

Laser-induced effects in Raman spectra of single-wall carbon nanotubes

S.N. Bokova, V.I. Konov, E.D. Obratsova, A.V. Osadchii, A.S. Pozharov, S.V. Terekhov

Abstract. Two effects induced by increasing power density of a probe laser beam are discovered in Raman spectra of single-wall nanotubes: the irreversible disappearance of the ‘breathing’ Raman modes of small-diameter nanotubes (0.8–1 nm) and the reversible appearance of additional ‘breathing’ modes from nanotubes with diameters 0.1–0.3 nm smaller than the diameters of nanotubes undergoing resonance Raman excitation at room temperature. The thermal nature of these effects is confirmed by their reproducibility upon heating of the material in an optical oven.

Keywords: carbon nanotubes, laser-induced effects, Raman scattering.

1. Introduction

The basic requirement imposed usually on exciting laser radiation in Raman spectroscopy is that it should not affect the structure and parameters of substances under study. For this reason, low-power probe laser beams are used in experiments. However, Raman spectroscopy can also provide interesting information when high-power beams are employed. In this case, a unique possibility appears to observe *in situ* laser-induced effects in materials.

Single-wall carbon nanotubes are suitable objects for such studies. This new nanostructured material [1] consisting of defect-free cylinders of diameter 0.4–2 nm and length 1–10 μm (Fig. 1), which are folded from a two-dimensional graphite plane, possesses many unique quantum properties [2]. Of special interest are its electronic properties. The density of one-electron states of a nanotube is a discrete set of van Hove singularities (Fig. 2), whose position is determined by the diameter and chirality of the nanotube [3, 4]. Depending on the geometry, nanotubes can be either semiconductors or metals. This property is crucial for the development of nanoelectronic elements and devices such as diodes, transistors, and logical circuits [5].

S.N. Bokova, V.I. Konov, E.D. Obratsova, A.V. Osadchii, A.S. Pozharov, S.V. Terekhov Center for Natural-Science Studies, A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; fax: 7 (095) 135 76 72; e-mail: elobr@kapella.gpi.ru

Received 23 January 2003
Kvantovaya Elektronika 33 (7) 645–650 (2003)
Translated by M.N. Sapozhnikov

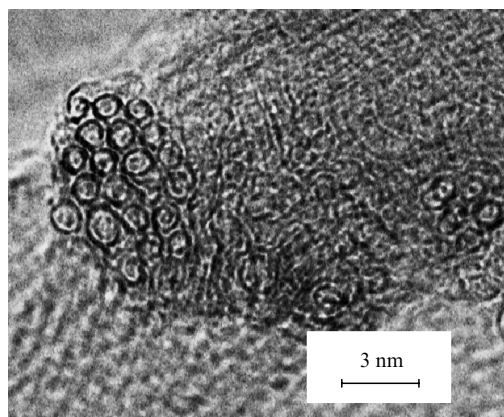


Figure 1. Electron-microscope image of the cross section of a bundle of single-wall nanotubes prepared by the high-pressure decomposition of CO (HipCO).

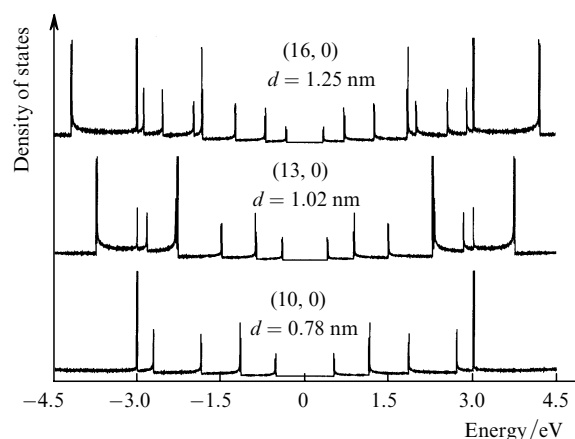


Figure 2. Distribution of the density of one-electron states for non-chiral ‘zigzag’ nanotubes ($m, 0$), where m is the number of carbon hexagons fitted in the nanotube circumference. The calculation was performed using a computer program allowing the simulation of the density of one-electron states for carbon nanotubes of any geometry [4]; d is the nanotube diameter.

