Spectroscopy and the structure of matter 3.
Raman spectroscopy

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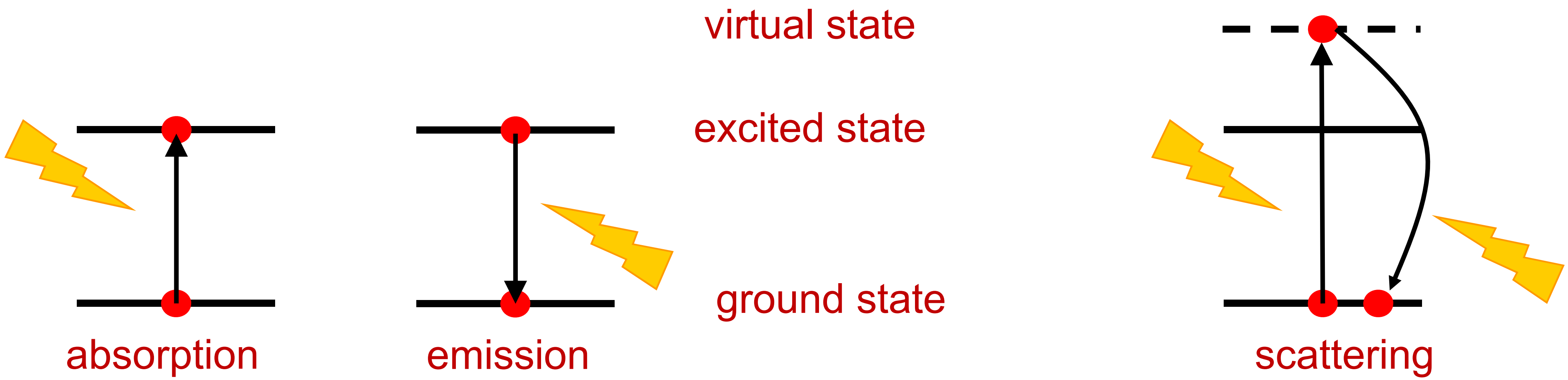
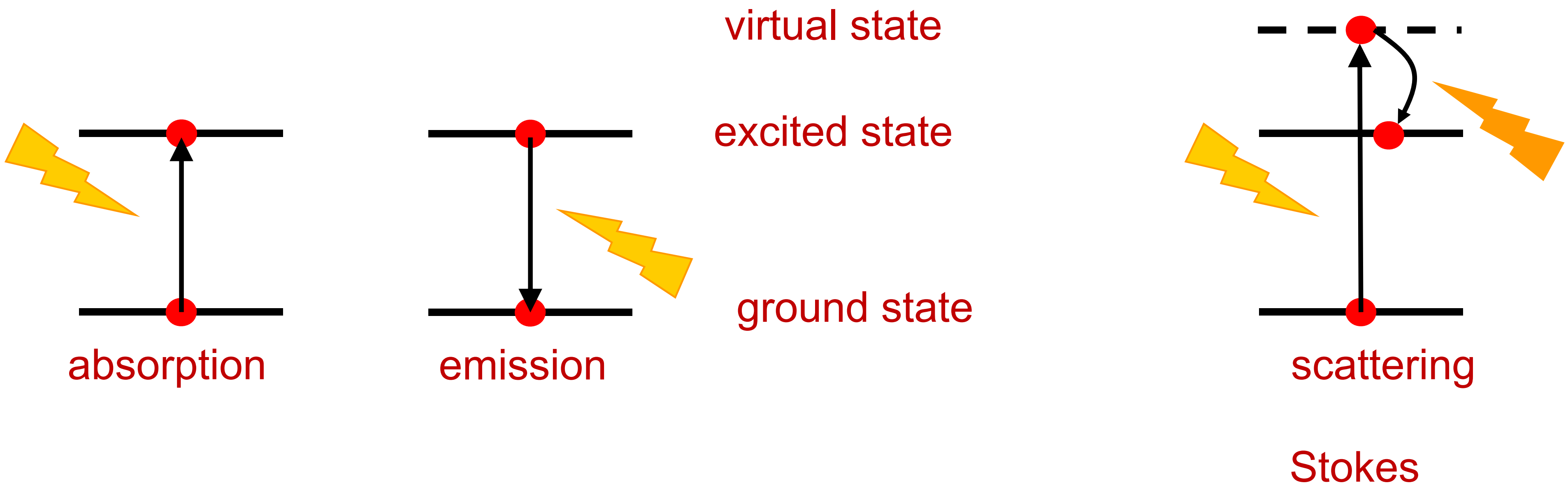
Raman scattering: history

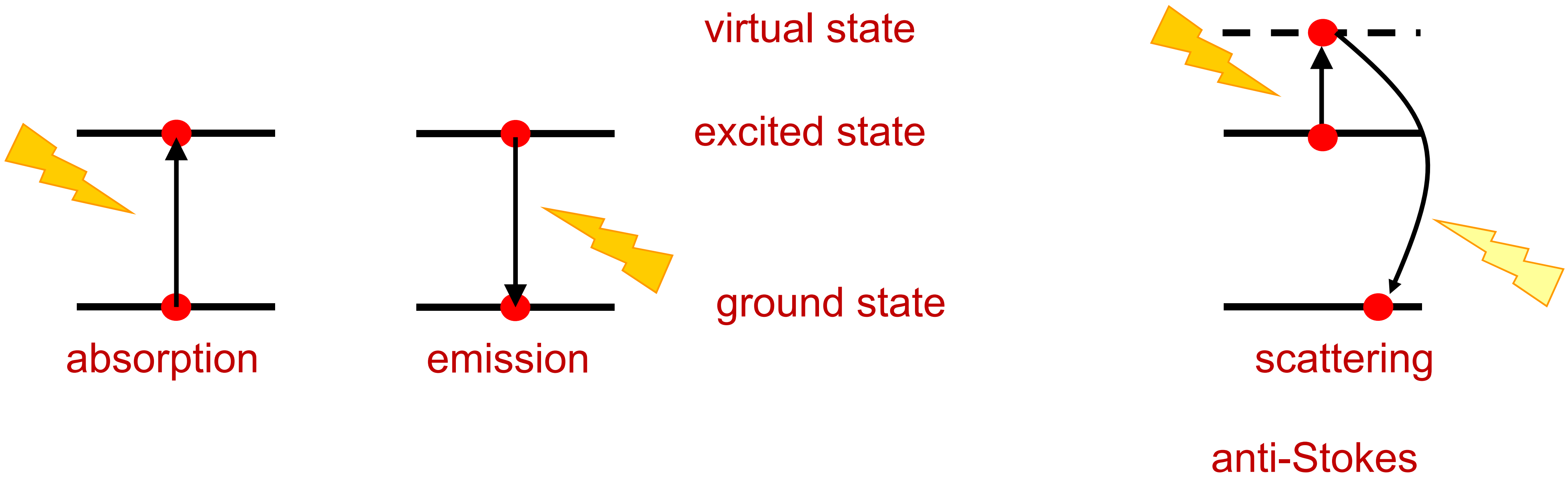
- C.V. Raman – K.S. Krishnan
- L. Mandelstam – G. Landsberg ("combination scattering")

Nobel prize for physics 1930



Rayleigh scattering


virtual state
excited state
ground state
absorption
emission
scattering
Stokes


virtual state
excited state
ground state
absorption
emission
scattering
anti-Stokes

