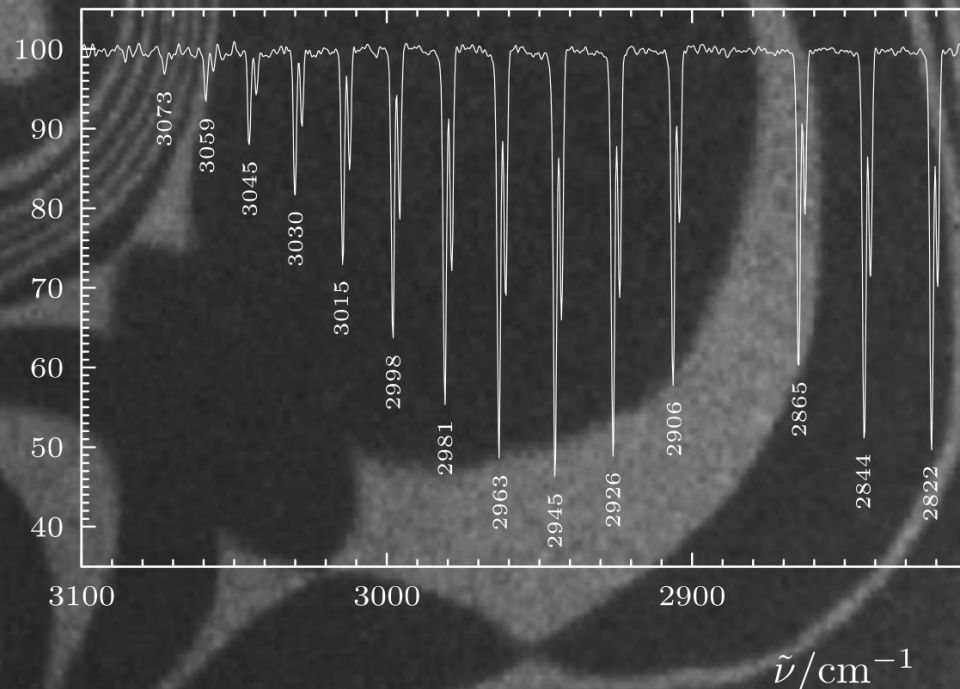# Iontové a vibrační spektroskopie
Ion and Vibrational Spectroscopies

(NEVF168)

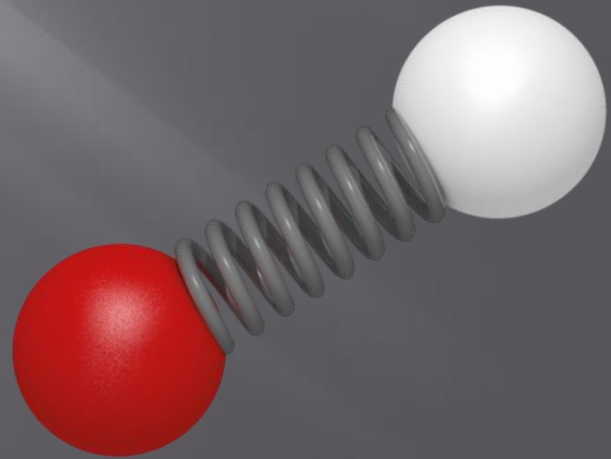*Viktor Johánek*
viktor.johanek@mff.cuni.cz

- Iontové spektroskopie *(doc. K. Mašek)*

- Vibrační spektroskopie
  - ✓ přehled a principy
  - ✓ IR vibrační spektroskopie
  - ✓ Ramanova spektroskopie

Vibrational spectroscopy
Vibrační spektroskopie

- Overview of vibrational spectroscopies
- Theoretical background
- Vibrational-Rotational modes

Vibrational spectroscopy
Introduction

Vibrational spectroscopy

– **non-invasive** label-free molecular spectroscopy
– provides **bond-specific** chemical analysis
– used in organic/anorganic chemistry, geology, material, environmental, and biomedical sciences etc.

Atoms in molecules vibrate with freqs. in the **IR range**

Vibrational spectroscopy methods

1) Photon-induced (optical)   IR, Raman

2) Electron-induced   HREELS, IETS

3) Neutron-induced   Inelastic neutron scattering

$h\nu$ **Light interaction with material:**
- Transmission
- Reflection
- Absorption → IR spectroscopy , UV-Vis
- Luminescence → Luminescence spectroscopies
- Elastic Scattering
- Inelastic Scattering → Raman

IR & Raman related textbooks:
- Larkin, P.: *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*, Elsevier, Waltham, 2011
- Schrader, B.: *Infrared and Raman spectroscopy: Methods and Applications,* VCH, Weinheim, 1995
- Griffiths, P. R. & De Haseth, J. A.: *Fourier Transform Infrared Spectrometry,* John Wiley & Sons, Hoboken, 2007
- Ferraro, J. R. & Nakamoto, K.: *Introductory Raman spectroscopy,* Academic Press, San Diego, 1994
- Gauglitz, G. & T. Vo-Dinh, T.: *Handbook of Spectroscopy*, Wiley-VCH Verlag GmbH & Co. Weinheim, 2003

Energy-level diagram of a **molecule**
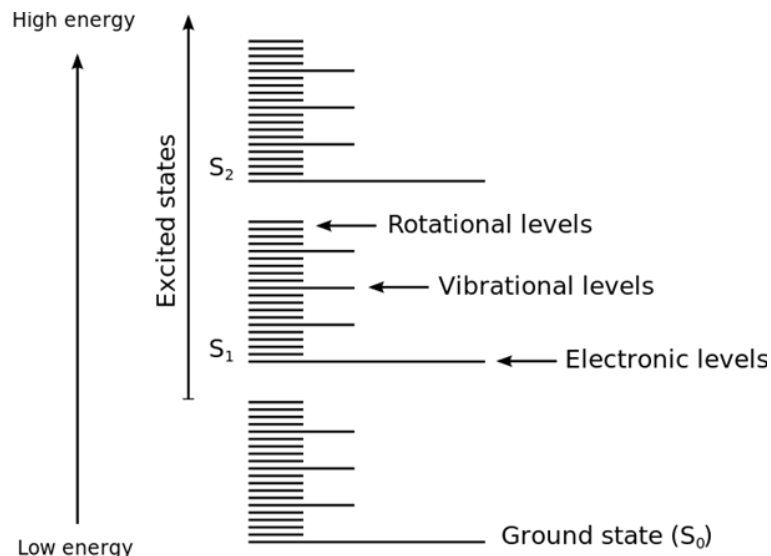
Internal energy

$$E_{int} = E_{el}(n) + E_v(v) + E_r(j)$$

Units

- Frequency [Hz]
- Wavelength [nm], [μm]
- Wavenumber (absolute, relative) [cm^{-1}]
- Energy [eV], [kJ/mol], [kcal/mol]

Basic conversions:
1 eV ≈ 96.5 kJ/mol ≈ 1.24 μm ≈ 8066 cm^{-1}
    ≈ 242 THz

Vibrational spectroscopy
Introduction

Chemical and structural analysis by vibrational spectroscopies

- Determination of chemical groups within molecule
- Compound identification (fingerprint match to spectral databases)
- Monitoring of chemical reactions *in-situ*

Vibrations => **Bond** specific analysis

Basic characteristics of optical vibrational spectroscopies:

Advantages

- non-invasive
- provides molecular specificity
- versatile: can work with solids, liquids, gases; crystals, powders, thin films, adsorbates, ...
- in-situ and microscopy capabilities
- easily adapted for operando experiments
- table-top instruments (often turn-key)
- large tunability of photon sources (or use of broadband sources)

Disadvantages

- minimal elemental specificity
- not all modes active (complementary methods can be used)
- at least partial optical transparency along the beam path required
- sensitivity strongly sample dependent and often low
- acquisition times sometimes long

Vibrational spectroscopy
Theory basics – optical processes

Optical response of matter upon light irradiation:

→ **Dielectric polarization density** (dipole moment per unit volume)

$$\vec{P}(t) = \varepsilon_0\left(\chi_1 \vec{E}(t) + \chi_2 \vec{E}^2(t) + \chi_3 \vec{E}^3(t) + \cdots\right) \qquad \text{(Taylor series)}$$

linear term   2nd order non-linearity   3rd order non-linearity

χ_n **n-th order susceptibility** ((n+1)-th-rank tensor)

Cross sections

- Electronic (UV-Vis) absorption spectroscopy: 10^{-20} m^2
- Fluorescence spectroscopies: $10^{-21} - 10^{-23}$ m^2
- Vibrational IR absorption spectroscopy: 10^{-23} m^2
- (Non-resonant) Raman spectroscopy: 10^{-33} m^2
- Resonance Raman spectroscopy: 10^{-29} m^2
- Surface enhanced Raman scattering: $10^{-21} - 10^{-27}$ m^2

=> **Optical spectroscopy methods**:

- **Linear** optical processes involving excitation:

  - IR absorption spectroscopy
  - Raman spectroscopy

  Vibrational spectroscopies

  - UV-Vis spectroscopy – electronic transitions

- **Non-linear** optical processes

  – typically *surface specific* (broken symmetry or alignment requirements)

  - Sum frequency generation (SFG) – for aligned molecules only (surfaces, crystals, in ext. el. fields, …)
  - Second-harmonic generation (SHG) – special case of SFG
  - Complementary vibrational spectroscopy (CVS) – simultaneous IR & Raman
  - Coherent anti-Stokes Raman scattering spectroscopy (CARS) – 3rd order
  - Third-harmonic generation (THG) – 3rd order

Vibrational spectroscopy
Linear optical vibr. spectroscopies – basics and classification

Infrared (IR) absorption spectroscopy

Raman scattering spectroscopy

Physical effect

Resonant effect – absorption upon transmission or reflection

Non-resonant effect – scattering from sample

Physical principle

Based on **variation of dipole moment** along normal coords
=> active for anti-symmetric vibrations that alter dipole moment (polar bonds)

$$I \propto \left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0}$$

Q … vibration coordinate ($Q = 0$ … near equilibrium)

$\vec{\mu}$ … **dipole moment**

1st rank tensor: vector $\left(\mu_x, \mu_y, \mu_z\right)$

- Bond is a "spring"

Based on **molecular polarizability** along normal coordinates
=> active for symmetric vibrations that alter polarizability

$$I \propto \left(\frac{\partial \alpha}{\partial Q}\right)_{Q=0}$$

$\vec{\mu} = \alpha \vec{E}$ … **induced** dipole moment under el. field $\vec{E}$

=> Depends on mutual field–molecule orientation
& $\vec{\mu}$ generally in different direction than $\vec{E}$

α … **polarizability**

2nd rank tensor: matrix $\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$

- 3D volume (polarizability ellipsoid: $1/\sqrt{\alpha}$ from c.o.g.)

Usage

- Often used for identification of functional groups of molecules

- Typically used for identification of skeletal structures
- Complementary information about molecular vibrations

Vibrational spectroscopy
Linear optical vibr. spectroscopies – basics

Rule of mutual exclusion

Fundamental (normal) vibrational modes of molecules with a **center** of symmetry (centrosymmetric molecule) cannot be both IR and Raman active

[some exceptions exist]

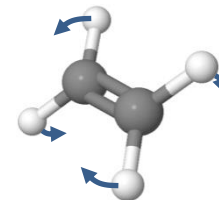=> *In turn, it allows to identify this symmetry element by comparison of IR & Raman*

– some vibrations can be inactive ("silent") in **both** methods – e.g. in ethylene (C_2H_4, 1 of 12), benzene (C_6H_6, 8 of 30), tetrachloroplatinate ion ($[PtCl_4]^{2-}$), fullerene (C_{60}, 32! of 46), …

– can be derived from group theory

C_2H_4 torsional mode
(out-of-plane twisting)
– No change in either dipole moment or polarizability
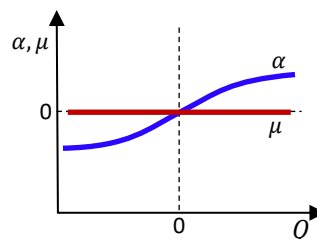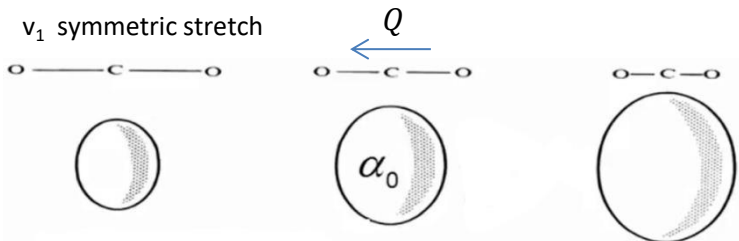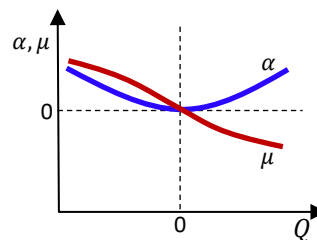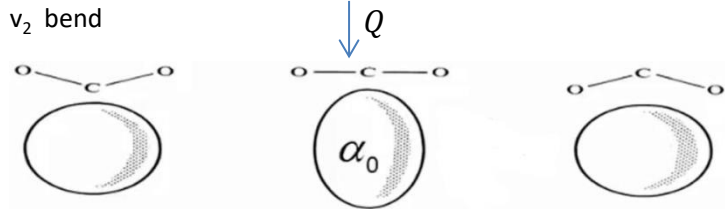
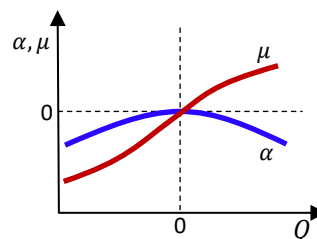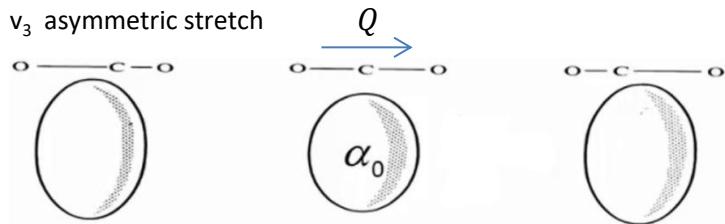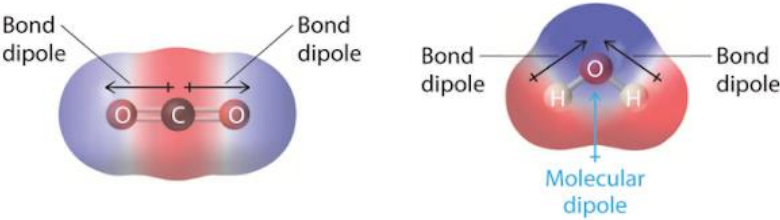|	**Infrared absorption spectroscopy**	**Raman scattering spectroscopy**
v_1 symmetric stretch	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} = 0$ **inactive**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} \neq 0$ **active**
v_2 bend	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$ **active**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} = 0$ **inactive** (Rayleigh scattering only)
v_3 asymmetric stretch	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$ **active**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} = 0$ **inactive** (Rayleigh scattering only)

Vibrational spectroscopy
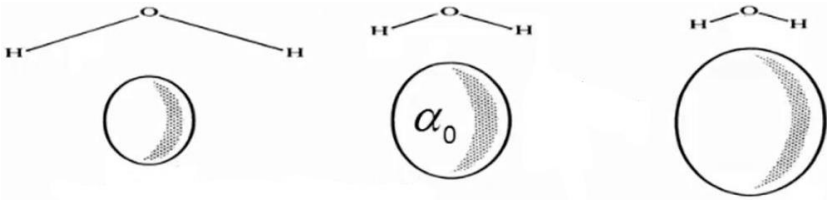## Linear optical vibr. spectroscopies – basics

When symmetry broken – vibrations can be **both** IR and Raman active

Bond dipole — Bond dipole

(a) No net dipole moment

Bond dipole — Bond dipole — Molecular dipole

(b) Net dipole moment
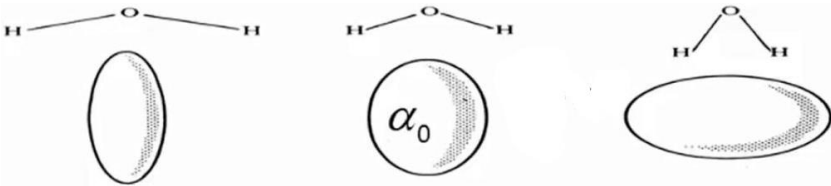
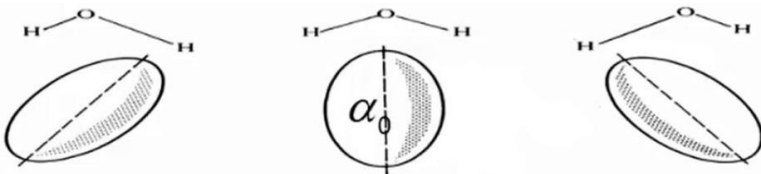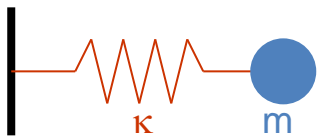|		Infrared absorption spectroscopy	Raman scattering spectroscopy
v_1 symmetric stretch	size	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$ **active**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} \neq 0$ **active**
v_2 bend	shape	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$ **active**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} \neq 0$ **active**
v_3 asymmetric stretch	orientation	$\left(\dfrac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} \neq 0$ **active**	$\left(\dfrac{\partial \boldsymbol{\alpha}}{\partial Q}\right)_{Q=0} \neq 0$ **active**

Vibrational spectroscopy
Theory basics – molecular vibrations

Harmonic oscillator
(no damping)

κ m

Classical mechanics

$F = -\kappa x$ ... Hooke's law
$F = m\ddot{x}$ ... Newton's 2nd law
$m\ddot{x} = -\kappa x$

$\Rightarrow x(t) = A\sin(\omega t)$

$\omega = \sqrt{\dfrac{\kappa}{m}}$ ... **natural frequency** of oscillator

$\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{\kappa}{m}}$ ... **angular (circular) frequency** [Hz]

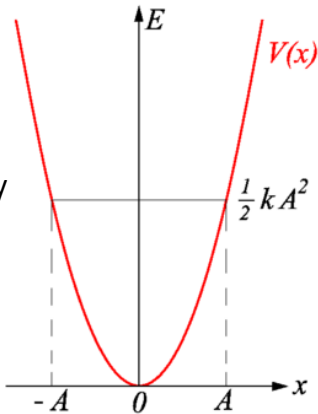Reciprocal wavelength [cm^{-1}]: $\bar{\nu} = \dfrac{\nu}{c}$

$\Rightarrow V(x) = \dfrac{1}{2}\kappa x^2$ ... Potential

$F = -\dfrac{dV}{dx}$

$E = \dfrac{1}{2}\kappa A^2$ ... Total energy

Quantum mechanics

$-\dfrac{\hbar}{2m}\psi''(x) + \dfrac{1}{2}\kappa x^2 \psi(x) = E\psi(x)$ ... Schrödinger equation (1D)
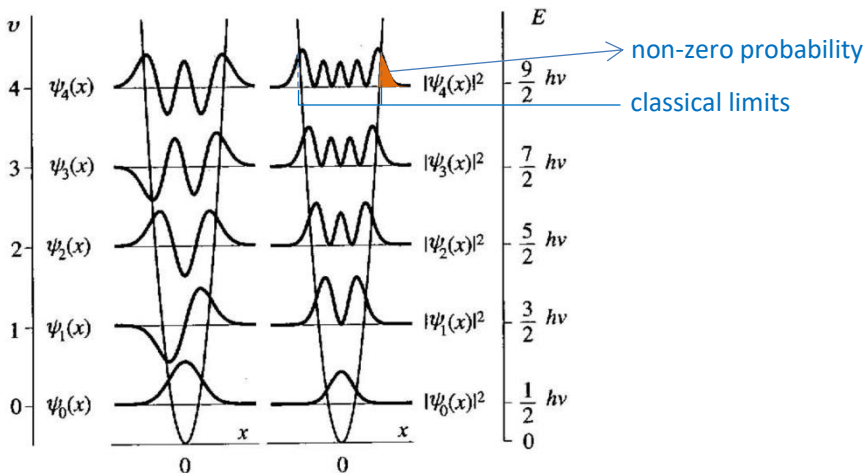
$\Rightarrow \boxed{E_n = \left(n + \dfrac{1}{2}\right)\hbar\omega}$ $\Rightarrow \Delta E = \hbar\omega = h\nu$

Energy levels quantized
$\Rightarrow n$ is molecular quantum number for vibration

$\psi_n(x) = \sqrt{\dfrac{\sqrt{\alpha}}{2^n n!\sqrt{\pi}}} H_n(\sqrt{\alpha}x)e^{-\alpha x^2/2}$

normalization constant

H_n ... Hermite polynomial, $\alpha = \sqrt{\dfrac{m\kappa}{\hbar^2}}$

non-zero probability

classical limits

Vibrational spectroscopy
Theory basics – molecular vibrations

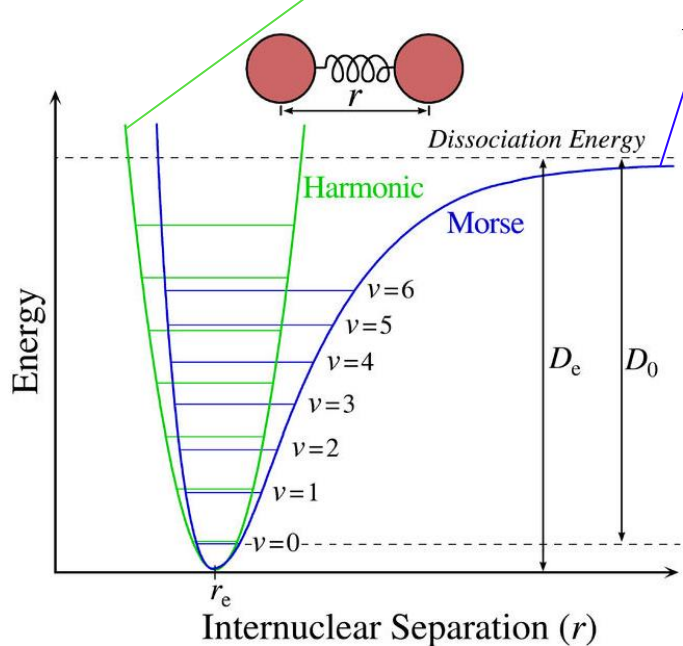**Harmonic vs. anharmonic potential (QM)**

- **Harmonic**:

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{m}}$$

- **Anharmonic**: **Morse potential** => vibrational levels not spaced equally

$$E_v = \left(v + \frac{1}{2}\right) h\nu - \frac{1}{4D_e}\left[\left(v + \frac{1}{2}\right) h\nu\right]^2 (+ \cdots)$$

1st anharmonic correction

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa_e}{m}}$$

Selection rules

$$\Delta v = \pm 1 \quad \Rightarrow \quad \Delta E = h\nu$$

(from properties of Hermit. polynomials – wavefunctions form an orthonormal set)

$\Delta v = \pm 1$ … fundamental band
$\Delta v = \pm 2$ … 1st overtone band
$\Delta v = \pm 3$ … 2nd overtone band
…..

HCl molecule as an anharmonic oscillator vibrating at energy level E_3

Morse potential

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$

$$a = \sqrt{\kappa_e / 2D_e}$$

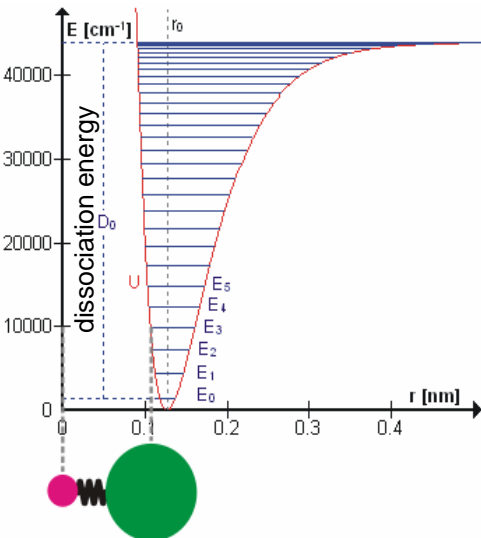κ_e … force constant near well minimum
a … well "width"
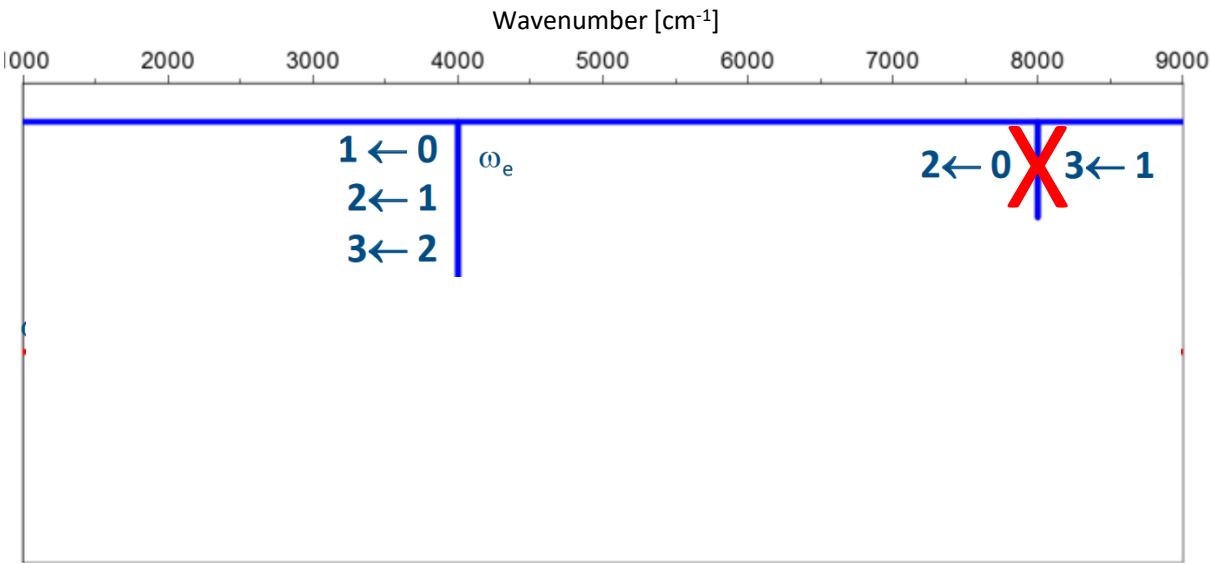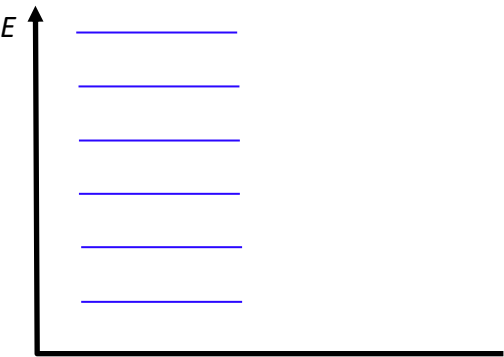
Vibrational spectroscopy
Theory basics – molecular vibrations

Harmonic vs. anharmonic spectrum

Diatomic molecule

harmonic
approximation

$$E_v = \boxed{\left(v + \frac{1}{2}\right)\omega_e} - \left(v + \frac{1}{2}\right)^2 \omega_e \chi_e$$

E

Wavenumber [cm^{-1}]

| 1000 | 2000 | 3000 | 4000 | 5000 | 6000 | 7000 | 8000 | 9000 |

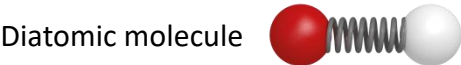**1 ← 0** ω_e

2 ← 1

3 ← 2

2 ← 0 **3 ← 1**

- degeneration
- strict selection rule

Vibrational spectroscopy
Theory basics – molecular vibrations

Harmonic vs. anharmonic spectrum

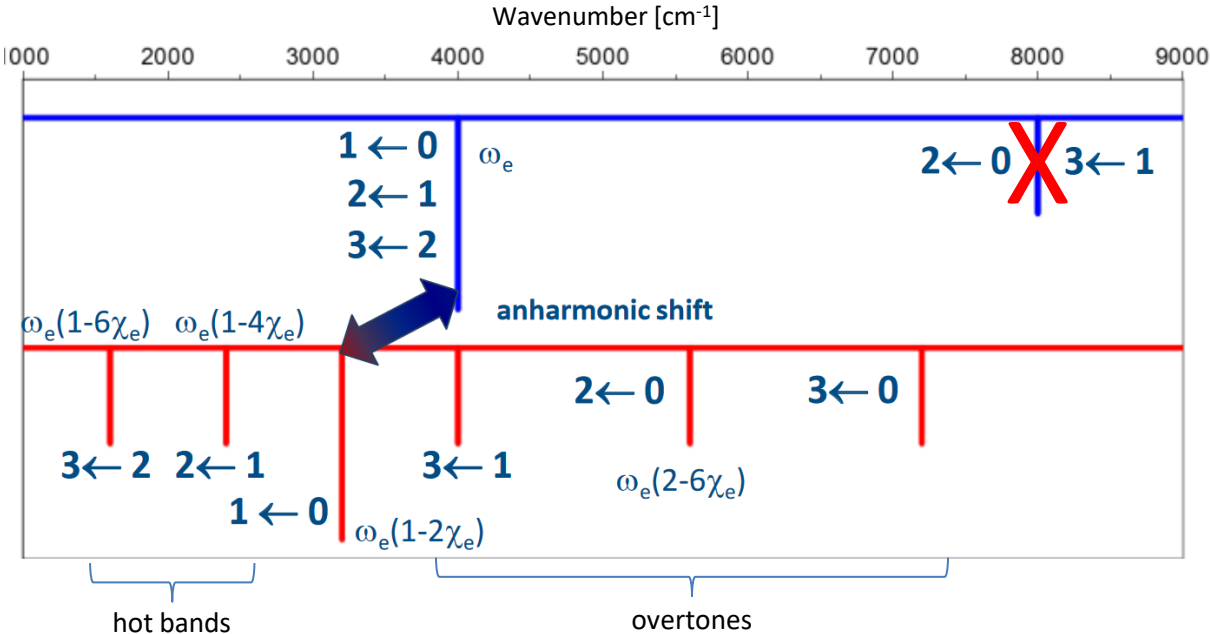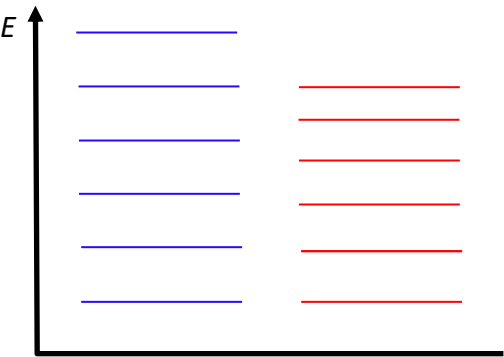Diatomic molecule

harmonic
approximation

$$E_v = \boxed{\left(v + \frac{1}{2}\right)\omega_e} - \left(v + \frac{1}{2}\right)^2 \omega_e \chi_e$$

incl. anharmonic contribution

ω_e ... harmonic frequency $(= h\nu_e)$
χ_e ... anharmonicity constant

Wavenumber [cm^{-1}]

$1 \leftarrow 0$ ω_e
$2 \leftarrow 1$
$3 \leftarrow 2$

$2 \leftarrow 0$ ✗ $3 \leftarrow 1$

anharmonic shift

$\omega_e(1-6\chi_e)$ $\omega_e(1-4\chi_e)$

$2 \leftarrow 0$ $3 \leftarrow 0$

$3 \leftarrow 2$ $2 \leftarrow 1$
$1 \leftarrow 0$ $3 \leftarrow 1$ $\omega_e(2-6\chi_e)$
$\omega_e(1-2\chi_e)$

hot bands   overtones

- degeneration
- strict selection rule

- anharmonic shift
- no selection rule
- separation (degeneration removed)
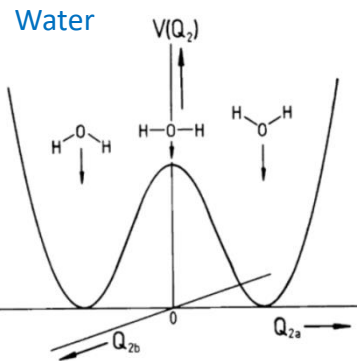 => more complex spectrum

