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Vibrational Properties and Structure of Carbon Nanotubes Based on C_{60} Molecule and Its Symmetry

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ABSTRACT

Carbon nanotubes based on molecule C_{60} are analysed. These tubes can be considered as an approximation of the smallest possible diameter for carbon fiber. The tubes symmetry is lower than that of the icosahedral C_{60} molecule and therefore the infrared- and Raman-active modes are expected to split. We used this symmetry classification to consider the vibrational problem of the graphene nanotubes as quasi one-dimensional (1D) objects.

1. INTRODUCTION

Nanotube structure is 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 a rolled graphite sheet with a diameter of a few nanometers. The carbon-atom hexagons on the nanotube are usually arranged in helical fashion about the nanotube axis.

These graphitic nanotubes may possess some 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 the high efficiency of production [1]. Recent theoretical studies have shown that the electronic properties of a graphitic nanotube depend strongly on its helical structure [2-4]. It can be metallic or semiconducting, which implies that electronic properties of nanotube can be tuned by changing its geometrical parameters.

The structure and electronic properties of graphitic nanotubes are intensively studied. Relationship between the structural symmetry and lattice dynamics of graphitic nanotube has been discussed [1].

The special interest of graphene nanotubes in relation to the broad field of carbon-fiber science and technology is motivated by the fact that a graphene nanotube can be considered as one-atomic-layered carbon fiber of the smallest possible diameter. Graphene nanotubes are thus of interest for model calculations for structure property relations. In this paper we consider the properties of various types of carbon fibers based on C_{60}, particularly those based on a fivefold or threefold axis, because of higher symmetry of these fibers.

2. SYMMETRY CLASSIFICATION OF GRAPHENE NANOTUBES

Higher-order fullerenes can be considered as the first members of a series of fullerenes which form single-layer carbon fiber for the limit of large *j*. There are three major classifications of the graphene nanotube, based on the C_{60} molecule, depending on whether they are related to *fivefold*, *threefold*, or *twofold* axes relative to C_{60}. Generally speaking all graphene nanotubes consist of a graphene sheet rolled up around an axis to form a cylinder with top and bottom edges that fit perfectly on to a C_{60} cap at either end, the caps being formed by cutting appropriately the C_{60}

molecule in half. Both C_{60+10j} and C_{60+18j}, j=1,2... types of graphene nanotubes can be considered as a limiting case of a vapour-grown carbon fiber with a monolayer thickness [1,2]. The diameter of this fiber is 0.683 nm, assuming an average C-C distance of 0.143 nm. Generally, diameter of a nanotube can be larger, and the nanotubes can be closed or opened. The larger the diameter the more similar are the properties of cylinder to the properties of graphene sheet: no infrared active and one Raman active mode.

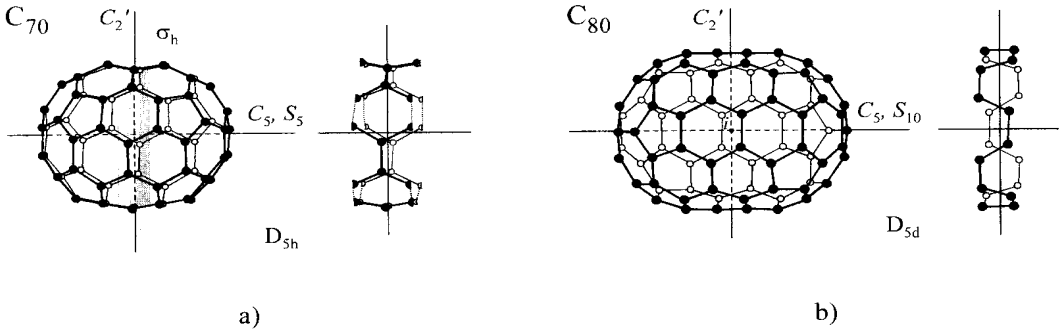

Fig. 1. Structure of a) molecule C_{70} as a first member of class C_{70+20j} fibers and (right) 20 atoms repeating part of cylinder, and b) molecule C_{80} as a first member of class C_{80+20j} fibers and (right) 20 atoms repeating part of cylinder.

