

Phonons and symmetry properties of (4,4) picotube crystals

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Abstract. The recently grown picotube crystals are the closest to a monochiral nanotube sample achieved up to now. We present an experimental and theoretical study of the vibrational properties of these crystals, including polarization dependent Raman spectra and *ab initio* calculations. We assign symmetries to the most intense peaks, A_1 in most cases. From *ab initio* calculations we obtain the underlying atomic displacements. We find, among others, modes related to the high-energy mode and the radial-breathing mode of carbon nanotubes.

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Much of the existing knowledge about carbon nanotubes stems from the zone-folding of graphite properties[1]. In this way, many regularities of the nanotube properties can be explained, but the effect of the curvature of the nanotube walls is completely neglected. A complementary approach is to study the properties of very short molecule-like nanotubes: the system we present here is a realization of this idea. A picotube is a highly symmetric hydrocarbon which resembles a very short (4,4) nanotube. The synthetic procedure guarantees the existence of only one "chirality" and uniform geometry in the samples which facilitates the comparison with theory[2]. The achievement of growing picotube crystals offers currently the closest approximation to a monochiral nanotube crystal.

We present an experimental and theoretical study of the vibrations of picotube crystals. For the polarization-dependent micro-Raman measurements we used a single grating LABRAM spectrometer and an excitation laser wavelength of 633 nm in backscattering geometry. *Ab initio* calculations were performed with the SIESTA code using the local-density approximation[3, 4, 5]. The core electrons were replaced by nonlocal, norm-conserving pseudopotentials[6]. A double- ζ singly polarized (DZP) basis set of localized atomic orbitals was used for the valence electrons. The cut off radii were determined from an energy shift of 50 meV by localization. For the calculation of the picotube molecule we used a grid cutoff of ≈ 100 Ry in real space (≈ 200 Ry for the phonon calculation).

In Fig. 1 we show the structure of a picotube as obtained from X-ray measurements of a picotube crystal[7]. It can be seen as a (4,4) hexagon ring with eight benzene-like wings. Due to the repulsion of these wings the inversion symmetry is broken: two of the upper wings bend towards the main axis of rotation (C_2), and the other two bend

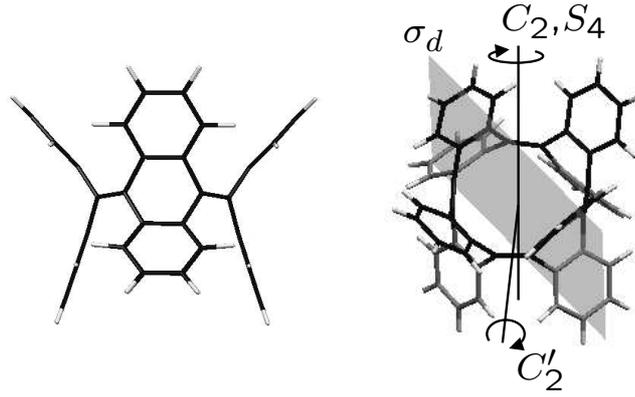


FIGURE 1. Structure of a picotube molecule. Side view: note the asymmetry of the upper and lower wings of each anthracene-like unit. Four of these wings bend towards the main rotational axis, and four away from it, forming an alternating structure. Top view: The black (gray) C atoms are in the image foreground (background). The H atoms are white. The symmetry axes and planes are indicated.

away from it, complementarily on the lower side. The molecule does not have D_{4h} but the lower D_{2d} symmetry. *Ab initio* relaxation of a single molecule yields a structure in excellent agreement with the measurements[8, 7].

In Fig. 2 we show Raman spectra for incident and outgoing light polarization parallel to one edge of a picotube crystal. It is dominated by a feature around 1600 cm^{-1} , typical for sp^2 carbon compounds. Taking a closer look we can differentiate two peaks at 1601 and 1592 cm^{-1} , plus a lower peak at 1569 cm^{-1} (see inset). The intermediate frequency range is dominated by a peak at 1131 cm^{-1} and a group of three peaks at 1066 , 1056 , and 1042 cm^{-1} . At low frequencies we find a band around 480 cm^{-1} and a group of peaks around 270 cm^{-1} .

The dots in Fig. 3(a) show the intensity of the peak at 1601 cm^{-1} as function of the angle ψ between the polarization of the incident light and the x axis of the crystal. The trained eye will guess an A_1 symmetry for this mode. However, the intensity does not go to zero at $\psi = 45^\circ$ for parallel incident and scattered light. Neither a single A_1 nor any other single Raman tensor can explain this behavior. Therefore, inspired by X-ray measurements we propose a unit cell with perpendicular molecules interacting weakly and scattering independently[7]. In this case the Raman intensity can be calculated as

$$I \propto (\mathbf{e}_i \cdot R_{PT} \cdot \mathbf{e}_s)^2 + (\mathbf{e}_i \cdot R_{PT}^\perp \cdot \mathbf{e}_s)^2 \quad (1)$$

where R_{PT} is the Raman tensor of a picotube molecule and R_{PT}^\perp the same Raman tensor rotated by 90° with respect to the latter. $\mathbf{e}_{i(s)}$ denote the polarization of the incoming (scattered) light. We fitted the data for the 1601 cm^{-1} peak with the function obtained by applying Eq. (1) to the case of an A_1 Raman tensor. The resulting fit is excellent, as shown in Fig. 3. Therefore, we assign this peak to an A_1 symmetry mode from identical molecules with alternating orientations. Using this method we assigned the symmetries of the most intensive peaks, mostly A_1 . The peak at 1592 cm^{-1} is an exception. It can only be explained as the sum of different symmetries, including necessarily E or B_2 . Infrared