The geometrical parameters of nanotubes should be strictly controlled in manufacturing such elements. However, up to now, there have been no methods for synthesis of monodisperse nanotubes with a specified diameter. The homogeneity of a material can be substantially improved by performing its structuring using, for example, laser

radiation. Laser radiation can be simultaneously used to modify the material and excite its Raman spectrum, which characterises this modification. It is known that Raman spectra give information on the diameter and chirality of individual nanotubes, the type of their conductivity and the size of their bundles, the distribution of nanotubes over their diameters in a particular sample, and the purity of the material [6–8]. Because of the resonance character of scattering, the intensity of Raman lines of single-wall nanotubes is so high that a signal from one nanotube (one polyatomic molecule) can be detected [7]. In recent years several papers were published devoted to laser-induced effects observed in Raman spectra of graphite-like materials: graphite [9], multiwall [10, 11], and single-wall [12–15] carbon nanotubes.

The aim of this paper was to find the features in Raman spectra related to the variation in the structure and properties of single-wall carbon nanotubes caused by irradiation by a cw argon laser.

2. Experimental

We studied single-wall carbon nanotubes of three types synthesised by the methods of laser ablation [16], arc synthesis [17], and the catalytic high-pressure decomposition of CO (HipCO) [18]. All the materials were preliminarily investigated by the methods of high-resolution electron microscopy and Raman spectroscopy using low-power laser excitation. The Raman spectra were studied with a triple Jobin–Yvon S-3000 monochromator equipped with an attachment for microscopic samples. The spectral slit width was 2 cm^{-1} . The spectra were detected with a CCD array.

Radiation from a cw argon laser at 488.0 nm (2.54 eV), 495.5 nm (2.50 eV), and 514.5 nm (2.41 eV) was used both to act on the material (in air) and to excite Raman scattering. The laser beam power was varied from 1 to 1000 mW. The size of the laser spot on a sample was $20\ \mu\text{m}$. The thermal annealing of nanotubes was performed in an optical oven equipped with a temperature controller for temperature varying in the range from 20 to $800\text{ }^\circ\text{C}$.

3. Experimental results and discussion

3.1 Irreversible changes in Raman spectra of single-wall carbon nanotubes caused by laser radiation

Fig. 3 shows the Raman spectra of nanotubes recorded by an argon laser at 514.5 nm at different excitation power densities. The spectrum obtained at a low (non-perturbing) power density is presented in Fig. 3a. This spectrum is typical for single-wall carbon nanotubes. The first specific feature of the spectrum is the splitting of the tangential Raman mode, which includes atomic vibrations parallel to the nanotube surface, into several components. The frequency of this mode at room temperature is 1592 cm^{-1} . In the case of HipCO nanotubes, one of the components (1565 cm^{-1}) is enhanced, which gives an asymmetric shape of the Fano resonance to the total line profile and leads to a slight shift of the dominant frequency (1591 cm^{-1}). Such a spectrum reflects the presence of the electron–phonon interaction and corresponds to metal nanotubes [7]. Therefore, 2.41-eV photons excite resonantly Raman scattering in one or several nanotubes possessing the metallic conduction.

