# UV-Raman spectroscopy on nanotubes@zeolite

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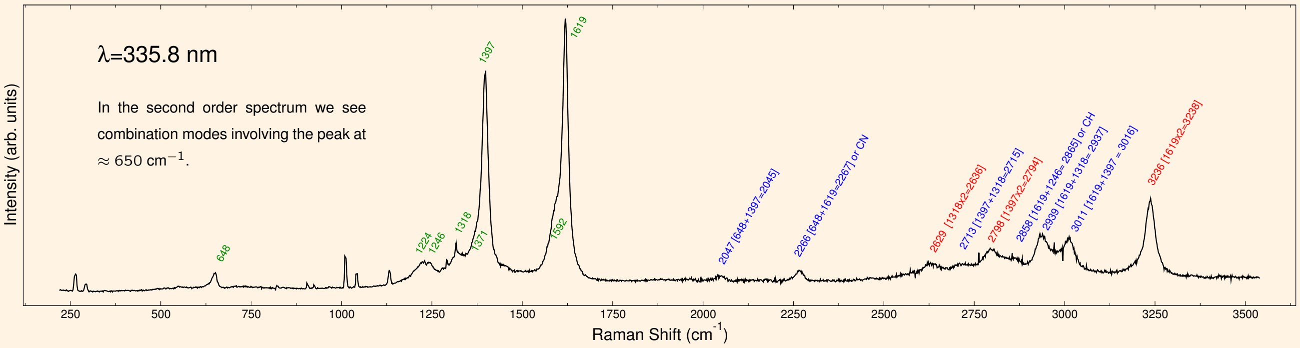
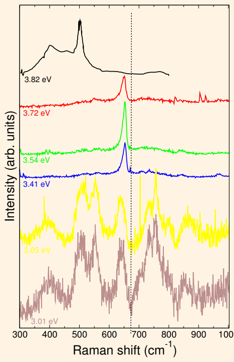
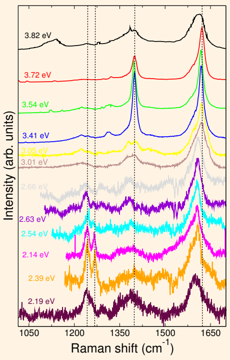
Nanotubes grown inside the channels of zeolite crystals are constrained to diameters around 4 Å. We observe a Raman mode at $\approx 650\,\mathrm{cm}^{-1}$, resonant at an energy close to 3.5 eV. With help of *ab initio* and double-resonance calculations we discuss the possible existance of smaller nanotubes than assumed up to now.



In the second order spectrum we see combination modes involving the peak at $\approx 650$ cm$^{-1}$.

## Wavelength dependence

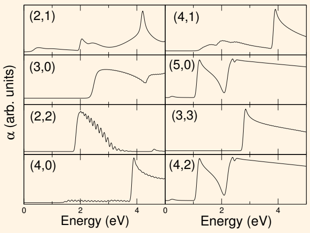


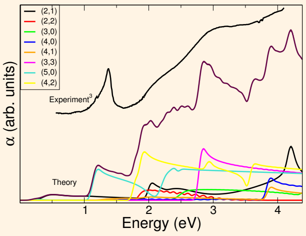


We observe a mode at 650 cm$^{-1}$ in the UV-region. The high frequency and resonant energy suggest the radial breathing mode of an ultrasmall nanotube.

- ≈1600 cm$^{-1}$: double peak.
- ≈1400 cm$^{-1}$ and ≈1250 cm$^{-1}$.
- No shift with the laser energy.

## *Ab initio* calculations





Several ultrasmall nanotubes have absorption maxima in the visible range, some only in the UV range.

|  | d (Å) | $\omega_{\mathrm{RBM}}$ | $\omega^{(T)}_{\mathrm{HEM}}$ | $\omega^{(L)}_{\mathrm{HEM}}$ |
|---|---|---|---|---|
| (2,1) | 2.4 | 731 | 1154 | 1456 |
| (3,0) | 2.6 | 793 | 1227 | **1574** |
| (2,2) | 2.8 | 720 | **1293** | 1292 |
| (4,0) | 3.4 | 625 | 1336 | **1612** |
| (3,2) | 3.6 | 636 | 1432 | 1542 |
| (4,1) | 3.8 | 565 | 1386 | 1561 |
| (5,0) | 4.1 | 524 | 1430 | **1601** |
| (3,3) | 4.2 | 545 | **1554** | 1486 |
| (4,2) | 4.3 | 524 | 1492 | 1604 |

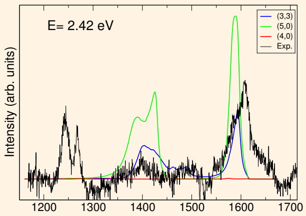
All frequencies in cm$^{-1}$.

If we add up the absorptions from all calculated ultrasmall nanotubes we obtain a reasonable agreement with the experimental data.

- The frequencies at 1200-1300 cm$^{-1}$ are due to the high pyramidalization angle of the smallest nanotubes.
- The low frequency of $\omega^{L}_{\mathrm{HEM}}$ for the (3,3) nanotube is due to a strong electron-phonon coupling.

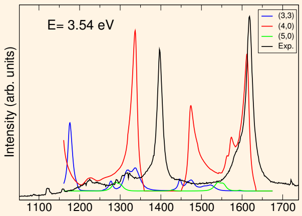
## Double-resonant Raman

We calculate the contribution to the spectrum of three selected nanotubes using the expression:
$I \propto |\sum_{a,b,c} \frac{\mathcal{M}}{(E_l - E_{ai} - i\gamma)(E_l - \hbar\omega_{ph} - E_{bi} - i\gamma)(E_l - \hbar\omega_{ph} - E_{ci} - i\omega)}|^2$.

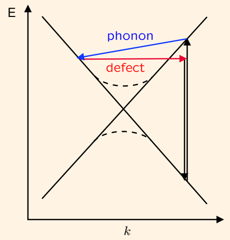


In contrast to bigger tubes there is no D-mode. We can exlain peaks at 1400-1500 $cm^{-1}$ using the $A_1$ modes of the 4 Å nanotubes, but not the peaks at 1200 cm$^{-1}$.

Contributions from tubes which are not in full resonance can yield the less intense peaks which appear in wide energy ranges.



Double-resonant process



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## Conclusions

- The appearance of a peak at ≈ 650 cm$^{-1}$ suggests that nanotubes with diameter below 4 Å could be present in the zeolite.
- Further peaks cannot be explained by only 4 Å-diameter nanotubes.
- Calculations of the optical absorption and vibrational spectrum of nanotubes with diameters below 4 Å suggest that the middle-range-peaks could be naturally explained.

## References

[1] *Reich, Thomsen, and Maultzsch, Carbon nanotubes, basic concepts and physical properties, WILEY-VCH (2004)*

[2] All calculations were performed with the SIESTA code
*P. Ordejón et al., PRB* **53***, R10 441 (1996)*
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[3] Li *et al. Phys. Rev. Lett.* **87**, 127401 (2001)

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