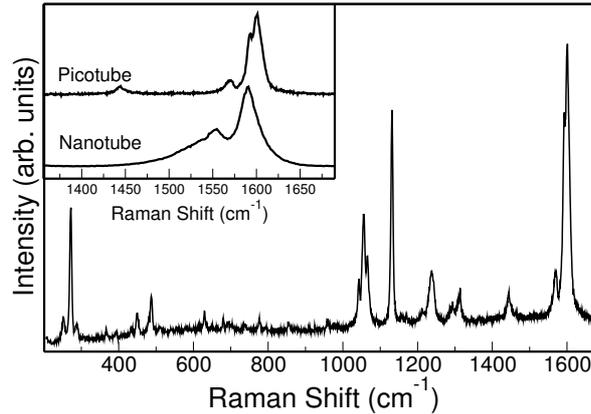


FIGURE 2. Raman spectrum of a picotube molecule along its x axis. Inset: Zoom of the high-energy region for the same picotube spectrum and the spectrum of a nanotube bundle (diameter around 1 nm) .

Fourier Raman measurements show more than three peaks in this region, which confirms our observation[9].

We are now interested in the atomic displacements underlying the measured peaks. By *ab initio* calculations, we found three A_1 vibrational modes in the high-energy region shown in Fig. 3(b). The mode at 1621 cm^{-1} is equivalent to the high-energy mode of armchair carbon nanotubes, derived from the in-plane optical phonon of graphite. The high-energy mode of single-walled nanotubes has a double peak structure similar to the one found in the picotubes. However, in the case of armchair nanotubes it stems from only one phonon branch due to a double resonance process[10, 11, 1]. This is not the case for the picotubes, but the band shape is due to several modes. The lower symmetry of the molecule, for example the absence of inversion symmetry, allows more phonons to be Raman active. In addition, if we think of the picotube as a very short nanotube, we can see the picotube vibrations as the result of "folding" the Brillouin zone of the (4,4) nanotube. Therefore, for each Raman active branch of the nanotube, several modes will be found in the vibrational spectrum of the picotube. The number of active modes in the Raman spectrum of carbon nanotubes is further reduced by the antenna effect[1].

The fourth mode shown in Fig. 3(b), at a 262 cm^{-1} and with A_1 symmetry, is clearly related to the radial breathing mode of carbon nanotubes. The frequency is in good agreement with the measured peaks at 272 or 253 cm^{-1} . *Ab initio* calculations for the (4,4) nanotube yield a much higher frequency of 413 cm^{-1} . The frequency softening in the case of the picotube is related to its lower symmetry. All atoms in a nanotube are equivalent by symmetry. The radial-breathing mode is totally symmetric, therefore all atomic displacements must be equal. In the case of the picotube this condition is strongly relaxed. The wings are not equivalent and they are not connected by bonds. Part of the C-C bonds are not stretched since the mode is strongly mixed with a translation along the molecular axis, which lowers the frequency of the vibration.

Summarizing, we presented a study of the vibrational properties of picotube crystals. From polarization-dependent Raman measurements we inferred a low interaction between the molecules, supported by the excellent agreement between the theoretical structure of an isolated molecule and the measured structure in crystalline form. We

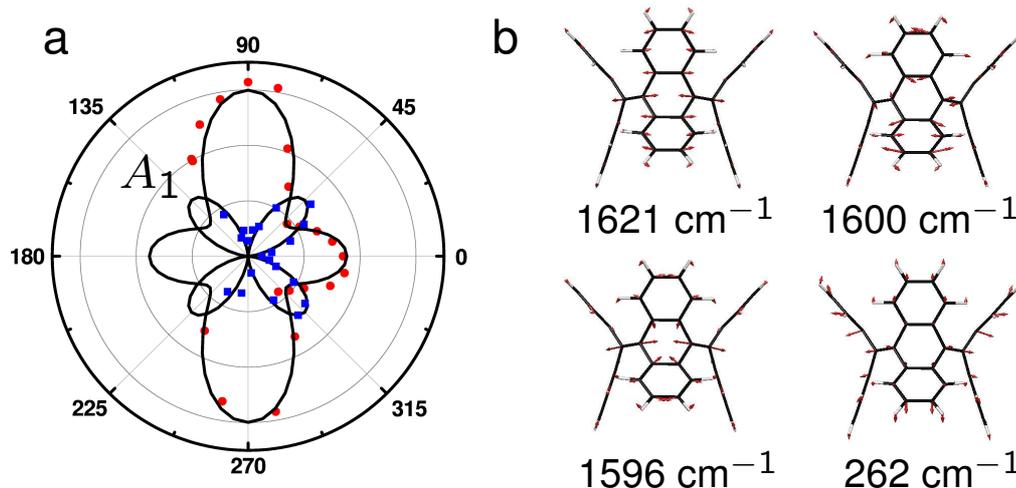


FIGURE 3. (a) Intensity of the peak at 1601 cm^{-1} as a function of the angle ψ between the polarization of the incident light and the x edge of the picotube crystal. The circles (squares) correspond to parallel (perpendicular) incident and scattered light. The lines are fits to a A_1 symmetry scattered by two perpendicular, non interacting picotube molecules. (b) Selected *ab initio* calculated vibrations of the picotube molecule.

were able to assign the symmetry of the most intensive peaks, mostly A_1 . Comparing to *ab initio* calculations we found vibrations related to the in-plane optical phonon of graphite and a breathing-like mode, in strong analogy with carbon nanotubes.

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