Optical spectroscopy in materials science 7.

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

https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/ramaneffect.html

virtual state

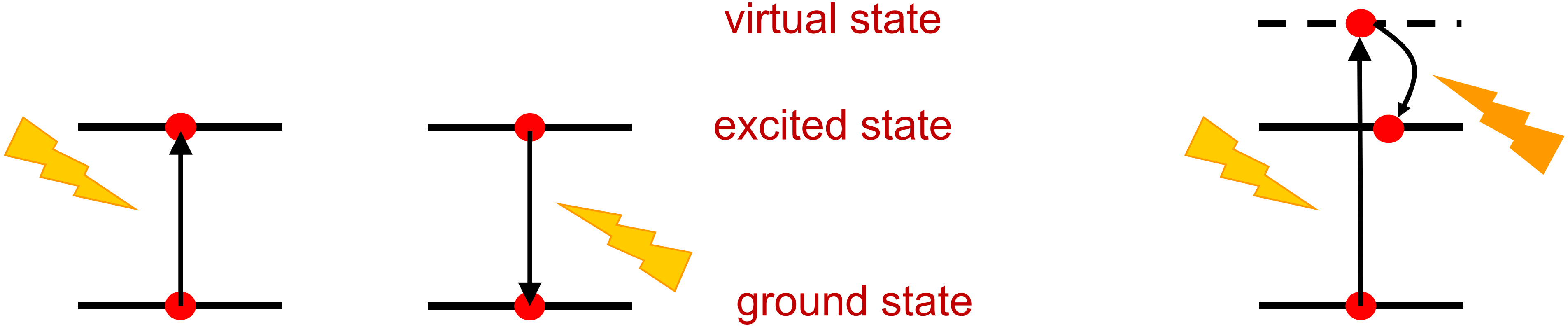
excited state

ground state

absorption

emission

Rayleigh scattering



virtual state

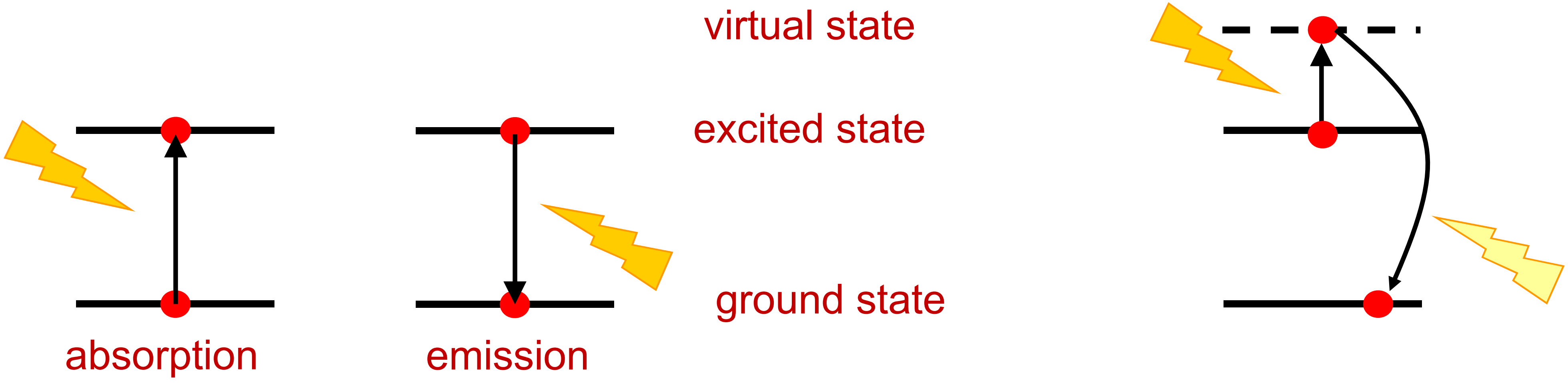
excited state

ground state

absorption

emission

Stokes scattering



virtual state

excited state

ground state

absorption

emission

anti-Stokes scattering

Infrared absorption and Raman scattering

IR: $\mu = \mu_0 + (\Delta\mu)\cos\omega_0 t = \mu_0 + \left(\frac{\partial\mu}{\partial r}\right)_0 r\cos\omega_0 t$ change of dipole moment during the vibration

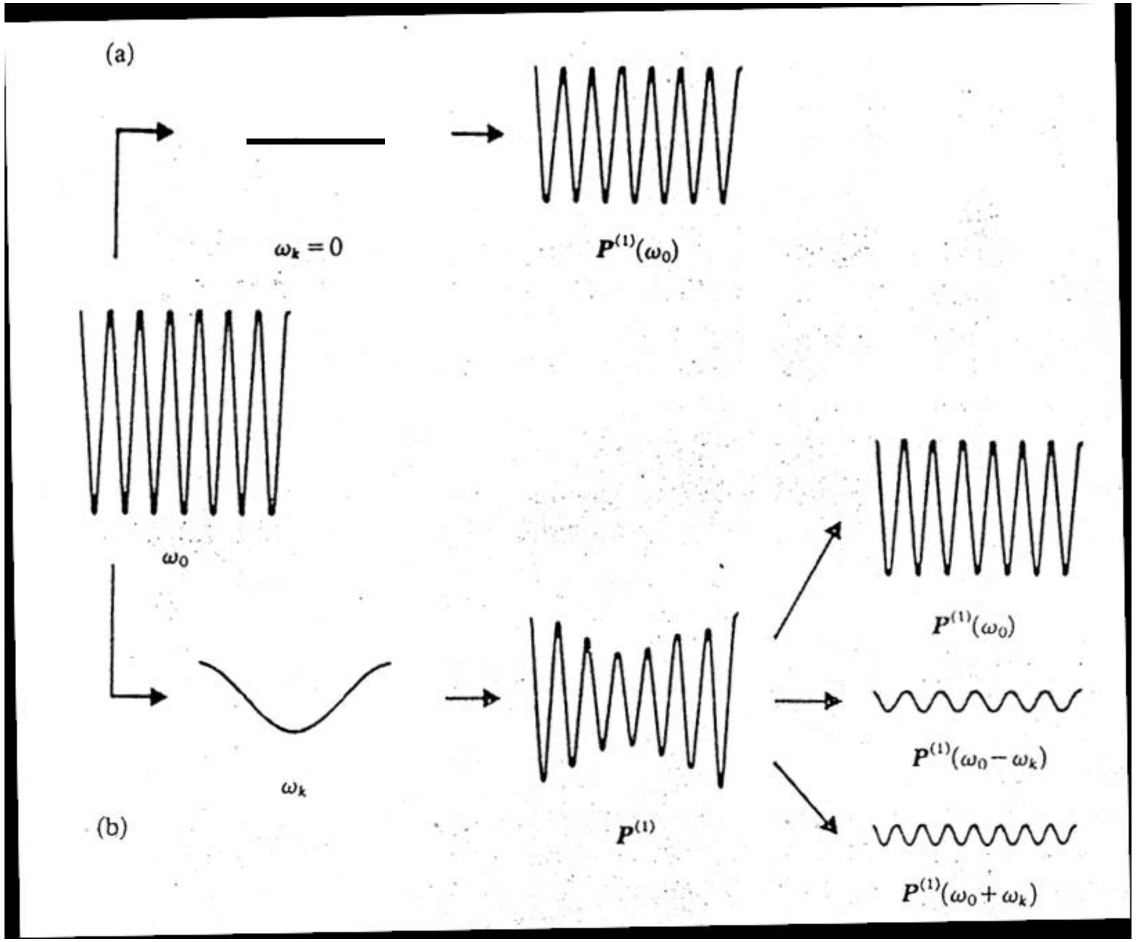
For deformable objects: $\mu_{ind} = \alpha(r)E,$ where α is the polarizabiity

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

$$\Delta\alpha = \left(\frac{\partial\alpha}{\partial r}\right)_0 r$$

Rayleigh anti-Stokes Stokes

The Raman effect – classical picture



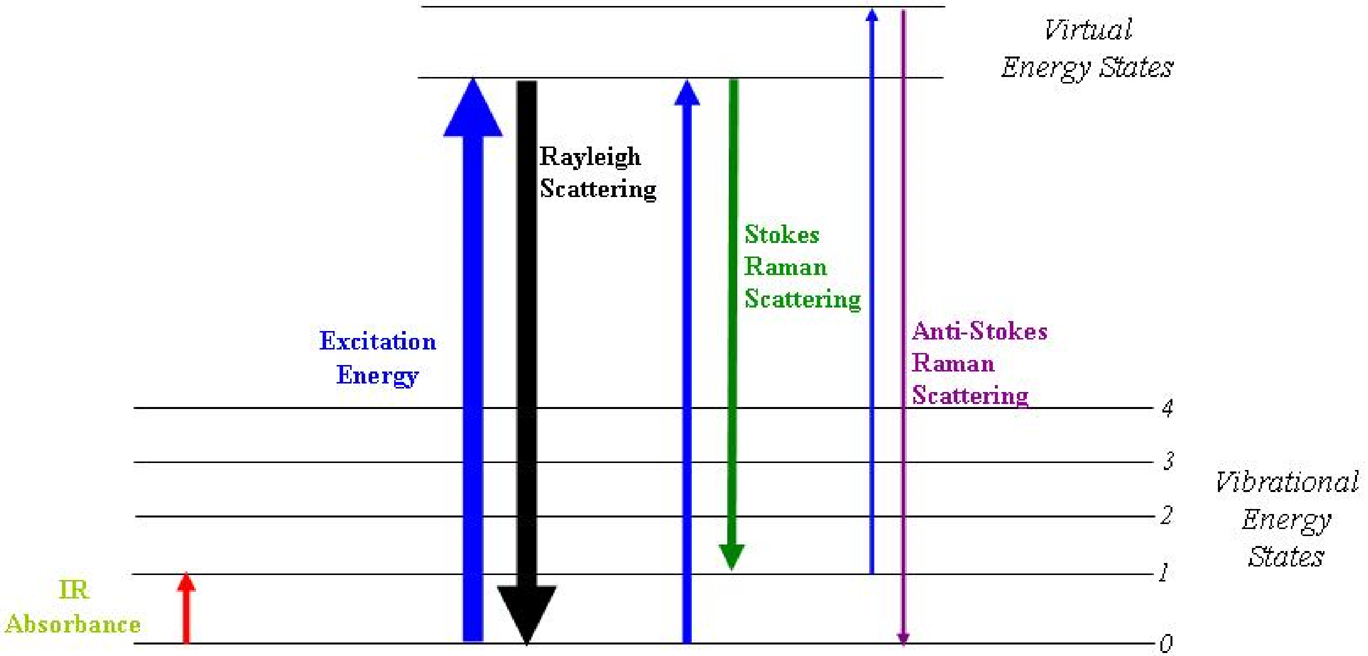
D. A. Long: Raman spectroscopy
McGraw-Hill, 1977