Fibers formed along a *fivefold* axis can be considered as molecules represented by the formula C_{60+10j} where j is a positive integer. We can think of C_{60+10j} fiber as composed of a rolled graphene sheet containing j rows of armchair hexagons, each row containing five full armchairs. These rows of hexagons are joined at their zigzag ends to form a cylinder with *fivefold* periodic boundary conditions. Here, we need to distinguish the C_{60+20j} which have inversion symmetry (D_{5d}) and even number of armchair rows of carbon atoms from C_{50+20j} fibers which have mirror plane symmetry (D_{5h}) and an odd number of armchair rows in their cylinders.

If we assume formulae C_{70+20j} (if j=0 we have C_{70}) and C_{80+20j} (if j=0 we have C_{80}) for these two classes of molecules, the number and types of vibrational modes for the entire molecules are:

- C_{70+20j}

$\chi_v=(12+3j)A_1'+(9+3j)A_2'+(21+6j)E_1'+(22+6j)E_2'+(9+3j)A_1''+(10+3j)A_2''+(19+6j)E_1''+(20+6j)E_2''$;
A_1', E_2' and E_1'' are Raman active, and E_1' and A_2'' are infrared active;

- C_{80+20j}

$\chi_v=(13+3j)A_{1g}+(10+3j)A_{2g}+(23+6j)E_{1g}+(24+6j)E_{2g}+(11+3j)A_{1u}+(12+3j)A_{2u}+(23+6j)E_{1u}+(24+6j)E_{1u}$;
A_{1g}, E_{1g} and E_{2g} modes are Raman active, and A_{2u} and E_{1u} are infrared active.

Fibers based on the *threefold* symmetry axis can be described as C_{60+18j}, j=1,2,... For j an odd integer, the symmetry is D_{3h} and for j, an even integer, the symmetry is D_{3d}. If we assume that the smallest molecules in these groups are C_{96} and C_{78}, these two classes can be described as C_{96+36j}, j=1,2... and C_{78+36j}, j=1,2,... The number and types of vibrational modes are:

- C_{96+36j}

$\chi_v=(27+10j)A_{1g}+(20+8j)A_{2g}+(47+18j)E_g+(21+8j)A_{1u}+(26+10j)A_{2u}+(47+18j)E_u$;
A_{1g} and E_{2g} are Raman active, and A_{2u} are E_u are infrared active;

- C_{78+36j}

$\chi_v=(22+10j)A_1'+(16+8j)A_2'+(38+18j)E'+(17+8j)A_1''+(21+10j)A_2''+(38+18j)E''$;
A_1', E' and E'' are Raman active, and E' and A_2'' are infrared active.

Nanotubes with *twofold* axis cannot be fitted to C_{60} cap.

For large j we get very long molecules that must be studied as one-dimensional objects where influence of caps can be neglected, i.e. properties of cylinder dominate.

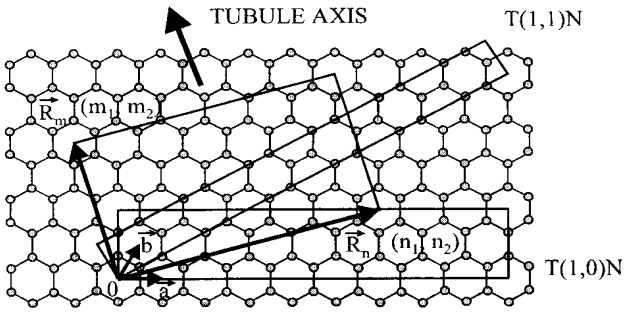

Fig. 2. Graphite sheet and graphitic nanotubes. Vector $\vec{R}_n$ defines the nanotube helicity and diameter. Vector $\vec{R}_m$ indicates the direction of the nanotube, and $|R_m|$ determines the length of a unit cell of the nanotube.

