Vibrational properties of double-walled carbon nanotubes

J. Maultzsch[*], S. Reich[*†], P. Ordejón[†], R. R. Bacsa[**], W. Bacsa[**], E. Dobardžić[‡], M. Damnjanović[‡] and C. Thomsen[*]

[*]*Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin, Germany*
[†]*Institut de Ciència de Materials de Barcelona (CSIC), Campus de la Universitat Autònoma de Barcelona, E-08193 Bellaterra, Barcelona, Spain*
[**]*Laboratoire de Physique des Solides, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex 4, France*
[‡]*Faculty of Physics, University of Belgrade, P.O. Box 368, 11001 Belgrade, Serbia*

Abstract. We study the vibrational properties of double-walled carbon nanotubes by *ab initio* calculations and Raman scattering. Furthermore, we investigate the stability of double-walled tube configurations with other interlayer distances than in graphite.

An increasing number of carbon nanotube studies focused very recently on double-walled tubes (DWNT). The interaction between the inner and outer tube, for example, has been investigated in relation to the breathinglike phonon modes [1, 2]. The comparatively small diameter of the inner tube in typical DWNT samples has led to a number of Raman studies which attempted an assignment of the inner tube chirality based on the radial breathing mode (RBM) frequencies [3, 4, 5]. In these investigations, the interaction between the tube walls is often modeled by adding a constant to the dependence of the RBM frequency on the inverse tube diameter. In both theoretical and experimental studies the distance between the tube walls is usually assumed the same as the interlayer distance in graphite, i.e., ≈ 3.4 Å.

In this paper we study the vibrational properties of double-walled carbon nanotubes first by an analytically solvable spring-constant model and second by *ab initio* density-functional calculations for several pairs of armchair tubes. We show that double-walled nanotubes with interwall distances different from the value in graphite may exist. In the DWNT with a smaller wall distance [(4,4)@(8,8)], the phonon modes exhibit a strong mixing; in all other investigated DWNTs each of the constituents vibrates independently. In the (3,3)@(8,8) tube, the change in phonon frequencies due to the wall interaction is larger for the high-energy optical phonon modes than for the RBM. Finally, we compare our results with Raman spectra.

In order to estimate the RBM frequecies in DWNT in a simple approximation, we modeled the tubes by homogeneous cylinders and the wall-wall interaction by an effective spring constant. If the inner tube diameter d_1 is below 10 Å, an analytical expression can be used for the RBM frequencies Ω_1 and Ω_2 of the out-of-phase and the in-phase

TABLE 1. Total energy per carbon atom after relaxation of the atomic positions.

	E_{tot} **eV/atom**	**radius Å**		E_{tot} **eV/atom**	**radius (inner) Å**	**radius (outer) Å**	**energy gain meV/atom**
(3,3)	-154.8697	2.102	(3,3)@(8,8)	-155.1776	2.103	5.458	195
(4,4)	-155.0691	2.769	(4,4)@(8,8)	-155.1983	2.725	5.546	-23
(8,8)	-155.2663	5.463	(3,3)@(9,9)	-155.1873	2.106	6.121	96
(9,9)	-155.2803	6.141	(4,4)@(9,9)	-155.2341	2.772	6.123	188

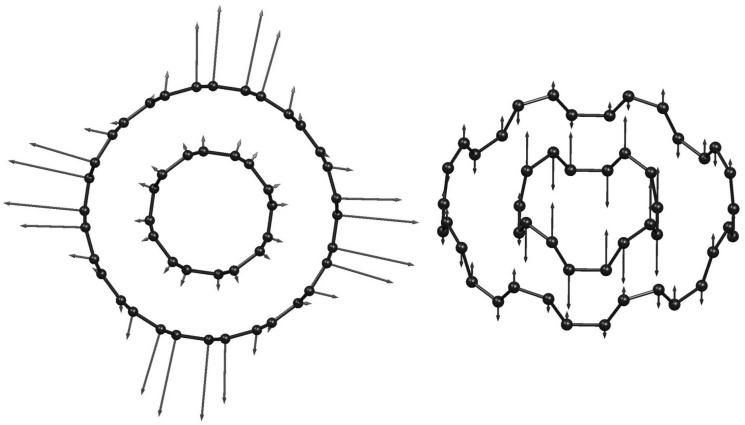

FIGURE 1. (4,4)@(8,8) tube: in-phase breathing mode at 232 cm^{-1} (left) and out-of-phase LO mode at 1582 cm^{-1} (right).

motion, respectively:

$$\Omega_{1/2} \approx \omega_{1/2} + \frac{\kappa d_1}{2 m_{1/2} \omega_{1/2}},$$

where $\kappa = 1.159 \cdot 10^5$ amu cm^{-2} Å^{-1} is found from the graphite B_{2g} mode at 127 cm^{-1}, $\omega_{1/2} \propto 1/d_{1/2}$ are the RBM frequencies and $m_{1/2}$ the linear mass densities of the inner/outer tube [6].

To investigate the full vibrational spectrum of DWNT, we performed *ab inito* calculations using the SIESTA code within the local-density approximation [7]. A double-ζ, singly polarized basis set of localized atomic orbitals was used for the valence electrons. In Table 1 we summarize the total energy per carbon atom after the relaxation of the atomic positions in the investigated double-walled tubes. All of the four DWNTs, with the inter-wall distance ranging from 2.8 Å [(4,4)@(8,8)] to 4.0 Å [(3,3)@(9,9)], appear stable. The energy gain per carbon atom from the sum of the two isolated constituents to the double-walled tube is given in the last column of Table 1.