Rayleigh

Stokes

anti-Stokes

The Raman effect – quantum picture

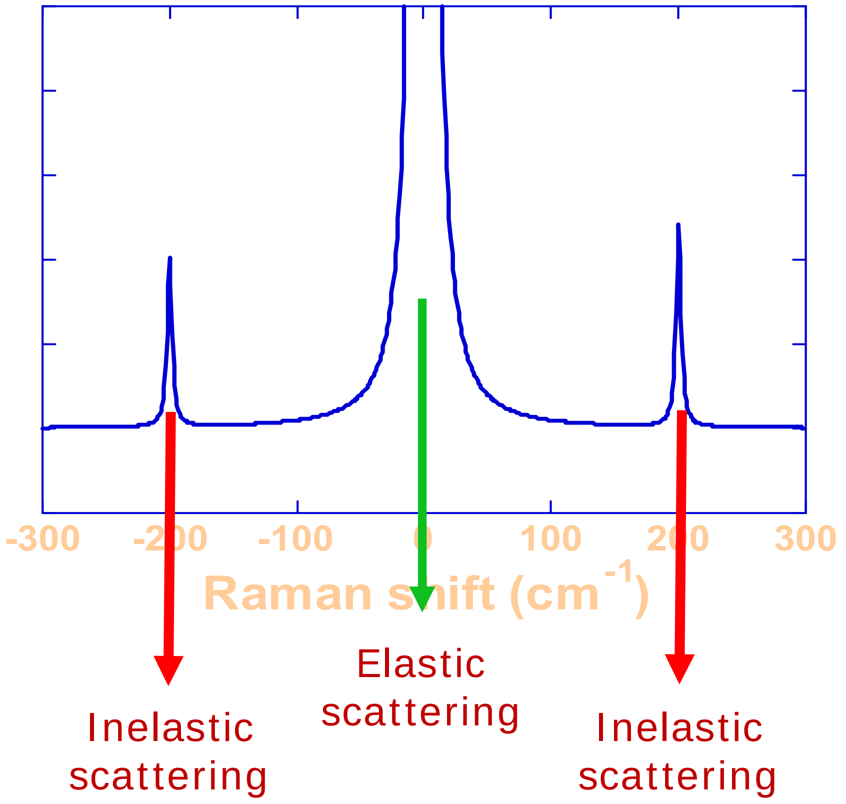


Álmosdi Péter, BME 2008
Source: Wikipedia

Raman spectroscopy

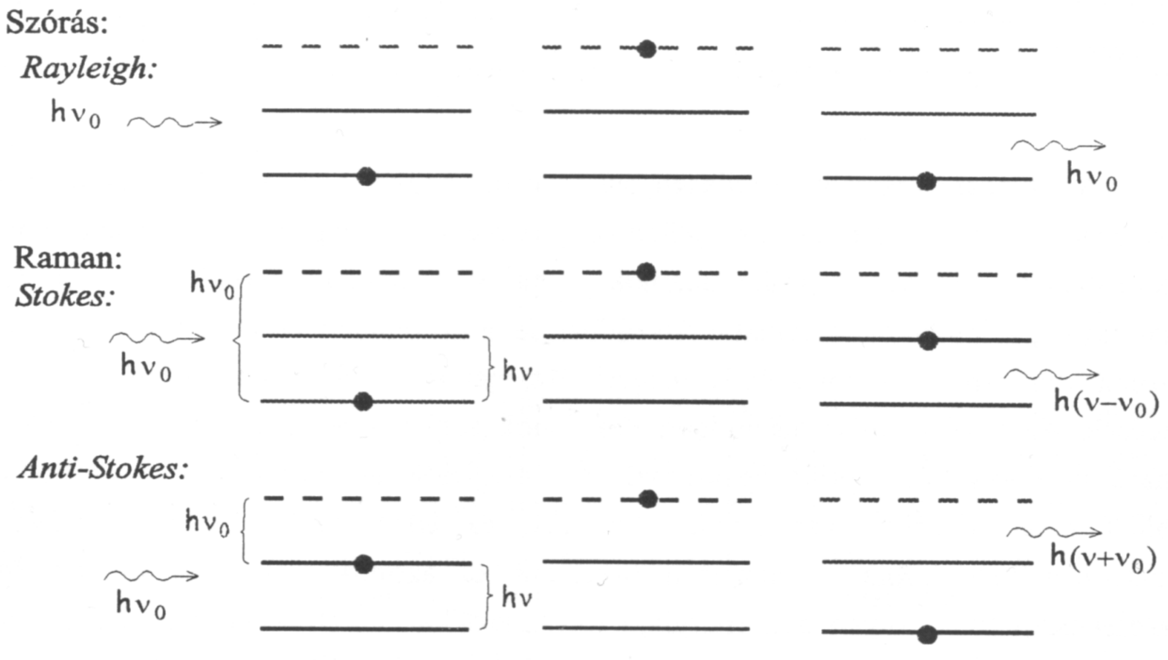
Light scattering by monochromatic light

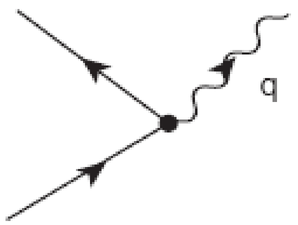
Spectrum of scattered light relative to the exciting light



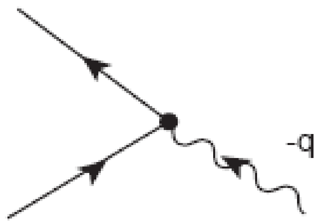
- Inelastic scattering can only be observed if the polarizability of the medium changes during the scattering process
- The magnitude of the shift does not depend on the frequency of the exciting light
- The probability of inelastic scattering is small, every one of 10^8 photons suffers inelastic scattering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

Raman scattering: energy and momentum conservation





Stokes



anti-Stokes

The change in wave vector of the photon has to be compensated by the phonon

$\mathbf{k}_L, \mathbf{k}_S \approx 10^4\ \mathrm{cm}^{-1}$

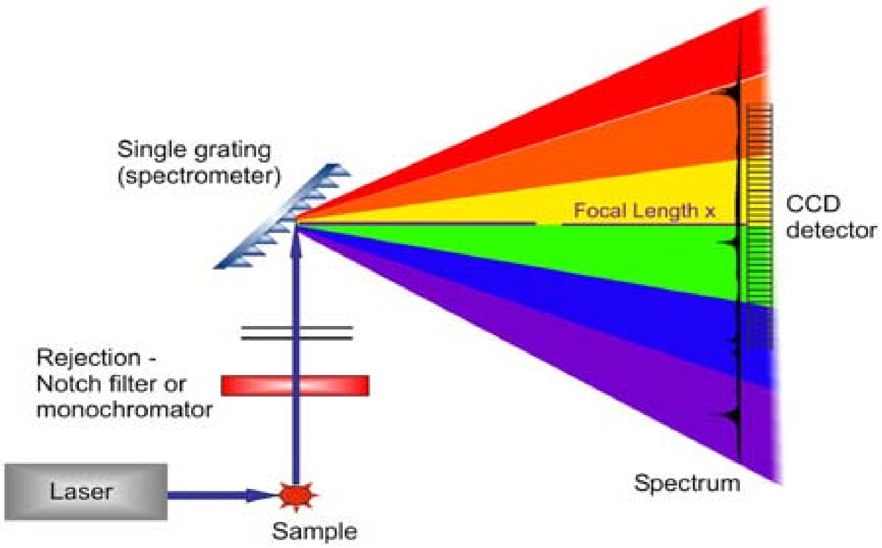
$\mathbf{q} \approx 10^{10}\ \mathrm{cm}^{-1}$

