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Symmetry properties of chiral carbon nanotubes

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The method of zone folding is applied to the calculation of the phonon mode frequencies in carbon nanotubules. The Raman and infrared-active mode frequencies are determined for nanotubules of different diameters and chiralities.

Carbon nanotubules form an important class of materials with many potential applications.[1–6] Extensive studies have been carried out on the electronic and lattice properties of these materials.[7–14] Some of the symmetry properties and their consequences for the electronic and lattice properties of nanotubes were recently investigated.[12–14] In this work, we study the vibrational properties of carbon nanotubes. In particular, the frequencies of Raman and infrared-active modes are calculated for various tubule sizes and different chiralities.

A carbon tubule is obtained by rolling a two-dimensional (2D) graphene sheet in such a way that two lattice points on the sheet, such as O and A in Fig. 1, will be folded one onto the other. Such a tubule is specified by a pair of integers (n,m) such that

$$\vec{OA} = \vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \; , \tag{1}$$

$\vec{a}_1$ and $\vec{a}_2$ being the lattice vectors on the 2D sheet. There is no loss of generality if we consider only cases where $n > m$.

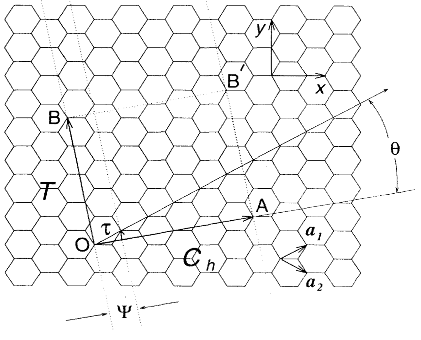

FIG. 1. Construction of the nanotube from the 2D graphene sheet. If the sheet is rolled such that the tip and tail of $\vec{C}_h$ coincide, a chiral nanotube results. The vector $\vec{T}$ is the fundamental lattice vector of the 1D nanotube, θ is the chiral angle, and $\mathbf{\Psi} = \mathbf{C}_h\psi/2\pi$, ψ being the angle defined in Eq. (3).

A nanotube can be viewed as a one-dimensional crystal with a fundamental lattice vector $\vec{T}$ along the direction of the tube axis. Denoting the highest common divisor d of n and m by the bracket $\langle n,m\rangle = d$, then T is given by[12,13] $T = \sqrt{3}C/d_R$, where

$$\begin{aligned} d_R &= d \quad \text{if } n-m \neq 3dr, \\ &= 3d \quad \text{if } n-m = 3dr, \end{aligned} \tag{2}$$

and r is any integer. It follows that the number of carbon atoms per unit cell of a tube specified by the integers (n,m) is $2N$ such that $N = 2(n^2+m^2+nm)/d_R$.

For a chiral nanotube, the fundamental symmetry operation is given by $R = (\psi, \vec{\tau})$, where $\vec{\tau}$ represents a translation along the tube axis and is equal to $\vec{T}d/N$, while ψ is the angle of rotation along this axis and is given by

$$\psi = 2\pi\frac{\Omega}{Nd} + 2\pi\frac{\lambda}{d}. \tag{3}$$

Here $\lambda = 0, 1, \ldots, d-1$, and

$$\Omega = \{p(m+2n) + q(n+2m)\}\,(d/d_R), \tag{4}$$

where p and q are integers that are uniquely determined by the equation

$$mp - nq = d, \tag{5}$$

subject to the conditions $q < m/d$ and $p < n/d$. The point reached from O by a translation vector $p\vec{a}_1 + q\vec{a}_2$ is at a distance τ from $\vec{C}_h$.

In order to find the space group of any chiral tube specified by (n,m), we first prove that $\langle\Omega, N\rangle = d$. To begin with, we consider the case where $d = 1$ and $n-m \neq$

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$3r$, so that $d_R = 1$ also. It follows from Eq. (5) that Ω is odd. We assume that $\langle \Omega, N\rangle = a$, where a must be odd since Ω is odd. In the following we show that $a = 1$.

