Introductory Lecture Series

Physics and Chemistry Graduate School Göttingen
2002-2005 *(-2011)*

Spectroscopy and Dynamics of Molecular Aggregates, Chains, Coils, and Networks

Part B: Aggregation in Solution (summer 2003)

Abel, Eckold, Roesky, *Schurtenberger*, Suhm

(FT)IR-spectroscopy in solution

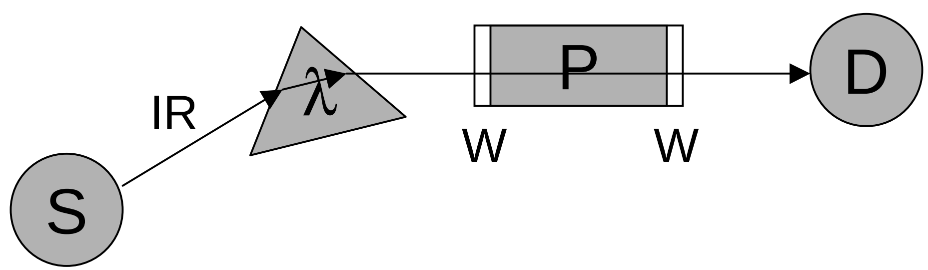
IR-spectroscopy:

universal tool for the study of molecular dynamics

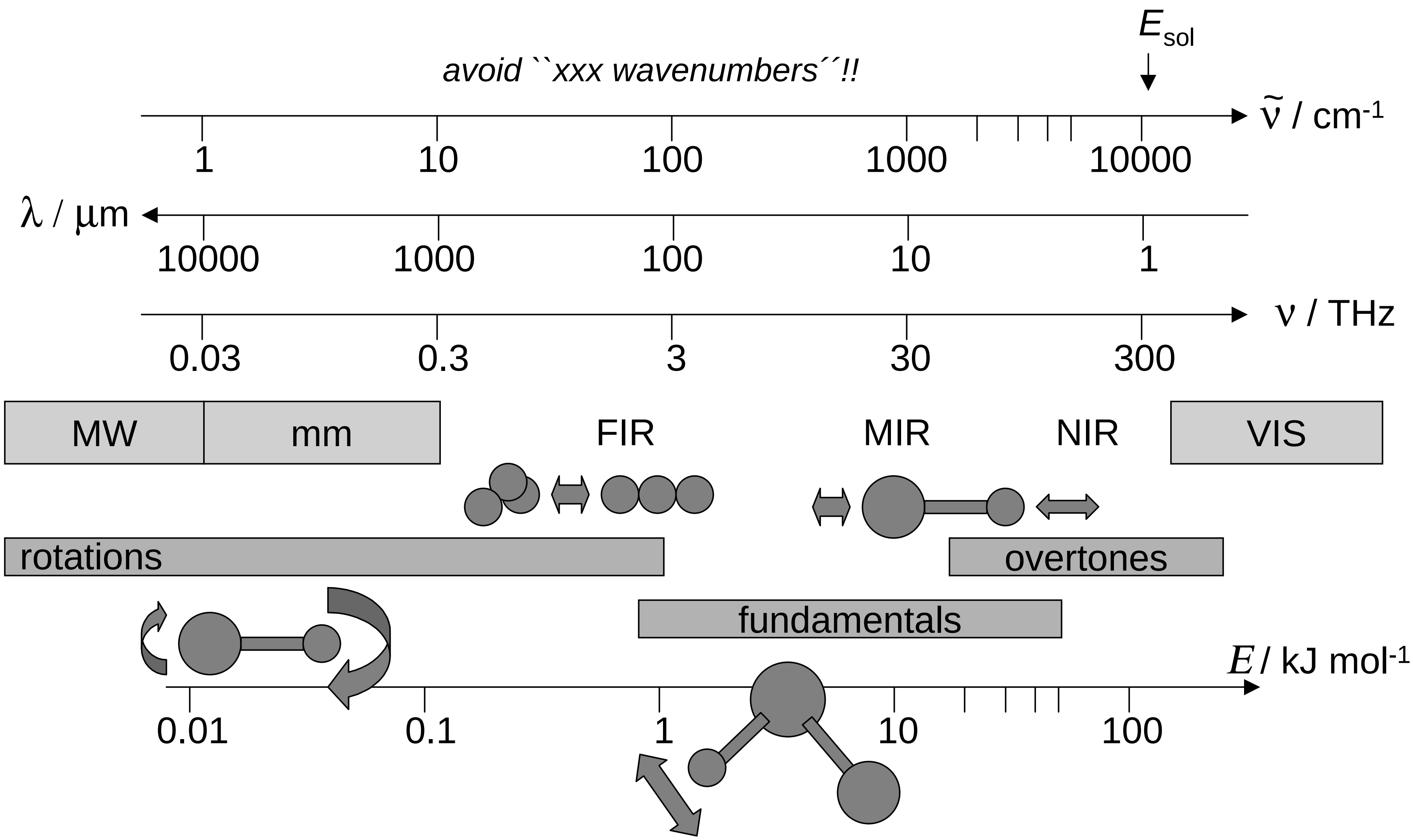
inexpensive, widespread use

works in all states of matter (can probe intermolecular interactions)

