

Vibrational Calculation of Single-Wall Armchair Carbon Nanotubes of Small Diameter

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ABSTRACT

The results of theoretical calculations of the vibrational infrared (IR) and Raman active modes of some armchair single-wall carbon nanotubes are presented. Nanotubes of very small diameter, considered as short clusters, and the calculated positions of IR and Raman active modes are analyzed, as well as their dependences on the cluster diameter.

1. INTRODUCTION

Special interest in graphite nanotubes is related to their structure and properties (mechanical, electronic and optical). Despite their great breakthrough in various fields of application, a number of challenging questions are still open and additional knowledge about their structure, chemical bonds, electron 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.

Indication in several theoretical works that nanotubes of diameters even smaller than the diameter of fullerene C₆₀ could be stable [1] has been confirmed: fullerenes smaller than C₆₀ and the corresponding nanotubes were synthesized [2]. In this paper the vibrational calculations of armchair nanotubes of very small diameter will be reported.

2. MODEL

Nanotube structure is usually described as a graphite sheet rolled in a specific manner into a cylinder, which further determines the nanotube properties [3]. Therefore, lattice vector $\vec{R}(n_1, n_2) = n_1\vec{a} + n_2\vec{b}$ of the graphite sheet, i.e. a pair of indices (n_1, n_2) is used to specify the nanotube structure. The diameter D of the cylinder is given by:

$$D = \frac{a}{\pi} \sqrt{n_1^2 + n_1n_2 + n_2^2},$$

where the lattice constant of graphite sheet is denoted by a . Rolled up graphite sheets are expected to have a lot of properties derived from the energy bands and lattice dynamics of graphite (the greater the diameter the closer the properties of the nanotube to the properties of the graphite sheet, so the effect of the curvature can be neglected, i.e. small hybridization between the sp^2 and the p_z orbitals can be assumed [4]). Approximate values of vibrational frequencies of the nanotubes are obtained from those of graphite sheet by the zone-folding method [3,4]. This approach includes the following limits. Vanishing frequencies at $q \rightarrow 0$ in two dimensional graphite sheet do not produce the corresponding modes in nanotubes, i.e. one of the frequencies must be calculated separately. This scheme also does not give rise to two zero-frequency tubule modes corresponding to the translational modes in the two directions perpendicular to the tubule axis (nanotube (5.5) has a limiting diameter for the model based on 2D dispersion relations, because of the significant influence of curvature for small-diameter nanotubes [4]).

Due to specific symmetry of the graphite sheet, there are two limiting cases in possible nanotube structure: the *zig-zag* type, denoted by $(n, 0)$, with C-C bonds parallel to the nanotube axis, and the *armchair* type (n, n) , with C-C bonds perpendicular to the nanotube axis. Among armchair nanotubes presented in this paper, nanotube (5.5) fits to the C_{60} caps with fivefold axis. Also, we focused here on the cylinders of mathematically smallest diameters, beyond those limited by C_{60} caps, assumed to be stable due to the absence of the pentagon isolation rule [1], and recently synthesized (for example, nanotube (4.4) corresponds to the recently synthesized small fullerene C_{36}) [2].

Cluster calculations are mainly used to overcome the problems in the mentioned model based on the 2D dispersion relations. The vibrational frequencies 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 parameters 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 [5].

Results of these calculations are vibrational frequencies and forms [6]. In this article vibrational frequencies of armchair nanotube (n, n) , $n = 3, 4, \dots, 9$ are presented. The smallest cluster (further on *unit ring*) for specified n , i.e. diameter, consists of n hexagons arranged around the axis. It is not the unit cell of the infinite nanotube (Fig. 1), but it is chosen to complete the appropriate field of force constants. Characteristic modes of these clusters are classified and

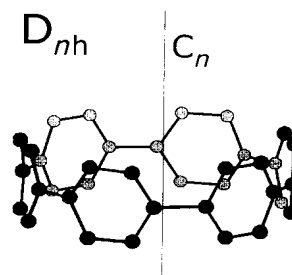


Fig. 1. Model of the smallest cluster of armchair nanotubes (n, n) , with $n = 3, 4, \dots, 9$.