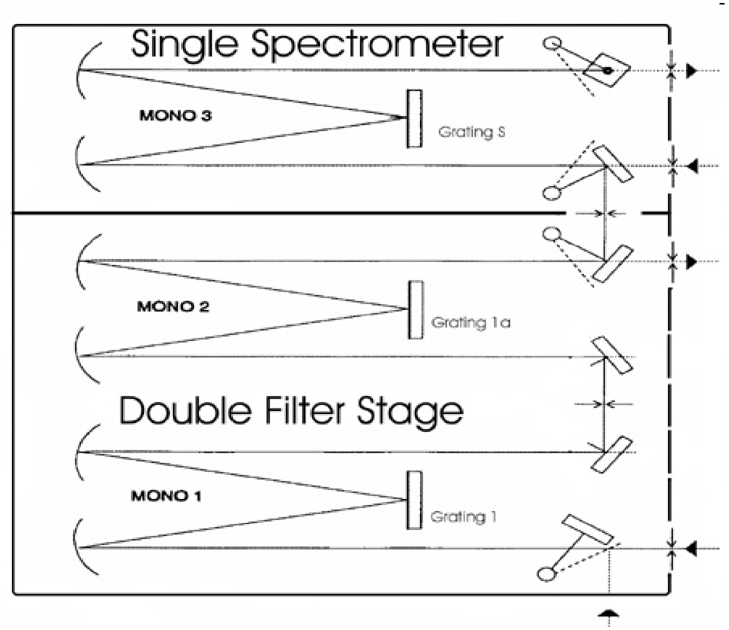
$\Rightarrow$ $\mathbf{k}_L, \mathbf{k}_S \ll \mathbf{q}$

Only phonons in the middle of the Brillouin zone take part in the scattering

Álmosdi Péter, BME 2008
Source: Wikipedia

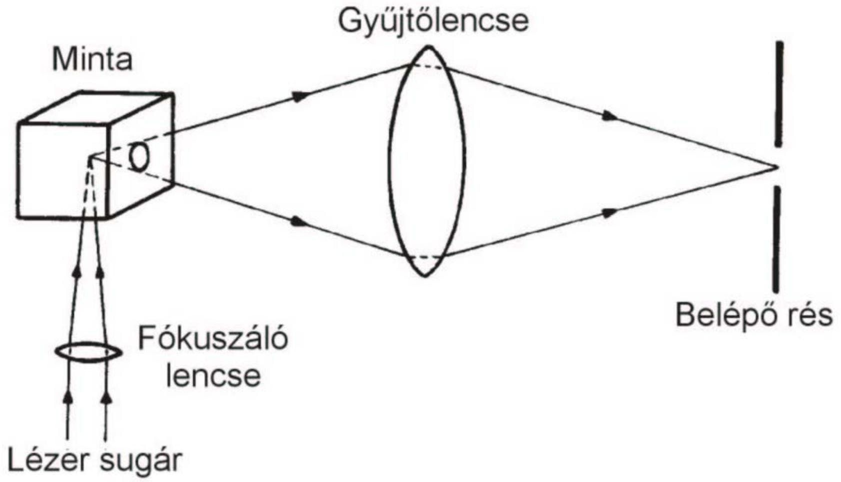
Experimental setup



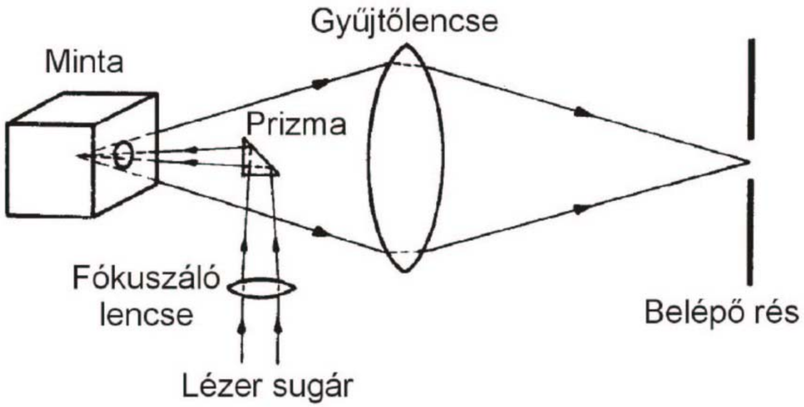


Excitation: visible, monochromatic light (laser) ~ 10^4 cm^{-1}
Frequency difference: infrared region, resolution: ~ 1 cm^{-1}
Resolution of monochromator critical!

Experimental arrangements



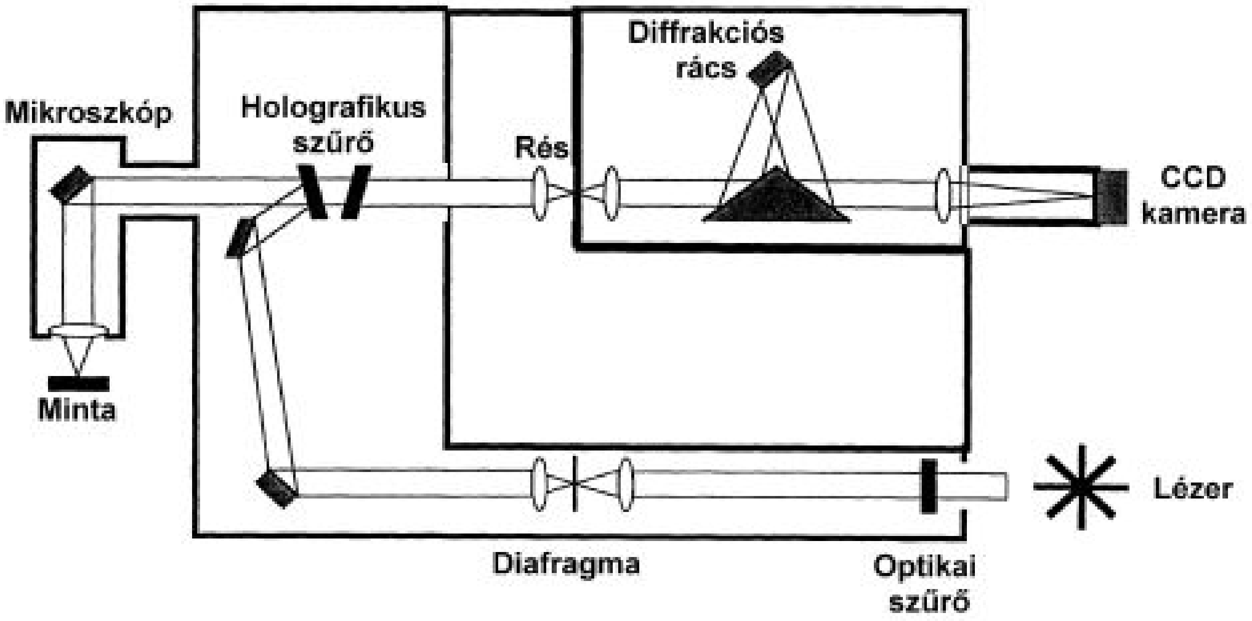
3.4a. ábra. A 90°-os gerjesztési elrendezésû mintatér.



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

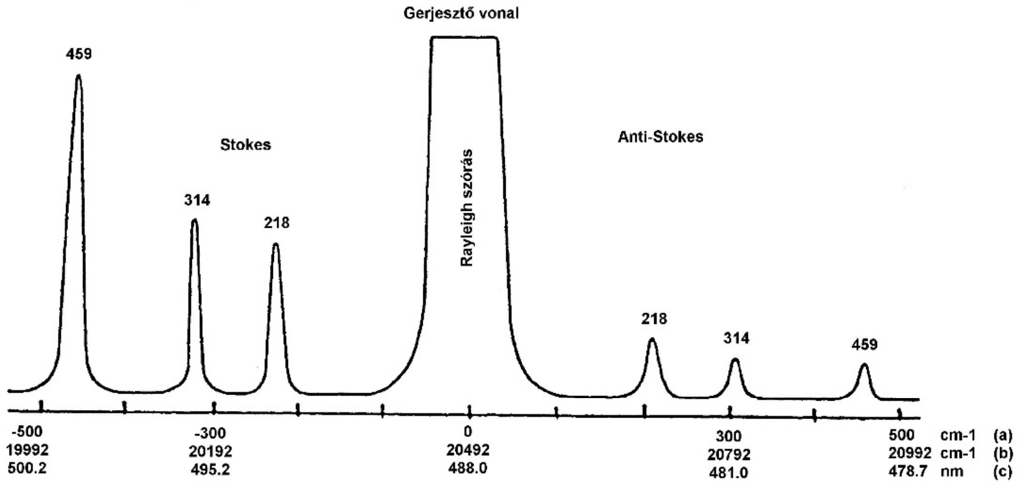
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

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)

