Optical spectroscopy in materials science 8.

Infrared spectroscopy 2.
Raman spectroscopy
Optical spectroscopy of anisotropic media

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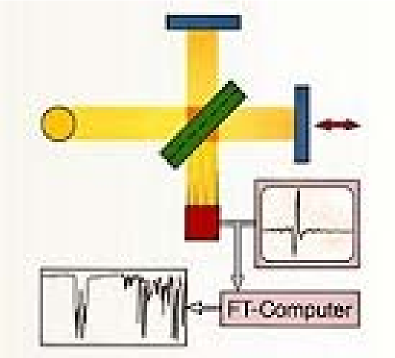
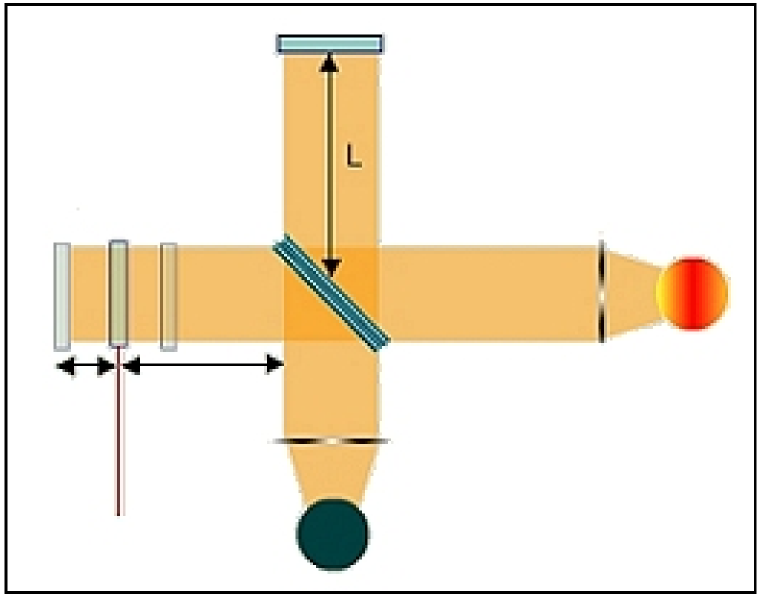
Fourier-transformation infrared (FTIR) spectroscopy

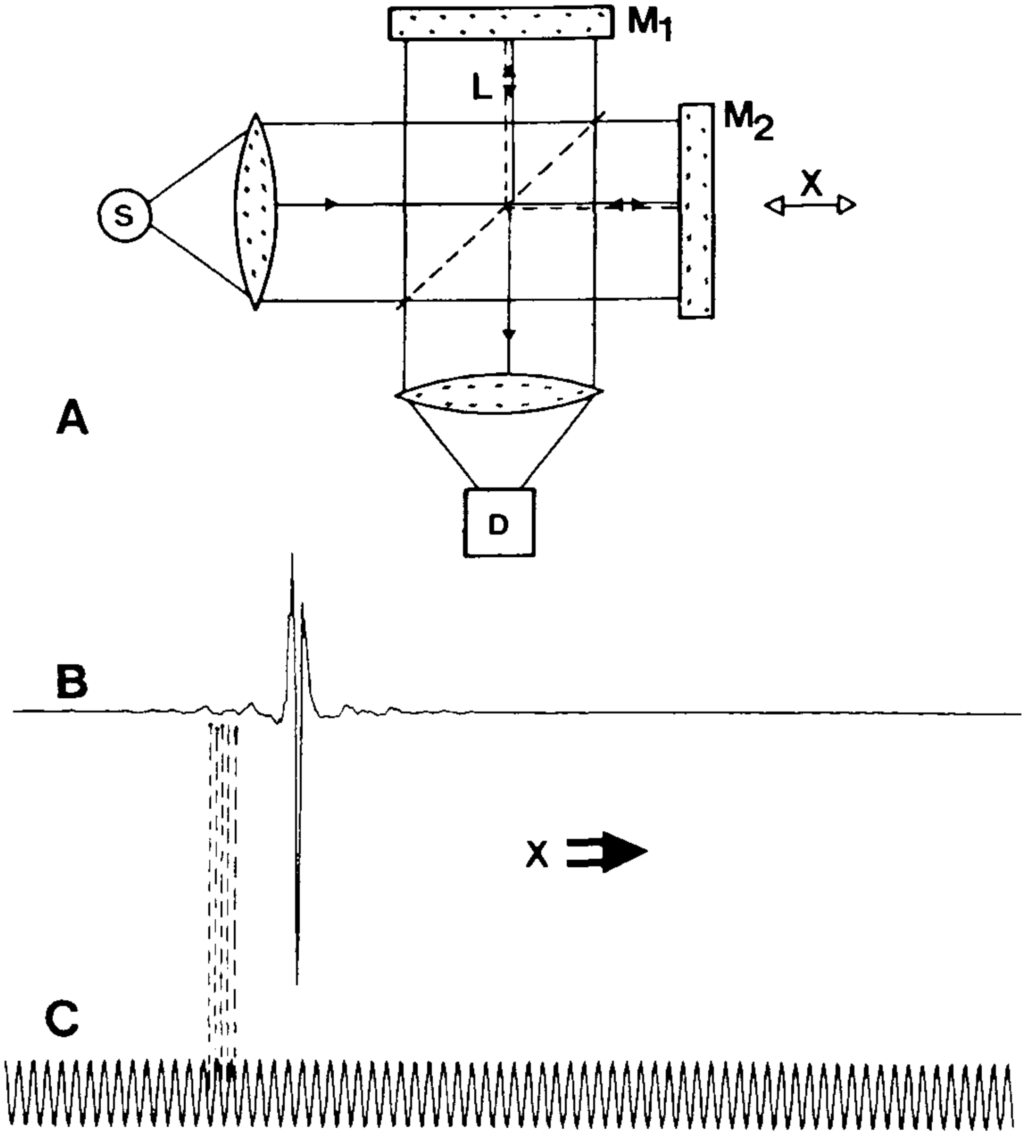




$$I(\nu^*) = \int_{-\infty}^{+\infty} I(x)\cos(2\pi\nu^* x)dx$$

$$i(\nu^*) = \Delta x \sum_{-M}^{M} I(m\Delta x)\cos(2\pi\nu^* m\Delta x)$$

Sampling control: He-Ne laser



Typical parameters

Mirror velocity: 0.5-60 mm/sec

He-Ne laser wavelength: 632.8 nm, wavenumber 15800 cm^{-1}

minimal distance of zero points: 316.4 nm n_{max} =15800 cm^{-1}

632.8 nm n_{max}= 7900 cm^{-1}

frequency of signal at detector: $f=2vn^{*}$

for f=1.58 mm/sec

400 cm^{-1} f=126 Hz

4000 cm^{-1} f=1260 Hz

Signal evaluation

Interferogram
Fourier transformation:
Apodization
Phase correction
Zerofilling

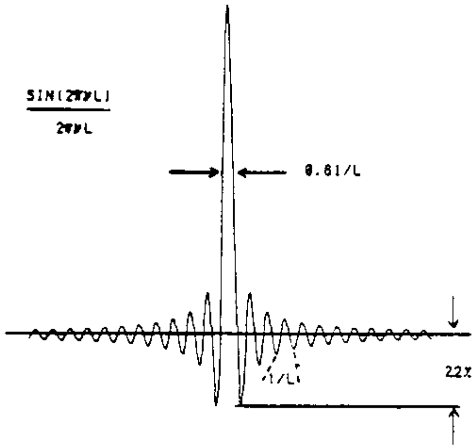
$$i(\nu^*) = \Delta x \sum_{-M}^{M} I(m\Delta x)\cos(2\pi\nu^* m\Delta x)$$

finite, discrete FT

Apodization

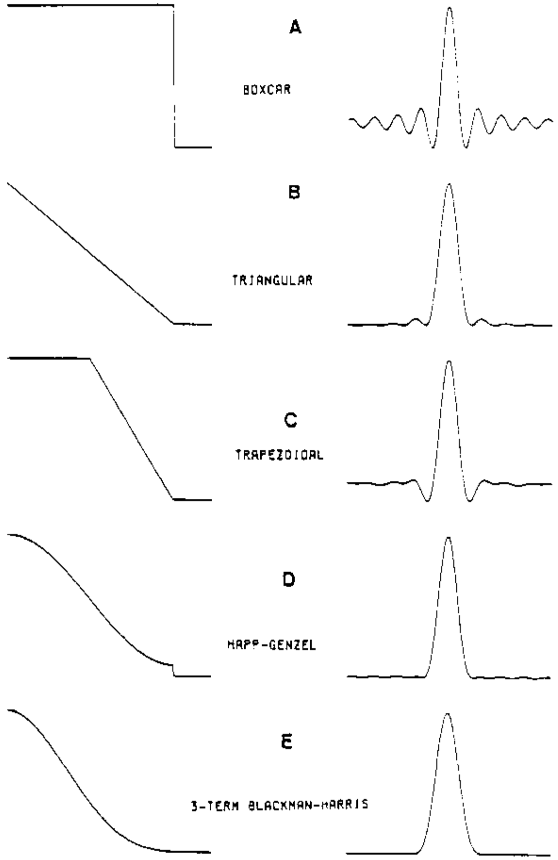
Instrumental lineshape:

$$I(\nu) = 2M\Delta x \frac{\sin(2\pi\nu M\Delta x)}{2\pi\nu M\Delta x} = 2M\Delta x\,\mathrm{sinc}(2\pi\nu M\Delta x)$$



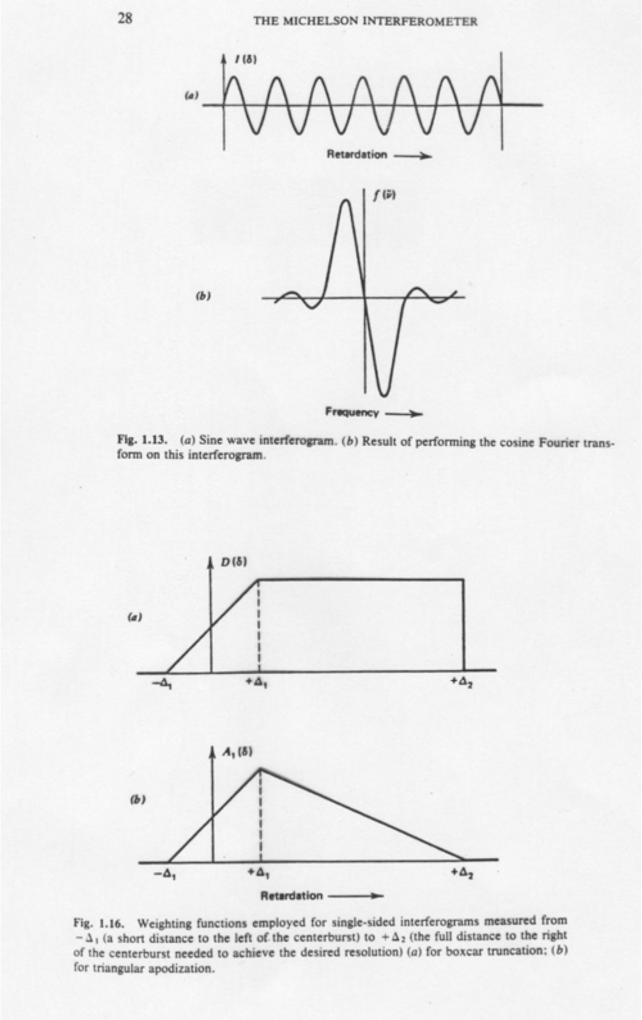
Fourier transform of the boxcar cutoff, known as the sinc function. Largest side lobe is 22 % of the main lobe amplitude. L = Optical Pathlength Difference.

Apodization
(French for
“cutting the feet off”:
convolution with
other functions



Several apodization functions (left) and the 'Instrumental Lineshape' produced by them (right). The cases *A - D* are commonly used in FT-IR.

Phase correction



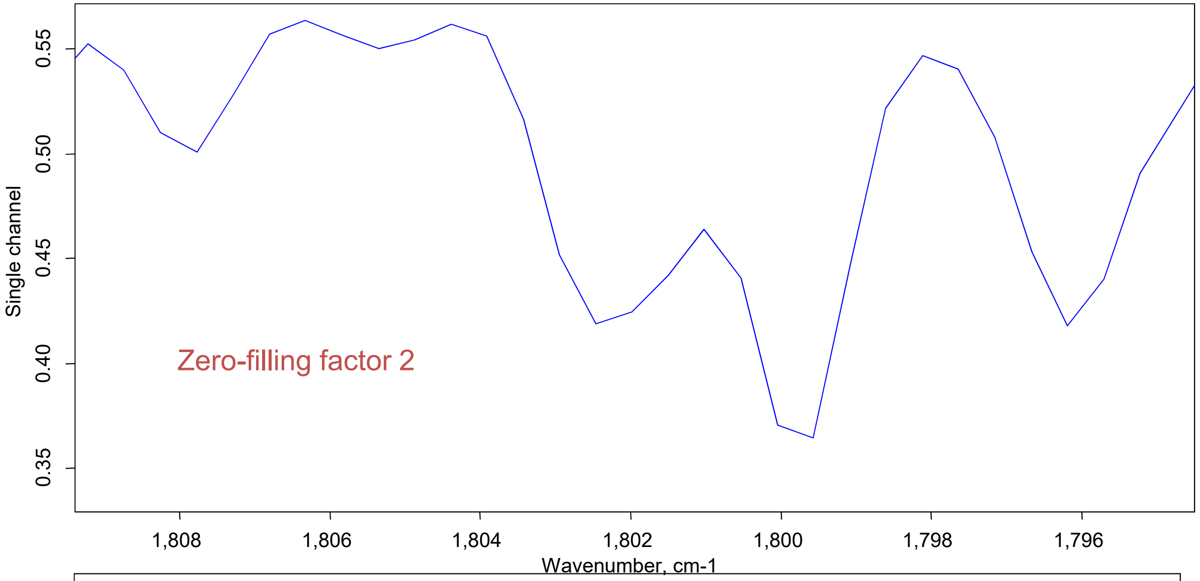
28 THE MICHELSON INTERFEROMETER

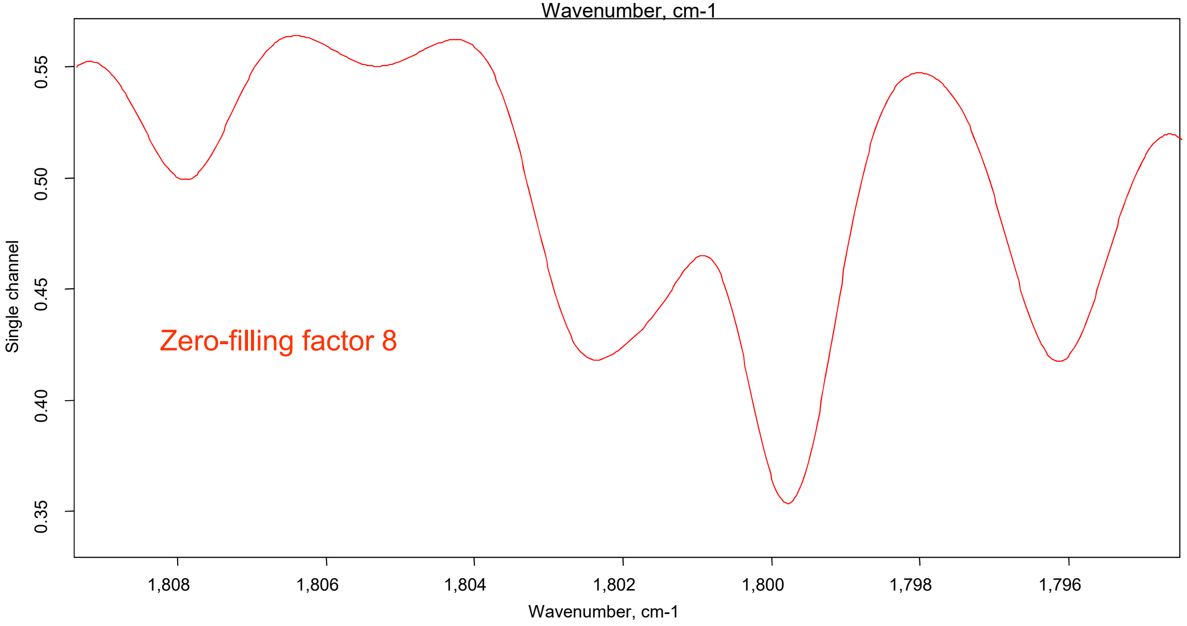
Fig. 1.13. (a) Sine wave interferogram. (b) Result of performing the cosine Fourier transform on this interferogram.

