Vibrational Cluster Calculations of Zig-Zag Carbon Single-Wall Nanotubes

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ABSTRACT

The results of theoretical cluster calculations of positions of the vibrational IR and Raman active modes of zig-zag carbon single-wall nanotubes of small diameter are presented. These results might be significant for fast diagnostics of the structure of synthesized carbon single-wall nanotubes.

1. INTRODUCTION

Carbon nanotube is assumed to be an infinitely long cylinder with a monolayer of hexagonally ordered carbon atoms in the tube wall. A carbon nanotube is, therefore, an one-dimensional system and the fourth member of the carbon family with a dimension of 1D (diamond in 3D, graphite in 2D, and fullerene in 0D). A nanotube is a form of graphite sheet with a diameter of a few nanometers.

These graphite nanotubes may poses unusual mechanical, electronic and optical properties with a wide range of technological applications such as nanoscale devices, light-weight and high strength composite materials, etc., connected with their crystalline perfection, various possible helical structures, dimensionality, and high efficiency of production. Theoretical studies have shown that the electronic properties of a graphite nanotube strongly depend on its helical structure. It can be metallic or semiconducting, which implies that electronic properties of nanotube can be tuned by changing its geometrical parameters [1].

The special interest of graphite nanotubes is related to the broad field of carbon-fiber science and technology, and motivated by the fact that a single-wall nanotube can be considered as one atomic-layered carbon fiber of the smallest diameter. Graphite nanotubes are thus of interest for model calculations for structure property relations. A number of challenging questions are still open and some additional knowledge about structure, chemical bonds, electronic distribution, etc. is still needed. Infrared and Raman spectroscopy combined with careful calculation of vibrational spectra are expected to provide such information for these structures.

The symmetry of the nanotubes is relevant both for deep insight into their physical properties and simplifying calculations. Due to their 1D translational periodicity along the axis, the resulting groups are the line groups and the lattice dynamic can be studied in this manner to classify normal modes [2,3].

On the other hand these rolled up graphite sheets are expected to have a lot of properties derived from the energy bands and lattice dynamics of graphite i.e. graphite sheet. Phonon dispersion calculations for 3D graphite and 2D graphite sheet are similar. Due to weak interplanar coupling in graphite there is a little dispersion in the k_z direction, and very little difference between the structure of 2D and 3D one-phonon density states is detected. Approximate values for vibration fre-

quencies of the nanotubes can be obtained from those of graphite sheet by the method of zone folding (two shortcomings: three modes with vanishing frequencies at $q{\to}0$ in 2D do not produce corresponding modes in nanotubes, i.e. one of the frequencies must be calculated separately; this scheme does not give rise to two zero-frequency tubule modes corresponding to the translational modes of the atoms in the two directions perpendicular to the tubule axis). The effect of the curvature on the force constants also has been neglected, i.e. the small hybridization between the sp2 and p_z orbitals has been assumed [4,5].

It is obvious that greater the diameter the closer the properties of the nanotube to the properties of the graphite sheet.

The fact that the nanotube samples synthesized in the laboratory typically are not so perfect, has led to some confusion in the interpretation of the experimental vibrational spectra. The presence of other carbonaceous materials in the samples contributes artifacts to the vibrational spectrum. Therefore, there is a strong necessity for model vibrational calculations and their comparison with IR [6] and Raman [7-10] experimental studies of single-wall nanotubes.

So, in this paper our results of the calculations for nanotubes of very small diameters will be reported.

2. MODEL CALCULATIONS

The structure of cylinder of graphite nanotube can be described by specifying two lattice points on graphite sheet which uniquely define the nanotube structure: a fixed lattice point denoted by O(0,0) and another lattice point denoted by R(n_1,n_2), which will fold onto O by rolling the graphite sheet (Fig. 1).
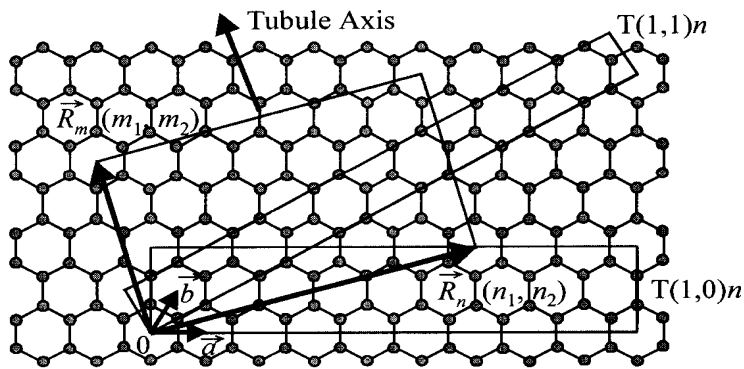

Fig. 1. Graphite nanotubes by rolling the graphite sheet: vector $\vec{R}_n$ defines the tube helicity and diameter; vector $\vec{R}_m$ indicates the direction of the nanotubes $|\vec{R}_m|$ determines the length of a unit cell of the nanotubes. Two limiting cases are also shown: the zig-zag T(1,0)n and the armchair direction, T(1,1)n.