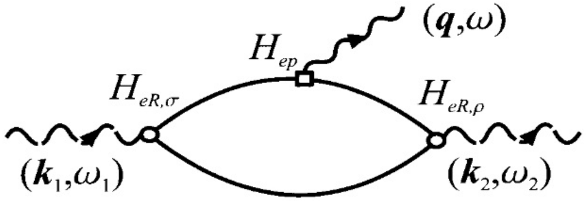
Intensity ratio:

$$\frac{I_{AS}}{I_S} \sim e^{\frac{-h\upsilon}{kT}}$$

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

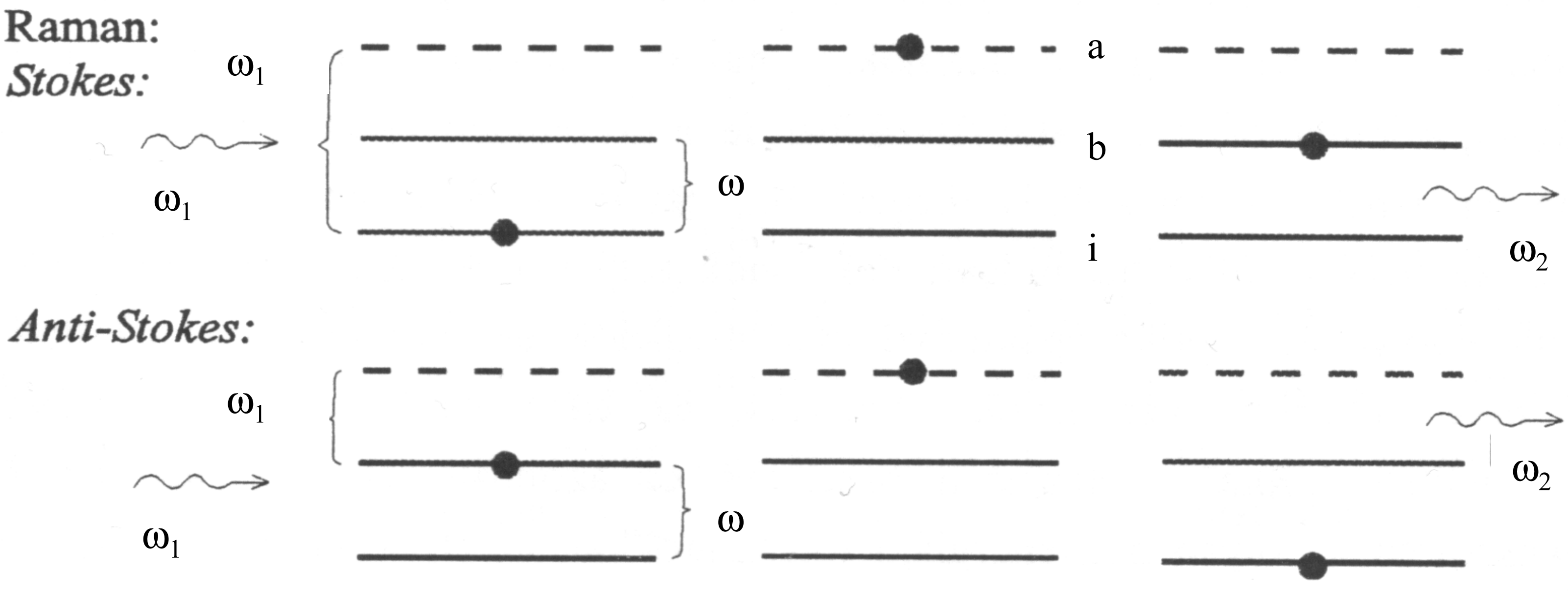
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

The Raman effect



Stokes scattering: $I \sim \left|K_{2f,10}\right|^2$

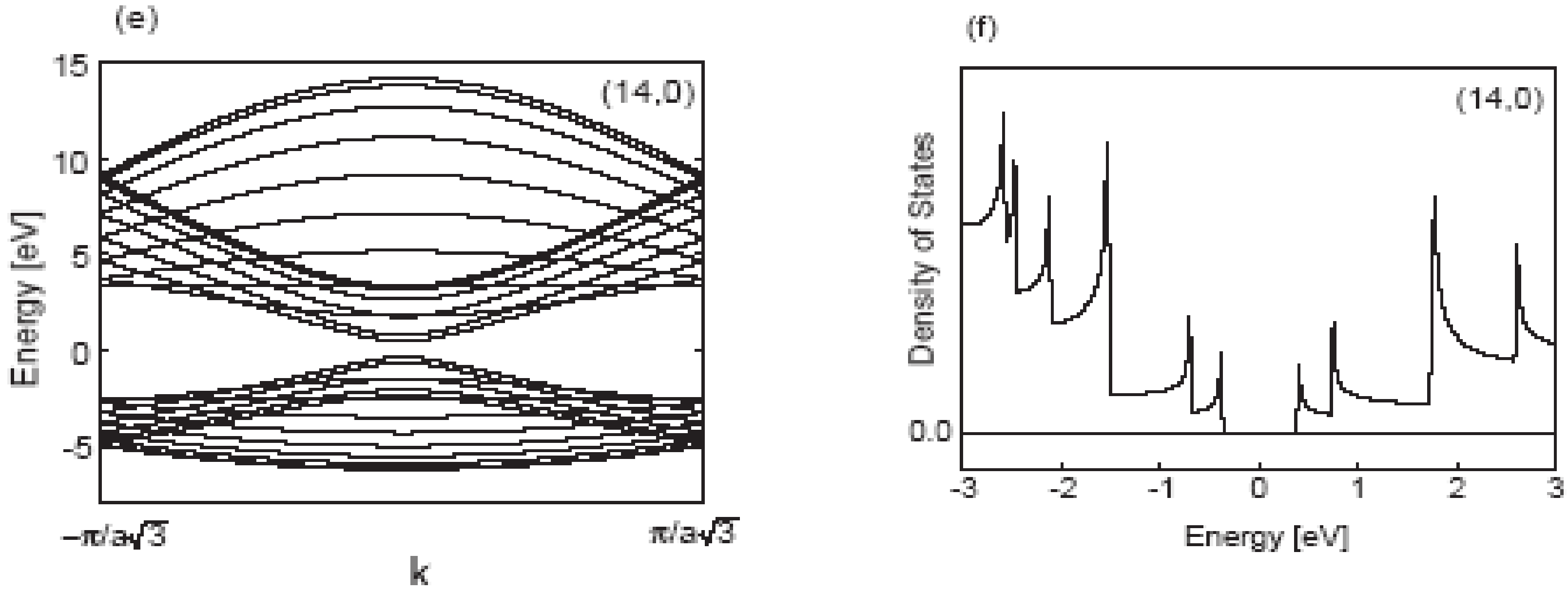
$$K_{2f,10} = \sum_{a,b} \frac{\langle \omega_2, f, i \,|\, H_{eR,\rho} \,|\, 0, f, b \rangle \langle 0, f, b \,|\, H_{ep} \,|\, 0, 0, a \rangle \langle 0, 0, a \,|\, H_{eR,\sigma} \,|\, \omega_1, 0, i \rangle}{(E_1 - E^e_{ai} - i\gamma)(E_1 - \hbar\omega - E^e_{bi} - i\gamma)}$$



Resonant Raman scattering

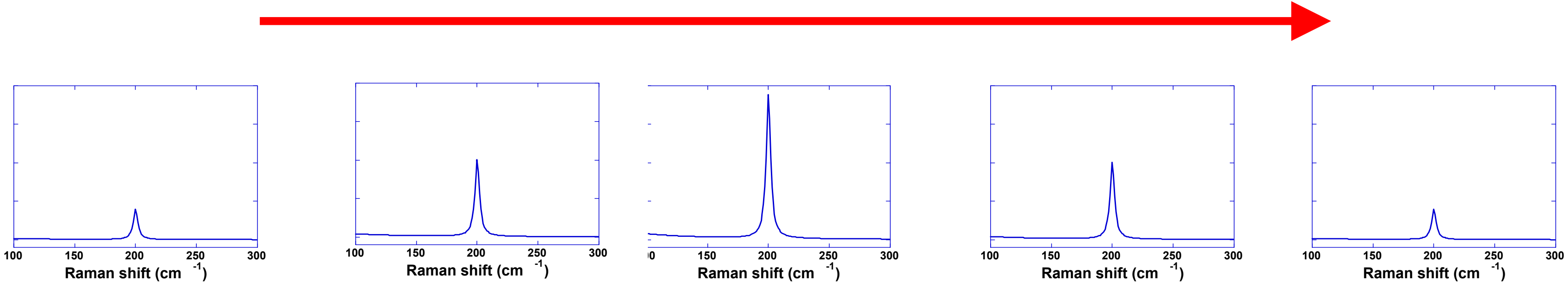
If the energy of the exciting laser approaches the energy of a real transition in the medium, the intensity of the Raman scattering increases by orders of magnitude. This is the **resonant Raman effect.**

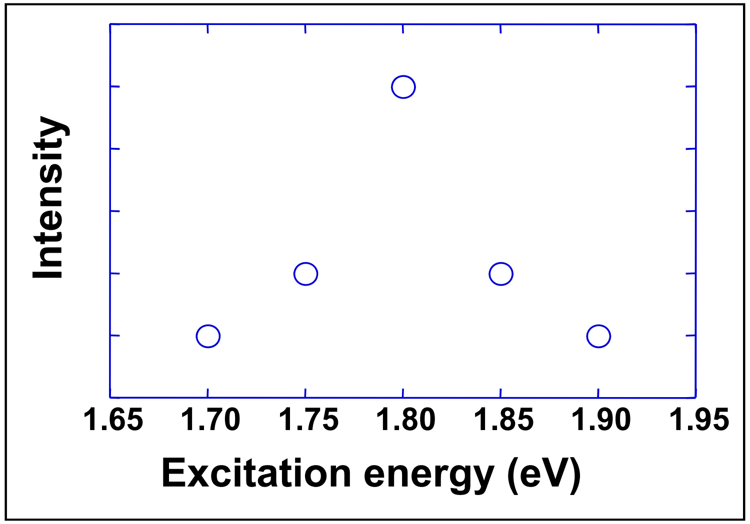
Resonant Raman scattering is the strongest close to maxima in the density of states.