Using Eqs. (3) and (5), we can write

$$(n+m)\Omega = (p+q)N + (n-m), \tag{6}$$

$$(n-m)\Omega = (p-q)N - 3(n+m). \tag{7}$$

Because $\langle \Omega, N\rangle = a$, it follows that $\langle n-m, 3(n+m)\rangle = ja$, where j is some integer. Since $n-m$ is not a multiple of 3, this implies that

$$\langle n-m, n+m\rangle = ja. \tag{8}$$

Defining the integers A and B such that $A = (n-m)/ja$ and $B = (n+m)/ja$, it follows that $n = ja(A+B)/2$ and $m = ja(B-A)/2$. Since a is odd, it follows that a is a common divisor of n and m. The assumption that $\langle n, m\rangle = 1$ then implies that $a = 1$.

For the case $d = 1$ and $n - m = 3r$, we can proceed similarly as above and show that $\langle \Omega, N\rangle = 1$. It is then readily apparent that in the general case for which $\langle n, m\rangle = d \neq 1$, we have

$$\langle \Omega, N\rangle = d. \tag{9}$$

For the case of $d = 1$, the space group of a chiral nanotube specified by (n, m) is the product of the translation group and a group $\mathcal{C}_{N/\Omega}$, denoting a cyclic chiral group of order N, given by

$$\mathcal{C}_{N/\Omega} = \{\mathcal{R}_{N/\Omega}, \mathcal{R}^2_{N/\Omega}, \ldots, \mathcal{R}^{N-1}_{N/\Omega}, \mathcal{R}^{N}_{N/\Omega} = E\}, \tag{10}$$

where $\mathcal{R}_{N/\Omega}$ is the symmetry operation $\left(2\pi\frac{\Omega}{N}, \vec{T}/N\right)$, and E is the identity element. Since $\langle \Omega, N\rangle = 1$ for $d = 1$, the angle of rotation in the operation $\mathcal{R}^{N-i}_{N/\Omega}$ is never an integral multiple of 2π for all integers i such that $0 < i < N$.

For the general case when $d \neq 1$, the cylinder is separated into d sections connected by the elements of the cyclic group of rotations $\mathcal{C}_d$. Thus we can write the chiral group of the nanotube as the product of two cyclic groups,

$$\mathcal{C} = \mathcal{C}_d \times \mathcal{C}'_{Nd/\Omega}, \tag{11}$$

where

$$\mathcal{C}_d = \{C_d, C_d^2, \ldots, C_d^d = E\} \tag{12}$$

and

$$\mathcal{C}'_{Nd/\Omega} = \{\mathcal{R}_{Nd/\Omega}, \mathcal{R}^2_{Nd/\Omega}, \ldots, \mathcal{R}^{N/d}_{Nd/\Omega} = E\}, \tag{13}$$

where the angles of rotation in $\mathcal{C}'_{Nd/\Omega}$ are defined modulo $(2\pi/d)$ instead of 2π, and $\mathcal{R}_{Nd/\Omega} = \left(2\pi\frac{\Omega}{Nd}, \vec{T}d/N\right)$.

The inconvenience of having angles defined modulo $2\pi/d$ instead of 2π may be removed according to the following scheme. Let us set $\langle \Omega/d, d\rangle = d'$. Then we can write $d = \alpha d'$, $\Omega/d = \beta d'$ where α and β are integers such that $\langle \alpha, \beta\rangle = 1$. We consider the group

$$\mathcal{L} = \{\mathcal{R}_{Nd/\Omega}, \mathcal{R}^2_{Nd/\Omega}, \ldots, \mathcal{R}^{N/d'}_{Nd/\Omega} = E\}, \tag{14}$$

where the angles are defined modulo 2π. We assert that $\mathcal{R}^{(N/d')-i}_{Nd/\Omega} \neq E$ for all integers i such that $0 < i < N/d'$. To show this, we first note that $\langle \Omega/d, d\rangle = d'$ and $\langle \Omega/d, N/d\rangle = 1$ implies that $\langle \Omega/d, N\rangle = d'$ which in turn implies that $\langle \Omega/dd', N/d'\rangle = 1$. Then the angle