Infrared absorption and Raman scattering

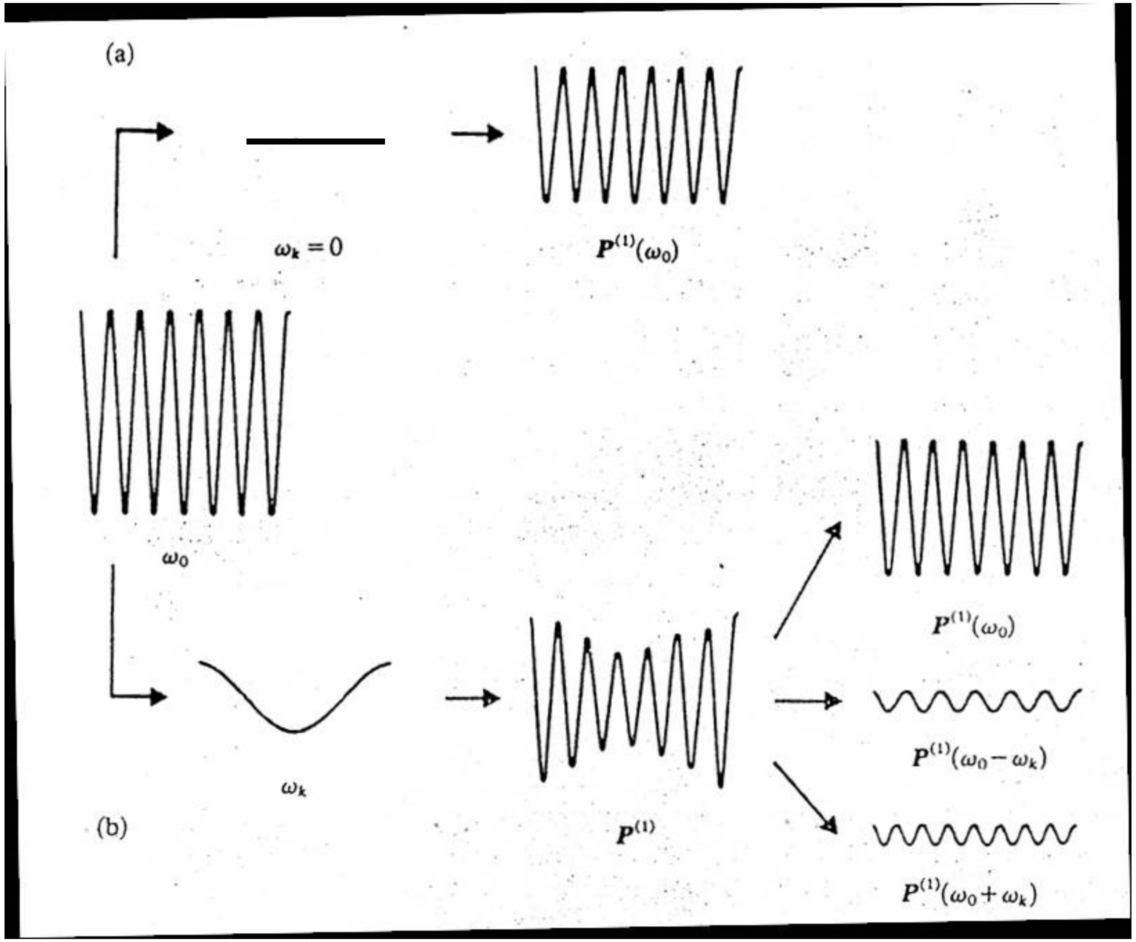
IR: $\mu = \mu_0 + (\Delta\mu)\cos\omega_0 t = \mu_0 + \frac{\partial\mu}{\partial r} r \cos\omega_0 t$ change of dipole moment during the vibration

For deformable objects: $\kappa \sim r,$ or

$$\mu_{ind} = [\alpha_0 + (\Delta\alpha)\cos\omega_0 t][E_0 \cos\omega t] = \alpha_0 E_0 \cos\omega t + \frac{1}{2}(\Delta\alpha)E_0[\cos(\omega+\omega_0)t + \cos(\omega-\omega_0)t]$$

Rayleigh — anti-Stokes — Stokes

The Raman effect – classical picture



D. A. Long: Raman spectroscopy
McGraw-Hill, 1977

Rayleigh

Stokes

anti-Stokes

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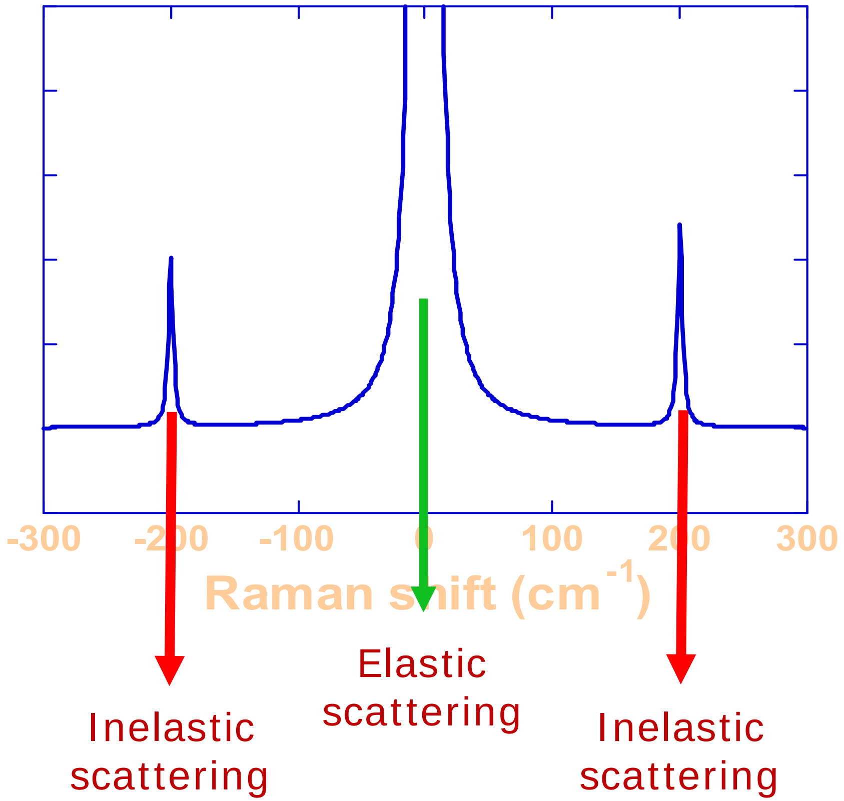
Raman spectroscopy