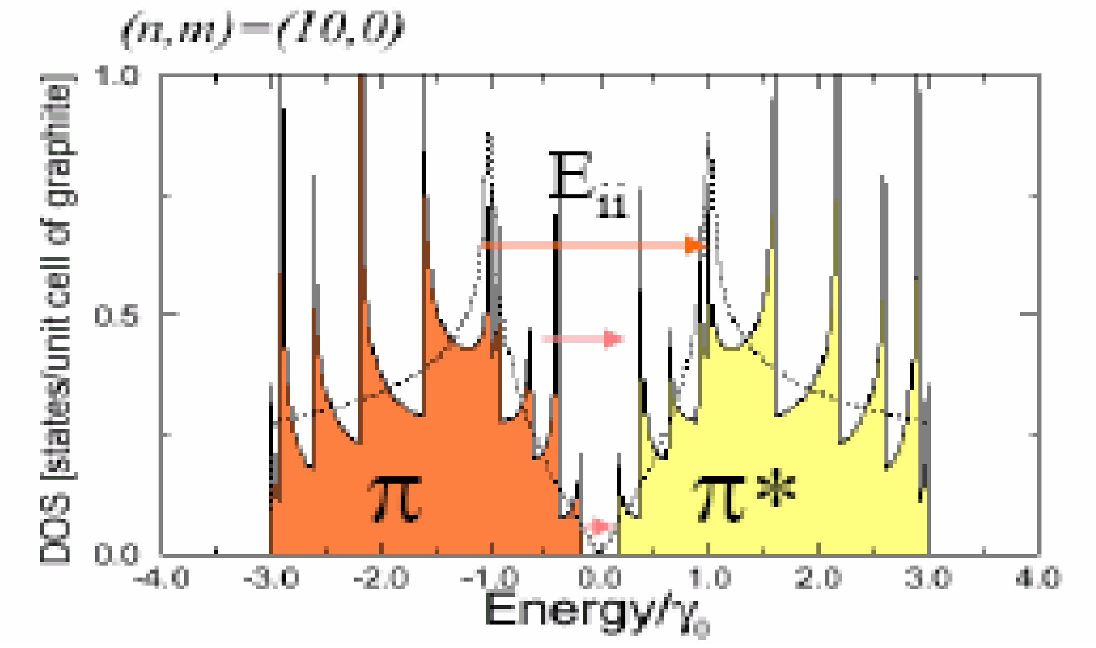


Resonant Raman excitation profile

Excitation energy

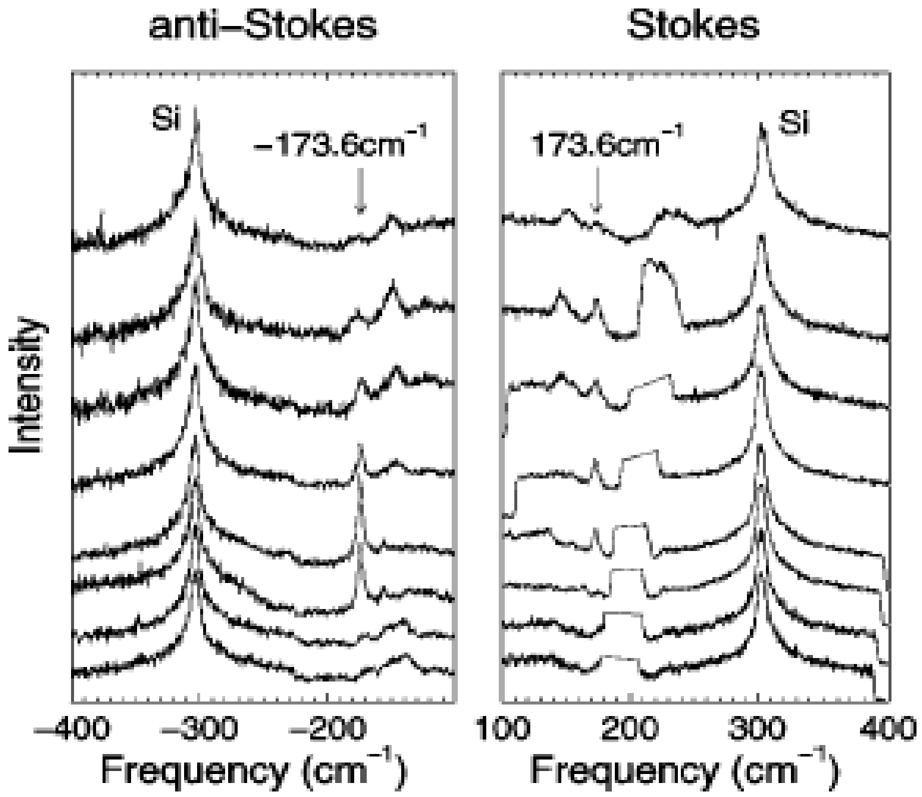




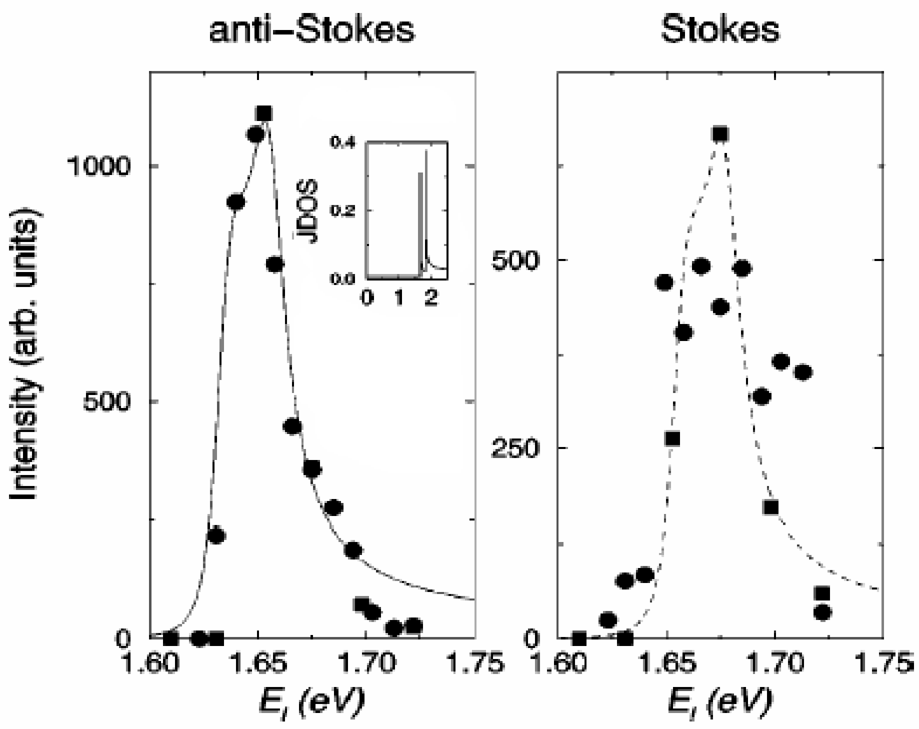


Excitation profile: example

Excitation: 1,623 - 1,722 eV



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

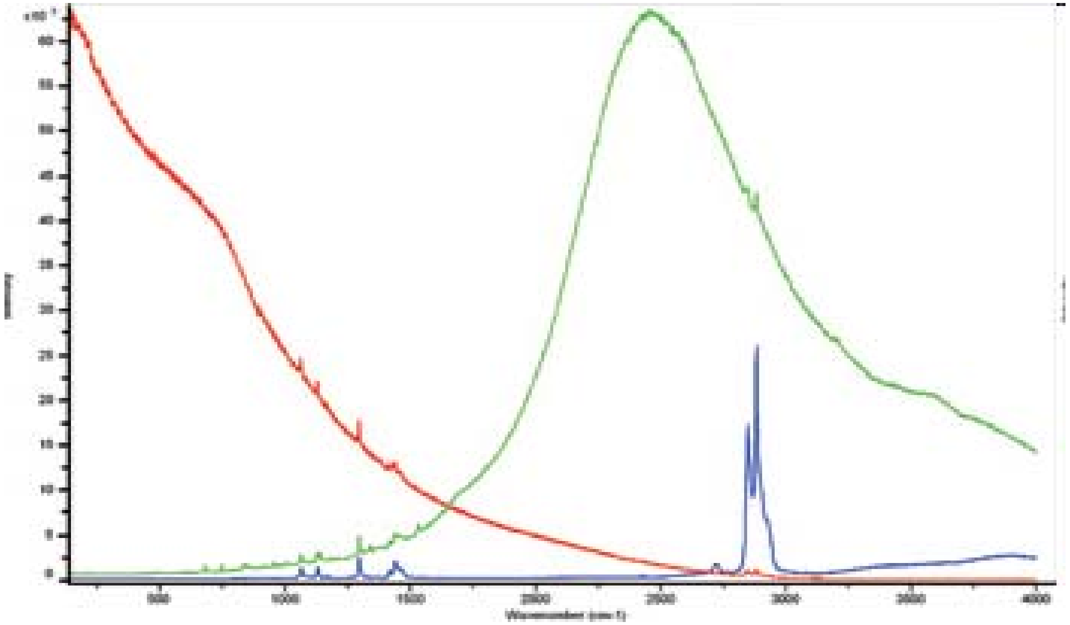


Veres Miklós, MTA Wigner FK

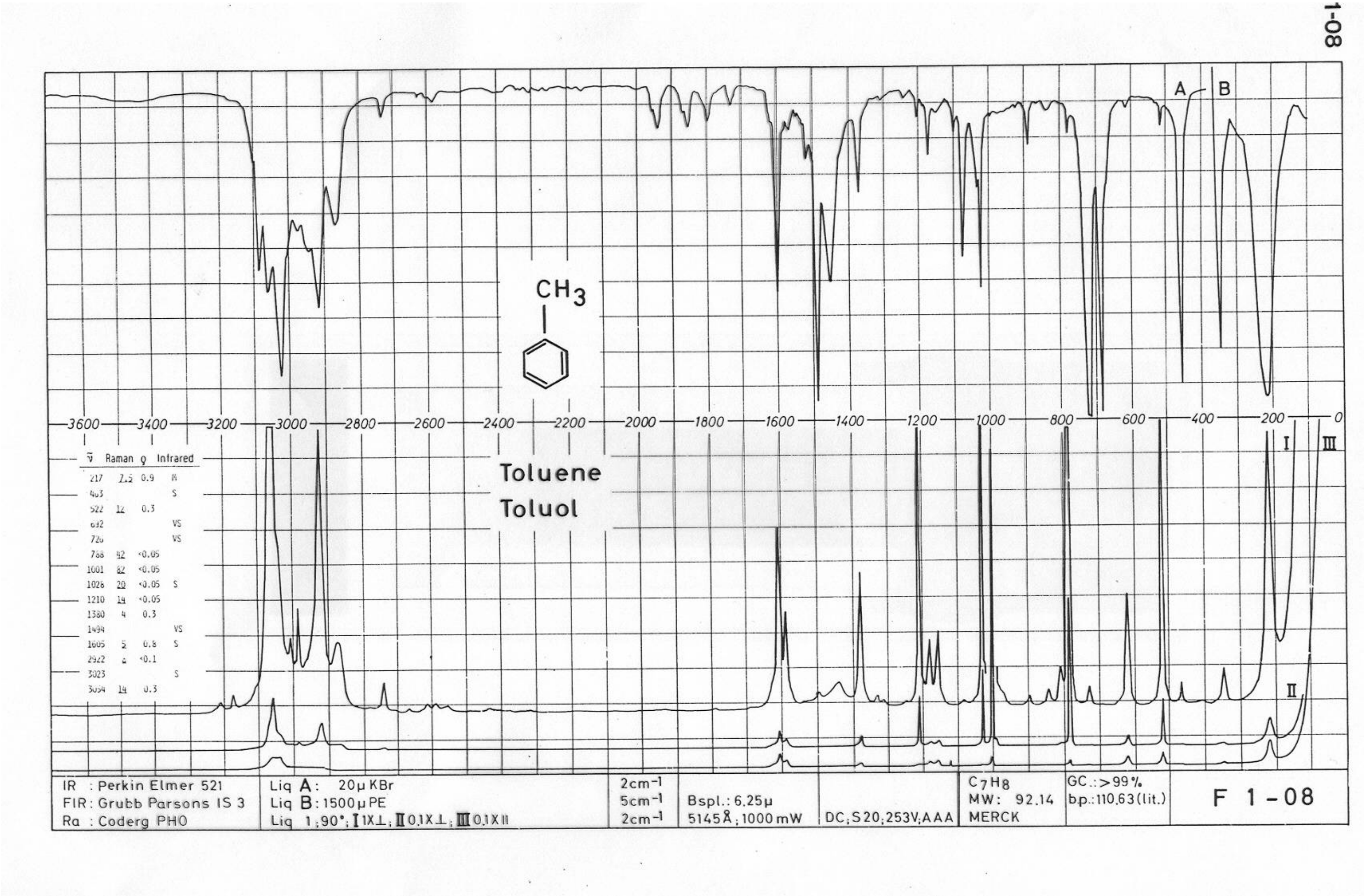
A.Jorio et al.
Phys. Rev. B 63 (2001) 245416

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



$\tilde{\nu}$	Raman	ρ	Infrared
217	7.5	0.9	M
463			S
522	12	0.3	
692			VS
726			VS
788	42	<0.05	
1001	82	<0.05	
1028	20	<0.05	S
1210	19	<0.05	
1380	4	0.3	
1494			VS
1605	5	0.8	S
2922	6	<0.1	
3023			S
3054	19	0.3	

IR

Raman

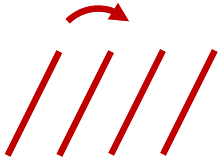
Birefringence, linear dichroism

T, R can be measured in independent directions
with light polarized in the respective direction

↓

max. 3 independent n, ε

- Kramers-Kronig relations hold in each direction independently
- selection rules depend on direction
- normal incidence: 3 measurements on at least two surfaces