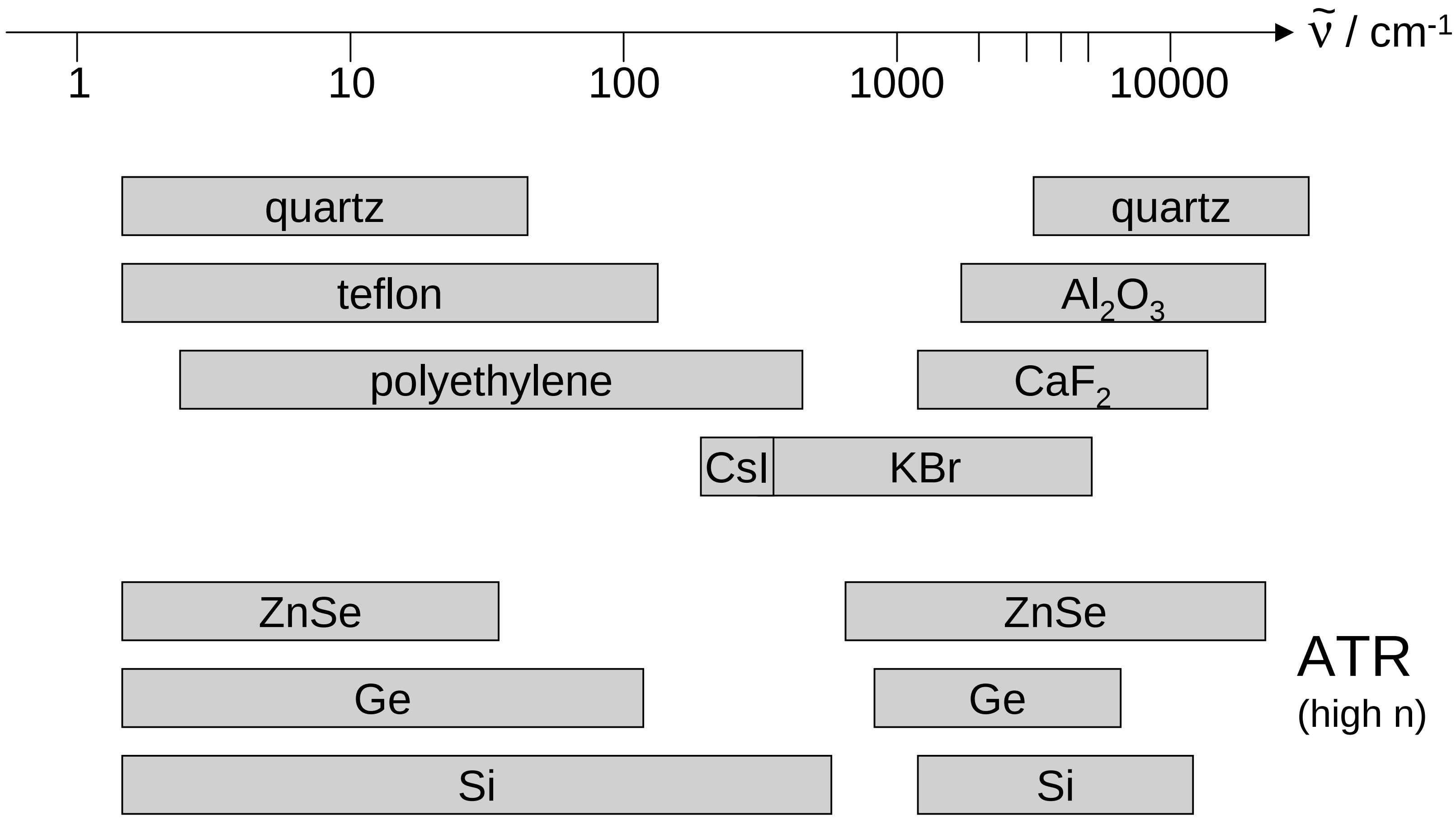
for structure determination superseeded by X-Ray, MS, NMR



Infrared spectrum



Infrared transparent materials



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Incoherent IR light sources

blackbody sources
$\tilde{\nu}_{max}/\mathrm{cm}^{-1} \approx 2\, T / \mathrm{K}$
$\rho(\nu_{max}) \sim T^3$
$\rho(\nu_{small}) \sim T$

source stability:

$\Delta T = 0.1\mathrm{K} \rightarrow$
$\Delta A = 0.0001$
($1000\text{-}3000\mathrm{cm}^{-1}$)

detection limit:
$\Delta A < 0.00001$

Globar® (glowbar): SiC (1800K)

Nernst glower: (Zr,Y,Ce)O (2000K)

Tungsten/quartz: (3000K) >$3000\mathrm{cm}^{-1}$

Mercury arc: (6000K,plasma) <$200\mathrm{cm}^{-1}$
(1000K,quartz) MIR

Synchrotron, FEL: Far IR

Infrared Detectors

IR-radiation (W) → electrical signal (A, V)

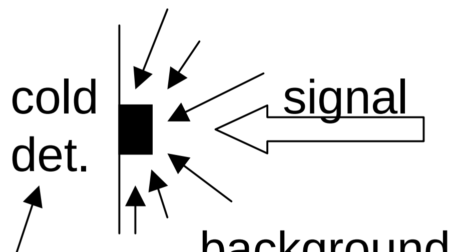
thermal det. (const)

photon det. (~λ)

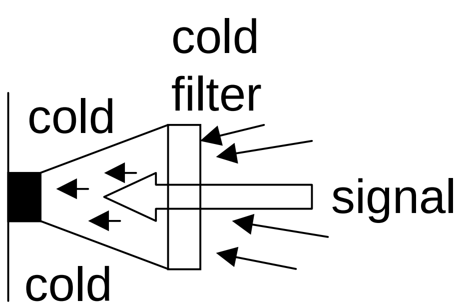
responsivity (A / W) (quantum efficiency, signal)

noise-equivalent power NEP (W / Hz$^{1/2}$) (signal-to-noise)

→ detectivity $D^* = A^{1/2}$ / NEP
(unit 1J(ones)=1cm Hz$^{1/2}$ W^{-1})



→ need ≈10^{10} IR photons



linearity!

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Detector types

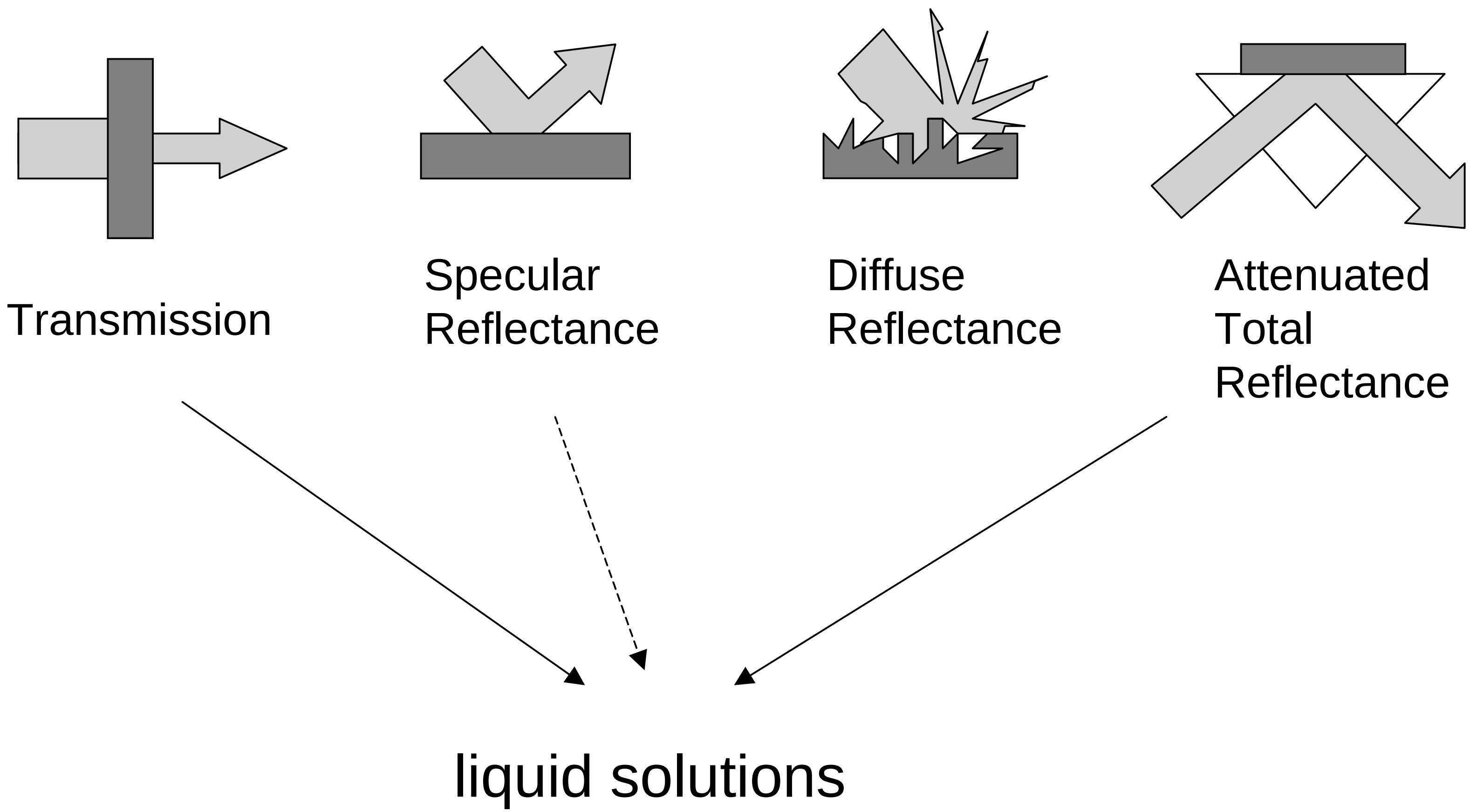
Pyroelectric: ΔT leads to temporary charge separation
e.g. deuterated triglycine sulfate (DTGS, T_{Curie} =60° C)
slow, insensitive ($D^* \approx 10^9$J), inexpensive, broad-band