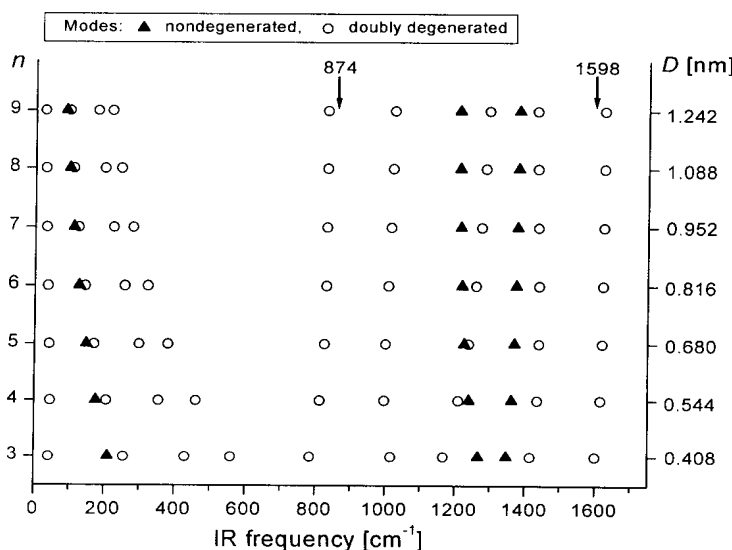


Fig. 2. Calculated vibrational frequencies of infrared active modes of the unit ring (cluster model) of armchair nanotubes, (n, n) , $n = 3, 4, \dots, 9$, of the corresponding diameters D

assigned in accordance to their point group (D_{nh}). Armchair clusters formed of few unit rings connected along nanotube axis simulate a part of the infinite nanotubes (n, n) ; the longer the cluster, the better the results corresponding to the infinite nanotubes of similar structures.

3. CALCULATION

The vibrational calculations are based on the force constants taken from benzene molecule [7]. The calculated frequencies of the characteristic IR and Raman modes for the smallest clusters of various diameters are presented in Figs. 2 and 3.

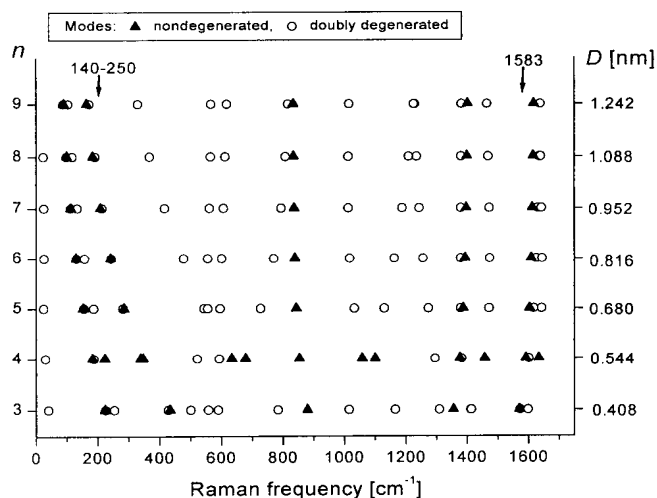


Fig. 3. Calculated vibrational frequencies of Raman active modes of the unit ring (cluster model) of armchair (n, n) nanotubes, $n = 3, 4, \dots, 9$, of the corresponding diameters D

nanotubes show expected trend of changes, and good agreement for $n \geq 5$, compared to Dresselhaus et al. [4].

Further on, the values of Raman active modes for $n \geq 9$ in armchair nanotubes can be predicted at ~ 1600 , ~ 1450 , ~ 1350 , ~ 1200 , ~ 1000 , ~ 800 , ~ 600 and below 600 cm^{-1} (Fig. 3), and compared with the experimentally detected Raman modes at $\sim 1583 \text{ cm}^{-1}$ and $\sim 140 - 250 \text{ cm}^{-1}$ [10,11]. The high-frequency Raman modes (over 600 cm^{-1}) in armchair nanotubes of $n > 5$ do not depend much on the diameter, but below 600 cm^{-1} characteristic frequencies drastically soften with the increase in diameter (which is in agreement with the results of the zone-folding calculations, too). As a real sample presumably consists of nanotubes of different types and diameters, each contributing proportionally to the Raman spectra, we expect to detect the diameter-sensitive groups of modes in the spectral area below 600 cm^{-1} [12].

