RAMAN SPECTROSCOPY ON ELECTROCHEMICALLY DOPED CARBON NANOTUBES

P. M. Rafailov[a,b*], C. Thomsen[a]

[a]Institut für Festkörperphysik der Technischen Universität Berlin, Sekr. PN 5-4, Hardenbergstr. 36, D-10623 Berlin, Germany
[b]Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

We studied the Raman response of electrochemically doped single-walled carbon nanotubes (SWNT), using different electrolyte solutions and excitation energies in the range 1.92 - 2.54 eV. The frequency shifts of the high-energy stretching graphite-like mode (HEM) and the disorder (D) mode were examined as a function of the doping level. We show that the actuation properties of nanotubes (strain vs. doping) can be determined from the HEM shift. The results, considered in the framework of a double-resonant model for Raman scattering, give evidence about the doping-induced shift of whole regions of phonon dispersion branches.

1. Introduction

Single-walled carbon nanotubes (SWNT) are promising materials for a variety of future applications ranging from reinforced fibers to field-emission flat panel displays. For many of these, a detailed knowledge of the doping behavior of the nanotubes is needed. A powerful method which can provide fine tuning of the mechanical and electronic properties of SWNTs is electrochemical doping [1]. This tuning can be monitored by Raman spectroscopy in a standard three-electrode cell. The shift of the high-energy SWNT mode (HEM) upon double-layer charging in an electrolytic solution has been intensively studied [1,2] at the most common laser excitation of 514.5 nm. The second-order of the D mode, $D*$, also exhibits a considerable shift upon doping [3]. Here we show that useful information on the bond length change can be obtained from doping-induced frequency shifts, as in the double-layer model the transferred charge can be quantified [1]. However, as the HEM and the D mode are double-resonant in nature [4,5], it should be taken into account that different laser excitations will probe different regions of the bond-stretching dispersion branches, whose shift upon doping may be wave-vector dependent. We also present a Raman investigation of the whole HEM dispersion branch, by excitation-energy dependent measurements of the HEM and the $D*$ mode of a SWNT bundle sample [6].

2. Experimental details

A stripe of SWNT paper [6] was prepared as a working electrode in a three-electrode cell. A Metrohm - Potentiostat was employed for charging at constant potentials. A platinum wire and

---

* Corresponding author: rafailov@physik.tu-berlin.de

Ag/AgCl/3M KCl served as auxiliary and reference electrode, respectively. The working electrode was only partly contaminated with the solution, and was electrically contacted at its dry end.

3. Results and discussion

The frequency of the high-energy graphite-like stretching mode scales linearly with doping, at least up to 1 V applied potential, as can be appreciated from Fig. 1. This frequency shift was found to be largely independent of the excitation energy, as well as of the particular counterion which forms the double layer. As doping leads to a homogeneous deformation, the dependence on the strain ε of the phonon frequency ω in a nanotube can be modelled similarly to the response under hydrostatic pressure [7]:

$$\frac{\omega(f) - \omega_0}{\omega_0} = \frac{\Delta\omega(f)}{\omega_0} = -2\gamma\varepsilon_{zz} \tag{1}$$

