# COMPUTER MODELLING OF THE OPTICAL ABSORPTION SPECTRUM OF SINGLE-WALLED CARBON NANOTUBE BUNDLES

YU.I. PRYLUTSKY, O.V. OGLOBLYA, P. SCHARFF[1]



**Taras Shevchenko Kyiv National University, Faculty of Biology**
*(64, Volodymyrska Str., Kyiv 01033, Ukraine),*

[1]**Institute of Physics**
*(TU Ilmenau, Ilmenau D-98684, Germany)*

The computer modelling of the optical absorption of single-walled carbon nanotube (SWCNT) bundles in the approximation of normal distributions of nanotube radii and chiral angles is carried out. The electronic and optical properties of SWCNT bundles are investigated with the use of the Su—Schrieffer—Heeger (SSH) theory under linear electron-phonon coupling. The localized states demonstrate the nonlinear aspects of excited states in SWCNTs. It is found that SWCNTs with different radii have a strong oscillatory dependence of the optical absorption on the incident light energy. A decrease in lengths and the uncapping of nanotube's ends shift the peaks of the optical absorption spectrum to the region of relatively high energies and suppress their height.

## Introduction

Until today, SWCNTs attract a significant attention both of the theorists and experimenters. The complexity of their isolation from various products of the synthesis is the main obstacle for the experimental study of SWCNTs. However, many research groups have recently obtained the significant quantities of SWCNTs of 1—2 nm in diameter with a narrow distribution of sizes, by using many different catalysts made of transition and lanthanide metals [1]. Therefore, it is important to study the optical properties of such SWCNT bundles. The possibility to work with the entire sample and to investigate the integral contribution from SWCNTs is the advantage of the optical methods. For the theoretical explanation of the experimental data obtained on the SWCNT bundles, it is necessary to possess a detailed information about the distribution of SWCNTs. The assumption about the Gaussian distributions of diameters and chirality angles of SWCNTs in a bundle is most probable [2]. The experimental studies [1] have shown also that, in the synthesis of carbon nanotubes, their caps may be destroyed partially or completely. Such an effect will greatly influence the optical and electronic structures of carbon nanotubes. Thus, in the present paper, the computer modelling of the optical absorption of SWCNT bundles in the approximation of the normal distributions of nanotube radii and chirality angles is carried out.

## 1. Results and Discussion

We consider the composition of disordered SWCNT bundles, i.e., the set of nanotubes of different chiralities. The content of nanotubes in the sample is described by the Gaussian distribution with a center which corresponds to a nanotube of the specific type of symmetry, whose content in the sample is maximum. Let us assume that the distribution of diameters is Gaussian with the average value $d_0$ and dispersion $\sigma_d^2$, and let the distribution of angles of chirality be also Gaussian with the average value $\theta_0$ and dispersion $\sigma_\theta^2$. To simplify the calculations, we consider the SWCNT bundles which contain only nanotubes with diameters $d_0 - \sigma_d < d < d_0 + \sigma_d$ and angles of chirality $\theta_0 - \sigma_\theta < \theta < \theta_0 + \sigma_\theta$. In the theoretical paper [3], it was shown that, in the composition of a disordered SWCNT bundle, the interaction between nanotubes corresponds to the localization of wave functions on the separate nanotubes, i.e., the energy spectrum of separate nanotubes is not changed. Therefore, we will statistically average the optical absorption of a nanotube $\alpha_{m,n}$ with the indices of chirality $(m,n)$ by the formula

$$\alpha(E) \approx \sum_{m,n} \exp\left[-\frac{(d_{m,n}-d_0)^2}{2o_d^2} - \frac{(\theta_{m,n}-\theta_0)^2}{2o_\theta^2}\right] \times$$

$$\times \alpha_{m,n}(E). \qquad (1)$$

We considered two SWCNT bundles: with a chirality angle of $15° \pm 15°$ and a diameter of $7.4 \pm 1.2$ Å (bundle A) and with a diameter of $9.4 \pm 1.3$ Å (bundle B). Bundle B contains such nanotubes: (6,6), (7,5), (7,6), (7,7), (8,4), (8,5), (8,6), (8,7), (9,3), (9,4), (9,5), (9,6),

