Monitoring the vibrational local character of SWCNTs by TERS

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ABSTRACT

Tip-enhanced Raman spectroscopy (TERS) is used for studying the vibrational local character of single-walled carbon nanotubes (SWCNT) on the nanometer scale. Working in STM-mode with an Au-tip, we discuss the intensity changes and the frequencies shift of the Raman features of SWCNTs upon approaching the tip to the sample surface. The TERS amplitude of the G-mode is strongly dependent on the tip-sample distance and the used excitation energy plays a key role in matching the plasmon resonance. Moreover, the Raman intensity of the D mode and radial breathing mode (RBM) are very sensitive to changes in the tip-sample distance in the first 1 nm contact region. Using the RBM and the G^--mode frequencies, an accurate chiral-index assignment is given, assuming that we observe predominantly tubes close to resonance.

BACKGROUND AND MOTIVATION

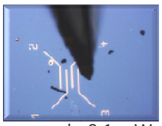
- Exponential decay of the TERS signal in the first 20 nm from the sample surface;
- Vibrational behavior in TERS:
  - two components of the G mode,
  - D mode,
  - 2D mode,
  - RBM;
- the possibility to better control the tip-sample distance using STM-mode;
- importance of resonance conditions;
- accuracy of the chiral index assignment.

TERS SETUP

AFM/STM XE-100 (*Park Systems*)

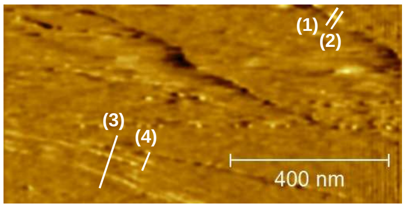
- Au-tip obtained by oblique cutting of an Au wire (0.9999 % purity, d = 0.2 mm);

LabRam HR800 spectrometer (*Horiba Jobin Yvon*)

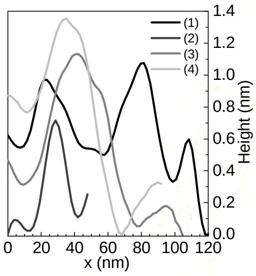


- microscope objective for tip illumination from the side;
- long distance microscope objective (50x):
  - mounted in a 60° to the surface normal,
  - N.A. = 0.35;
- Nd:YAG (532.2 nm) and He-Ne (632.8 nm) lasers: power on the sample 0.1 mW;
- spectral resolution of 2 cm^{-1};
- Peltier-cooled CCD camera;
- collection of the spectra in backscattering geometry.

SAMPLE

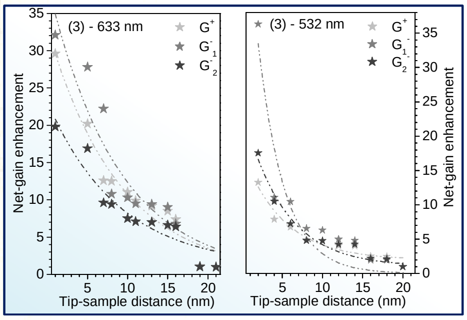


STM topography showing the measured regions. The Raman spectra were recorded with the 632.8 nm (1)-(4) and 532.2 nm (3)&(4) excitation laser lines.

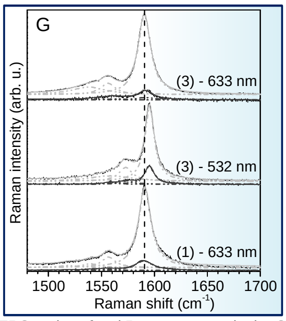


STM height profiles of the measured regions. The heights and the widths confirm the presence of SWCNTs in bundles. The heights between 0.7 and 1.4 nm agree very well with the calculated diameter [1] using the observed RBM frequency.

RESULTS AND DISCUSSION

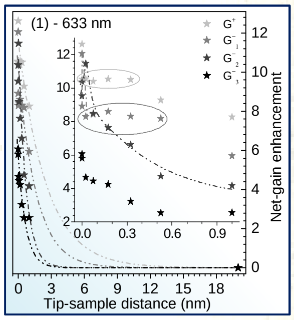


Net-gain enhancement of the G mode as a function of the tip-sample distance at position **(3)** excited @633 nm (left) and @532 nm (right).

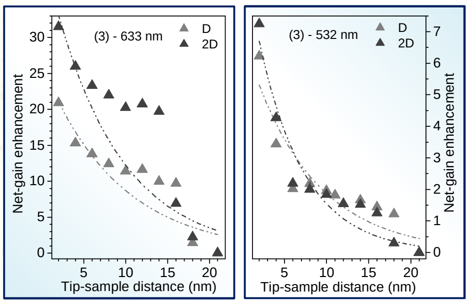


TERS and confocal Raman spectra in the G-mode region recorded at positions **(1)** & **(3)**.

- ❖ exponential decay of the G-mode TERS signal;
- ❖ resonance conditions are **not** important for the Raman spectra of G^- mode;
- ❖ higher enhancement factor of the transversal G^- mode;
- ❖ at contact: → tip presses the bundle;
- ❖ below 1 nm:
  - → bundle decompression,
  - → first an intensity increase of the transversal G^-_1 and G^-_2 mode, then a constant intensity, and afterwards an exponential decrease,
  - → exponential decrease in intensity of the G^+ and G^-_3 modes.

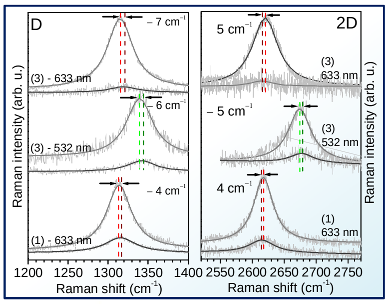


Net-gain enhancement as a function of the tip-sample distance at position **(1)** excited @ 633 nm.