Lattice vector $\vec{R}(n_1,n_2) = n_1\vec{a} + n_2\vec{b}$ or the indexes (n_1,n_2) are used to specify the graphite nanotube. The nanotube is denoted by T(n_1,n_2) or T(l_1,l_2)n, where n is the largest common divisor among n_1 and n_2 and the l_1 and l_2 determine the helicity of the nanotube. Parameters are confined by $n_1 \geq n_2 \geq 0$. If a is the lattice constant of graphite, then the tube diameter D is given by:

$$D = \frac{a}{\pi}\sqrt{n_1^2 + n_1 n_2 + n_2^2} \ .$$

There are two limiting cases: the *zig-zag* direction denoted by T(1,0)n, where C-C bonds are parallel to the nanotube axis, and the *armchair* direction denoted by T(1,1)n, where C-C bonds are normal to the nanotube axis. At the first step [11] special attention was paid on the nanotubes fitting to the C_{60} caps: T(1,1)5 fiber corresponds to the armchair cap with fivefold axis, while T(1,0)9 fiber corresponds to the zig-zag cap with threefold axis. Assuming an average C-C distance of 0.143 nm, the diameter of these nanotubes is 0.683 nm. We concentrated here to the cylinders of mathematically smallest diameters, even beyond diameters limited by C_{60} caps.

The infrared spectra of many molecules and polymers, including those with extended π-electron conjugation, have been successfully interpreted on the basis of the following theoretical model: the electrons and the nuclei are decoupled adiabatically; anharmonic effects are neglected; and the force constants and electrooptical param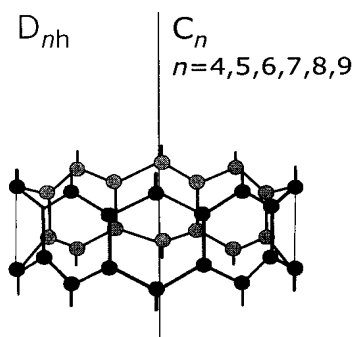eters in the framework of natural (internal) vibrational coordinates (valence bonds and angles, and out-of-plane dihedral and bond-plane angles) are assumed to be fairly local (i.e. independent of the structural details, except for the location and the type of the few nearest neighbors). Accordingly, force constants and electrooptical parameters can be transferred from small molecules of appropriate stereochemical structure [12].

D_{nh} | C_n
$n=4,5,6,7,8,9$

Fig. 2. Model of the smallest cluster (unit ring) of the zig-zag nanotubes.

As a first step in our nanotubes investigations, we started with vibrational calculations of the *cluster model* of zig-zag nanotube T(n,0), $n = 4,5,...,9$. Our results for $n = 9$ can be compared with experimental spectra and results of other calculations [4,5]. This is limiting diameter for model based on the 2D dispersion relations, because of the significant influence of curvature for small-diameter nanotubes.

On the other hand, our results for smaller n are interesting to show potential behavior of the system. The smallest cluster for specified n i.e. diameter consists of n hexagons arranged around axis and simulates the unit cell (further on *unit ring*) of the infinite nanotube (Fig. 2). Characteristic modes of these clusters may be classified and assigned in accordance to their point group (D_{nh}). The cluster formed of few unit rings connected along nanotube axis simulates a part of the infinite nanotube T(n,0). The longer the cluster is, the results correspond better to the infinite nanotube of similar structure. This vibrational calculation is currently limited by the dimension of the cluster i.e. the number of unit rings.

The calculation is based on force constants and electrooptical parameters taken from benzene molecule [13]. The calculated frequencies of characteristic IR and Raman modes for the smallest clusters of different type (unit rings of different diameter) are presented in Fig. 3.

For greater n, our model predicts IR active modes in regions ~1500–1600 cm^{-1}, ~ 1340 cm^{-1}, ~ 870 cm^{-1}, and below 400 cm^{-1}, in comparison with experimentally detected IR modes at ~ 1598 cm^{-1} and ~ 874 cm^{-1} [6], Fig. 3(a).

