Raman Spectroelectrochemistry - A Way of Switching the Peierls Transition in Metallic Single-walled Carbon Nanotubes

P. M. Rafailov, J. Maultzsch and C. Thomsen

Institut für Festkörperphysik, Technische Universität Berlin
Hardenbergstr. 36, 10623 Berlin, Germany

ABSTRACT. **The high-energy vibrational modes of metallic nanotubes are believed to be softened compared to the semiconducting ones by a Peierls-like transition [1]. We examined the frequency shifts and the intensity of the peaks of the high-energy band in SWNT Raman spectra in dependence on the doping level, as excited with a red laser to enhance the metallic tubes. The metallic modes were indeed found exceptionally sensitive to electrochemical doping, exhibiting large frequency shifts and intensity fluctuations. Our data may be interpreted as controlling the Peierls-like instability in metallic tubes with the applied potential.**

BACKGROUND. The shift of the high-energy SWNT mode (HEM) upon double-layer charging in an electrolytic solution has been intensively studied for both semiconducting and metallic nanotubes [2–5]. In the "metallic resonance window" (1.7 - 2.2 eV) doping successively restores the semiconducting-like HEM shape, causing the broad "metallic" band at the low frequency side of the HEM to vanish [3, 5]. This effect was attributed to a depletion of the first optical transition in metallic SWNTs [5], thus assuming intercalation-like doping levels (up to ≈ 0.1 holes/C-atom).

Driving the HEM-modes with electrochemical doping - essentially different response of metallic and semiconducting SWNTs

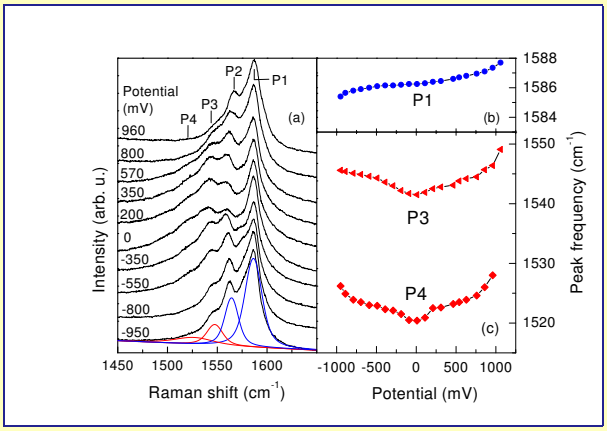

Figure 1: Raman spectra at 1.95 eV excitation energy of the high-energy mode (HEM) at several potentials applied to the SWNT electrode in 1 M NH_4Cl aqueous solution. Metallic modes undergo a strong non-linear hardening upon doping of either sign.

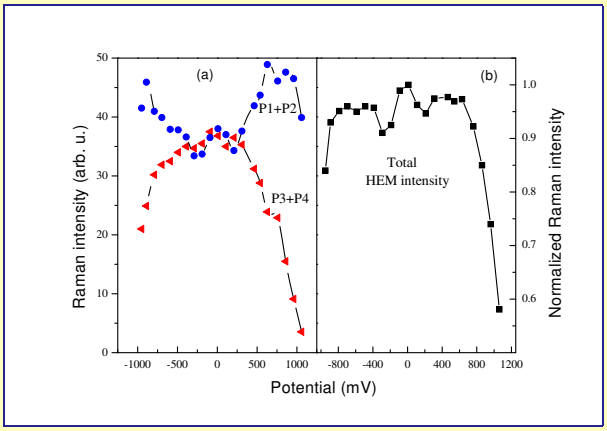

Figure 2: Integrated Raman intensities: The apparent loss of Raman intensity of metallic modes (P3+P4) essentially comprises an intensity transfer to P1 and P2. The total Raman intensity is preserved up to $\pm$900 mV at doping levels $\leq 0.005|e|$/C-atom. This rules out a depletion of the first "metallic" transition as a possible reason for the apparent vanishing of the metallic modes.