$$2\pi\frac{i\Omega}{Nd} = 2\pi i\frac{(\Omega/dd')}{(N/d')}$$

is not an integral multiple of 2π, and thus $\mathcal{R}^{(N/d')-i}_{Nd/\Omega} \neq E$. We note that since $\langle \alpha, \beta\rangle = 1$ and

$$\frac{N}{d}\left(2\pi\frac{\Omega}{Nd}\right) = 2\pi\beta/\alpha, \tag{15}$$

it follows that the sequence of rotations

$$\left\{\mathcal{R}^{N/d}_{Nd/\Omega}, \mathcal{R}^{2N/d}_{Nd/\Omega}, \ldots, \mathcal{R}^{\alpha N/d}_{Nd/\Omega} = E\right\}$$

is equivalent to a permutation of the sequence of rotations

$$\{C_\alpha, C_\alpha^2, \ldots, C_\alpha^\alpha = E\},$$

which is a subgroup of $\mathcal{C}_d$. The chiral group of the nanotube may be written as the product $\mathcal{C} = \mathcal{C}_d \times \mathcal{L}$ which is of order N since among the αN elements in the product, only N elements are distinct, because $\mathcal{L}$ contains a subgroup of $\mathcal{C}_d$ of order α. Further simplification may be achieved if $\langle \alpha, d'\rangle = 1$, for then $\mathcal{C} = \mathcal{L} \times \mathcal{C}_{d'}$ in which case the direct product has N elements that are all distinct.

In all the cases considered above, the irreducible representations of the group $\mathcal{C}$ are given by $A, B, E_1, E_2, \ldots, E_{N/2-1}$. In the E_n irreducible representation, the characters of any operation C corresponding to a rotation by an angle ξ are given by

$$\chi(C) = \begin{cases} e^{i2\pi\xi n} \\ e^{-i2\pi\xi n}. \end{cases} \tag{16}$$

The A representation is completely symmetric, while in the B representation, the characters for the product groups are $\chi(\mathcal{R}_{Nd/\Omega}) = -1$ and $\chi(C_d) = +1$. This follows by noting that if $\langle \Omega/d, d\rangle = d' \neq 1$, then the fact that d' must be odd, that N/d is even, that

$$\mathcal{C}_{d/d'} = \left\{\mathcal{R}^{N/d}_{Nd/\Omega}, \mathcal{R}^{2N/d}_{Nd/\Omega}, \ldots, \mathcal{R}^{Nd/dd'}_{Nd/\Omega} = E\right\}, \tag{17}$$

and that $C_{d/d'} = C_d^{d'}$ implies that if $\chi(\mathcal{R}_{Nd/\Omega}) = -1$, then $\chi(C_{d/d'}) = +1$ and $\chi(C_d) = +1$.

The phonon mode frequencies of the 1D tubule at the Γ point, $\omega_{\mathrm{1D}}(k=0)$, are approximately given in terms of the phonon frequencies in the 2D graphene sheet, $\omega_{\mathrm{2D}}(\vec{k})$, according to the following relationship

$$\omega_{\mathrm{1D}}(0) = \omega_{\mathrm{2D}}\left(\frac{2\pi\mu}{C_h}\hat{C}_h\right) \;,\quad \mu = 0, 1, \ldots, N-1\,. \tag{18}$$

The phonon frequencies of the 2D graphene sheet are obtained from a Born–von Karman force constant model which accounts for the results of Raman, infrared, neutron, and electron energy loss spectroscopies.[14]

At the Γ point in the Brillouin zone of the nanotube, we can classify all the phonon modes according to the irreducible representations of the relevant symmetry group. The nanotube modes, obtained by setting $\mu = 0$ in Eq. (18), correspond to the Γ-point modes of a graphene sheet; consequently, they are completely symmetric and thus they transform according to the A irreducible representation.