where γ is the Grüneisen parameter, f is the doping level, $\omega_0 = \omega(f=0)$ and ε_{zz} stands for the axial strain. Upon doping, a new equilibrium state of the SWNT is achieved with a minor change in the carbon-carbon bond length. In analogy to graphite, we take the axial strain to be approximately equal to the circumferential one, neglecting the nanotube curvature. Then, using $\gamma \approx 1.1$ as estimated for graphitic intercalation compounds and $\Delta\omega \approx 1.4$ cm^{-1} at 1 V applied potential (doping level $f \approx 0.005$ holes/C-atom), we obtain $\varepsilon_{zz} \approx -0.04\%$, in good agreement with theoretical estimates [8].
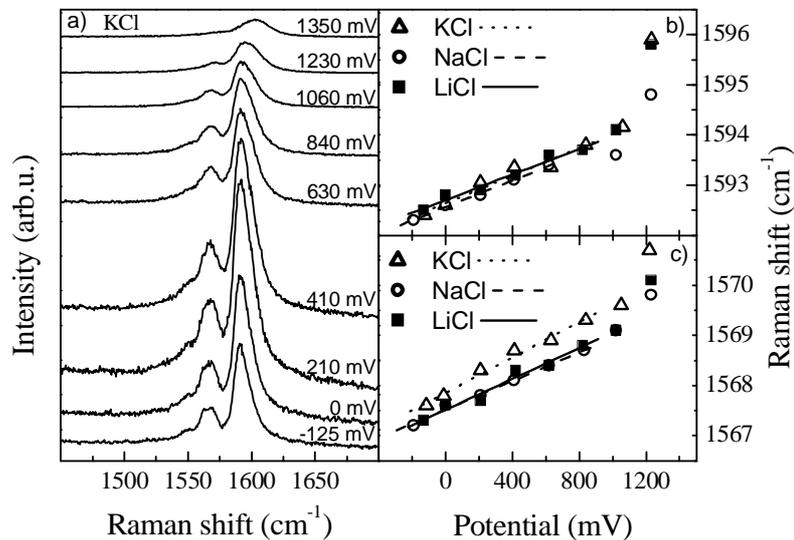

Fig. 1. *(a)* Raman spectra of the high-energy mode (HEM) at several potentials applied to the SWNT-mat (1 M KCl). *(b)* The frequency of the main HEM peak at 1593 cm^{-1}, as a function of the applied potential for three different solutions: LiCl (squares), NaCl (circles) and KCl (triangles). *(c)* The same as *(b)* for the second-strongest HEM peak at 1567 cm^{-1}.

We further checked the doping behavior of the second-order D mode: D^* (the D mode itself was too weak to be reliably fitted). With appropriately chosen laser excitation, the D^* mode exhibited a considerable shift upon doping, as seen in Fig. 2 *(a)* for $\lambda_{exc} = 568$ nm. We observed a surprisingly strong dependence of the doping-induced shift on the excitation energy: from no shift to above 4 cm^{-1}/V in going from blue to red excitation, as shown in Fig 2 *(b)*.

To explain the D^* mode behavior, we recall that both the D and the D^* mode originate from phonons in the vicinity of the graphite K-point and appear in the Raman spectra due to a defect-

induced double-resonant process [4]. A resonantly excited electron emits a phonon and is resonantly scattered across the Γ point. Then it is scattered back by a defect, thus compensating the large wave vector of the created phonon and recombines with a hole in a $\Delta k \approx 0$ transition [4]. Due to the steep dispersion of the high-energy TO phonon branch, increasing the excitation energy leads to smaller wave vectors and a higher frequency of the double-resonant phonon [4]. This is illustrated in Fig. 3 *(a)* and *(b)*.
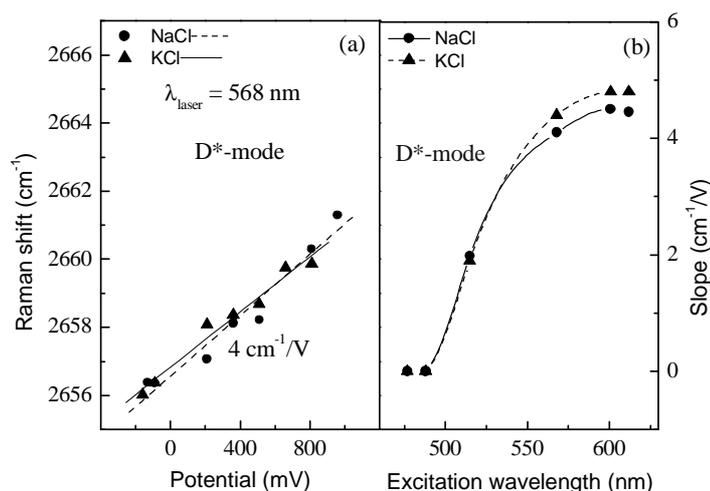

Fig. 2. *(a):* The frequency of the *D** mode as a function of the applied potential for two electrolyte solutions at λ_{exc} = 568 nm.   *(b): D** mode slopes (frequency shift per unit applied potential) as obtained for various laser excitation wavelengths. The connecting lines are guides to the eye.