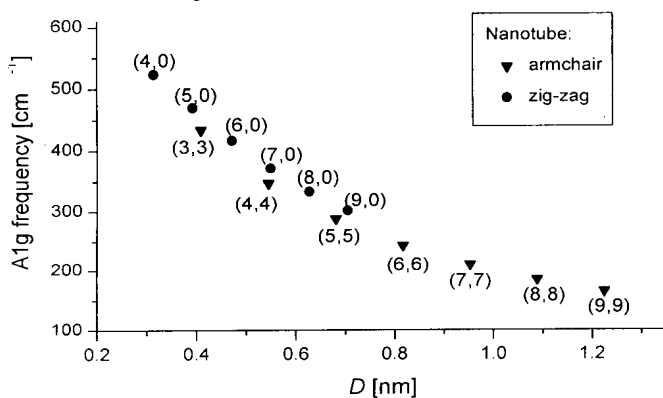


Fig. 4. The Raman active A_{1g} frequency dependence on the nanotube diameter D , for armchair (n, n) and zig-zag $(n, 0)$ structures

This model predicts infrared active modes for $n \geq 9$ in the following regions: $1200 - 1600 \text{ cm}^{-1}$, $\sim 1000 \text{ cm}^{-1}$, $\sim 800 \text{ cm}^{-1}$ and below 400 cm^{-1} (Fig. 2). Experimentally detected IR modes are at $\sim 1598 \text{ cm}^{-1}$ and $\sim 874 \text{ cm}^{-1}$, typically with poor IR intensities [8]. High frequency IR modes (over 800 cm^{-1}) do not change much with the diameter; therefore they are expected to stay almost independent of further changes in the diameter. This is generally expected behavior for nanotubes [3,4]; similar behavior is predicted for the zig-zag type nanotubes, both for IR and Raman spectra [9]. The low-frequency IR modes (below 600 cm^{-1}) strongly depend on the diameter and soften as the diameter increases. Therefore, the calculated frequencies for armchair

The most interesting among low frequency Raman active modes is the breathing A_{1g} mode. It is the most intense mode in this spectral region [12,13]. This frequency belongs to the silent region in the case of graphite and other carbon materials, therefore A_{1g} mode marks the existence of the nanotube geometry. It is, like all low lying modes, sensitive to nanotube diameter D , but not to nanotube chirality. Fig. 4 illustrates the dependence of A_{1g} frequency on the nanotube diameter: the calculated values of

A_{1g} frequencies for the armchair (n, n) and zig-zag ($n, 0$) [9] structures are presented in the same diagram. It is clear that the A_{1g} frequency is independent of the nanotube chirality [13-15].

The E_{1g} and A_{1g} modes exist in the same frequency region, as evident from Fig. 3. Since the intensity of A_{1g} is much stronger than that of E_{1g} , experimental spectra are dominated by A_{1g} mode.

It is clear that the cluster model has its own limits. We constructed longer clusters to simulate 1D objects. The results of these calculations show that characteristic frequencies do not change much, i.e. assumed unit rings represent the main vibrational properties of the nanotube with similar structure.

4. CONCLUSION

On the basis of vibrational calculations on the cluster models of armchair nanotubes of small diameters, (n, n), $n = 3, 4, \dots, 9$, the positions of their IR and Raman active modes were obtained. A good agreement with the results of the calculations based on the zone-folding of dispersion relations of the 2D graphite sheet is pointed out, as well as with the experimental results. Cluster model calculations allowed us to determine the behavior of all corresponding vibrational modes, out of which the low-frequency most intense Raman active A_{1g} breathing mode was of special interest.

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