Fig. 1.16. Weighting functions employed for single-sided interferograms measured from $-\Delta_1$ (a short distance to the left of the centerburst) to $+\Delta_2$ (the full distance to the right of the centerburst needed to achieve the desired resolution) (a) for boxcar truncation; (b) for triangular apodization.

Interferogram contains sin(x) contributions
Complex Fourier transformation
Determination of phase at chosen frequencies
(real resolution decreases)

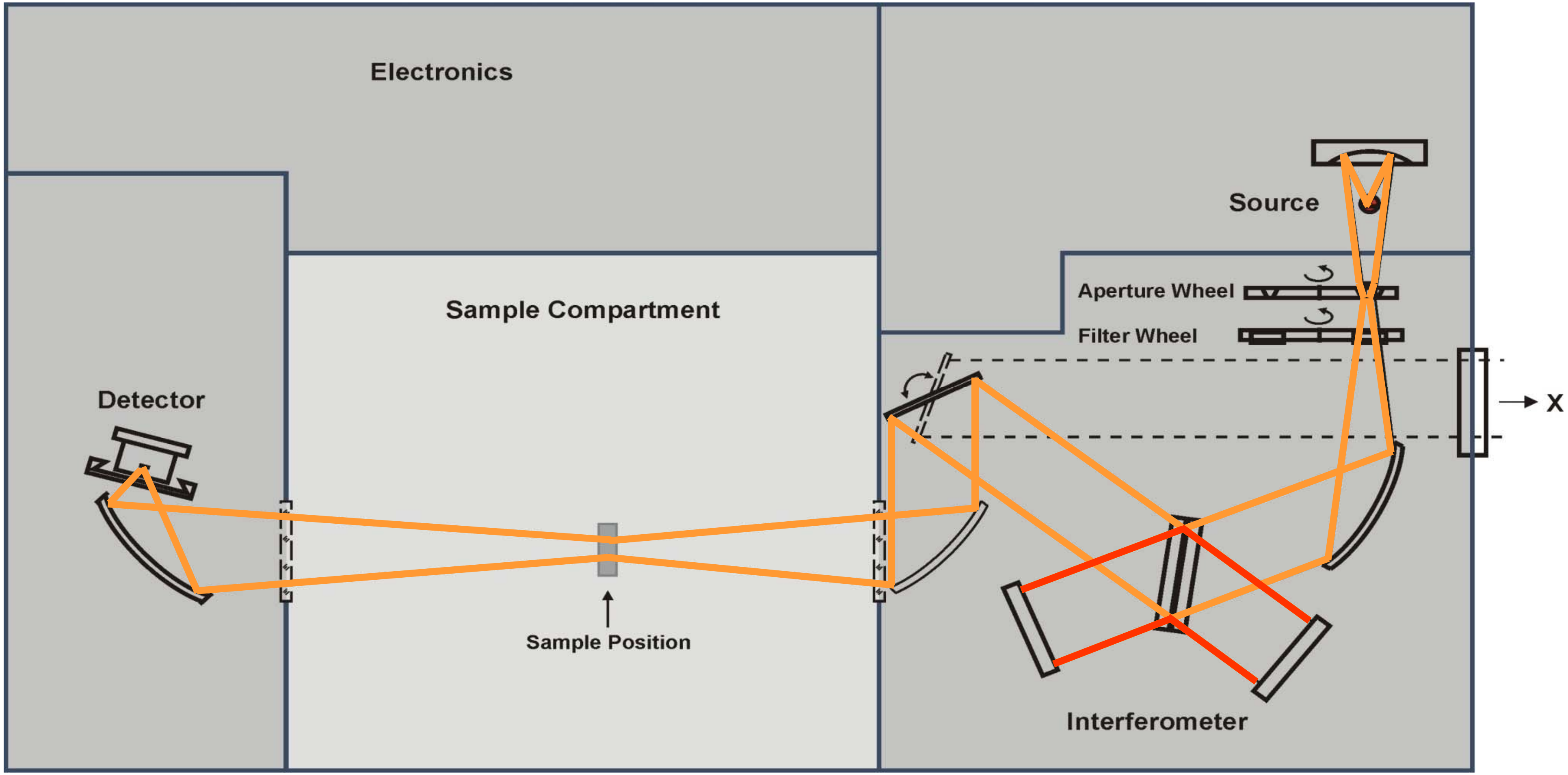
Zerofilling



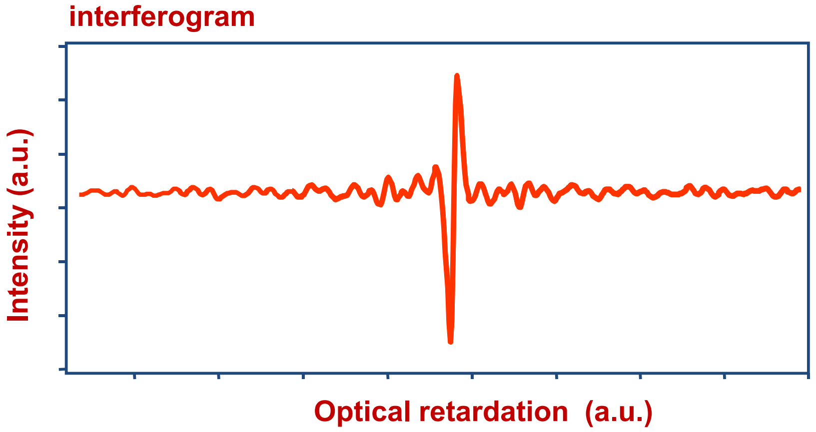


Adding zeroes to end of interferogram
“Spectrum-like” interpolation
Does not replace resolution!