High-frequency IR modes (over 800 cm^{-1}) do not change much with the diameter. For smaller values of n (diameter) calculated frequencies of IR active modes do change, but at $n = 8,9$ they converge, and it is expected to stay almost independent on the change of diameter. Therefore, these clearly recognizable features in absorbance or reflectance spectra are expected to appear for a variety of single-wall nanotubes.
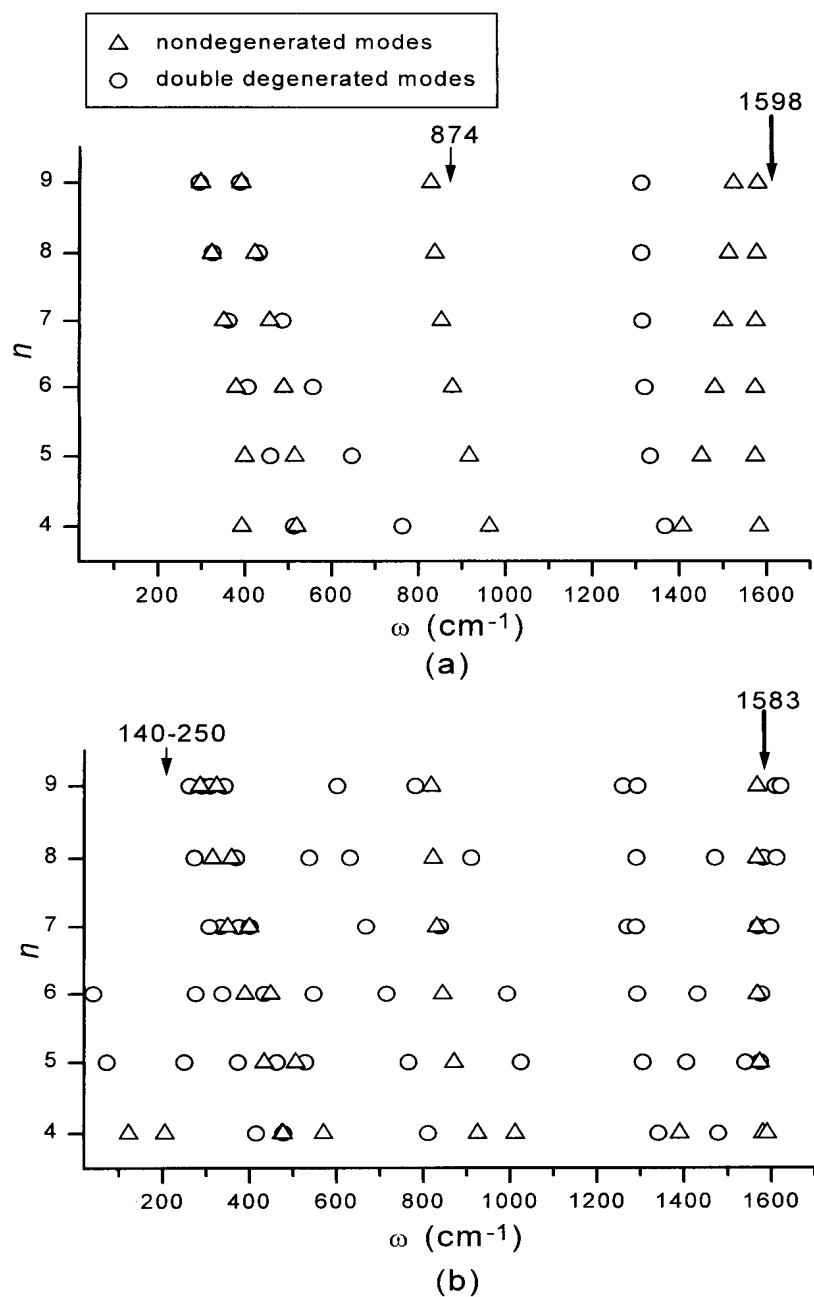
Fig. 3. Infrared (a) and Raman (b) active modes of the unit ring (cluster model) of zig-zag $T(n,0)$ nanotubes, $n = 4,5,6,7,8,9$; nanotube diameter is directly proportional to n (the number of hexagons inside the unit ring).

The low-frequency IR modes of the single-wall nanotubes (below 400 cm^{-1}) strongly depend on the diameter and soften as the diameter increases. We studied nanotubes of the diameters below those treated by Dresselhaus [4,5] and therefore only calculated frequencies for $n = 9$ could be compared. On the other hand, the very trend of changes for $n < 9$ is in agreement with their results.

So, different types of nanotubes are expected to have different spectra in this region, but typically with poor IR intensities.

Further, for greater n calculated values of Raman active modes can be grouped at ~ 1600 cm^{-1}, ~ 1300 cm^{-1} and ~ 820 cm^{-1}, and bellow 600 cm^{-1}, in comparison with experimentally detected Raman modes at ~ 1583 cm^{-1} and ~ 140 -250 cm^{-1} [7-10], Fig. 3(b).

Contrary to the IR spectra, the calculated Raman spectra for small diameters appear to depend more on the structure of nanotubes, being strongly influenced by the parity of n. While the modes at ~ 1600 cm^{-1}, ~ 1300 cm^{-1} and ~ 820 cm^{-1} do not depend much on the diameter, in the region below 600 cm^{-1} characteristic frequencies drastically soften with the increase of the diameter and it is expected for nanotubes for $n > 9$ to be under 200 cm^{-1} (which is in agreement with the results of zone-folding calculations too). As a real sample consists of nanotubes of different diameters, and each type of nanotube contributes proportionally to the Raman spectra, we expect to detect group of modes in this spectral area. For other types of nanotube the differences in calculated frequencies with the change in diameter are expected in the low frequency region too.

3. CONCLUSION

On the basis of the vibrational calculations on the cluster model of zig-zag nanotube $T(n,0)$ $n = 4,...,9$, we have predicted positions of their IR and Raman active modes. Comparing to experimental spectra, we found a good agreement. Our results are also in agreement with results of the calculations that come from the zone-folding of dispersion relations of 2D graphite sheet.

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