The structure of cylinder of graphitic nanotube can be described [5,6] by specifying two lattice points on a graphite sheet: denoting a fixed lattice point by O(0,0), another lattice point by R(n_1,n_2), which will fold onto O which uniquely defines the nanotube structure, Fig. 2. Lattice vector $\vec{R}(n_1,n_2) = n_1\vec{a} + n_2\vec{b}$ or the indexes (n_1,n_2) can be used to specify the graphitic nanotube. We denote it by T(n_1,n_2) or T(l_1,l_2)N; here N is the largest common divisor among n_1 and n_2, and n_1=l_1 ·N, n_2=l_2 ·N. The l_1 and l_2 determine the helicity of the nanotube and N determines the rotational symmetry of the nanotube; the nanotube axis is the C_N axis. For a given vector $\vec{R}_n$, which determines the nanotube diameter, there is always another vector $\vec{R}_m(m_1,m_2)$ so that $\vec{R}_n \cdot \vec{R}_m = 0$, which determines the unit cell length. Parameters are confined by $n_1 \geq n_2 \geq 0$, and there is no common divisor among m_1 and m_2. If a is the lattice constant of graphite, then the diameter D, the unit cell length L, and the number of carbon atoms per unit cell N_c are given by:

$$D = \frac{|\vec{R}_n|}{\pi} = \frac{a}{\pi}\sqrt{n_1^2 + n_1 n_2 + n_2^2},$$

$$L = |\vec{R}_m| = a\sqrt{m_1^2 + m_1 m_2 + m_2^2},$$

$$N_c = 2(n_1 m_2 - n_2 m_1) = 2N(l_1 m_2 - l_2 m_1),$$

The chiral fiber thus generated has no distortion of bond angles other than that caused by the cylindrical curvature of the fiber. The chiral angle θ defined as the angle between $\vec{R}_n$ and $\vec{R}(p,0)$ (p is an integer) is given by:

$$\theta = \arctan[-\sqrt{3}n_2 / (2n_1 + n_2)].$$

Consequently, there are only six definable angles for a fiber. Out of them, the limiting cases are the zigzag direction (θ=0), T(1,0)N, where C-C bonds parallel to the nanotube axis exist, and the armchair direction (θ=±30°), T(1,1)N, where C-C bonds normal to the nanotube axis exist - which only fit to C_{60} caps: T(1,1)5 fiber corresponds to cylinders of C_{60+20j} and C_{50+20j} (armchair cap) and T(1,0)9 fiber corresponds to cylinder of fibers with threefold axis (zigzag cap).

The factor group of the one-dimensional space group of the graphitic nanotubes T(1,1)N and T(1,0)N is isomorphic to the point group D_{Nd}. . There are two cases: N=even and N=odd. In the case of even N, there is the point group $D_{(2n)d}$ (E, $2(S_{2(2n)})^{(2j-1)}$ (j=1,...,n), $2(C_{2n})^{(j)}$ (j=1,...n-1), C_2, $(2n)C_2'$, $(2n)\sigma_d$). $8n$ elements of these groups are classified into 6 classes. There are $2n$-1 double degenerated irreducible representations. In the case of odd N, we have the point group $D_{(2n+1)d}$ (E, $2(C_{2n+1})^{(j)}$ (j=1,...,n), $(2n+1)C_2'$, i, $2(S_{2(2n+1)})^{(2n+1-2j)}$ (j=1,...,n), $(2n+1)\sigma_d$). $4(2n+1)$ elements of these groups are classified into 6 classes. There are $2n$ double degenerated irreducible representations.

For nanotubes T(1,1)N and T(1,0)N, there are N_C=4N particles per unit cell, and four unequivalent positions in unit cell. If we use character tables for isomorphic point groups D_{Nd}, having in mind that translational modes have E_1 and B_2 symmetries and the rotational mode has A_2 symmetry for even values of N, and that translational modes have E_{1u} and A_{2u} and the rotational mode has A_{2g} symmetry for odd N, vibrational modes have the following symmetries:

- T(1,1)N

for N=even χ_v= $3A_1+2A_2+3B_1+2B_2+5E_1+6E_2+6E_3+...+6E_{N-1}$

for N=odd χ_v= $3A_{1g}+2A_{2g}+6E_{1g}+6E_{2g}+...+6E_{(N-1)/2\,g}+3A_{1u}+2A_{2u}+5E_{1u}+6E_{2u}+...+6E_{(N-1)/2\,u}$

- T(1,0)N

for N=even χ_v=$4A_1+2A_2+2B_1+3B_2+5E_1+6E_2+6E_3+...+6E_{N-1}$

for N=odd χ_v=$4A_{1g}+A_{2g}+6E_{1g}+6E_{2g}+...+6E_{(N-1)/2\,g}+2A_{1u}+3A_{2u}+5E_{1u}+6E_{2u}+...+6E_{(N-1)/2\,u}$.

