Grid (1 , 1)

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

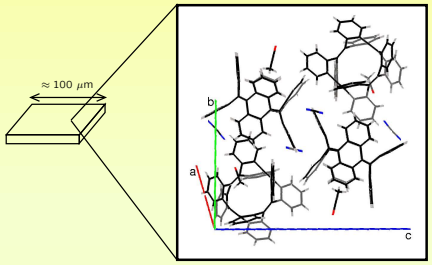
M. Machón[1], S. Reich[2], J. Maultzsch[1], P. Puech[3], Z. K. Tang[4], R. Herges[5], and C. Thomsen[1]

[1]Institut für Festkörperphysik, Technische Universität Berlin, [2]Department of Engineering, University of Cambridge, UK, [3]Laboratoire Physique des Solides de Toulouse, Université Paul Sabatier, Toulouse

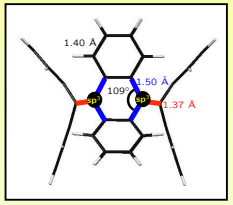
[4] Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Hong Kong, [5]Institut für Organische Chemie, Universität Kiel,

The recently grown picotube crystals are the closest to a monochiral nanotube sample achieved up to now [1]. The small diameter of the molecule allows the observation of curvature effects such as rehybridization.We present a thorough experimental and theoretical study of these molecules, including X-ray diffraction, polarization dependent Raman spectra, and *ab initio* SIESTA [4] calculations, and compare the properties of picotubes to those of carbon nanotubes [2].

CRYSTAL STRUCTURE



PICOTUBE MOLECULE



Formula: $C_{56}H_{32}$.

Symmetry group: D_{2d}.

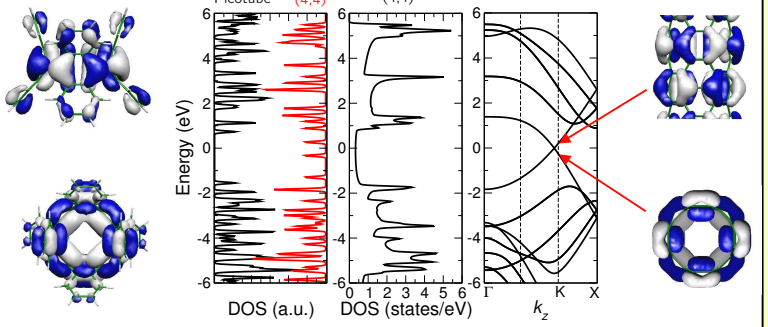
Diameter = 5.4 Å

Calculated (4,4) NT diameter=5.5 Å.

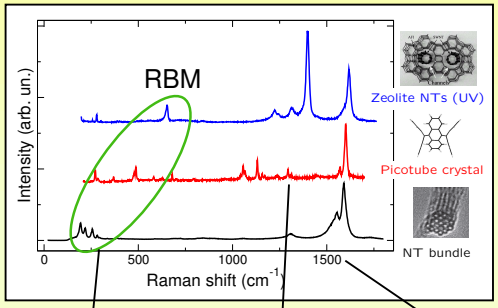
The atoms in the central ring rehybridize due to curvature. The angle of 109°, as well as the length of the blue marked bonds, indicate sp^3 character. The bonds in the ring show the typical double bond length.

ELECTRONIC PROPERTIES

The HOMO and LUMO wavefunctions show similarities to the (4,4) nanotube, but are shifted away from the Fermi level. The picotube crystals are transparent for most of the visible range [$E_g = 2.3$ eV].



RAMAN SPECTRA



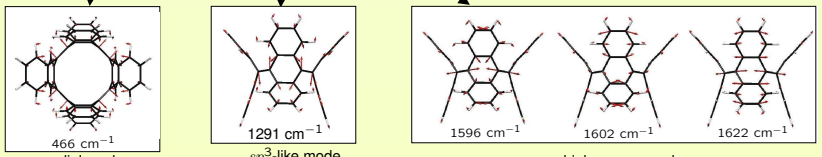
Double peak structure at ≈ 1601 cm^{-1} observed up to now only in SWNTs.

Group of three peaks at ≈ 480 cm^{-1}.

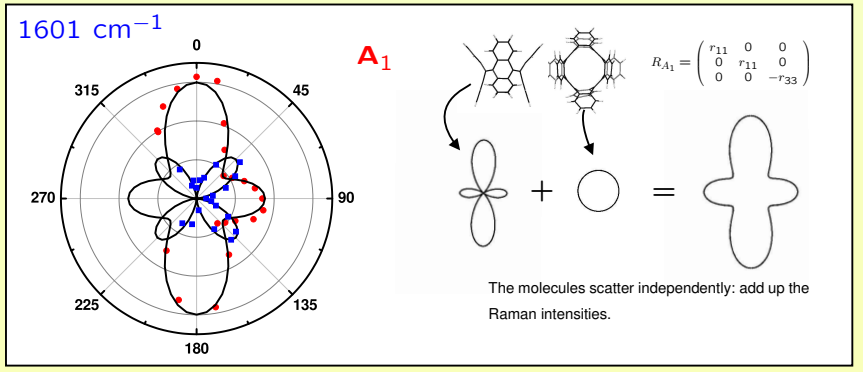
ω_{RBM}-diameter relationship (constants from Ref.[3]):

$\omega_{RBM} = \frac{214}{d}$ cm^{-1}nm + 19 cm^{-1}=416 cm^{-1}

in fairly good agreement with the measurement. The *ab initio* calculations of the RBM-like eigenmode and frequency (466 cm^{-1}) confirm this analogy. The eigenvectors of the high energy modes, also shown, resemble the nanotube eigenvectors.



POLARIZATION-DEPENDENT RAMAN



The molecules scatter independently: add up the Raman intensities.

Conclusions

- Picotube crystals are the best approximation available to monochiral nanotube crystals.
- Curvature effects are observed in the picotube structure and the Raman spectrum in form of rehybridization.
- An analogy can be established between several properties of the (4,4) nano- and picotubes.

References

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[2] *Reich, Thomsen, and Maultzsch, Carbon nanotubes, basic concepts and physical properties, WILEY-VCH (2004)*

[3] *H. Telg et al., PRL* **93**, *177401 (2004)*

[4] All calculations were performed with the SIESTA code
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maria@physik.tu-berlin.de

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