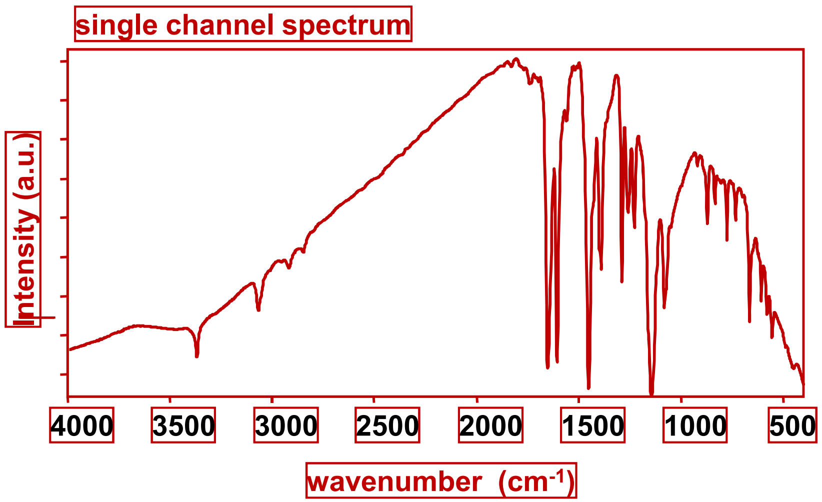
FTIR spectrometer

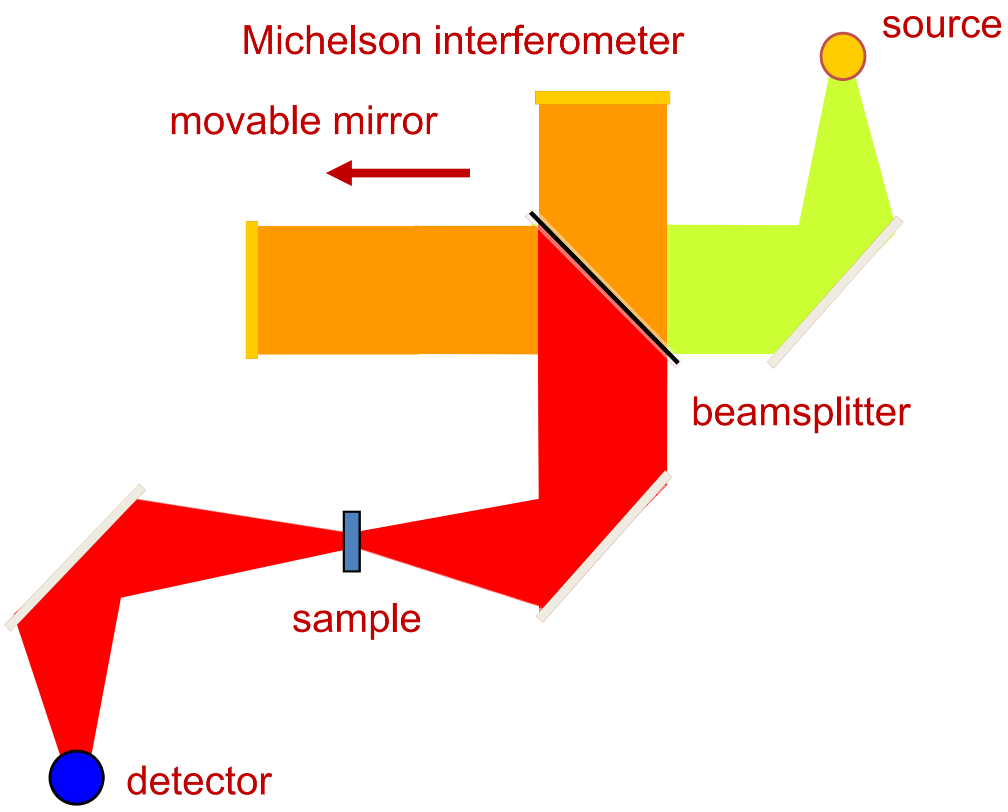


FTIR measurement

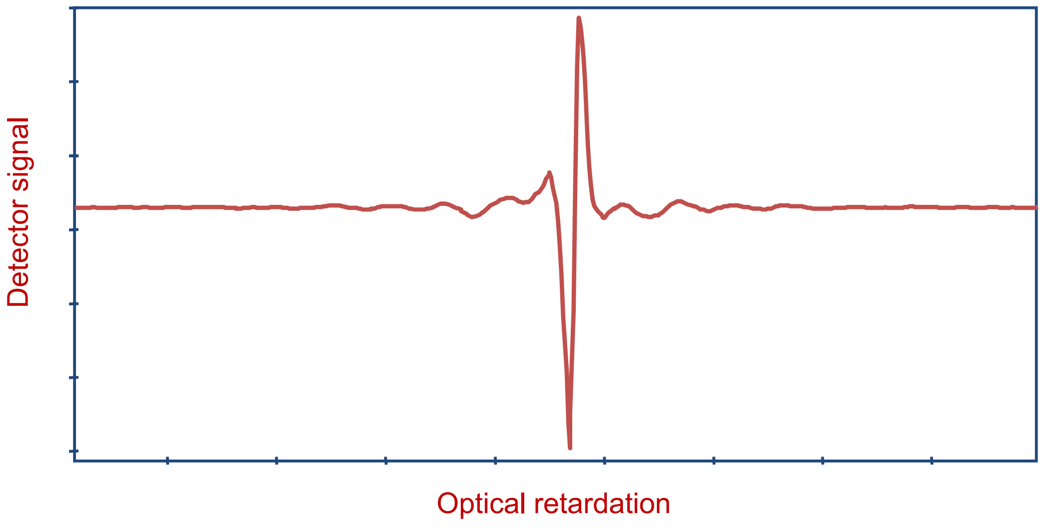


Fourier-Transformation

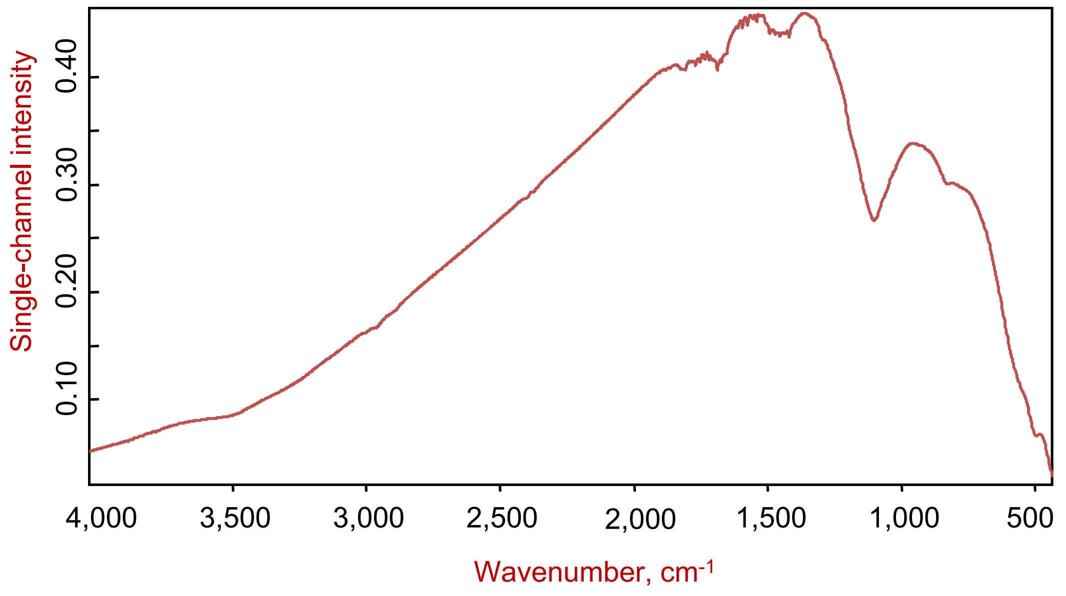




Reference spectrum

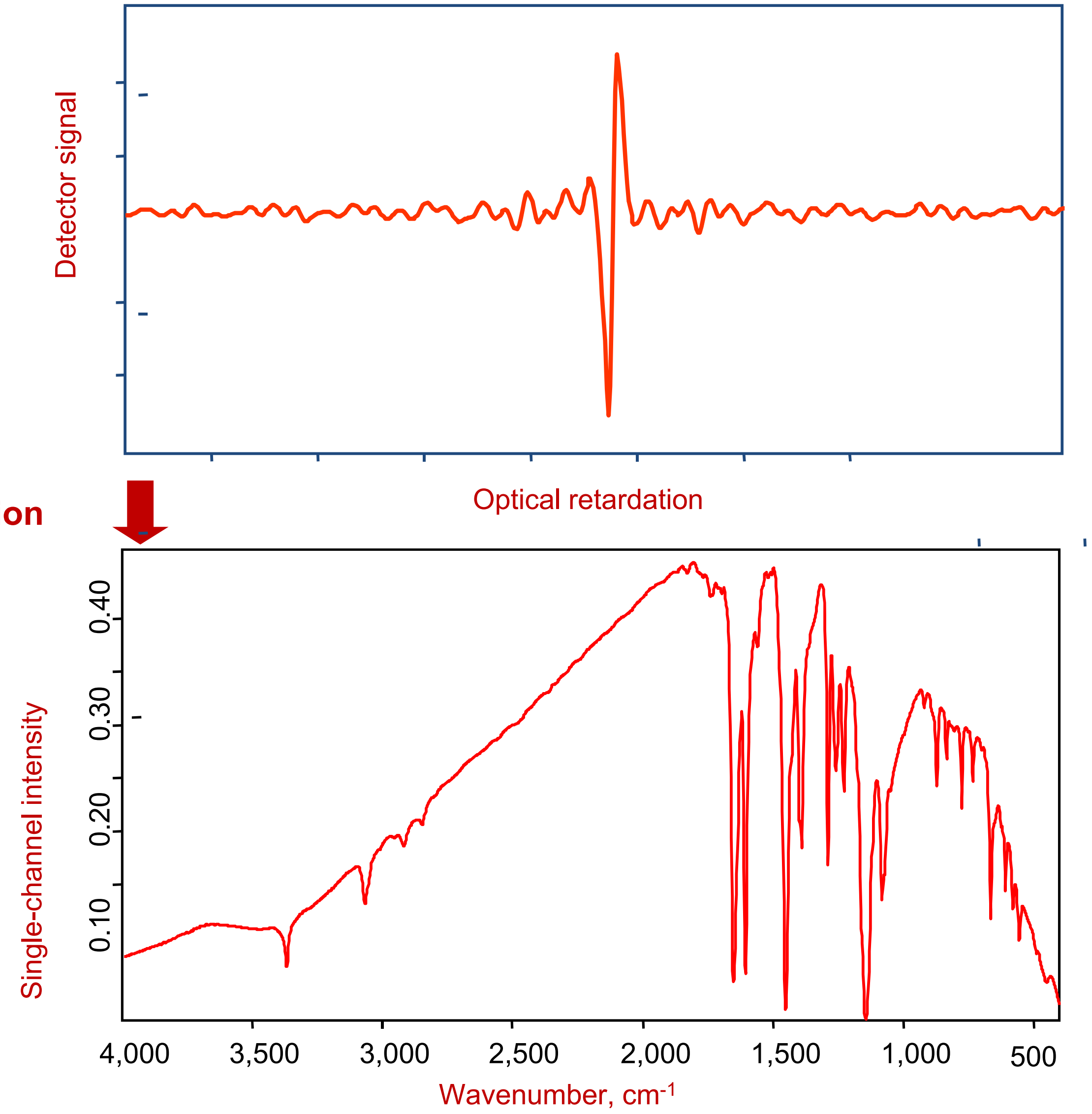


Fourier transformation

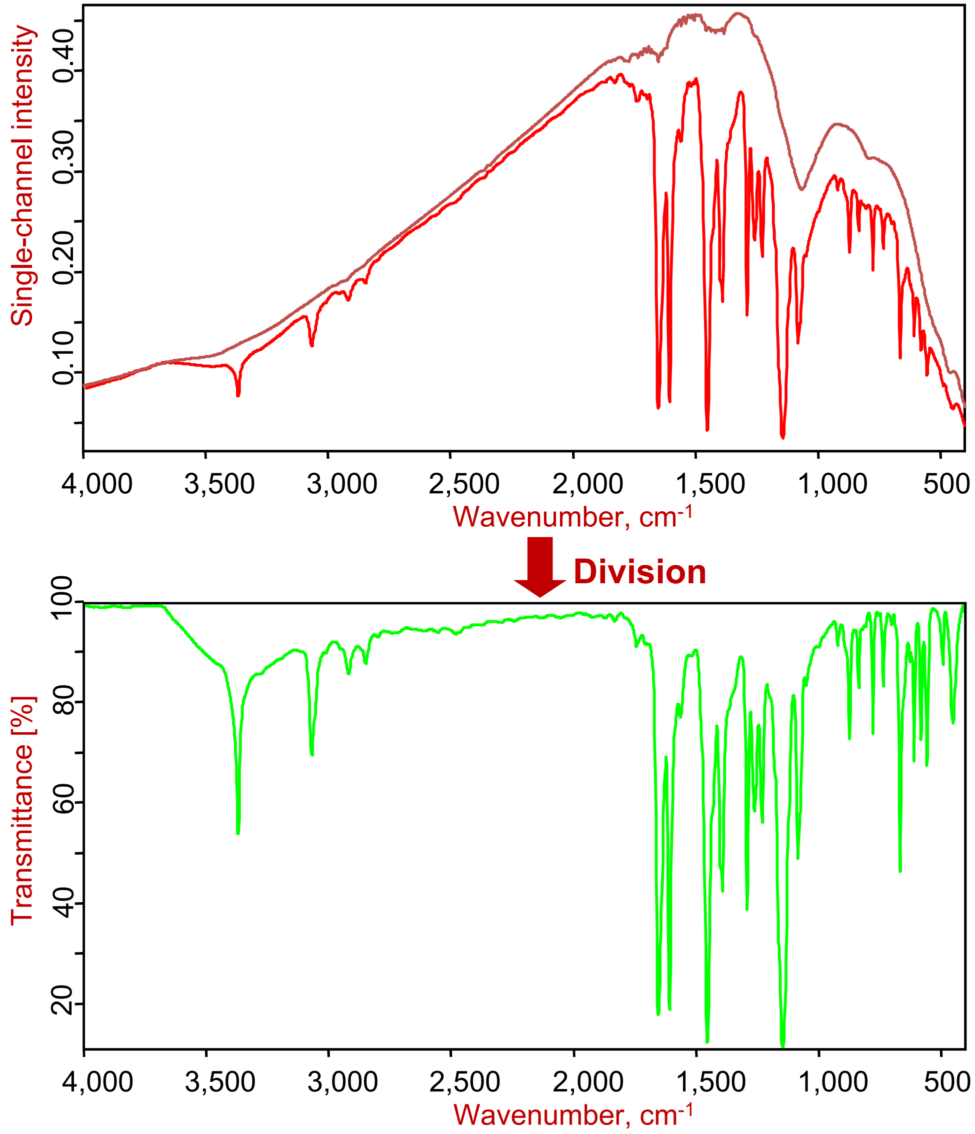


Sample spectrum

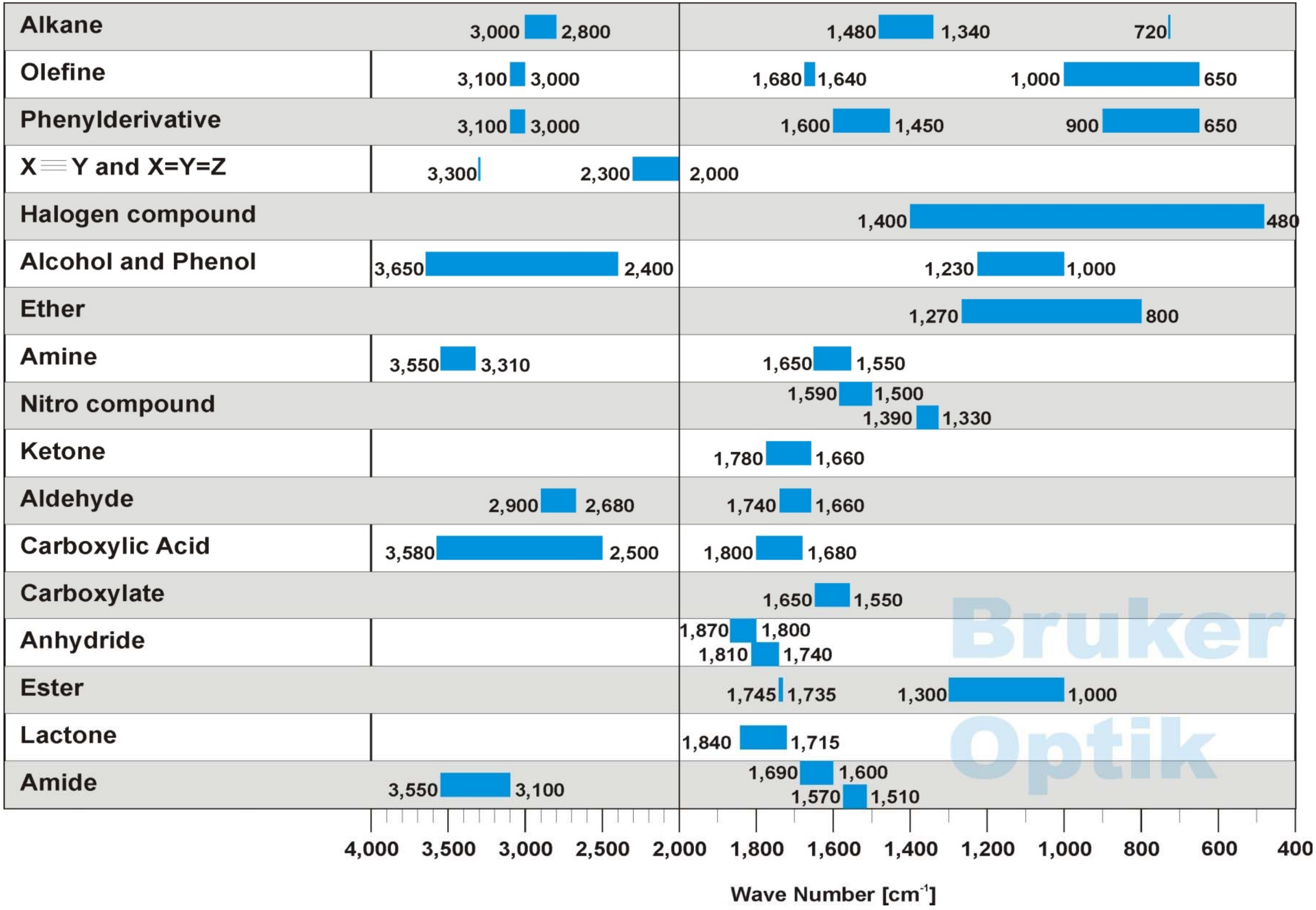
Fourier transformation



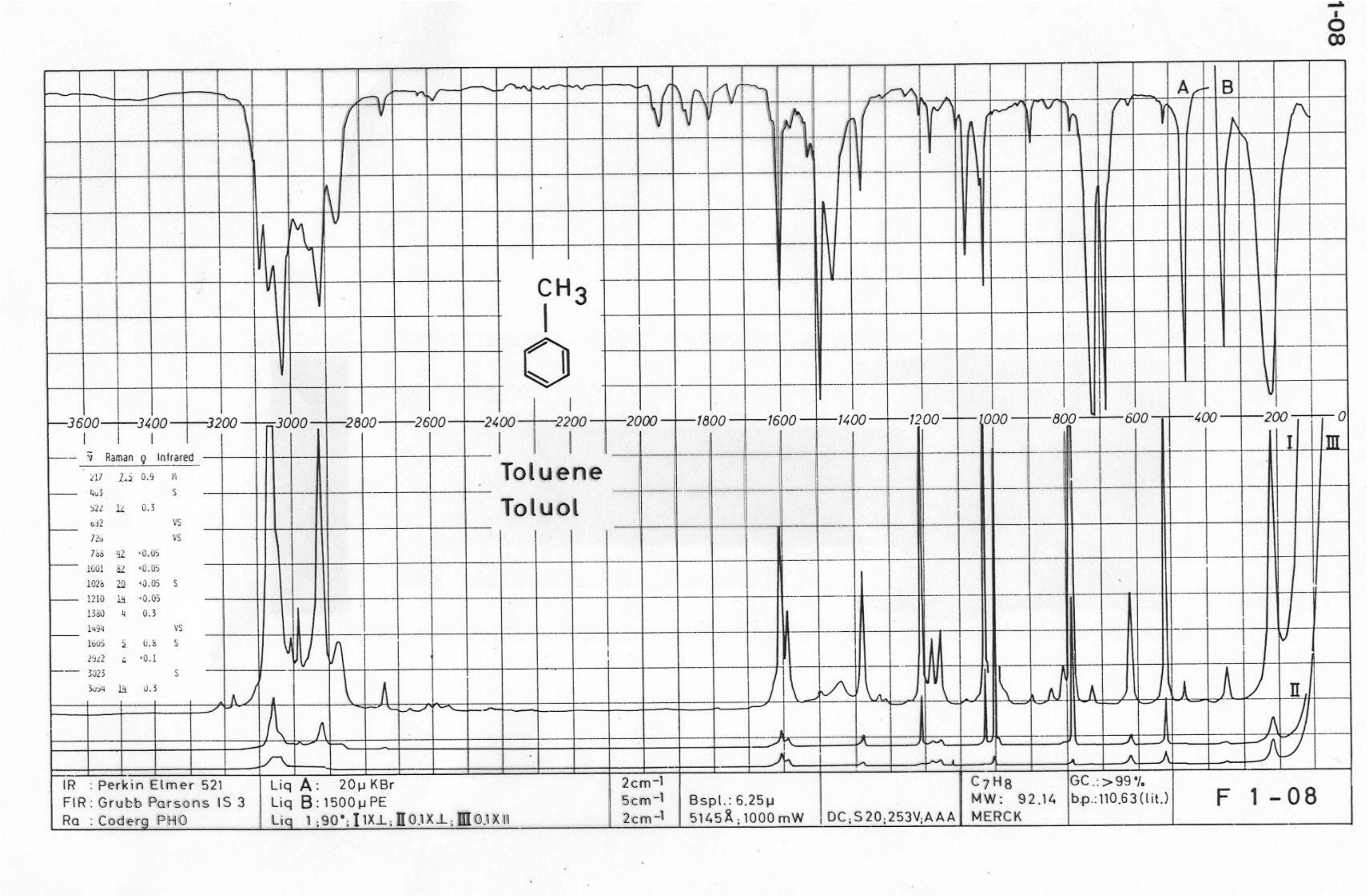
Transmission spectrum



Group frequencies



Typical infrared and Raman spectrum



$\tilde{\nu}$	Raman	ϱ	Infrared
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403			S
522	12	0.3	
692			VS
726			VS
768	42	<0.05	
1001	82	<0.05	
1026	20	<0.05	S
1210	14	<0.05	
1380	4	0.3	
1494			VS
1605	5	0.8	S
2922	6	<0.1	
3023			S
3054	14	0.3	