Doping shifts the phonon branch. This alters the double-resonance condition, as only a unique pair of electronic-transition energy and phonon energy can fulfil it. The different frequency slopes of the *D** mode at different excitation energies thus imply that the doping-induced shift varies with wave-vector. This is schematically shown in Fig. 3 *(b)*: The phonon state at wave-vector k_{ph1} is involved in the Raman process by, e.g., blue laser excitation, and exhibits no doping-induced shift (see Fig. 2(b)), while the state at k_{ph2} is excited by, e.g., yellow laser light and shifts considerably upon doping.
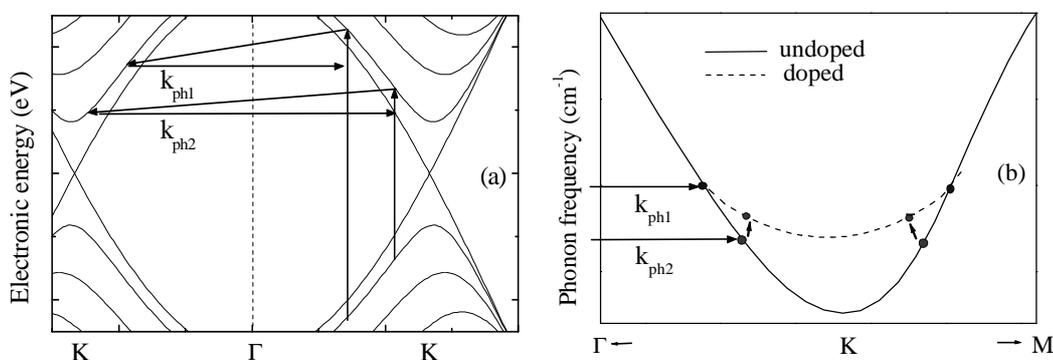

Fig. 3 *(a):* A double-resonant Raman process that reveals the *D* and *D** modes for two different excitations. *(b):* Phonon dispersion relation without (solid line) and with doping (dashed line) and the corresponding double-resonantly excited phonon states (filled circles). k_{ph1} and k_{ph2} are the same phonon k-vectors as in *(a)*.

4. Conclusions

We performed a Raman investigation of the high-energy modes of SWNTs upon electrochemical doping for various excitation energies. We introduced a simple model by means of which the actuation properties of carbon nanotubes can be estimated from the doping-induced shift of the high-energy graphite-like mode. The doping-induced shift of the $D*$ mode was found to be strongly k-vector dependent and thus unsuitable for strain estimates. This leads us to conclude that the k-vector dependence of the doping-induced shift is stronger in those regions of the Brillouin zone where the phonon branches are more dispersive.

References

[1] L. Kavan, P. Rapta, L. Dunsch, M. Bronikowski, P. Willis, R. Smalley, J. Phys. Chem. B **105**, 10764 (2001).
[2] M. Stoll, P. M. Rafailov, W. Frenzel, C. Thomsen, Chem. Phys. Lett. **375**, 625 (2003).
[3] S. Gupta, M. Hughes, A. H. Windle, J. Robertson, J. Mater. Res. **13**, 2418 (1998).
[4] J. Maultzsch, S. Reich, C. Thomsen, Phys. Rev. B **65**, 233402 (2002).
[5] J. Maultzsch, S. Reich, C. Thomsen, Phys. Rev. B **64**, 121407(R) (2001).
[6] Free-standing nanotube paper (mean diameter 1.3 nm) from S. Roth, MPI - Stuttgart
[7] S. Reich, H. Jantoljak, C. Thomsen, Phys. Rev. B **61**, R13389 (2000).
[8] G. Sun, J. Kürti, M. Kertesz, R. H. Baughman, J. Phys. Chem. B **107**, 6924 (2003).