Bolometer: Resistance increases strongly with temperature
e.g. Ga-doped (for absorption) Ge-detector at 2-4K (l-He)
slow, best for far IR, down to 0.3THz ($D^* \approx 10^{12}$J)

Photoconductor: Conductivity increases upon illumination (val.->cond. band)
e.g. HgCdTe at 77K, band gap changes with composition
non-linear, bias current, fast, best for MIR ($D^* \approx 10^{10}$J)

Photovoltaic: pn-boundary generates current upon irradiation
e.g. InSb at 77K
fast, best below 5.5μm, D^* up to 10^{11} cm $Hz^{1/2}$ W^{-1}

Sampling Techniques in IR Spectroscopy



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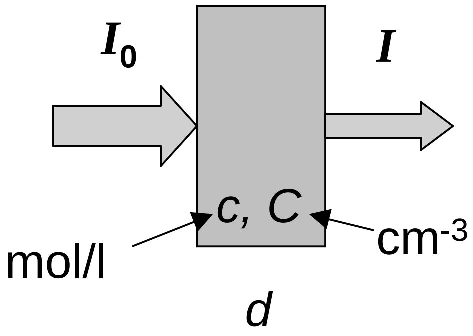
Transmission



Lambert-Beer

$-\ln I/I_0 = \alpha d = \kappa c d$

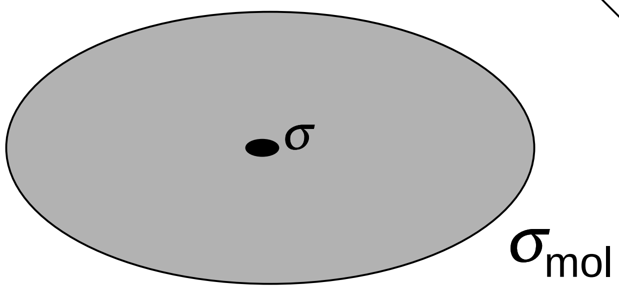
$-\ln I/I_0 = \alpha d = \sigma C d$

α → linear absorption coefficient

κ = molar absorption coefficient → up to 10^3 l mol^{-1} cm^{-1}

σ = absorption cross section → up to 100 pm^2

→ Absorbance A (often $\log_{10}$)



gas:	$C = 10^{19}$cm^{-3}	d=1mm	$\ln I/I_0 = -1$
liquid:	$C = 10^{22}$cm^{-3}	d=1µm	$\ln I/I_0 = -1$

d=1µm → solutions, overtones, ATR

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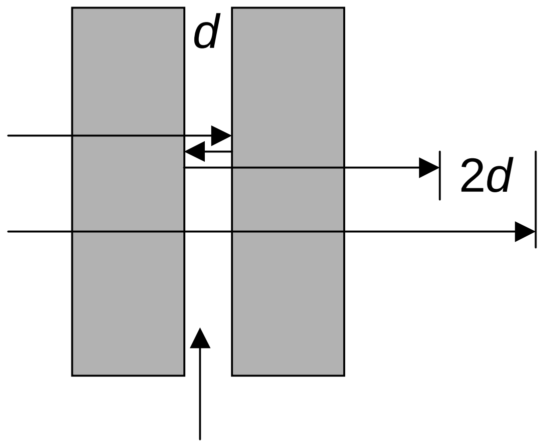
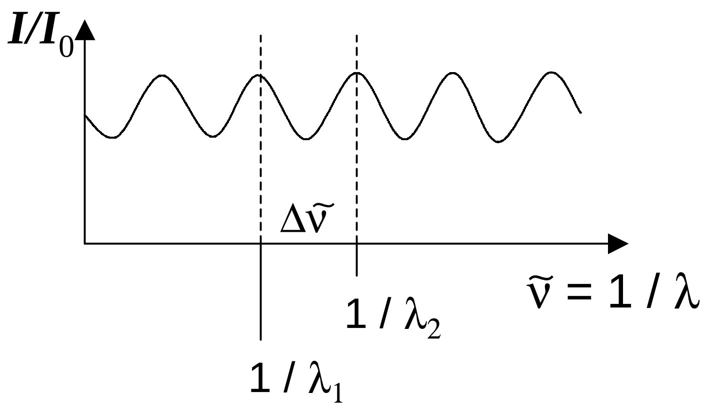
How to measure cell thickness



constructive interference:

$2\,d = n\,\lambda_1$
$2\,d = (n+1)\,\lambda_2 \quad (\lambda_2 < \lambda_1)$



thin films: include the refractive index *n*!

$2\,d / \lambda_2 - 1 = 2\,d / \lambda_1$

$2\,d\ \Delta\tilde{\nu} = 1$

$d = 1 / (2\,\Delta\tilde{\nu})$

frequently used solvents:

CCl_4: 4000 - 1350 cm^{-1} (1550 cm^{-1})
CS_2 : 1350 - 400 cm^{-1} (850 cm^{-1})
(acetone, THF, water, ...)