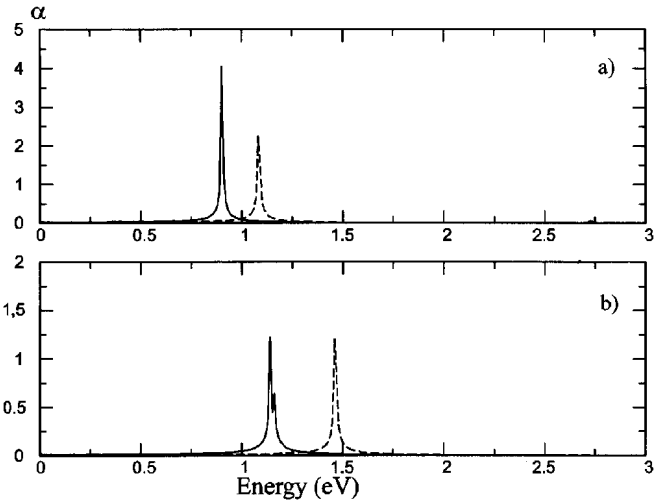


Fig. 1. Optical absorption of SWCNTs with a fullerene cap (solid line) and without it (dotted line) for (9,0) nanotube with the length of (*a*) 7 and (*b*) 5 translational periods

(10,1), (10,2), (10,3), (10,4), (10,5), (11,0), (11,1), (11,2), (11,3), (11,4), (12,0), (12,1), (12,2), (13,0), (13,1).

The table shows the nanotubes presented in bundle A and gives the fundamental geometric characteristics of these tubes: $(m, n)$ are the indices of chirality, $d$ is a diameter, $\theta$ is the angle of chirality, $T$ is the quantity of translational periods, the column "capped" indicates an open or closed nanotube, $\tau$ is the length of a unit cell, $N$ is the quantity of atoms in the unit cell. The numerical calculations were carried out with the use of personal programs. The frequency filtration (library libfftw) was used for constructing the density of electronic states (DOS) on discrete levels.

**Composition of SWCNT bundle A**

| $(m,n)$ | $d$ (Å) | $\theta$ | $T$ | Capped | $\tau$ (Å) | $N$ |
|---|---|---|---|---|---|---|
| (5,5) | 6.78 | 30.01 | 20 | not | 2.46 | 410 |
| (6,3) | 6.21 | 19.11 | 5 | not | 11.27 | 432 |
| (6,4) | 6.82 | 23.42 | 2 | not | 18.56 | 316 |
| (6,5) | 7.47 | 27.00 | 1 | not | 40.63 | 376 |
| (6,6) | 8.14 | 30.00 | 20 | not | 2.46 | 492 |
| (7,2) | 6.41 | 12.22 | 2 | not | 34.87 | 550 |
| (7,3) | 6.96 | 17.00 | 1 | not | 37.86 | 330 |
| (7,4) | 7.55 | 21.06 | 3 | not | 13.65 | 386 |
| (7,5) | 8.17 | 24.51 | 1 | not | 44.48 | 450 |
| (8,0) | 6.26 | 0.00 | 8 | not | 4.26 | 272 |
| (8,1) | 6.69 | 5.82 | 1 | not | 36.40 | 308 |
| (8,2) | 7.17 | 10.89 | 6 | not | 6.51 | 352 |
| (8,3) | 7.71 | 15.30 | 1 | not | 41.96 | 404 |
| (8,4) | 8.28 | 19.11 | 3 | not | 11.27 | 352 |
| (9,0) | 7.04 | 0.00 | 7 | yes | 4.26 | 348 |
| (9,1) | 7.47 | 5.21 | 1 | not | 40.64 | 382 |
| (9,2) | 7.94 | 9.83 | 1 | not | 43.23 | 430 |
| (9,3) | 8.47 | 13.90 | 3 | not | 15.36 | 486 |
| (10,0) | 7.83 | 0.00 | 6 | yes | 4.26 | 340 |
| (10,1) | 8.25 | 4.71 | 2 | not | 14.96 | 316 |