IR : Perkin Elmer 521 FIR: Grubb Parsons IS 3 Ra : Coderg PHO	Liq A: 20µ KBr Liq B: 1500µ PE Liq 1; 90°; I 1X⊥; II 0.1X⊥; III 0.1X∥	2cm⁻¹ 5cm⁻¹ 2cm⁻¹	Bspl.: 6.25µ 5145Å; 1000 mW	DC; S20; 253V; AAA	C_7H_8 MW: 92.14 MERCK	GC.: >99% b.p.: 110.63 (lit.)	F 1-08

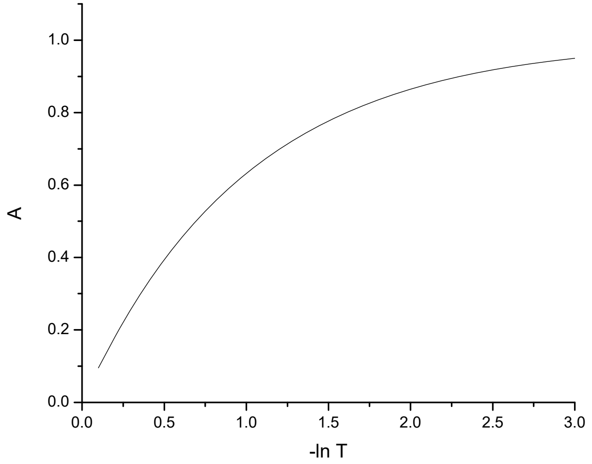
B. Schrader: Raman/Infrared Atlas of Organic Compounds. VCH Publishers, 1989.

Absorption spectroscopy

if R<<1, $T = \frac{I_T}{I_0} = e^{-\alpha d}$ $A \cong -\log T = \alpha d = \varepsilon c d$ Beer's law
log, ln?

$[\alpha] = cm^{-1}$ $[\varepsilon] = 1/cm/konc.$ ↓ specific (molar) absorption coefficient

Concentration can be determined:
known coefficient
calibration



Instruments

FIR/MIR

MIR/NIR

Near field/SNOM

Take-home message

- vibrational spectra: vibrations of atoms, damped harmonic oscillator with reduced mass $m_r = \frac{m_+ m_-}{m_+ + m_-}$ and relative displacement $r = (u_+ - u_-)$
- eigenfrequency of oscillator $\omega_0 = \sqrt{\frac{\kappa}{m_r}}$ κ interatomic interaction strength
- ionic crystals: Reststrahlen region with high reflectivity around ω_0
- longitudinal excitation if $\varepsilon_{rel}(\omega_l) = 0$, $\omega_l^2 = \omega_0^2 + \frac{\Omega^2}{\varepsilon_\infty}$, LO-TO splitting measure of intensity
- FTIR spectroscopy: Michelson interferometer, $I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi \nu^* x) dx$
- throughput and multiplex advantage
- interferogram of monochromatic source: cosine function, of continuous source: peaked
- FTIR spectrometer: source – beamsplitter – sample – detector
- measurement: interferogram → single-beam spectrum → transmission spectrum
- resolution depends on mirror pathlength, frequency range on sampling interval
- signal evaluation from interferogram: apodization, phase correction, zerofilling
- infrared spectral analysis: qualitative (group frequencies), quantitative (Beer’s law)

Összefoglalás

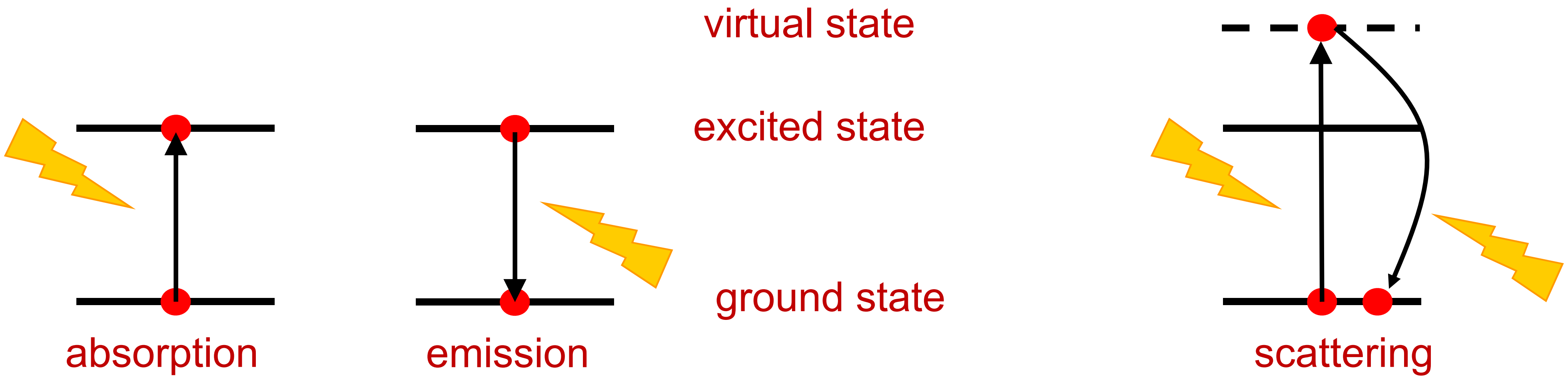
- rezgési spektrumok: atomok rezgései, csillapított harmonikus oszcillátor, redukált tömeg $m_r = \frac{m_+ m_-}{m_+ + m_-}$, relatív elmozdulás $r = (u_+ - u_-)$
- sajátfrekvencia $\omega_0 = \sqrt{\frac{\kappa}{m_r}}$ κ az atomok közti kölcsönhatás erőssége
- ionos kristályok: Reststrahlen tartomány ω_0 körül nagy reflexió
- longitudinális gerjesztés $\varepsilon_{rel}(\omega_l) = 0$, $\omega_l^2 = \omega_0^2 + \frac{\Omega^2}{\varepsilon_\infty}$, LO-TO felhasadás intenzitást mér
- FTIR spektroszkópia: Michelson interferométer, $I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi\nu^* x) dx$
- átbocsátás és multiplex előny
- monokromatikus forrás interferogramja: cosinusfüggvény, folytonos forrásé: egy csúcs
- FTIR spektrométer: forrás – nyalábosztó – mintatér – detektor
- mérés: interferogram → egysugaras spektrum → transzmissziós spektrum
- a felbontást a tükörúthossz, a frekvenciatartományt a mintavétel gyakorisága határozza meg
- jelfeldolgozás: interferogram – apodizáció – fáziskorrekció - zerofilling
- infravörös analízis: kvalitatív (csoportfrekvenciák), kvantitatív (Lambert - Beer törvény)

Raman spectroscopy

Raman scattering: history

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

Nobel prize for physics 1930



virtual state

excited state

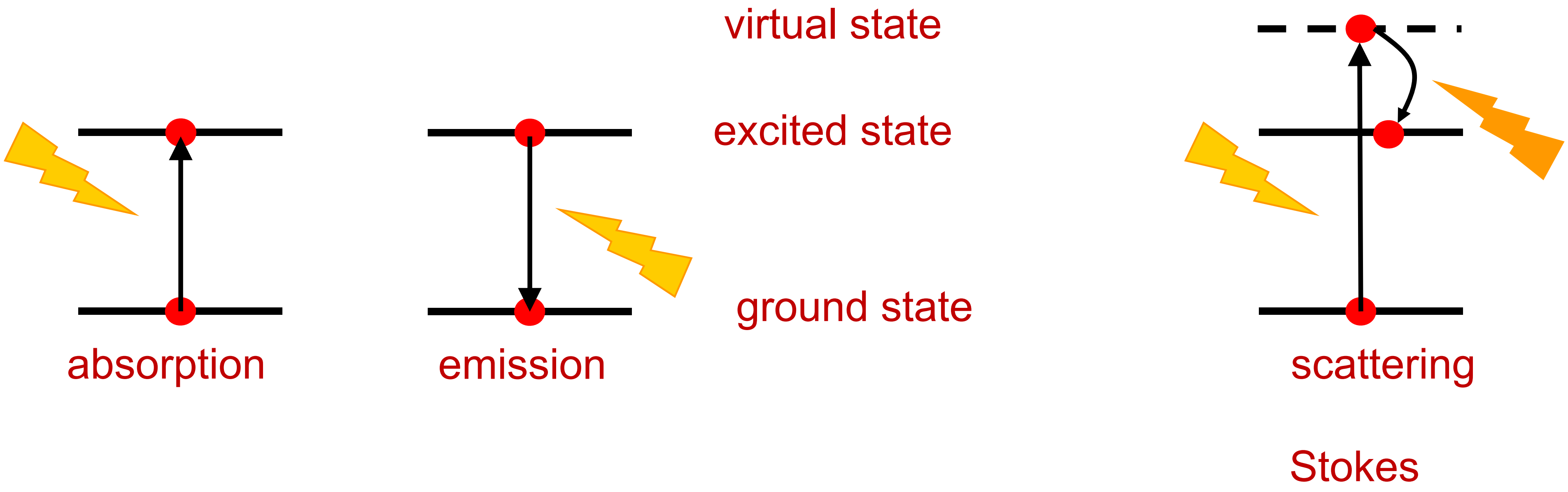
ground state

absorption

emission

scattering

Rayleigh scattering



virtual state

excited state

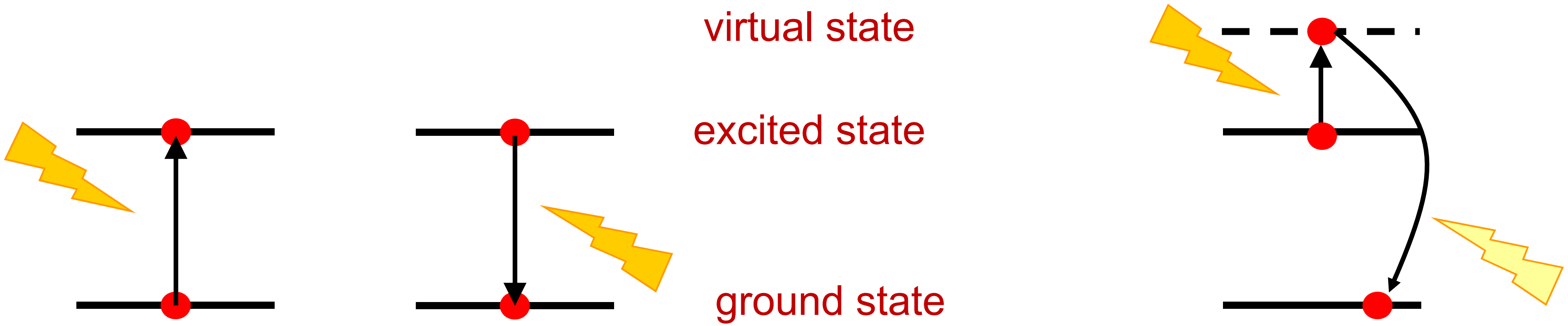
ground state

absorption

emission

scattering

Stokes



virtual state

excited state

ground state

absorption

emission

scattering

anti-Stokes

Infrared absorption and Raman scattering

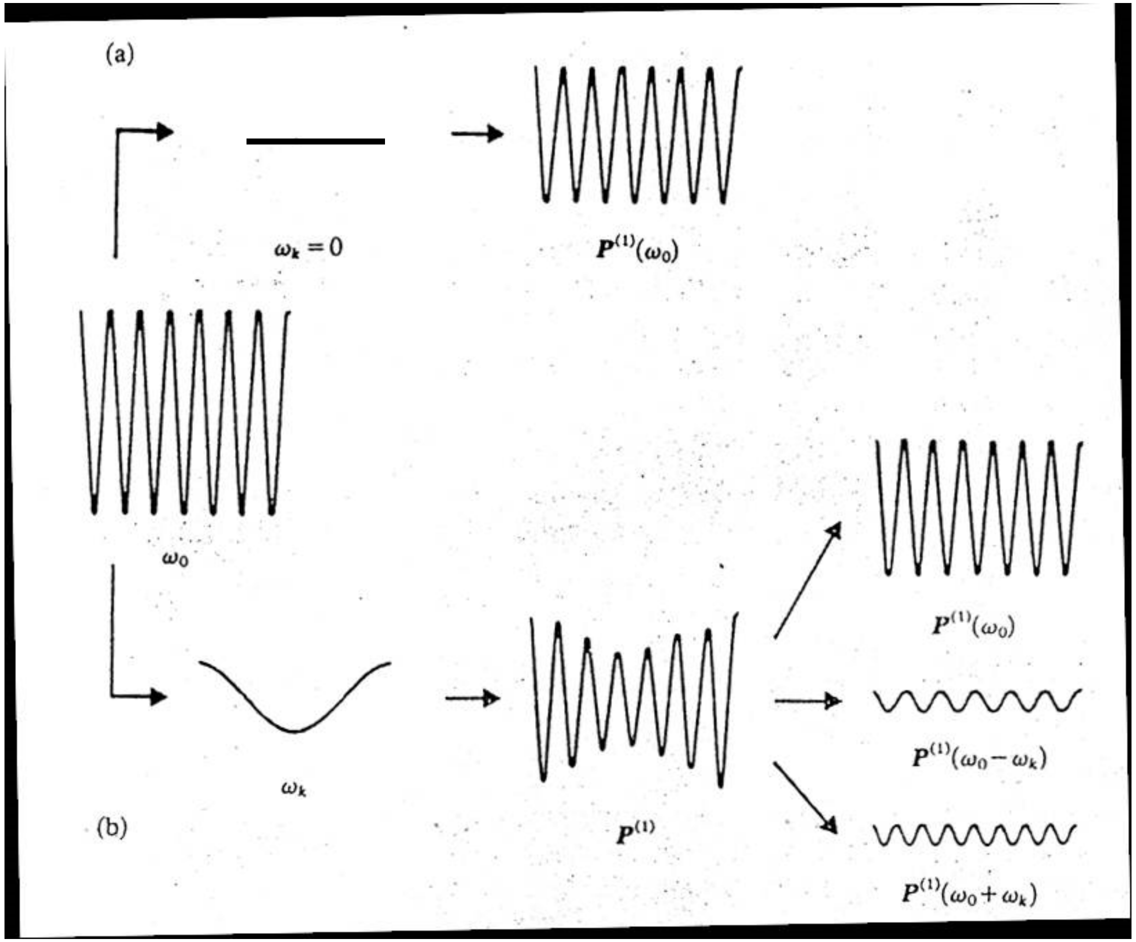
IR: $\mu = \mu_0 + (\Delta\mu)\cos\omega_0 t = \mu_0 + \frac{\partial\mu}{\partial r} r \cos\omega_0 t$ change of dipole moment during the vibration