- polarizer, analyzer in the same direction (one can be omitted)



Spectrum of one-dimensional organic conductor

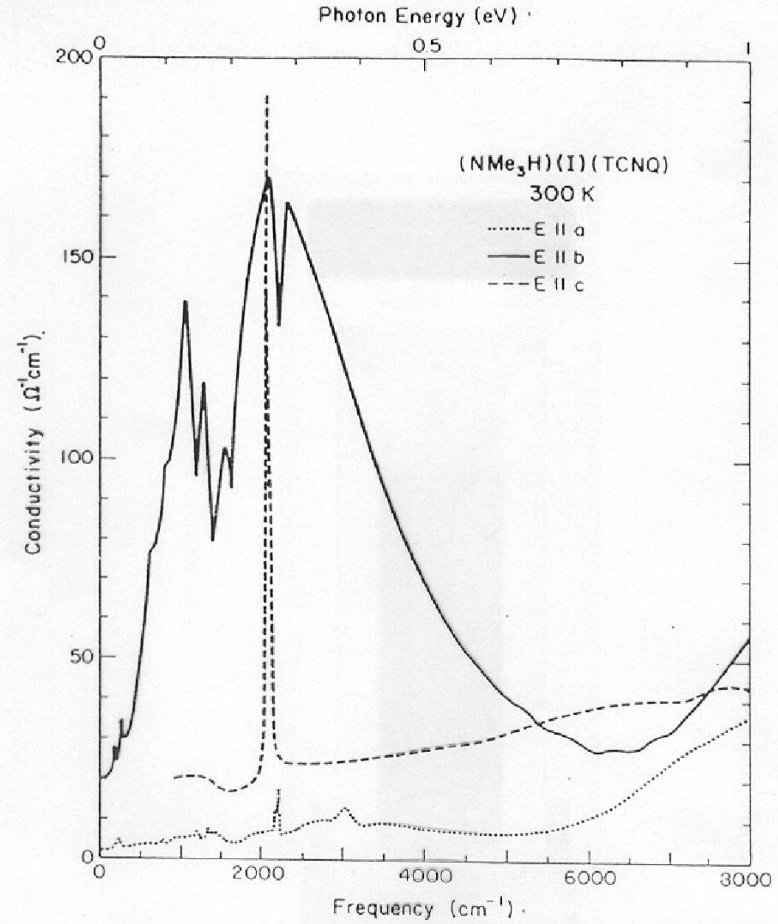
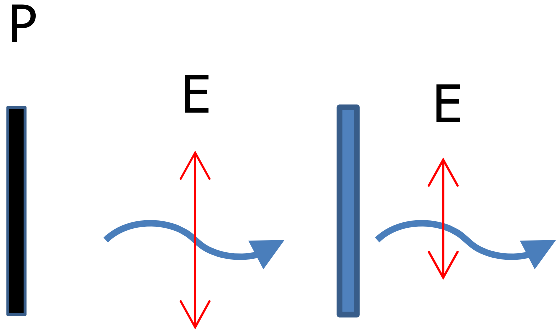


FIG. 41. Frequency-dependent conductivity determined by Kramers–Kronig analysis of the reflectance of (NMe$_3$H)(I)(TCNQ). The chain axis is *b* (solid lines). [From Tanner *et al.* (1979).]

Anisotropy in infrared and Raman spectra

IR $\frac{\partial \mu}{\partial Q} \neq 0$

$$\frac{\partial \mu}{\partial Q} = \begin{bmatrix} \frac{\partial \mu_x}{\partial Q} \\ \frac{\partial \mu_y}{\partial Q} \\ \frac{\partial \mu_z}{\partial Q} \end{bmatrix}$$



Raman $\frac{\partial \alpha}{\partial Q} \neq 0$

$$\frac{\partial \alpha}{\partial Q} = \begin{bmatrix} \frac{\partial \alpha_{xx}}{\partial Q} & \frac{\partial \alpha_{xy}}{\partial Q} & \frac{\partial \alpha_{xz}}{\partial Q} \\ \frac{\partial \alpha_{yx}}{\partial Q} & \frac{\partial \alpha_{yy}}{\partial Q} & \frac{\partial \alpha_{yz}}{\partial Q} \\ \frac{\partial \alpha_{zx}}{\partial Q} & \frac{\partial \alpha_{zy}}{\partial Q} & \frac{\partial \alpha_{zz}}{\partial Q} \end{bmatrix}$$