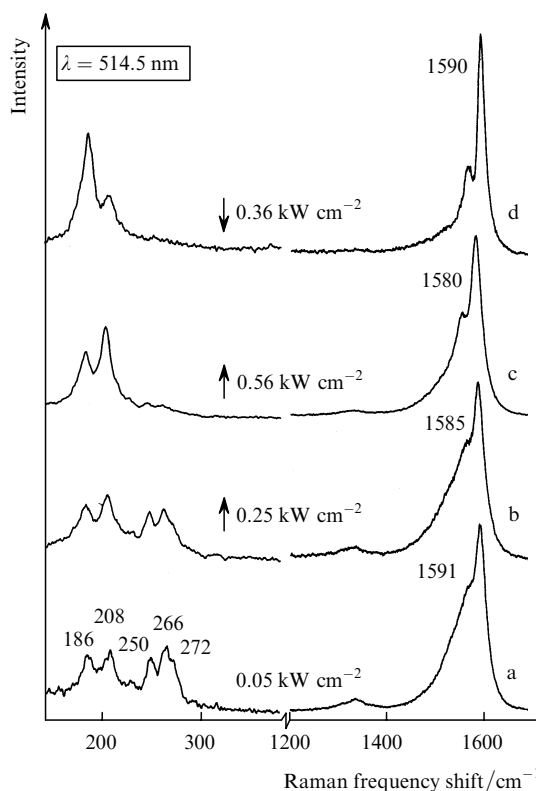


Figure 3. Raman spectra of HipCO nanotubes in the region of breathing and tangential modes recorded by increasing the 515.5-nm radiation power density of an argon laser (a–c) and decreasing it (d). Raman mode frequencies at bands are presented here and in Figs 4, 6, 7 in cm^{-1} .

Another feature of the spectrum is the presence of a group of lines in the region $100\text{--}300\text{ cm}^{-1}$ (the so-called breathing modes) for nanotubes of different geometries. Each of these modes represents the radial vibrations of a nanotube as a whole. The specific feature of the HipCO material is a broad distribution of nanotubes over their diameters, including small-size nanotubes ($\sim 0.8\text{ nm}$), which are absent in materials synthesised by other methods. The recorded spectrum exhibits five breathing modes at frequencies 186, 208, 250, 266, and 272 cm^{-1} .

In the general case, the breathing mode frequency in Raman spectrum depends on the nanotube diameter as [19, 20]

$$\omega = \frac{C_1}{d} + C_2, \quad (1)$$

where ω is the Raman frequency (in cm^{-1}), d is the nanotube diameter (in nm); and C_1 and C_2 are constants. The constant C_1 is determined by the dispersion curve of graphite, while the constant C_2 gives the frequency shift of radial vibrations of an individual nanotube after its inclusion into a bundle (caused by the van der Waals interaction between nanotubes in the bundle). Electron microscopy showed that nanotubes in materials we studied are combined, as a rule, in bundles. The best agreement with experimental data is achieved for $C_1 = 234$ [19] and $C_2 = 10\text{ cm}^{-1}$.

We calculated from (1) the diameters of nanotubes corresponding to the frequencies of breathing modes shown

in Fig. 3a: $d = 1.33, 1.18, 0.98, 0.91,$ and 0.8 nm for $\omega = 186, 208, 250, 266,$ and 272 cm^{-1} , respectively. One can see from Figs 3b, c that, as the power density P of laser radiation increases, the relative intensity of breathing modes corresponding to nanotubes of the smallest diameter (0.8 – 1.0 nm) decreases down to zero at $P = 0.56$ kW cm^{-2} . The shape of a tangential mode changes simultaneously with the weakening of breathing modes. The asymmetry of the line profile disappears, and the mode acquires the shape that is typical for semiconductor nanotubes. Fig. 3d shows that these changes are irreversible: the Raman signal from small-diameter nanotubes is not recovered after decreasing the power density of the laser beam.

The only reversible change in the spectrum is the frequency of the tangential mode of nanotubes. It was shown earlier that this frequency depends linearly on temperature [8, 21] and can be used as an intrinsic temperature indicator in Raman spectra of nanotubes. A standard estimate of the temperature from the ratio of the Stokes and anti-Stokes Raman components cannot be applied for nanotubes because in the case of resonance Raman scattering, the Stokes and anti-Stokes photons are under different resonance conditions [7, 21].

The thermally induced shift of Raman modes at a constant pressure is determined by the thermal coefficient of volume expansion of a material and anharmonicity [9]. The degree of nanotube imperfection and, hence, its thermal coefficient of volume expansion depends on the method of synthesis. This leads to the variation in the coefficient of the thermal shift of a tangential Raman mode from material to material, its linearity being retained. For this reason, each type of nanotubes requires calibration measurements in an optical oven.

We also studied the influence of laser radiation of different power on HipCO nanotubes in vacuum (the experiment was similar to that demonstrated in Fig. 3). However, the Raman signal from small-diameter nanotubes did not vanish with increasing laser radiation power density. Therefore, the presence of oxygen is necessary for observing spectral transformations described above.

