PHYSICAL REVIEW B, VOLUME 63, 201403(R)

Number of Raman- and infrared-active vibrations in single-walled carbon nanotubes

Ofir E. Alon*
Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel

(Received 23 October 2000; revised manuscript received 20 March 2001; published 4 May 2001)

By analyzing the point groups of the (nonsymmorphic) rod-groups of carbon nanotubes we show, for the first time, to the best of our knowledge, that all achiral carbon nanotubes possess only 8 Raman-active and 3 infrared-active phonon modes. This is in contrast to previously predicted 15–16 and 7-8 active modes, respectively. On the same ground we show that all chiral carbon nanotubes have 14 (instead of 15) Raman-active and 6 (instead of 9) infrared-active phonon modes.

DOI: 10.1103/PhysRevB.63.201403 PACS number(s): 73.61.Wp, 31.15.Hz, 63.20.Dj

Since their discovery in 1991 (Ref. 1) carbon nanotubes have attracted enormous attention of both experimentalists and theoreticians for their properties (see, e.g., Refs. 2,3 and references therein). The classification of carbon nanotube symmetries is an essential stage in predicting their physical properties, among which are active infrared (IR) and Raman vibrations (see Ref. 4 and references therein). For example, there are 15–16 Raman-active phonon modes predicted for infinitely long armchair carbon nanotubes,[4] with frequencies up to about 1600 cm^{-1}. Of them 7 modes are intense (in the low and high frequency zones), while the rest (in the intermediate frequency zone) have no intensity for infinite nanotubes,[5] but do have some intensity for finite nanotubes.[6] Such predictions have clear fingerprints in Raman scattering experiments from carbon nanotube ropes.[7,8]

So far, the determination of optically active phonon modes in achiral carbon nanotubes has been performed with symmorphic rod groups.[4,9,10] In order to account for the inversion symmetry operation, unit cells possessing the point-groups $\mathcal{D}_{nh}$ or $\mathcal{D}_{nd}$ for even or odd n, respectively, were chosen for the $(n,0)$-zigzag and (n,n)-armchair carbon nanotubes. However, achiral carbon nanotubes possess in addition a screw-axis of order $2n$ and n glide planes.[11] Due to these operations the symmetry of achiral carbon nanotubes is described by nonsymmorphic rod-groups, as elucidated recently by Damnjanović *et al.*[11] Dynamically speaking, the lower symmetry employed in Refs. 4, 9, and 10 implies that an additional degree of freedom is, in fact, introduced in choosing the *relative* position of the two carbon atoms comprising the hexagonal cell. The higher symmetry identified in Ref. 11 fixes the position of all carbon atoms within the nanotubes if the position of only one atom is chosen. As will be shown below, this has a dramatic effect on vibrational spectra in achiral carbon nanotubes, namely, reducing the number of optically active phonon modes. Especially, it is shown that armchair carbon nanotubes possess only 8 Raman-active vibrations, which corroborates the recent experimental data.[7,8]

Consider the achiral carbon nanotubes possessing the rotation axis of order n, that is the $(n,0)$-zigzag or (n,n)-armchair carbon nanotubes. The nonsymmorphic rod-group describing achiral carbon nanotubes with *either* odd or even index n can be decomposed in the following manner:

$$\mathcal{G}[n]=\mathcal{L}_{T_z}\times[\mathcal{D}_{nh}|_{z=0}\oplus(\mathcal{D}_{nd}|_{z=T_z/4}\ominus\mathcal{C}_{nv})\oplus\mathcal{C}_{nv}\times\mathbf{S}_{2n}], \tag{1}$$

where the reference point $z=0$ denotes the crossing of horizontal, σ_h, and vertical, σ_v, reflection planes (see Fig. 1). $\mathcal{L}_{T_z}$ is the one-dimensional (1D) translation group with $T_z=|\mathbf{T}_z|$. The screw axis $\mathbf{S}_{2n}$ is an operation which involves the lattice smallest nonprimitive translation (and rotation), $\mathbf{S}_{2n}=(z\rightarrow z+T_z/2,\varphi\rightarrow\varphi+\pi/n)$. The subtraction of the point group $\mathcal{C}_{nv}$ in Eq. (1) reflects the set relation between the point groups $\mathcal{D}_{nh}|_{z=0}$ and $\mathcal{D}_{nd}|_{z=zT_{z0}/4}$, $\mathcal{D}_{nh}|_{z=0}\cap\mathcal{D}_{nd}|_{z=T_z/4}=\mathcal{C}_{nv}$, for all n's. A glide plane $\mathbf{g}$ is also presented in Fig. 1. It fulfills the multiplication relation $\mathbf{g}=\mathbf{S}_{2n}\sigma_v$. Note that $\mathbf{g}$ contains a nonprimitive translation of length $T_z/2$. The existence of n distinct glide planes in $\mathcal{G}[n]$ stems from the last term in Eq. (1).