A little remark on absorbance *A*

$A_e = \ln I_0/I$	Napierian absorbance favored for weak absorptions (gas phase, IR) $A_e \approx (I_0 - I)/I_0$ for small A_e (1% absorption means $A_e \approx 0.010$) (2% absorption means $A_e \approx 0.020$)
$A_{10} = \log_{10} I_0/I$	Decadic absorbance favored for strong absorptions (condensed phase, VIS/UV) order of magnitude of attenuation (100x attenuation means $A_{10} = 2$) (1000x attenuation means $A_{10} = 3$)
of course:	$A_e = A_{10} \log_{10} e \approx 2.3026\, A_{10}$

Optical properties in Physics and Chemistry

complex refractive index → $\mathbf{n} = n(\tilde{\nu}) + i\,k(\tilde{\nu})$

refractive index $n = c_v / c_m$

absorption index $k = \alpha / 4\pi\tilde{\nu}$

Maxwell relation

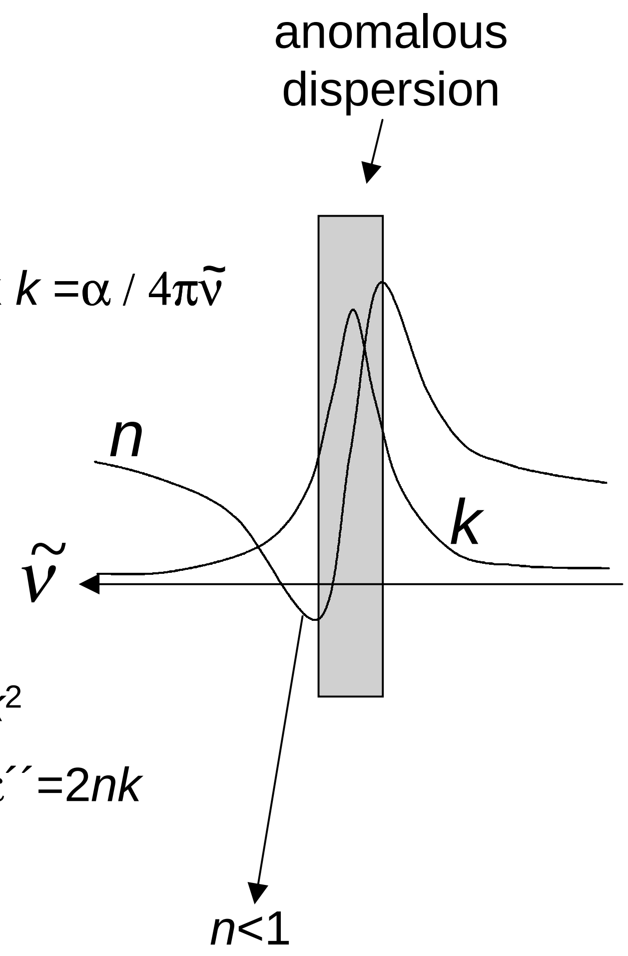
$$\varepsilon = \mathbf{n}^2$$

complex dielectric constant → $\varepsilon = \varepsilon' + i\,\varepsilon''$

dielectric constant $\varepsilon' = n^2 - k^2$

dielectric loss $\varepsilon'' = 2nk$

Kramers-Kronig



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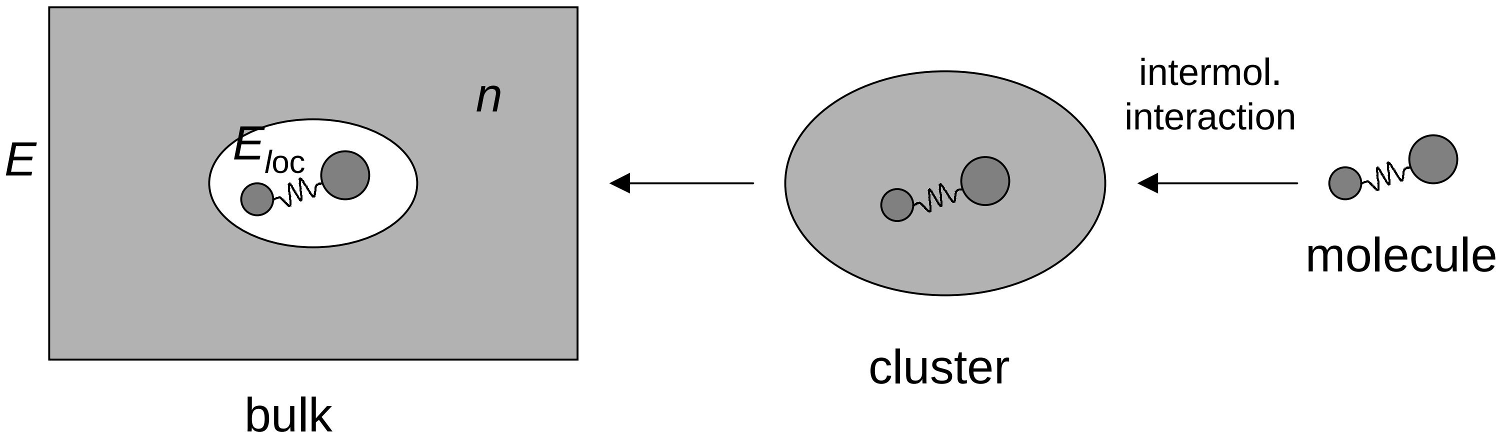
Relating bulk properties to molecular properties

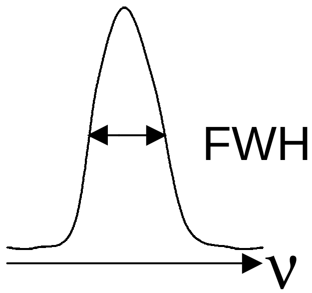


H_2O, OH stretch, in cm^{-1}:

α_{max} =3413
k_{max} =3406 → corrected: 3427 3756
ε''_{max} =3389
(300K)

absorption coefficient ≠ absorption index ≠ dielectric loss

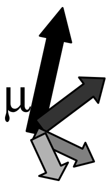
IR spectral bandwidths in solution



gas phase: rotational fine structure (high *T*)
lifetime (τ) broadening (low *T*)
$\Gamma = 1/(2\pi\tau) \rightarrow$ Lorentzian

in solution:

rotation is (often) diffusional $\Gamma_{rot} = 1/\pi\tau_{or}$



vibrational dephasing due to fluctuations in the local environment (ν,φ) $\Gamma_{de} = 1/\pi T_2^*$