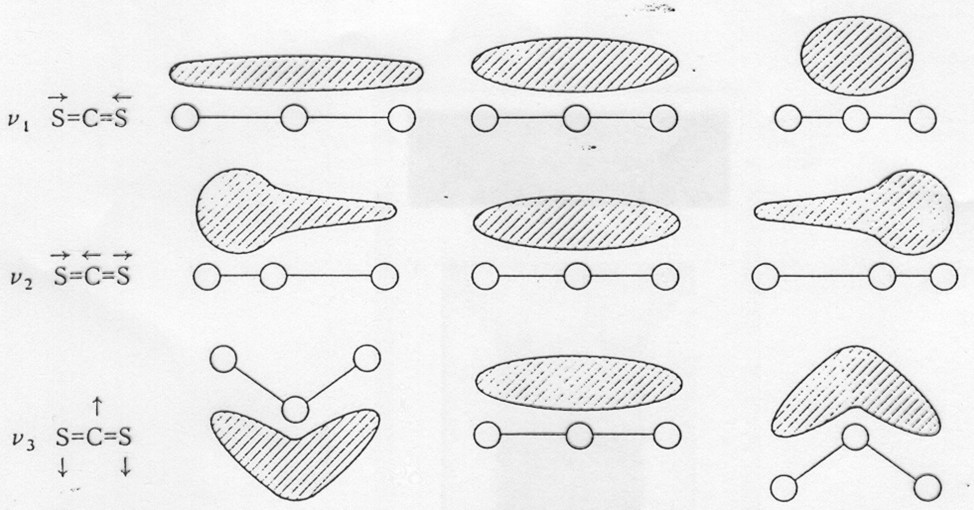
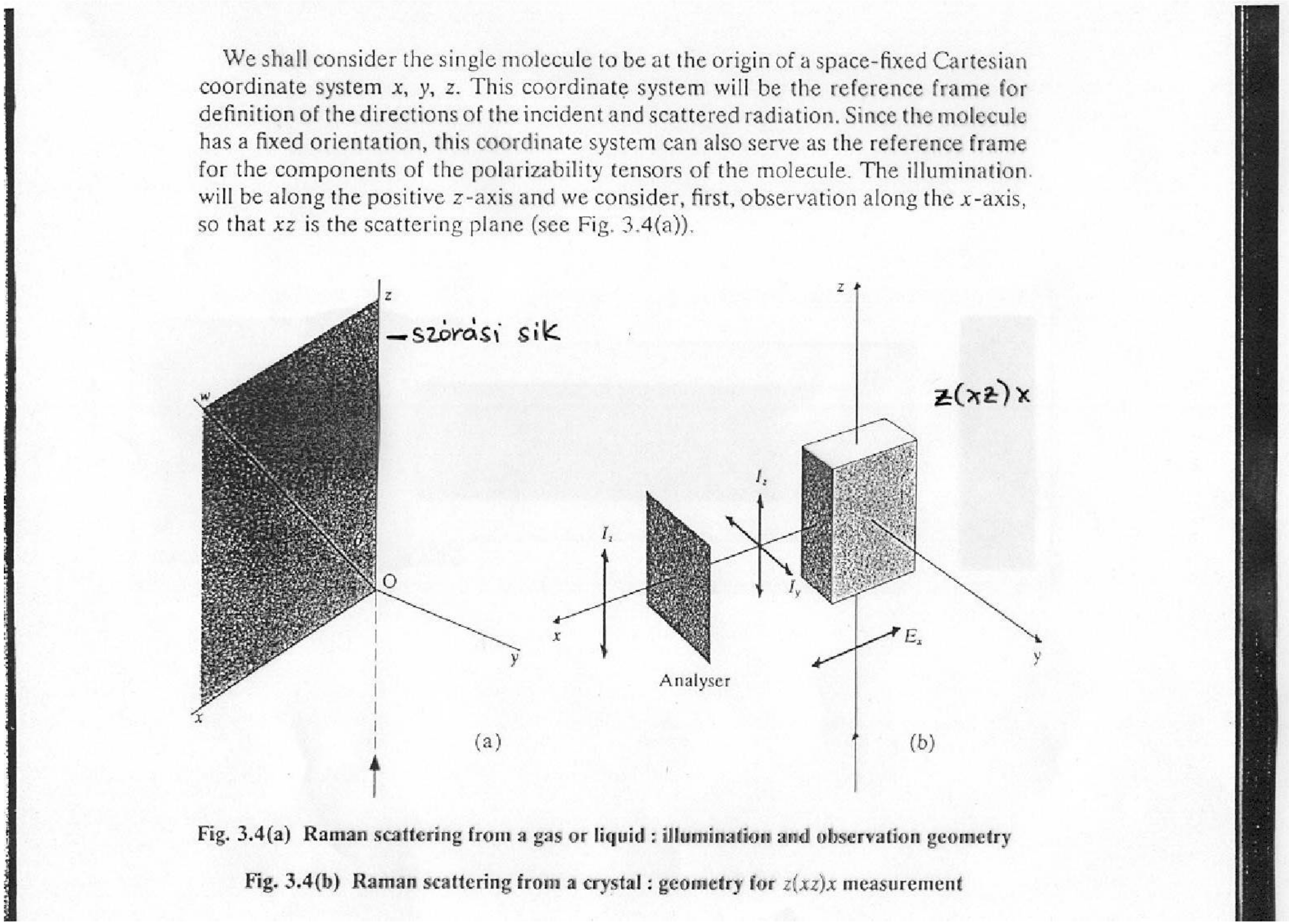


Fig. 5.2 Vibrations of carbon disulfide and accompanying changes in polarizability. Bending vibration ν_3 is degenerate, the other ν_4 being perpendicular to the paper plane.

Polarization of incident and scattered light can differ
Need both polarizer and analyzer

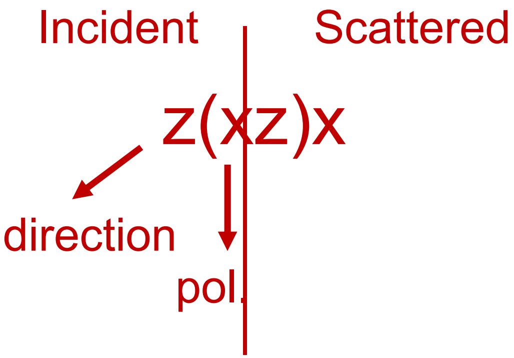
Scattering plane, scattering geometry



We shall consider the single molecule to be at the origin of a space-fixed Cartesian coordinate system x, y, z. This coordinate system will be the reference frame for definition of the directions of the incident and scattered radiation. Since the molecule has a fixed orientation, this coordinate system can also serve as the reference frame for the components of the polarizability tensors of the molecule. The illumination will be along the positive z-axis and we consider, first, observation along the x-axis, so that xz is the scattering plane (see Fig. 3.4(a)).

Fig. 3.4(a) **Raman scattering from a gas or liquid : illumination and observation geometry**

Fig. 3.4(b) **Raman scattering from a crystal : geometry for** $z(xz)x$ **measurement**



Depolarization ratio:

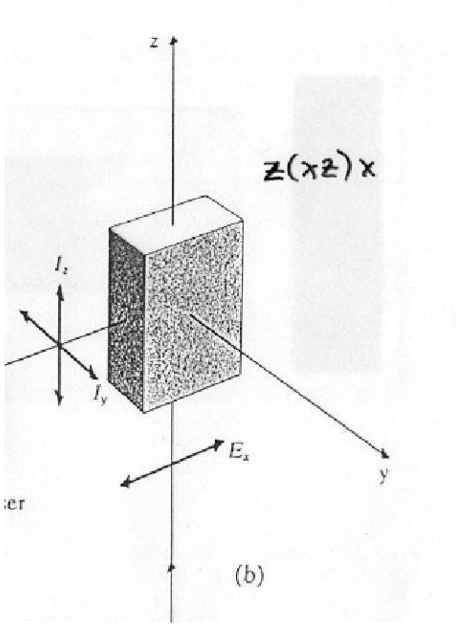
$$\rho_{\parallel}(\theta) = \frac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)}$$

θ angle between incident and scattered light
upper index: polarization of incident light
lower index: polarization of scattered light
(**E** relative to scattering plane)

Depolarization ratio

$$\rho_{\parallel}(\theta)=\frac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)} \qquad \rho_{\perp}(\theta)=\frac{{}^{\perp}I_{\parallel}(\theta)}{{}^{\perp}I_{\perp}(\theta)}$$

for “natural” light: $$\rho_{n}(\theta)=\frac{{}^{n}I_{\parallel}(\theta)}{{}^{n}I_{\perp}(\theta)}$$



in z(xz)x geometry:

$$\rho_{\parallel}(\frac{\pi}{2})=\frac{{}^{x}I_{y}}{{}^{x}I_{z}} \qquad \rho_{\perp}(\frac{\pi}{2})=\frac{{}^{y}I_{z}}{{}^{y}I_{y}} \qquad \rho_{n}(\frac{\pi}{2})=\frac{{}^{n}I_{z}}{{}^{n}I_{y}}$$

$$\rho_{\parallel}(\frac{\pi}{2})=\frac{(\alpha_{yx}')^{2}}{(\alpha_{zx}')^{2}} \qquad \rho_{\perp}(\frac{\pi}{2})=\frac{(\alpha_{zy}')^{2}}{(\alpha_{yy}')^{2}} \qquad \rho_{n}(\frac{\pi}{2})=\frac{(\alpha_{zx}')^{2}+(\alpha_{zy}')^{2}}{(\alpha_{yx}')^{2}+(\alpha_{yy}')^{2}} \qquad \alpha_{xy}'=\left(\frac{\partial\alpha_{xy}}{\partial r}\right)$$

α_{zz}’, α_{xx}’ from other orientation; since α and α’ are symmetric, α_{xy}’$=\alpha_{yx}$’

the relative values of the matrix elements
can be obtained from 6 measurements

Polarizability tensor for randomly oriented objects

$$\alpha = \alpha_{iso} + \alpha_{aniso} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} + \begin{pmatrix} \alpha_{xx} - a & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} - a & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} - a \end{pmatrix}$$

$$a = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\gamma^2 = \frac{1}{2}\left\{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)\right\}$$

α and γ^2 are invariant to coordinate transformations

Depolarization ratio for randomly oriented objects

$$\rho_\perp(\theta) = \frac{{}^{\perp}I_{\parallel}(\theta)}{{}^{\perp}I_{\perp}(\theta)}$$