The point group of the rod group, $\mathcal{G}_0[n]$, is obtained by setting all translations (including the nonprimitive ones) in $\mathcal{G}[n]$ equal to zero. From Eq. (1) we obtain

$$\mathcal{G}_0[n]=\mathcal{D}_{nh}|_{z=0}\oplus(\mathcal{D}_{nd}|_{z=0}\ominus\mathcal{C}_{nv})\oplus(\mathcal{C}_{nv}\times C_{2n})=\mathcal{D}_{2nh}, \tag{2}$$

where $C_{2n}\equiv(\varphi\rightarrow\varphi+\pi/n)$ is the rotation embedded in $\mathbf{S}_{2n}$.

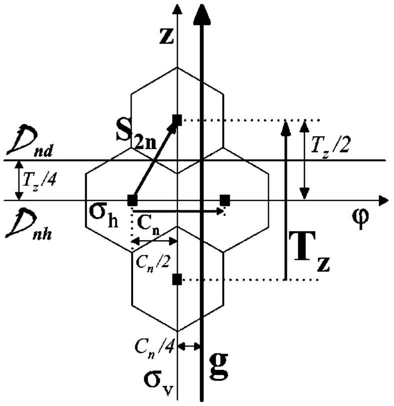

FIG. 1. 2D projection of various symmetries in achiral carbon nanotubes (without loss of generality, a zigzag carbon nanotube segment is presented): $\mathbf{T}_z$ is the primitive translation; $\mathbf{S}_{2n}$ is the screw axis with nonprimitive translation and rotation, denoted by $T_z/2$ and $C_n/2$, respectively; $\mathbf{g}$ is a glide plane; $\mathcal{D}_{nh}|_{z=0}$ and $\mathcal{D}_{nd}|_{z=T_z/4}$ stand for the corresponding point-group operations, among which σ_h, σ_v, and $\mathbf{C}_n$ are denoted. Note the $T_z/4$ shift between $\mathcal{D}_{nh}|_{z=0}$ and $\mathcal{D}_{nd}|_{z=T_z/4}$, that coexist in all achiral carbon nanotubes.

0163-1829/2001/63(20)/201403(3)/$20.00

Aiming at characterizing the symmetry of phonons at the $\Gamma(k=0)$-point, we would like to discuss the irreducible representations (IRREPS) of $\mathcal{G}[n]$ at Γ. As known from the theory of space groups,[12] these IRREPS are in a one-to-one correspondence with the IRREPS of the factor group of the wave vector $k=0$, which is isomorfic to $\mathcal{G}_0[n]=\mathcal{D}_{2nh}$. Recall that the character table of $\mathcal{D}_{2nh}$ possesses $2n+6$ IRREPS,[13]

$$\Gamma_{\mathcal{D}_{2nh}}=A_{1g}\oplus A_{2g}\oplus B_{1g}\oplus B_{2g}\oplus A_{1u}\oplus A_{2u}$$
$$\oplus B_{1u}\oplus B_{2u}\oplus \sum_{j=1}^{n-1}\{E_{jg}\oplus E_{ju}\}.$$

Next, we would like to determine the symmetries of the $6N$ phonon modes at the Γ point and how many modes are Raman or IR active. N is the number of hexagons within a unit cell (there are 2 carbon atoms per each hexagon). Recall that for achiral nanotubes $N=2n$. At this point we have to differentiate between $(n,0)$-zigzag and (n,n) armchair carbon nanotubes, due to the differences in atom arrangements inside their unit cells.