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



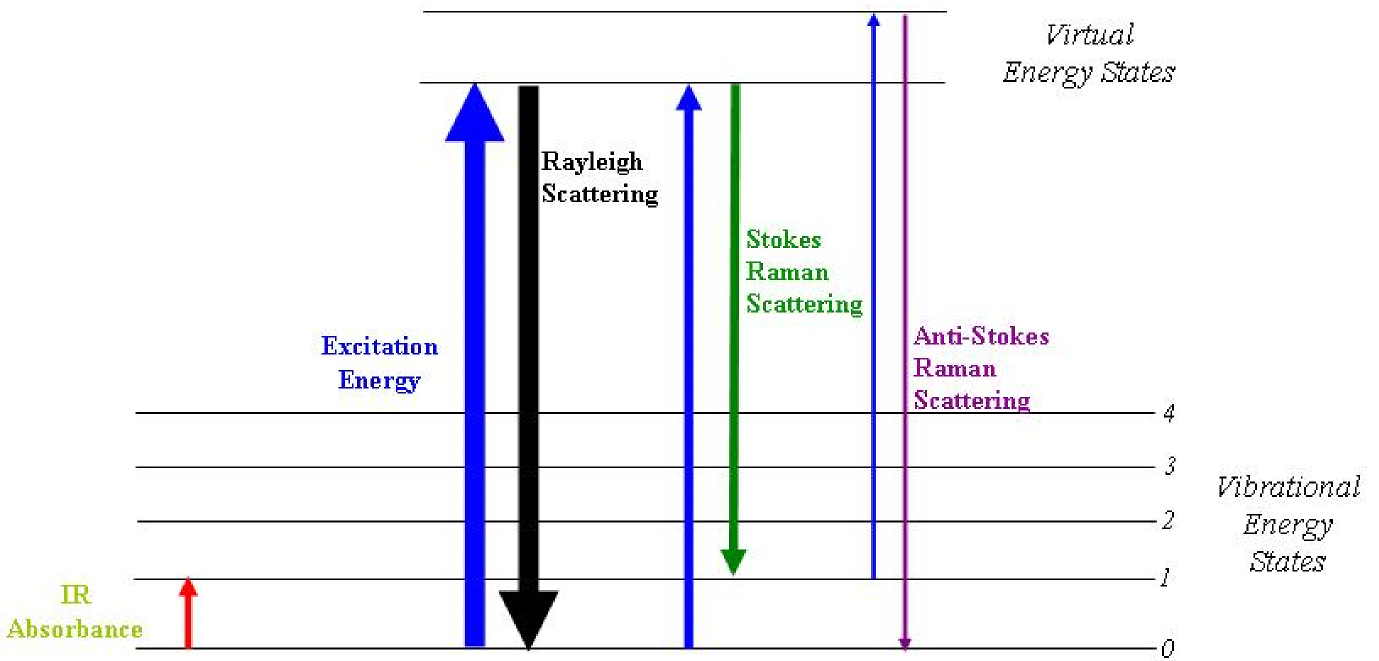
D. A. Long: Raman spectroscopy
McGraw-Hill, 1977

Rayleigh

Stokes

anti-Stokes

The Raman effect – quantum picture

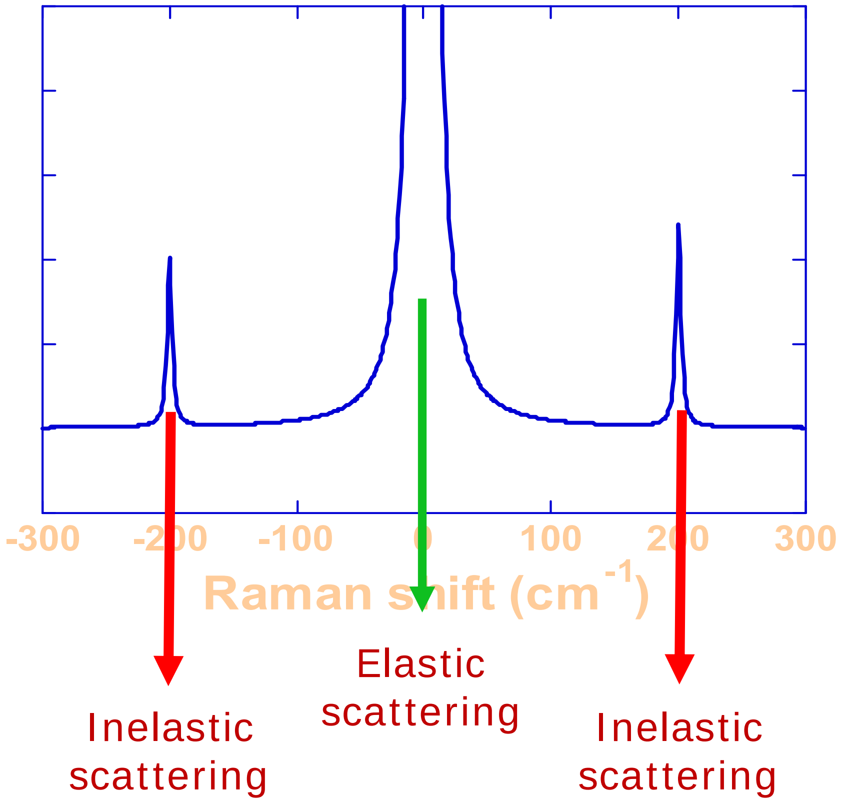


Álmosdi Péter, BME 2008
Source: Wikipedia

Raman spectroscopy

Light scattering by monochromatic light

Spectrum of scattered light relative to the exciting light



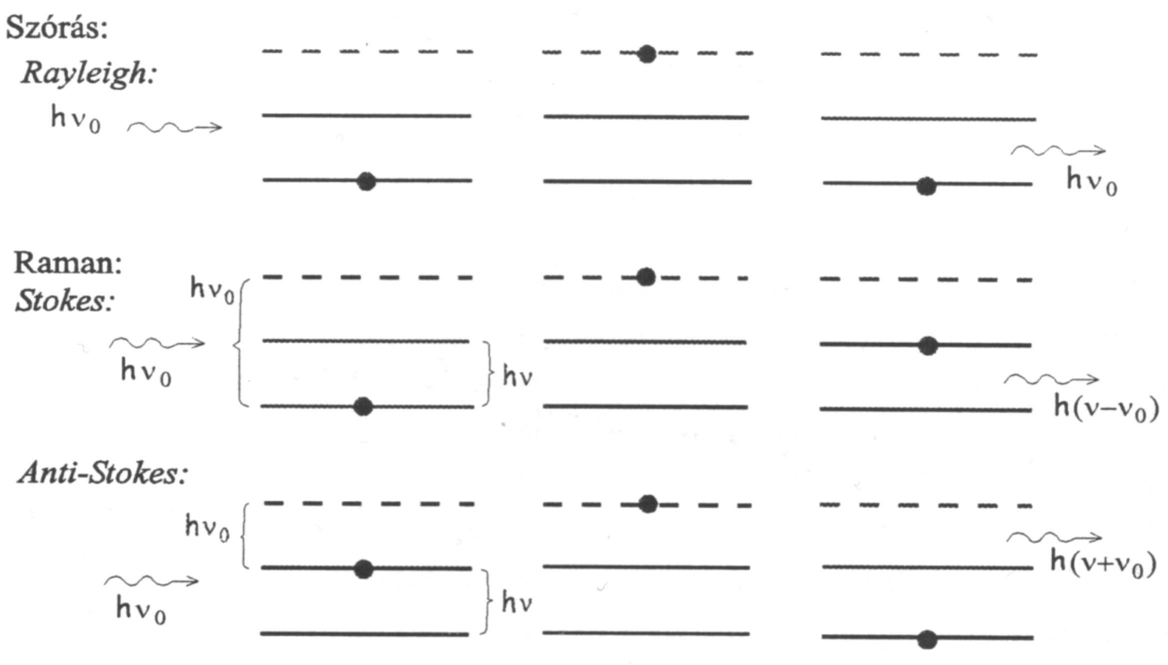
Inelastic scattering

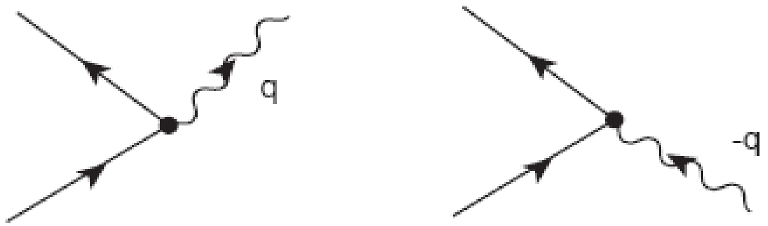
Elastic scattering

Inelastic scattering

- 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





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

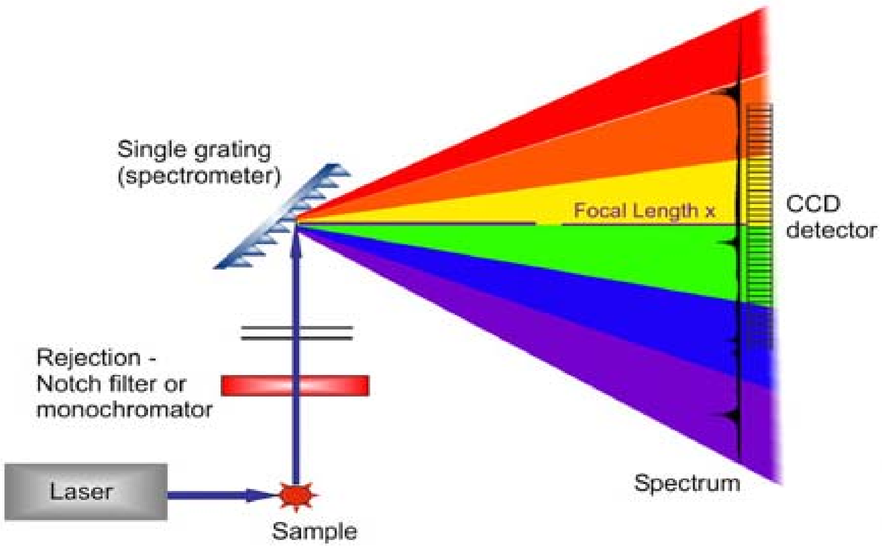
$\mathbf{k}_L, \mathbf{k}_S \approx 10^4\ \mathrm{cm}^{-1}$ $\Rightarrow$ $\mathbf{k}_L, \mathbf{k}_S << \mathbf{q}$

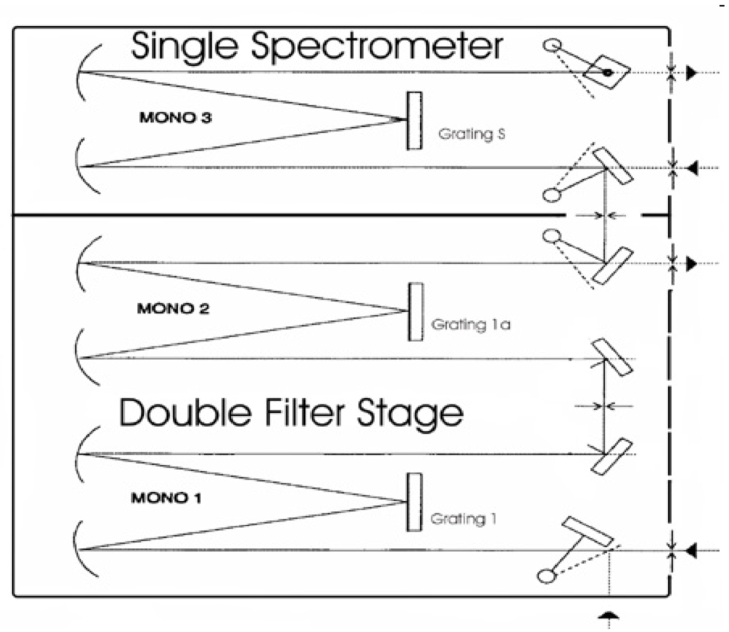
$\mathbf{q} \approx 10^{10}\ \mathrm{cm}^{-1}$

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

Álmosdi Péter, BME 2008
Source: Wikipedia

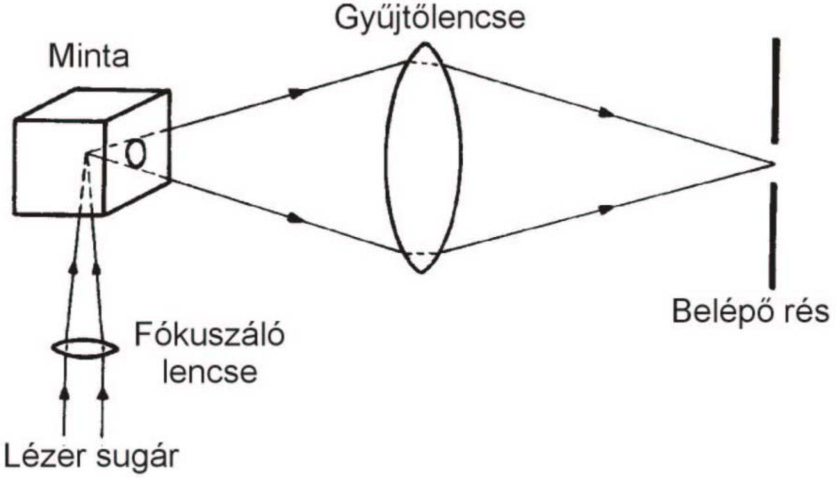
Experimental setup



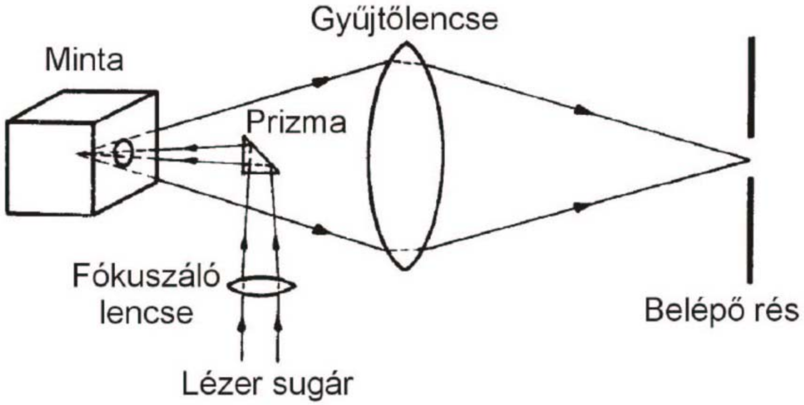


Excitation: visible, monochromatic light (laser) ~ 10^4 cm^{-1}
Frequency difference: infrared region, resolution: ~ 1 cm^{-1}
Resolution of monochromator critical!

