

Symmetry of the high-energy modes in carbon nanotubes

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(Submitted June 3, 1999)

Introduction. Group theory predicts 15 or 16 Raman active modes for single-walled nanotubes, irrespective of their diameter [1]. In the carbon-bond stretching region ($\approx 1600 \text{ cm}^{-1}$) several peaks are observed in the Raman spectra. Based on lattice dynamical calculations these peaks have been assigned to A_{1g} , E_{1g} and E_{2g} modes [1, 2]; *ab initio* calculations also find modes of these symmetries at these energies [3]. Calculations of the Raman polarizability predict the E_{1g} modes to be the strongest [4, 5]. No polarized Raman spectra from crystals of nanotubes have been published to confirm this assignment. Recently, Sun *et al.* produced samples with aligned small-diameter tubes ($d \approx 5 \text{ \AA}$) embedded in a host with cylindrical holes [6]. From their spectra they identify an A_{1g} , an E_{1g} , and an E_{2g} mode. Single crystals not being available, a way to determine the symmetries of modes in Raman scattering is through depolarization ratios (D) [7]. While in general it is not possible to uniquely derive the sign or magnitude of the tensor elements, one can distinguish traceless tensors (E_{1g} and E_{2g}) from fully symmetric tensors (A_{1g}).

Experimental Results. We determined $D=I_{\perp}/I_{\parallel}$ of several unoriented samples of single-walled nanotubes ($d \approx 14 \text{ \AA}$) with $\lambda_{exc}=488 \text{ nm}$ (Fig. 1). Assuming that the largest peaks correspond to two modes we find $D=0.40 \pm 0.04$ at 1592 and 1566 cm^{-1} , which is incompatible with strict E_{1g} or E_{2g} symmetry (for which $D \equiv 0.75$; small deviations ϵ from perfect symmetry change D only to order ϵ^2). Instead, it indicates that these modes of the nanotubes are of A_{1g} symmetry, where D can vary between 0 and 0.75 depending on the tensor elements. The data of Sun *et al.* agree with the peaks at 1592 and 1566 cm^{-1} being A_{1g} modes although they conclude differently (i.e., A_{1g} for the highest frequency mode, E_{2g} symmetry for the second strongest peak in their spectra) [6]. For the point groups of the nanotubes, D_{nh} , D_{nd} , or $C_{N/\Omega}$, we derive from the depolarization ratios the A_{1g} phonon Raman tensors [8]

$$A_{1g}^{1592} : \begin{pmatrix} \mp 0.06 & & \\ & \mp 0.06 & \\ & & \pm 1 \end{pmatrix} \text{ and } A_{1g}^{1566} : \begin{pmatrix} \pm 0.36 & & \\ & \pm 0.36 & \\ & & \mp 0.21 \end{pmatrix}$$

We normalized with $|\alpha_{zz}^{1592}|=1$ [9]; the error in the last digit is 4.

Discussion and Conclusions. It thus appears that we can describe the two peaks in the high-energy spectra of SWNT with A_{1g} modes. The predicted E_{1g} and E_{2g} modes apparently are much weaker. A similar situation occurs in C_{60} [10] and in high-temperature superconductors [11], where cancellations in the Raman polarizability of the traceless eigenmodes result in 10 to 100 times weaker signals than of the fully symmetric modes.

It is interesting to speculate about the origin of the A_{1g} modes in Fig. 1. There is only one A_{1g} mode expected in this high-energy region in armchair or zigzag nanotubes. Different diameters, at least in the simple zone-folding scheme, cannot yield new frequencies for A_{1g} modes. On the other hand, in *ab initio* and force-constants calculations, the highest A_{1g}

frequencies for similar diameters come out differently for armchair and zigzag tubes [3, 4]. The higher-energy mode in Fig. 1 could thus result from zigzag, the other from armchair nanotubes or all high-energy peaks may even correspond to a distribution of tube chiralities. Resonance Raman spectra [12] suggest the 1566-cm^{-1} and lower modes to be metallic, i.e. mostly armchair tubes, leaving the 1592-cm^{-1} peak to originate from semiconducting zigzag or chiral nanotubes.

Acknowledgements. We thank P. Bernier, C. Journet, J.-P. Salvetat and L. Forró for providing us with samples of single-walled nanotubes.

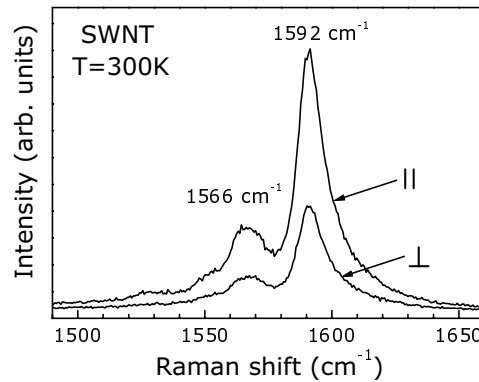


Figure 1: Raman spectra for parallel and crossed polarizations in the carbon-stretching region of single-walled nanotubes.

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- [9] We could have also normalized to $\alpha_{xx}^{1592}=\pm 1$ and obtained $\alpha_{zz}^{1592}=\mp 0.64$. Likewise, even for a fixed A_{1g}^{1592} , there is a second solution for the lower mode. For $\alpha_{zz}^{1592}=\pm 1$ this solution is: $\alpha_{xx}^{1566}=\mp 0.03$ and $\alpha_{zz}^{1566}=\pm 0.56$. The results of Ref. [6] imply, however, $|\alpha_{zz}| \gg |\alpha_{xx}|$ for the higher and $|\alpha_{zz}| \approx |\alpha_{xx}|$ for the lower mode.
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