The $6N$ phonon modes transform according to the following IRREPS for zigzag and armchair carbon nanotubes:

$$\Gamma_{6N}^{zig}=\Gamma_{\rm a}^{zig}\otimes\Gamma_{\rm v}=2A_{1g}\oplus A_{2g}\oplus B_{1g}\oplus 2B_{2g}\oplus A_{1u}\oplus 2A_{2u}$$
$$\oplus 2B_{1u}\oplus B_{2u}\oplus \sum_{j=1}^{n-1}\{3E_{jg}\oplus 3E_{ju}\}, \tag{3}$$

$$\Gamma_{6N}^{arm}=\Gamma_{\rm a}^{arm}\otimes\Gamma_{\rm v}=2A_{1g}\oplus 2A_{2g}\oplus B_{1g}\oplus B_{2g}\oplus A_{1u}\oplus A_{2u}$$
$$\oplus 2B_{1u}\oplus 2B_{2u}\oplus 2E_{1g}\oplus 4E_{2g}\oplus 2E_{3g}\oplus 4E_{4g}\oplus \dots$$
$$\oplus(3+(-1)^{n-1})E_{(n-1)g}\oplus 4E_{1u}\oplus 2E_{2u}\oplus 4E_{3u}$$
$$\oplus 2E_{4u}\oplus \dots \oplus(3-(-1)^{n-1})E_{(n-1)u}, \tag{4}$$

where

$$\Gamma_{\rm a}^{zig}=A_{1g}\oplus B_{2g}\oplus A_{2u}\oplus B_{1u}\oplus \sum_{j=1}^{n-1}\{E_{jg}\oplus E_{ju}\} \tag{5}$$

and

$$\Gamma_{\rm a}^{arm}=A_{1g}\oplus A_{2g}\oplus B_{1u}\oplus B_{2u}$$
$$\oplus 2\sum_{j=2,4,6,\dots}^{n-1}E_{jg}\oplus 2\sum_{j=1,3,5,\dots}^{n-1}E_{ju} \tag{6}$$

stand for the reducible representations of the carbon-atom positions inside the unit cells.[14] $\Gamma_{\rm v}=A_{2u}\oplus E_{1u}$ is the vector representation. Of these modes, the ones that transform according to $\Gamma_{\rm t}=A_{1g}\oplus E_{1g}\oplus E_{2g}$ (the tensor representation) or $\Gamma_{\rm v}$ are Raman or IR active, respectively. Out of the $6N$ phonon modes, four (which transform as $\Gamma_{\rm v}$ and $\Gamma_{R_z}=A_{2g}$) have vanishing frequencies.[15] Consequently, the symmetries and number of optically active phonon modes in zigzag carbon nanotubes are given by

$$\Gamma_{\rm Raman}^{zig}=2A_{1g}\oplus 3E_{1g}\oplus 3E_{2g}\Rightarrow n_{\rm Raman}^{zig}=8, \tag{7}$$

$$\Gamma_{\rm IR}^{zig}=A_{2u}\oplus 2E_{1u}\Rightarrow n_{\rm IR}^{zig}=3 \tag{8}$$

and in armchair carbon nanotubes:

$$\Gamma_{\rm Raman}^{arm}=2A_{1g}\oplus 2E_{1g}\oplus 4E_{2g}\Rightarrow n_{\rm Raman}^{arm}=8, \tag{9}$$

$$\Gamma_{\rm IR}^{arm}=3E_{1u}\Rightarrow n_{\rm IR}^{arm}=3. \tag{10}$$

Thus, the number of Raman- and IR-active phonon modes is fixed for all zigzag and armchair carbon nanotubes, as previously predicted by Dresselhaus and co-workers using the *subgroup* point groups $\mathcal{D}_{nh},\mathcal{D}_{nd}\subseteq\mathcal{D}_{2nh}$.[4,9,10] However, due to the higher rod-group and factor group symmetries there are much fewer active modes: 8 (Raman) and 3 (IR), instead of 15–16 and 7-8, respectively.[4,9,10]