The SSH model [4] was used in the numerical calculations of the electronic and optical properties of an individual SWCNT. In the approximation of the self-consistency field, the model Hamiltonian takes the form

$$H_{\rm HF} = \sum_{\langle i,j\rangle,s} (-t - \alpha y_{ij})(c_{is}^{+} c_{is} + \text{h.c.}) +$$

$$+ \frac{K}{2} \sum_{\langle i,j\rangle} y_{ij}^2 + U \sum_i \Big(\sum_s \rho_{i,-s} c_{is}^{+} c_{is} - \rho_{i\uparrow}\rho_{i\downarrow}\Big). \qquad (2)$$

Eigenvalues $\varepsilon_{ks}$ and functions $\psi_{ks}$ are found from the equation

$$\varepsilon_{ks}\psi_{ks}(i) = \sum_{\langle i,j\rangle} (-t - \alpha y_{ij})\psi_{ks}(j) + U\rho_{i,-s}\psi_{ks}(i). \qquad (3)$$

Here, $\rho_{is} = \langle c_{is}^{+} c_{is}\rangle = {\sum_k}' \psi_{ks}(i)\psi_{ks}(j)$ is the electron density (the prime near the sum stands for the summation only over the populated levels). From the limitation $\sum\limits_{\langle ij\rangle} y_{ij} = 0$, it is possible to obtain the self-consistency relation for $y_{ij}$ as

$$y_{ij} = \frac{2\alpha}{K} {\sum_{k,s}}' \psi_{ks}(i)\psi_{ks}(j) - \Delta y, \qquad (4)$$

where

$$\Delta y = \frac{2\alpha}{KN} \sum_{\langle ij\rangle} {\sum_{k,s}}' \psi_{ks}(i)\psi_{ks}(j). \qquad (5)$$

Here, $N$ is the number of $\pi$ bonds. The following parameters were used in the numerical calculations: $\alpha = 6.3$ eV/Å, $K = 49$ eV/Å$^2$, $t = 2.7$ eV.

Fig. 1 gives the results of calculations of the optical absorption of SWCNTs with different lengths, being closed (solid line) and open (dotted line) ones. As seen, the peaks of optical absorption for SWCNTs of greater lengths are shifted to the side of smaller energies. The presence of fullerene caps (closed nanotubes) has the same influence on the optical absorption, i.e., it is equivalent to an increase in the effective dimensionality of the system. The effect of caps is greater for SWCNTs of smaller lengths.

Fig. 2 shows the optical absorption of SWCNTs (10,0) with different lengths which are closed by the fullerene caps. As seen, the dependence of a position of the first peak for the SWCNT (10,0) on length is the inversely proportional one, which agrees with the results in [4]. Moreover, the presence of caps considerably influences the electronic properties of SWCNTs (10,0).

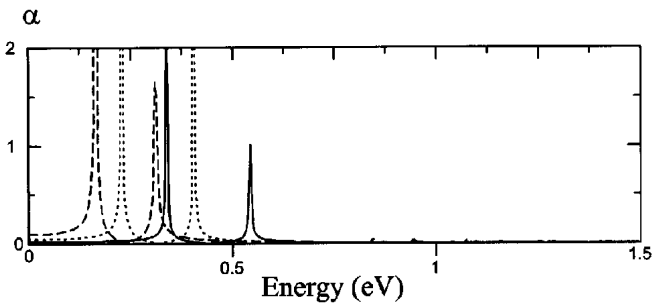


Fig. 2. Optical absorption of SWCNT (10,0) with different lengths closed by the fullerene caps: 4 translational periods (solid line); 6 translational periods (point line); and 8 translational periods (dotted line)