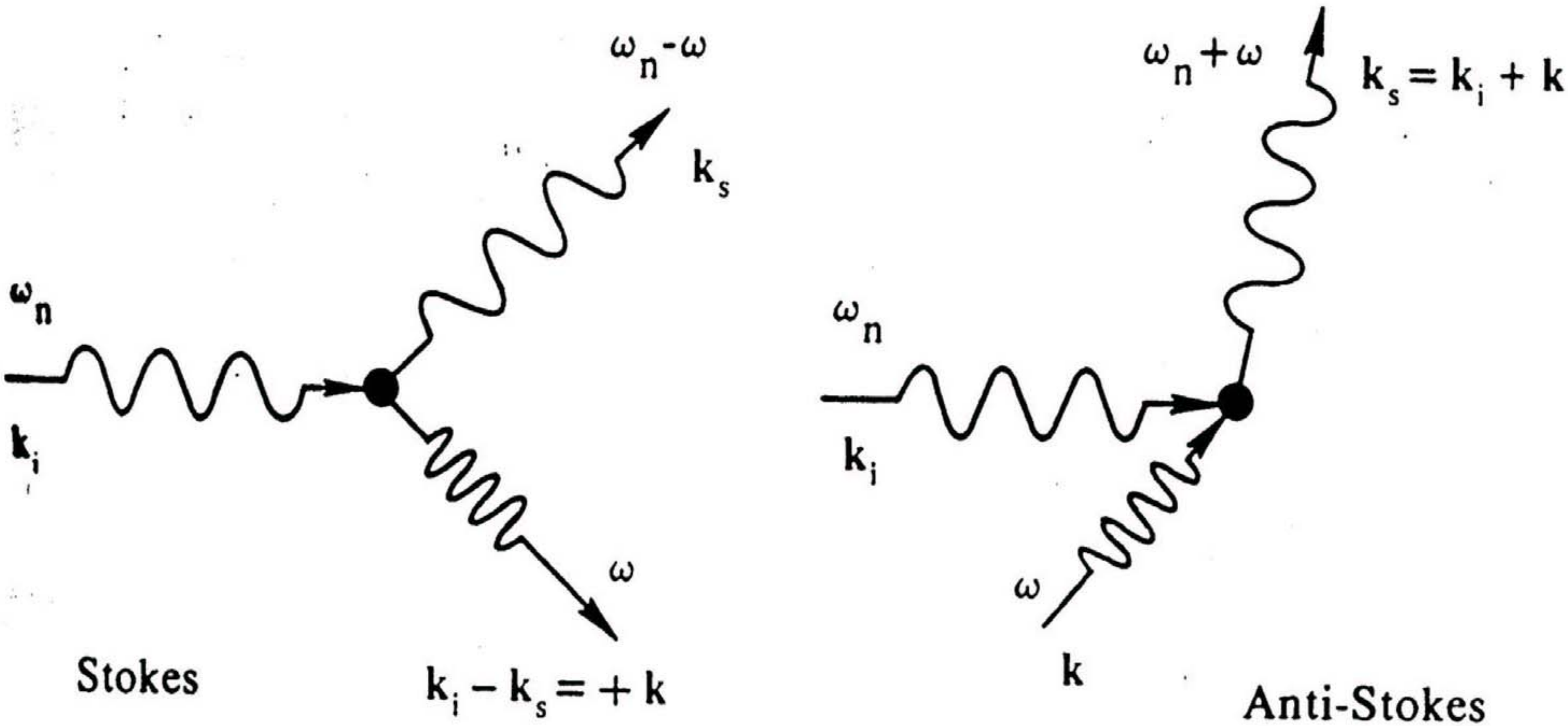
Light scattering by monochromatic light

Spectrum of scattered light relative to the exciting light

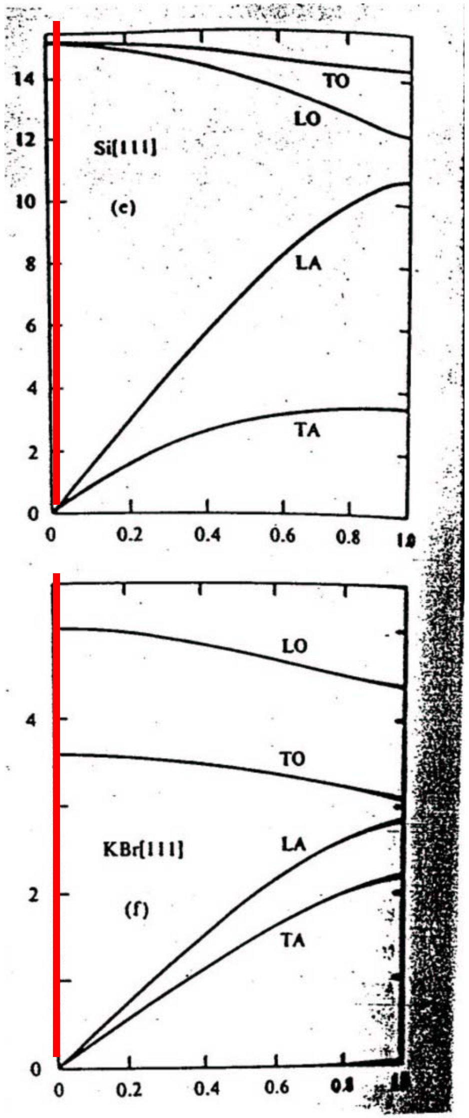


- Inelastic scattering can only be observed if the polarizability of the medium changes during the scattering process
- The magnitude of the shift does not depend on the frequency of the exciting light
- The probability of inelastic scattering is small, every one of 10^8 photons suffers inelastic scattering
- The magnitude of the shift depends on the properties of the medium
- Inelastic scattering happens on elementary excitations of the medium (usually phonons)

Conservation of momentum



Interaction of vibrations with light



Dispersion of vibrations in a solid

Dispersion of light

Momentum:
infrared light λ = 6000 nm
E = 0.2 eV ≈ 50 THz

$$k = \frac{\omega}{c} = \frac{2\pi}{\lambda} \cong 10^4 cm^{-1}$$

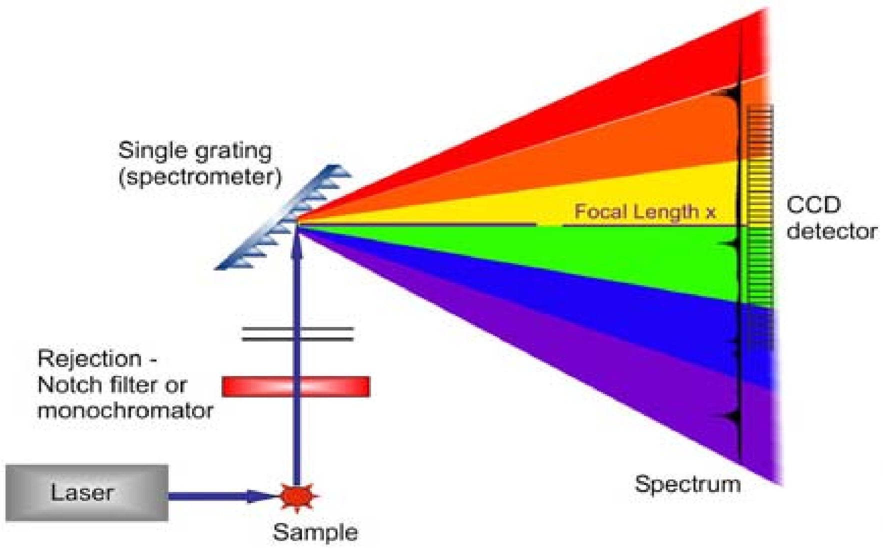
Typical Brillouin zone:
a = 0.6 nm

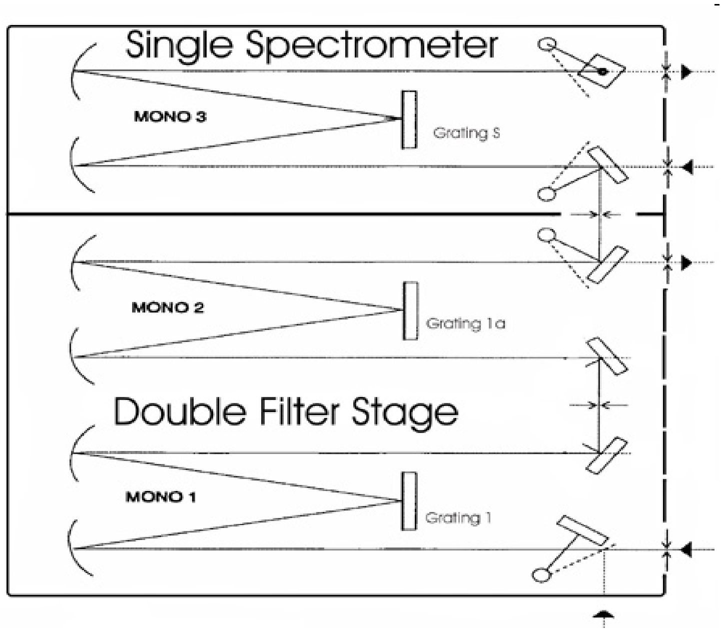
$$k_{\max} = \frac{2\pi}{a} \cong 10^8 cm^{-1}$$

Zone-center optical phonons detected

Álmosdi Péter, BME 2008
Source: Wikipedia

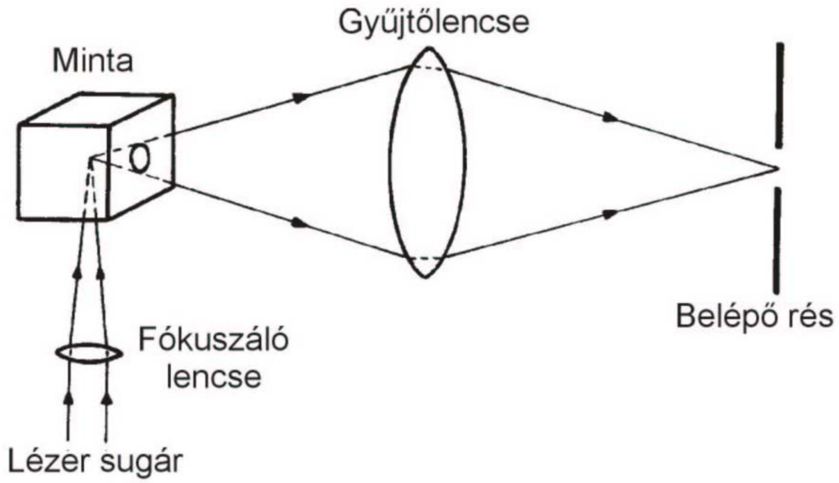
Experimental setup



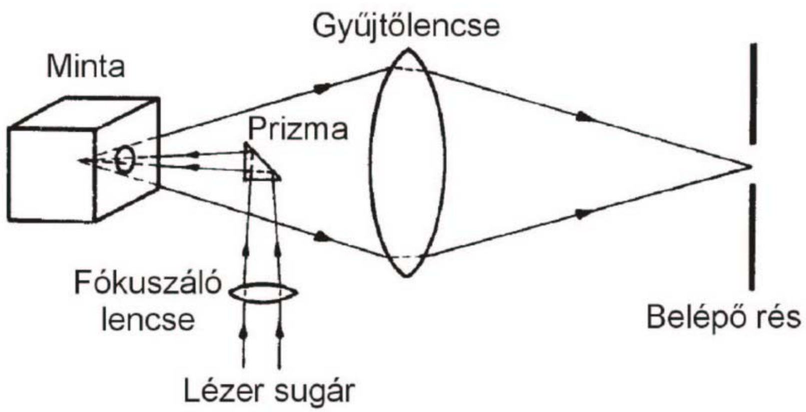


Excitation: visible, monochromatic light (laser) ~ 10^4 cm^{-1}
Frequency difference: infrared region, resolution: ~ 1 cm^{-1}
Resolution of monochromator critical!