To explain this effect, the authors of Ref. [22] proposed the mechanism of selective oxidising annealing of single-wall carbon nanotubes in a laser beam with the threshold annealing temperature dependent on the nanotube diameter. In this case, the role of the laser beam was reduced to the heating of the material, and it could be expected that the breathing Raman modes of small-diameter nanotubes would also vanish exclusively due to the material heating.

To verify this assumption, Raman spectra corresponding to different heating temperatures of HipCO nanotubes in an optical oven in air were recorded (Fig. 4). One can see that the Raman modes at frequencies above 250 cm^{-1} disappeared with increasing temperature, along with a change in the Fano profile of the tangential mode. These two spectral transformations occurring simultaneously suggest that the selectively removed small-diameter nanotubes had the metallic conduction.

We found the threshold temperature for annealing nanotubes of diameter 0.8 – 1 nm during measurements in the oven. It was ~ 400 $^{\circ}\text{C}$. Raman lines from larger nanotubes of diameter 1.1 – 1.4 nm preserved at the first stage of annealing disappeared completely at a temperature of 650 $^{\circ}\text{C}$. This value coincided in fact with the value obtained by the method of thermogravimetry [23]. We calibrated the

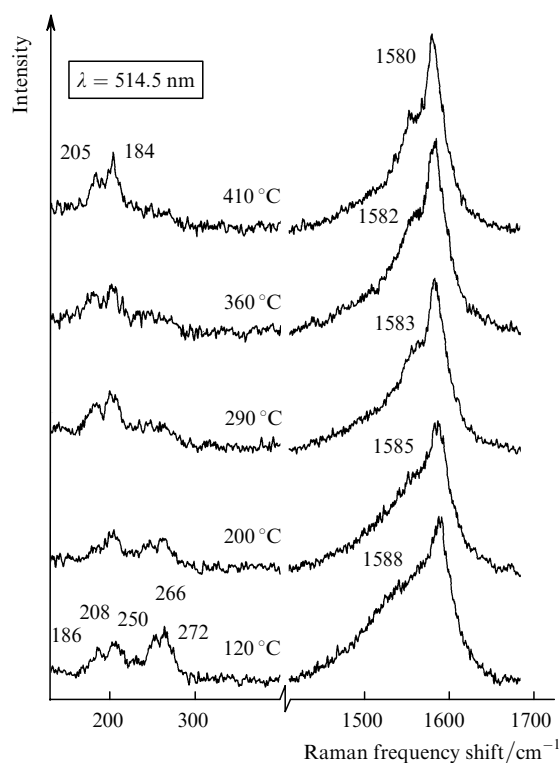


Figure 4. Raman spectra of HipCO nanotubes in the region of breathing modes recorded upon heating in an optical oven in air. Raman modes at frequencies above 250 cm^{-1} disappear irreversibly with increasing temperature.

linear shift of the tangential Raman mode of HipCO nanotubes subjected to thermal treatment in air (Fig. 5). The coefficient of thermal shift was -0.03 $\text{cm}^{-1} \text{ } ^{\circ}\text{C}^{-1}$. Using this value, we estimated the temperature at the instant of the disappearance of the breathing modes of small-diameter

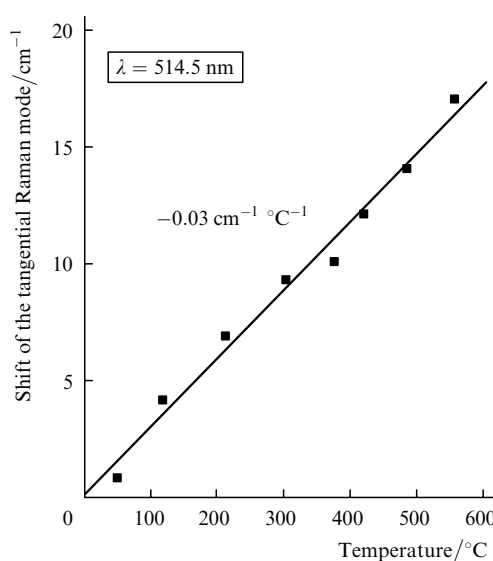


Figure 5. Temperature shift of the tangential Raman mode for single-wall carbon HipCO nanotubes measured upon heating in an optical oven in air (squares). The solid straight line is a linear approximation. The mode frequency at room temperature is 1591 cm^{-1} .

nanotubes in the Raman spectrum of the material heated by the laser (Fig. 3). The threshold annealing temperature (400°C) coincided with that measured in the oven.