vibrational relaxation (IVR, emission, etc.) $\Gamma_{rel} = 1/2\pi T_1$

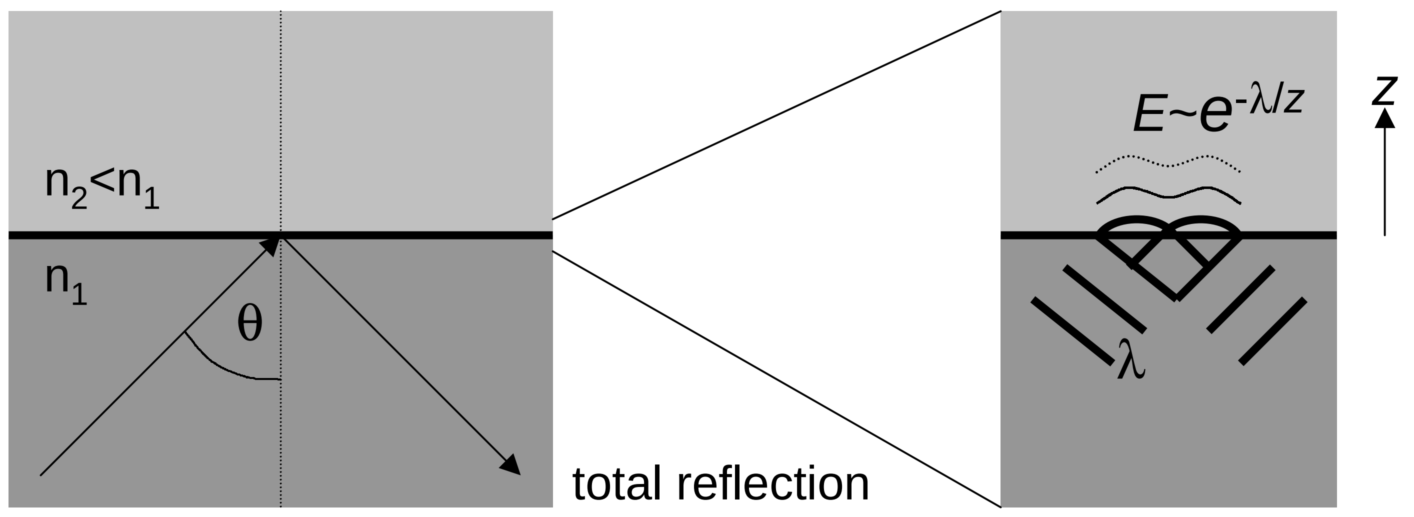
total $\Gamma = \Gamma_{rot} + \Gamma_{de} + \Gamma_{rel}$

ps-ns (NMR,Raman) ← ps (fs-ns) ← fs-s (N_2)

+inhomogeneous contributions
(often small in room temperature liquids)
from long-lived local geometries
(H-bonds, low-T matrices, glasses)

→analysis with time-domain experiments

Attenuated Total Reflection (ATR) Spectroscopy



total reflection
for $\theta>\theta_c$ with
$\sin\theta_c=n_2/n_1$

penetration depth ($E=E_o/e$): $d_p=\lambda/(2\pi n_1(\sin^2\theta-(n_2/n_1)^2)^{1/2})$

effective thickness: $d\approx 3d_p$

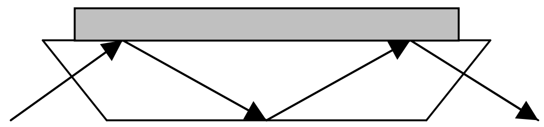
Ge (n_1=4), H_2O (n_2=1.3), λ=3µm, θ=60° : d_p=185nm
ZnSe (n_1=2.4), Polymer (n_2=1.5), λ=10µm, θ=45° : d_p= 2µm

Advantages and Disadvantages of ATR

+ short optical path for strong absorbers

+ no interference fringes

+ selective to surface (but µm)



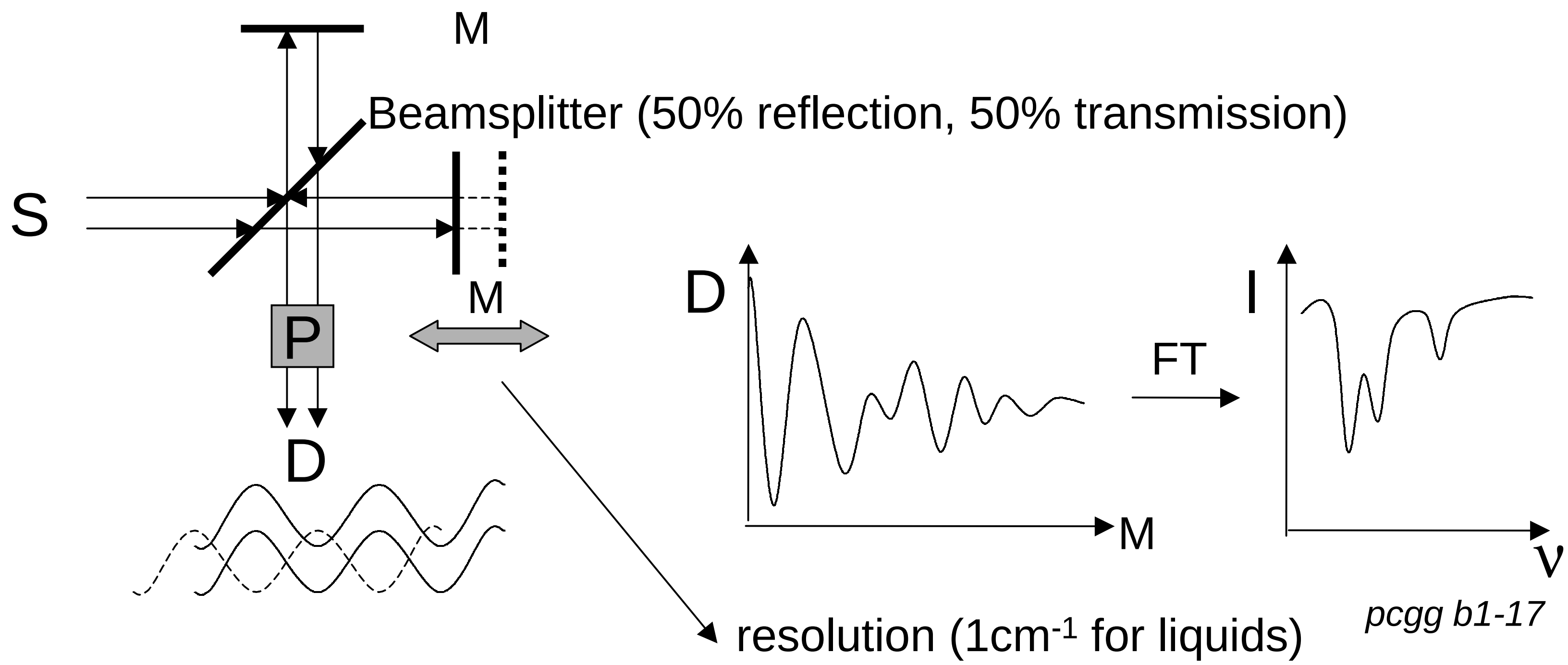
- n_2,λ-dependence of *d*

- surface contaminations

- contacting problems

Wavelength discrimination

tunable IR-lasers:	expensive, limited range, one λ at a time (wavelength resolution, time resolution)
dispersive elements:	prisms (NaCl) gratings (monochromators, NIR) one λ at a time, small throughput
interferometers:	F(ourier) T(ransform) IR spectroscopy