Vibrational spectroscopy
Theory basics – molecular vibrations

Vibrational potentials with multiple minima
– can occur for polyatomic molecules
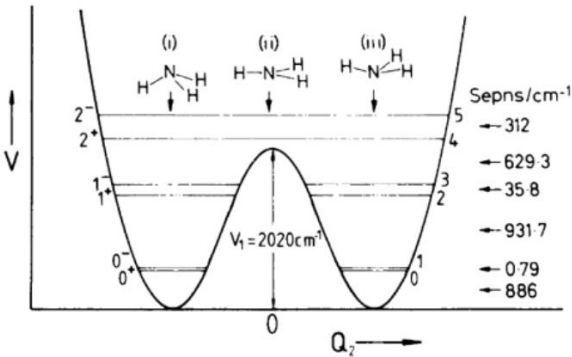
Barrier to planarity/linearity:

infinite   low   zero

tunelling possible

Wavefunction overlaps => splits
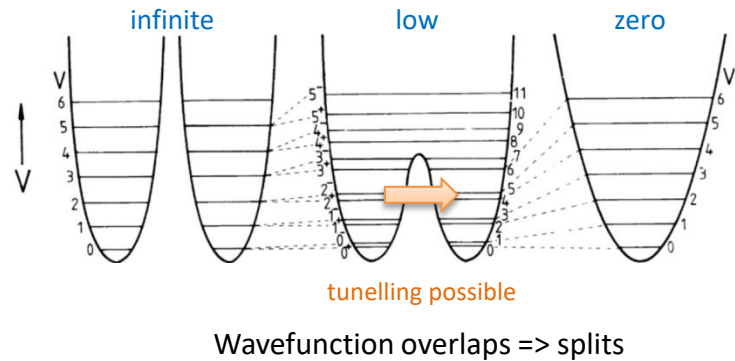
Bends of triatomic non-linear molecules

Water

Inversion vibrations

Ammonia – 2 pyramidal configurations, can switch via planar conf.
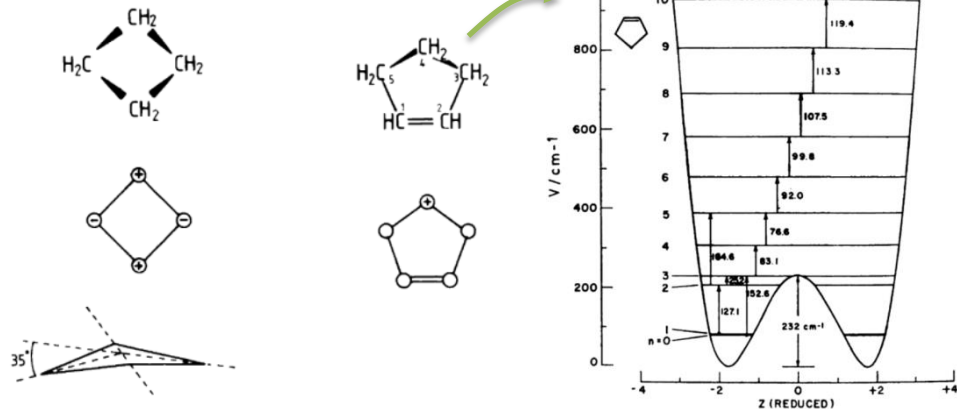
$V_1 = 2020\,cm^{-1}$

Ring-puckering vibrations

– Bending vibrations out of the plane of the ring
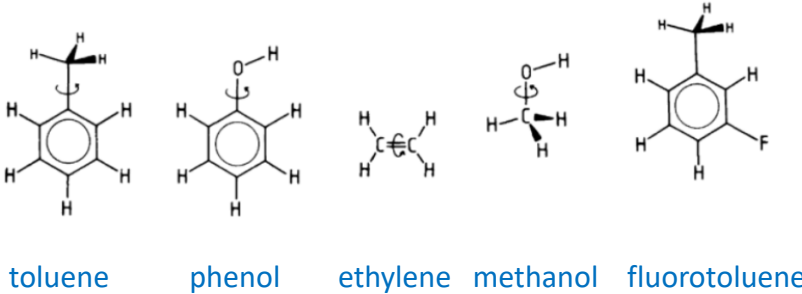
cyclobutane   cyclopentene

Torsional vibrations

– twisting motion between 2 rigid parts of a molecule

toluene   phenol   ethylene   methanol   fluorotoluene

Vibrational spectroscopy
Theory basics – Fermi resonance

Fermi resonance
– anharmonic effect: interaction (coupling) of vibrations with (coincidentally) similar frequency (quantum mixing)

Criteria for Fermi resonance:
1) The 2 vibrations must have the same symmetries
2) The transitions have almost the same energy

Fermi resonance effects:
1) The high energy mode shifted to higher energy and vice versa (=> larger split)
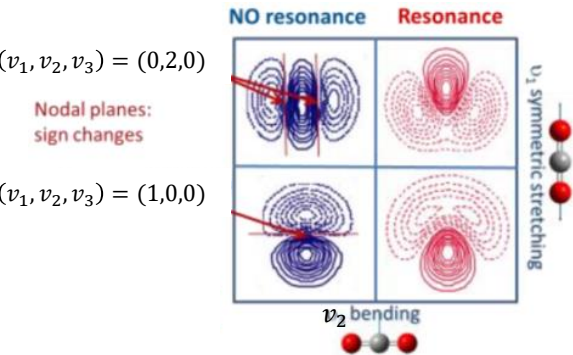2) Intensity gain for the weaker band and vice versa

- Often occurs between normal and overtone modes
- Closer the energies, stronger the interaction
- The two transitions can be thought of as a linear combination of the parent modes (wavefunctions), forming a diad
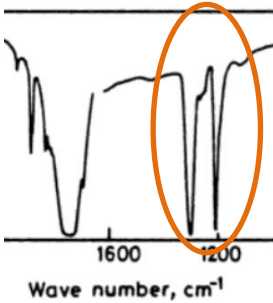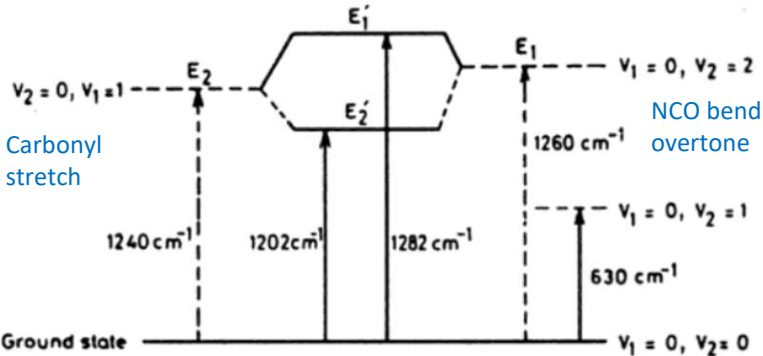- Quantified by Fermi coupling constant   F. vazebná konstanta

no resonance   resonance

hv $2hv'$ $h(v+x)$ $2h(v+x)'$

hv'
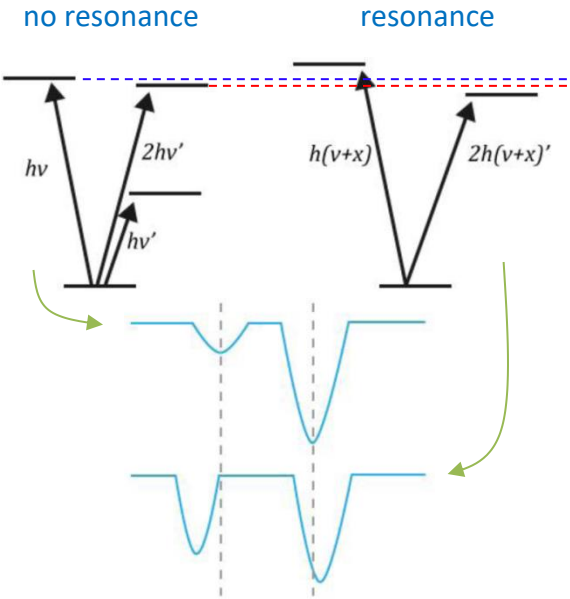
Fermi diad („doublet")
(generally polyad)

„Classical" example (Fermi): **CO_2**

v_1 (sym. stretch) $\approx 2v_2$ (bend)

Potassium cyanate (KNCO)

NO resonance   **Resonance**

$(v_1, v_2, v_3) = (0,2,0)$

Nodal planes:
sign changes

$(v_1, v_2, v_3) = (1,0,0)$

v_1 symmetric stretching

v_2 bending

E_1'

E_2 E_1 $V_1 = 0, V_2 = 2$

$V_2 = 0, V_1 = 1$ E_2'

NCO bend
overtone

Carbonyl
stretch   1260 cm^{-1}

1240 cm^{-1} 1202 cm^{-1} 1282 cm^{-1} $V_1 = 0, V_2 = 1$

630 cm^{-1}

Ground state $V_1 = 0, V_2 = 0$

1600   1200

Wave number, cm^{-1}
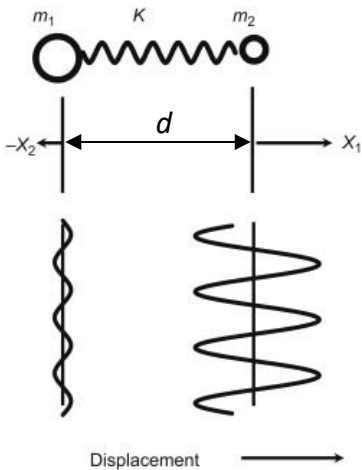
Vibrational spectroscopy
Molecular vibrations and rotations

The simplest case: diatomic molecule, stretching vibration (**harmonic oscillator**), **rigid rotor** (no centrifugal distortion)
Vibrations and rotations assumed **independent** (Born-Oppenheimer approximation)

Vibrations

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{… reduced mass}$$

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

v … **vibrational quantum number**

$$\Delta v = \pm 1$$

RT: $\Delta v = +1$ (1←0 transition)
(almost only $v = 0$ populated)*

→ Fundamental band allowed only

Selection rules

From Fermi's golden rule:
Transition probability

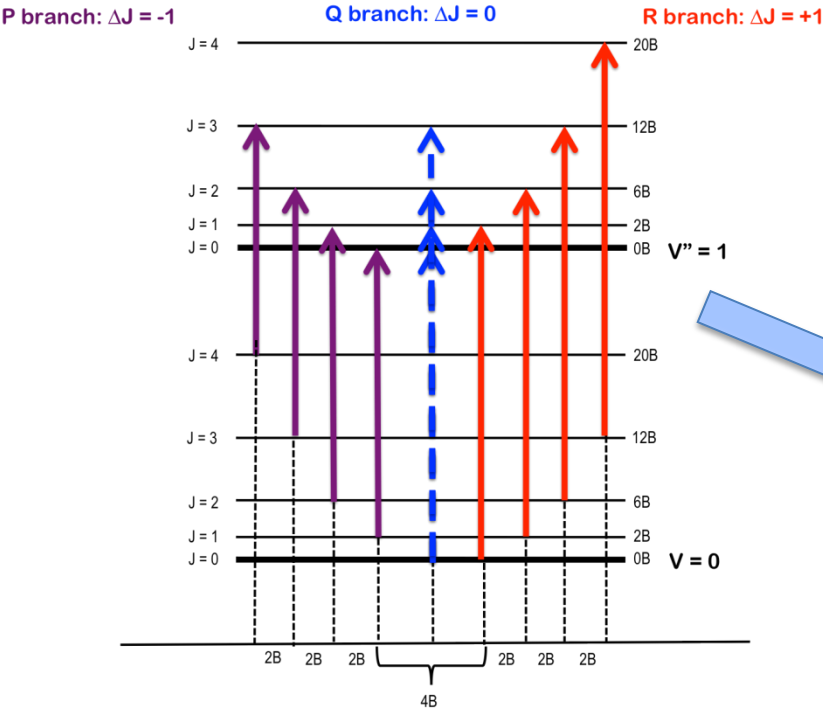$$\wp \propto \rho_{fin} \int \varphi_{fin}{}^* \delta \varphi_{ini} dv$$

ρ_{fin} … density of final states
φ … wavefunctions
δ … perturbation operator
    (interaction)

horké přechody
* Hot bands – bands involving excited states
Important for T comparable to characteristic
vibrational temperature (typ. 10^3 K)

Rotations

$$I = \mu d^2 \qquad \text{… moment of inertia}$$

In wavenumbers:

rotational constant of a molecule

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$F(J) = \frac{E_r}{hc} = B\,J(J+1) \quad, B = \frac{h}{8\pi^2 cI}$$

J … **rotational quantum number**
    (belonging to ang. momentum along axis of rotation)

$$\Delta J = \pm 1$$

Energy conservation: photon carries
1 quantum of angular momentum

$\Delta J = 0$ allowed for perp. momentum transition
(shift of rotation axis => $\Delta K \neq 0$)

K … projection of J to symmetry axis

- *Diatomic*: some (mostly those with odd # of unpaired electrons)
- *Linear polyatomic*: Perpendicular bands only
- *More complex*: Both parallel and perpendicular

"Ground state" at common temperatures

Room temperature => typically in ground
state, but rotation levels can be populated

$$k_B T_{(RT)} \doteq 25 meV$$

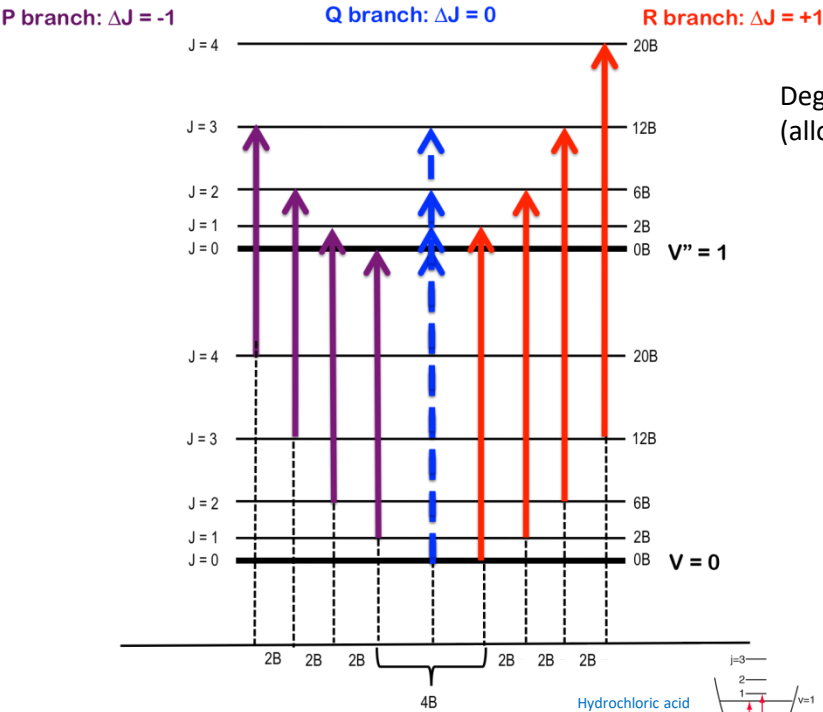# Vibrational spectroscopy
Molecular vibrations and rotations

Rotational branches

P-branch ("poor"): $\Delta J = -1$
R-branch ("rich"): $\Delta J = +1$
Q-branch: $\Delta J = 0$

Hydrochloric acid

General nomenclature for "branches"

Branch	O	P	Q	R	S
ΔJ	-2	-1	0	+1	+2

Vibrational spectroscopy
Molecular vibrations and rotations

Rotational branches

P-branch ("poor"): $\Delta J = -1$
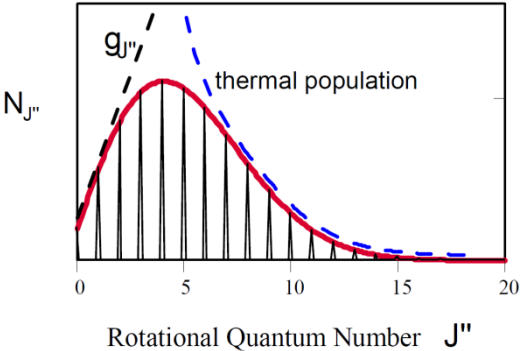**R**-branch ("rich"): $\Delta J = +1$
Q-branch: $\Delta J = 0$

Intensity distribution

– no thermal population in upper (final) state => intensity scales with population of lower (initial) state:

$$N(J'') \propto g(J'')\; e^{-\frac{E_{J''}}{kT}} = (2J'' + 1)\; e^{-\frac{hcBJ''(J''+1)}{kT}}$$

Degeneracy of the J''th level
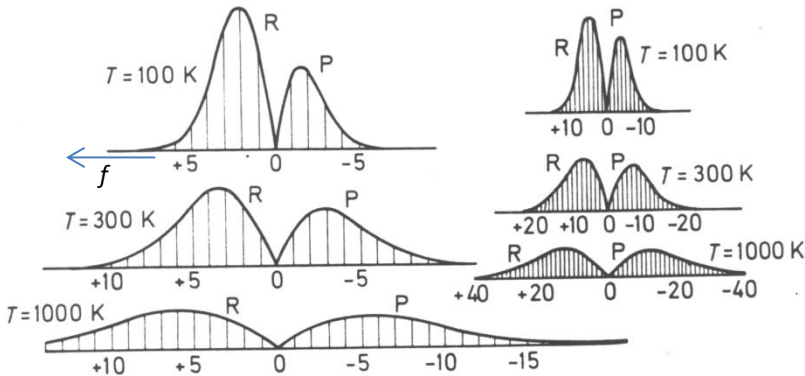(allowed levels of $M_{J''}: -J''\ldots +J''$)

Boltzmann distribution

Rotational Quantum Number J''

Overall intensity $\propto$ vibr. transition dipole moment

Examples: HCl (B=10.44 cm^{-1})   CO (B=1.94 cm^{-1})

P branch: $\Delta J = -1$ Q branch: $\Delta J = 0$ R branch: $\Delta J = +1$

General nomenclature for "branches"

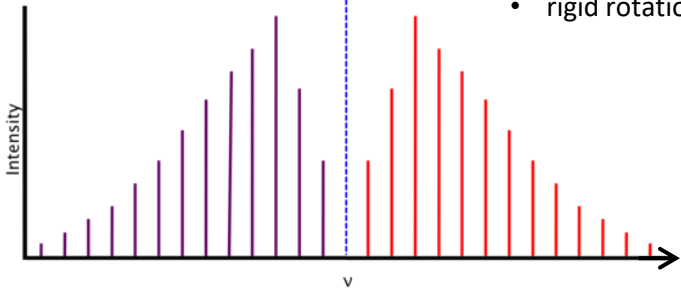| Branch	O	P	Q	R	S
ΔJ	-2	-1	0	+1	+2

Hydrochloric acid

Vibrational spectroscopy
Molecular vibrations and rotations

Ideal spectrum

- Equidistant lines
- Symmetric bands

Assumptions recall:
- harmonic oscillator
- vibrations and rotations independent
- rigid rotation

Total nuclear energy of the combined rotation-vibration motion

$$E(v,J) = h\nu_0 \left(v + \frac{1}{2} \right) + BJ(J+1)$$

vib   rot

Real spectrum

- Spacing higher on P side, lower on R side
- Asymmetric bands
- P-branch less intensive
- Lines appear as peaks

Rotational-Vibrational Coupling   rotačně-vibrační vazba
– Moment of inertia depends on bond length, which changes by vibration
   => rotational constant (B) changes
      → correction via rotational-vibrational coupling constant (α_e)

Centrifugal distortion   odstředivá distorze
– Molecular bond length change due to centrifugal force
   → $d \uparrow \Rightarrow I \uparrow \Rightarrow B \downarrow$
      → correction via centrifugal distortion constant (δ_e)

Anharmonic vibrations
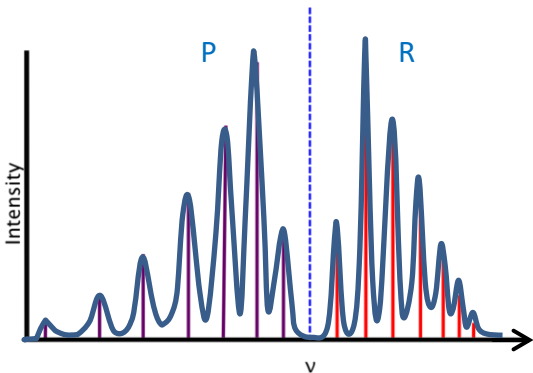– Affect band center position

Thermal distribution of electrons
=> Dependence on the population of the lower J state

Line broadening
– *Natural:* Variability of chem. environment, lifetime broadening, Doppler (thermal), collisions, proximity broadening
– *Instrument:* Aperture size, frequency, grating & path length (DIR), mirror amplitude (FTIR), …

vib   rot   rot-vib   cent.dist.

$$E(v,J) = h\nu_0 \left(v + \frac{1}{2} \right) + B_e J(J+1) + \alpha_e \left(v + \frac{1}{2} \right) J(J+1) - \delta_e [J(J+1)]^2$$

Vibrational spectroscopy
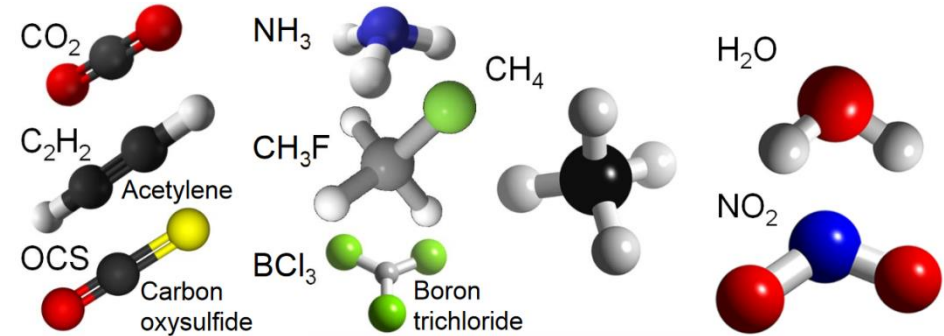## Molecular vibrations and rotations

Polyatomic molecules

3 principal axes => 3 principal moments of inertia: I_A, I_B, I_C

Symmetry classification

Type:

Linear molecules	Symmetric tops	Spherical tops	Asymmetric
$I_B = I_C$, $I_A \approx 0$	$I_B = I_C \neq I_A$, $I_A \neq 0$	$I_A = I_B = I_C$	$I_A \neq I_B \neq I_C$

examples

CO_2

C_2H_2 — Acetylene

OCS — Carbon oxysulfide

NH_3

CH_3F

BCl_3 — Boron trichloride

CH_4

H_2O

NO_2

Relatively simple

No dipole moment
Not microwave active

Most complex
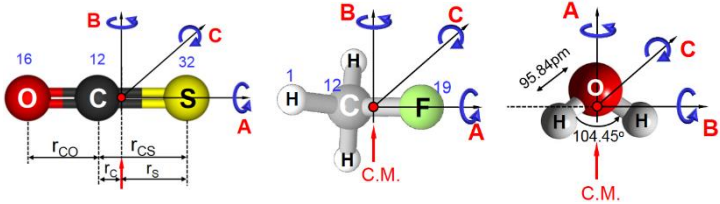
Q-branch allowed
– Intensity proportional to projections of l

16   12   32
O — C — S
r_{CO} r_{CS}
r_G r_s

1   12   19
H — C — F
H
H
C.M.

95.84pm
O
H   H
104.45°
C.M.
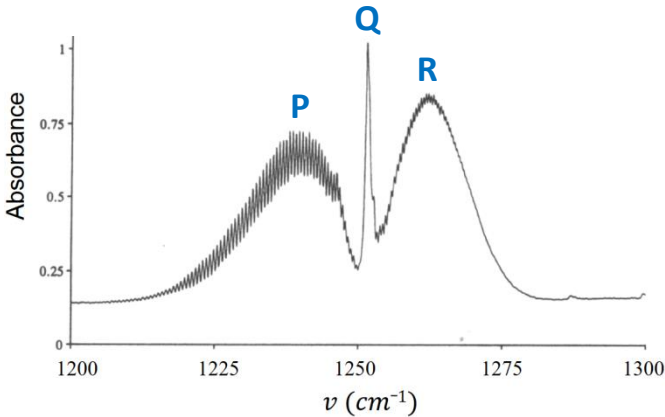
Linear molecules must be **asymmetric** to have electric dipole moment (isotopic substitution does not help – bond length unchanged)

OCS   HCN CO_2 C_2H_2 HC_2Cl
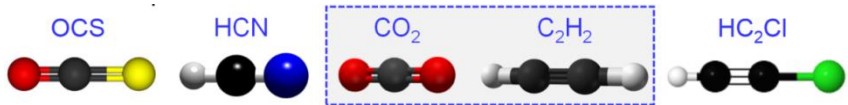
Symmetric => no dipole moment

Vibrational spectroscopy
Rotational-vibrational spectrum

Example: Carbon monoxide
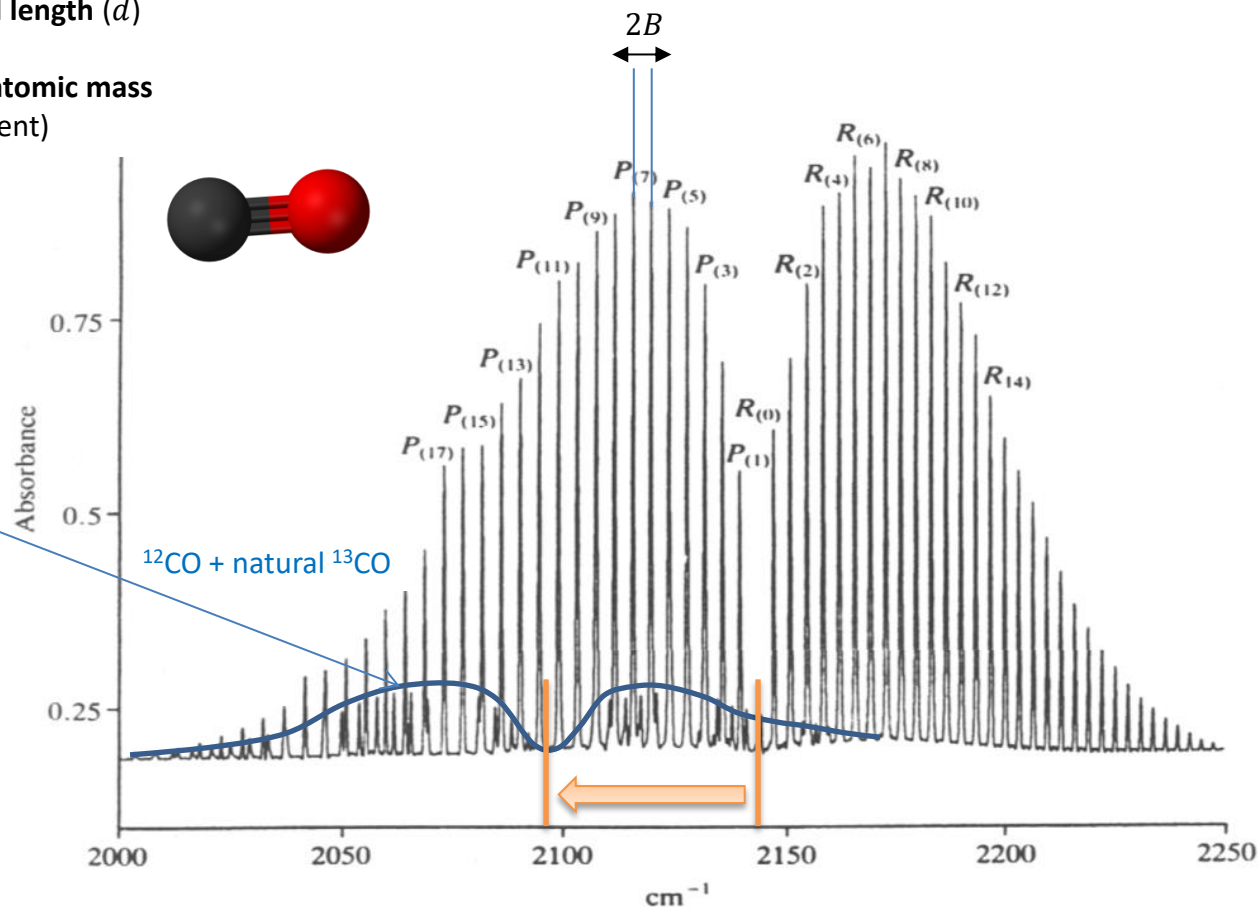
- (Almost) uniform spacing => easy to interpret

- $B = \frac{h}{8\pi^2 cI}, \ \ I = \mu d^2$

  => straight-forward determination of **bond length** (d)

- Isotopic substitution → determination of **atomic mass**
  (d is mass independent for the same element)

Isotopic effect:

$$\nu \propto \sqrt{\frac{1}{\mu}}, \ \ B \propto \frac{1}{\mu}$$

^{12}CO + natural ^{13}CO

Vibrational spectroscopy
Theory basics – molecular bonds

Force constants and bond orders – selected compounds

Bond A-B	Force Const. f [N cm⁻¹]	Bond Order	Compound	Bond A-B	Force Const. f [N cm⁻¹]	Bond Order	Compound
H-H	5.14	0.77	H_2	H-O	7.40	1.0	HO^-
Li-Li	1.24	1.2	Li_2	H-F	8.85	1.1	HF
B-B	3.58	1.2	B_2	H-Al	1.76	0.60	AlH_4^-
C-C	16.5	3.2	HCCH	H-Si	2.98	0.84	SiH_4
N-N	22.42	3.2	N_2	H-P	3.11	0.82	PH_3
O-O	11.41	1.4	O_2	H-S	4.29	1.0	H_2S
F-F	4.45	0.58	F_2	H-Cl	4.81	1.0	HCl
Na-Na	0.17	0.24	Na_2	H-Ge	2.81	0.82	GeH_4
Si-Si	4.65	2.0	Si_2	H-As	2.85	0.81	AsH_3
Si-Si	~1.7	~0.9	Si_2H_6	H-Se	3.51	0.93	H_2Se
P-P	5.56	2.1	P_2	H-Br	3.84	0.98	HBr
P-P	2.07	0.95	P_4	H-Sn	2.03	0.76	SnH_4
S-S	4.96	1.7	S_2	H-Sb	2.09	0.77	SbH_3
S-S	2.5	0.99	S_8	H-I	2.92	0.97	HI
Cl-Cl	3.24	1.1	Cl_2	C-H	5.50	1.0	CH_4
Ni-Ni	0.11	0.2	Ni solid	C-B	3.82	1.1	$B(CH_3)_3$
As-As	3.91	1.8	As_2	C-C	16.5	3.2	HCCH
Se-Se	3.61	1.6	$^{80}Se_2$	C-C	9.15	1.9	H_2CCH_2
Br-Br	2.36	1.1	Br_2	C-C	7.6	1.7	C_6H_6
Rb-Rb	0.08	0.2	Rb_2	C-C	4.4	1.1	H_3CCH_3
Cd-Cd	1.11	1.0	Cd_2^{2+}	C-N	18.07	3.0	HCN
Sb-Sb	2.61	1.9	Sb_2	C-N	11.84	2.1	CN_2^-
Te-Te	2.37	1.7	Te_2	C-N	6.54	1.3	$NNCH_2$
I-I	1.70	1.2	I_2	C-O	18.56	2.8	CO
Hg-Hg	1.69	1.5	Hg_2^{2+}	C-O	15.61	2.4	CO_2
Pb-Pb	4.02	3	Pb_2	C-O	12.76	2.0	OCH_2
Bi-Bi	1.84	1.6	Bi_2	C-O	7.86	1.3	CO_3^{2-}
H-B	2.75	0.68	BH_3	C-O	5.1	0.96	$O(CH_3)_2$
H-C	5.50	1.0	CH_4	C-F	6.98	1.1	CF_4
H-N	7.05	1.1	NH_3	C-P	8.95	2.4	HCP
H-O	8.45	1.1	H_2O	C-S	7.67	2.0	CS_2

