

# Raman spectroscopy of carbon nanotubes with electrostatically attached cytochrome c



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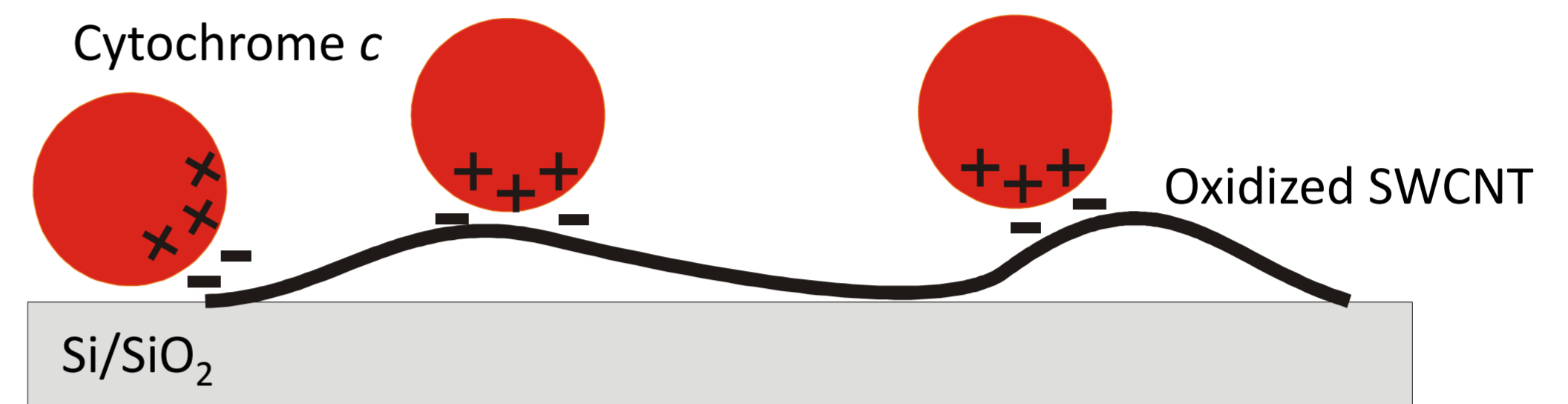
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## Motivation

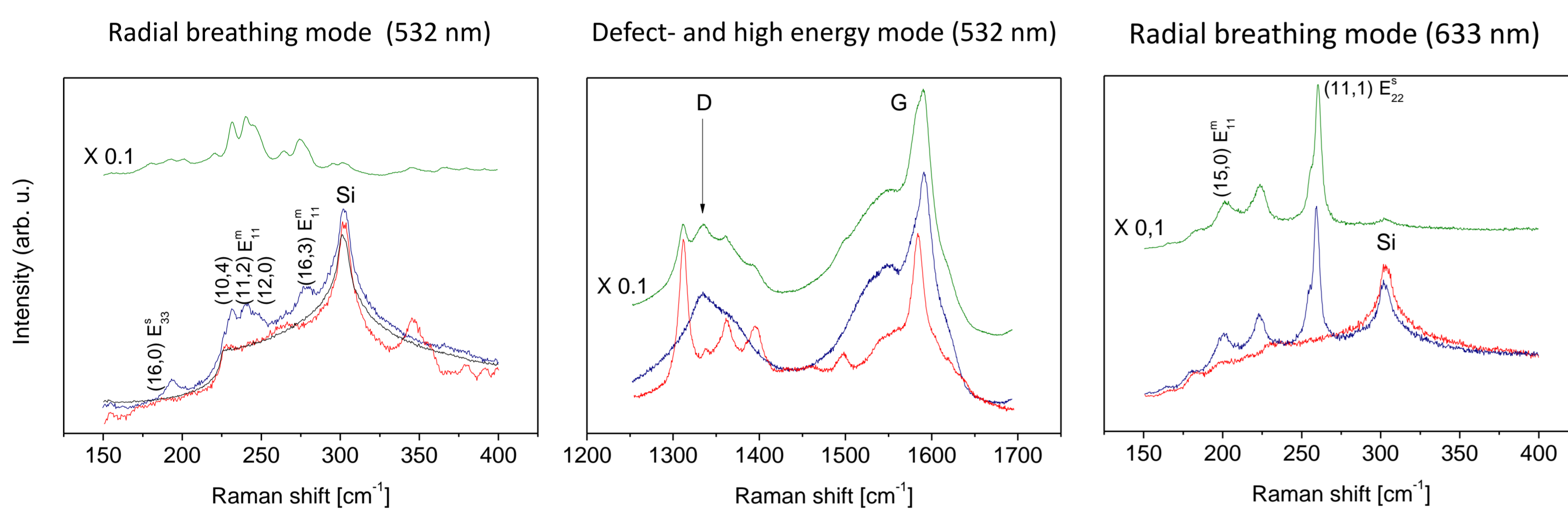
- Nanotubes as electrode for enzymes
- Here: Cytochrome c (Cc) coupled to single-walled carbon nanotubes (SWCNTs) as a model system
- Interaction between SWCNTs and Cc?
- Effect on the vibrational properties of SWCNTs and/or Cc?