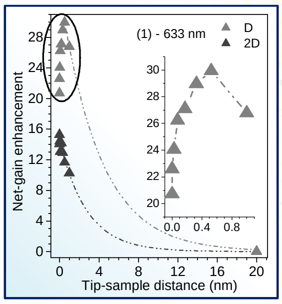


Net-gain enhancement of the D and 2D modes as a function of the tip-sample distance at position **(3)** excited @633 nm (left) and @532 nm (right).

- ❖ exponential decay of the D- and 2D-modes TERS signal;
- ❖ resonance conditions **are** important;
- ❖ D mode is blue shifted;
- ❖ 2D mode exhibits:
  - → red shift @633 nm,
  - → blue shift @532 nm;
- ❖ at contact, the tip:
  - → presses the bundle,
  - → creates/enlarges the defects;
- ❖ below 1 nm:
  - → first an intensity increase of D, then an exponential decay;
- ❖ the 2D mode is not sensitive to the pressure exerted by the tip on the sample.

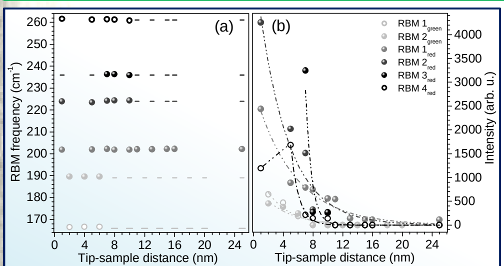


TERS and confocal Raman spectra in the D (left) and 2D (right) modes regions recorded at positions **(1)** & **(3)**.

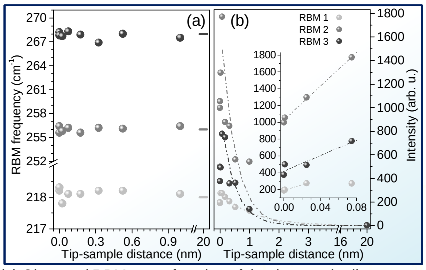


Net-gain enhancement as a function of the tip-sample distance at position (1) excited @633 nm.

- ❖ retracting the tip from the "contact" position, the RBMs intensity increases for distances smaller than 1 nm, decreasing afterwards exponentially;
- ❖ resonance conditions **are** important;
- ❖ RBM are slightly shifted from TERS to the confocal Raman;
- ❖ in the first 1 nm, the tip presses the bundle:
  - → the tubes cannot breathe properly,
  - → larger ν_{RBM} shifts;
- ❖ only one RBM (RBM 1_{red}) was observed in confocal Raman;
- ❖ RBMs occur at different tip-sample distances.

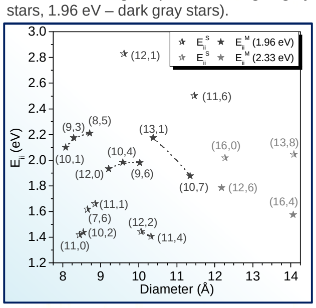


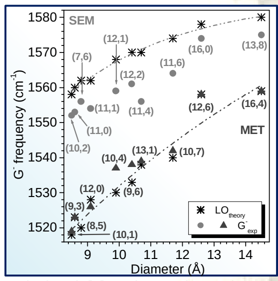
(a) Observed RBMs as a function of the tip-sample distance at position **(3)**. (b) Intensity as a function of the tip-sample distance. Data presented in (a) & (b) are summarized for 633 nm and 532 nm.



(a) Observed RBMs as a function of the tip-sample distance at position **(1)**. (b) Intensity as a function of the tip-sample distance. Data presented in (a) & (b) are summarized for 633 nm.

Kataura plot of the theoretical E_{ii} [1,2] used for the chiral-index assignment *as a* function of the tube diameter. The plot includes assignment values for two different excitation energies (2.33 eV – light gray stars, 1.96 eV – dark gray stars).





Calculated [3] and experimental TERS and confocal Raman G^--mode frequencies dependences as a function of the calculated tube diameter. The dashed lines are drawn to guide the eye, for the theoretical data: SEM – semiconducting, MET – metallic.

CONCLUSIONS

- ✓ Using TERS we have probed the variation of the Raman signal of SWCNTs at different tip-sample distances;
- ✓ TERS intensities of the tangential G^-- mode and RBMs (having different origins) in carbon nanotubes are strongly sensitive for tip-sample distances ‹1 nm (the tip presses the tube);
- ✓ The increase in intensity of the D mode for tip-sample distances ‹1 nm can be due to the fact that new defects appear;
- ✓ A blue shift of the D mode, from TERS to the confocal Raman, was observed for both excitation energies, whereas the 2D mode was red shifted by using 1.96 eV and blue shifted when exciting with 2.33 eV;
- ✓ With TERS it is possible to differentiate between SWCNTs by using the RBM and G^--mode frequencies;
- ✓ Different TERS enhancements factors using two excitation energies for different Raman features of SWCNTs were observed.

REFERENCES

[1]. C. Thomsen, H. Telg, J. Maultzsch, and S. Reich, *PSS B* **242**, 1802 (2005).
[2]. V. N. Popov, L. Henrard, and P. Lambin, *Phys. Rev. B* **72**, 035436 (2005).
[3]. O. Dubay, G. Kresse, and H. Kuzmany, *Phys. Rev. Lett.* **88**, 235506 (2002).

Acknowledgements

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