Experimental arrangements



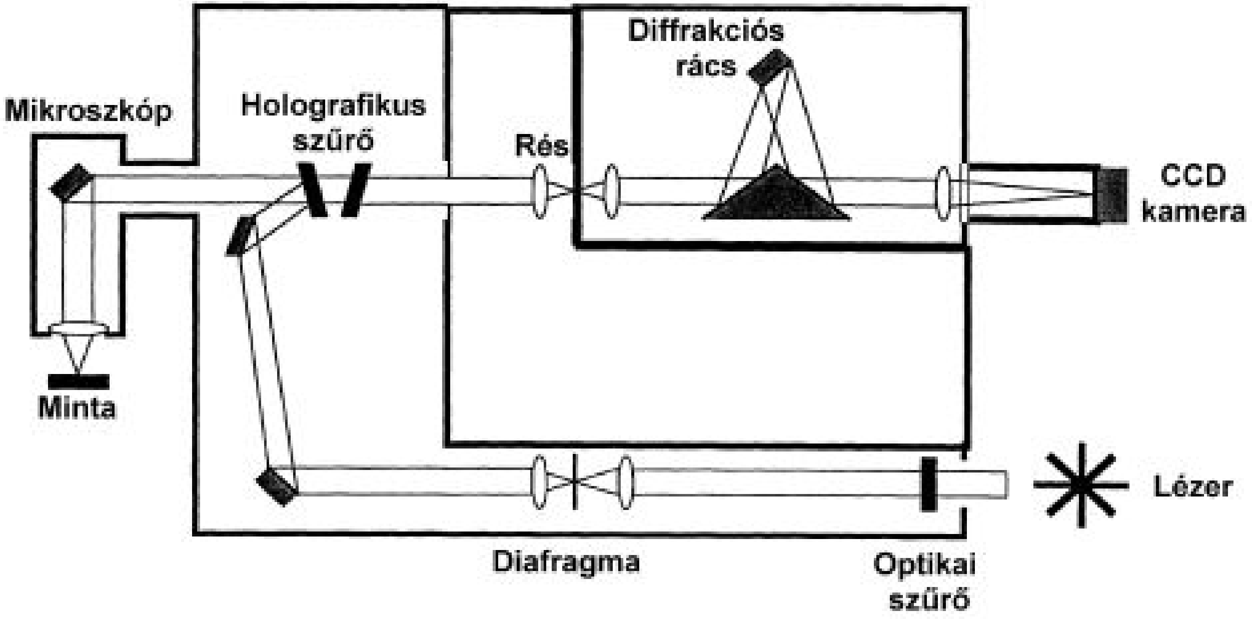
3.4a. ábra. A 90°-os gerjesztési elrendezésû mintatér.



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

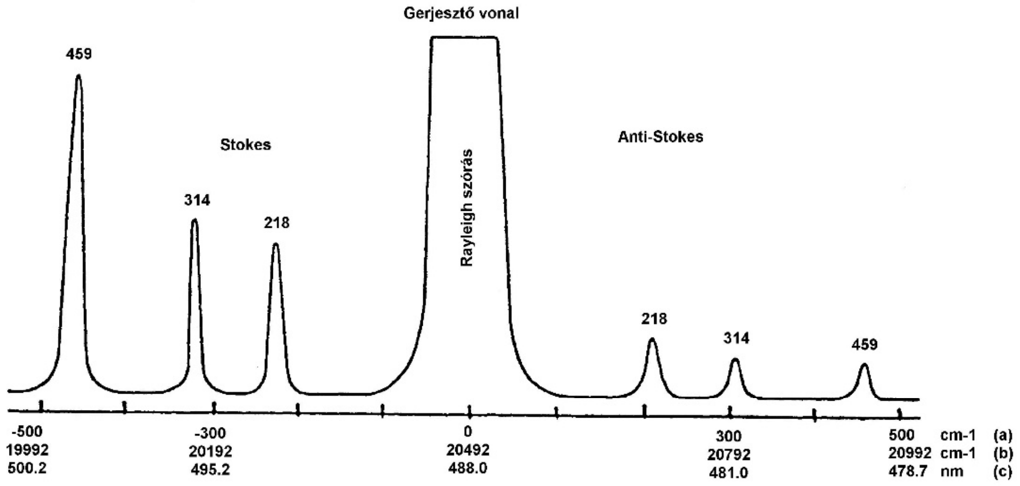
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

Raman microscope



3.11. Diódasoros detektorral működő Raman mikroszkóp.

Raman spectrum of CCl_4



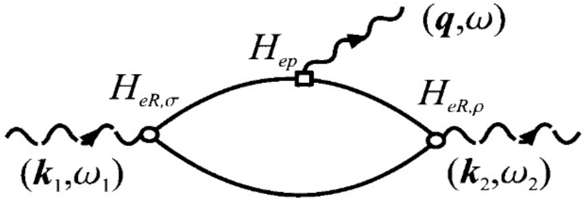
3.2. ábra. A CCl_4 folyadék Raman színképe a gerjesztõ vonal (Ar-ion lézer 488,0 nm) mindkét oldalán.

(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)

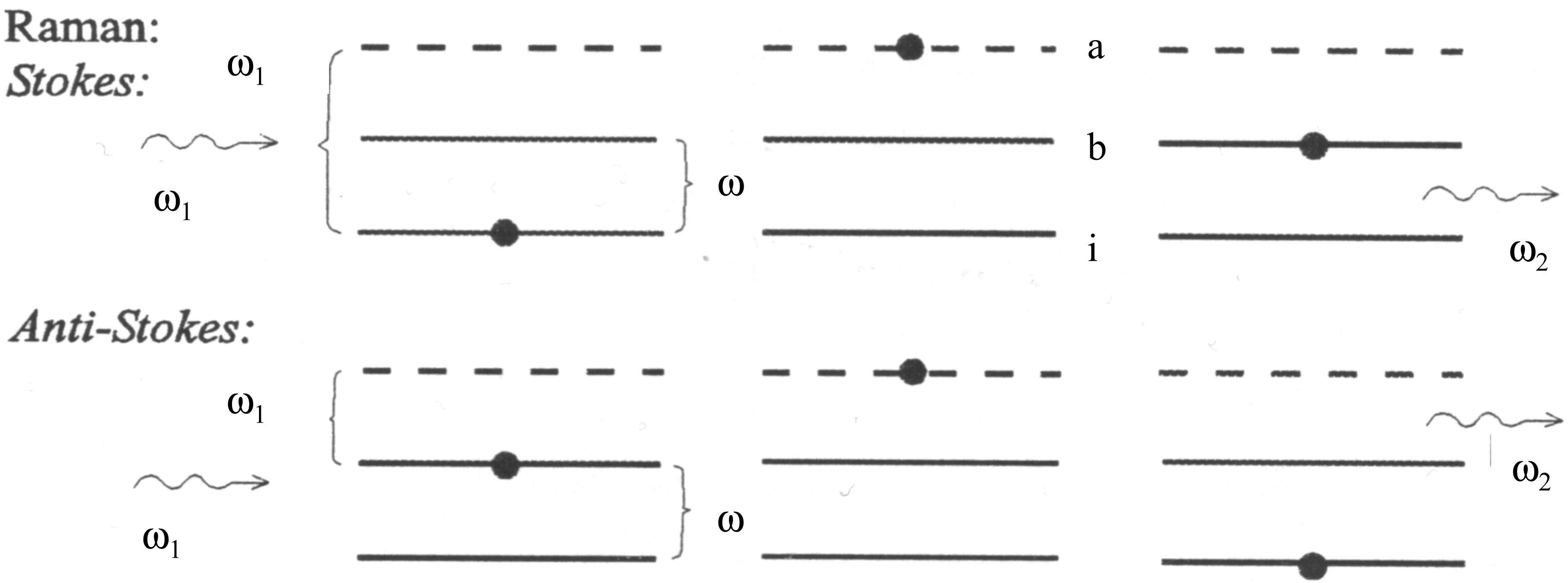
Mink János: Az infravörös és Raman spektroszkópia alapjai. Veszprémi Egyetem Analitikai Kémiai Tanszék

The Raman effect



Stokes scattering:

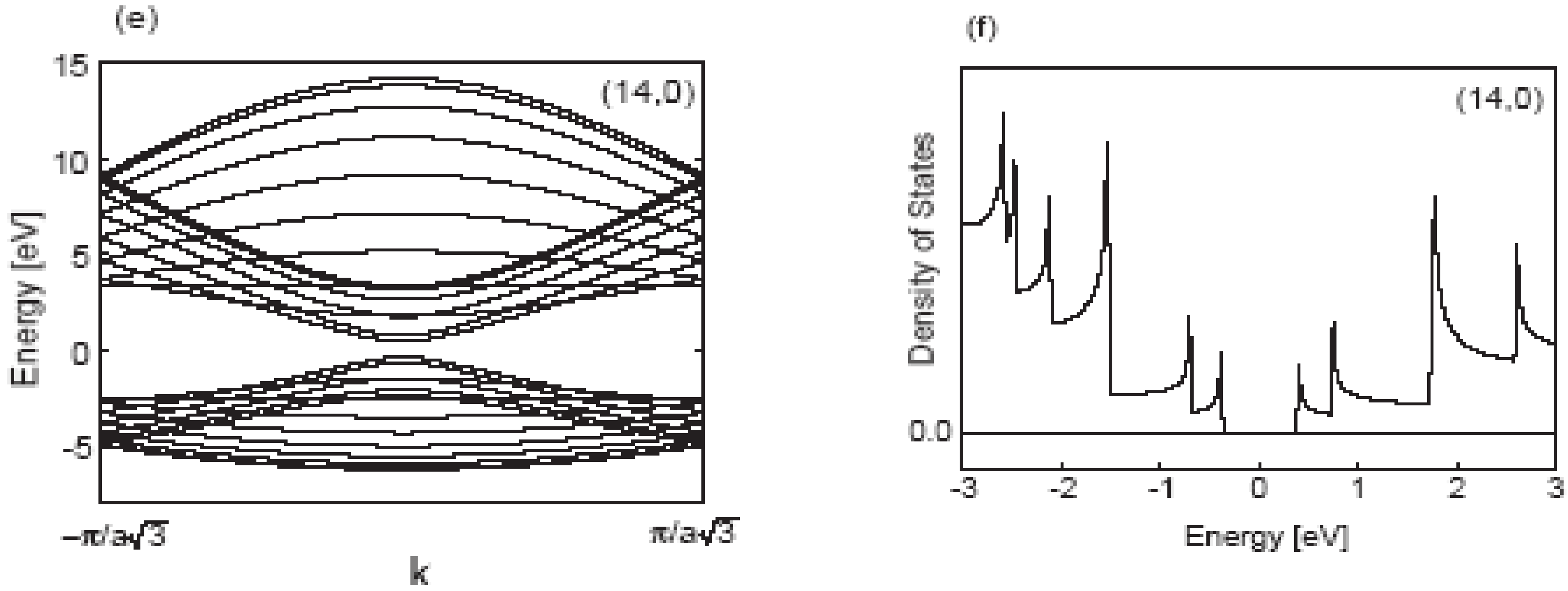
$$K_{2f,10} = \sum_{a,b} \frac{\langle \omega_2, f, i \,|\, H_{eR,\rho} \,|\, 0, f, b \rangle \langle 0, f, b \,|\, H_{ep} \,|\, 0, 0, a \rangle \langle 0, 0, a \,|\, H_{eR,\sigma} \,|\, \omega_1, 0, i \rangle}{(E_1 - E^e_{ai} - i\gamma)(E_1 - \hbar\omega - E^e_{bi} - i\gamma)}$$



Resonant Raman scattering

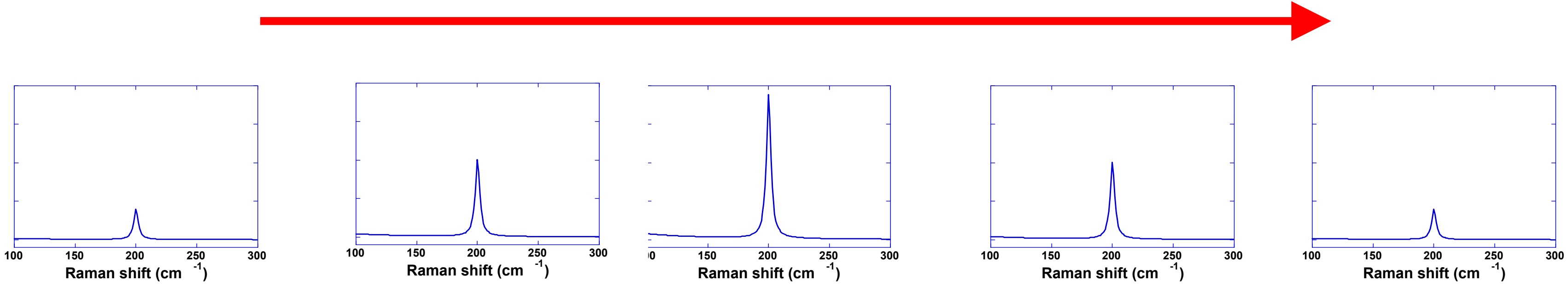
If the energy of the exciting laser approaches the energy of a real transition in the medium, the intensity of the Raman scattering increases by orders of magnitude. This is the **resonant Raman effect.**

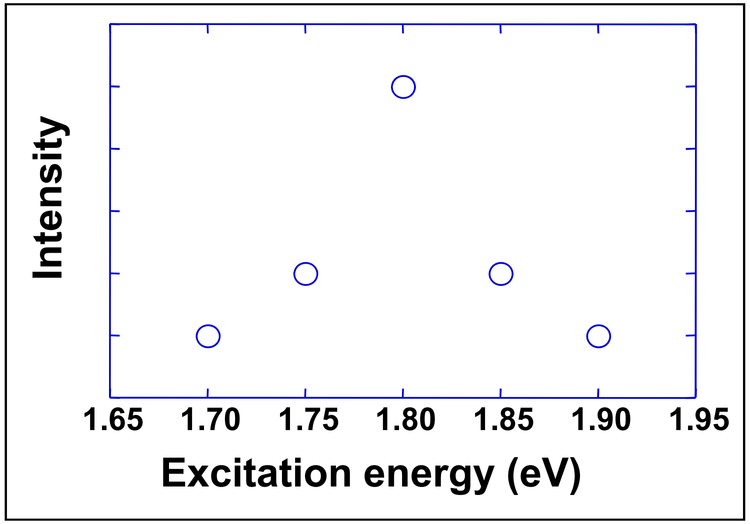
Resonant Raman scattering is the strongest close to maxima in the density of states.