References

[1] O. Dubay and G. Kresse, *Phys. Rev. B*, **67**, 035401 (2003).

[2] L. Kavan *et al.*, *J. Phys. Chem. B*, **105**, 10764 (2001).

[3] C. P. An, Z. V. Zardeny, Z. Iqbal, G. Spinks, R. H. Baughman and A. Zakhidov, *Synth. Met.*, **116**, 411 (2001).

[4] M. Stoll, P. M. Rafailov, W. Frenzel and C. Thomsen, *Chem. Phys. Lett.*, **375**, 625 (2003).

[5] P. Corio *et al.*, *Chem. Phys. Lett.* **370**, 675 (2003).

[6] J. Maultzsch, S. Reich, U. Schlecht and C. Thomsen, *Phys. Rev. Lett.*, **91**, 087402 (2003).

[7] J. Maultzsch, S. Reich and C. Thomsen, *Phys. Rev. B*, **65**, 233402 (2002).

[8] S. Reich, C. Thomsen and J. Maultzsch, *Carbon Nanotubes: Basic Concepts and Physical Properties*, Wiley-VCH (Weinheim, 2004).

Discussion

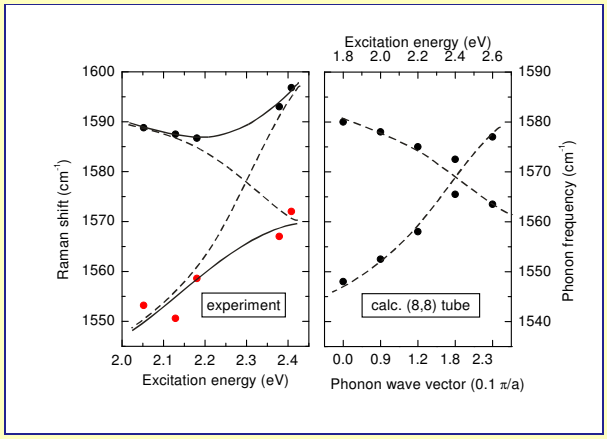

Figure 3: (From Ref. 6) *Left:* Measured HEM frequencies as a function of excitation energy. *Right:* Calculated HEM frequencies of the (8,8) tube as a function of laser energy (top axis) and of the double-resonant phonon wave vector [7,8] (bottom axis). A red laser excitation combined with electrochemical doping that shifts the LO branch Γ-point states to higher energies should have the same effect as a blue laser excitation.

Limits of the Double-Layer Regime

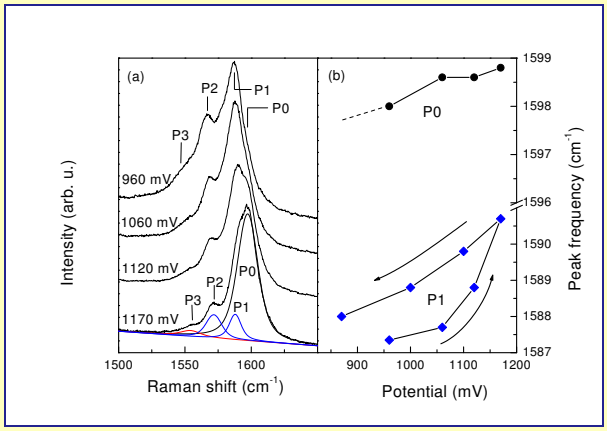

Figure 4: Raman spectra at 1.95 eV excitation of the HEM upon electrochemical doping at several high potentials - a spectroscopic evidence for a transition from a low-doping double-layer charging to hysteretic intercalative doping.

Conclusions

- Due to band crossover at the Fermi level Raman modes of metallic SWNTs are very sensitive to electrochemical doping. We tentatively ascribe the exceptionally strong shift of the peaks **P3** and **P4** to a removal of the Peierls-like instability which lowers the Γ-point frequency of the LO-branch in metallic SWNTs [1].
- At double-layer potentials higher than 1 V a transition from double-layer charging regime to hysteretic intercalative doping takes place.

March 2005