It is instructive to trace the origin of the above findings in the *restriction* of IRREPS from high down to lower symmetry. Let us analyze the single-walled achiral carbon nanotubes with even index *n* (similar analysis can be carried out for odd n's). The restriction of Γ_{6N}^{zig} and Γ_{6N}^{arm} from the point group $\mathcal{D}_{2nh}$ to its subgroup $\mathcal{D}_{nh}$ doubles the number of 1D IRREPS, on the expense of the 6 2D IRREPS of the type $E_{(n/2)g}$ and $E_{(n/2)u}$. Nevertheless, the number of 1D IRREPS corresponding to *optically-active* modes is not affected (for $n>4$) by the above splitting. Rather, the 1D IRREPS B_{1g} and B_{2u} of $\mathcal{D}_{2nh}$ transform, upon restriction, as the 1D IRREPS A_{1g} (Raman active) and A_{2u} (IR active) in $\mathcal{D}_{nh}$, respectively. Consequently, the frequencies of A_{1g} and A_{2u} are doubled. Finally, the frequencies of the *remaining* 2D IRREPS, among them are E_{1g}, E_{2g} (Raman-active), and E_{2u} (IR active), are also doubled, since the 2D IRREPS $E_{(n-j)g}$ and $E_{(n-j)u}$ $(j=1,\dots,n/2-1)$ in $\mathcal{D}_{2nh}$ transform, upon restriction, as E_{jg} and E_{ju} in $\mathcal{D}_{nh}$. This correlation analysis (between IRREPS of a group and its subgroup) gives the factor of about 1/2 between the number of optically active vibrations found by the present higher-symmetry analysis and the corresponding number found in Refs. 4, 9, and 10.

Our findings corroborate the recent experimental data (see Refs. 7 and 8) and theoretical predictions of Raman-line intensities (Refs. 5 and 6), where only 7 intense lines were identified for armchair nanotubes. For this, examine the atomic displacements of the 7 intense Raman-active modes of the (10,10)-armchair carbon nanotube (see Fig. 2 in Ref. 7, or Fig. 10.6 in Ref. 4). This reveals that they transform according to $\Gamma_{\rm t}$, not only with respect to the lower-symmetry $\mathcal{D}_{10h}$ point group, but also with respect to the higher-symmetry $\mathcal{D}_{20h}$ factor group. In other words, these 7 out of 16 modes (frequencies) are among the 8 modes which we predict to be Raman active, on the basis of the higher nonsymmorphic rod-group symmetry identified in armchair carbon nanotubes. A complete $\mathcal{D}_{2nh}$-symmetry-based analysis of a force-constant model for phonon modes in achiral carbon nanotubes[5] will be given elsewhere.

Next, we would like to discuss the number of Raman- and IR-active vibrations in chiral carbon nanotubes. So far, the determination of optically active phonon modes in chiral carbon nanotubes has been performed with commutative nonsymmorphic rod-groups.[4,10,16] The point group of the rod-group of the (n,m)-chiral carbon nanotube has been shown to be $\mathcal{C}_N$, where N (the number of hexagons within a unit cell) is a function of n and m.[4,10,16]. Recently, chiral carbon nanotubes were shown to possess in addition perpendicular C_2 axes.[11] The existence of these ''overlooked'' symmetry operations constitutes the geometrical proof that chiral carbon nanotubes possess the structure of noncommutative nonsymmorphic rod groups.[11] Consequently, the point group of the rod-group for the (n,m)-chiral carbon nanotube is $\mathcal{D}_N$. As will be presented below, this higher symmetry ($\mathcal{C}_N \subseteq \mathcal{D}_N$) leads to the reduction of the number of optically-active phonon modes in chiral carbon nanotubes.

Analogously to the treatment given above for achiral carbon nanotubes, we would like to discuss the IRREPS of the factor group of the wave vector $k=0$, being $\mathcal{D}_N$ for chiral carbon nanotubes. Recall that the character table of $\mathcal{D}_N$ possesses $N/2+3$ (N is always even for carbon nanotubes) IRREPS,[13]

$$\Gamma_{\mathcal{D}_N} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus \sum_{j=1}^{N/2-1} E_j .$$