For even N, A_1, E_2 and E_{N-1} are Raman active and B_2 and E_1 are infrared active. For odd N, A_{1g}, E_{1g} and E_{2g} are Raman active and A_{2u} and E_{1u} are infrared active. In the T(1,1)N graphitic nanotubes there are 15 distinct Raman active modes and 7 distinct infrared active modes. In the T(1,0)N graphitic nanotubes there are 16 Raman active modes and 8 distinct infrared active modes. The symmetries of the Raman and infrared active modes are different.

The factor group of the one dimensional space group of the general chiral graphitic nanotube T(l_1,l_2)N is isomorphic to point group C_N . In the general chiral graphitic nanotube there are 15 distinct Raman frequencies ($4A+5E_1+6E_2$) and 9 distinct infrared frequencies ($4A+5E_1$). Infrared active modes are also Raman active modes.

3. VIBRATIONAL PROBLEM AND SYMMETRY CLASSIFICATION OF GRAPHENE NANOTUBES

Infrared spectra of many polymers, including those with extended π-electron conjugation, have been successfully interpreted on the basis of the following theoretical model: (a) a single chain is considered to be infinite, extended and translationally periodic; (b) the electrons and the nuclei are decoupled adiabatically; (c) anharmonic effects are neglected, and (d) the force constants and electro-optical 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 neighbours), and hence can be transferred from small molecules of appropriate stereochemical structure [8].

The invariant electro-optical parameters can be obtained by representing the polymeric dipole moment in the form of vector sum, $\vec{\mu} = \sum_k \mu_k \vec{e}_k$, where μ_K are some scalar parameters which have a meaning of dipole moments of the valence bonds for fully additive bonds and effective parameters in other cases like here, and $\vec{e}_k$ are the unit vectors of valence bonds. Intensity of α-th normal mode is $I_\alpha \approx \left(\partial\vec{\mu}/\partial Q\right)_\alpha^2$. After differentiation one obtains that $\left(\partial\vec{\mu}/\partial Q\right)_0$ depends on $\left(\partial\mu/\partial q_\beta\right)$, $\left(\partial\vec{e}_k/\partial q_\beta\right)$ and $l_{\alpha\beta}$, where $l_{\alpha\beta}$ are elements of the α-th column of the orthogonal unitary matrix L_q (relating natural q and normal vibrational coordinates Q: q=L_qQ, corresponding to the form of normal vibration Q_α. The matrix column $l_q^{(\alpha)}$ is the eigenvector of the matrix vibrational eigenproblem $\left(T_pU_q-\omega_\alpha^2 I\right)l_q^{(\alpha)}=0$ for a dynamical vibrational matrix D=T_pU_q; ω_α are fundamental vibrational frequencies of the polymer, T_p is the matrix of polymeric kinematical coefficients (dependent on the polymer geometry and mass distribution), and U_q is the matrix of polymeric force constants (dependent on the near-equilibrium charge density distribution). Due to the translational symmetry of polymers, matrices T_p and U_q have quasiperiodic forms, enabling quasidiagonal form of the dynamical matrix. Force constants u_{ij} and electro-optical parameters

represent a system of semiempirical parameters, which can be simultaneously obtained from experimental data for characteristic chemical groups of small molecules. If we have K identical units, for one unit we have to solve k-dimensional vibrational problem and for a polymer of K units, according to the structure of dynamical matrix D, we have to solve K vibrational problems of k-th dimensionality each. We get $K \cdot k$ frequencies $\omega_i^{(s)}$ (i=1,...k, s=1,..K). Frequencies are grouped into k vibrational branches, frequencies s=1,...k belong to one branch. Influence of inter-segment interaction on one vibration mode of a monomer depends on the form of that mode; dispersion of the corresponding vibration branch of the polymer determines the strength of coupling.