Therefore, we have found by the method of Raman spectroscopy that the threshold temperature of selective oxidising annealing of HiPCO nanotubes by laser radiation depends on the nanotube diameter and can be determined from the frequency of a tangential Raman mode of nanotubes at the instant of disappearance of the corresponding breathing mode. Such a controllable selective annealing can be successfully used for homogenisation of nanotubes.

3.2 Reversible changes in Raman spectra of single-wall carbon nanotubes caused by laser radiation

From the very beginning of the development of Raman diagnostics of carbon nanotubes, one of the main advantages of this method is the high intensity of Raman lines provided by the possibility of selective resonance excitation of nanotubes of different geometry [6]. Each material contains nanotubes of different diameters [24]. The distribution of nanotubes over their diameter is usually described by a Gaussian with the half-width $0.1\text{--}0.4\text{ nm}$. The average diameter is determined by synthesis parameters: the catalyser, temperature, pressure, and the buffer gas [25]. Each of the nanotubes has its own electronic structure (Fig. 2). When the energy of an exciting laser photon coincides with the energy gap between symmetric van Hove peaks in the distribution of the density of one-electron states of an individual nanotube, the resonance Raman signal can be excited. This is manifested in the Raman spectrum as the dominating breathing mode of this nanotube. As the laser photon energy increases, the resonance condition is satisfied for a smaller-diameter nanotube (Fig. 6a).

We found in our experiments that the selective resonance response of nanotubes can be tuned not only by scanning the laser excitation frequency but also by varying the laser power density (the laser wavelength being fixed) [26]. Fig. 6b shows the Raman spectra of paper-like samples of single-wall carbon nanotubes obtained by the laser ablation method. The spectra were recorded at different 514.5-nm excitation power densities. In the first spectrum excited at a power density of 10 kW cm^{-2} , the 187-cm^{-1} breathing mode dominates, which corresponds to nanotubes of diameter 1.32 nm . One can see that, as the excitation power density is increased, new breathing modes appear in the spectrum, which correspond to smaller-diameter nanotubes having resonance energies that exceed the energy of exciting photons (2.41 eV). Although the excitation wavelength remains fixed, the spectrum changes similarly to the dependence of the spectrum on the excitation wavelength shown in Fig. 6a. The mode frequencies are somewhat shifted to the red due to sample heating. These spectral variations are reversible, the initial shape of the spectrum being recovered when the laser excitation power is decreased.

As in the case described in section 3.2, to verify the thermal nature of laser action on nanotubes, it was necessary to perform measurements in the optical oven. Fig. 7 shows the Raman spectra of the same nanotubes as in Fig. 6b, which were recorded *in situ* upon heating of samples in the optical oven in air. To exclude the influence of the 514.5-nm probe laser radiation on samples, the spectra were recorded at a low laser power density (50 W cm^{-2}). Two characteristic modes were observed in the spectrum at room