The $6N$ phonon modes transform according to the following reducible representation:

$$\Gamma_{6N}^{ch} = \Gamma_{\mathrm{a}}^{ch} \otimes \Gamma_{\mathrm{v}} = 3A_1 \oplus 3A_2 \oplus 3B_1 \oplus 3B_2 \oplus \sum_{j=1}^{N/2-1} 6E_j , \qquad (11)$$

where

$$\Gamma_{\mathrm{a}}^{ch} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus \sum_{j=1}^{N/2-1} 2E_j \qquad (12)$$

stands for the reducible representation of the carbon-atom positions inside the unit cell. $\Gamma_{\mathrm{v}} = A_2 \oplus E_1$ is the vector representation. Of these modes, the ones that transform according to $\Gamma_{\mathrm{t}} = A_1 \oplus E_1 \oplus E_2$ and/or Γ_{v} are Raman and/or IR active, respectively. Four of the $6N$ phonon modes, those which transform as Γ_{v} and $\Gamma_{R_z} = A_2$ have vanishing frequencies.[15] Consequently, the symmetries and number of optically-active phonon modes are given by

$$\Gamma_{\mathrm{Raman}}^{ch} = 3A_1 \oplus 5E_1 \oplus 6E_2 \Rightarrow n_{\mathrm{Raman}}^{ch} = 14, \qquad (13)$$

$$\Gamma_{\mathrm{IR}}^{ch} = A_2 \oplus 5E_1 \Rightarrow n_{\mathrm{IR}}^{ch} = 6. \qquad (14)$$

Thus, the number of Raman- and IR-active phonon modes is independent of the chiral nanotube indices, (n,m), as previously predicted by Jishi *et al.* using the *subgroup* factor group $\mathcal{C}_N \subseteq \mathcal{D}_N$.[16] However, due to the higher rod-group and factor-group symmetries, fewer modes are active: 14 (Raman) and 6 (IR), instead of 15 and 9, respectively.[16]

In conclusion, by utilizing the higher-symmetry factor group $\mathcal{D}_{2nh}$ for the symmetry analysis of phonon modes in achiral carbon nanotubes we find that the number of Raman- and IR-active vibrations is about half from what was previously predicted: 8 (Raman) and 3 (IR), rather than 15–16 and 7-8, respectively. This result corroborates the recent experimental results and theoretical predictions of Raman-line intensities for armchair carbon nanotubes. Our findings also allow for the reverse conclusion that vanishing intensities for those vibrational modes previously predicted to be active might indicate that the higher nonsymmorphic symmetry is (well) realized in experimental samples of single-walled carbon nanotubes. Finally, by applying the factor group $\mathcal{D}_N$ for the analysis of optically active vibrations in chiral carbon nanotubes we find that fewer modes are active: 14 (Raman) and 6 (IR), instead of 15 and 9, respectively.

ACKNOWLEDGMENTS

The author wishes to thank Professor N. Moiseyev, Dr. V. Averbukh, and Dr. U. Peskin for many helpful discussions and comments.

---

*Email address: ofir@tx.technion.ac.il

[1] S. Iijima, Nature (London) **345**, 56 (1991).

[2] C. Dekker, Phys. Today **52** (5), 22 (1999).

[3] M. Terrones, W. K. Hsu, H. W. Kroto, and D. R. M. Walton, Top. Curr. Chem. **199**, 189 (1999).

[4] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).

[5] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **57**, 4145 (1998).

[6] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **59**, 2388 (1999).

[7] A. M. Rao *et al.*, Science **275**, 187 (1997).

[8] C. Journet *et al.*, Nature (London) **388**, 756 (1997).

[9] R. A. Jishi, L. Venkataraman, M. S. Dresselhaus, and G. Dresselhaus, Chem. Phys. Lett. **209**, 77 (1993).

[10] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

[11] M. Damnjanović, I. Milošević, T. Vuković, and R. Sredanović, Phys. Rev. B **60**, 2728 (1999).

[12] J. F. Cornwell, *Group Theory and Electronic Energy Bands in Solids* (North-Holland, Amsterdam, 1969).

[13] D. C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy: an Introduction to Vibrational and Electronic Spectroscopy* (Dover, New York, 1989).

[14] The reducible representations in Eqs. (3)–(6) are given for odd n's. For even n's, one should interchange $B_{2g} \leftrightarrow B_{1g}$, $B_{1u} \leftrightarrow B_{2u}$ in Eqs. (3) and (5) and $B_{1u} \leftrightarrow B_{1g}$, $B_{2u} \leftrightarrow B_{2g}$ in Eqs. (4) and (6). Such differences would have no fingerprints in the number of active modes, since these 4 IRREPS correspond to optically inactive vibrations (for $n>2$).

[15] C. Y. Liang and S. Krimm, J. Chem. Phys. **25**, 543 (1956).

[16] R. A. Jishi, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **47**, 16 671 (1993).