNTs synthesized by low-velocity spraying within the range of photon energies (a) from 1.0 up to 1.4 eV and (b) from 1.7 up to 2.7 eV.

THG and 50 for SHG under conditions of our experiments, offering THG and SHG as sensitive techniques for CNT detection in transparent materials. The second and third harmonics produced by a linearly polarized pump field were also linearly polarized, with their polarization vectors oriented along the polarization direction of the pump field. The fact that linearly polarized pump radiation gives rise to linearly polarized second and third harmonics with a very low depolarization degree opens the ways to analyze the structure properties of CNTs via polarization measurements on the second and third harmonics.

Our experimental data, however, give no access to the absolute values of the quadratic and cubic nonlinear susceptibilities responsible for SHG and THG. The measurement of nonlinear-optical susceptibilities usually involves a calibration against the harmonic yield from a reference sample with known nonlinear susceptibility. Such a procedure, which was earlier employed to estimate the nonlinear susceptibility of CNTs in suspensions [17], becomes inapplicable in the case of CNTs on a substrate, leading to considerable errors because of spatial inhomogeneities and strong scattering in the CNT sample.

In view of an amazing diversity of carbon nanotubes, featuring different point-group symmetries and broadly tunable, structure-sensitive band gaps [33], nonlinear-optical techniques offer much promise as a tool for local probing of CNTs capable for detecting the band gap and identifying the spatial structure of nanotubes. In particular, second-harmonic generation is governed by the second-order nonlinear susceptibility $\chi^{(2)}(2\omega; \omega, \omega)$, which vanishes for centrosymmetric media. Second-harmonic generation thus allows the detection of nanotubes in a host made of centrosymmetric material with no background related to the nonlinearity of the host. The second harmonic can be generated in CNT materials through surface nonlinear-optical interactions, as well as due to nondipole nonlinear terms or the chirality of some types of CNTs. Methods of measurements distinguishing between these SHG mechanisms would allow SHG to be used to identify the type of CNTs and to detect chiral nanotubes in a sample. Ensembles of chiral CNTs are of special interest for practical implementation of concepts related to the nonlinear optics of media with broken mirror symmetry and observation of a new class of nonlinear-optical phenomena inherent in chiral materials [34–38].

The results of our experiments show that quasi-one-dimensional CNT structures offer new possibilities for optical harmonic generation. Quantum confinement gives rise to singularities in the density spectrum of electron states. Such systems possess strong nonlinearities, which can be enhanced due to one- or multiphoton resonances (Fig. 4), suggesting the ways of creating solid-state generators of optical harmonics. An illuminating and comprehensive overview of the role of one-

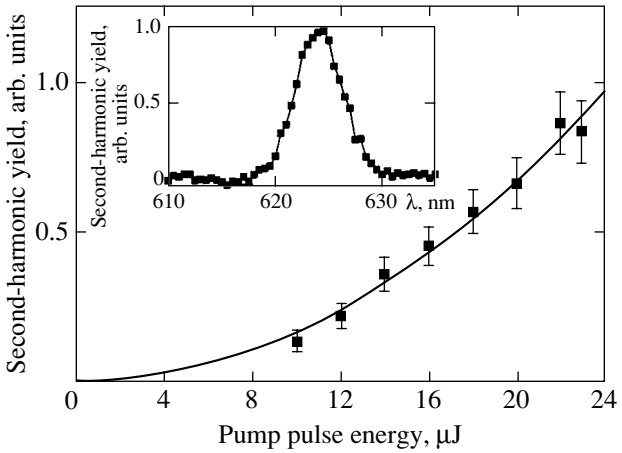

Fig. 6. The yield of the second harmonic generated in a layer of single-wall CNTs on a glass substrate in transmission as a function of the energy of a 75-fs Cr:forsterite laser pump pulse. The diameter of the focused pump beam on the surface of the CNT sample is 120 μm. The solid line represents the quadratic scaling law of the pump pulse energy, which is typical of the perturbative regime of second-harmonic generation. The inset shows the spectrum of the second harmonic.

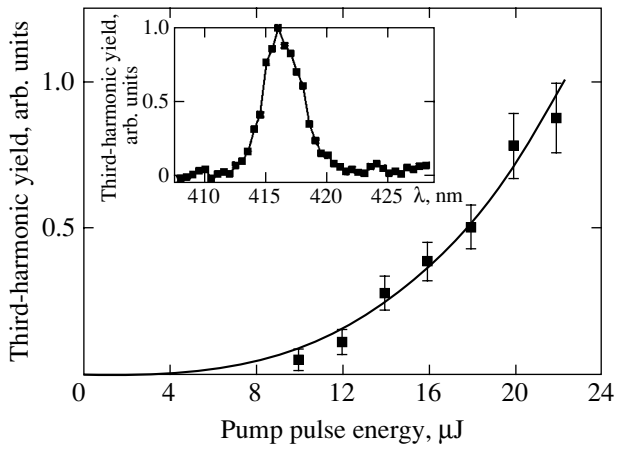

Fig. 7. The yield of the third harmonic generated in a layer of single-wall CNTs on a glass substrate in transmission as a function of the energy of a 75-fs Cr:forsterite laser pump pulse. The diameter of the focused pump beam on the surface of the CNT sample is 120 μm. The solid line represents the cubic scaling law of the pump pulse energy, which is typical of the perturbative regime of third-harmonic generation. The inset shows the spectrum of the third harmonic.

and multiphoton resonances in optical-harmonic generation is provided in classical textbooks on nonlinear optics [39, 40]. In our experimental situation, we do not expect any effects related to the interference of one- and multiphoton excitation pathways [41–44] since the conditions of one- and multiphoton resonances for the same pump frequency can be simultaneously satisfied in our case only for physically different CNTs (CNTs of different structure). The frequencies of optical van Hove transitions are determined by the CNT diameter d and the chiral angle α. In particular, the frequencies ν_i of the first ($i = 1$) and second ($i = 2$) van Hove transitions $v_1 \longrightarrow c_1$ and $v_2 \longrightarrow c_2$ (Fig. 4) are given by the following approximate expression [26]:

$$\nu_i = \frac{a}{b_i + c_i d} + \frac{A_{nm}\cos 3\alpha}{d^2},$$

where a is a constant, b_i and c_i are parameters varying for different optical transitions, and A_{nm} is the parameter depending on the CNT indices m and n. Methods of nonlinear spectroscopy can thus be employed to probe the structure and determine the sizes of CNTs.

6. CONCLUSIONS

The table puts the experimental results presented in this work in the context of earlier studies on the nonlinear optics of CNTs. Amplified 75-fs pulses of a Cr:forsterite laser were employed in our experiments to generate the second and third harmonics in a system of single-wall CNTs. The second- and third-harmonic yields in our experiments scaled as $(I_p)^n$, where I_p is the pump intensity and n is the harmonic number, within the range of pump intensities up to at least 10^{12} W/cm^2, indicating the perturbative regime of nonlinear-optical interactions and suggesting a convenient calibration for the second and third harmonics employed as spectroscopic tools in CNT systems. High-contrast second- and third-harmonic signals observed in our experiments suggest optical harmonics as a highly sensitive probe for the diagnostics of carbon nanotubes. The fact that linearly polarized pump radiation gives rise to linearly polarized second and third harmonics with a very low depolarization degree opens ways to analyze the structural properties of CNTs via polarization measurements on the second and third harmonics.

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