Bond A-B	Force Const. f [N cm⁻¹]	Bond Order	Compound	Bond A-B	Force Const. f [N cm⁻¹]	Bond Order	Compound
C-S	3.3	1.0	$S(CH_3)_2$	O-O	6.18	0.89	O_2
C-Cl	3.12	0.93	CCl_4	O-O	5.70	0.83	O_3
C-Ni	2.91	1.2	Ni_4CO	O-Na	~3.2	~1.1	Na-OH
C-Ni	1.43	0.68	NiCO	O-Mg	3.5	1.1	MgO
C-Se	5.94	1.8	CSe_2	O-Al	5.66	1.5	AlO
C-Br	2.42	0.86	CBr_4	O-Al	3.8	1.1	$Al(OH)_4$
C-Rh	2.4	1.2	$(Rh(CN)_6)^{3-}$	O-Si	9.25	2.1	SiO
C-Ag	2.0	0.99	$(Ag(CN)_2)^-$	O-Si	4.75	1.2	SiO_4^{4-}
C-I	1.69	0.79	CI_4	O-P	9.41	2.0	PO
N-H	7.05	1.1	NH_3	O-P	6.16	1.4	PO_4^{3-}
N-B	7.2	1.6	BN_2	O-S	10.01	2.0	SO_2
N-C	18.07	3.0	HCN	O-Cl	4.26	1.0	ClO_2
N-N	22.42	3.2	N_2	O-Cl	3.30	0.82	ClO^-
N-N	16.01	2.4	N-NNH	O-Ca	2.85	1.2	CaO
N-N	13.15	2.0	$N-N-N^-$	O-Ti	7.19	2.4	TiO
N-O	25.07	3.1	$N-O^+$	O-V	7.36	2.3	VO
N-O	17.17	2.3	NO_2^+	O-Cr	5.82	1.9	CrO
N-O	15.49	2.1	NO	O-Mn	5.16	1.6	MnO
N-O	15.18	2.0	ONCl	O-Fe	5.67	1.7	FeO
N-O	11.78	1.7	NNO	O-Cu	2.97	0.93	CuO
N-F	4.16	0.66	NF_3	O-Ge	7.53	1.8	^{74}GeO
N-Si	3.8	1.1	$((CH_3)_3Si)_2NH$	O-Se	6.45	1.5	SeO
N-S	12.54	2.5	NSF_3	O-Mo	3.05	1.2	Ba_2CaMoO_6 (solid)
N-S	8.3	1.9	HNSO	O-Ru	6.70	2.2	RuO_4
N-S	3.1	0.87	H_3N-SO_3	O-Ag	2.00	0.79	AgO
O-Li	1.58	0.66	LiO	O-Sn	5.53	1.7	SnO
O-Be	7.51	1.8	BeO	O-Te	5.31	1.6	TeO
O-B	13.66	2.5	BO	O-Ba	3.79	1.8	BaO
O-B	6.35	1.3	BO_3^{3-}	O-Ce	6.33	2.6	CeO
O-O	16.59	2.0	O_2^+	O-Pr	5.68	2.4	PrO
O-O	11.41	1.4	O_2	O-Nd	3.5	1.6	$NdAc_3 \cdot H_2O$ (polymer)

Vibrational spectroscopy
Vibrational modes of polyatomic molecules

Degrees of vibrational modes of a free molecule

- Linear molecules: **3N–5**

- Nonlinear molecules: **3N–6**

    N … number of atoms within the molecule
   3N total
        3 translational, 3 (2) rotational

Theory of normal vibrations

Polyatomic molecules → coupled oscillators
Cannot be QM solved (even for harmonic osc.)
  => linear transformation to a coordinate system leading to
      a set of independent oscillators
      (1st aproximation – good for low vibr. states of stable molecules)

Normal modes = collective modes
with indentical frequency and phase

Common types of normal vibrations: stretching & bending motions (3-atom group within a molecule, e.g. =CH_2)

stretching ν
valenční

bending δ
in-plane   out-of-plane
rovinné   mimorovinné
deformační
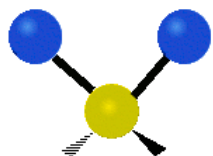
stretching symmetric ν_s
valenční symetrická
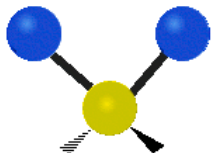
scissoring δ
nůžková
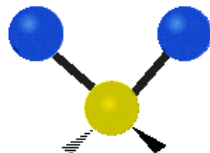
wagging ω
vějířová
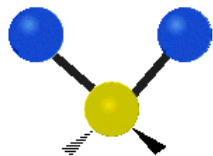
stretching asymmetric ν_{as}
valenční asymetrická
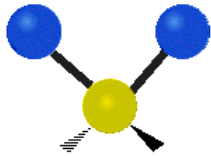
rocking ρ
kyvadlová
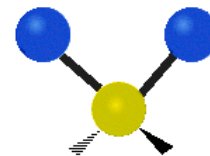
twisting τ
kroutivá

Cartesian vs. Internal coordinates:

Coordination system based on
internal coordinates – defined
according to chemical "common sense"
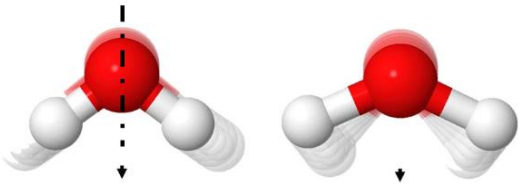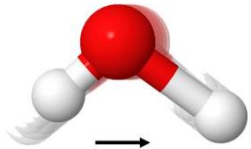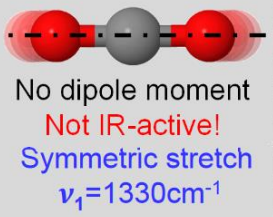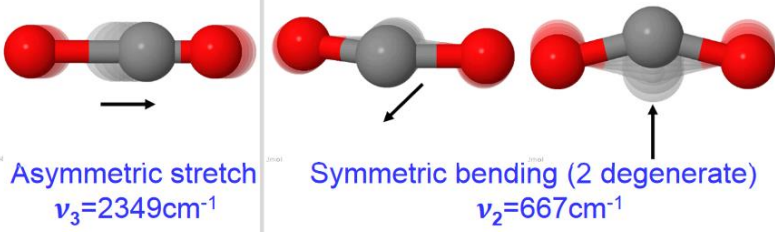
+ combinations
+ Fermi resonances

Generally
$f(\nu) > f(\delta)$

Vibrational spectroscopy
Vibrational modes

Parallel and perpendicular modes of symmetrical molecules

Examples:	**Parallel (‖)** Dipole changes are ‖ to the main axis of symmetry		**Perpendicular (⊥)** Dipole changes are ⊥ to the main axis of symmetry
H_2O (3x3-6=3 vib. modes)	Symmetric stretch $\nu_1 = 3652 cm^{-1}$	Symmetric bending $\nu_2 = 1595 cm^{-1}$	Asymmetric stretch $\nu_3 = 3756 cm^{-1}$
CO_2 (3x3-5=4 vib. modes)	No dipole moment Not IR-active! Symmetric stretch $\nu_1 = 1330 cm^{-1}$	Asymmetric stretch $\nu_3 = 2349 cm^{-1}$	Symmetric bending (2 degenerate) $\nu_2 = 667 cm^{-1}$

Molecular symmetry **preserved** during vibration   Molecular symmetry **broken** due to vibration

Important for rotation-vibrational spectroscopy – different **selection rules**:

$\Delta J = \pm 1$ $\Delta J = 0$ or ± 1

Vibrational spectroscopy
Group theory and vibrational spectroscopy

Group theory → symmetry operations is a finite group containing:

Symmetry elements Prvky symetrie
– basic geometrical entities

- *Point* – inversion center
- *Line* – Rotation axis
- *Plane* – Mirror plane

Symmetry operations Operace symetrie
– geometrical transformations
– can be represented by matrixes
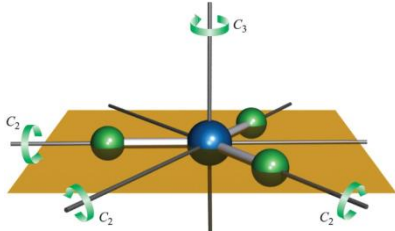
Principal axis = axis with the largest n of C_n

Group relationships
uzavřenost grupy
- Closure: $A \in G$ & $B \in G$ => $AB \in G$
- Associativity: $(AB)C = A(BC)$
- Identity: $\exists E: EA = AE = A$
- Inverses: $\forall A \exists A^{-1}: AA^{-1} = A^{-1}A = E$

Some symmetry operation relationships

$C_n{}^n = E$
$\sigma^2 = E$
$\sigma^{-1} = \sigma$
$\sigma^k = \sigma$ (odd k) or E (even k)
$i^k = i$ (odd k) or E (even k)
$S_n = C_n \sigma_h = \sigma_h C_n \Rightarrow S_1 = \sigma_h, S_2 = i$

nevlastní rotace
(rotačně-reflexní operace)

Symmetry element	Symbol used	Example*
Identity	E	
Rotation axis (rotation by 360°/n)	C_n	
Horizontal mirror plane (reflection about xy plane, i.e. perpendicular to principal axis)	σ_h	
Vertical mirror plane (reflection about xz or yz plane, i.e. containing principal axis)	σ_v	
Diagonal (dihedral) mirror plane (reflection between xz and yz planes)	σ_d	
Inversion center	i	
Improper rotation axis (rotation by 360°/n followed by reflection perpendicular to rotation axis)	S_n	

Vibrational spectroscopy
Group theory and vibrational spectroscopy
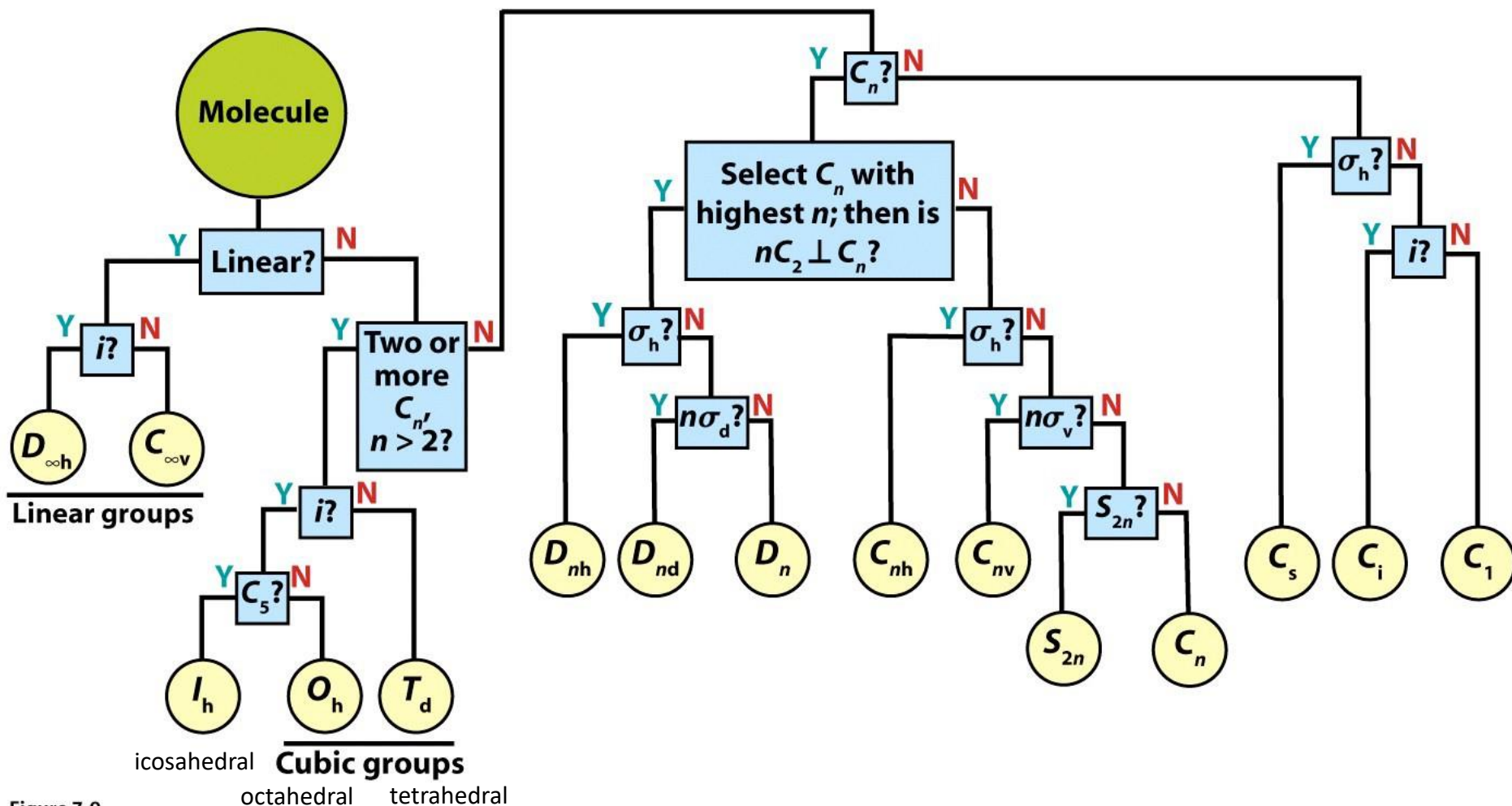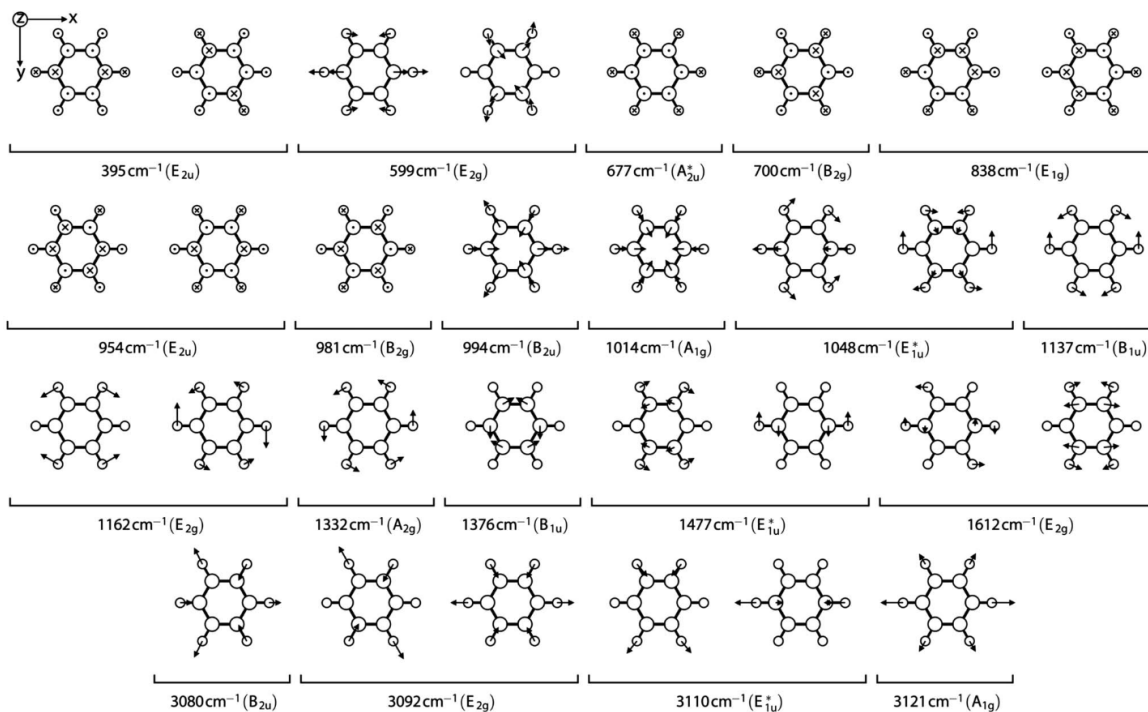
Point group determination chart

Figure 7-9
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong
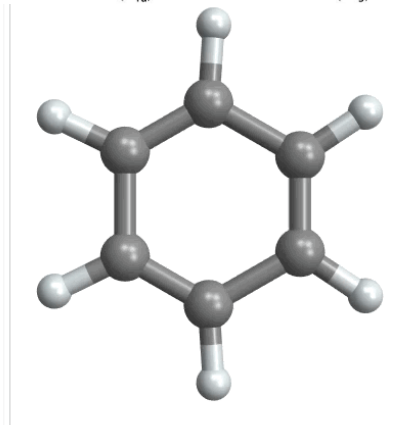
Vibrational spectroscopy
Vibrational modes

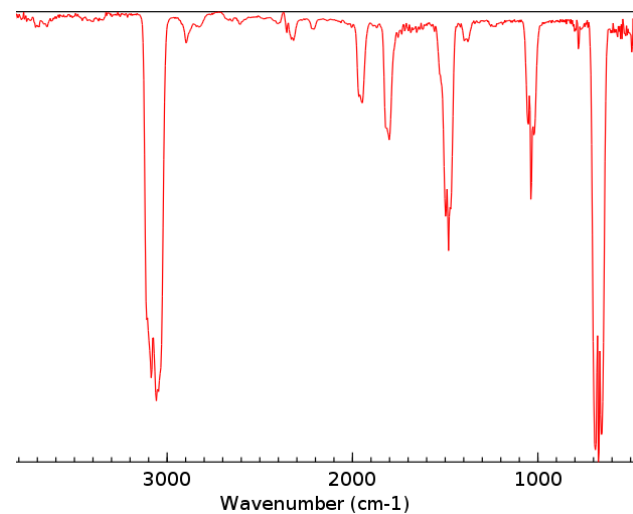**More complex case: Benzene** – highly conjugated system

395 cm^{-1} (E_{2u})   599 cm^{-1} (E_{2g})   677 cm^{-1} (A_{2u}^*)   700 cm^{-1} (B_{2g})   838 cm^{-1} (E_{1g})

954 cm^{-1} (E_{2u})   981 cm^{-1} (B_{2g})   994 cm^{-1} (B_{2u})   1014 cm^{-1} (A_{1g})   1048 cm^{-1} (E_{1u}^*)   1137 cm^{-1} (B_{1u})

1162 cm^{-1} (E_{2g})   1332 cm^{-1} (A_{2g})   1376 cm^{-1} (B_{1u})   1477 cm^{-1} (E_{1u}^*)   1612 cm^{-1} (E_{2g})

3080 cm^{-1} (B_{2u})   3092 cm^{-1} (E_{2g})   3110 cm^{-1} (E_{1u}^*)   3121 cm^{-1} (A_{1g})

Ring collective stretches = "breathing"

Ring bends = "puckering"

gas

solution (10% in CCl_4/CS_2) vs. solvent

NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)
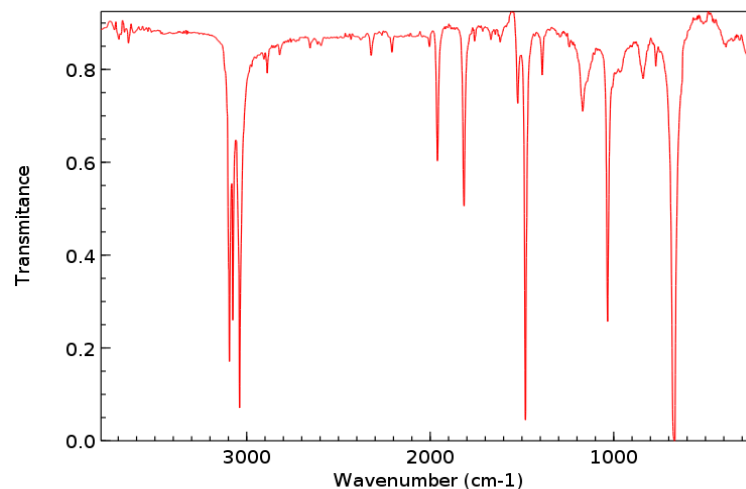
Infrared vibrational spectroscopy
Infračervená vibrační spektroskopie

- Method overview and principle
- Instrumentation
- Fourier Transform IR spectroscopy
- Interpretation of IR spectra
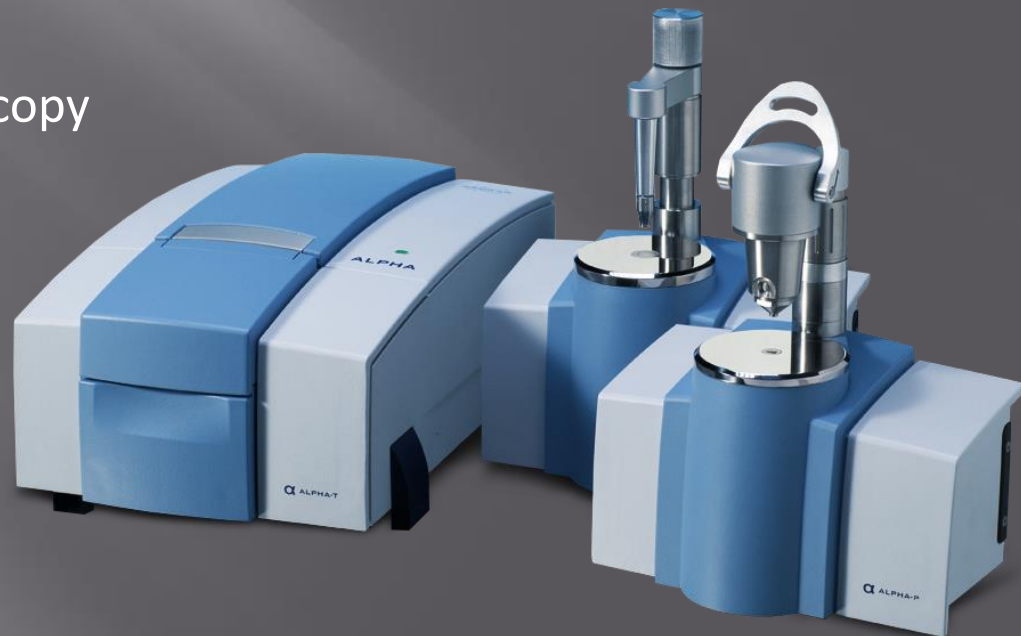
Infrared vibrational spectroscopy
Basics and classification

Infrared light spectrum
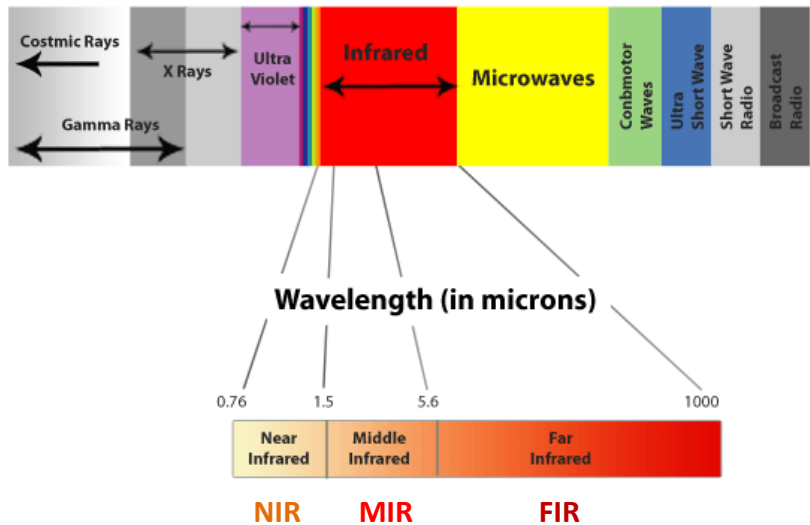
Wavelength [μm]	0.75	3	50	1000
Wavenumber [cm⁻¹]	13333	3333	200	10
Frequency [THz]	400	100	6	0.3
Photon Energy [meV]	1653	413	25	1.24

Division scheme of IR regions varies slightly – ISO, CIE, astronomy, telecommunications, …

Methods

Transmission
  – transparent samples

Reflection
- Specular reflection   *spekulární reflexe*
  – low incidence angle (~20-60°) specular refl. on highly-refl. sample
  – bulk optical properties, thin layers
- Reflection-absorption (**RAIRS / IRAS**)
  – grazing incidence reflection on highly-refl. sample (typ. metal)
  – thin films, adsorbates, ...
- Diffusive reflection (**DRIFTS**)   *difúzní reflexe*
  – diffusely scattered IR collected and refocused
  – typically for powders or rough surfaces
- Attenuated Total Reflectance (**ATR**)   *zeslabená úplná reflexe*
  or Multiple Internal Reflection (**MIR**)
  – total internal reflection in IR transmitting sample
  – absorption on surface-adsorbed species

Light absorption quantification

Transmittance
$$T = I/I_0$$

Absorbance
$$A = \log I_0/I$$
$$A = -\log T$$

Reflectance
Refl.→Abs.: Kramers-Kronig transformation
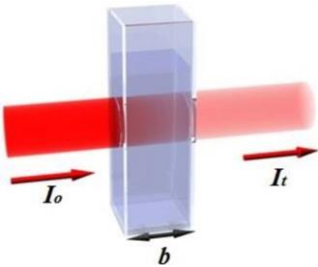
Infrared vibrational spectroscopy
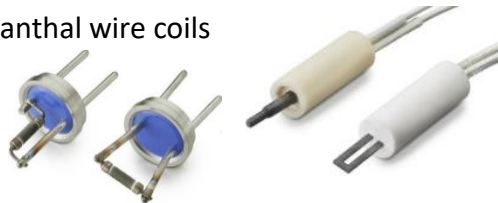## Instrumentation

✓ **Light (irradiation) sources**
   – Typically an ellectrically heated inert solid → continuous radiation (black body)
   – High stability and intensity required
   – Polarization modulation possible

- Nernst or Glower filament lamp
- Globar (SiC)
- Ni-Cr (Nichrome) or Kanthal wire coils
- Rh wire
- CO_2 laser w/ tuning

Special case: **Synchrotron source**

- High brightness – smaller samples, better signal-to-noise
- Essentially a point source:
   Can be focussed (diffraction-limited size) → Microscopy
- Pulsed source (light from electron bunches)
   → fast timing measurements (~ns)

✓ **Sampling devices**
   – Different for solids, liquids, gases
   – Solvents, mulls (oil paste) or salt (KBr, NaCl, …) buffers used

✓ **Monochromator** or **frequency modulator**
   1) Dispersion + monochromator → Dispersive IR
   2) Signal modulation and collection in time domain → Fourier transform IR

✓ **Transducers** or **detectors**
   – Can be cooled for lower noise and higher stability

   1) Thermal transducers: Thermocouples and bolometers
   2) Pyroelectric transducers
   3) Photoconducting transducers

✓ **Signal processing and recording device**

Vibrational spectroscopy
Instrumentation – samples

Transmission measurements

- KBr or CsI pellet
- Cuvette with KBr or NaCl windows (ZnSe, Si, AgCl, ... for water) – liquids, gases
- Thin film or precipitate on KBr or NaCl window
- Suspension in Nujol (parrafine oil) or Fluorolube (fluorinated hydrocarbon) – powders
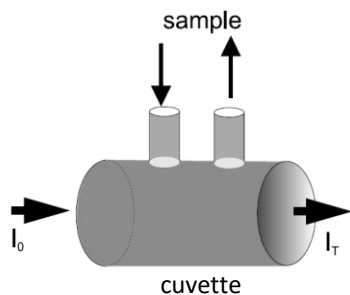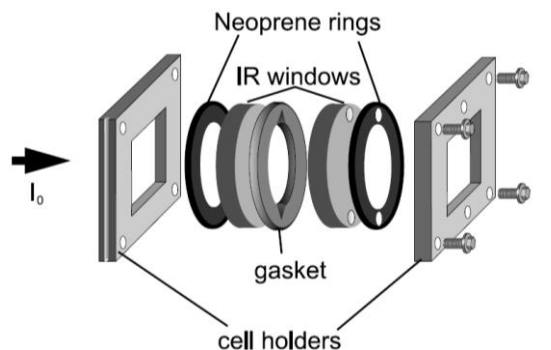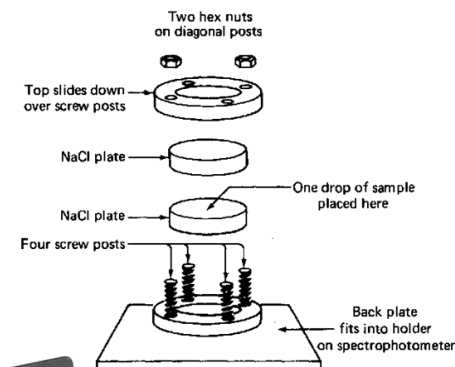
Samples

- solid, liquid, gas
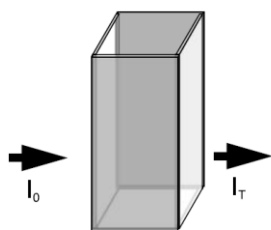
UV/Vis liquid cell   Flow cell (liquids, gases)   IR liquid cell   Solids, precipitates

- pellet (salt+sample powder)
- thin film
- droplet on a plate

Vibrational spectroscopy
Instrumentation – samples

Reflection measurements

- External (specular) reflection
- Reflection absorption (RAIRS/IRRAS)
- Internal reflection – attenuated total reflection (ATR)
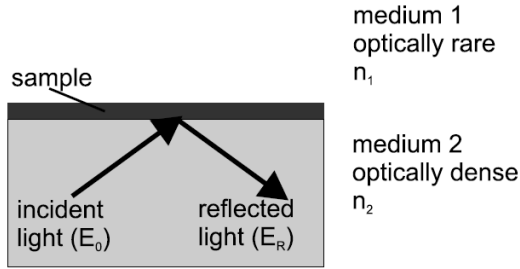- Diffuse (DRIFTS)

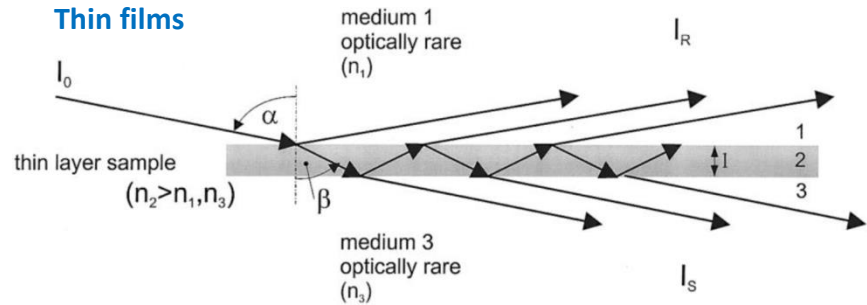### Samples
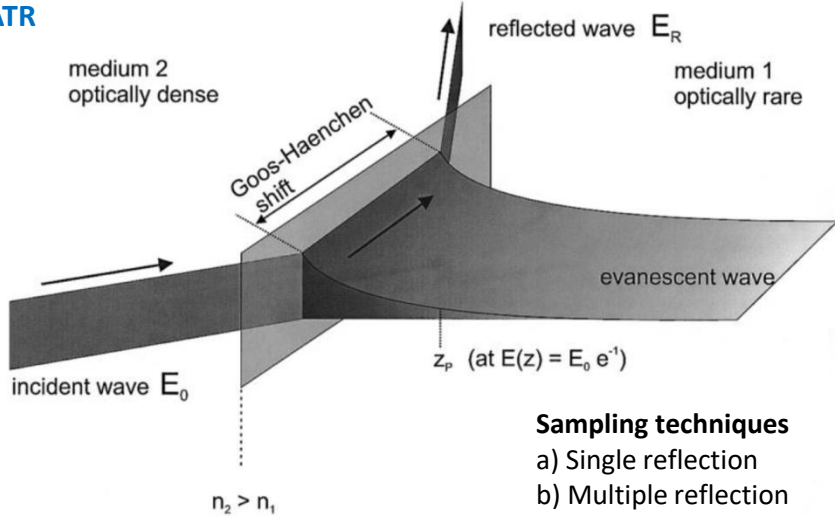
- Solids – most common
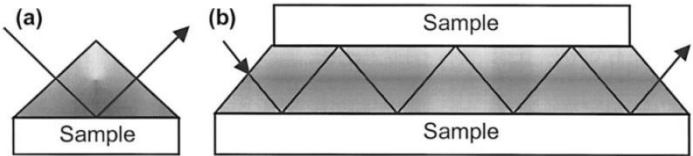- Liquids (ATR)