Experimental arrangements



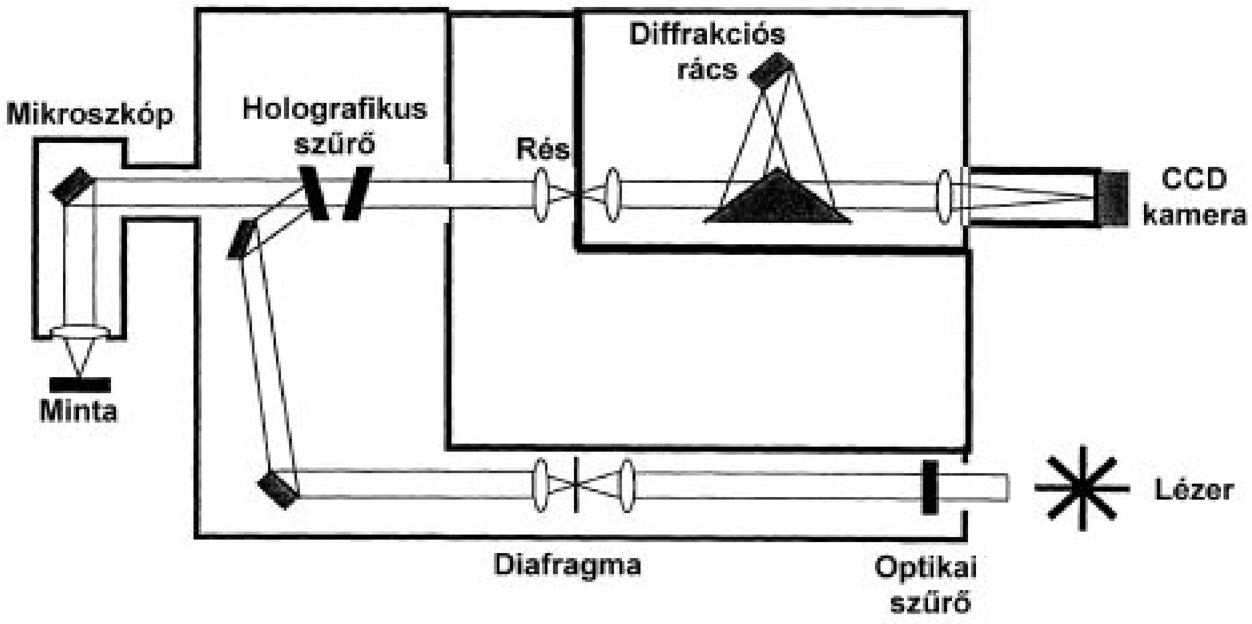
3.4a. ábra. A 90°-os gerjesztési elrendezésû mintatér.



3.4b. ábra. A 180°-os gerjesztési elrendezésû mintatér.
(a kis prizma helyett kisméretû síktükör is használható)

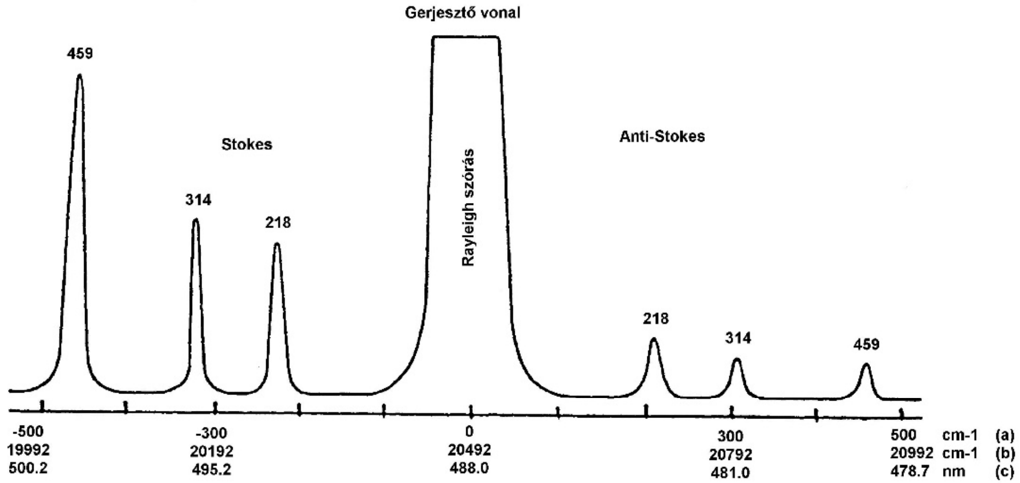
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

Raman microscope



3.11. Diódasoros detektorral mûködõ Raman mikroszkóp.

Raman spectrum of CCl_4



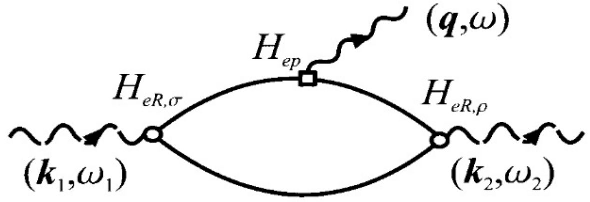
3.2. ábra. A CCl_4 folyadék Raman színképe a gerjesztõ vonal (Ar-ion lézer 488,0 nm) mindkét oldalán.

(a) Raman eltolódás (cm^{-1})
(b) Abszolút hullámszám skála (cm^{-1})
(c) Hullámhossz skála (nm)

a) Raman shift (cm^{-1})
b) Absolute wavenumbers (cm^{-1})
c) Wavelength (nm)

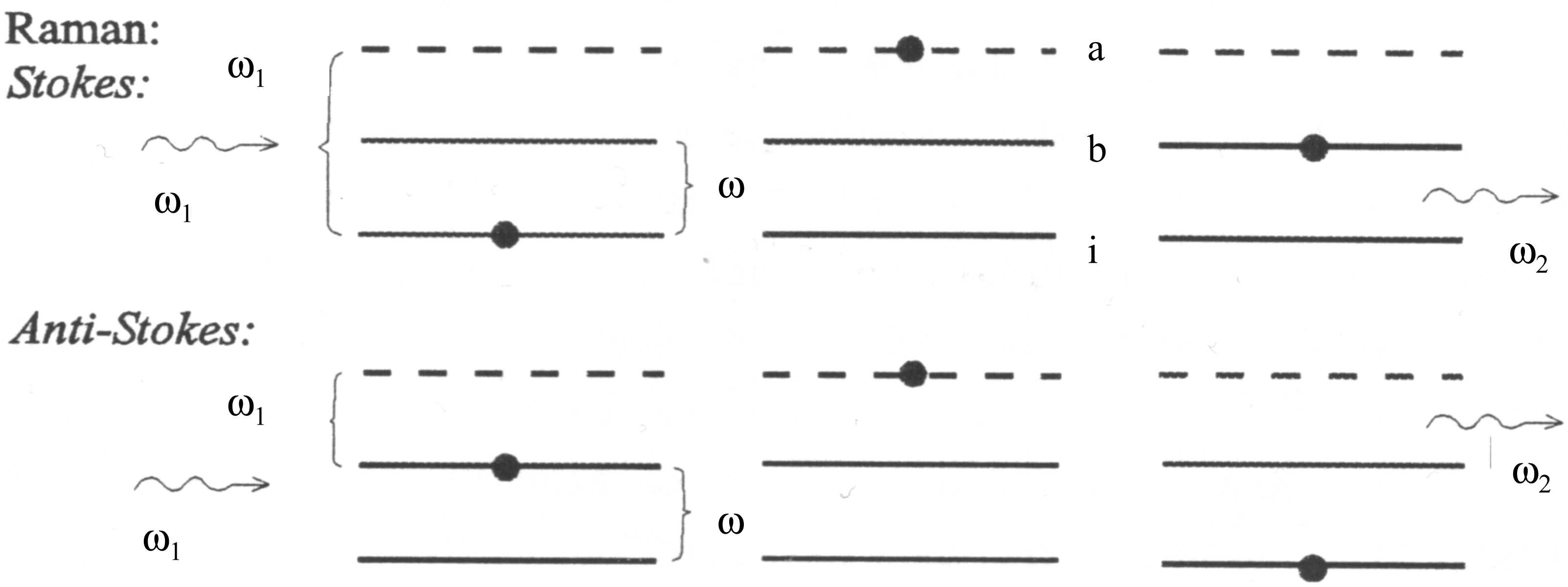
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

The Raman effect



Stokes scattering:

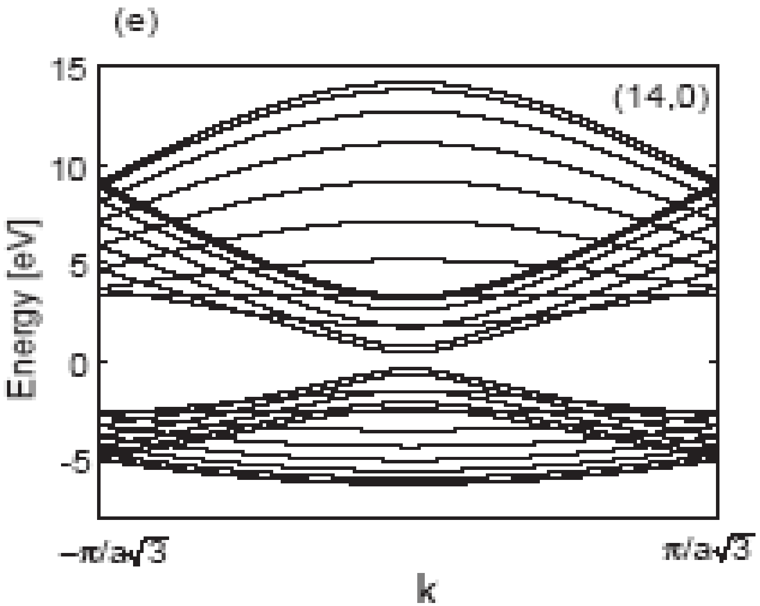
$$K_{2f,10}=\sum_{a,b}\frac{\langle \omega_2,f,i\,|H_{eR,\rho}\,|0,f,b\rangle\langle 0,f,b\,|H_{ep}\,|0,0,a\rangle\langle 0,0,a\,|H_{eR,\sigma}\,|\omega_1,0,i\rangle}{(E_1-E^e_{ai}-i\gamma)(E_1-\hbar\omega-E^e_{bi}-i\gamma)}$$