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Advantages

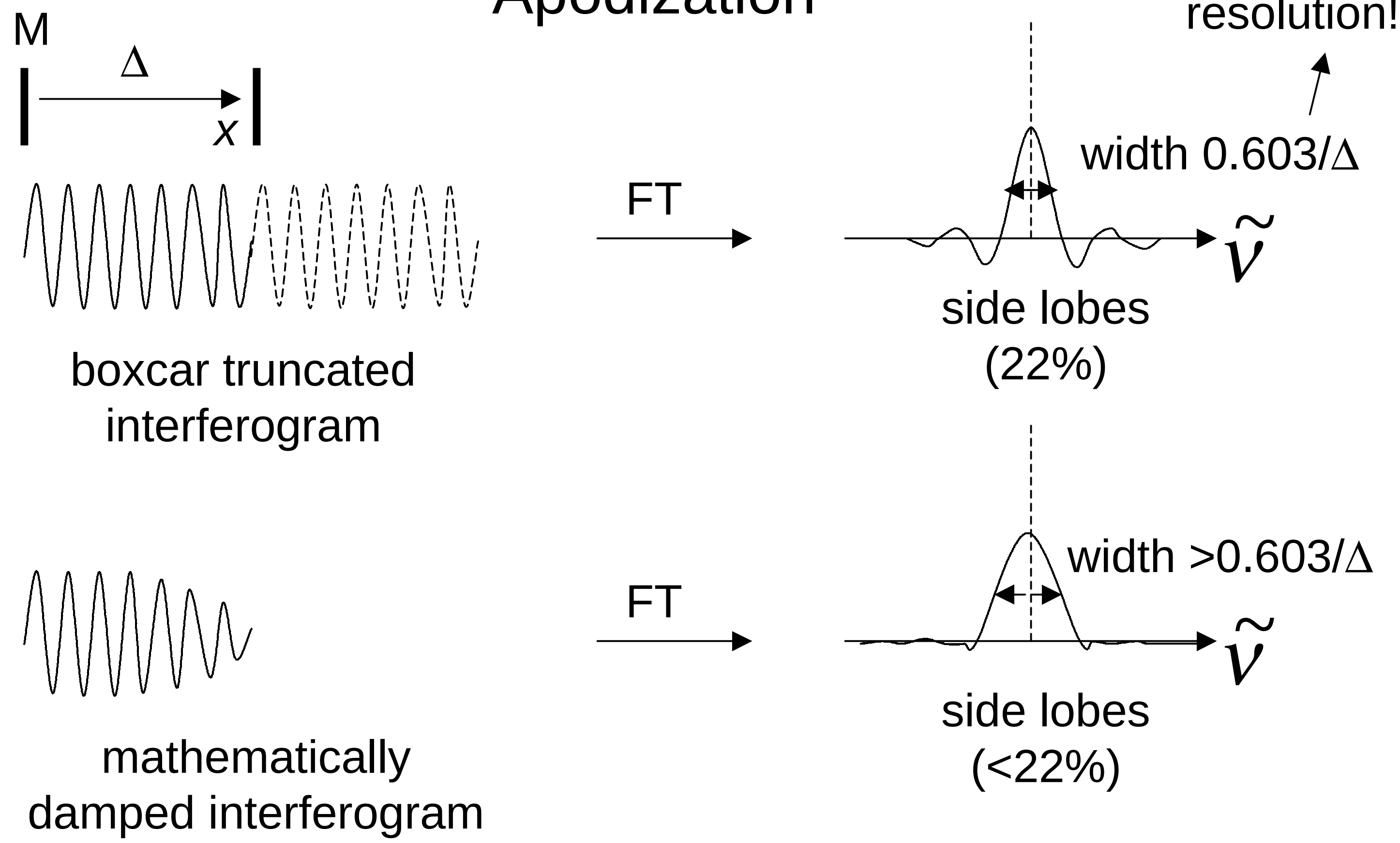
Throughput (étendue) advantage: (Jacquinot, †2002)

The slit in a dispersive instrument wastes most of the radiation, at least more than the circular aperture of an interferometer, for a given resolution (cylindrical vs. 2D symmetry)

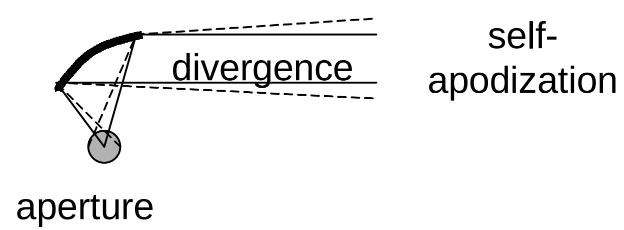
Multiplex advantage: (Fellgett)

Dispersive instruments are typically sequential (but: CCD arrays), whereas interferometers record all frequencies at the same time ($N_{1/2}$)
(in particular FIR, where detector noise dominates over photon noise)

Apodization



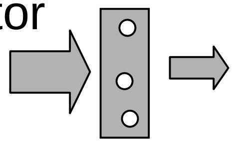
Blackmann-Harris: 1.137/Δ, 0.03%
Norton-Beer (medium): 0.845/Δ, 1.4%



(FT)IR artifacts

atmospheric absorptions: CO_2 (2350,667cm^{-1}), H_2O (3700,1600,$<400cm^{-1}$)

interference fringes: parallel plates, layers, windows, etc. 

stray light: shortcutting to the detector  nonlinearity

nonlinear detectors:
signal below the detector cutoff (MCT)
appearance of bands at exactly 2x the frequency

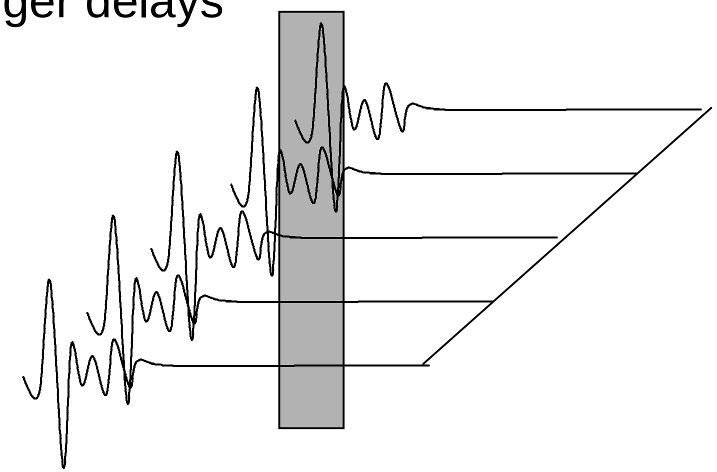
aliasing: folding of spectral features due to coarse sampling (Nyquist theorem)

non-horizontal baseline: temperature effects

digitization noise: insufficient noise due to slow scanning, low amplification

Time-resolved FTIR

>10ms	rapid scan FTIR, up to 100 spectra/s
>10µs	stroboscopic FTIR, assembling of interferogram sections from scans with different trigger delays