Thin films

Rough surfaces, powders
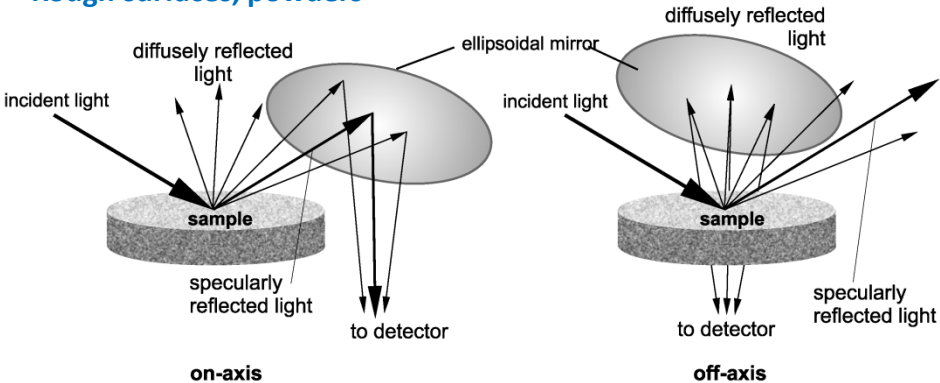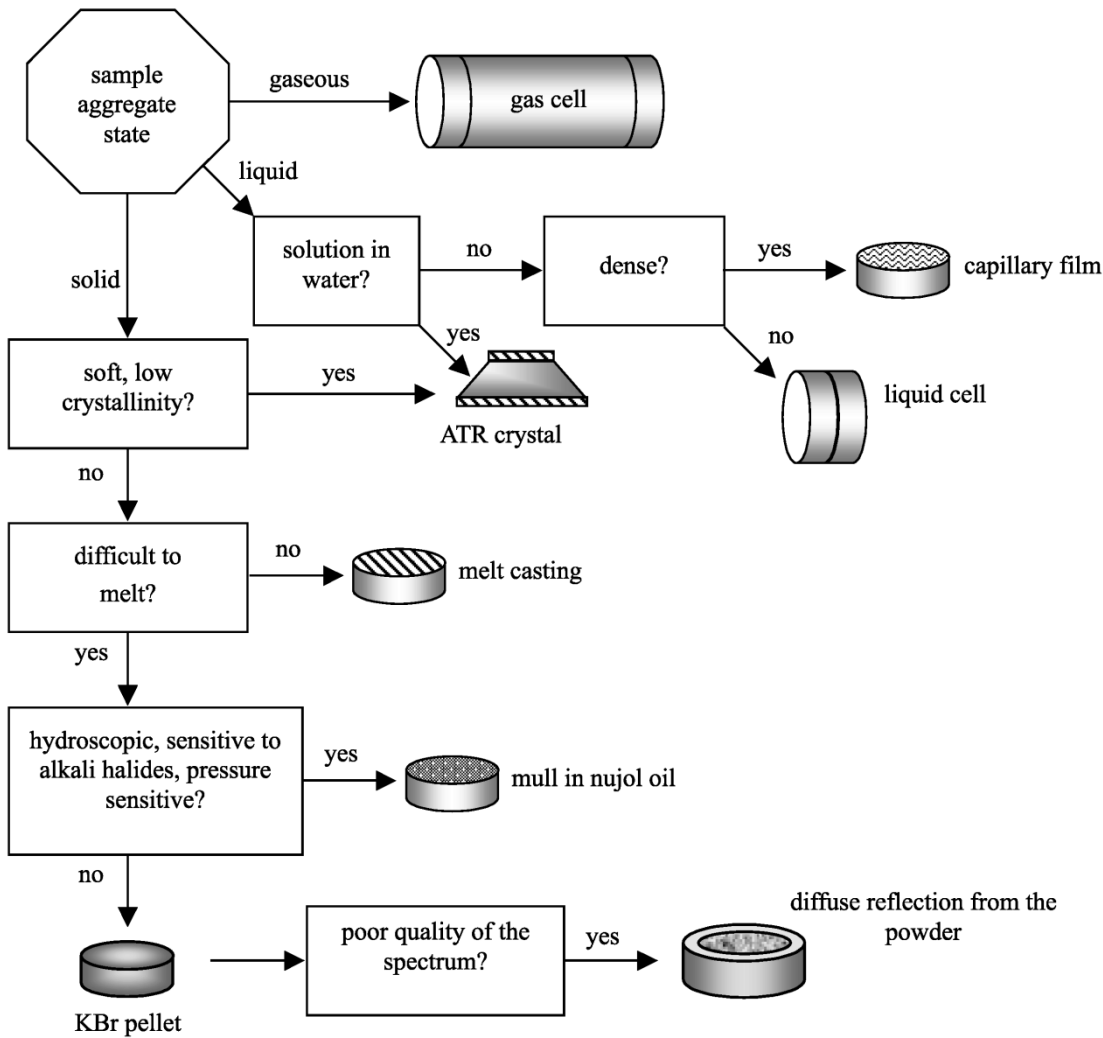
ATR

Sampling techniques
a) Single reflection
b) Multiple reflection

Vibrational spectroscopy
Instrumentation – samples

IR sampling techniques – decision chart for „bulk" samples

Infrared vibrational spectroscopy
Instrumentation – Dispersive IR spectrometry

Dispersive IR spectrometer

– Good for qualitative work
– Sample between source and monochromator
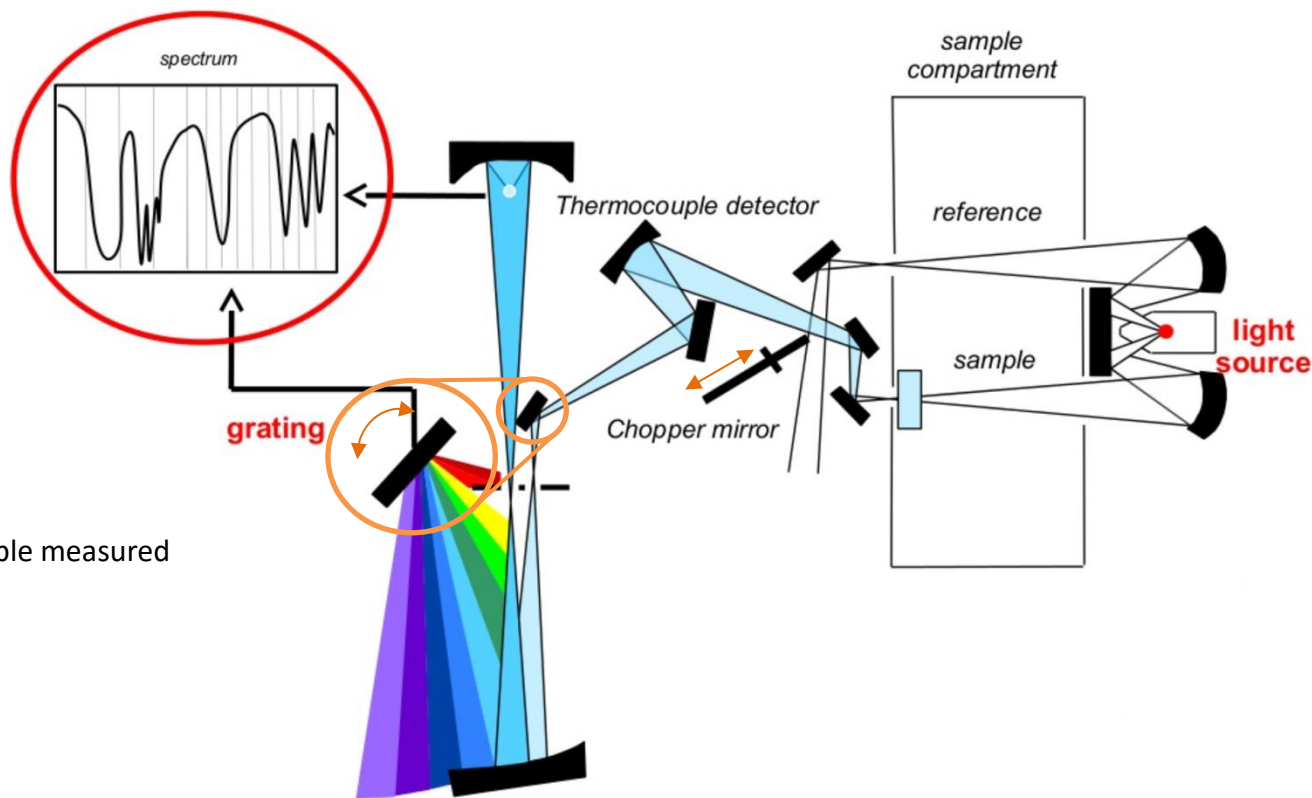 (elimination of scattered radiation)
– Nowadays outdated

Double beam DIR – simultaneous sample and reference

Advantages

- Less expensive than FTIR
- In DB-DIR: both reference and sample measured

Diadvantages

- Single frequency at a time
- Slow scan speed
- Low signal (narrow aperture)

Non-dispersive IR spectrometer

– The same construction except the source is intrinsically monochromatic and tunable

Infrared vibrational spectroscopy
Instrumentation – Fourier Transform IR spectroscopy

IR spectroscopy with Fourier transform (FTIR)

- Fast measurements (sub-second spectra possible)
- Better sensitivity and S/N ratio
- Better frequency resolution and reproducibility
- Better reliability (less moving parts)

Main advantages (from dispersive sp.):

- Jacquinot (throughput) adv.   Výhoda světelnosti
  – wider beam spot size: no narrow slits

- Felgett (multiplex) adv.   Multiplexová výhoda
  – response at all wavelengths measured simultaneously

- Connes[F] (precision) adv.   Výhoda jednoduché kalibrace
  – automatic internal calibration: HeNe laser (<0.01 cm^{-1} accuracy)

Time-resolved IR spectroscopy
*(measurement modes for fast processes)*

Rapid Scan technique

- time-resolved spectroscopy of **non-reproducible** experiments (e.g. many chemical reactions)

- Interferometer mirror moves very fast
- More scans can be averaged
- Low resolution (short path)

Up to ~100 spectra/s possible!

Step Scan technique

- monitoring of very fast **reproducible** events (transients)

- Interferometer mirror consecutively steps to separate interferogram points and the experiment is restarted again
- High time resolution
- Very long path possible => high spectral resolution
- Low signals => synchronous detection (lock-in)
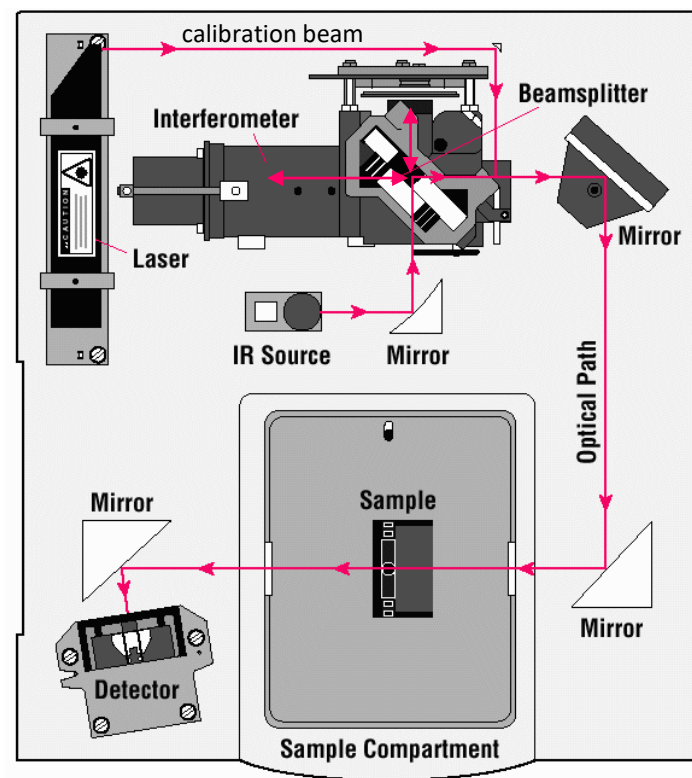
Applications

- Electron transfer studies
- Gas-phase kinetics
- Spectroscopy of radical intermediates
- Dynamics of combustion processes
- Photolysis experiments
- Pump–probe experiments
- Time-resolved emission spectroscopy (photoluminescence, fluorescence, pulsed laser emission, …)
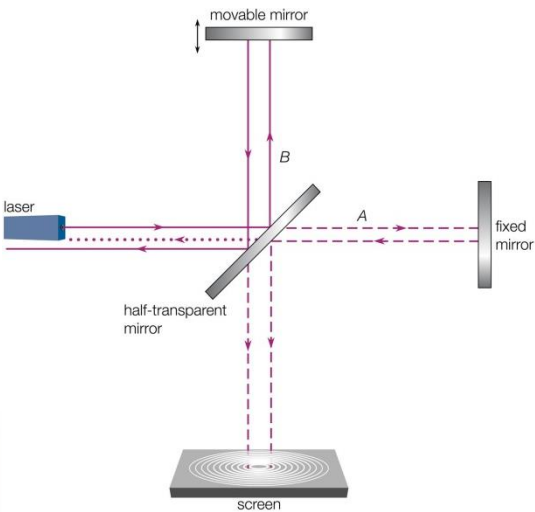
Infrared vibrational spectroscopy
Instrumentation – Fourier Transform IR spectroscopy

FTIR interferometer

- Optical device to produce interference of 2 light beams with variable phase difference
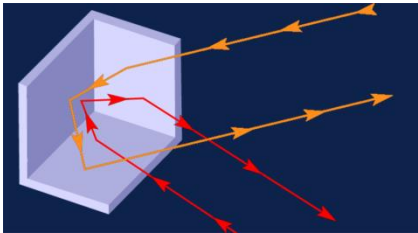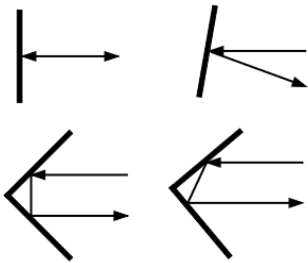
Standard Michelson interferometer

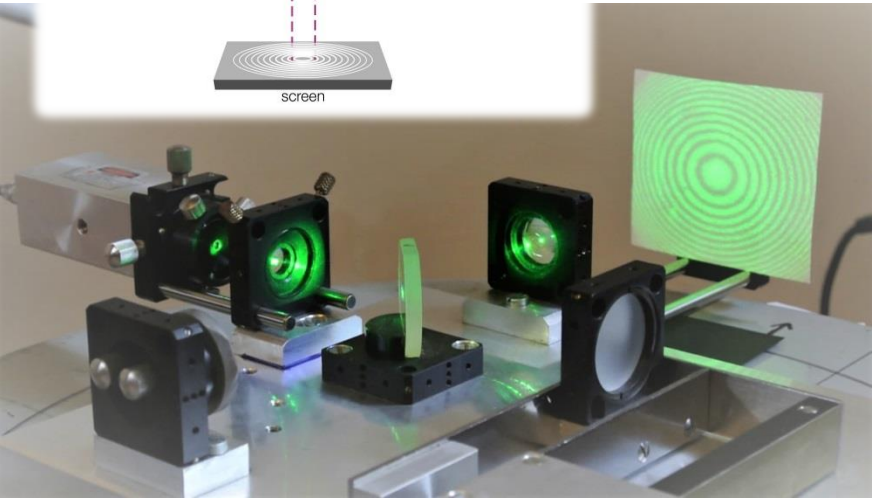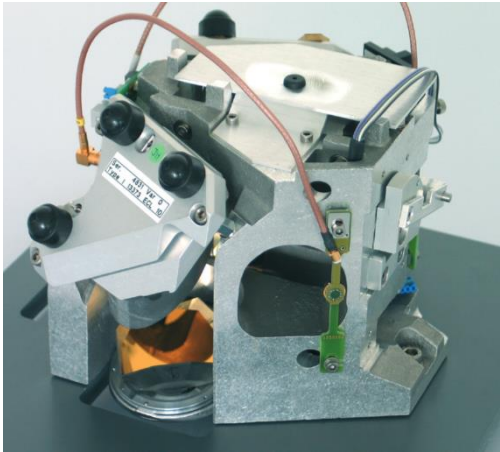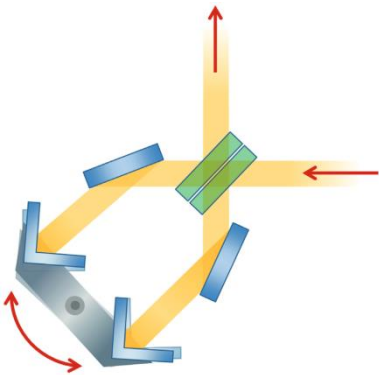- Flat mirrors
- Tilt alignment needed – e.g. by piezo transducers

Cube corner mirror interferometer

- Dual retroreflecting cube corner mirrors   koutový odražeč
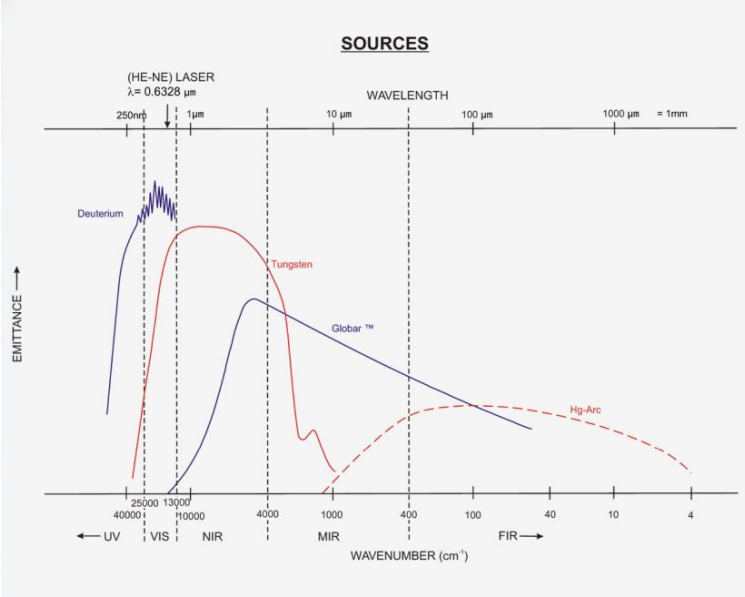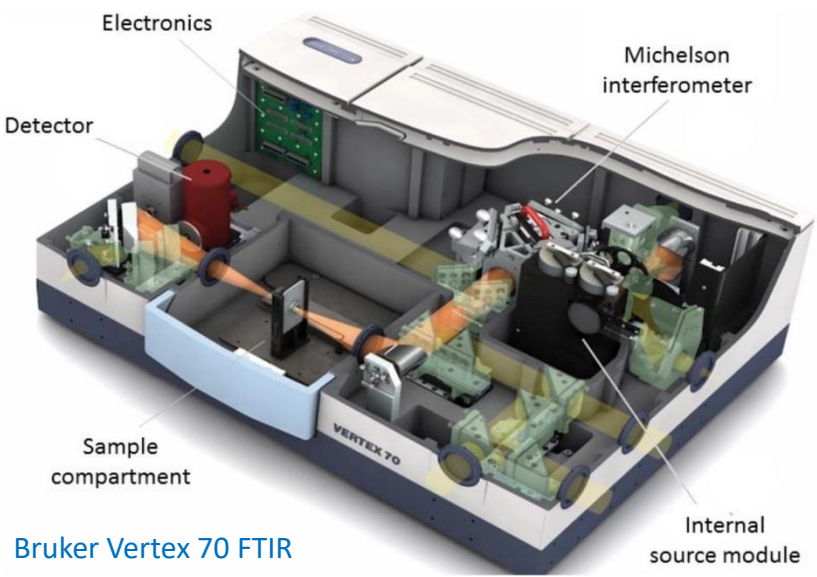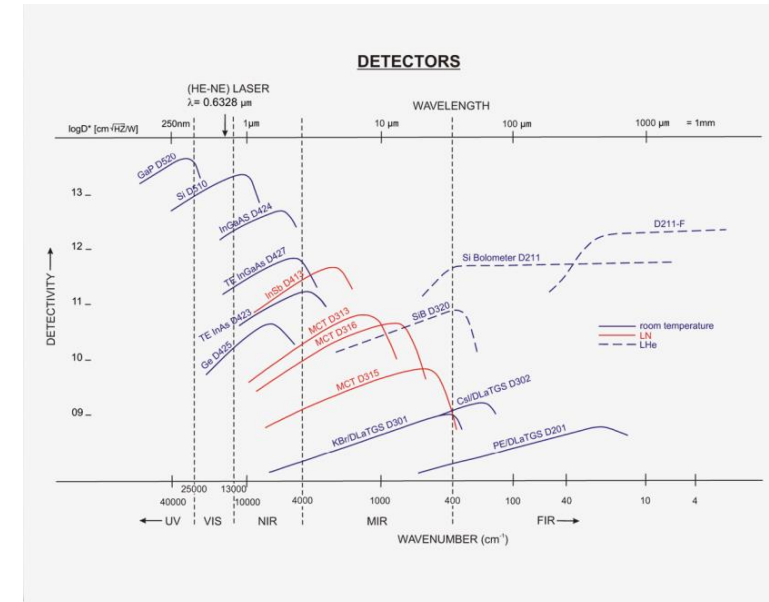- Tilt invariant => More stable

RockSolid^{TM} interferometer (Bruker)

Infrared vibrational spectroscopy
Instrumentation – Fourier Transform IR spectroscopy

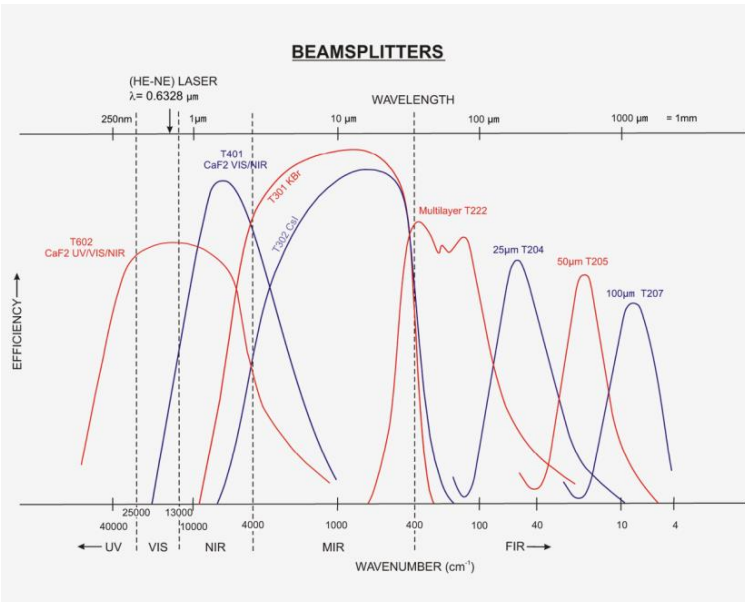Bruker Vertex 70 FTIR

Infrared vibrational spectroscopy
Fourier Transform IR spectroscopy – Theory

Detected intensity of 2 monochromatic plane waves with the same frequency:

$$I = \left|\vec{E}\right|^2 = \left|\vec{E_1}\right|^2 + \left|\vec{E_2}\right|^2 + 2\left|\vec{E_1}\right| \cdot \left|\vec{E_2}\right| \cos \Theta$$

Normal incidence, $\Theta = kx$, $k = 2\pi/\lambda$, x … pathlength difference

$$\frac{1}{2}\left|\vec{E_1}\right|^2 = \frac{1}{2}\left|\vec{E_2}\right|^2 \equiv G$$

$$\Rightarrow \quad I(x) = G[1 + \cos(kx)]$$

For non-monochromatic light: Spectral function $G(k)$

Short reminder:

$$e^{ikx} = \cos(kx) + i\sin(kx) \qquad \text{Euler's formula}$$
$$\cos(kx) = \frac{1}{2}\left(e^{ikx} + e^{-ikx}\right)$$
$$\sin(kx) = \frac{1}{2i}\left(e^{ikx} - e^{-ikx}\right)$$

$$I(x) = \int_0^\infty [1 + \cos(kx)]G(k)dk$$
$$= \int_0^\infty G(k)dk + \int_0^\infty G(k)\frac{1}{2}\left(e^{ikx} + e^{-ikx}\right)dk$$
$$= \frac{1}{2}I(0) + \frac{1}{2}\int_{-\infty}^\infty G(k)e^{ikx}dk$$

$$W(x) \equiv \frac{2I(x) - I(0)}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty G(k)e^{ikx}dk$$

$\Rightarrow G$ is a **Fourier transform** of W

$$G(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty W(x)e^{-ikx}dx$$

I(x) → G(k)

FFT Calculations

%T

Polystyrene run as film

Wavenumbers (cm-1)

Interferograms   CPU   Spectrum
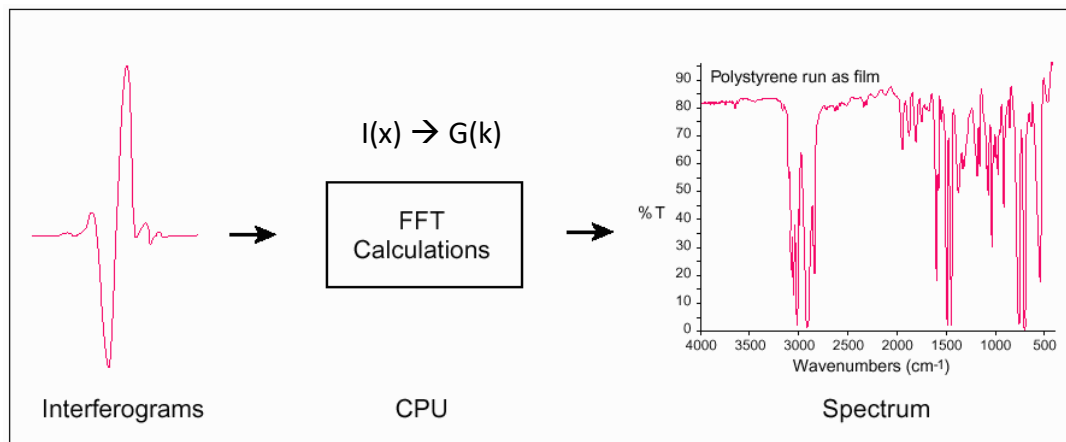
$(1/\sqrt{2\pi}$ constant from angular freq. and k relation & symmetry of direct and inversion Fourier)

Infrared vibrational spectroscopy
Fourier Transform IR spectroscopy – Theory
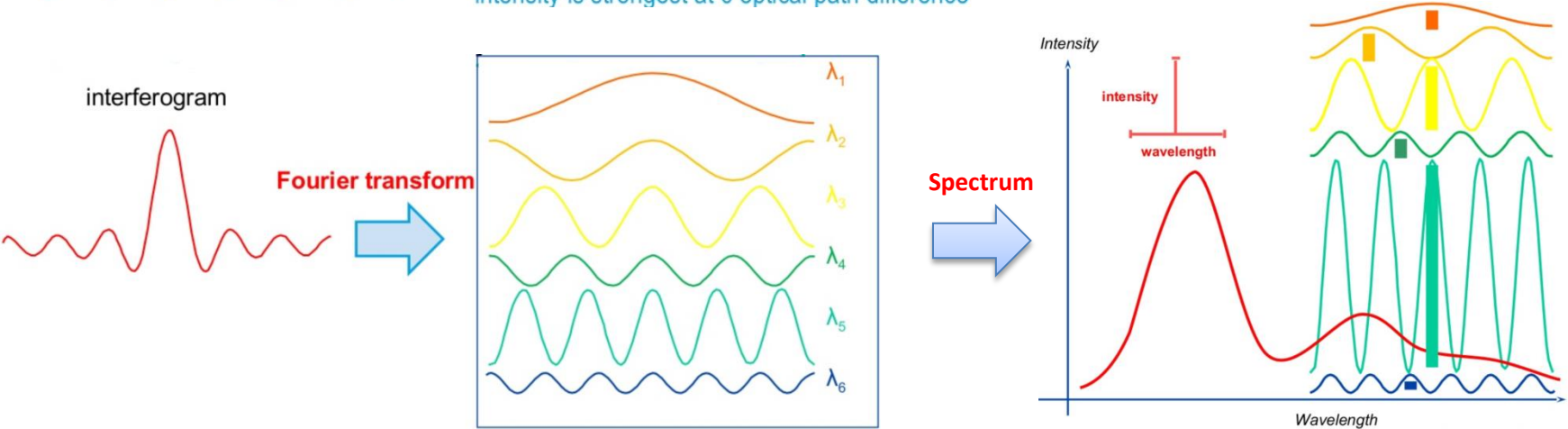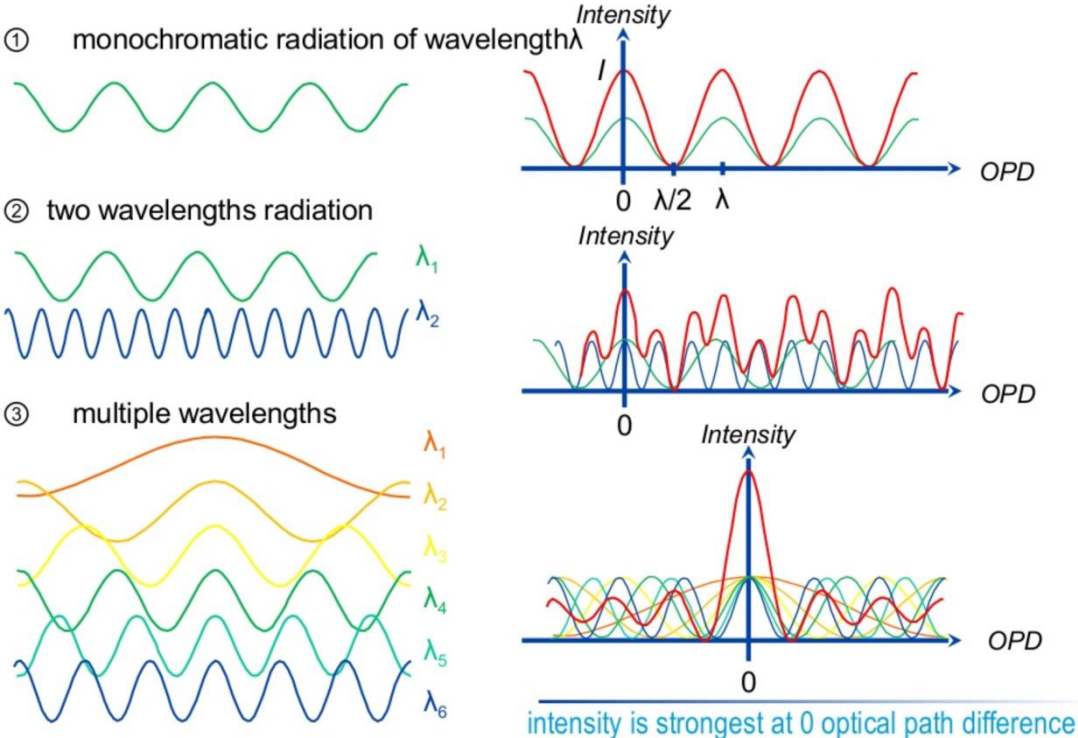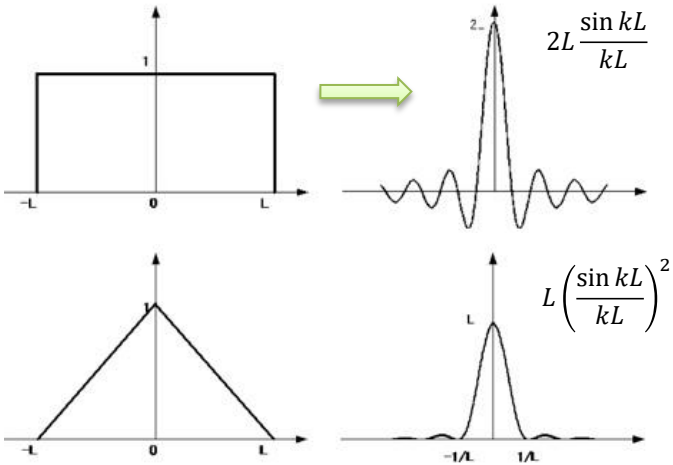
Infrared vibrational spectroscopy
Fourier Transform IR spectroscopy – Theory