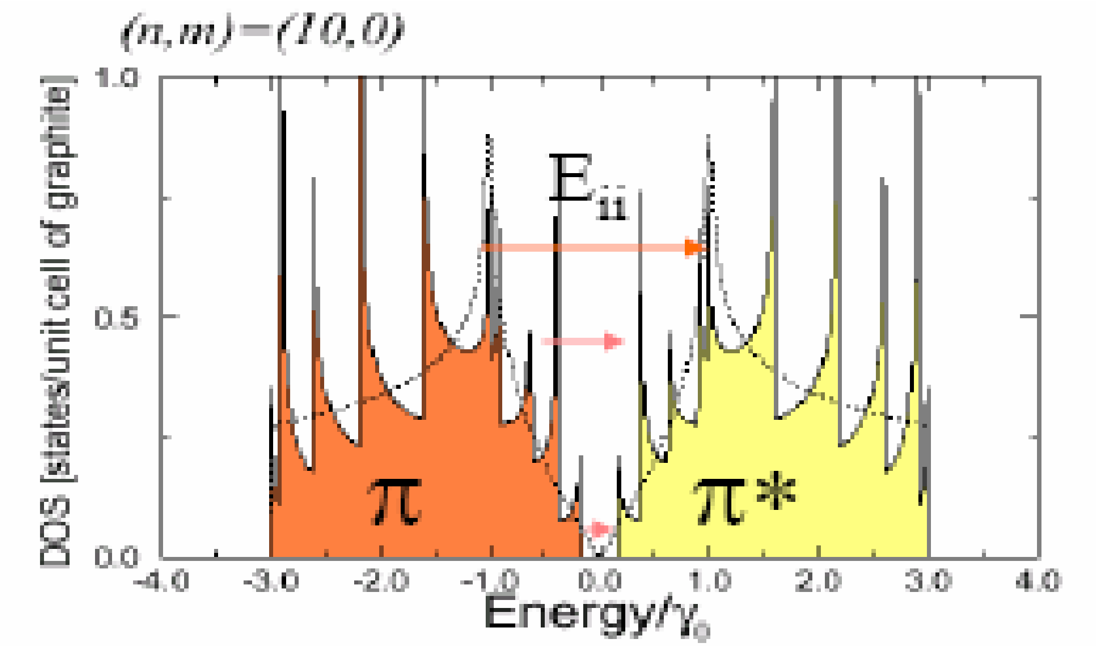


Resonant Raman excitation profile

Excitation energy

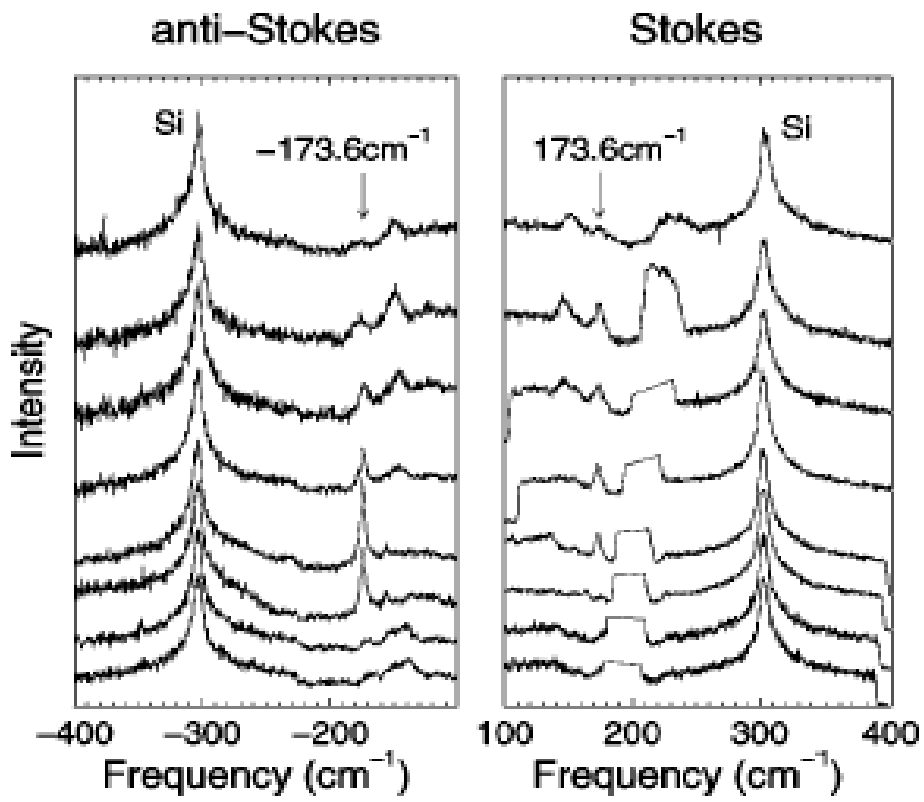




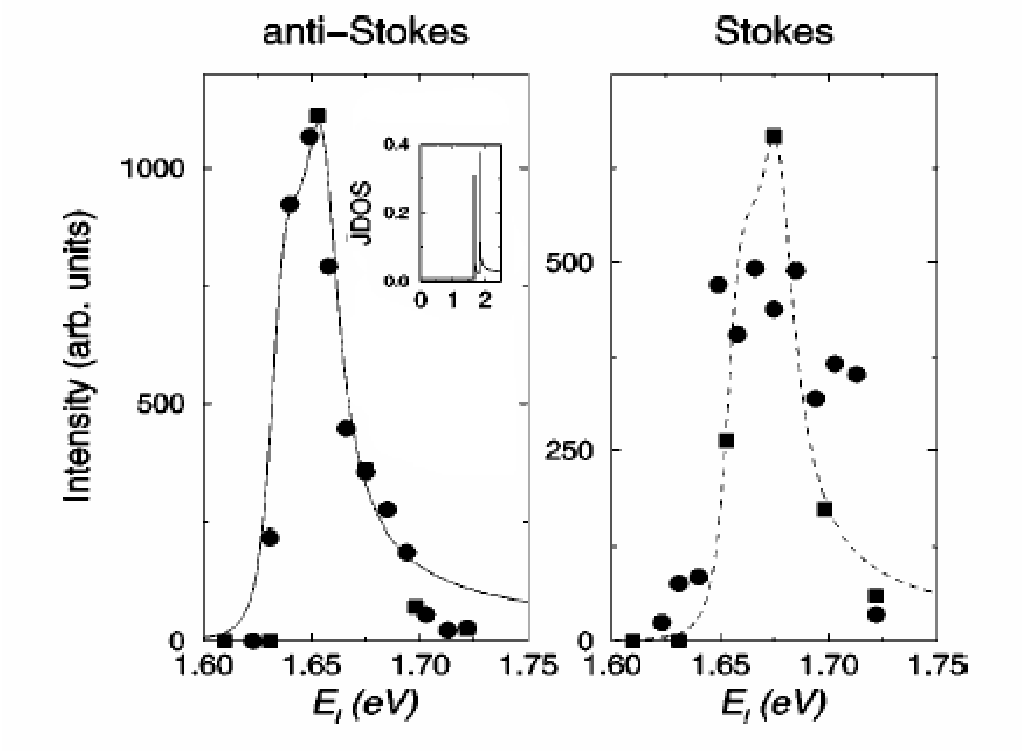


Excitation profile: example

Excitation: 1,623 - 1,722 eV



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

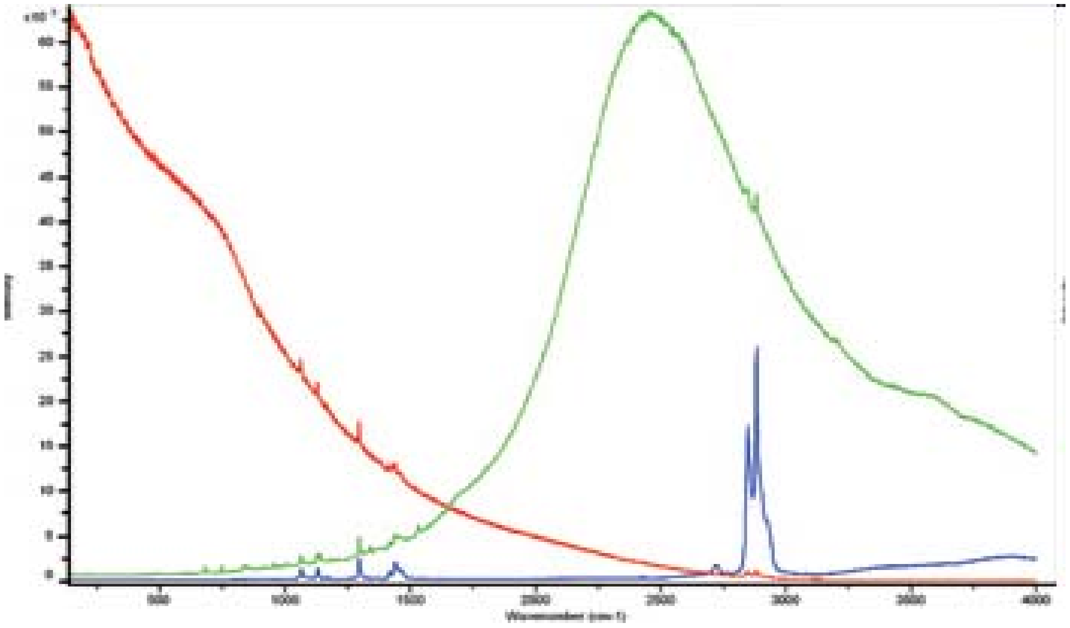


A.Jorio et al.
Phys. Rev. B 63 (2001) 245416

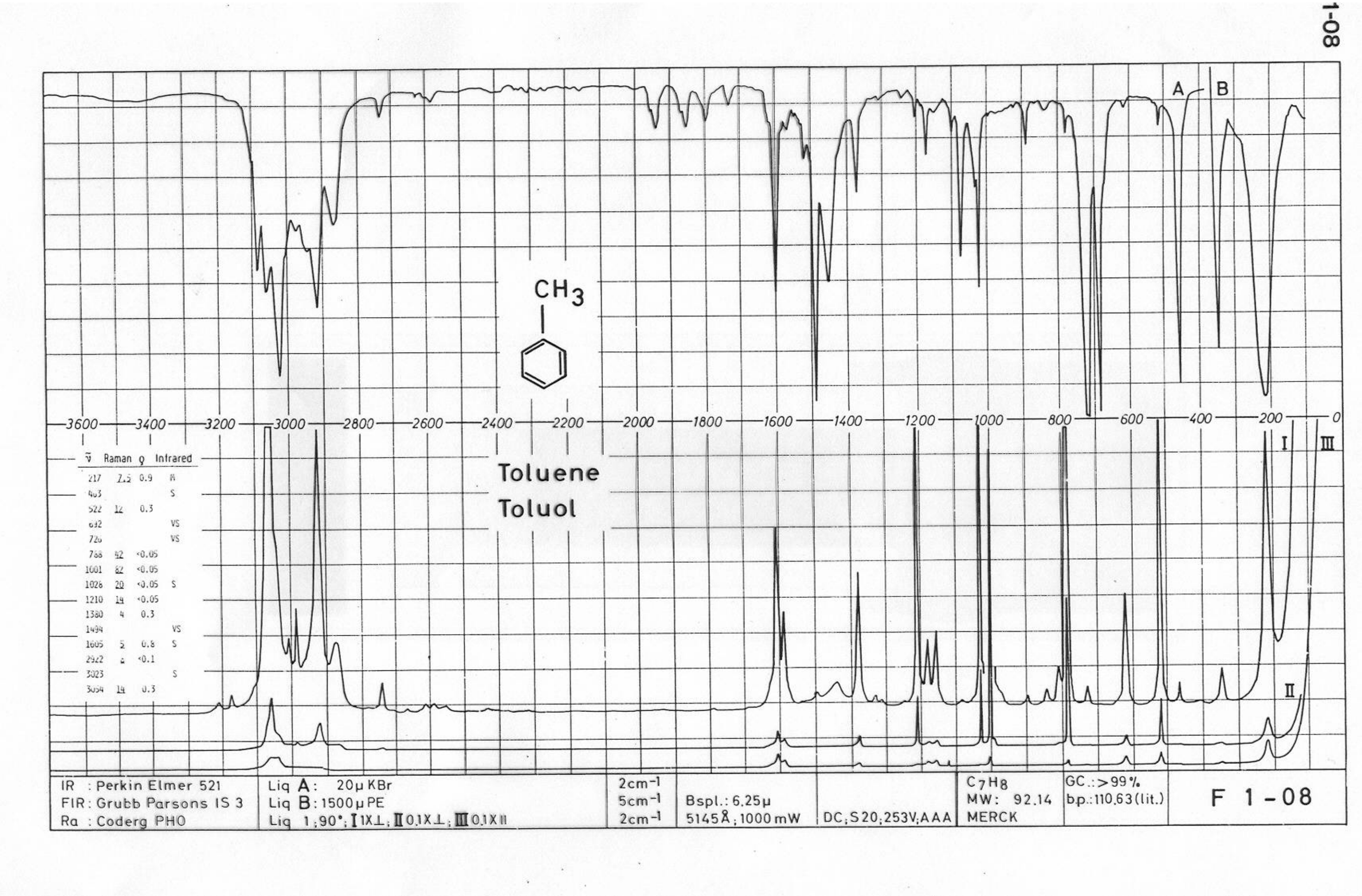
Veres Miklós, MTA Wigner FK

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



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3023			S
3054	14	0.3	

IR : Perkin Elmer 521
FIR: Grubb Parsons IS 3
Ra : Coderg PHO

Liq A: 20µ KBr
Liq B: 1500µ PE
Liq 1;90°; I 1X⊥; II 0,1X⊥; III 0,1X∥

2cm⁻¹
5cm⁻¹
2cm⁻¹

Bspl.: 6,25µ
5145Å; 1000 mW

DC; S20; 253V; AAA

C_7H_8
MW: 92.14
MERCK

GC.: >99 %
b.p.: 110,63 (lit.)

