A Resonant Raman Study of SWNTs under Electrochemical Doping

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

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

Abstract. The first and second-order high-energy Raman modes of single-walled carbon nanotubes were investigated as a function of electrochemical doping for excitation energies in the range 477 – 780 nm. In the metallic resonance window (560 – 740 nm) a new peak was detected in the HEM region and found to exhibit spectacular shifts upon doping. For excitation energies above and below the metallic resonance range this new peak is absent. The second-order D mode also shifts with doping; the shift, however, strongly depends on excitation energy. In double resonance this corresponds to a wave-vector dependence of the doping-induced shift of the phonon branches.

INTRODUCTION

Electrochemical doping via double layer charging in a electrolyte solution can provide a fine tuning of the mechanical and electronic properties of carbon nanotubes[1]. This tuning can be monitored with Raman spectroscopy by means of a standard three-electrode cell equipped with a quartz window. The shift of the high-energy SWNT mode (HEM) upon double-layer charging in an electrolytic solution has been intensively studied[1, 2, 3] at the most common laser excitation of 515 nm and was found to be ≈ 250 cm^{-1}/hole/C-atom (1.5 cm^{-1}/V). The second-order D mode also exhibits a considerable shift upon doping[4]. From doping-induced frequency shifts useful information on the bond length change can be obtained[2, 5] as in the double-layer model the transferred charge can be quantified. However, as the HEM and the D mode are double-resonant in nature, 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. Here we present a Raman investigation of the whole HEM dispersion branch by excitation-energy dependent measurements of the HEM and the second order of the D mode of a SWNT bundle sample[6].

EXPERIMENTAL

A stripe of SWNT paper with surface density of $\approx 5 \cdot 10^{-5}$ g[6] was prepared as a working electrode in a three-electrode cell equipped with quartz windows. A Metrohm - Potentiostat was employed for charging at constant potentials. A platinum wire and Ag/AgCl/3 M KCl served as auxiliary and reference electrode, respectively. The work-
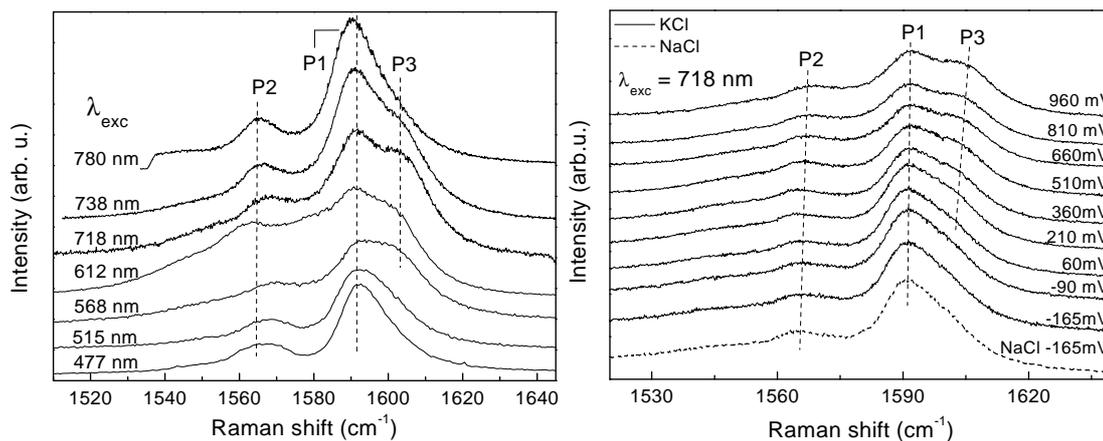
FIGURE 1. **Left**: The HEM band as excited with various laser wavelengths at a constant doping level of ≈1 V (0.005 holes/C-atom).
Right: The HEM band at $\lambda_{exc} = 718$ nm. At this wavelength the developtment of the new peak P3 on increasing the doping level can be followed best.

ing electrode was only partly dived into the solution and was electrically contacted at his dry end.

Several different aqueous solutions (concentration 1 M) were applied in the voltammetric measurements: LiCl, NaCl and KCl. The Raman spectra were recorded with a DILOR triple grating spectrometer equipped with a CCD detector. The 477, 488, 514.5 and 568 nm lines of an Ar^+/Kr^+ laser, as well as a dye laser and a Titanium-Sapphire laser were used for excitation and the spectral resolution was 2 - 6 cm^{-1}.

RESULTS AND DISCUSSION

As can be appreciated from Fig. 1, outside the metallic resonance window (560 – 740 nm) the HEM band in the doped state preserves its well known shape [main peak at 1593 cm^{-1} (P1) and a second-strongest peak at 1567 cm^{-1} (P2)]. In contrast, upon red excitation of the doped SWNTs we observe a qualitative change of what is known as the resonant HEM band of metallic tubes: a new peak (P3) emerges and separates from high-frequency side of P2. The appearance of this peak can either be attributed to an onset of an intercalation process, or it can be assumed that phonons in metallic tubes shift more strongly upon doping. The former suggestion is based on the similarity to the Raman spectrum of p-type graphitic intercalation compounds, where an additional peak appears above 1600 cm^{-1}[7]. However, intercalation may be ruled out as in no Raman experiment on intercalated nanotubes thus far the influence of the charge transfer showed up only upon red excitation and was completely absent outside the metallic resonance window. We therefore tentatively attribute P3 to phonons from the high-energy dispersion branch of metallic tubes (note that because of the double resonance[8] a whole section of the dispersion branch can contribute to the HEM when varying the doping level). From fitting the spectra to Voigt profiles a shift between 3 and 4 cm^{-1}/V