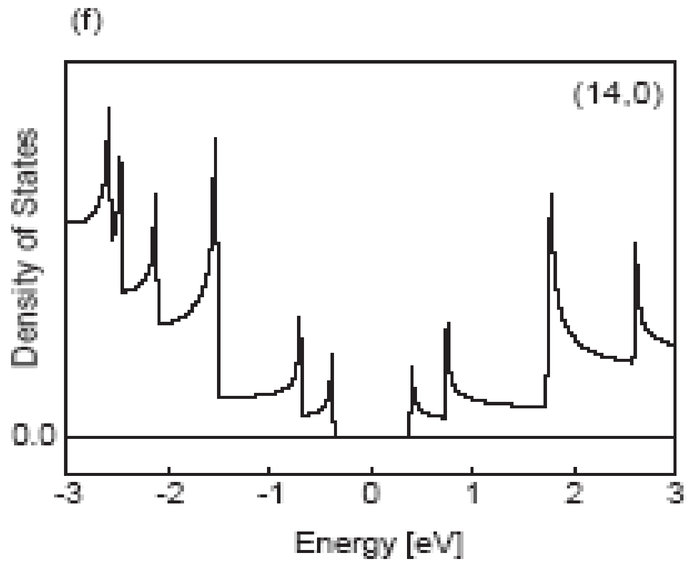


Resonant Raman scattering

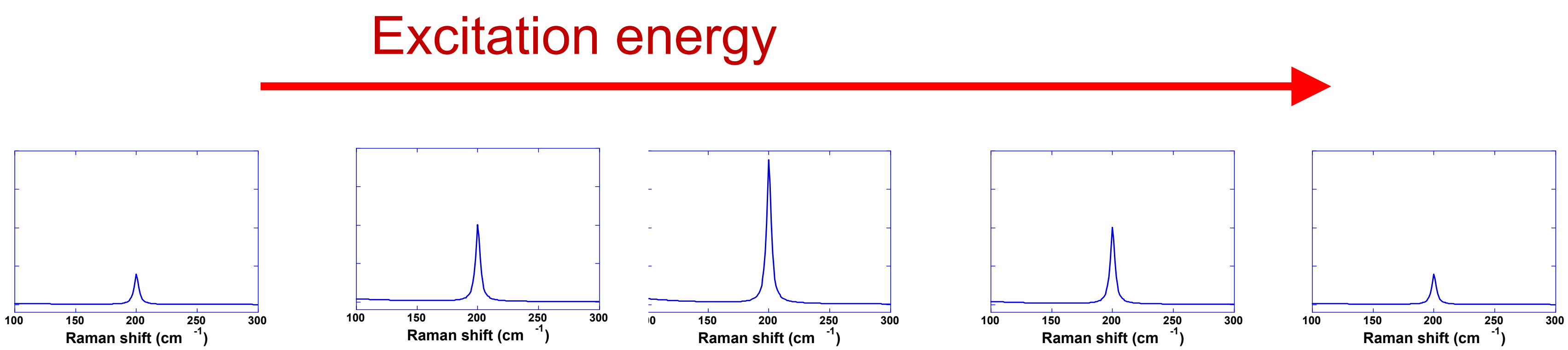
If the energy of the exciting laser approaches the energy of a real transition in the medium, the intensity of the Raman scattering increases by orders of magnitude. This is the **resonant Raman effect.**

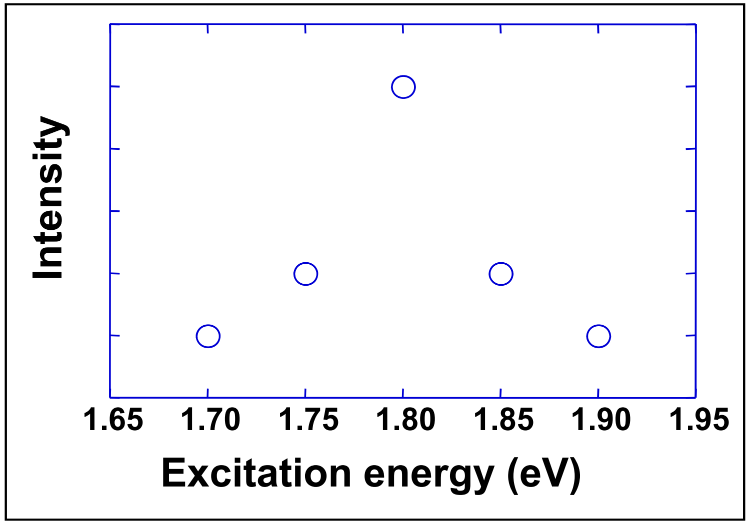
Resonant Raman scattering is the strongest close to maxima in the density of states.