## SWCNTs with cytochrome c

- Oxidation of SWCNTs by HNO<sub>3</sub>: Creation of carboxylic groups at the end and at the sidewall-defects of the SWCNTs
- Deprotonation: Negative charging of the carboxylic groups
- Binding of the positively charged lysine domains of Cc to the SWCNTs

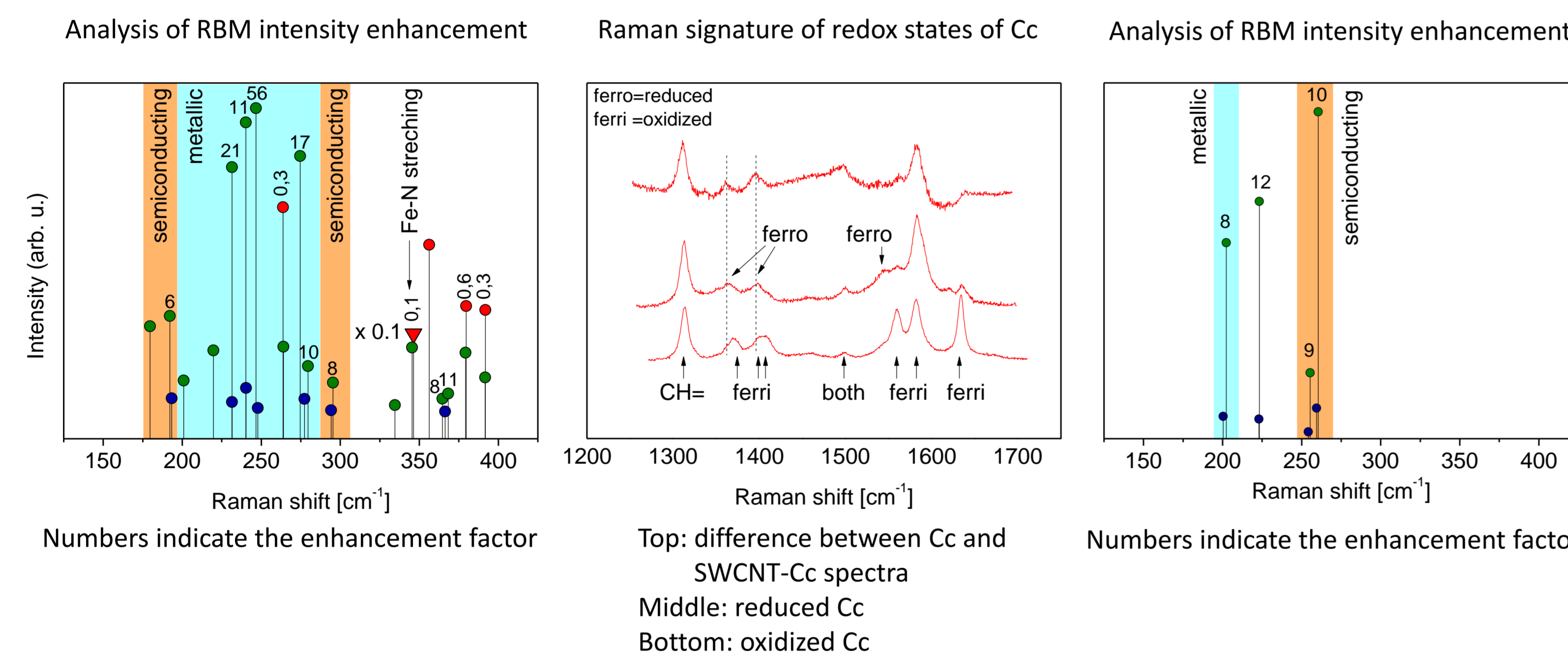


## Results

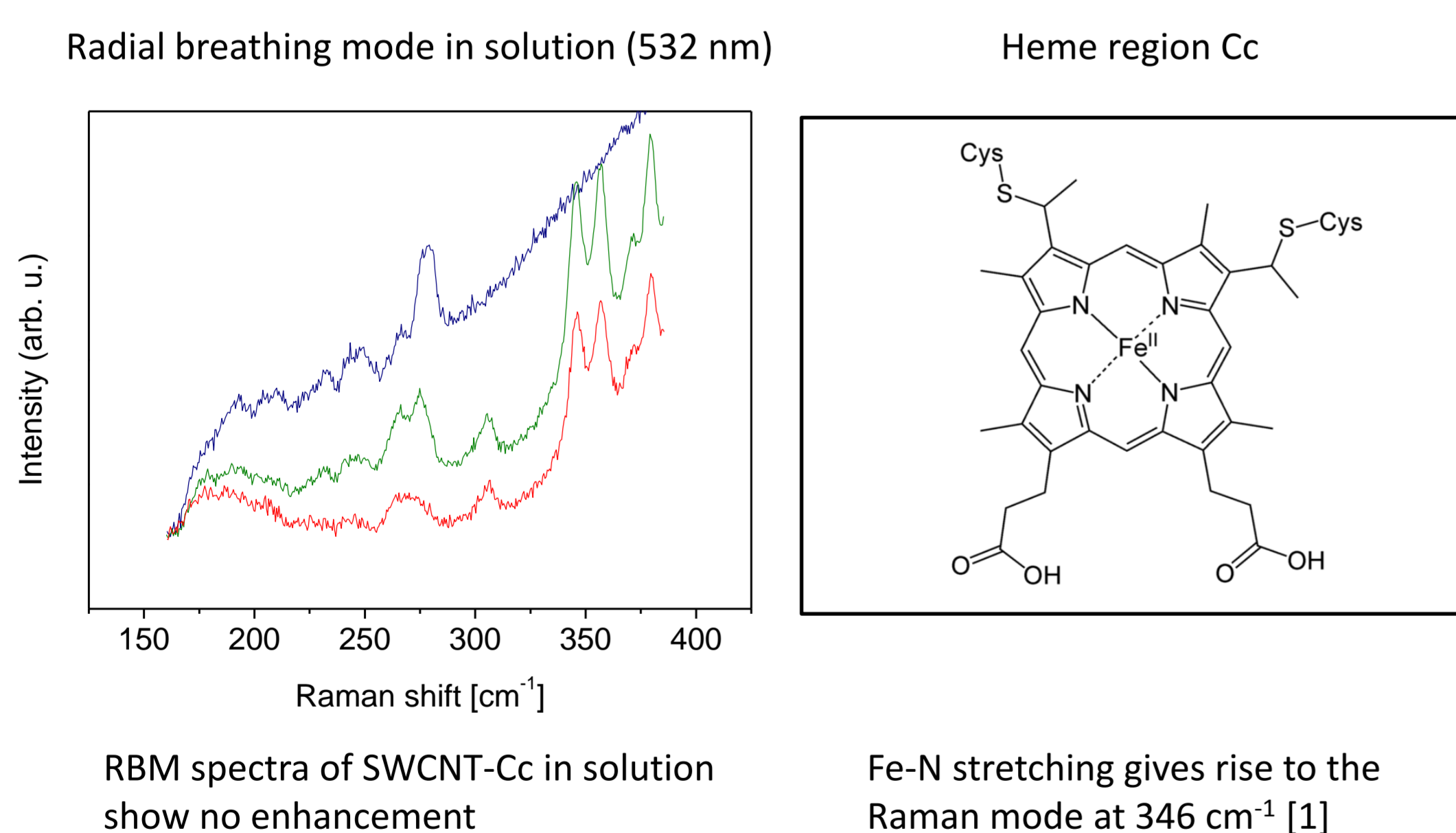


Legend: Oxidized SWCNTs with cytochrome c (green), Oxidized SWCNTs (blue), Cytochrome c (red), Silicon (black)

- Raman spectra recorded with 532 nm and 633 nm laser wavelength
- A signal enhancement (approx. factor 10) is visible for spectra of SWCNT with attached Cc



- Intensity analysis of the RBM shows different enhancement factors for SWCNT coupled to Cc.
- The highest enhancement factors are observed for metallic tubes excited at 532nm
- At 633nm excitation, the enhancement factors are overall smaller than at 532nm
- A strong decrease of the Cc peak at 346 cm<sup>-1</sup> (Fe-N stretching mode [1]) is observed compared to the other Cc peaks
- Comparison of oxidized and reduced Cc spectra shows that the Cc attached to the SWCNT is a mixture of oxidized and reduced state [2]



## Conclusion

RBM enhancement observed for metallic SWCNT at 532nm excitation wavelength  
 → assumption: effect is caused by attachment of Cc  
 → Cc has absorption band around 520nm

No selective enhancement for metallic SWCNT observed at 633nm excitation  
 → Cc has no absorption band in this region [2]  
 → overall moderate enhancement might be due to inhomogeneities of the sample (signal from higher-density region on the substrate)

No enhancement of RBMs for SWCNT-Cc in solution  
 → excessive Cc in the solution absorbs laser light at 532nm, leading to an overall decrease of the Raman signal

Outlook:  
 → preparation of diluted SWCNT-Cc samples on substrate, for measurements at the same nanotube before and after attachment of Cc  
 → further analyze changes of Cc peaks (e.g. decrease of the 346cm<sup>-1</sup> mode) through attachment to SWCNT

## References

[1] Hu, S.; Morris, I.; Singh, J.; Smith, K. & Spiro, T. JACS, 115, 12446-12458 (1993)  
 [2] Friedrich Siebert, F. and Hildebrandt, H. Vibrational Spectroscopy in Life Science (Wiley-VCH, Weinheim, 2008)