In the (4,4)@(8,8) and the (3,3)@(9,9) tube, the two constituents have a fourfold and threefold rotational axis in common, respectively, i.e., they are commensurate with respect to rotations about the tube axis. In the other two DWNTs, the only symmetry operations besides the translation along the tube axis are the horizontal mirror plane and

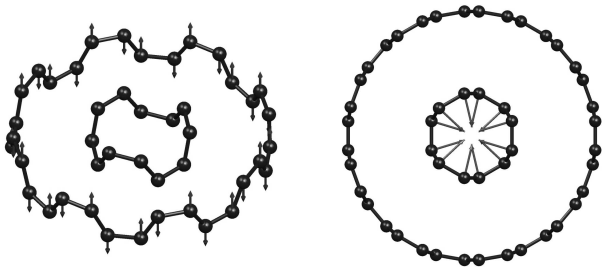

FIGURE 2. Longitudinal optical mode in the (3,3)@(8,8) tube (left) and RBM mode in the (3,3)@(9,9) tube (right). In both DWNT, the inner and outer tube vibrate independently.

the U axis [8, 9]. Thus for the incommensurate DWNTs a very low friction between the walls is expected if the tubes are rotated against each other, but there is interaction between the walls in the commensurate ones [10]. Since the calculation of the acoustic phonon frequencies is not accurate enough, we investigated this prediction by rotating the inner tube in the (4,4)@(8,8) and the (3,3)@(8,8) and comparing the total energy before and after the rotation. We found a change in total energy less than 1 meV/atom for the (3,3)@(8,8) when the (3,3) tube was rotated; in the (4,4)@(8,8) tube the total energy increased by several meV per carbon atom upon rotation of the (4,4) tube, in agreement with the group-theoretical prediction.

We calculated the Γ-point phonon frequencies of the DWNTs, of their isolated constituents and, for comparison, of their constituents with the same (unrelaxed) atomic positions as in the DWNTs. As expected because of their small interwall distance and the commensurability, the RBM frequencies in the (4,4)@(8,8) tube are upshifted by 25-55 cm^{-1} with respect to the RBM in single-wall tubes. The longitudinal optical (LO) phonon mode is upshifted as well by up to 100 cm^{-1}. Moreover, the phonon displacements exhibit a strong mixing in the (4,4)@(8,8) tube. The in-phase and out-of-phase displacements of the two tubes are clearly seen (Fig. 1). Due to the symmetry reduction in the double-walled tube, the amplitude of the RBM vibration does not neccessarily remain constant along the circumference of the tube, e.g., the in-phase RBM amplitude exhibits a modulation by $\pi/2$ along the circumference.

In the (3,3)@(8,8) tube, we found no significant change in the RBM frequencies. Surprisingly, the transversal optical (TO) phonon mode of the (8,8) tube exhibits a downshift by 30 cm^{-1}. Most of the phonon eigenvectors in this DWNT are independent vibrations of their constituents; either the inner or the outer tube is displaced, while the amplitude of the other tube's displacement is zero (see Fig. 2). Also in the (3,3)@(9,9) tube the RBM frequencies are not affected by a wall-wall interaction. This might partly be due to the large interwall distance of 4 Å. On the other hand, from the commensurability of the tubes we would expect some interaction between the walls.

For comparison, we show in Fig. 3 the Raman spectra from two different spots of the same DWNT sample, both of which were typically found. The spectrum to the right is "metallic"-like, however, the downshift of the upper peak to below the graphite

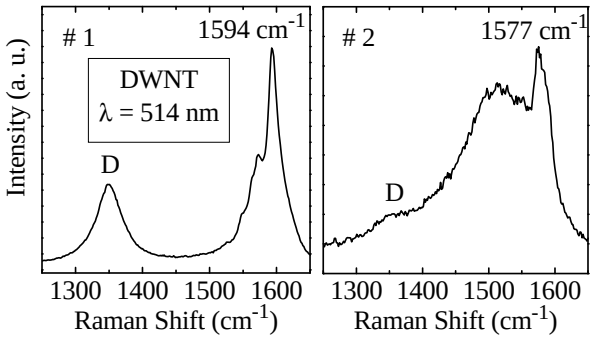

FIGURE 3. Raman spectra of different spots on the same sample of CVD-grown double-walled carbon nanotubes. The laser wavelength is 514 nm.

frequency is even for a metallic tube very unusual. This could be a hint to the downshift of the TO mode in the (3,3)@(8,8) tube predicted by the *ab initio* calculations.

In summary, we have shown that double-walled nanotubes with interwall distances between 2.8 and 4.0 Å may exist. We found from *ab initio* calculations that for some DWNTs the high-energy optical phonon modes are even more affected by the wall-wall interaction than the RBM modes. Since the effect on the RBM frequency of the inner tube is predicted to increase strongly with the tube diameter [1, 2, 6], *ab initio* calculations for larger DWNTs are neccessary. The effect of the symmetry of the tubes and of their interwall distance on the wall-interaction has to be investigated by future experiments and calculations.

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