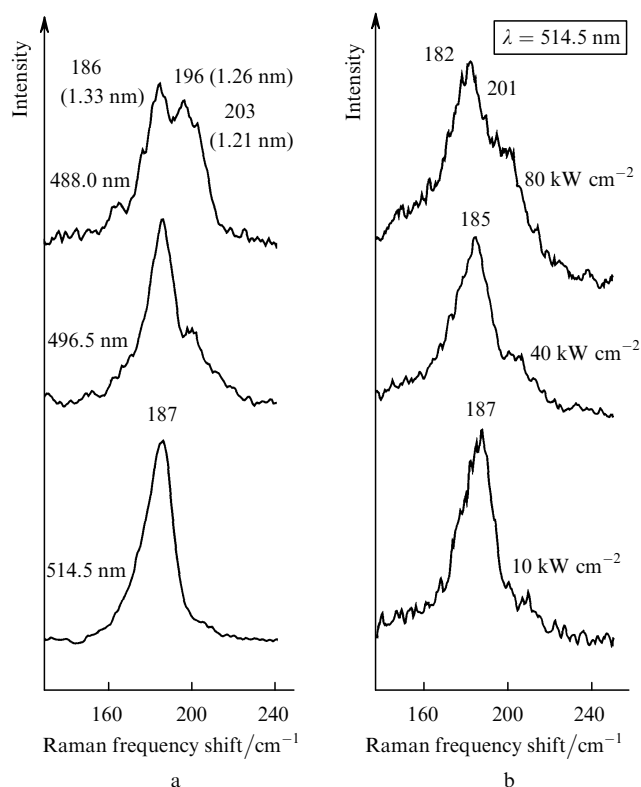


Figure 6. Dependences of the shape of breathing Raman modes of single-wall carbon nanotubes synthesised by the method of laser ablation on the laser excitation wavelength (a) and the 514.5-nm laser power density (b). The nanotube diameter is indicated in parentheses.

temperature: a single 187-cm^{-1} breathing mode and a split 1592-cm^{-1} tangential mode. The tangential mode shifted to the red with increasing temperature. As in the case of

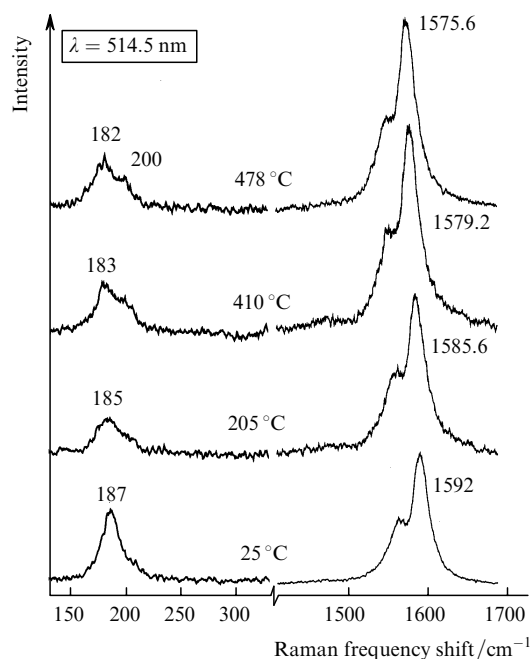


Figure 7. Thermally induced changes in the breathing Raman modes of single-wall carbon nanotubes synthesised by the laser ablation method and heated in an optical oven in air.

HipCO nanotubes, the shift of the tangential mode was linear, with the coefficient equal to $-0.038 \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$. This allows us to estimate the temperature in previous experiments on the laser heating of the paper-like sample of nanotubes.

The shape of the breathing Raman mode changed with increasing temperature in the same way as upon increasing the power density of exciting laser radiation (Fig. 6b). The frequency of the main breathing mode decreased with temperature. However, the thermal shift coefficient equal to $-0.011 \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$ proved to be substantially lower than that for the tangential mode. At a temperature of $\sim 200 \text{ }^\circ\text{C}$, along with the main breathing mode, the 203-cm^{-1} mode appeared, corresponding to smaller-diameter nanotubes. The intensity of the new mode increased with temperature and the mode slightly shifted to the red.

Thus, our experiments have shown that excitation of the Raman signal of nanotubes, whose resonance energy exceeds the energy of exciting photons, can be caused exclusively by increasing temperature. This means that laser radiation heats a sample, and the appearance of a signal from smaller-diameter nanotubes can be considered as a thermally induced resonance. The absence of optical effects is also confirmed by the linear dependence of the tangential-mode intensity on the power density of laser radiation.