In real device: we cannot measure from -∞ to ∞

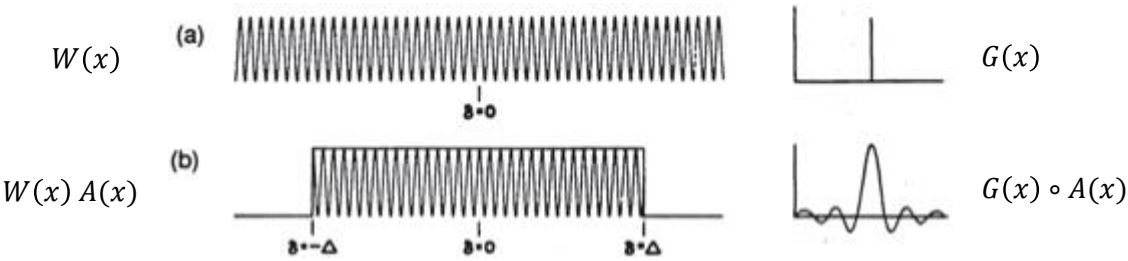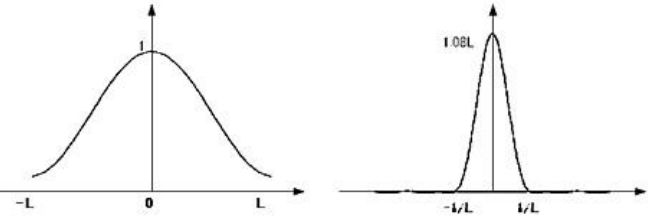$$\Rightarrow \quad resolution \propto \frac{1}{2\pi x_{max}}$$

+ limits in x create ripples around peaks

$W(x)$ (a)
$W(x) A(x)$ (b)
$G(x)$
$G(x) \circ A(x)$

Apodization function

$2L \dfrac{\sin kL}{kL}$

$L \left(\dfrac{\sin kL}{kL} \right)^2$

Happp-Genzel function

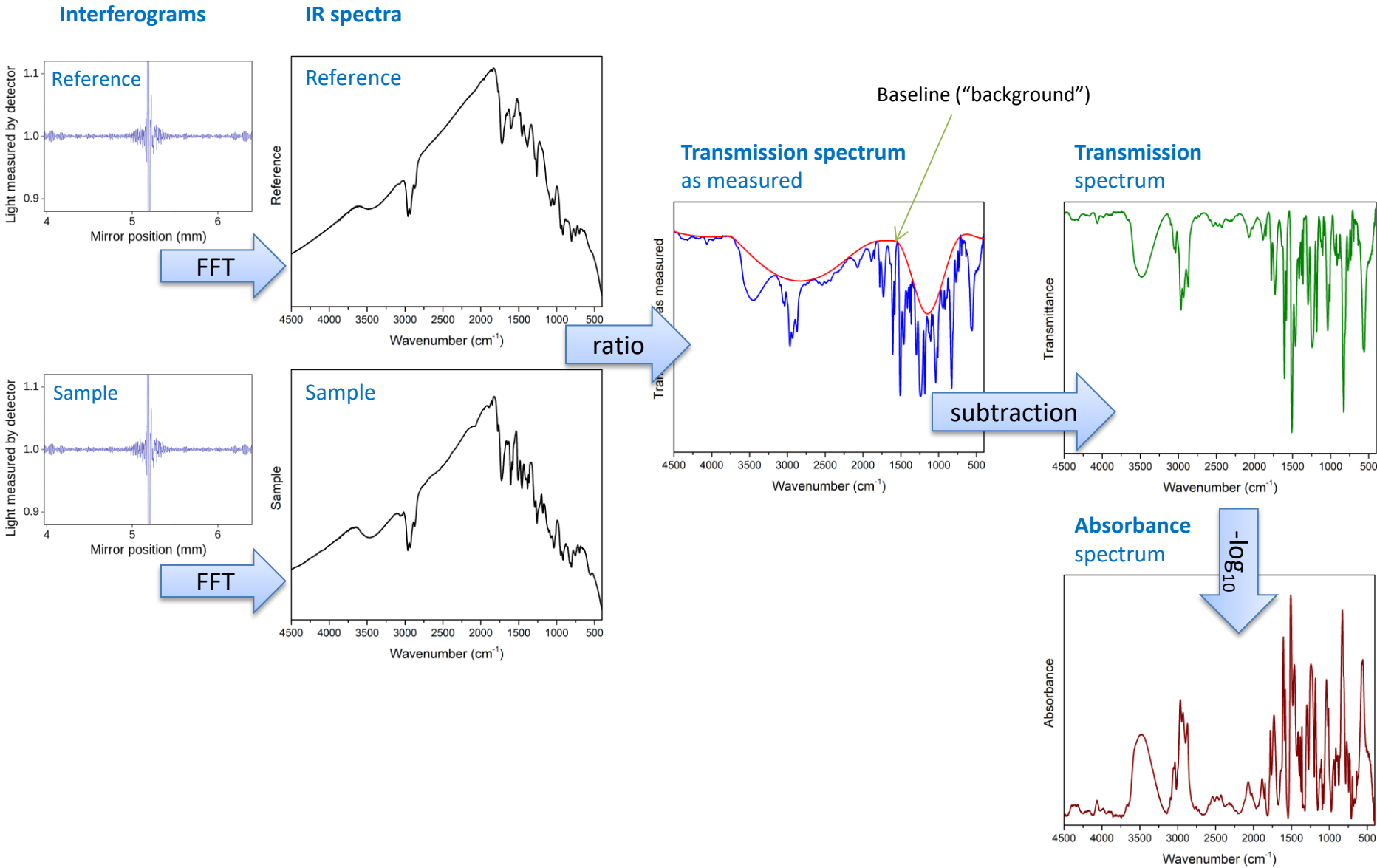| Apodization Function ($|x| \leq L$)		Fourier Transform Image	FWHM	Resolution	Peak Height	Ripple
Box-car	1	$2L \dfrac{\sin 2\pi vL}{2\pi vL}$	0.60/L	0.68/L	2.0L	-0.215
Triangular	$1 - \dfrac{|x|}{L}$	$L \left(\dfrac{\sin \pi vL}{\pi vL} \right)^2$	0.88/L	0.88/L	1.0L	+0.045
Happ-Genzel	$0.54 + 0.46\cos\left(\dfrac{\pi x}{L}\right)$	$\left\{ \dfrac{0.54}{\pi v} + \dfrac{0.46 \times 4\pi vL^2}{\pi^2 - (2\pi vL)^2} \right\} \sin(2\pi vL)$	0.91/L	0.89/L	1.08L	-0.006
Cosine (Cos)	$\cos\left(\dfrac{\pi x}{2L}\right)$	$\dfrac{\pi L}{(\pi/2)^2 - (2\pi vL)^2} \cos(2\pi vL)$	0.82/L	0.85/L	1.27L	-0.067
Lorenz	$\exp\left(-\dfrac{|x|}{L}\right)$	$\dfrac{2L}{1 + (2\pi vL)^2} \times [+e^{-1}\{2\pi vL \sin(2\pi vL) - \cos(2\pi vL)\}]$	0.71/L	0.73/L	1.26L	-0.055
Gaussian	$\exp\left\{-\left(\dfrac{2.24x}{L}\right)^2\right\}$	$\dfrac{L\sqrt{\pi}}{2.24} \exp\left\{-\left(\dfrac{\pi vL}{2.24}\right)^2\right\}$	1.17/L	1.16/L	0.79L	-0.000

Phase correction

FT generally yields complex spectrum (interferogram asymmetry): $G_R(x) + iG_I(x)$

→ Can be removed by calculation of square root of power spectrum: $G(x) G^*(x)$ (Mertz method)

Infrared vibrational spectroscopy
Fourier Transform IR spectroscopy – Workflow
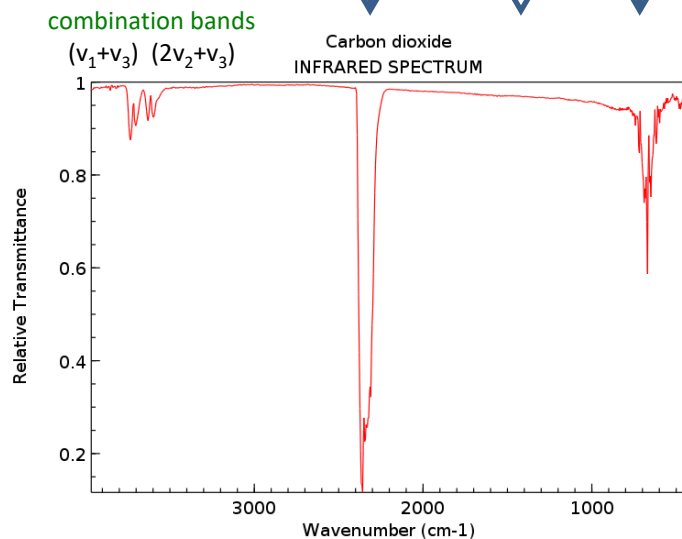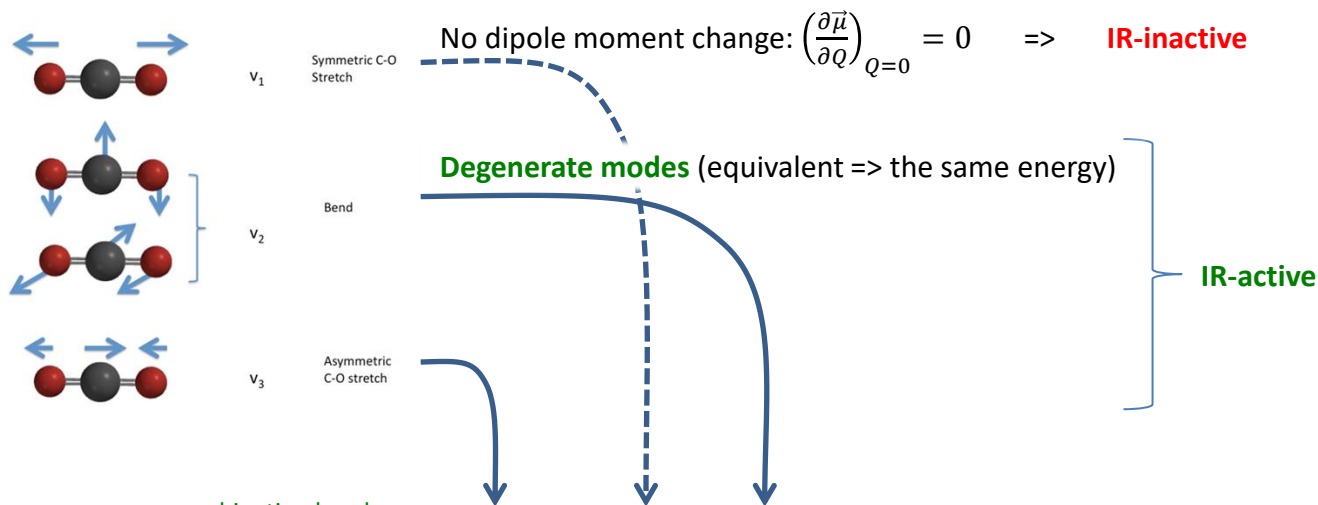
Interferograms

IR spectra

Reference

Reference

FFT

Sample

Sample

FFT

Baseline ("background")

Transmission spectrum
as measured

ratio

subtraction

Transmission
spectrum

-log$_{10}$

Absorbance
spectrum

Infrared vibrational spectroscopy
IR active vibrational modes

Example: Carbon dioxide (CO_2)

4 vibr. modes, but only **2** IR bands

Dipole moment = charge imbalance in the molecule

No dipole moment change: $\left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0} = 0$ =>   **IR-inactive**

v_1 — Symmetric C-O Stretch

Degenerate modes (equivalent => the same energy)

v_2 — Bend

IR-active

v_3 — Asymmetric C-O stretch

combination bands
(v_1+v_3) ($2v_2+v_3$)

Carbon dioxide
INFRARED SPECTRUM

Relative Transmittance

Wavenumber (cm-1)

NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Infrared vibrational spectroscopy
Interpretation of spectra

Interpretation of IR spectra – 2 interconnected tasks

1. Assignment of peaks and bands
2. Characterization of vibrations with respect to molecular geometry

Not all peaks are diagnostically valuable

Group frequency concept

Atomic group vibrates independently of other groups

(not exactly valid: differences treated as relatively small shifts)

⚠️ Not applicable to **coupled vibrations**

Ethanol
CH₂CH₃OH

Infrared vibrational spectroscopy
Interpretation of spectra

Interpretation of IR spectra – 2 interconnected tasks

1. Assignment of peaks and bands
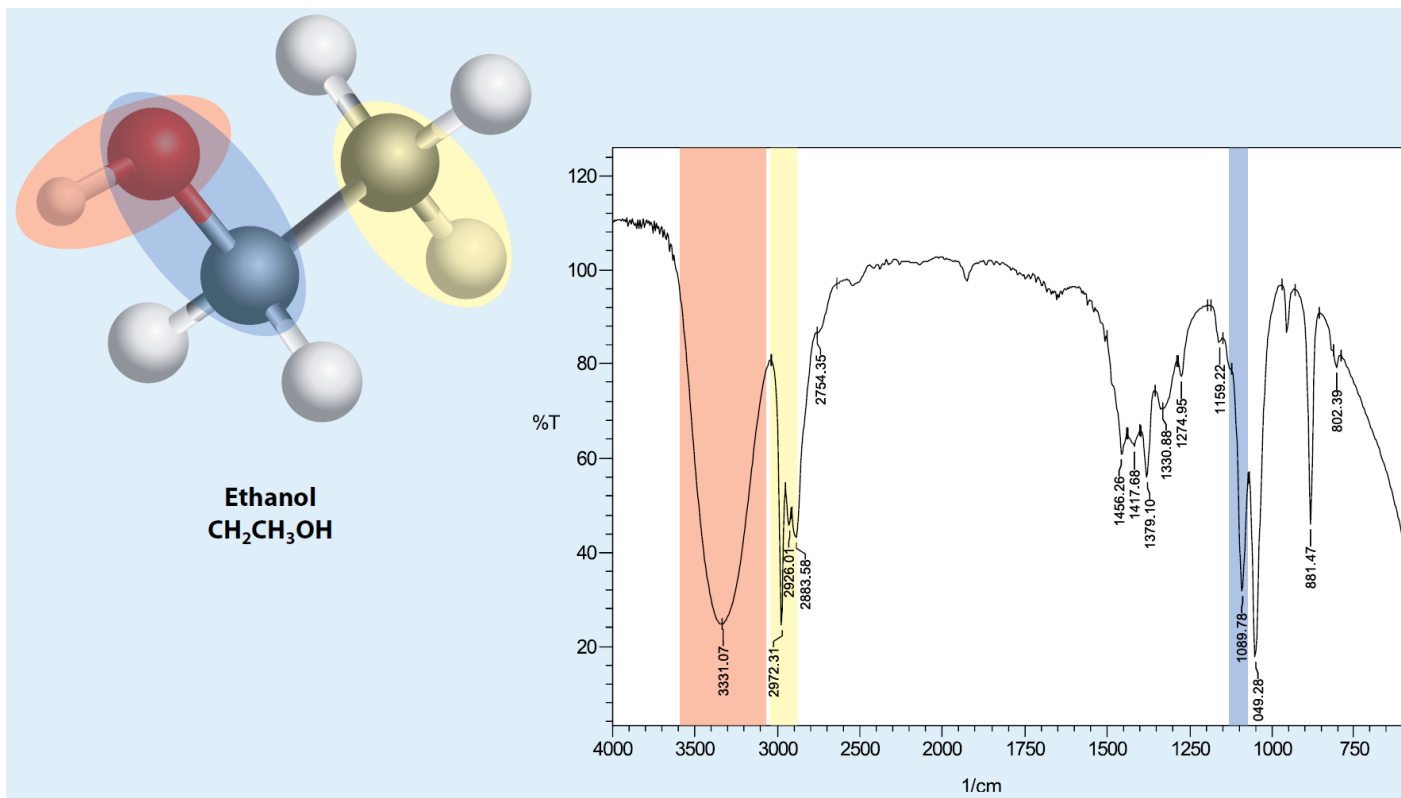2. Characterization of vibrations with respect to molecular geometry

Not all peaks are diagnostically valuable

Group frequency concept

Atomic group vibrates independently of other groups

(not exactly valid: differences treated as relatively small shifts)

⚠ Not applicable to **coupled vibrations**

Stretching vibration regions

- 3700-2500 cm^{-1} Single bonds to H
- 2300-2000 cm^{-1} Triple bonds
- 1900-1500 cm^{-1} Double bond
- 1400-650 cm^{-1} Single bonds (other than H)

Characteristic peak/band assignments
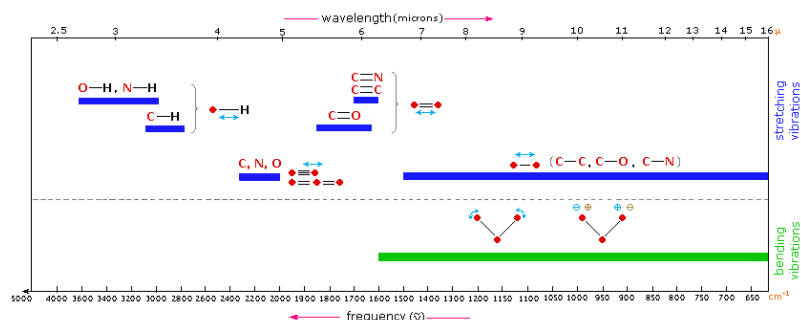→ **Functional groups**

„**Fingerprint region**"

Bond strength generally more important than mass

(unless very diff. as with H)
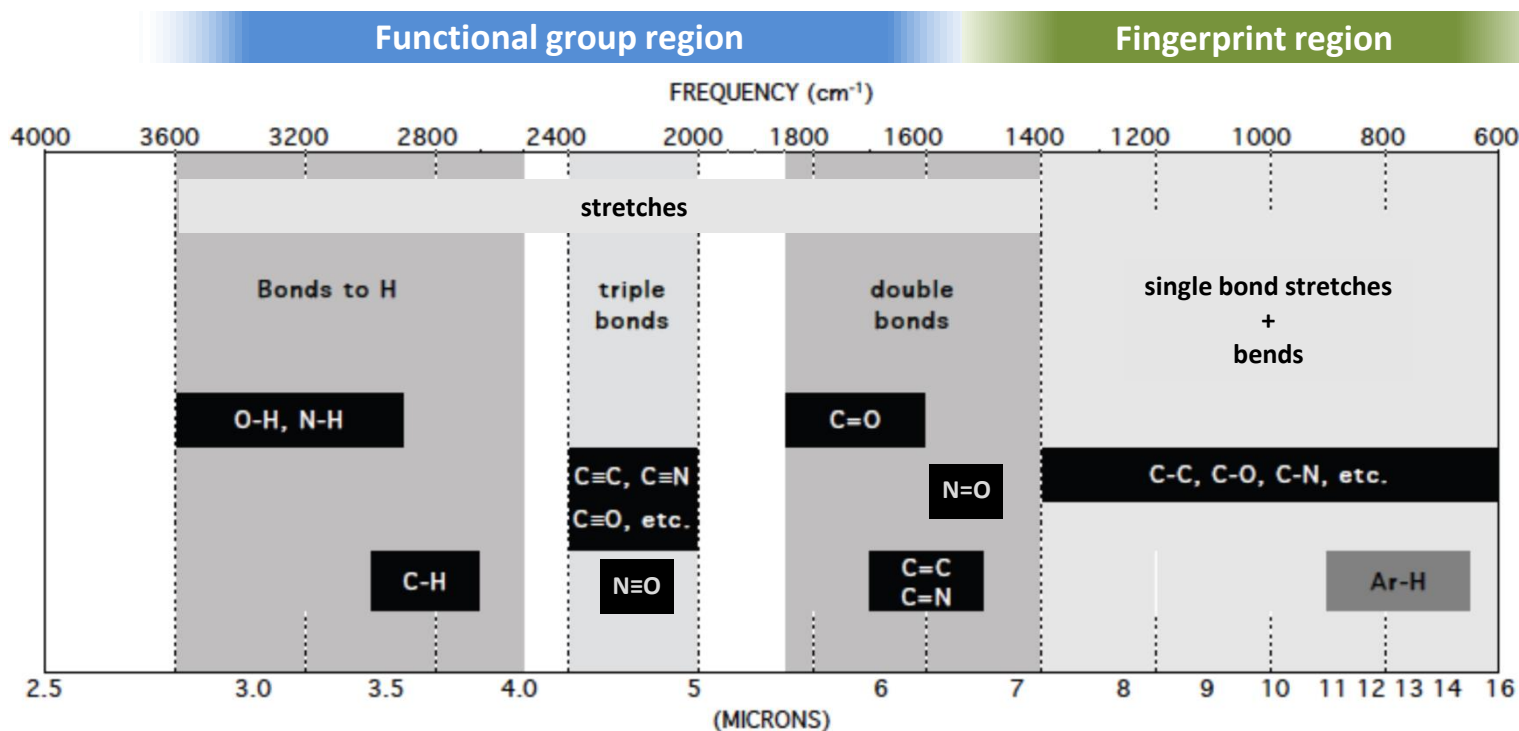
Infrared vibrational spectroscopy
Interpretation of spectra

Exact band position depends on the **bond environment** (type of molecule)

Single Bonds to Hydrogen

Bond	Wavenumber/cm^{-1}	Notes
C–H	3000 – 2850	Saturated alkanes, limited value as most organic compounds contain C–H
=C–H	3100 – 3000	Unsaturated alkene or aromatic
≡C–H	3300	Terminal Alkyne
O=C–H	2800 and 2700	Aldehyde, two weak peaks
O–H	3400 – 3000	Alcohols and Phenols. If hydrogen bonding present peak will be broad 3000–2500 (*e.g.* carboxylic acids)
O–H (free)	~3600	
N–H	3450 – 3100	Amines: Primary - several peaks, Secondary - one peak, tertiary - no peaks

Single Bonds (not to Hydrogen)

Bond	Wavenumber/cm^{-1}	Notes
C–C	Variable	No diagnostic value
C–O, C–N	1400 – 1000	Difficult to assign
C–Cl	800 – 700	Difficult to interpret
C–Br, C–I	Below 650	Often out of range of instrumentation

Double Bonds

Bond	Wavenumber/cm^{-1}	Notes
C=O	1840 – 1800 & 1780 – 1740	Anhydrides
C=O	1815 – 1760	Acyl halides
C=O	1750 – 1715	Esters
C=O	1740 – 1680	Aldehydes
C=O	1725 – 1665	Ketones
C=O	1720 – 1670	Carboxylic acids
C=O	1690 – 1630	Amides
C=C	1675 – 1600	Often weak
C=N	1690 – 1630	Often difficult to assign
N=O	1560 – 1510 & 1370 – 1330	Nitro compounds

Triple Bonds

Bond	Wavenumber/cm^{-1}	Notes
C≡C	2260 – 2120	Alkynes, bands are weak
C≡N	2260 - 2220	Nitriles

Bending Vibrations

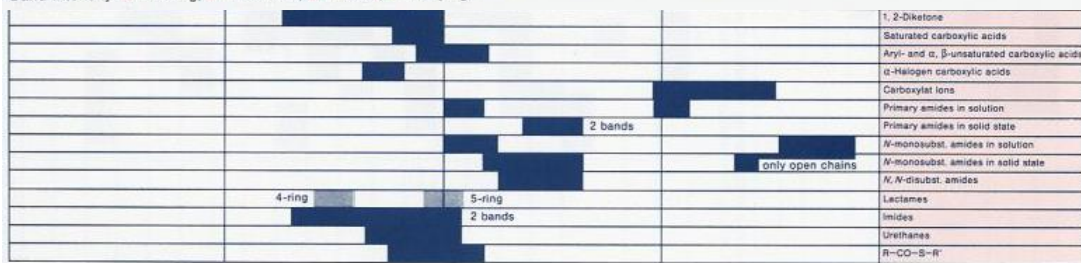| Bond	Wavenumber/cm^{-1}	Notes
R–N–H	1650 – 1500	Take care not to confuse N–H bend with the C=O stretch in amides
R–C–H	1480 – 1350	Saturated alkanes and alkyl groups
R–C–H	1000 – 680	Unsaturated alkenes and aromatics

Hard to make specific peak–group assignment
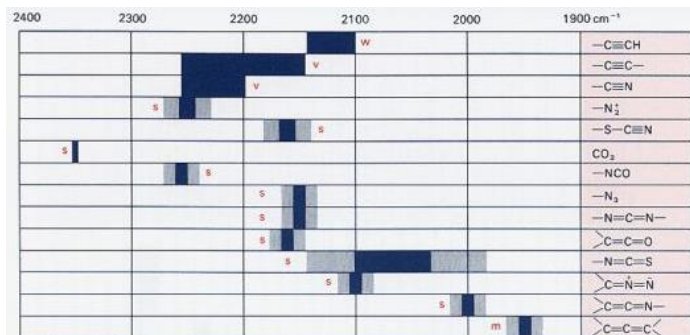
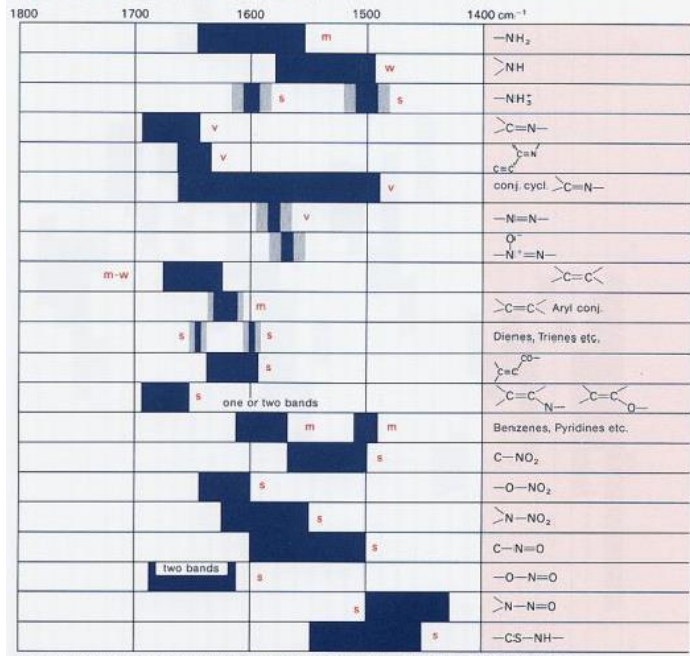# Infrared vibrational spectroscopy
Interpretation of spectra
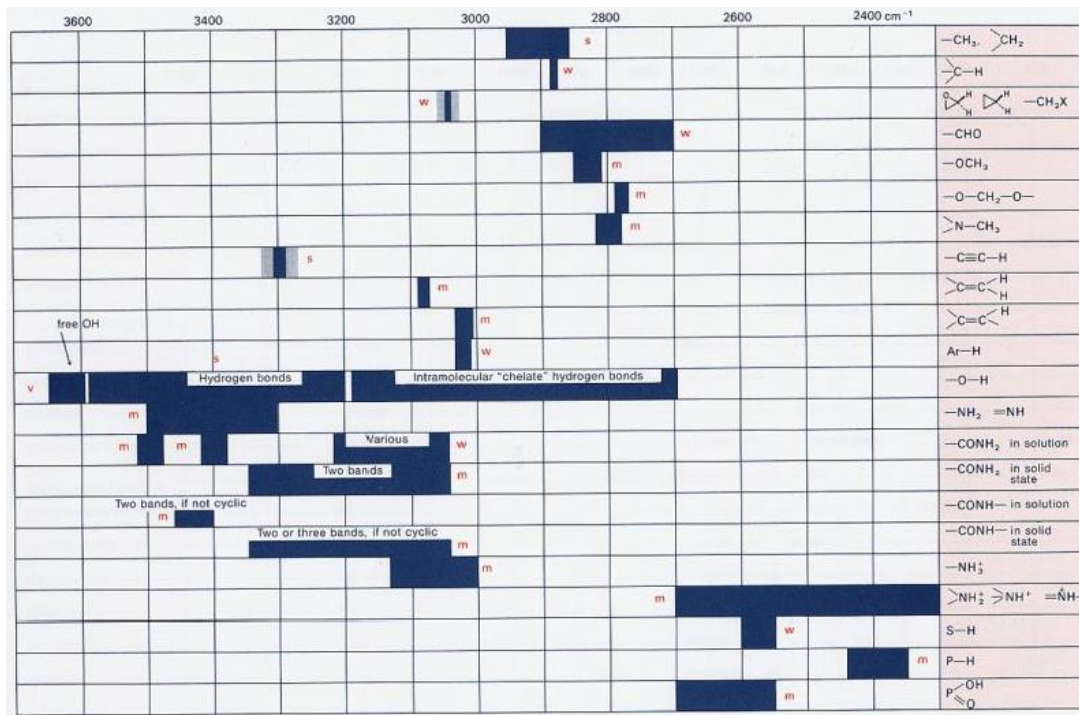
Modern techniques:
- Use of spectral libraries and recognition software (rule-based expert systems, fuzzy logic, artificial neuron networks ...)
- Theoretical simulation of IR spectra

Infrared vibrational spectroscopy
Interpretation of spectra

Fundamental, Overtone, and Combination Bands

fundamentální přechod
- **Fundamental** transition: between v=0 and v=1 ν_i

svrchní tón
- **Overtone**: between v=0 and v=2, 3, 4, … $\approx 2\nu_i$
  - typically 10-100x less intense than fundamental
    => only those of intense fund. tr. will appear

- **Combination** band: more than one vibration excited at the same time $a\nu_i + b\nu_j$

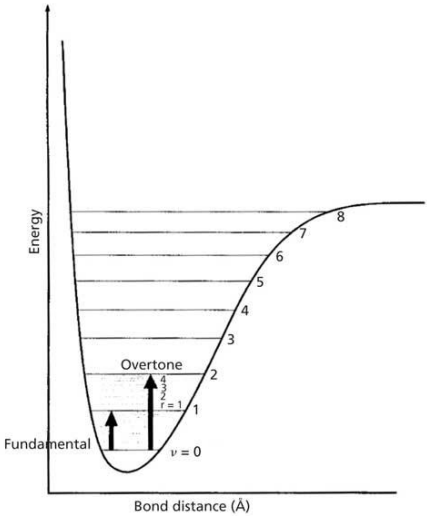- **Difference** band: quantum number changes with diff. signs $a\nu_i - b\nu_j$