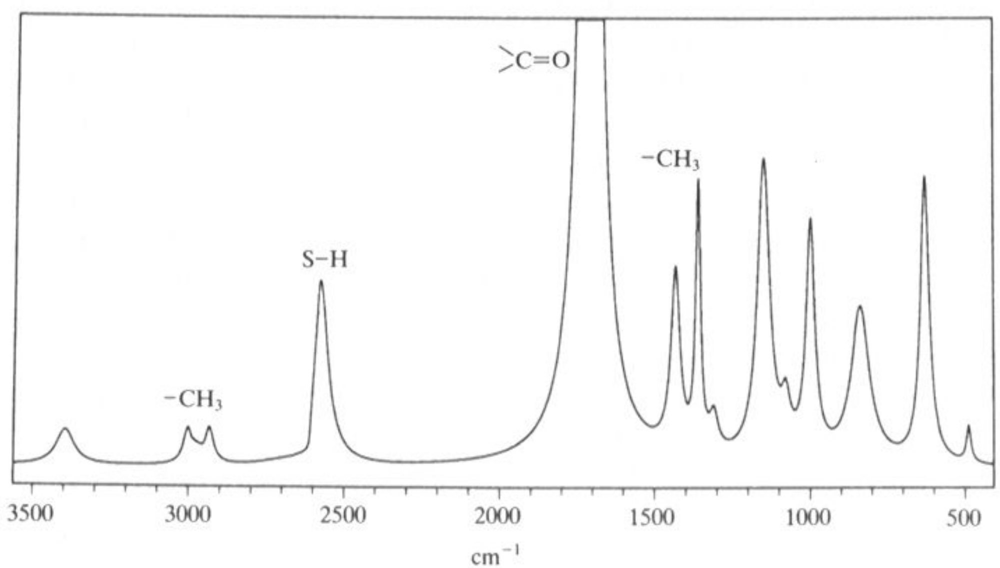


>10ns	step-scan FTIR, mirror held at ±1nm, signal measured with transient recorder, decrease in sensitivity
fs-ps	ultrafast lasers (pump-probe) instead of FTIR

IR group frequencies

in general: 3N-6 fundamental vibrations involving all N atoms (normal modes), apart from symmetry issues

true for low-frequency „fingerprint“ region



light atoms& strong bonds: characteristic group frequencies of functional groups e.g. X-H, C=O

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \qquad \tilde{\nu}\,/\,\mathrm{cm}^{-1} = 130\sqrt{\frac{f\,/(\mathrm{N/m})}{\mu\,/(\mathrm{u})}}$$

Stretching frequencies

C=O
1200 N/m
1700 cm^{-1}

O-H
600-800 N/m
(aggregation!)
3300-3700 cm^{-1}

C≡C
1600 N/m
2100 cm^{-1}

$$\tilde{\nu}\,/\,\mathrm{cm}^{-1} \approx 130\sqrt{\frac{f\,/(\mathrm{N/m})}{\mu\,/(\mathrm{u})}}$$

single:
200-900 N/m
double:
900-1400 N/m
triple:
1500-2300 N/m

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

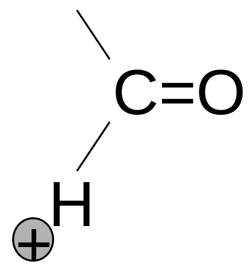
XH 0.9u-1u
CC 6u
CO 7u

but not IR-active for HCCH (no change of dipole moment)

symmetry issues!