Next we consider the modes obtained from Eq. (18) by setting $\mu = N/2$. These modes in the nanotube correspond to modes in a graphene sheet at the point $\vec{k} = N\vec{K}_1/2$ in the 2D hexagonal Brillouin zone, where $\vec{K}_1 = (2\pi/C_h)\hat{C}_h$.

Under the action of the symmetry operation $R_{Nd/\Omega}$, an atom is carried into another atom separated from it, in the 2D graphene sheet, by the vector $\vec{r} = p\vec{a}_1 + q\vec{a}_2$, where p and q are integers defined by Eq. (5). It is readily shown that

$$(N\vec{K}_1/2)\cdot\vec{r} = \pi\Omega/d\,, \tag{19}$$

and since Ω/d is odd, it follows that for the phonon mode with wave vector $N\vec{K}_1/2$, two atoms in the graphene 2D sheet separated by $\vec{r}$ have displacements that are completely out of phase. Thus $\chi(R_{Nd/\Omega}) = -1$. Similarly, we can show that $\chi(C_d) = 1$, and we deduce that the nanotube modes obtained by setting $\mu = N/2$ transform according to the B irreducible representation of the chiral symmetry group $\mathcal{C}$. Similarly, we can show that nanotube modes at the Γ point obtained from Eq. (18) by setting $\mu = \eta$, where $0 < \eta < N/2$, transform according to the E_η irreducible representation of the chiral symmetry group. The Raman-active modes transform according to the A, E_1, or E_2 irreducible representations of $\mathcal{C}$, while the infrared-active modes transform according to the A or E_1 irreducible representations.

As an example, we have calculated the frequencies of the Raman- and infrared-active modes, for two nanotubes whose chiralities are specified by $(n,m) = (7,4)$ and $(n,m) = (8,3)$. The (7,4) tubule was selected to illustrate the case $n - m = 3d$ while for the (8,3) tubule $n - m \neq 3d$. In Figs. 2 and 3, we show, respectively, the calculated frequencies of the Raman and infrared modes for nanotubes specified by $(n,m) = (7,4)$ as a function of the nanotube diameter, by considering multiples of (n,m), namely (14,8), (21,12), etc. The corresponding mode frequencies for nanotubes specified by $(n,m) = (8,3)$, calculated as a function of the nanotube diameter, are shown in Figs. 4 and 5.

Inspection of Figs. 2 and 4 indicates that the calculated Raman spectra for both chiralities are similar, and the same observation applies to the calculated infrared spectra. It is also observed that if a bundle of nanotubes, all with the same chirality and diameter, is synthesized, it will be possible to observe many Raman-and infrared-active modes, spread over a large frequency range. For a bundle composed of nanotubes with different chiralities

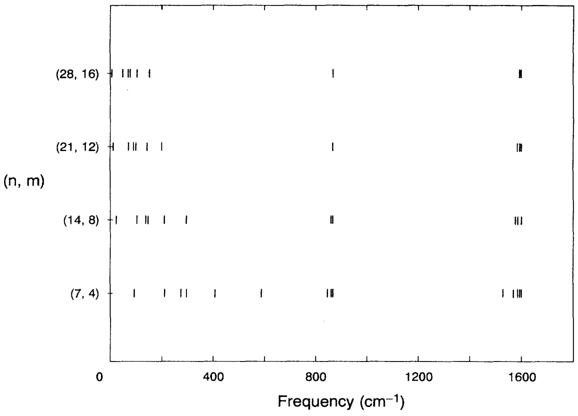

FIG. 2. Calculated Raman-active mode frequencies for nanotubes specified by (n,m) given by (7,4), (14,8), (21,12), and (28,16). All these nanotubes have the same chirality but different diameters.