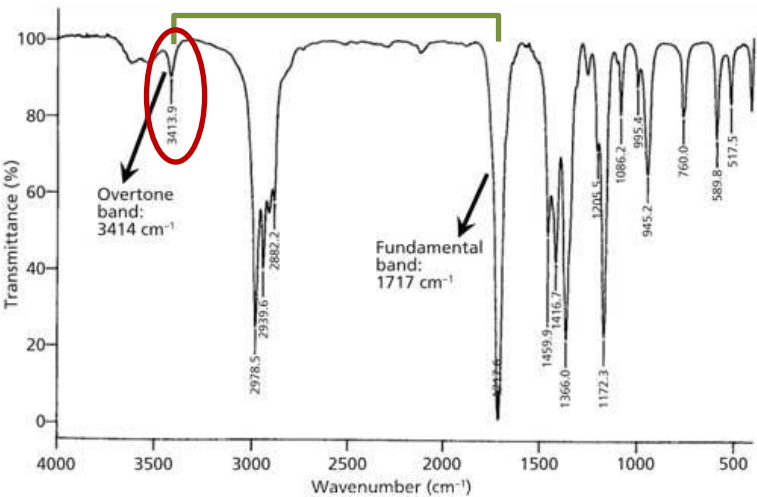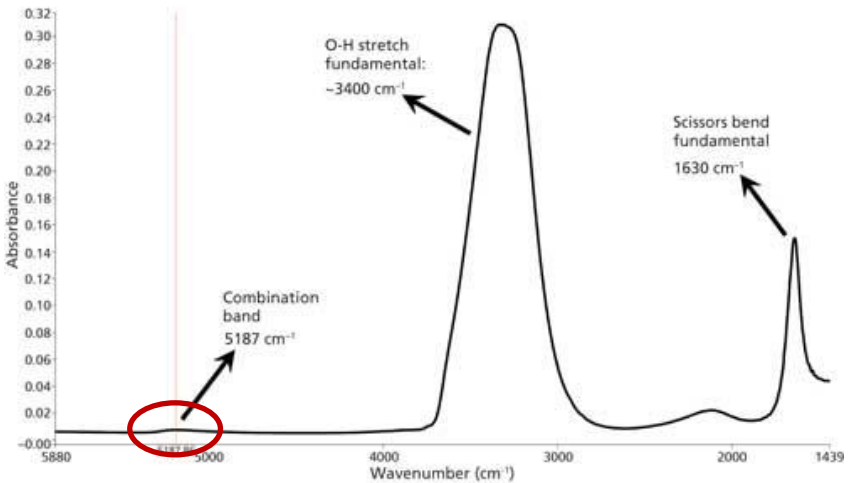… or **mixed**: $a\nu_i + b\nu_j - c\nu_k$

- weak
- often in NIR region

methyl ethyl ketone

water (liquid)

Infrared vibrational spectroscopy
Interpretation of spectra

Overtones and Near infrared
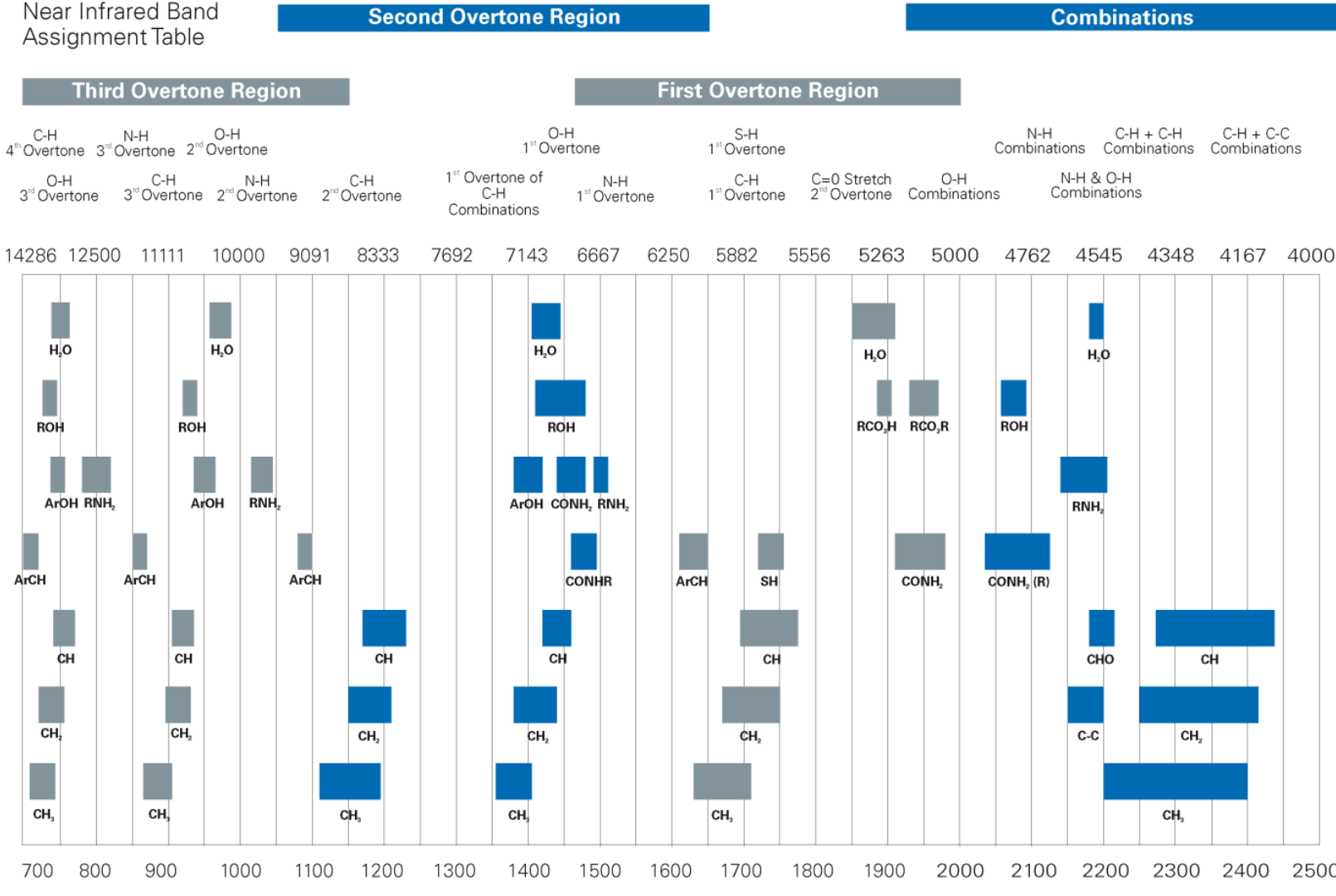
Infrared vibrational spectroscopy
Interpretation of spectra – functional groups

Basic identification of functional groups

O-H stretch (free)

C-H stretch (aliphatic – sp³)

no C≡C stretch

no C=O str.
no C=C str.

C-O stretch

C-H$_{2,3}$ bends

gas

C-C stretch (non-diag.)

OH stretch (H-bonded)

liquid

solid

Infrared vibrational spectroscopy
Interpretation of spectra – chain vs. cyclic
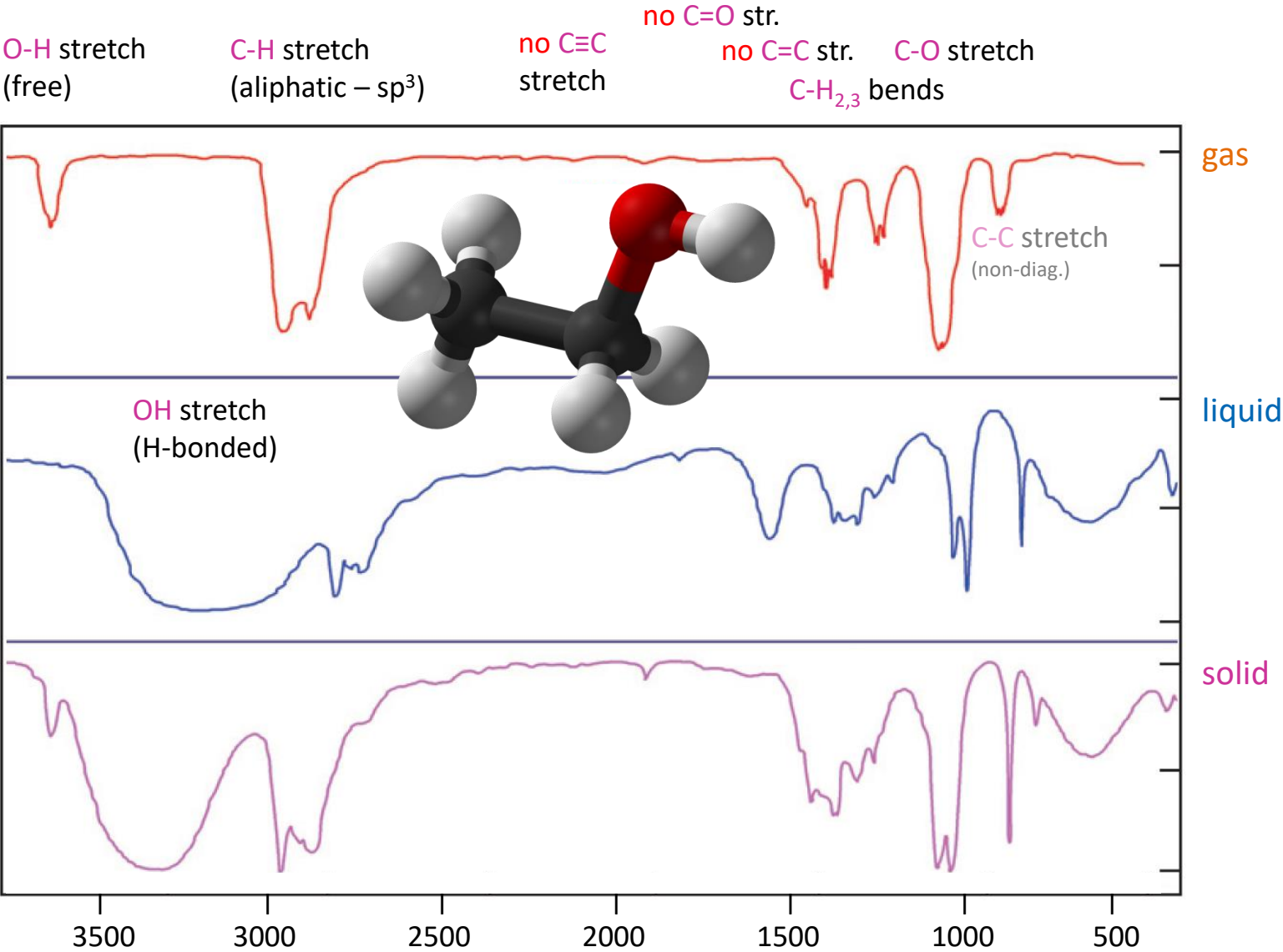
Aliphatic non-cyclic

decane

$CH_3(CH_2)_8CH_3$

(aliphatic)
sp^3 C–H stretch

CH_2 bend
(scissoring)

(CH_3 methyl rock –
„umbrella" mode)
CH_3 bend

long-chain band
(CH_2 methyl rock on long chain)

no sp^2 C-H

Aliphatic cyclic

cyclohexane

sp^3 C–H stretch

no CH_3

CH_2 bend
(scissoring)

C–H bend (wag)
(out-of-plane)

no long-chain band
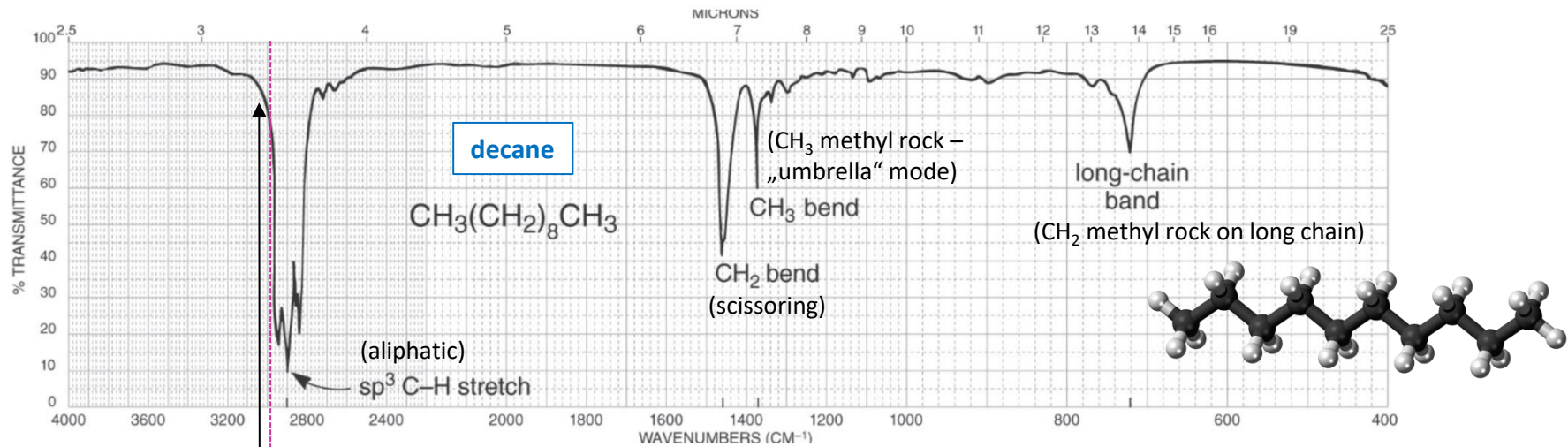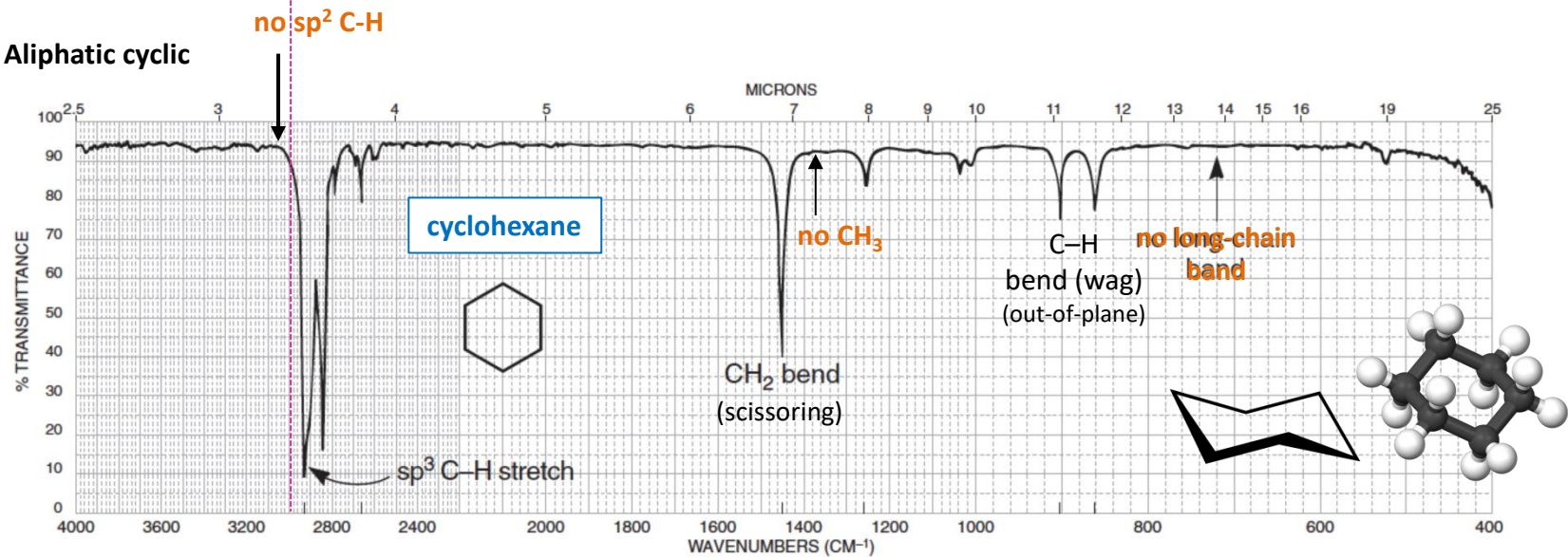
Infrared vibrational spectroscopy
Interpretation of spectra – bond order

Linear hydrocarbons

Alkane

$-C-H$ 2850–2960 cm^{-1}

$-C-C-$ 800–1300 cm^{-1}

-C-H stretch

C-C stretch

CH_3 bend

$CH_3(CH_2)_4CH_3$

overtone

Alkene

$=C-H$ 3020–3100 cm^{-1}

$C=C$ 1640–1680 cm^{-1}

$RCH=CH_2$ 910 and 990 cm^{-1}

$R_2C=CH_2$ 890 cm^{-1}

$=C-H$

C=C str.

$C=C$

$CH_3(CH_2)_3CH=CH_2$

$-CH=CH_2$ bend (out-of-plane)

$-CH=CH_2$ bend (in-plane)

Alkyne

$-C\equiv C-$ 2100–2260 cm^{-1}

$\equiv C-H$ 3300 cm^{-1}

$C\equiv C$ stretch

$-C\equiv C-$

$\equiv C-H$

$CH_3(CH_2)_3C\equiv CH$

$\equiv C-H$ bend

⚠️ Triple bond of substituted alkynes ($R_1-C\equiv C-R_2$) hardly detectable by IR: No $\equiv C-H$, $C\equiv C$ weak
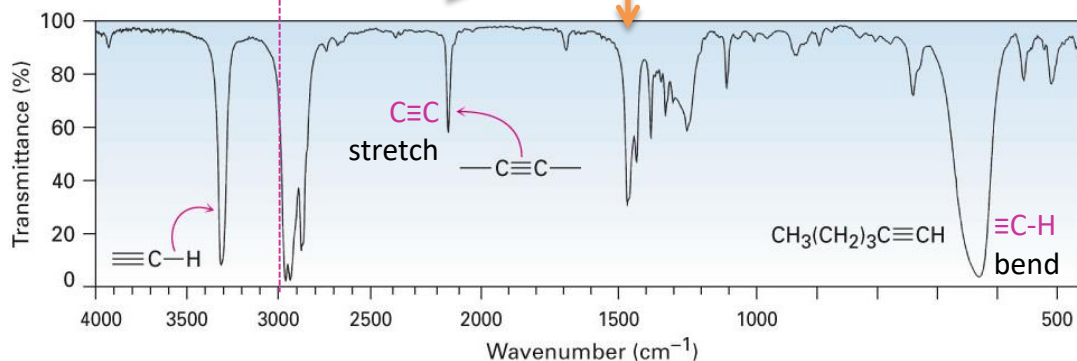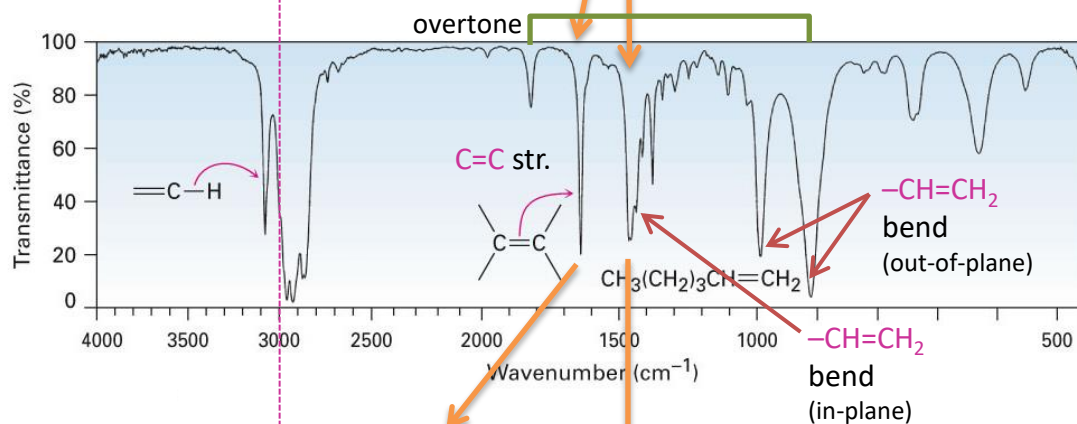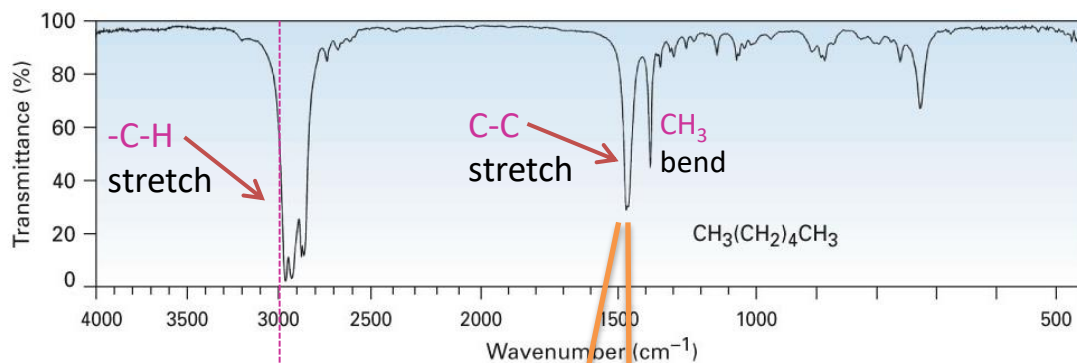
Infrared vibrational spectroscopy
Interpretation of spectra – molecular substitutions

Aromatic compounds

Benzene ⟹ Phenylethyne

Overtone and summation bands ("benzene fingers") – correlated with subst. pattern; rare example of diagnostically useful sum. bands

C−H (unsatur.) stretch

(C≡)C-H stretch

C-H stretch

-C≡C- stretch

C−H bends (in-plane)

C=C (benzene ring) stretch modes

C-H scissoring

(C≡)C-H

C−H bend (wag)

Aromatic C=C stretch slighly lower than pure C=C (delocalized electrons, formal bond order 1½)

Position sensitive to substitution pattern

Benzene substitution patterns

2000   1667 cm⁻¹

Mono-
Di-
o-
m-
p-
Tri- 1,2,3-
1,3,5-
1,2,4-
Tetra- 1,2,3,4-
1,2,4,5-
1,2,3,5-
Penta-
Hexa-

mono   ortho   meta   para

720-680 cm⁻¹
720-685 cm⁻¹
770-730 cm⁻¹   770-735 cm⁻¹   810-750 cm⁻¹   860-800 cm⁻¹
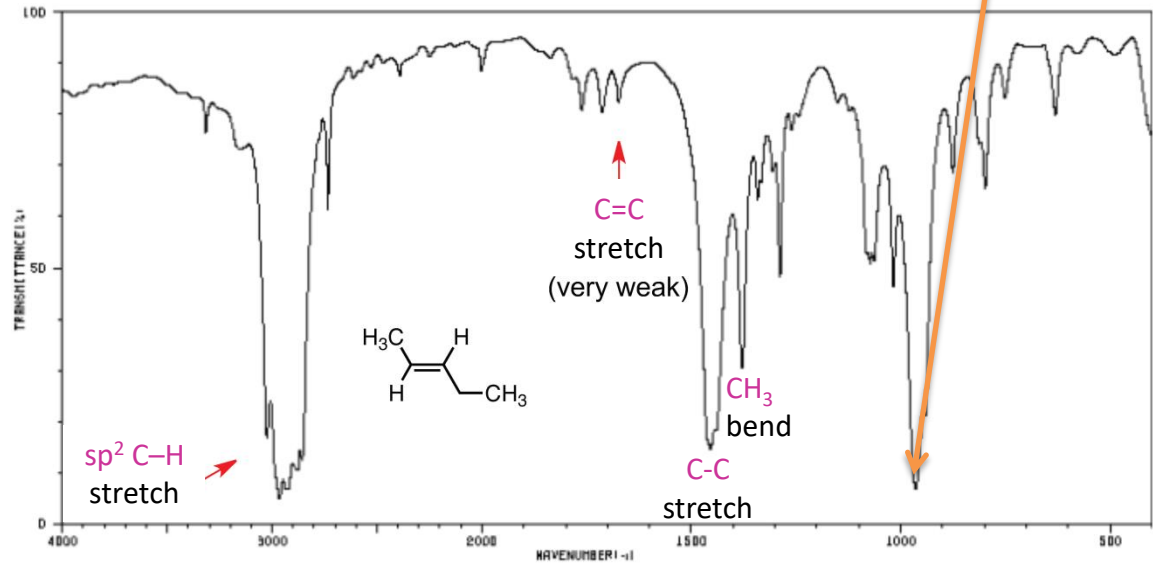1000   500   1000   500   1000   500   1000   500

Infrared vibrational spectroscopy
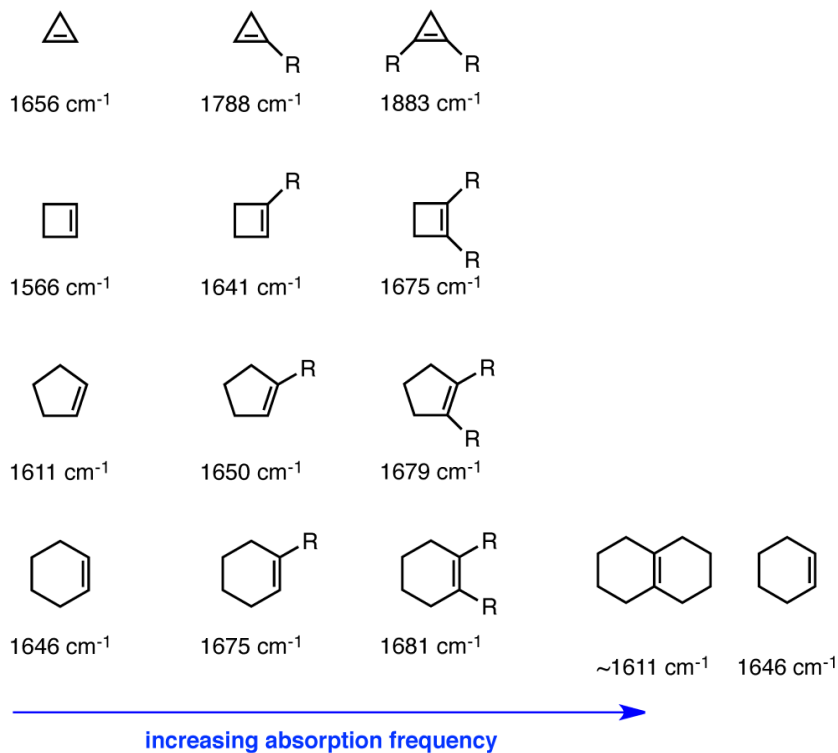## Interpretation of spectra – molecular isomers

cis-2-pentene
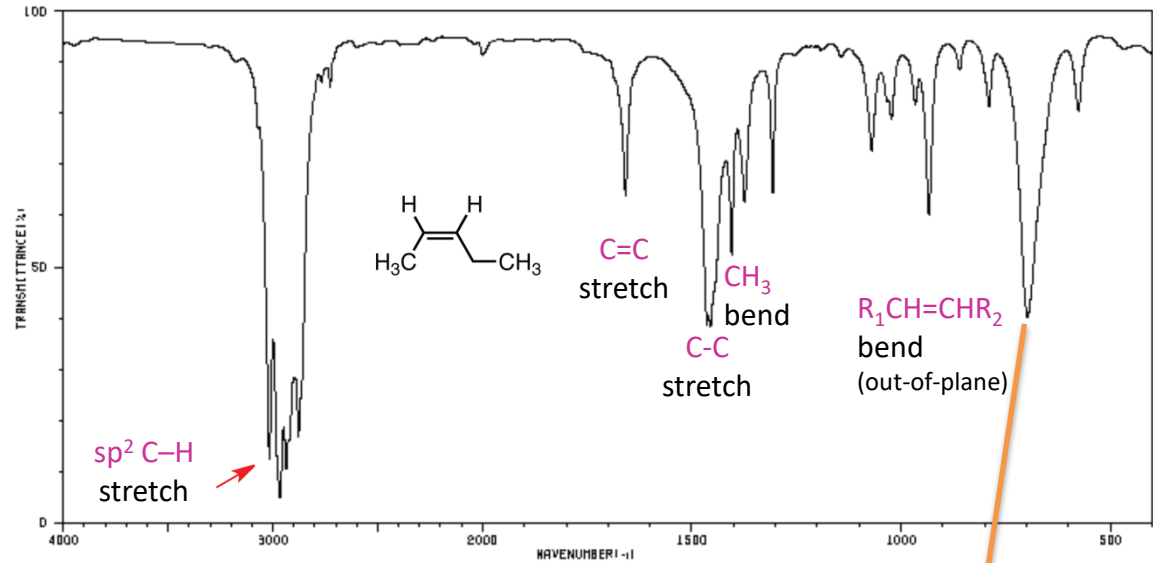
trans-2-pentene
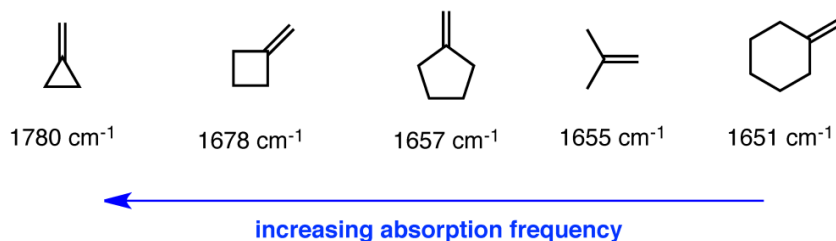
Infrared vibrational spectroscopy
Interpretation of spectra

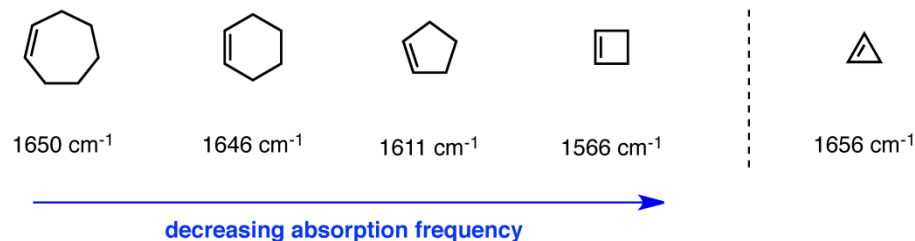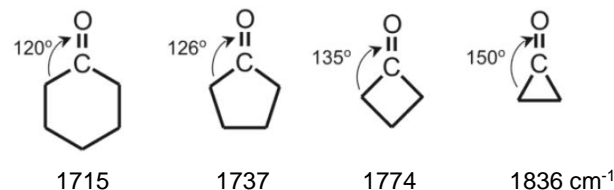**Susbstituent effect** – influence on C=C stretch

endocyclic alkenes

1656 cm^{-1} 1788 cm^{-1} 1883 cm^{-1}

1566 cm^{-1} 1641 cm^{-1} 1675 cm^{-1}

1611 cm^{-1} 1650 cm^{-1} 1679 cm^{-1}

1646 cm^{-1} 1675 cm^{-1} 1681 cm^{-1} ~1611 cm^{-1} 1646 cm^{-1}

→ increasing absorption frequency

exocyclic alkenes

1780 cm^{-1} 1678 cm^{-1} 1657 cm^{-1} 1655 cm^{-1} 1651 cm^{-1}

← increasing absorption frequency

Strain effect

– influence on C=C stretch in endocyclic alkenes

1650 cm^{-1} 1646 cm^{-1} 1611 cm^{-1} 1566 cm^{-1} 1656 cm^{-1}

→ decreasing absorption frequency

– strained ring carbonyls: bond angle is critical factor

120°   126°   135°   150°

1715   1737   1774   1836 cm^{-1}

Field effect
– greater O electronegativity → weaker carbonyl C=O bond force

$R-C(=O)-R$ $R-C(=O)-Cl$ $Cl-C(=O)-Cl$

1715 cm^{-1} 1800 cm^{-1} 1828 cm^{-1}

more s character

more p character
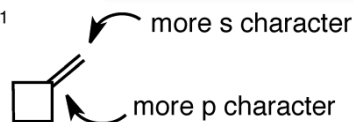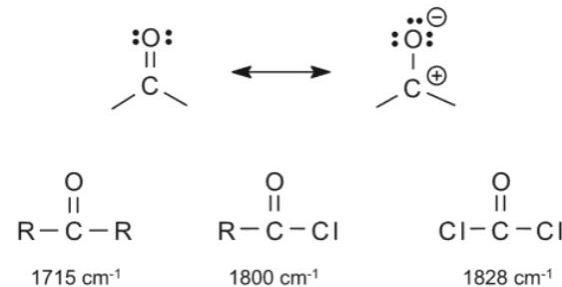
Infrared vibrational spectroscopy
Interpretation of spectra – isotopic substitutions