was established for P3. Although the error in determination of the P3 peak positions is especially high, it is obvious that its doping-induced shift is about twice as high as that of P1 and P2 (≈ 1.5 cm^{-1}/V for all wavelengths). The stronger shift of P3 may arise from a peculiar redistribution of phonon states upon shifting the Fermi level from its special position at the band-crossing point in metallic SWNTs[9].
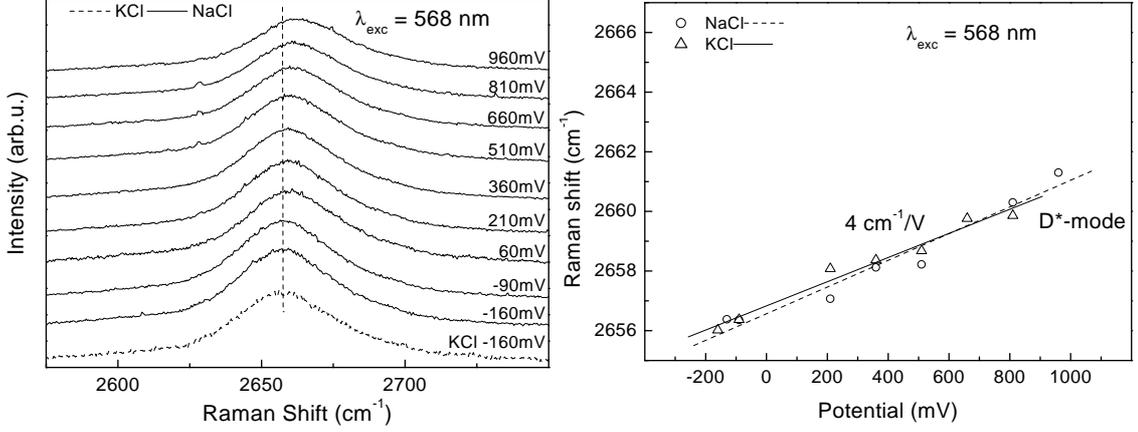
FIGURE 2. **Left**: Raman spectra of the D^* mode at several doping levels for $\lambda_{exc} = 568$ nm. **Right**: The frequency of the D^* mode as a function of the applied potential for two different solutions: NaCl (circles) and KCl (triangles).

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 exhibits a considerable shift upon doping as is seen from Fig. 2 for $\lambda_{exc} = 568$ nm. We observe 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. The following table summarizes the D^* shift slopes (in cm^{-1}/V) found in the examined spectral range:

Electrolyte / λ_{exc}	477 nm	488 nm	514.5 nm	568 nm	601 nm	612 nm
NaCl	0	0	2	4.1	4.5	4.4
KCl	0	0	1.9	4.4	4.8	4.8

Table 1: Doping-induced D^* shift (in cm^{-1}/V) at several excitation wavelengths.

To explain the D^* mode behavior we recall that both D and 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[11]. Due to the steep dispersion of the high-energy TO phonon branch[10], increasing the excitation energy leads to smaller wave vectors and higher frequency of the doubly-resonant phonon[11]. This is illustrated in Fig. 3a.

Doping shifts the phonon branch. This alters the double-resonance condition as only a unique pair of electronic-transition energy and phonon energy can fulfill it. 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. 3b.
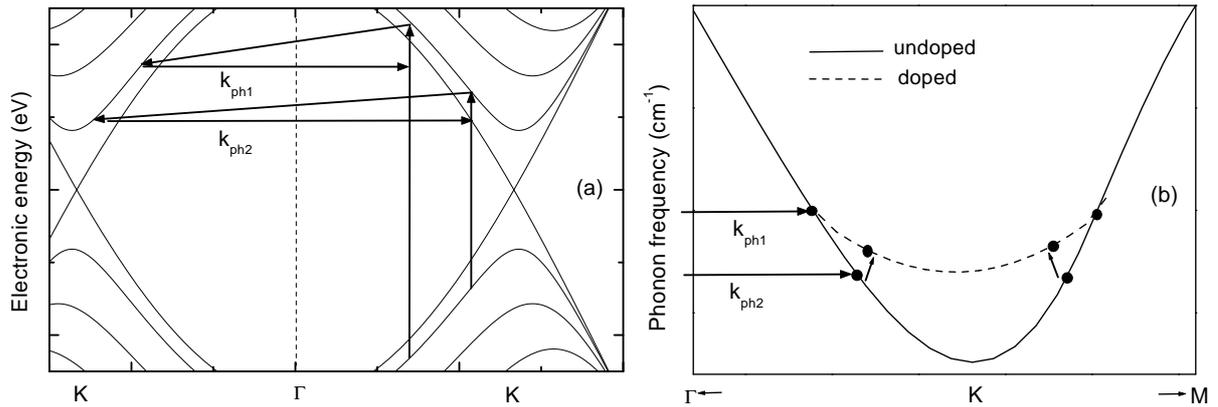
FIGURE 3. **a**: Double-resonant Raman scattering process that reveals the D and D^* modes for two different excitations.
b: Phonon dispersion relation without (solid line) and with doping (dashed line) and the corresponding double-resonantly excited phonon states. Arrows denote the same phonon wave-vectors as in **a**.

CONCLUSIONS

The main peak P1 of the HEM contains a contribution from modes of metallic SWNT (P3) that are revealed in the Raman spectra via electrochemical doping. Furthermore, the high-energy bond-stretching phonon branches of SWNTs shift non-uniformly upon electrochemical doping depending on the k-vector. One important implication from these results is that estimates of doping-induced strain from frequency shifts should take into account the different shift slopes of the HEM constituents and of the D^* mode itself at different excitation energies. Especially the D^* mode shift is unsuitable for such estimates and the HEM shift should be used at higher energy excitations where, the metallic tubes are not resonant.

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