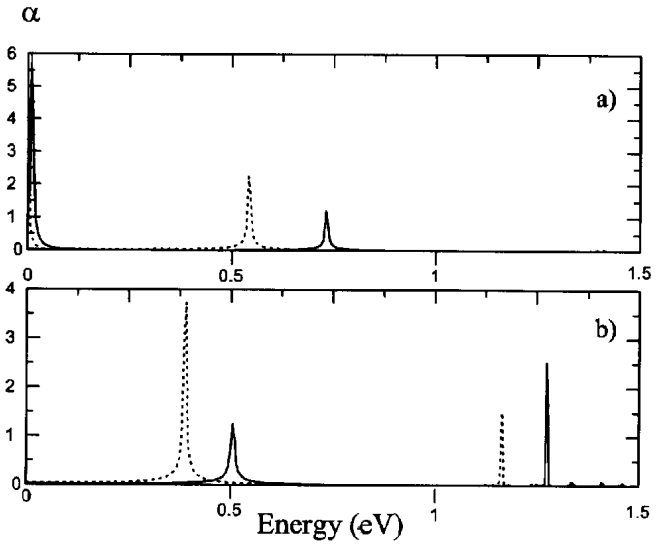


Fig. 3. Optical absorption of open nanotubes (15,0) (*a*) and those with a fullerene cap (*b*) with the lengths of 5 (solid line) and 7 (dotted line) translational periods

The calculations of the optical absorption of SWCNTs (15,0) with different lengths, open and closed ones, are presented in Fig. 3. As seen, the open nanotubes have infinitely large static optical absorption $\alpha(0)$.

It is known that the optical properties of $C_{60}$ is mainly defined by delocalized $\pi$-electrons like in conjugated polymers. However, the three-dimensional character of $C_{60}$ makes the optical absorption to be smaller than that of linear polymers containing a similar number of carbon atoms. For a capped nanotube, a $\pi$-electron on the site at the edge of a cylinder can only transfer to two neighbors of the site. Obviously, this kind of the edge effect reduces the effective space dimensions

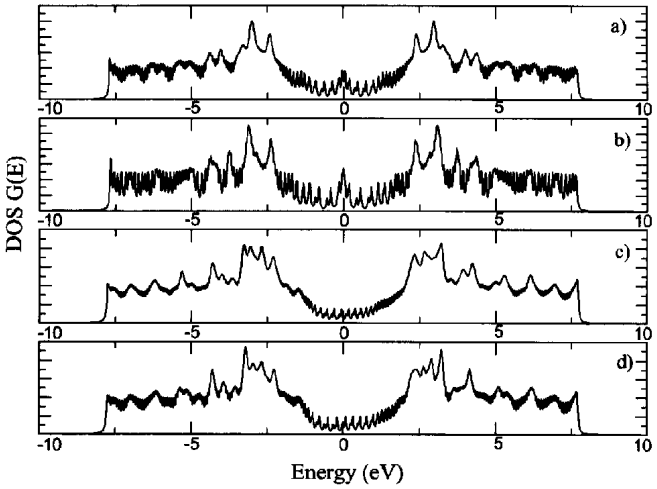


Fig. 4. Density of the electronic states of nanotube (15,0) without a fullerene cap *a*), *b*) and with it *c*), *d*) with lengths of 7 *a*), *c*) and 5 *b*), *d*) translational periods

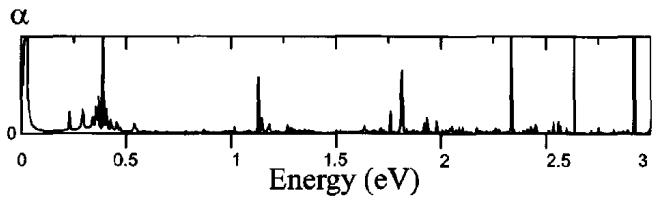


Fig. 5. Optical absorption of SWCNT bundle A

of $\pi$-electrons and thus enhances the static optical absorption of nanotubes.

As we can see from Fig. 4, the DOS of the open nanotubes, which have infinitely large static optical absorption $\alpha(0)$, reveals the sharp peaks of electron density near the Fermi level.

After the averaging of a composition over the nanotubes which can be present in a bundle, we obtain the results shown in Figs. 5 and 6. In particular, Fig. 6 gives the results of the averaging over different weighting factors of the spectra of SWCNTs, which are contained in bundle B. As seen, the method of averaging slightly influences the form of the first peak. Furthermore, the optical absorption peaks are grouped into clusters. It follows from the analysis of the maps of electron density that two first clusters correspond to the semiconductor nanotubes, and the third cluster corresponds to the metallic nanotubes, which is coordinated with the conclusion of [5].