CO (weakly adsorbed)
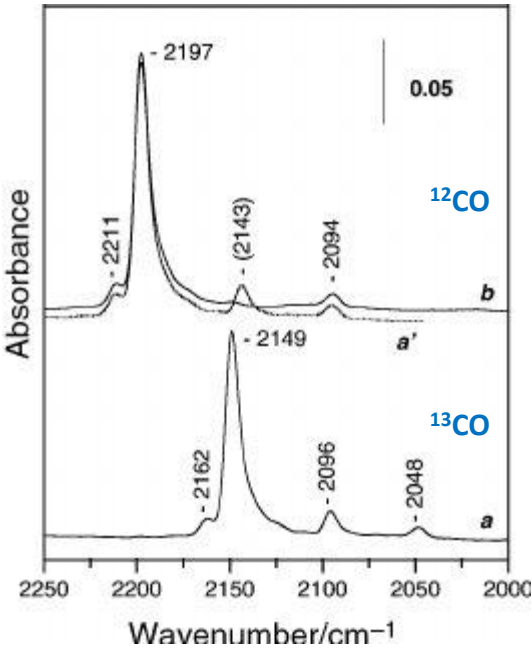
Harmonic approximation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$
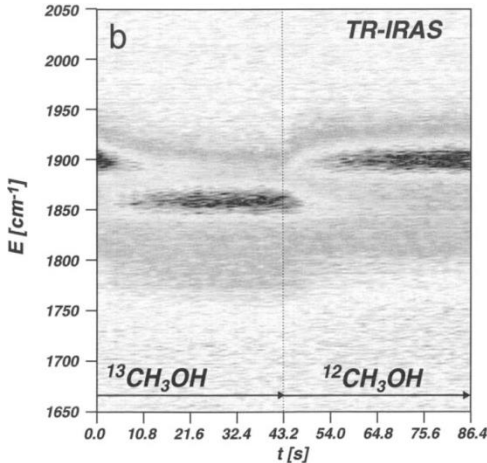
$$\mu_1 = \frac{12 \cdot 16}{12 + 16} = 6.857$$

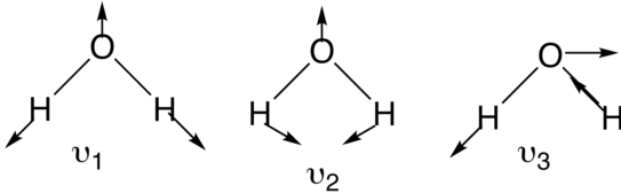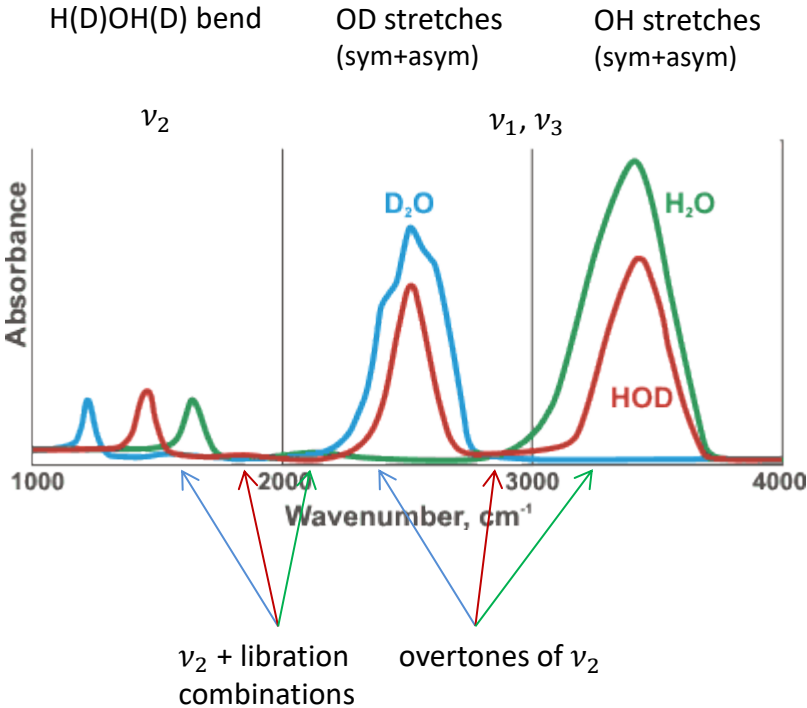$$\mu_2 = \frac{13 \cdot 16}{13 + 16} = 7.172$$

$$\sqrt{\frac{\mu_2}{\mu_1}} \doteq 1.0227$$

$$\frac{\nu_1}{\nu_2} \doteq 1.0223$$

=> Isotopic labelling possible – exchange reactions, specific site identification, molecular tracking, …

Liquid water

H(D)OH(D) bend   OD stretches (sym+asym)   OH stretches (sym+asym)

ν_2 ν_1, ν_3

ν_2 + libration combinations   overtones of ν_2

Infrared vibrational spectroscopy
Specular reflection analysis

Grazing angle (~70-85°) specular reflection:

– spectra similar to transmission ones
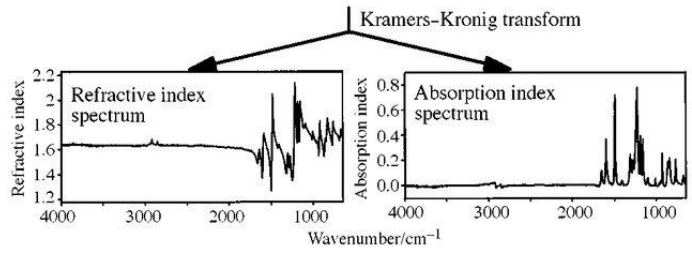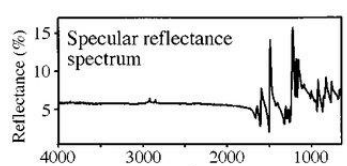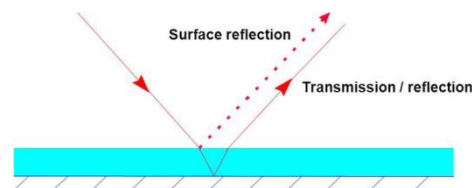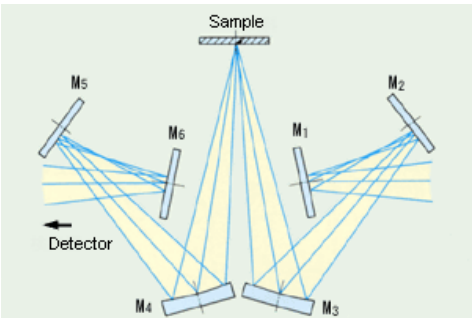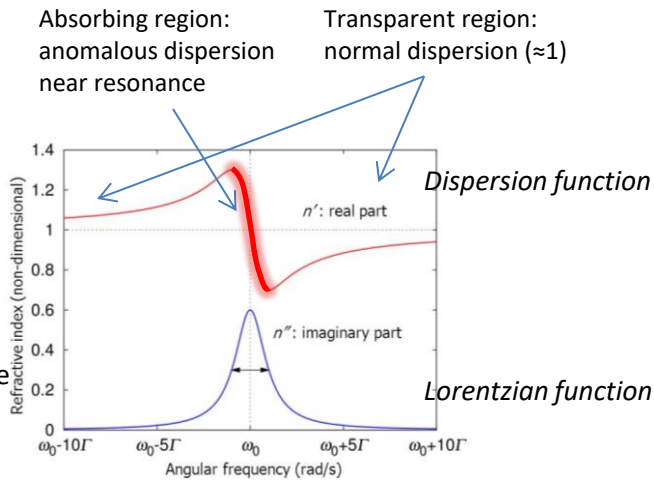– monolayers, adsorbates, (powders)

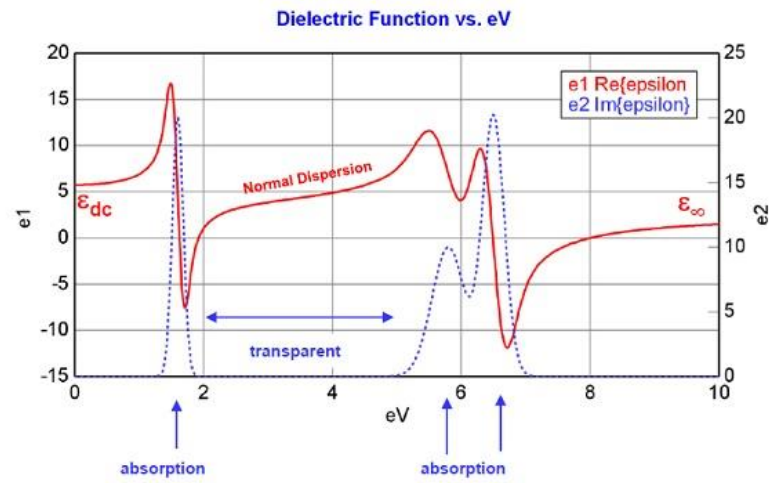**Near-normal** (~5-30°) specular reflection of dielectrics:

– spectra predominatly a function of refractive index
→ derivative shape of the bands (arising from superposition of extinction (absorption) coefficient and dispersion of refractive index) – conversion to absorbance-like spectra by Kramers-Kronig transformation
– thick transparent solids, thin layers – transmission-reflection (transflectance)

Dispersion
→ (Real part of the) refractive index

Absorption
→ Imaginary part of the refractive index

Absorbing region: anomalous dispersion near resonance

Transparent region: normal dispersion (≈1)

Dispersion function

Lorentzian function

Kramers–Kronig transform

Specular reflection spectrum

Infrared vibrational spectroscopy
Quantitative analysis

Light absorption quantities:

Transmittance

$$T = \frac{I}{I_0}$$

Absorbance

$$A = \log I_0/I$$
$$A = -\log T$$

Specular reflectance

Refl.→Abs.: *Kramers-Kronig transformation*

Angle of incidence influences
- Effective pathlength
- Polarized light response
- Projection to bonds (adsorbates)

Peak intensity factors

- Light intensity (freq. dependent)
- Magnitude of dipole moment change: $\left(\frac{\partial \vec{\mu}}{\partial Q}\right)_{Q=0}$
- Bonds orientations (esp. for polarized light)
- Concentration
- Attenuation due to absorption (Beer-Lambert / Beer's law):
  $A = \varepsilon l c$ (ε … absorptivity, l … pathlength, c … concentration)
  In gas: $A = \varepsilon l \frac{P}{RT}$
- Fermi resonance
- ATR: number of reflections, penetration depth, refractive index, quality of crystal-sample contact, ATR crystal optical properties

Absolute concentrations:
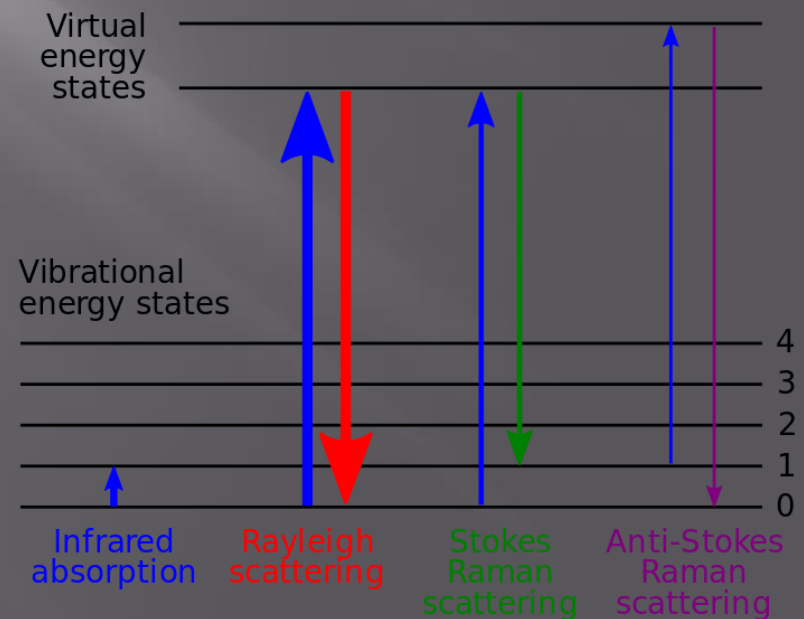– Calibration against known samples of the same volume/pressure (solutions, gases, …)

Relative concentrations:
– Normalization against a selected peak

Raman spectroscopy
Ramanova spektroskopie

- Method overview and principle
- Instrumentation
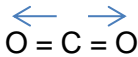- Interpretation of Raman spectra
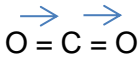
Raman spectroscopy
Basics

Raman spectroscopy

- Complementary to IR spectroscopy – both involve vibrational modes
- Based on frequency shifts due to scattering, exciting (ro-)vibrations

Anisotropic polarizability required

$\overset{\leftarrow}{O} = C = \vec{O}$
IR inactive
Raman active

$\vec{O} = C = \vec{O}$
IR active
Raman inactive

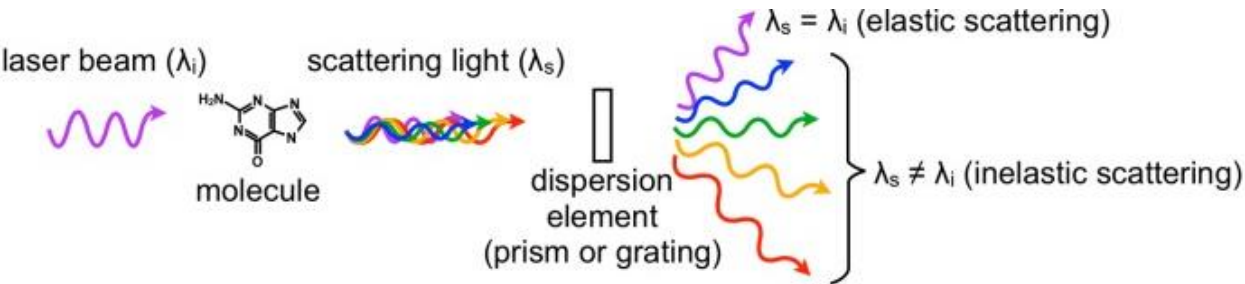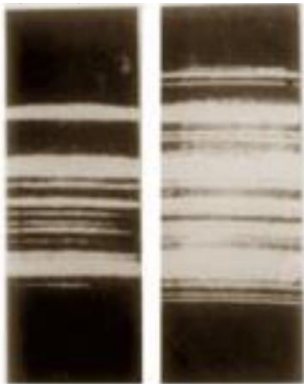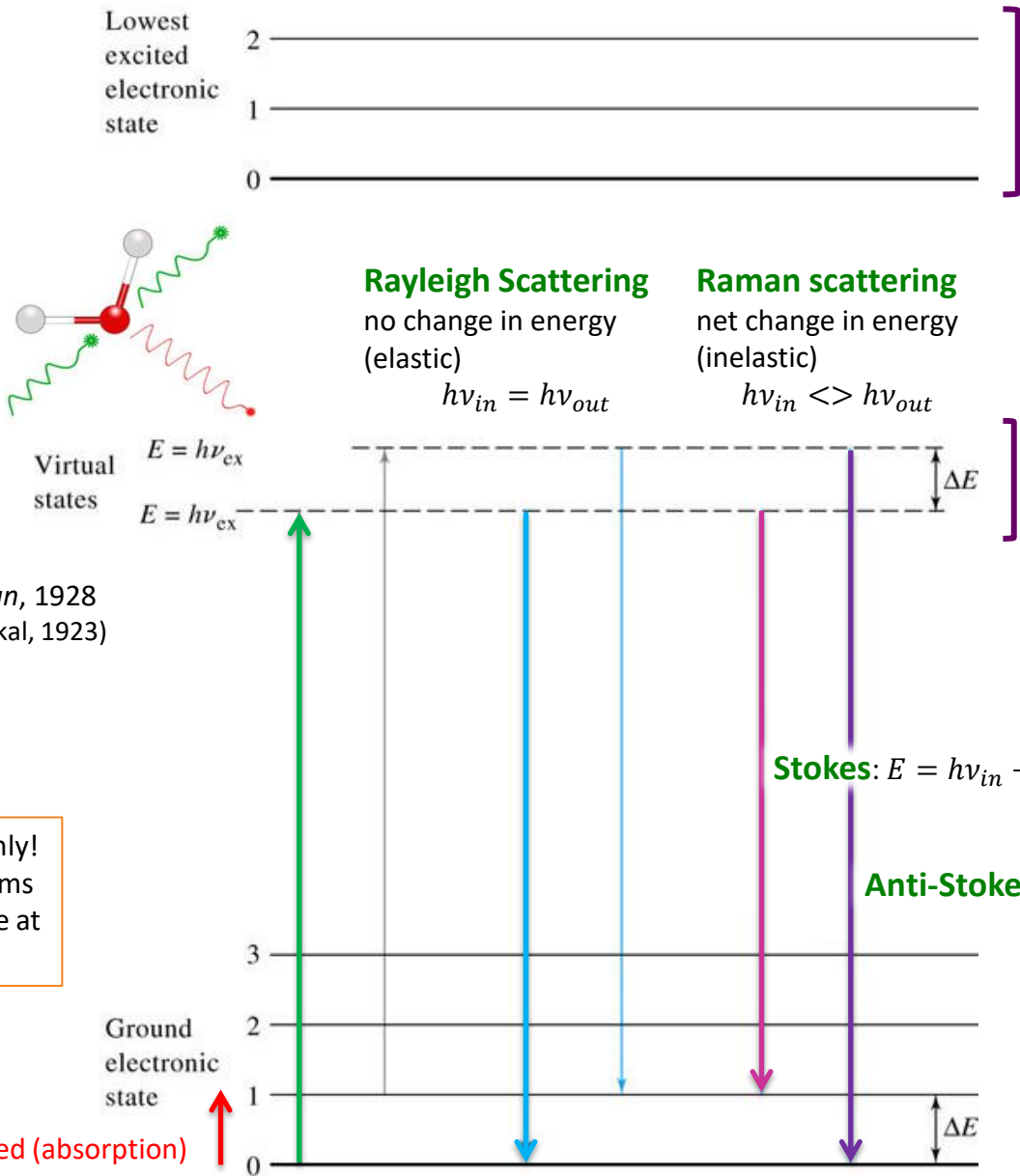| IR spectroscopy	Raman spectroscopy
1-photon process	2-photon process (ν_{ex}, ν_{scat})
change in dipole	change in polarizability
relatively strong	weak (~10^{-6}–10^{-7} of IR)
polarization useful for bond geometry	polarization features can aid identification
low spatial resolution	good spatial resultion possible
penetration depth dependence on freq.	essentially freq. independent penetration depth

laser beam (λ_i)   scattering light (λ_s)

molecule

dispersion element (prism or grating)

$\lambda_s = \lambda_i$ (elastic scattering)

$\lambda_s \neq \lambda_i$ (inelastic scattering)

Raman spectroscopy
Basic principle

Lowest excited electronic state — 2, 1, 0

No change in electronic states

Hg lamp   +Benzene

- Rotational Raman
- Vibrational Raman
- Electronic Raman

Rayleigh Scattering
no change in energy (elastic)
$$h\nu_{in} = h\nu_{out}$$

Raman scattering
net change in energy (inelastic)
$$h\nu_{in} <> h\nu_{out}$$

Virtual states
$E = h\nu_{ex}$
$E = h\nu_{ex}$

ΔE

Infinite number of virtual states
=> energy absorbed by molecule from photon **not quantized**

Chandrasekhara Venkata Raman, 1928
(predicted theoreticaly by A. Smekal, 1923)
→ Nobel prize in 1930

(Virtual state: not eigenfunction of any operator)

Stokes: $E = h\nu_{in} - \Delta E$

Anti-Stokes: $E = h\nu_{in} + \Delta E$

Atoms – Raleigh scattering only!
Isotropic polarizability => atoms act like an antenna: re-radiate at the incident frequency

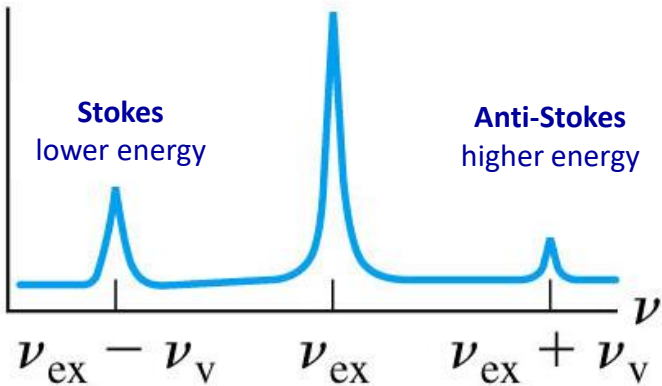Ground electronic state — 3, 2, 1, 0
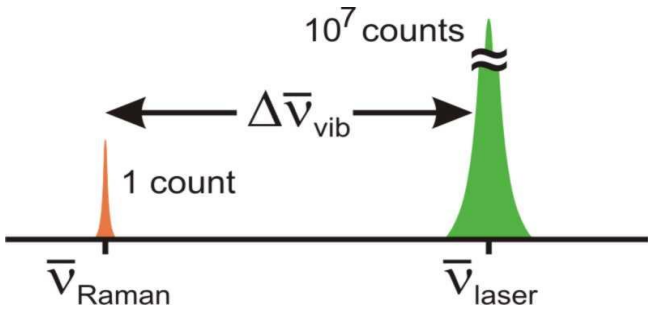
ΔE

Infrared (absorption)

Raman spectroscopy
Basics

Resulting Raman spectrum
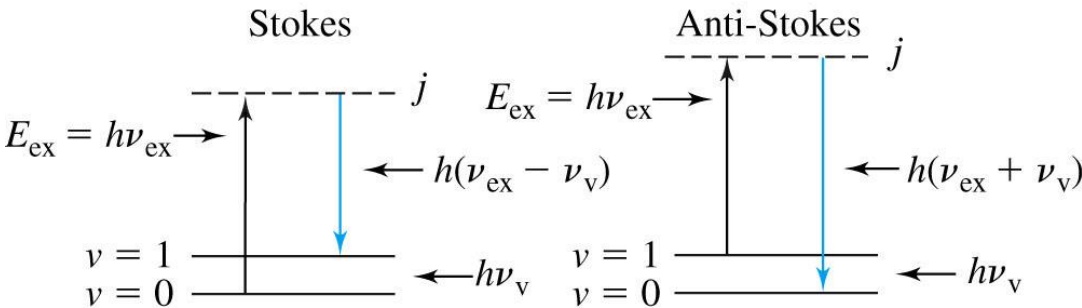
$\pm\Delta E$ … 1st vibrational level energy =>
Raman frequency shift = IR absorption frequency

Stokes | Anti-Stokes

$E_{ex} = h\nu_{ex}$

$E_{ex} = h\nu_{ex}$

$\leftarrow h(\nu_{ex} - \nu_v)$

$\leftarrow h(\nu_{ex} + \nu_v)$

$v = 1$
$v = 0$

$v = 1$
$v = 0$

$\leftarrow h\nu_v$

$\leftarrow h\nu_v$

Stokes
lower energy

Anti-Stokes
higher energy

$\nu_{ex} - \nu_v \quad \nu_{ex} \quad \nu_{ex} + \nu_v$

Only **1 in ~10^7 photons** is scattered inelastically!

10^7 counts

$\Delta\bar{\nu}_{vib}$

1 count

$\bar{\nu}_{Raman}$

$\bar{\nu}_{laser}$

Observed intensity $\propto$ Probability of emission

Raleigh scattering >> Stokes >> Anti-Stokes

Low wavenumber peaks ($\lesssim 200\ cm^{-1}$) can overlap with the Rayleigh wings of the excitation line

Vibrational spectroscopy
Linear optical vibr. spectroscopies – basics

The origin of the polarizability requirement in Raman (classical theory, linear effects only)

$\vec{\mu} = \alpha \vec{E}$ $\qquad\qquad$ $\vec{\mu}$ … induced polarization, α …polarizability

$|\vec{E}| = E_0 \cos(\omega_{src} t)$

$\alpha = \alpha_0 + \dfrac{d\alpha}{dQ} \cos(\omega_{vibr} t)$ $\qquad$ … polarizability along Q-coordinate (vibrational coord.) – linear component only

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Stokes $\qquad\qquad\qquad$ Anti-Stokes

$\Rightarrow \; |\vec{\mu}| \equiv \mu = \alpha_0 E_0 \cos(\omega_{src} t) + E_0 \dfrac{d\alpha}{dQ}\dfrac{1}{2} (\cos(\omega_{src} t + \omega_{vibr} t) + \cos(\omega_{src} t - \omega_{vibr} t))$

$\qquad\qquad$ Rayleigh

$\qquad\qquad\qquad\qquad\qquad\qquad$ sidebands (Raman scattering)

$\left(\dfrac{\partial \alpha}{\partial Q}\right)_{Q=0} = 0 \;\Rightarrow\; \mu = \alpha_0 E_0 \cos(\omega_{src} t)$ $\qquad$ – Rayleigh scattering only

Polarization energy ellipsoid

Polarization tensor can be measured by measuring the energy required to polarize the crystal/molecule in various directions

For E-field with only $x-$ and $y-$component:

$\mu = \dfrac{1}{2}\left[\alpha_{xx} E_x^{\,2} + (\alpha_{xy} + \alpha_{yx})E_x E_y + \alpha_{yy} E_y^{\,2}\right]$, $E^2 = E_x^{\,2} + E_y^{\,2}$

$\alpha_{xy} = \alpha_{yx}$ (polariz. tensor is symmetric) $\Rightarrow \mu = \dfrac{1}{2}(\alpha_{xx} E_x^{\,2} + 2\alpha_{xy} E_x E_y + \alpha_{yy} E_y^{\,2})$
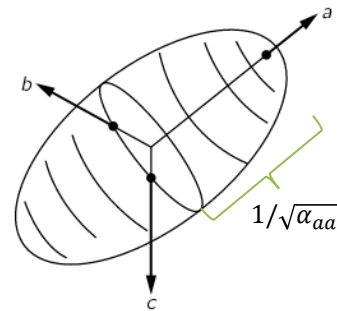
For a given polarization μ_0 we can plot an energy ellipse as a visualization of the polarization tensor

In 3D → ellipsoid

With principal axes a, b, c : $\qquad\qquad \alpha_{aa} E_a^{\,2} + \alpha_{bb} E_b^{\,2} + \alpha_{cc} E_c^{\,2} = 2\mu_0$

and with coords normalized to E: $\quad \alpha_{aa} a^2 + \alpha_{bb} b^2 + \alpha_{cc} c^2 = 1 \quad$ or $\quad \dfrac{a^2}{1/\sqrt{\alpha_{aa}^2}} + \dfrac{b^2}{1/\sqrt{\alpha_{bb}^2}} + \dfrac{c^2}{1/\sqrt{\alpha_{cc}^2}} = 1$

$\Rightarrow$ polarization tensor then has only 3 non-zero components: $\alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
  and polarizability in the direction of axis i is: $1/\sqrt{\alpha_i}$

Raman spectroscopy
Basics

$$\mu = \alpha_0 E_0 \cos(2\pi v_{src} t) + \frac{1}{2} E_0 \frac{d\alpha}{dQ} [\cos 2\pi(v_{src} t + v_{vibr} t) + \cos 2\pi(v_{src} t - v_{vibr} t)]$$

$\frac{d\alpha}{dQ}$ ... change in polarizability must be $\neq 0$

Classical description: no difference between Stokes and Anti-Stokes intensities

QM => **Stokes to Anti-Stokes intensity ratio**:
      Difference in population of energy levels of vibrational transitions
      (*Boltzmann distribution*)

$$\frac{N_{Stokes}}{N_{Anti-Stokes}} = \left(\frac{v_{src} - v_{vibr}}{v_{src} + v_{vibr}}\right)^4 e^{\frac{hv_{vibr}}{kT}}$$

Ex.: v_{vibr}=1440 cm^{-1} (CH$_2$ scis.), T=300K, $N_S/N_{AS} \approx 10^3$
v_{vibr}=216 cm^{-1} (CCl$_4$ vibr.), T=300K, $N_S/N_{AS} \approx 2.5$

Selection rules

$\Delta v = \pm 1$

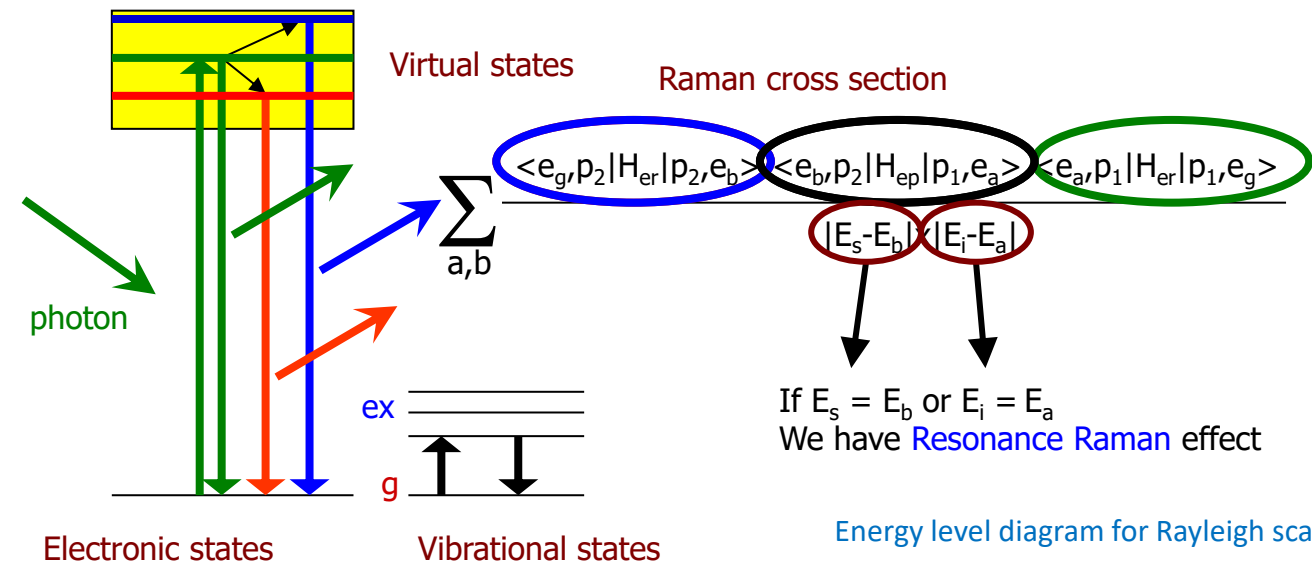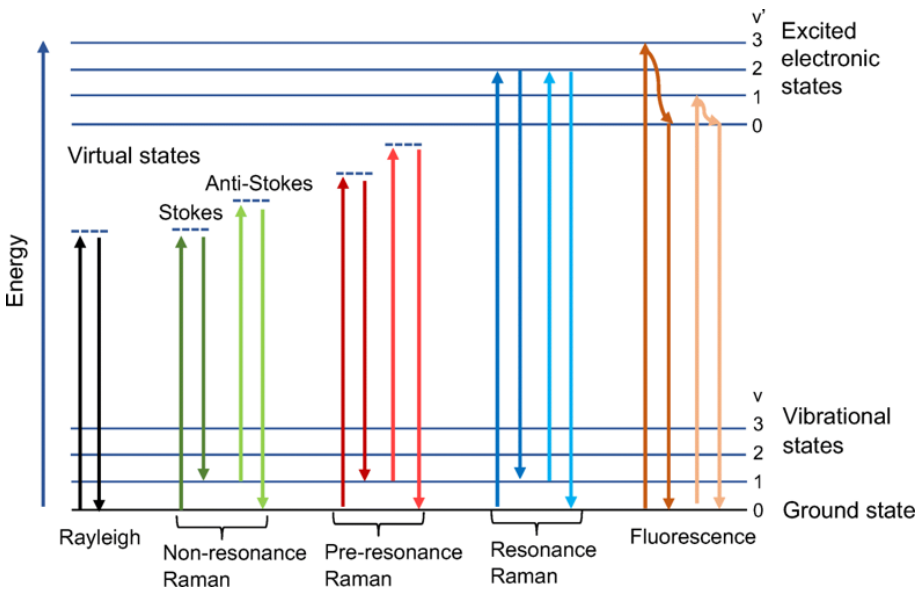|	
$\Delta v = \pm 1$	... fundamental band
$\Delta v = \pm 2$	... 1st overtone band
$\Delta v = \pm 3$	... 2nd overtone band
.....	

anharmonic   harmonic

Depolarization ratio

Simple case: direction of the scattered light (polarization direction) = that of incident light => no depolarization

General case: Non-zero component of scattered light perpendicular to incident light (perpendicular component) =>