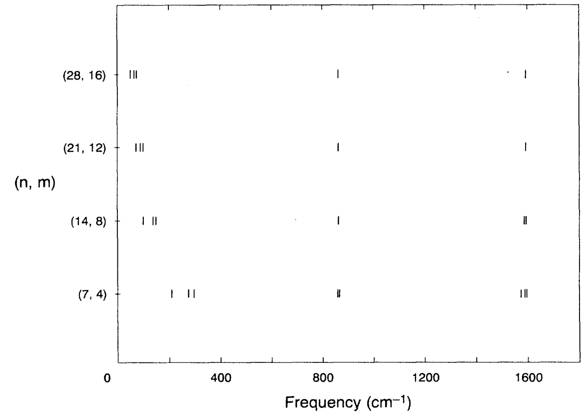

FIG. 3. Calculated infrared-active mode frequencies for nanotubes specified by (n,m) given by (7,4), (14,8), (21,12), and (28,16).

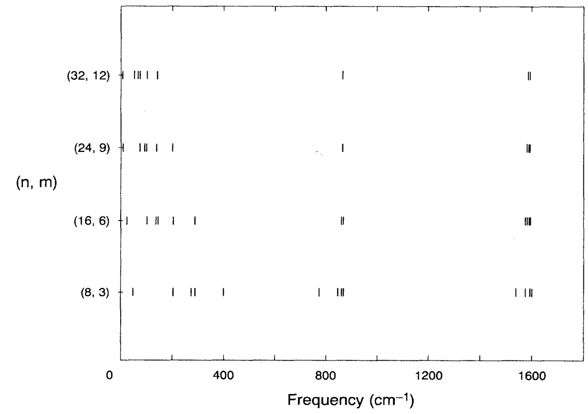

FIG. 4. Calculated Raman-active mode frequencies for nanotubes specified by (n,m) given by (8,3), (16,6), (24,9), and (32,12).

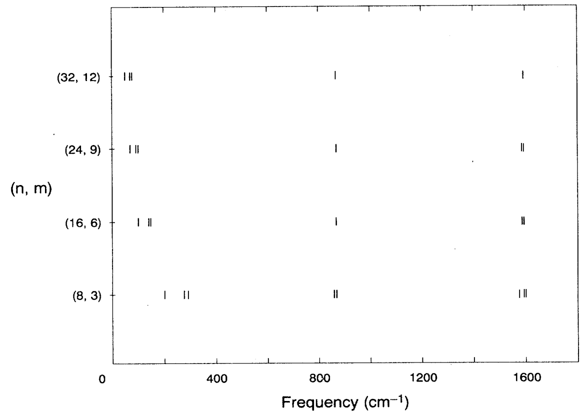

FIG. 5. Calculated infrared-active mode frequencies for nanotubes specified by (n,m) given by (8,3), (16,6), (24,9), and (32,12).

and diameters, on the other hand, the figures indicate that only the modes with frequencies $\sim$1590 cm^{-1} and $\sim$865 cm^{-1} will be observed, since these modes are Raman and infrared active for all nanotubes regardless of their chiralities of diameters.

Raman scattering experiments on nested nanotubes of various diameters and chiralities obtained by the dc arc process[15] have revealed the existence of a somewhat broad feature at 1574 cm^{-1} in the first-order spectrum. Raman spectra taken on wall deposits containing single-walled nanotubes of various diameters and chiralities produced in the presence of Co in the core of the carbon anode[16] exhibit additional features. A strong doublet is observed at 1566 cm^{-1} and 1592 cm^{-1}, as well as a broadband at 1341 cm^{-1}. The existence of a doublet near 1580 cm^{-1} is consistent with our calculations for all chiralities that have been considered, if we assume that the nanotube diameters are not too large. The observation of a broad Raman feature near 1341 cm^{-1} is not readily explained by the present calculations for chiral nanotubes of small diameter. Contributions near 1340 cm^{-1} might arise from nanotubes of larger diameter than considered here, or from the presence of other graphitic material within the sample volume. A large concentration of (n,m) armchair tubules could also give rise to weak Raman scattering intensity near 1340 cm^{-1}.

In conclusion, the results presented in this work should be useful in guiding experiments which might be used to characterize the type and size of fullerene tubules. Presently there are no published experimental infrared spectra for carbon nanotubes. Hopefully, the calculations presented here might stimulate such work.

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