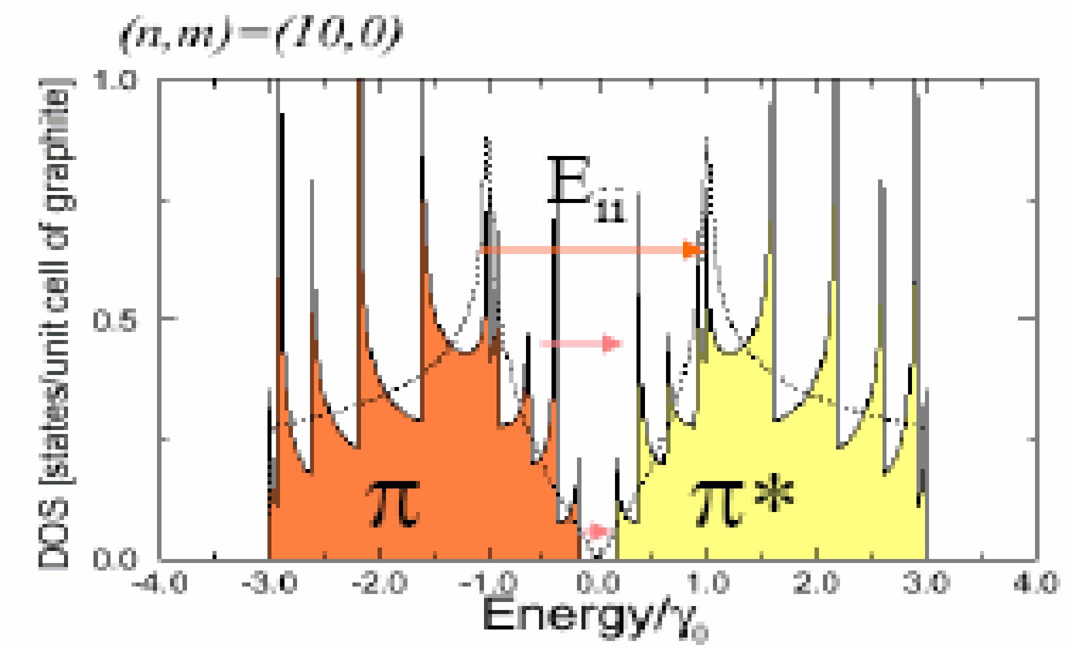




Resonant Raman excitation profile

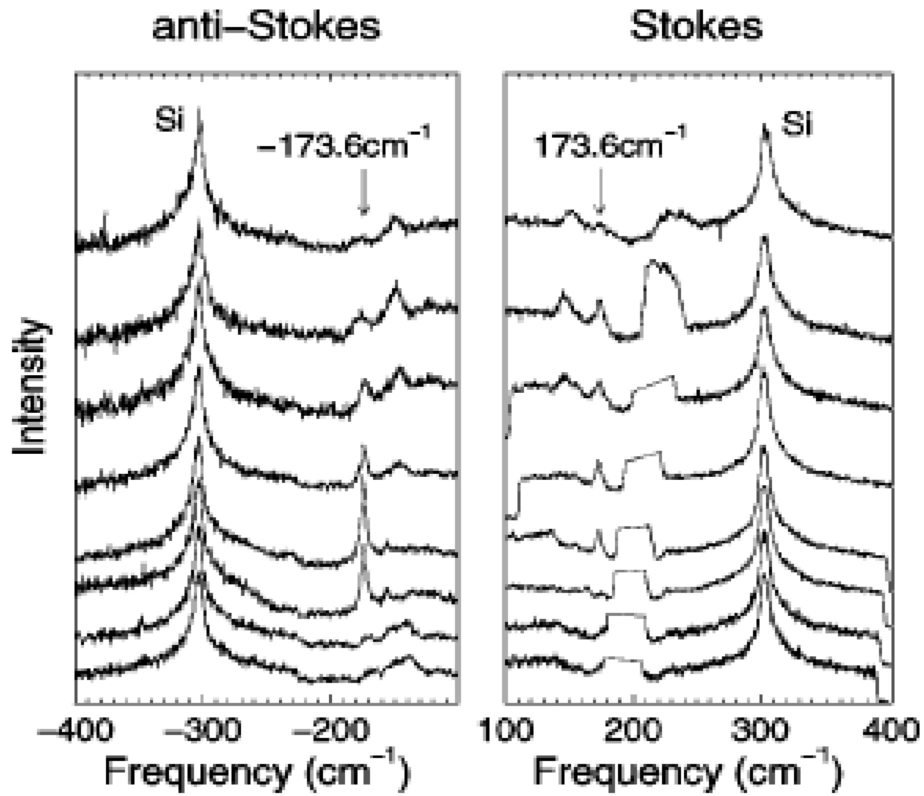




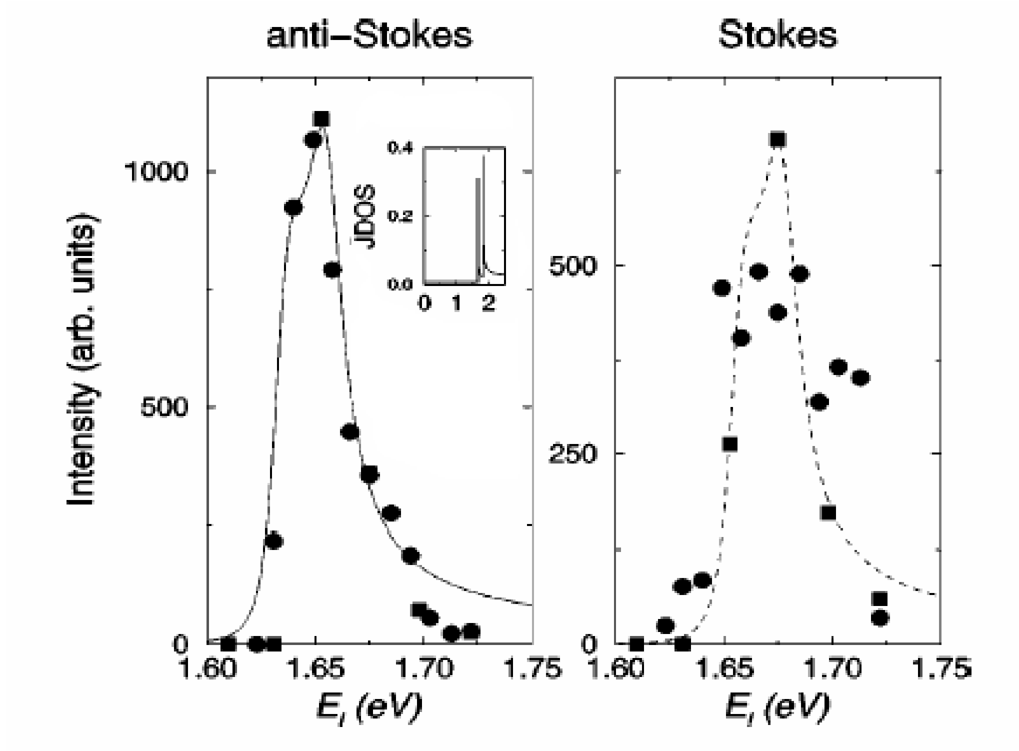


Excitation profile: example

Excitation: 1,623 - 1,722 eV



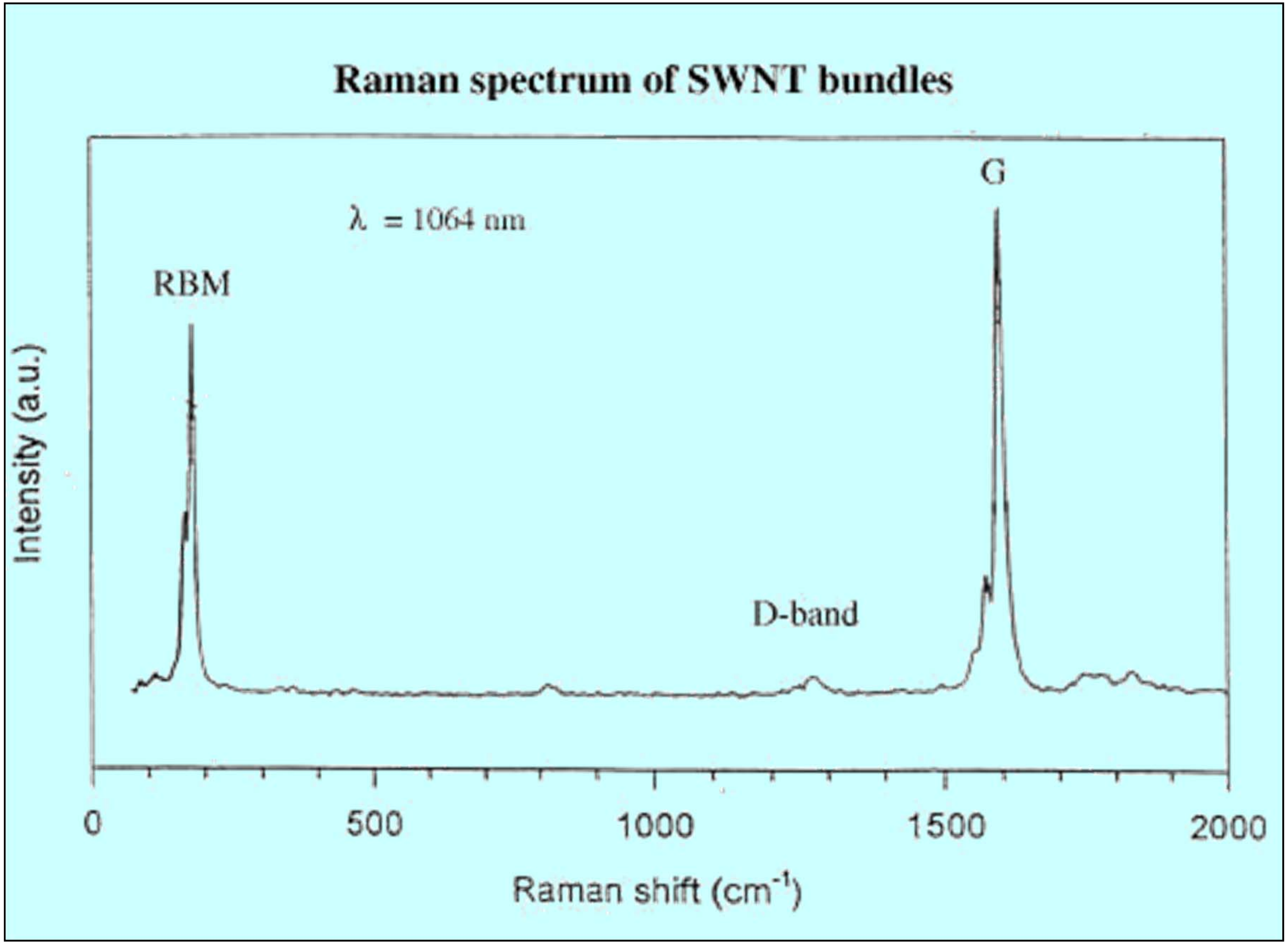
Excitation profile of the 173,6 cm^{-1} mode



A.Jorio et al.
Phys. Rev. B 63 (2001) 245416

Veres Miklós, MTA Wigner FK

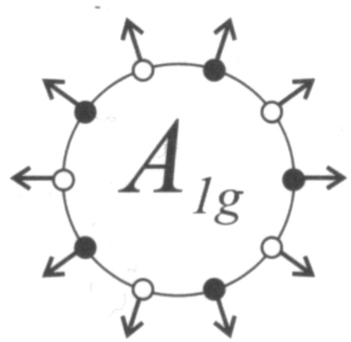
Raman spectra of carbon nanotubes



Radial breathing mode (RBM)

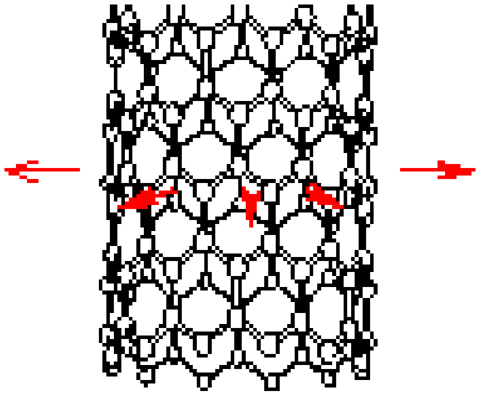
- Does not exist in graphite and other forms of carbon, typical of nanotubes
- Diameter dependence: decreasing with increasing diameter (decreasing curvature)
- Approximately proportional to 1/d