We can propose the following mechanism for excitation of a thermally induced resonance. At room temperature, a selective resonance Raman response is observed from nanotubes of diameter 1.32 nm whose electronic structure has the energy gap between symmetric van Hove singularities that coincides with the laser photon energy (2.41 eV). Nanotubes of a smaller diameter are not observed in the Raman spectrum because they have a large energy gap (Fig. 8). However, the thermal broadening of the edges of van Hove singularities [$\sim(2-3)kT$] results in a strong narrowing of the energy gap. The initial laser energy becomes also resonant for nanotubes with diameters that are smaller than the initial diameters by 0.1–0.2 nm. This leads to the appearance of new breathing Raman modes at frequencies exceeding the initial resonance frequencies by $10-15 \text{ cm}^{-1}$.

The resonance Raman response thermally induced by laser radiation was also observed for nanotubes synthesised by the arc method. Because the average diameter of nano-

tubes in this case was different, the effect was most distinct upon excitation by an argon laser at 488.0 nm (2.54 eV).

Thermally induced excitation of resonance Raman scattering in single-wall carbon nanotubes gives new information on the composition and electronic structure of materials, allowing a continuous ‘switching’ of the resonance response between nanotubes of different diameters by varying temperature rather than the laser excitation wavelength.

4. Conclusions

We have found the effect of annealing of single-wall carbon nanotubes of a small diameter (0.8–1 nm) at substantially lower temperatures ($400 \text{ }^\circ\text{C}$) than the annealing temperature for nanotubes of diameter 1.1–1.4 nm ($650 \text{ }^\circ\text{C}$). The effect was observed in the Raman spectra of HipCO nanotubes recorded at elevated temperatures, both in a laser beam and in an oven. It was manifested in the fact that breathing Raman modes at highest frequencies (above 250 cm^{-1}), corresponding to small-diameter nanotubes, gradually disappeared irreversibly with increasing temperature. The frequency of a tangential Raman mode can be used as an intrinsic temperature indicator. The linear shift of this frequency was calibrated in measurements performed in a thermally stabilised optical oven. Our results have shown that oxidising annealing performed at a given temperature can provide the homogenisation of nanotubes over their diameters.

Along with the Raman signal from nanotubes resonantly excited at room temperature, we have found thermally induced resonance excitation of breathing Raman modes in nanotubes of a smaller diameter. This effect was observed independently of the heating method (by a laser beam or in an optical oven) and the method of synthesis of nanotubes. We have proposed the mechanism of thermally induced Raman scattering that takes into account the thermal broadening of van Hove singularities in the distribution of the density of one-electron states of nanotubes resulting in a change in the resonance condition with increasing temperature. This effect can be used for tuning a selective resonance Raman response of a system of nanotubes by varying temperature rather than the excitation wavelength.

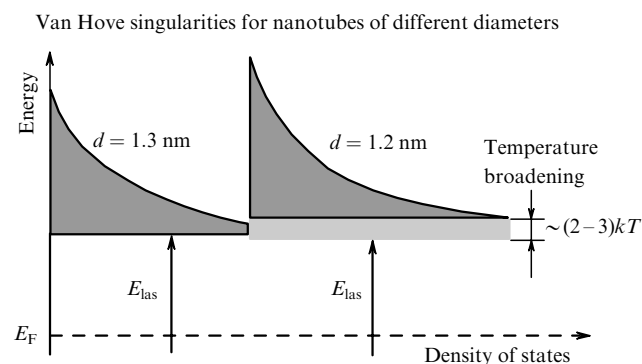


Figure 8. Energy diagram explaining the appearance of a thermally induced Raman resonance due to the thermal broadening of the edges of van Hove singularities in the distribution of the density of one-electron states for a nanotube with the resonance energy exceeding the threshold (E_{las} is the laser photon energy, E_{F} is the Fermi energy).

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 01-02-17358), INTAS (Grant No. 01-254), ISTC (Grant No. 1400), and the RAS program ‘Optical Spectroscopy and Frequency Standards’. A.V.S. was also supported by an ISSEP post-graduate grant and the Moscow Government. The authors thank V.I. Zaikovskii and V.L. Kuznetsov (Institute of Catalysis, Siberian Branch, RAS, Novosibirsk) for the electron-microscope study of nanotube materials and U. Dettlaff-Veligovska (Max-Planck-Institute für Festkörperforschung, Stuttgart, Germany) for donating HipCO samples.