Cylinders of carbon nanotubes can be also studied as periodic structures with screw axis $\overline{C}_p$. The nanotube axis coincides with the z-axis of coordinate system. The screw rotation around the z-axis is by the angle

$$\frac{2\pi}{p} = 2\,\mathrm{arctg}\left(\frac{\pi}{2}\frac{n_1 + 2n_2}{n_1^2 + n_1 n_2 + n_2^2}\right),$$

while the translation along the z-axis is by

$$t = \frac{\sqrt{3}n_1 a}{2\sqrt{n_1^2 + n_1 n_2 + n_2^2}}.$$

If one investigates carbon nanotubes in the above manner one must solve vibrational problem for a small molecule, in this case C_{60}, C_{70} , C_{78} or C_{80} .

Considering the fiber formed along the fivefold axis we find that the three bond angles are 120.09°, 118.35° and 118.35°. This is quite different from the C_{60} case where one of the angles is 108°. The fact that the bond angles in the C_{60}-based fibers are so close to 120° implies that the hybrid orbitals are essentially sp^2 ones, while the radial orbital is essentially the p_z orbital. Constants influencing the out-of plane modes in graphite are responsible for radial phonon modes in C_{60}-based fibers, and would be shifted up in comparison with the corresponding modes in C_{60} molecule, but slightly down-shifted from a graphene sheet.

For fibers we expect wide vibrational branches.

Let ω_i be one of the characteristic frequencies of translational unit with characteristic intensity I_i dependant on electro-optical parameters and $l_{\alpha\beta}$. I_i can be separated into I_{ix} , I_{iy} and I_{iz} projections. Intensities $I_i^{(s)}$ of characteristic frequencies on the branch $\omega_i^{(s)}$ s=1,...,K, depend on the structure. For translational symmetry:

$$s = \text{even} \quad I_i^{(s)} = 0,$$

$$s = \text{odd} \quad I_i^{(s)} = \frac{2}{K+1} I_i \,\mathrm{ctg}^2 \frac{s\pi}{2(K+1)},$$

$I_i^{(1)}$ is the maximal intensity on the branch, and mode will be observable in infrared spectrum, and x,y,z projections can also be separated. In the case of screw axis C_p along z, for I_z the situation is the same as for translational symmetry:

$$s = \text{even} \quad I_{i_z}^{(s)} = 0,$$

$$s = \text{odd} \quad I_{i_z}^{(s)} = \frac{2}{K+1} I_i \,\mathrm{ctg}^2 \frac{s\pi}{2(K+1)},$$

but for any s

$$I_{i_x}^{(s)} = \frac{1}{4(K+1)} I_{i_{xy}} \left[\frac{1}{\frac{s\pi}{2(K+1)} - \frac{\pi}{p}} \cos\frac{\pi}{p} \right],$$

$$I_{i_y}^{(s)} = \frac{1}{4(K+1)} I_{i_{xy}} \left[\frac{1}{\frac{s\pi}{2(K+1)} - \frac{\pi}{p}} \sin\frac{\pi}{p} \right],$$

i.e. $I_{i_z}^{(1)}$, $I_{i_x}^{(2(K+1)/p)}$, and $I_{i_y}^{(2(K+1)/p)}$ are maximal intensities, where $I_{i_{xy}}$ is the intensity projection in the xy plane. So we have dichroism. In unpolarized infrared spectra we have two bands: one at $\omega_i^{(1)}$ and one at $\omega_i^{(2(N+1)/p)}$. In polarized spectra we will see: $\omega_i^{(1)}$ for $E \| z$ and $\omega_i^{(2(N+1)/p)}$ for $E \perp z$. This dichroism becomes more visible with greater branch dispersion.

4. CONCLUSION

Vibrational problem of graphene nanotubes as 1D objects, based on the symmetry classification is analysed. Rich and characteristic spectral features of nanotubes revealed in this paper as compared with C_{60} and graphite show that infrared and Raman spectroscopy [7] may be specific and informative spectral tool to analyse their nanometer-scale properties in terms of size and symmetry dependent vibrational and electronic states.

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