θ angle between incident and scattered light
upper index: polarization of incident light
lower index: polarization of scattered light
(**E** relative to scattering plane)

α and γ are symmetric towards rotation of coordinates:

$$\alpha_{xy} = \sum_{x',y'} \alpha_{x',y'} \cos(xx')\cos(yy')$$

x,y can be x,y,z

Since α is a symmetric tensor (and we assume it to be real), $\alpha_{xy} = \alpha_{yx}$
and averaging on the spatial orientation of the molecules:

$$\overline{\alpha_{xx}^2} = \overline{\alpha_{yy}^2} = \overline{\alpha_{zz}^2} = \frac{45a^2 + 4\gamma^2}{45} \qquad \overline{\alpha_{yx}^2} = \overline{\alpha_{yz}^2} = \overline{\alpha_{zx}^2} = \frac{\gamma^2}{15} \qquad \overline{\alpha_{xx}\alpha_{yy}} = \overline{\alpha_{yy}\alpha_{zz}} = \overline{\alpha_{zz}\alpha_{xx}} = \frac{45a^2 - 2\gamma^2}{45}$$

The quantity determining the intensity: $\left(\dfrac{\partial \alpha_{xy}}{\partial r}\right) = \alpha_{xy}'$

similar relations can be derived for these using α' and γ', from where $\rho_\perp\left(\dfrac{\pi}{2}\right) = \dfrac{3(\gamma')^2}{45(a')^2 + 4(\gamma')^2}$

Depolarization ratio

a'=0 ⟶ $\rho = \frac{3}{4}$ depolarized

$$\rho_{\perp}\left(\frac{\pi}{2}\right) = \frac{3(\gamma')^2}{45(a')^2 + 4(\gamma')^2}$$

γ'=0 ⟶ $\rho = 0$ fully polarized

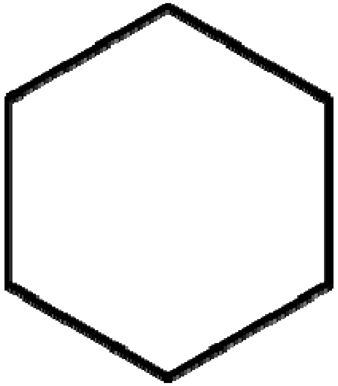
$0 < \rho < \frac{3}{4}$ partially polarized

Fully polarized mode: $\rho=0$

e.g. $\alpha = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$ and $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$

„totally symmetric" mode (A, A_g)

Depolarization ratio: example



cyclohexane

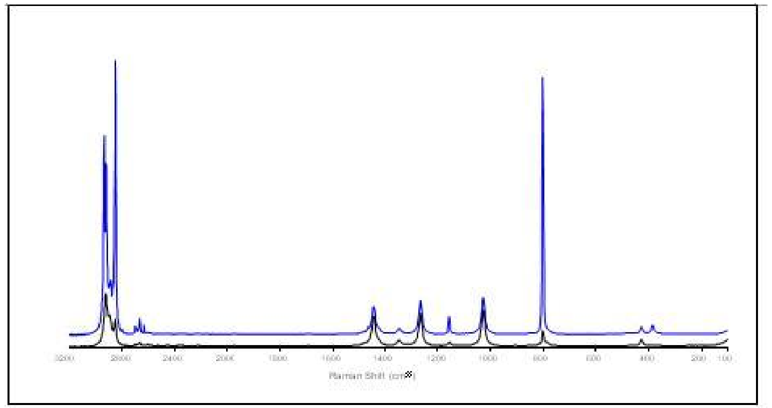


Figure 1, Raman spectra of cyclohexane arising from analysis Parallel (Blue) and Perpendicular (Black) to the excitation laser polarisation.

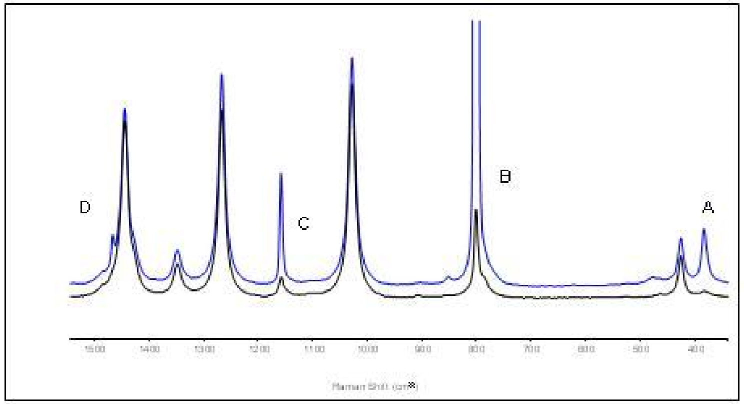
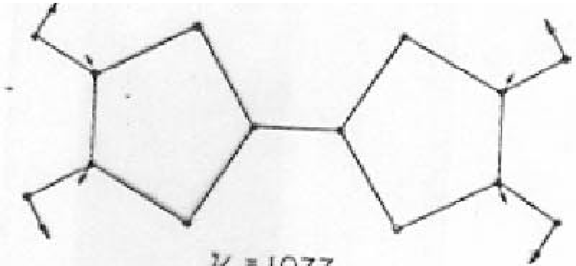
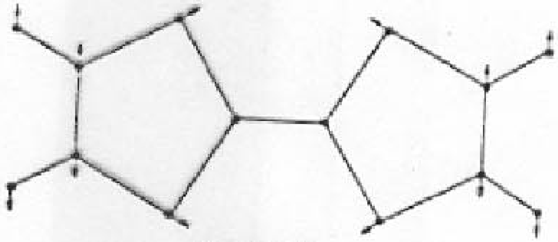


Figure 2. Zoom in on fingerprint region of cyclohexane, large changes in peaks A-D can be readily observed, this signifies that these peaks arise from totally symmetric vibrations.

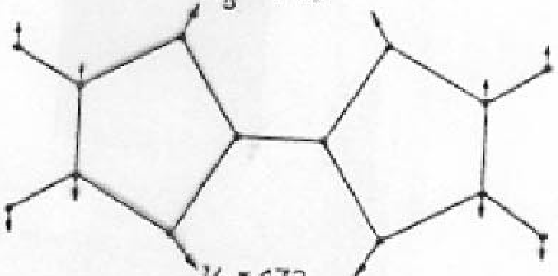
Totally symmetric vibrational modes



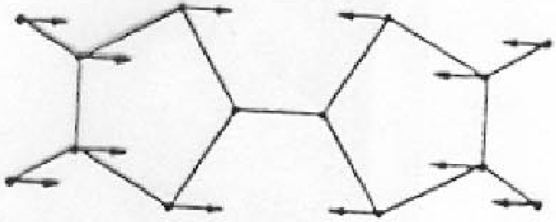
$\nu_4 = 1077$



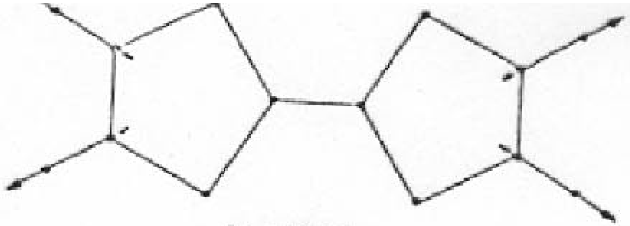
$\nu_5 = 740$



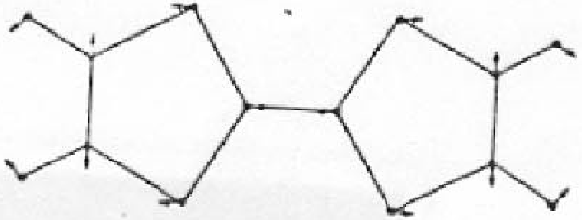
$\nu_6 = 472$



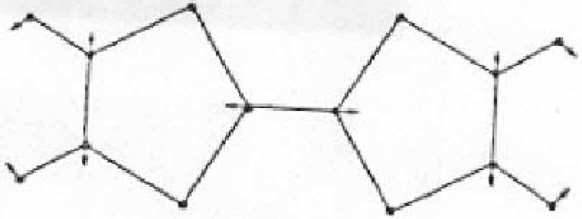
$\nu_7 = 253$



$\nu_1 = 3099$



$\nu_2 = 1559$



$\nu_3 = 1518$

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
- polarization-dependent effects: three incoming, three scattered directions, two polarizers
- scattering plane, scattering geometry e.g. z(xz)x
- Depolarization ratio $\rho_{\parallel}(\theta) = \frac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)}$
- Polarizability tensor for anisotropic materials $\alpha = \alpha_{iso} + \alpha_{aniso}$
- Depolarization ratio 0 → totally symmetric modes
- qualitative analysis as with IR, quantitative is hindered by scattering into the whole space and by resonance effects

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
- Polarizációfüggő jelenségek: három bejövő, három szórt irány, két polarizátor
- szórási sík, szórási geometria, pl. z(xz)x
- Depolarizációs arány $\rho_{\parallel}(\theta) = \dfrac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)}$
- Polarizálhatósági tenzor anizotróp anyagokra $\alpha = \alpha_{iso} + \alpha_{aniso}$
- Depolarizációs arány 0 → teljesen szimmetrikus módusok
- kvalitatív analízis mint az infravörösben, kvantitatív meghatározást akadályozza a teljes térbe kibocsátott szórt fény és a rezonancia-effektusok