References

- [doi>1.](#) Iijima S. *Nature*, 354, 56 (1991).
- Dresselhaus M.S., Dresselhaus G., Eklund P.C., in *Science of Fullerenes and Carbon Nanotubes* (New York, San Diego: Academic Press, 1996).
- [doi>3.](#) Mintmire J.W., White C.T. *Phys. Rev. Lett.*, 81, 2506 (1998).

4. Osadchii A.V., Obraztsova E.D., Terekhov S.V., Yurov V.Yu. *Pis'ma Zh.Eksp. Teor. Fiz.*, **77**, 479 (2003). [doi>](#)
5. Dresselhaus M.S., Dresselhaus G., Avouris P., in *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Berlin, Heidelberg: Springer, 2001). [doi>](#)
6. Rao M., Richter E., Bandow S., et al. *Science*, **275**, 187 (1997). [doi>](#)
7. Dresselhaus M.S., Dresselhaus G., Jorio A., Souza Filho A.G., Saito R. *Carbon*, **40**, 2043 (2002). [doi>](#)
8. Terekhov S.V., Obraztsova E.D., Lobach A.S., Konov V.I. *Appl. Phys. A*, **74**, 393 (2002). [doi>](#)
9. Tan P., Deng Y., Zhao Q., Cheng W. *Appl. Phys. Lett.*, **74**, 1818 (1999). [doi>](#)
10. Huang F., Yue K.T., Tan P., et al. *J. Appl. Phys.*, **84**, 4022 (1998). [doi>](#)
11. Huang P.V., Cavagnat R., Ajayan P.M., Stephan O. *Phys. Rev. B*, **51**, 10048 (1995). [doi>](#)
12. Li H.D., Yue K.T., Lian Z.L., Zhan Y., et al. *Appl. Phys. Lett.*, **76**, 2053 (2000). [doi>](#)
13. Yu Z., Brus L.E. *J. Phys. Chem.*, **104**, 10995 (2000). [doi>](#)
14. Zhang L., Li H., Yue K.-T., Zhang S.-L., et al. *Phys. Rev. B*, **65**, 073401 (2002). [doi>](#)
15. Corio P., Santos P.S., Pimenta M.A., Dresselhaus M.S. *Chem. Phys. Lett.*, **360**, 557 (2002). [doi>](#)
16. Thess A., Lee R., Nikolaev P., et al. *Science*, **273**, 483 (1996). [doi>](#)
17. Journet K., Maser W.K., Bernier P., et al. *Nature*, **388**, 756 (1997). [doi>](#)
18. Nikolaev P., Bronikovski M.J., et al. *Chem. Phys. Lett.*, **313**, 91 (1999). [doi>](#)
19. Kuzmany H., Plank W., Hulman M., et al. *Eur. Phys. J. B*, **22**, 307 (2001). [doi>](#)
20. Henrard L., Hernandez E., Bernier P., Rubio A. *Phys. Rev. B*, **60**, R8521 (1999). [doi>](#)
21. Obraztsova E.D., Terekhov S.V., Osadchy A.V., in *AIP Conf. Proc.* (Melville, 2000) Vol. 544, p. 276. [doi>](#)
22. Bokova S.N., Obraztsova E.D., Terekhov S.V., Dettlaff-Veglikovska U. *Proc. XI Intern. Laser Physics Workshop 2002 (LPHYS-02)* (Bratislava, 2002) p. 9. [doi>](#)
23. Chiang I.W., Bruns B.E., Smalley R.E., et al. *J. Phys. Chem. B*, **105**, 1157 (2001). [doi>](#)
24. Obraztsova E.D., Yurov V.Yu., Shevlyuga V.M., et al. *Nanostructured Materials*, **11**, 295 (1999). [doi>](#)
25. Kuznetsov V.L., Usoltseva A.N., Chuvilin A.L., Obraztsova E.D., Bonard J.-M. *Phys. Rev. B*, **64**, 235401 (2001). [doi>](#)
26. Obraztsova E.D., Bonard J.-M., Kuznetsov V.L., et al. *Nanostructured Materials*, **12**, 567 (1999). [doi>](#)



Aleksandr Mikhailovich Prokhorov and his wife Galina Alekseevna.