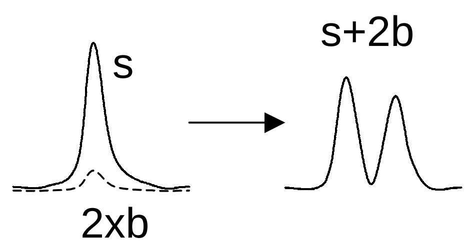
Some other aspects

bending modes: e.g. oop CH bend ≈1400cm^{-1}



overtones: e.g. 2x CH bend ≈2800cm-1, normally weak

intensity stealing from C-H stretch (2800cm^{-1}):
Fermi resonance

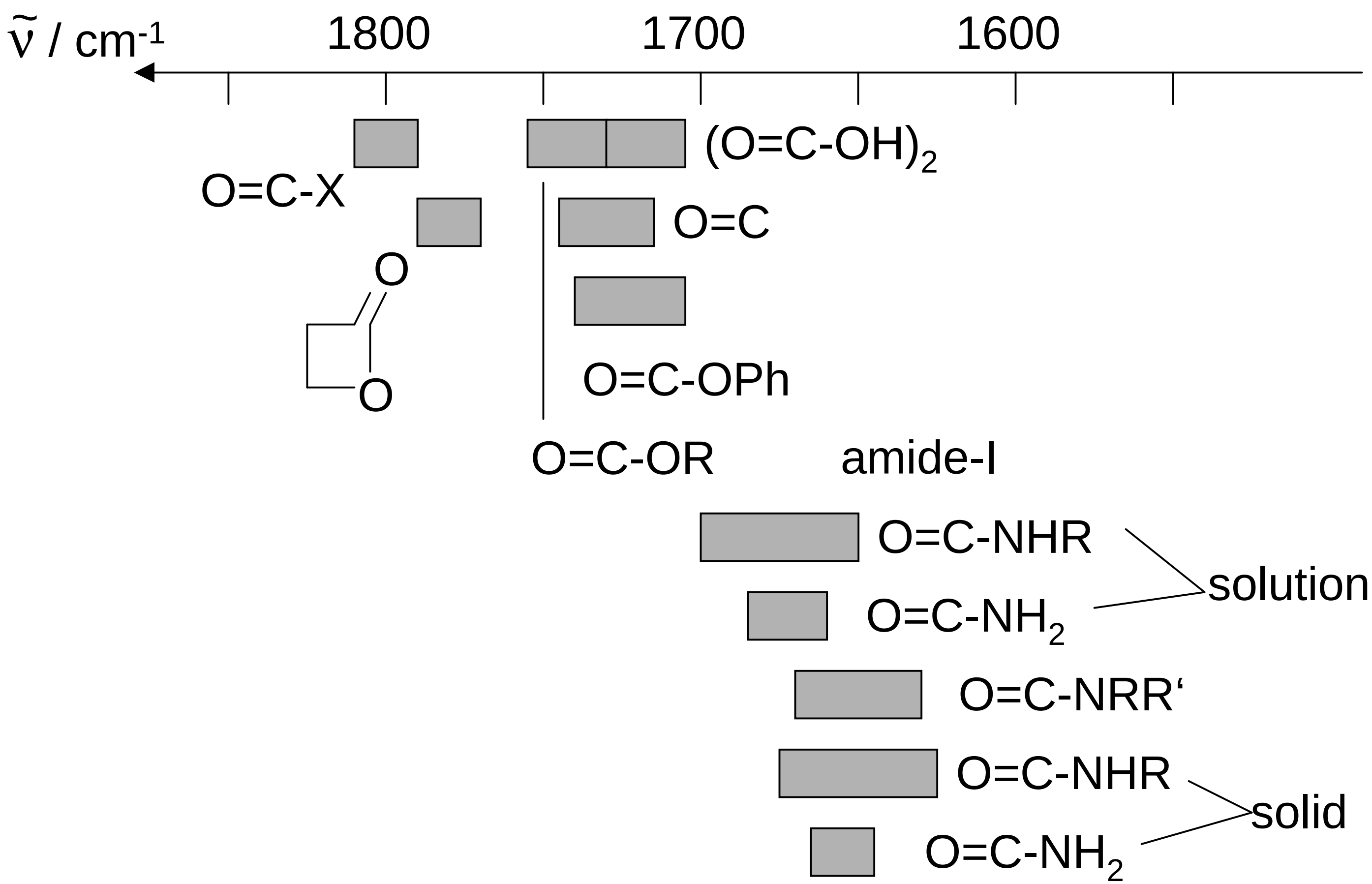


mechanical coupling: H-C≡C-H (C-H at 3330cm^{-1})

← → symm. (3375)

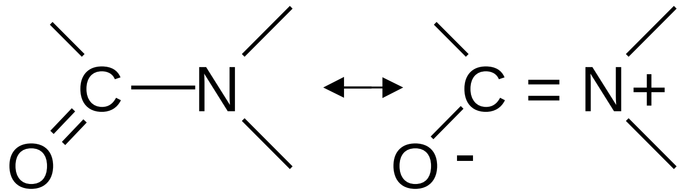
← ← antisymm. (3280, IR)

An example: C=O stretch fundamental

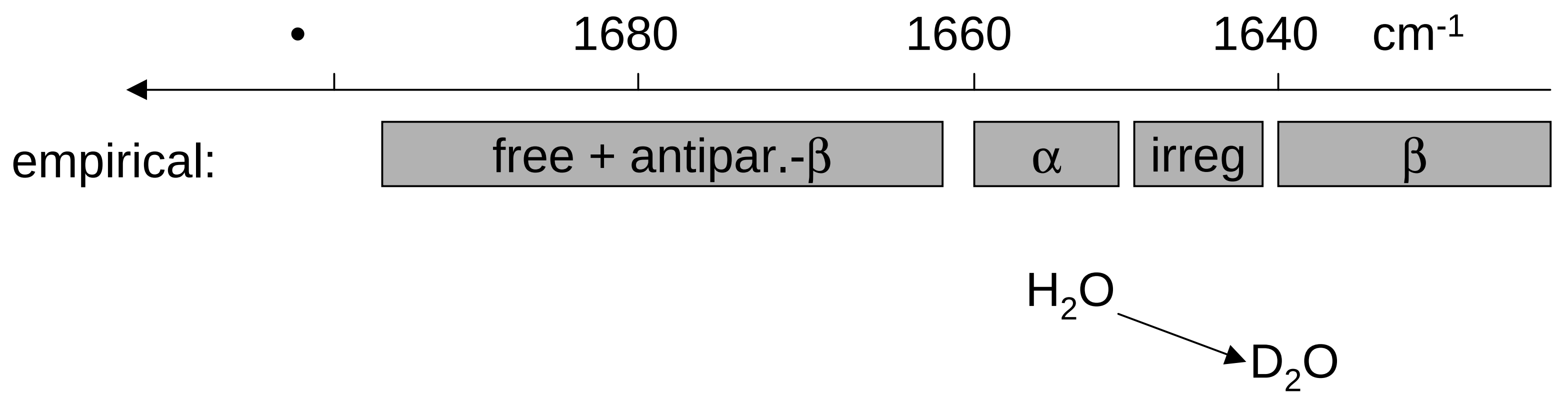


see e.g. G. Socrates, Infrared and Raman Characteristic Group Frequencies, Wiley, 2001

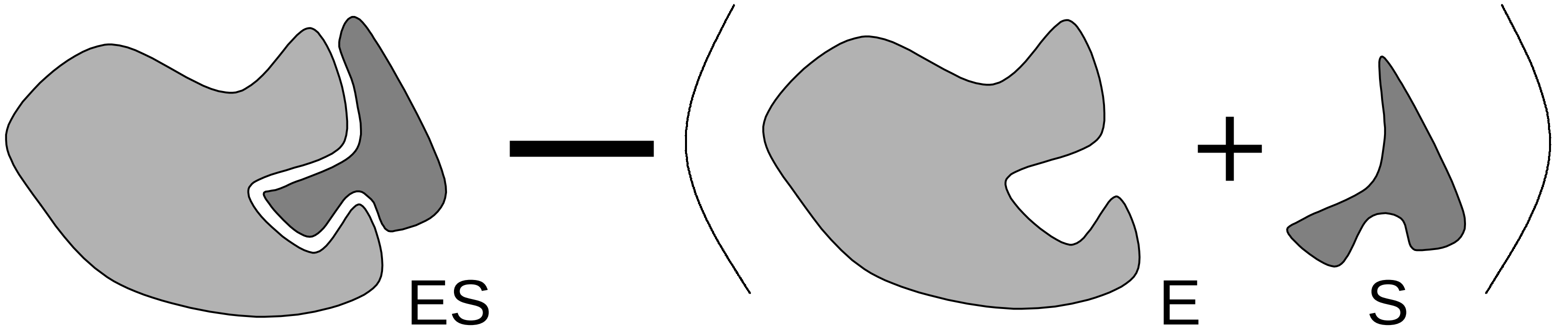
Amide I band (C=O)



strong charge flux associated
with the out-of-phase combination



IR-spectroscopy of biomolecular interactions



structure (complementing NMR- and X-ray studies):
only 10^{-5}g, comparison of crystal and solution, study of membranes

binding:
structure+interaction
e.g. respiratory proteins (hemoglobin) – binding of CO, cysteine S-H stretch

kinetics (time-resolved IR-spectroscopy):
difference techniques (before / after excitation) can select a certain functional group / interaction zone

Literature on FTIR spectroscopy in solution

survey:

Handbook of Vibrational Spectroscopy, 5 Volumes, Wiley 2002

tables:

e.g. Socrates, IR and Raman Characteristic Group Frequencies, Wiley 2001

physical background:

Chantry, Long-wave optics, 2 volumes, Academic Press 1984
Griffiths+de Haseth, Fourier Transform Spectrometry, Wiley 1986
Wilson, Decius, Cross, Molecular Vibrations, Dover 1980