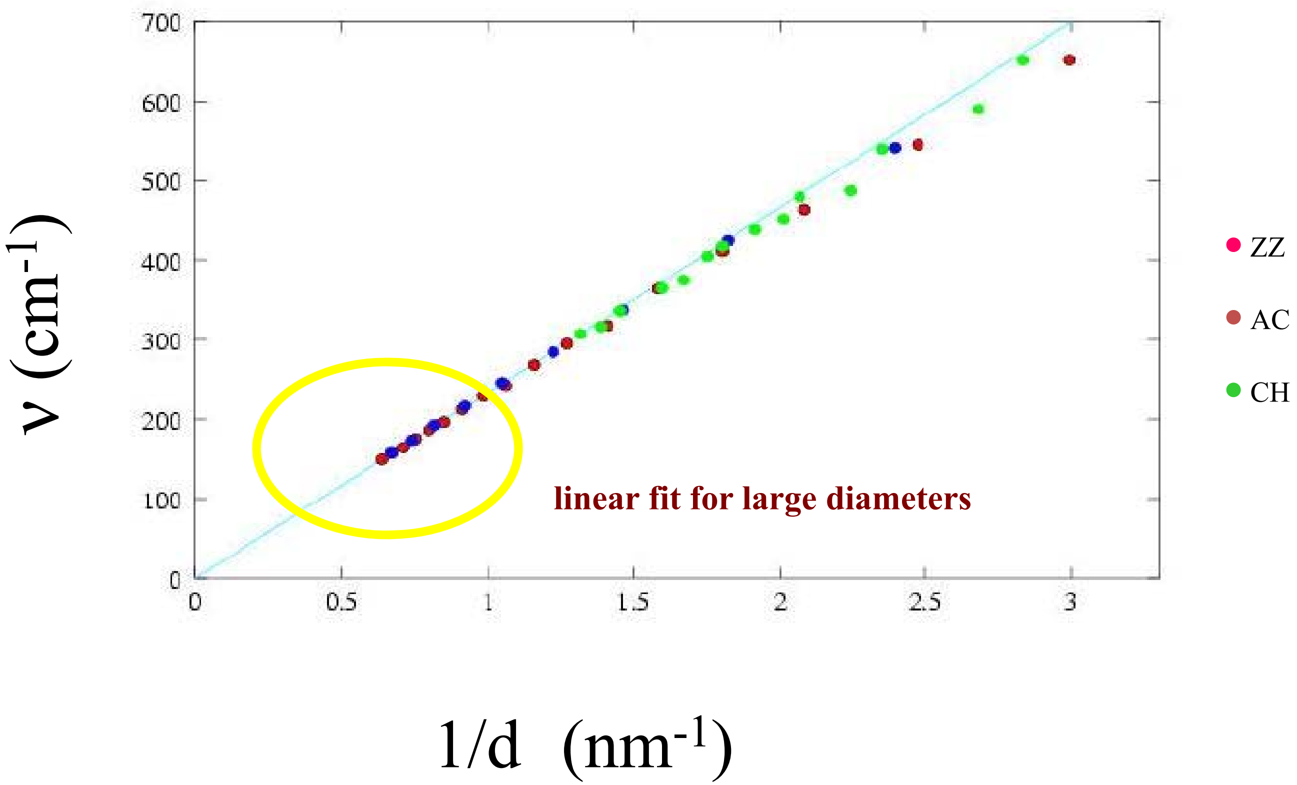
armchair



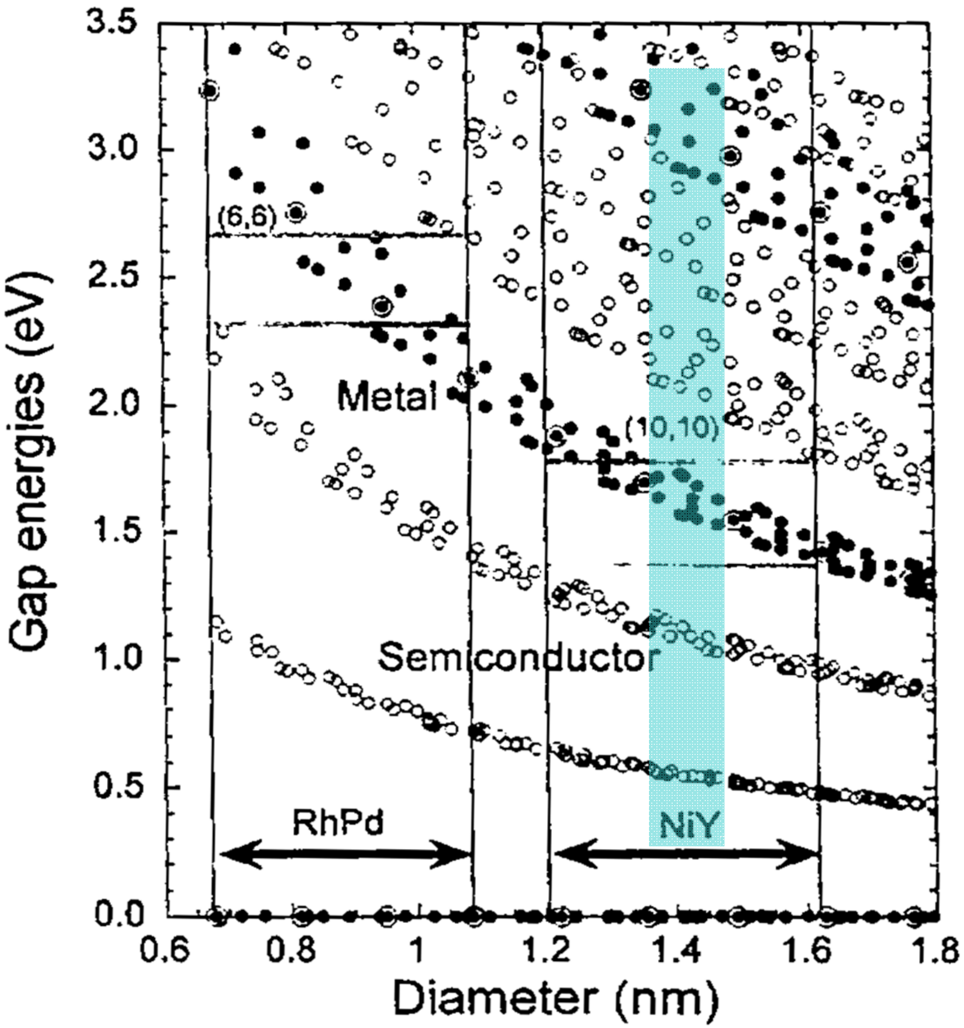
zig-zag

Diameter dependence of RBM frequency





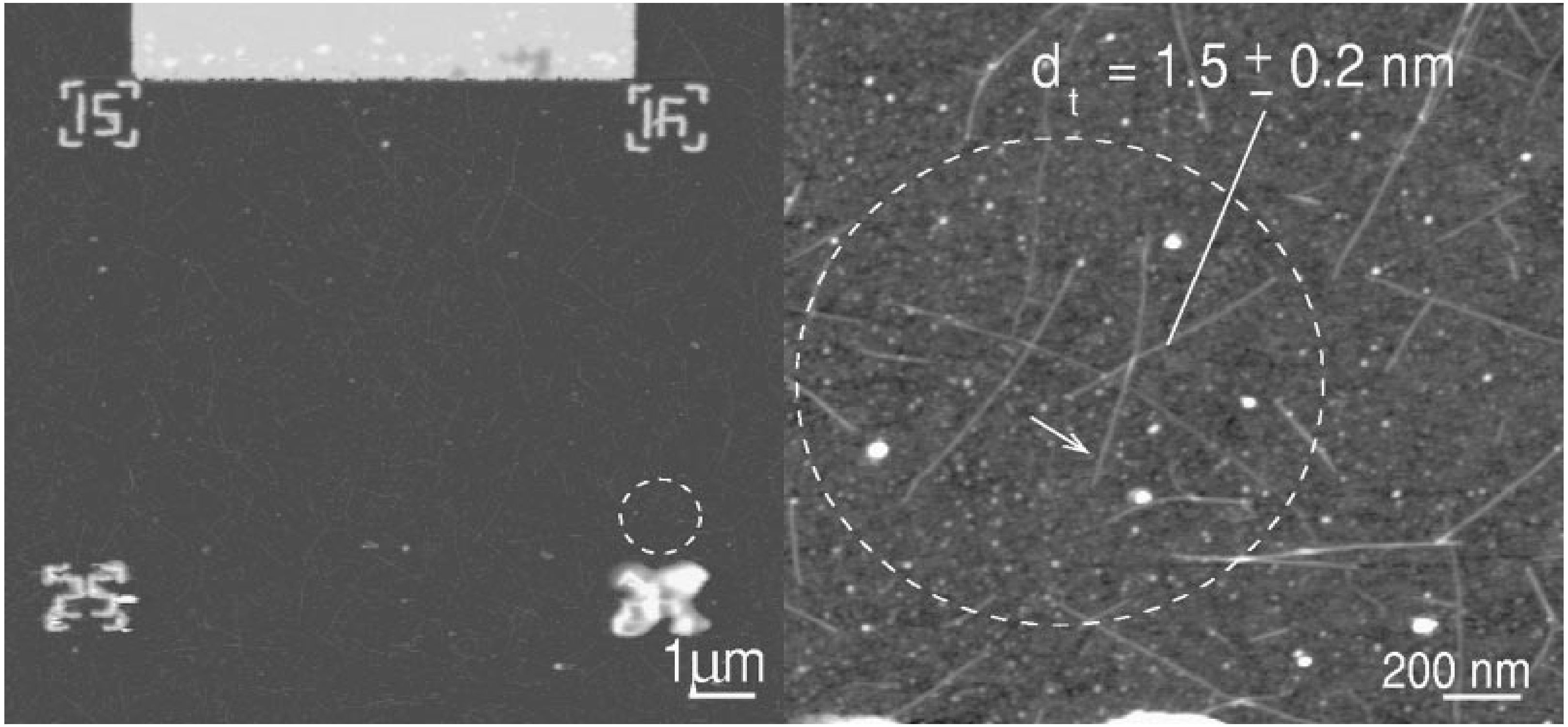
Theoretical Kataura plot



≈ 1/d dependence

H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu,S. Suzuki, Y. Ohtsuka, Y. Achiba: **Synthetic Metals 103**, 2555 (1999)

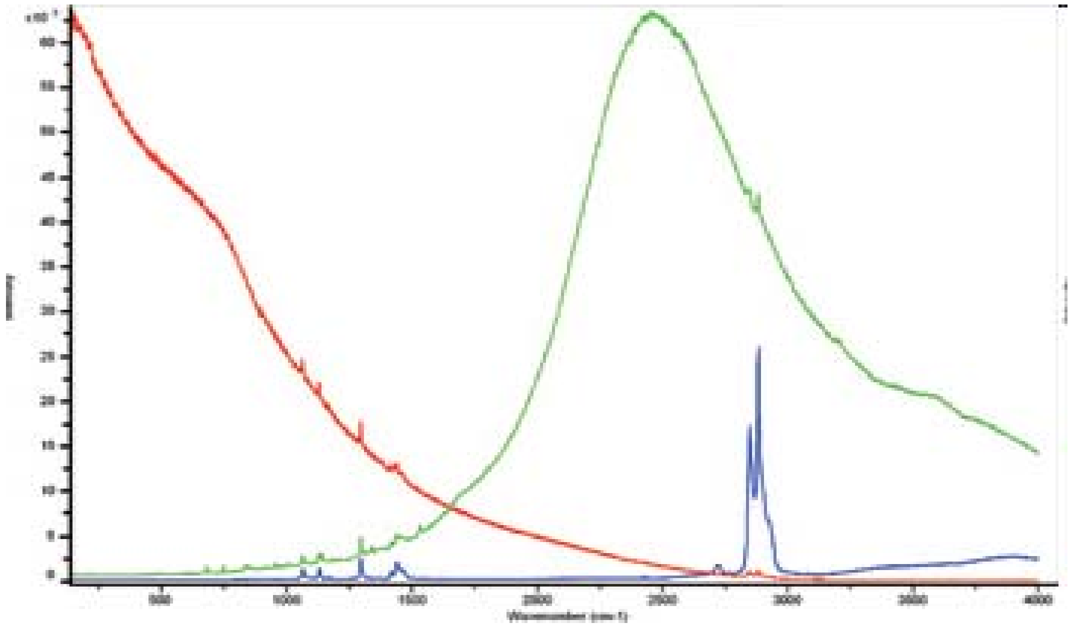
Individual nanotubes: Raman spectrum



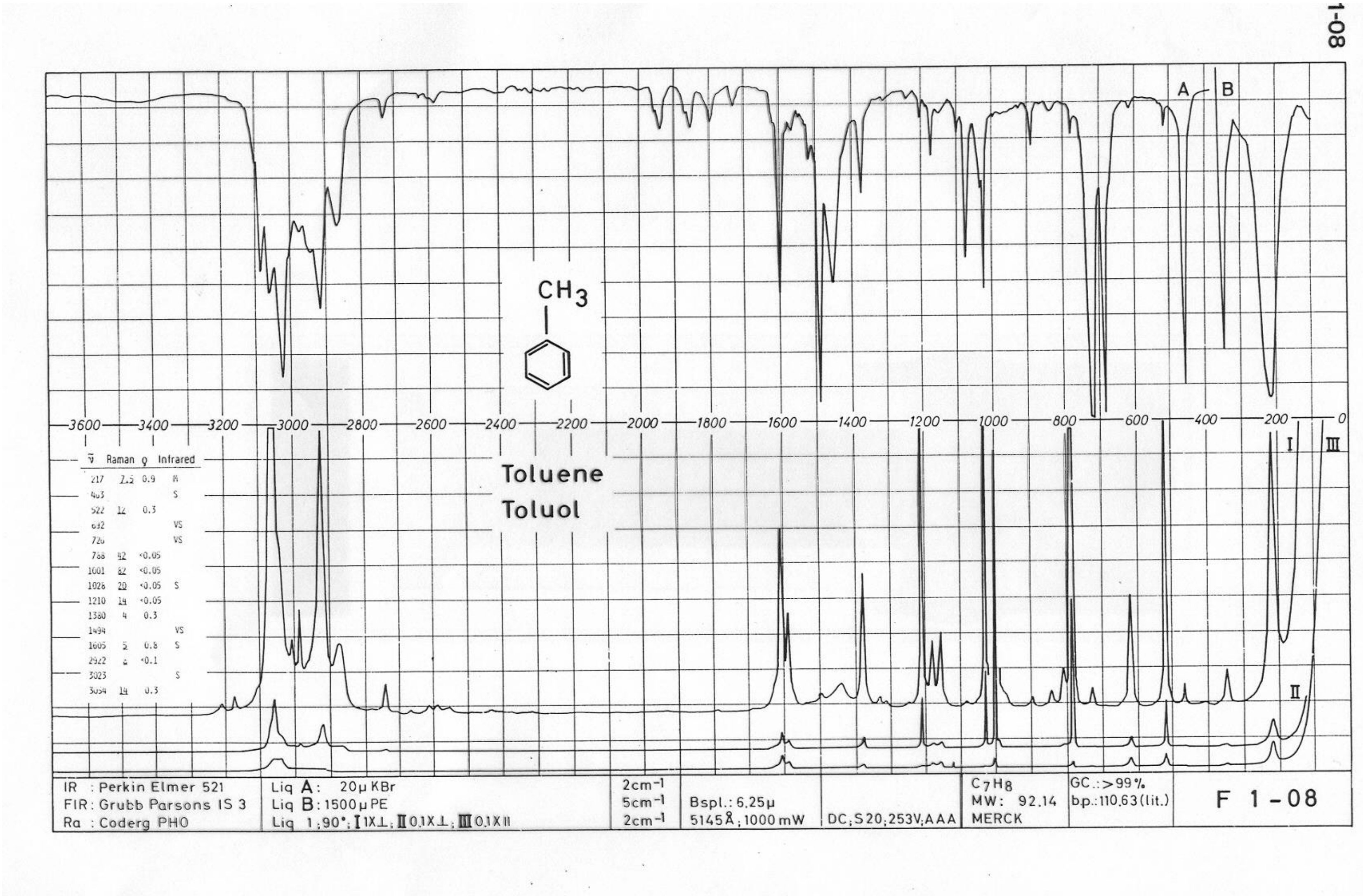
AFM images, sample localization

Choice of laser for eliminating fluorescence

If the excited state exhibits fluorescence, that can suppress the Raman lines. In this case one has to find the ideal laser.



Qualitative analysis



IR

Raman

Take-home message

- Raman scattering: two-photon process (exciting photon – virtual excited state – photon emission)
- measurement: with visible/NIR laser
- Raman shift is the difference of emitted and absorbed photon frequency, resolution depends on monochromator efficiency
- resonance Raman scattering: exciting light frequency matches a real excitation in the system
- qualitative analysis as with IR, quantitative is hindered by scattering into the whole space and by resonance effects
- IR and Raman activity:

  symmetry analysis – selection rules – principle of mutual exclusion

Összefoglalás

- Raman-szórás: kétfotonos folyamat (gerjesző foton elnyelése – virtuális gerjesztett állapot – fotonkibocsátás)
- gerjesztés látható/NIR lézerrel
- a Raman-eltolódás a kibocsátott és elnyelt foton frekvenciakülönbsége, a felbontást a monokromátor felbontása határozza meg
- rezonáns Raman-szórás: a gerjesztő fény frekvenciája megfelel a rendszer egy valódi gerjesztésének
- kvalitatív analízis mint az infravörösben, kvantitatív meghatározást akadályozza a teljes térbe kibocsátott szórt fény és a rezonancia-effektusok