F 1-08

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

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

Optical spectroscopy of anisotropic media

Optical anisotropy

- χ, ε, n are tensors
- if the medium is not isotropic, there is different response to excitations of different polarization

Polarization	**Quantity**	**Notation**	
linear	*n'*	**(linear) birefringence** ***(lineáris) kettőstörés***	
linear	*n"*	**(linear) dichroism** ***(lineáris) dikroizmus***	
circular	*n'*	**optical rotation** ***optikai forgatás***	**optical activity** ***optikai aktivitás***
circular		**Or: circular birefringence** ***cirkuláris kettőstörés***	
	n"	**circular dichroism** ***cirkuláris dikroizmus***	

Dielectric tensor

If ε is symmetric, it can be diagonalized by principal axis transformation:

$$\varepsilon = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}$$

ε_{11}, ε_{22}, ε_{33} are the *principal values* of the dielectric tensor

$n^{(1)} = \sqrt{\varepsilon_{11}}$ $n^{(2)} = \sqrt{\varepsilon_{22}}$ $n^{(3)} = \sqrt{\varepsilon_{33}}$ *the principal values of the index of refraction*

Crystals: if the crystallographic axes are mutually perpendicular (orthorhombic or higher symmetry space group), both the real and imaginary part of the optical functions can be diagonalized on the basis of the axes

Optical anisotropy in crystals

Isotropic *cubic*	$\varepsilon = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$	$n = \sqrt{a}$
uniaxial *trigonal (rhombohedral)* *tetragonal* *hexagonal*	$\varepsilon = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$	$n_o = \sqrt{a}, n_e = \sqrt{b}$
biaxial *triclinic* *monoclinic* *orthorhombic*	$\varepsilon = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$	$n^{(1)} = \sqrt{a}$ $n^{(2)} = \sqrt{b}$ $n^{(3)} = \sqrt{c}$

Uniaxial systems: $n_e > n_o$ positive, $n_e < n_o$ negative

Anisotropy in infrared and Raman spectra

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

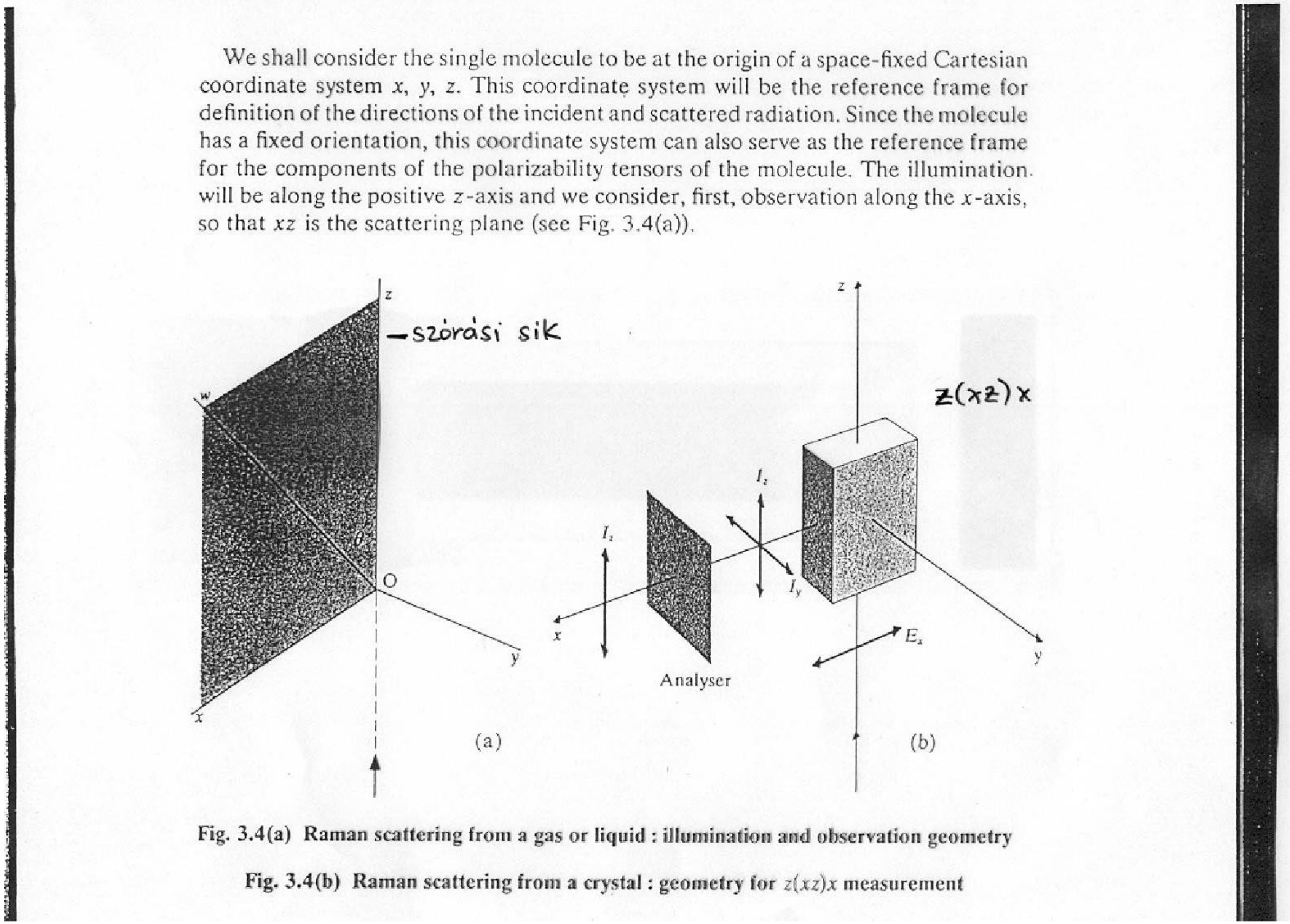
$$\frac{\partial \mu}{\partial Q} = \begin{bmatrix} \frac{\partial \mu_x}{\partial Q} \\ \frac{\partial \mu_y}{\partial Q} \\ \frac{\partial \mu_z}{\partial Q} \end{bmatrix}$$

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

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

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

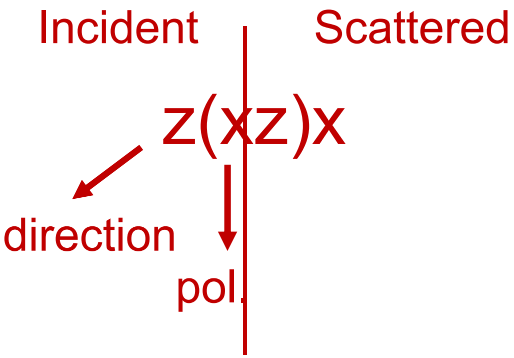
Scattering plane, scattering geometry



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**



Incident

Scattered

z(xz)x

direction

pol.

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

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

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

in z(xz)x geometry:

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

$$\rho_\parallel(\frac{\pi}{2}) = \frac{{}^x I_y}{{}^x I_z} \qquad \rho_\perp(\frac{\pi}{2}) = \frac{{}^y I_x}{{}^y I_y} \qquad \rho_n(\frac{\pi}{2}) = \frac{{}^n I_z}{{}^n I_y}$$

$$\rho_\parallel(\frac{\pi}{2}) = \frac{(\alpha_{yx}')^2}{(\alpha_{zx}')^2} \qquad \rho_\perp(\frac{\pi}{2}) = \frac{(\alpha_{zy}')^2}{(\alpha_{yy}')^2} \qquad \rho_n(\frac{\pi}{2}) = \frac{(\alpha_{zx}')^2 + (\alpha_{zy}')^2}{(\alpha_{yx}')^2 + (\alpha_{yy}')^2}$$

α_{zz}, α_{xx} from other orientation

Polarizability tensor for anisotropic materials

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

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

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

Depolarization ratio for non-oriented samples

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

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

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: $\left(\frac{\partial \alpha_{xy}}{\partial Q}\right) = \alpha_{xy}'$

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

Depolarization ratio

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

γ'=0 ⟶ $\rho = 0$ fully polarized

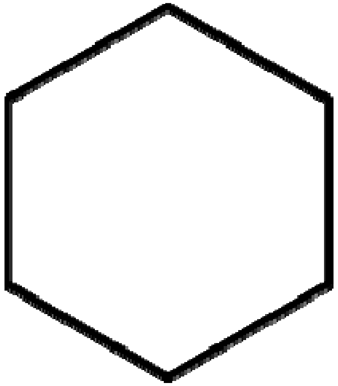
$0 < \rho < \frac{3}{4}$ partially polarized

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

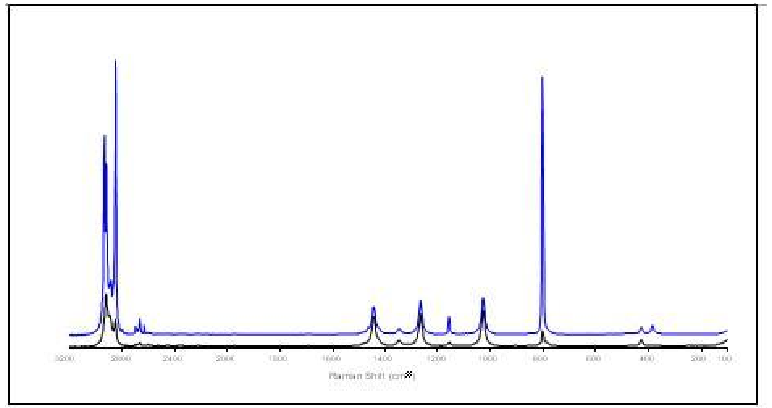


Figure 1, Raman spectra of cyclohexane arising from analysis Parallel (Blue) and Perpendicular (Black) to the excitation laser polarisation.

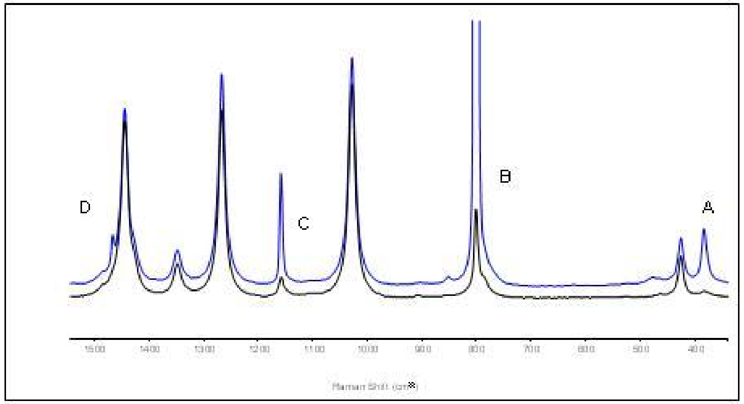
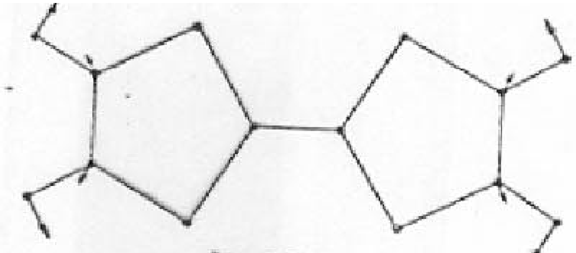
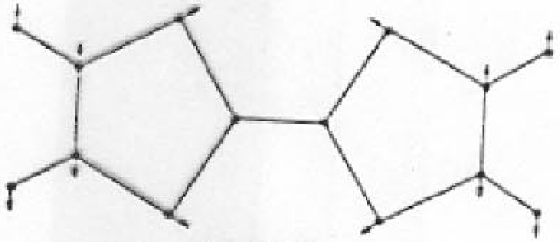


Figure 2. Zoom in on fingerprint region of cyclohexane, large changes in peaks A-D can be readily observed, this signifies that these peaks arise from totally symmetric vibrations.

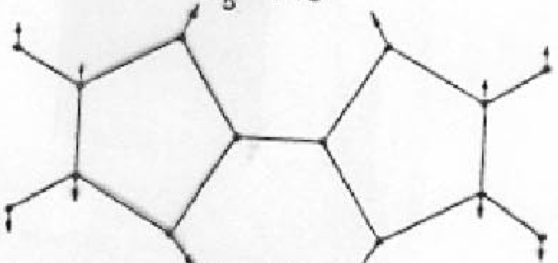
Totally symmetric vibrational modes



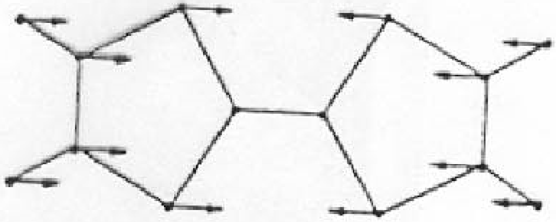
$\nu_4 = 1077$



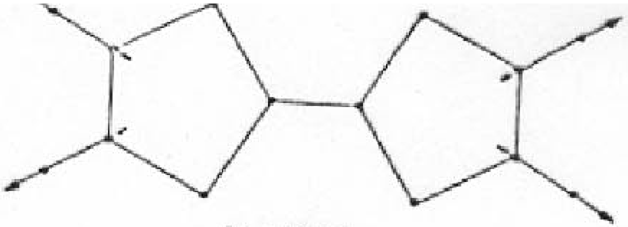
$\nu_5 = 740$



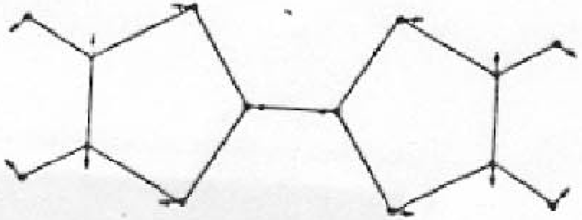
$\nu_6 = 472$



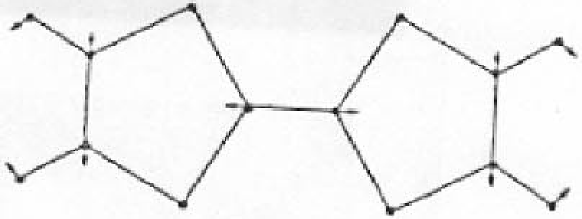
$\nu_7 = 253$



$\nu_1 = 3099$



$\nu_2 = 1559$



$\nu_3 = 1518$

Take-home message

- Anisotropy: linear, circular, dispersion, absorption
- **Linear birefringence and dichroism;**
- IR: three directions, one polarizer; Raman: three incoming, three scattered directions, two polarizers
- Raman: scattering plane, scattering geometry e.g. z(xz)x
- Depolarization ratio $\rho_{\parallel}(\theta) = \dfrac{{}^{\parallel}I_{\perp}(\theta)}{{}^{\parallel}I_{\parallel}(\theta)}$
- Polarizability tensor for anisotropic materials: $\alpha = \alpha_{iso} + \alpha_{aniso}$
- Depolarization ratio 0 → totally symmetric modes

Összefoglalás

- Anizotrópia: kettőstörés, dikroizmus, optikai forgatás, cirkuláris dikroizmus
- **Lineáris kettőstörés és dikroizmus:**
- IR: három irány, egy polarizátor; Raman: három bejövő, három szórt irány, két polarizátor
- Raman: 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