Polarised Raman measurements of β-carotene in photosystem II and carotene encapsulated in SWNTs

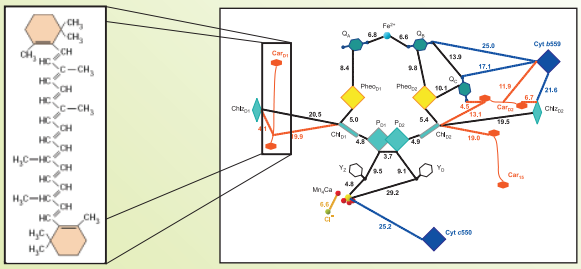
Katharina Brose[1], Norman Tschirner[1], Athina Zouni[2], Frank Müh[2], Kazuhiro Yanagi[3], Hiromichi Kataura[4], Janina Maultzsch[1]

[1] Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany
[2] Institut für Chemie, Max-Volmer-Laboratorium TU Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
[3] Department of Physics, Tokyo Metropolitan University, Japan
[4] Nanotechnology Research Institute, Institute of Advanced Industrial Science and Technology, Japan

Motivation:

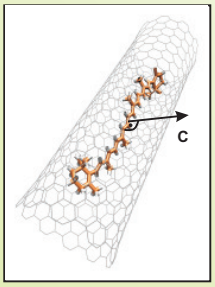
The pigment molecule β-carotene is of great importance for light harvesting complexes. It is used as one of the antenna pigments to collect the sunlight and send it to the reaction center. A second role is to protect the photo-system molecule complex.
In order to understand the function of the different β-carotene molecules in the reaction center, it is important to know the orientation of them in the reaction center. Therefore we performed polarisation dependent Raman spectroscopy on β-carotene in different environments.

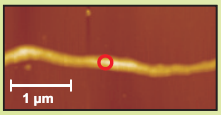
β-carotene in the different structures:



We investigated two different β-carotene systems: a dimeric photosystem II crystal and single walled nanotube (SWNT) bundles with encapsulated β-carotene.
The crystal unit cell includes four dimers. Each dimer is one PS II complex and has 12 β-carotene molecules inside, three in the reaction center. Because of their well-defined orientations, it should be possible to separate the Raman signals of mutually perpendicular β-carotene molecules.

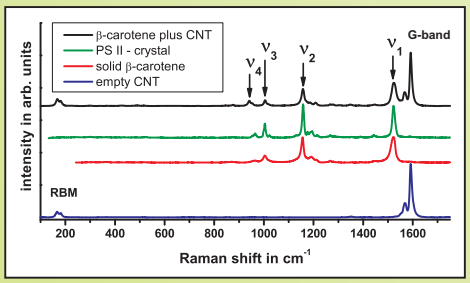
In order to analyse a single molecule with well-defined orientation, we measured the Raman signal of β-carotene encapsulated in SWNT bundles [1]. For this configuration, we know that the pseudo symmetry axis C perpendicular to the β-carotene backbone is always perpendicular to the nanotube axis.





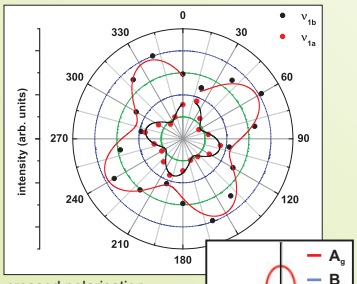
The Raman spectra of solid β-carotene, the PS II crystal and β-carotene in the SWNTs are very similar. The most prominent difference is the strongly enhanced intensity of the ν_4 band for β-carotene inside SWNT. This signal enhancement can be attributed to out-of-plane C - H wagging modes due to the influence of the nanotube wall [1]. The ν_4 peak indicates that the β-carotene molecule in the nanotube adapts a twisted conformation, since the ν_4 mode is not allowed for planar molecules [2]. It is the signature for successful incorporation of β-carotene into SWNTs.

The ν_1 band consists of two vibrational bands called ν_{1a} and ν_{1b}. [3,4] For the comparison of the polarised Raman measurements we refer to these two β-carotene modes.



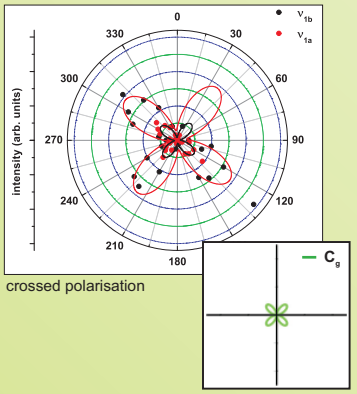
Polarised Raman measurements:

β-carotene in the PS II-crystals:



The two β-carotene modes in PS II crystal show fourfold polarisation dependence in crossed configuration. The two peaks can be distinguished by a 45° phase shift in their polarisation dependence. Based on their polarisation dependence, they were assigned to A_g and B_g symmetry (C_{2h} symmetry group of the β-carotene backbone). [4]

β-carotene encapsulated in SWNTs:



The ν_1 carotene peaks show fourfold polarisation dependence in crossed configuration as in the PS II crystal, but there is no 45° phase shift between ν_{1a} and ν_{1b}. For parallel polarisation, the intensity has a twofold polarisation dependence with the maximum at polarisation along the tubeaxis.

We attribute this polarisation behavior to a reduction of symmetry of the β-carotene inside the nanotube. Due to the twisting of the tube, the local C_2 axis is not present any more, resulting in C_i symmetry.

$$A_g = \begin{pmatrix} a & \frac{1}{2}a & 0 \\ -\frac{1}{2}a & a & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad B_g = \begin{pmatrix} 0 & 0 & \frac{1}{2}a \\ 0 & 0 & 0 \\ \frac{1}{2}a & 0 & 0 \end{pmatrix} \quad C_g = \begin{pmatrix} a & \frac{1}{2}a & \frac{1}{2}a \\ -\frac{1}{2}a & a & 0 \\ \frac{1}{2}a & 0 & 0 \end{pmatrix}$$

Conclusions:

We show that the polarised Raman spectra of β-carotene in PS II crystals and encapsulated in SWNTs can be simulated with the same Raman tensor entries even though the twisted molecules in the tubes show a reduction of symmetry.

References:

[1] K. Yanagi, Adv. Materials **18**, 437 - 441 (2006).

[2] B. Robert, in *The Photochemistry of Carotenoids*, Kluwer, Dordrecht, The Netherlands 1999, Ch. 10.

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katharina.brose@physik.tu-berlin.de