Thus, optical spectroscopy can be used to rapidly determine the detailed composition of bulk carbon nanotube samples providing the distributions of both tube diameters and chiral angles.

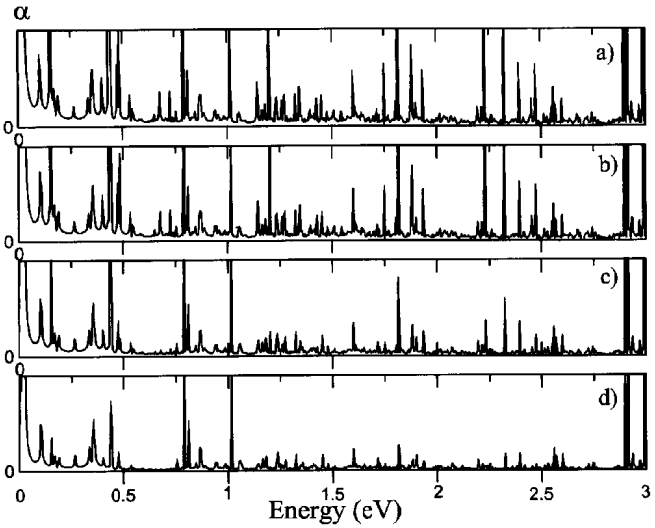


Fig. 6. Optical absorption of SWCNT bundle B: arithmetical averaging (*a*), Gaussian averaging with $2\sigma_0$ (*b*), $\sigma_0$ (*c*), and $\sigma_0/2$ (*d*) over the spectra of individual nanotubes

## Conclusions

The numerically calculated optical absorption spectra of the SWCNT bundles of various compositions have the strong oscillatory dependence of the optical absorption on the incident light energy, which is caused by the complex electron structure of SWCNTs. A decrease in the length and the uncapping of nanotube's ends shift the peaks of the optical absorption spectrum to the region of relatively high energies and decrease their height. The first and second peaks of optical absorption appear from the transition between van Hove's singularities on the maps of the density of states of SWCNTs with semiconductor properties, and the third peak appears from similar transitions for metallic SWCNTs. The obtained spectra of optical absorption for SWCNT bundles are in good agreement with the experimental data derived in measurements of the position of the first two peaks of absorption [2].

1. *Maiti A., Brabec C.J., Bernholc J.* // Phys. Rev. B. — 1997. — **55.** — P.R6097—R6100.
2. *Kuzmany H., Plank W., Hulman M. et. al.* // Europ. Phys. J. B. — 2001. — **22**, N 3. — P.307—320.
3. *Maarouf A.A., Kane C.L., Mele E.L.* // Phys. Rev. B. — 2000. — **61.** — P.11156—11171.
4. *Jun Ma, Ren-kuan Yuan* // Ibid. — 1998. — **57.** — P.9343—9348.
5. *Hertel T., Fasel R., Moos G.* // App. Phys. A. — 2002. — **75.** — P.449—465.

КОМП'ЮТЕРНЕ МОДЕЛЮВАННЯ СПЕКТРА ОПТИЧНОГО ПОГЛИНАННЯ В'ЯЗКАМИ ОДНОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК

*Ю.І. Прилуцький, О.В. Оглобля, П. Шарфф*

Р е з ю м е

Виконано комп'ютерне моделювання оптичного поглинання в'язок одношарових вуглецевих нанотрубок (ОВНТ) у наближенні нормальних розподілів радіусів нанотрубки та їх хіральних кутів. Електронні та оптичні властивості ОВНТ-в'язок досліджено в рамках моделі Зу—Шриффера—Хігера із застосуванням лінійної електрон-фононної взаємодії. Локалізовані стани демонструють нелінійність збуджених станів у ОВНТ-в'язках. Знайдено, що ОВНТ з різними радіусами мають сильну осцилюючу залежність оптичного поглинання від енергії падаючого світла. Зменшення довжини та відкриття кінців нанотрубки зміщує піки оптичного спектра поглинання в бік вищих енергій і зменшує їх інтенсивність.