$\rho = {I_\perp}/{I_\parallel}$ $I_\parallel$ ... parallel component

Depends on molecular symmetry: $\rho = 0$ for total symmetric vibr. modes

parallel-polarized
cross-polarized
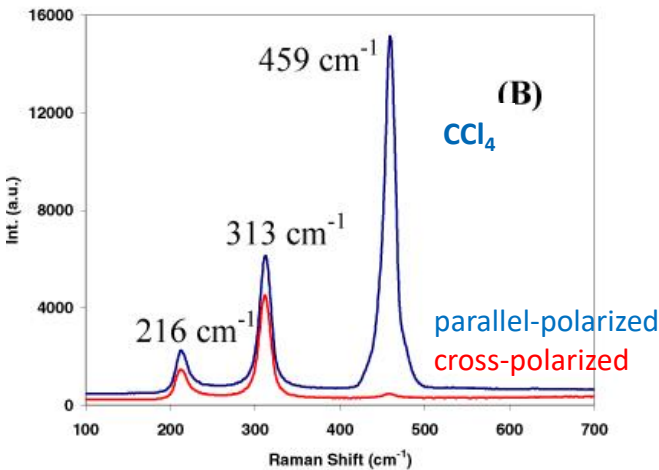
Raman spectroscopy
Resonance Raman – Basics

Quantum treatment and energy diagram

Virtual states

Raman cross section

$$\sum_{a,b} \frac{<e_g,p_2|H_{er}|p_2,e_b> <e_b,p_2|H_{ep}|p_1,e_a> <e_a,p_1|H_{er}|p_1,e_g>}{|E_s-E_b| |E_i-E_a|}$$

photon

ex

g

If $E_s = E_b$ or $E_i = E_a$
We have Resonance Raman effect

Electronic states   Vibrational states

Energy level diagram for Rayleigh scattering, Raman scattering, and fluorescence

Resonance Raman

wavelength of the incoming light is selected to coincide with an *electronic* transition of the molecule or material
(=> excitation to higher electronic levels)
- vibr. modes of el. excited states show larger polarizability
- 10-10⁵ intensity enhancement
- **selective**: Only few vibr. modes contribute to resonance (such molecular parts are called *chromophores*)
  => spectrum usually greatly simplified
- Drawback: Greatly increased probability of fluorescence

Raman spectroscopy
Basics

Raman visible to unaided eye!
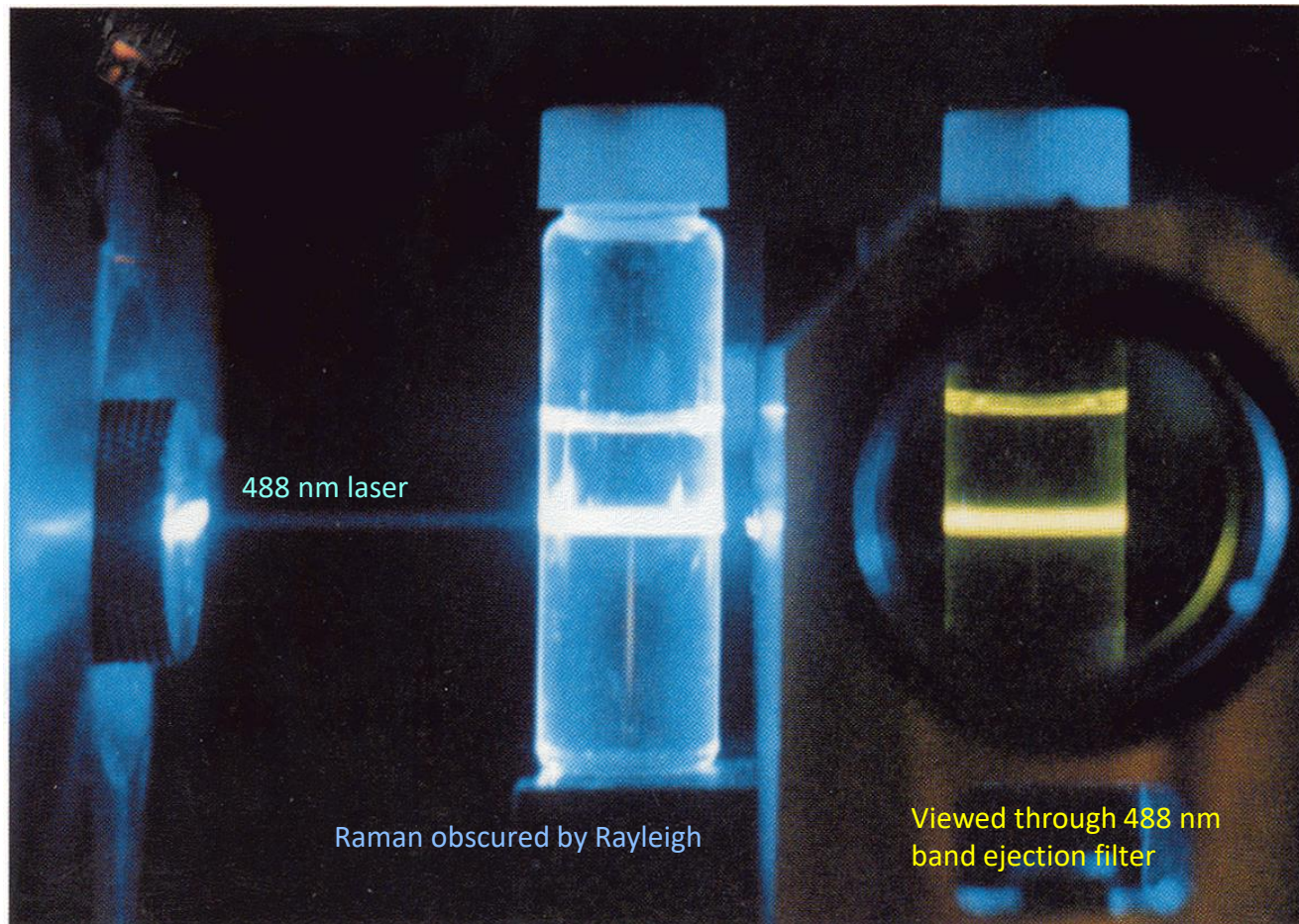
Raman spectroscopy
Instrumentation

Basic experimental setup

Main components:

- Laser excitation source
- Excitation delivery optics
- Sample
- Collection optics
- Wavelength separation device
  - notch filter (blocks ν_{src})
  - edge filters:
    longpass (transmits Stokes),
    shortpass (transmits Anti-Stokes)
- Detector

Advantages

- Non-destructive technique
- Wide selection of sources (from UV to NIR)
- Lower wavenumbers accessible – solid state analysis
- No special sample preparation required
- Aqueous solutions possible in Raman (water is weak Raman scatterer, but strong absorber in IR)
- Wide concentration range (concentration from <<1% to 100% without sample dilution measurable)
- Compatible with common windows

Classical (dispersive) Raman: monochromator + photomultiplier
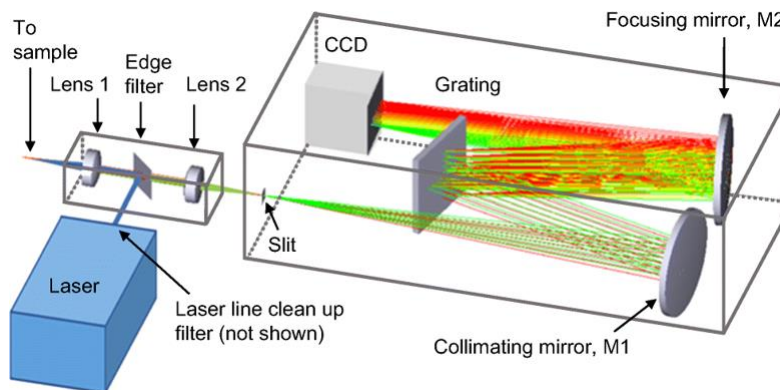
- narrow slits
- large instrument
- resolution vary across spectrum

- higher sensitivity => better for microscopy

FT-Raman: interferometer
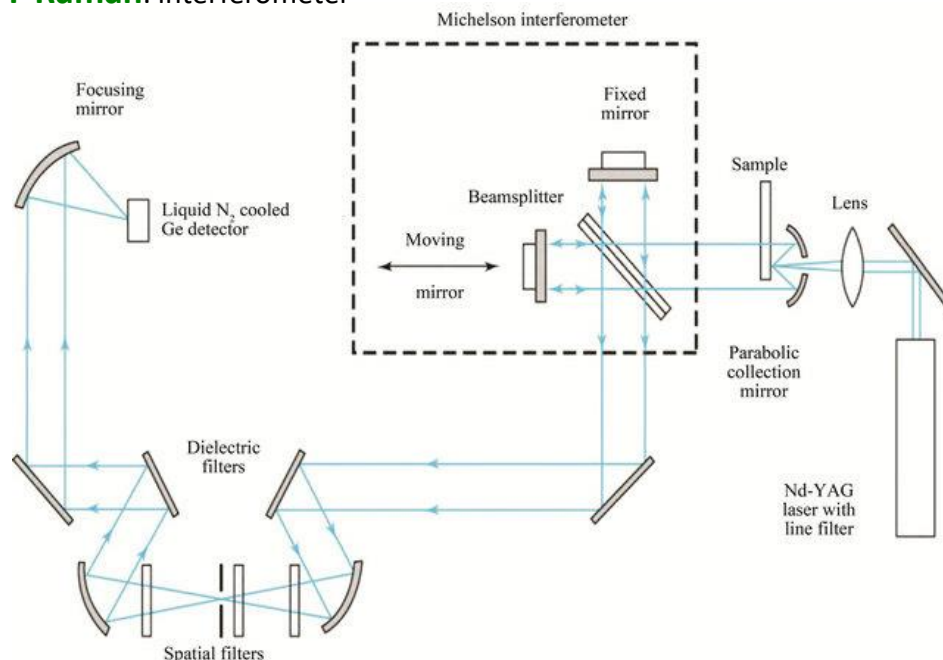
Raman spectroscopy
Instrumentation – properties

Requirements for **classical Raman technique** to determine peak position, peak shift, bandwidth and intensity:

- Laser Excitation
- Reduction of stray light
- Collecting optics
- Spectral resolution and spectral coverage
- Spatial resolution and confocality
- Sensitivity: subject to detector
- Light flux: subject to dispersion

Spectral resolution is a function of
1. dispersion
2. width of entrance slit
3. pixel size of the CCD

Dispersion is a function of
1. focal length of spectrometer
2. groove density of the grating
3. excitation wavelength

- In general, long focal length & high groove density grating → high spectral resolution.
- Raman line widths typically >3 cm^{-1} => 1cm^{-1} resolution sufficient

Spatial resolution

Lateral Resolution of confocal Raman microscopy (Raman sp. + confocal microscope):
- Theoretical lateral resolution: Rayleigh criterion.
- Confocal microscopes with high NA (numerical aperture) – $\Delta x \sim \lambda / NA$; down to 250 – 300 nm

Depth Resolution:
- Confocal microscope: $\Delta d \sim \lambda / NA^2$; <1 µm possible

Grating

Focal Length x

Filter

Detector (CCD)
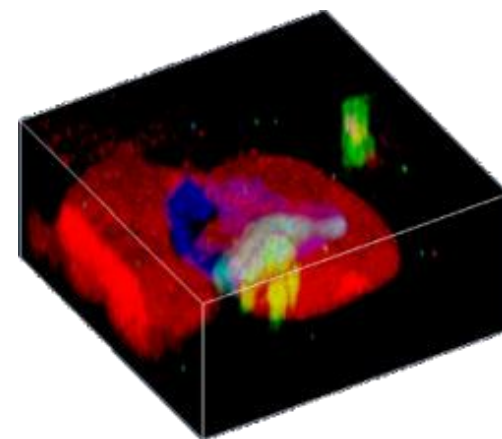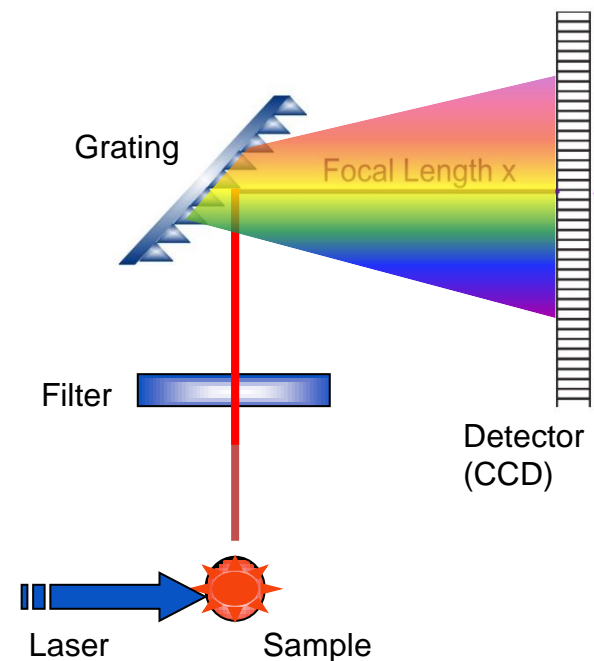
Laser   Sample

Raman spectroscopy
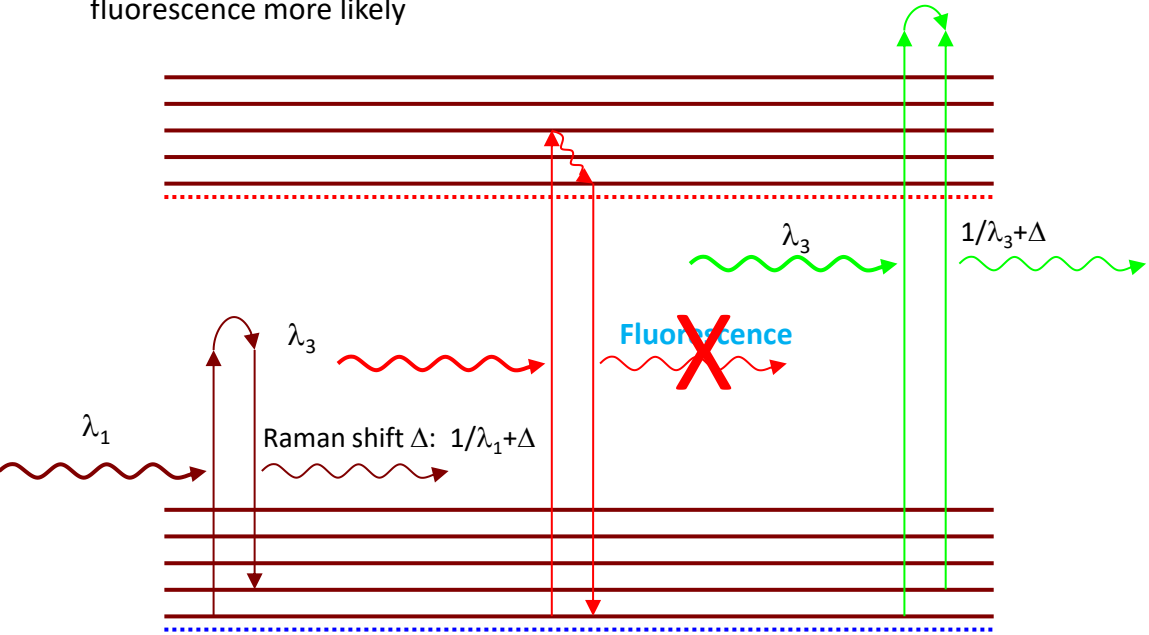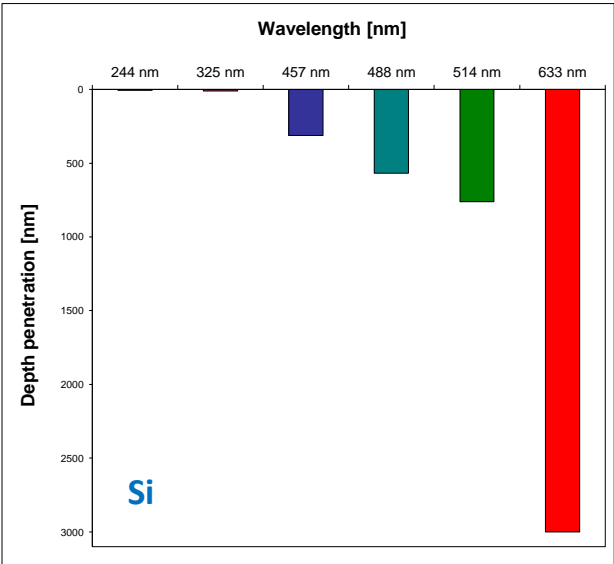## Instrumentation – source

Light source
- generally a laser to get required intensity
- doesn't have to be in IR region
  - visible or UV sources used
  - allows use of glass/quartz sample cells & optics
  - UV/Vis type detectors (photomultiplier tubes)

Laser selection
- Avoid fluorescence
- Avoid extensive heating and photo-induced changes
- Spatial resolution/Probing volume:
   spot size and material penetration depth
- Raman scatter probability $\propto 1/\lambda^4$ => UV lasers best, but fluorescence more likely

λ_3

$1/\lambda_3+\Delta$

Fluorescence

λ_3

λ_1

Raman shift Δ: $1/\lambda_1+\Delta$

Laser wavelengths: $\lambda_3 < \lambda_2 < \lambda_1$

Penetration depth ~ λ
=> **Depth profiling** possible

Wavelength [nm]

244 nm   325 nm   457 nm   488 nm   514 nm   633 nm

Depth penetration [nm]

Si

Raman spectroscopy

Instrumentation – source

Green spectrum: 532 nm laser
Red spectrum: 633 nm laser
Dark red spectrum: 785 nm laser

Fluorescence is wavelength **dependent**
Ordinary Raman is wavelength **independent**
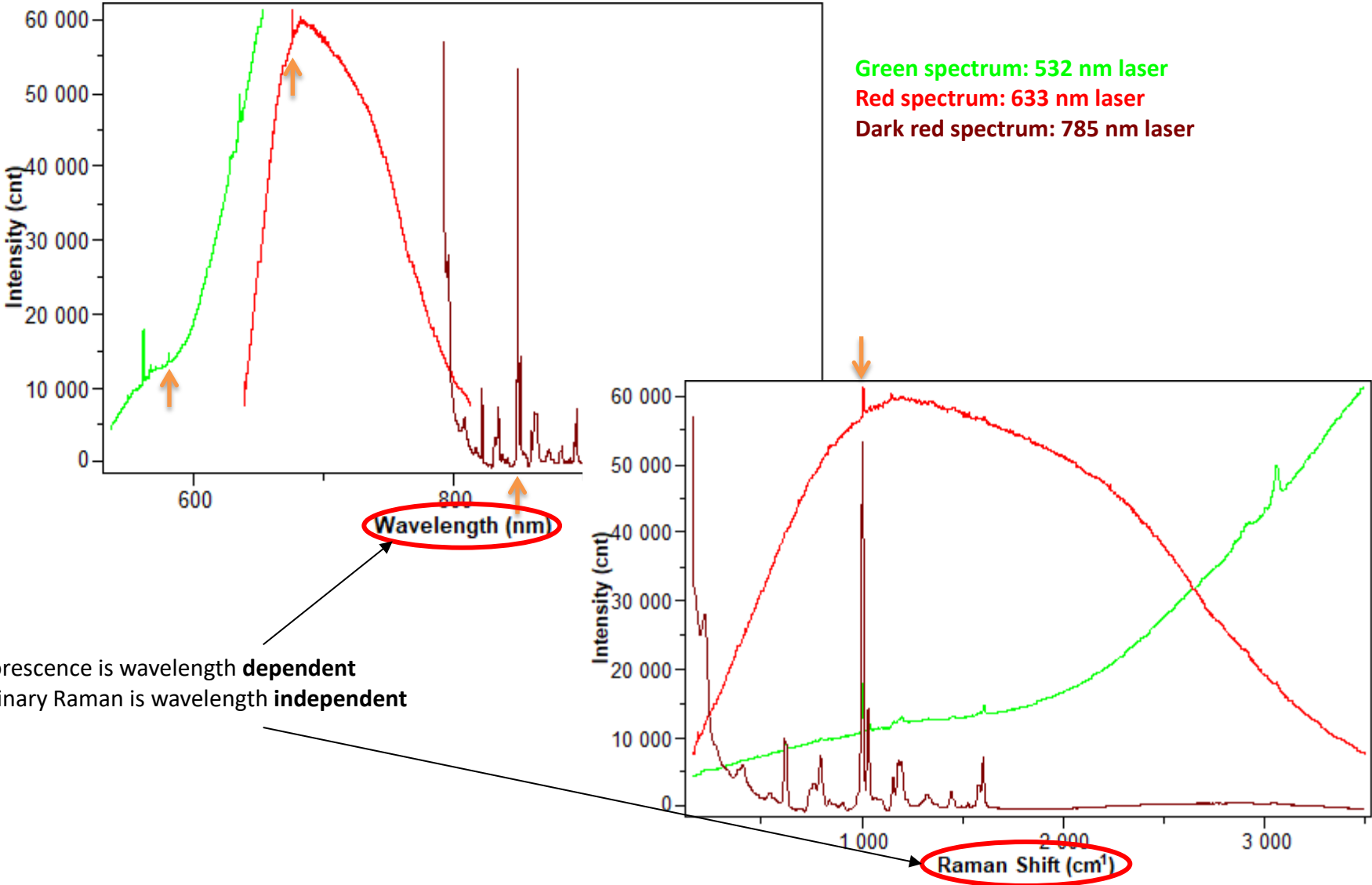
Raman spectroscopy
Raman and IR comparison

Mutually exclusive principle

Symmetric molecules:

Vibrational modes are either IR or Raman active

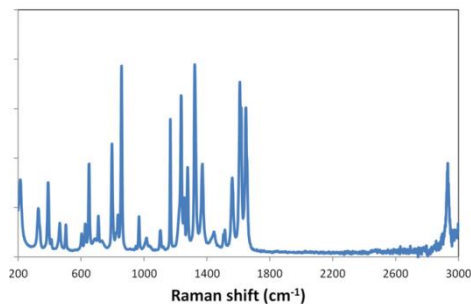**More complex molecules**:

Some modes both IR and Raman active

Example: CS_2
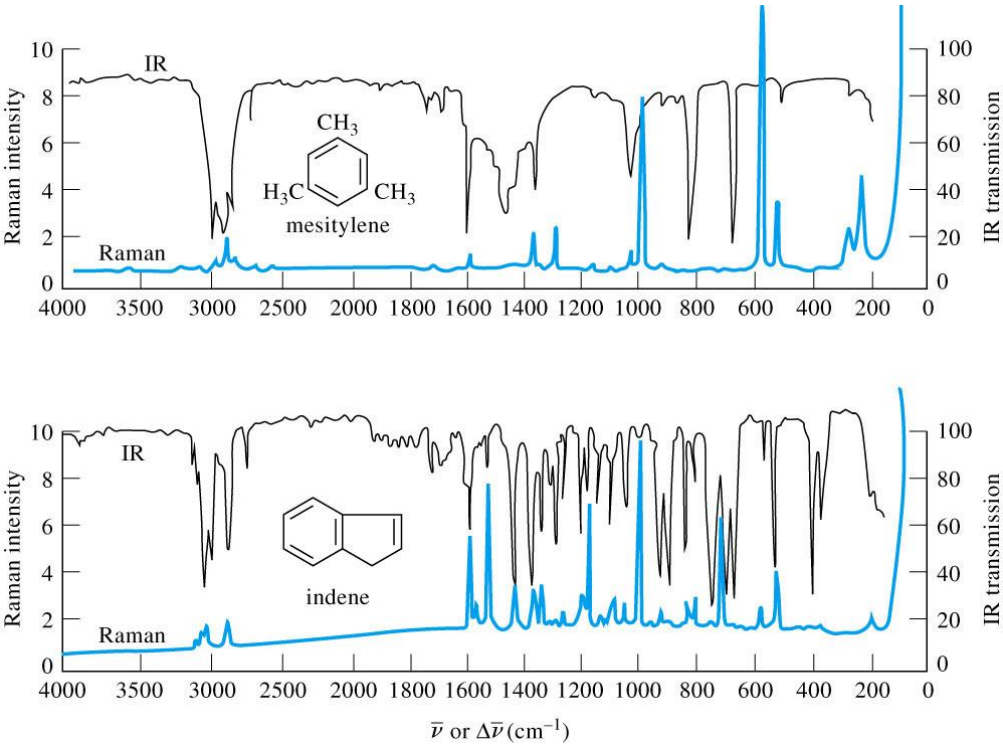
+ Some modes can be **silent**!

Raman spectroscopy
Interpretation of spectra

Information contained in the Raman spectrum

- Unique spectral fingerprint – **chemical identification**

- Peak intensity – information about the **quantity** of a specific compound
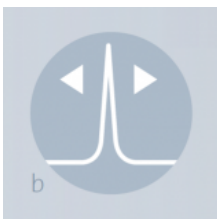
- Peak shift – can identify changes in **bond environment** and **stress and strain** states (constraints)
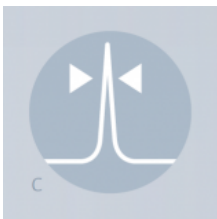
- Peak width – reveals the degree of **crystallinity** (**structural (dis)order**)

- Polarization state – information regarding molecule or crystal **symmetry and orientation**

Raman spectroscopy
Interpretation of spectra

Chemical identification
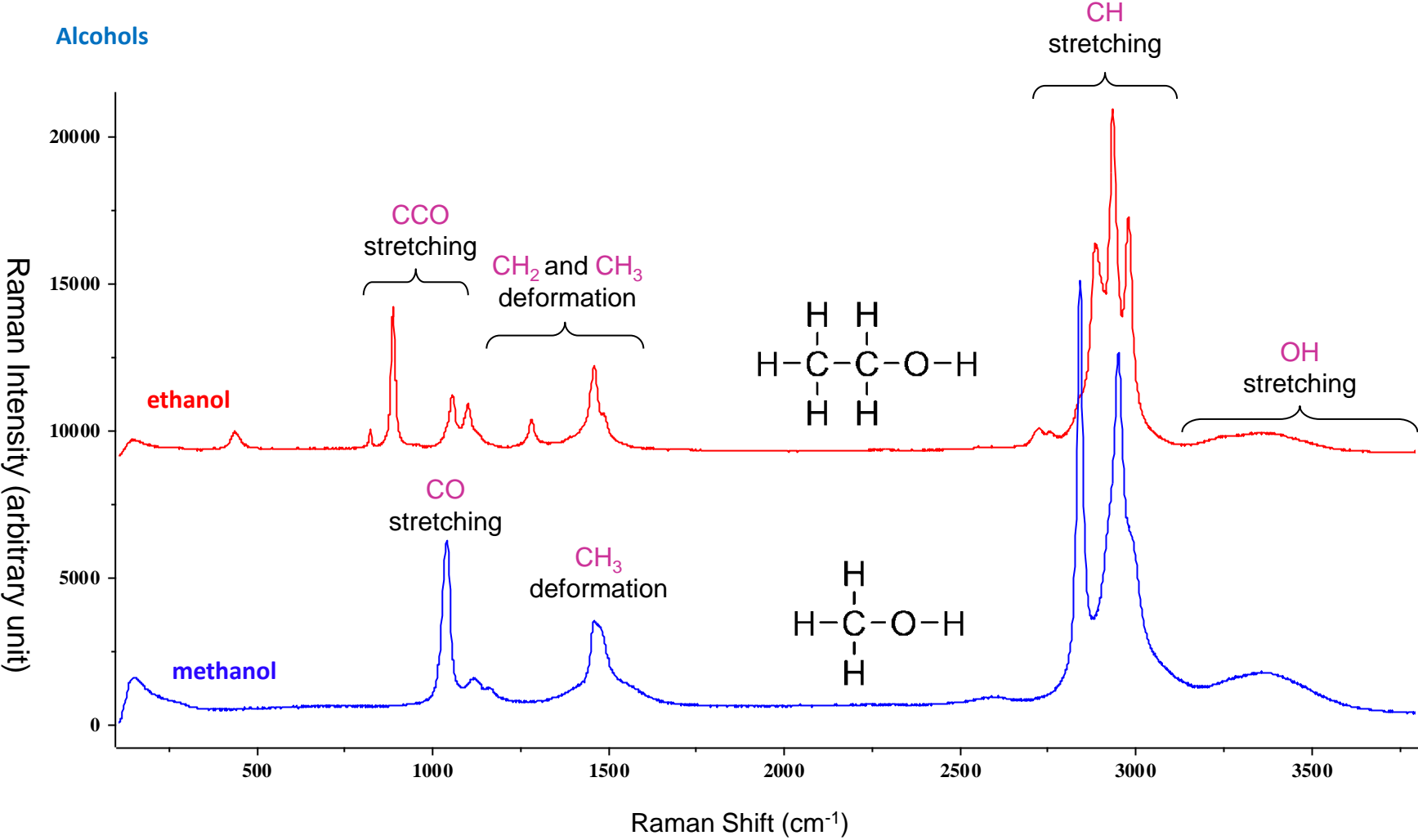
Raman spectroscopy
Interpretation of spectra

Mass effect

→ Peak position change

Mg - SO_4
Na_2 - SO_4

Isotopic shift

CH$_3$^{13}CN
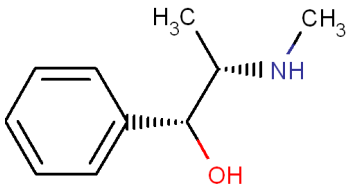CH$_3$^{12}CN
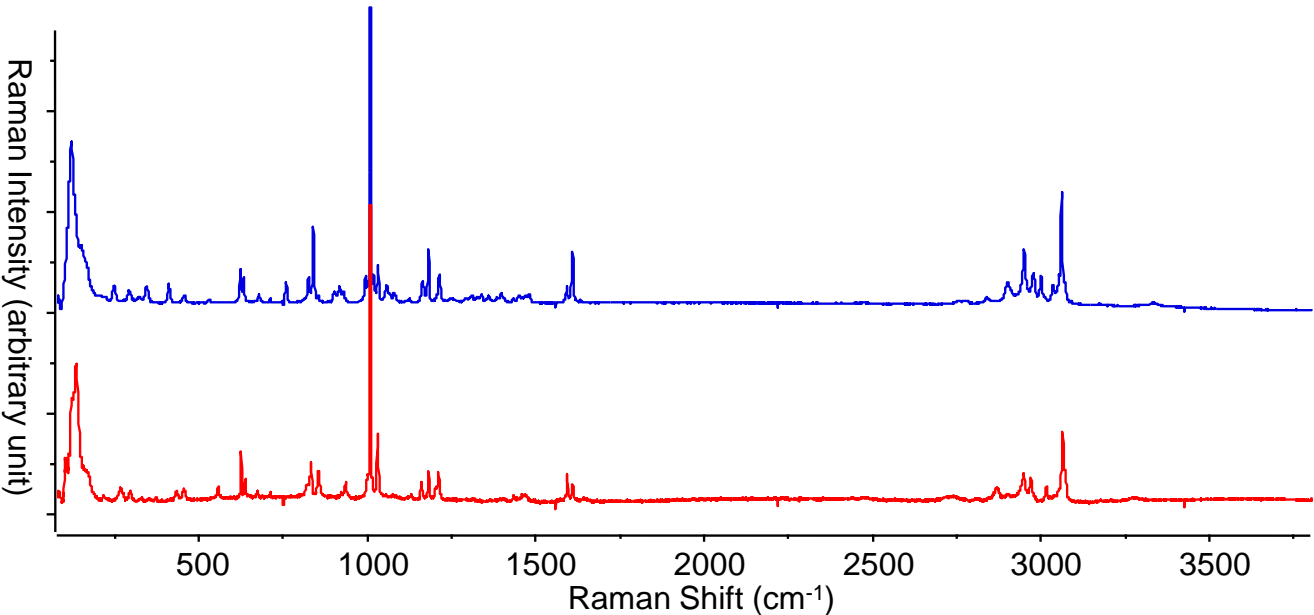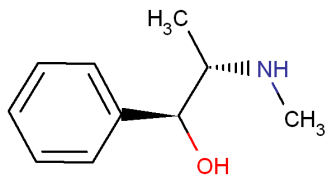
30.5 cm^{-1}

1564.3   1594.8
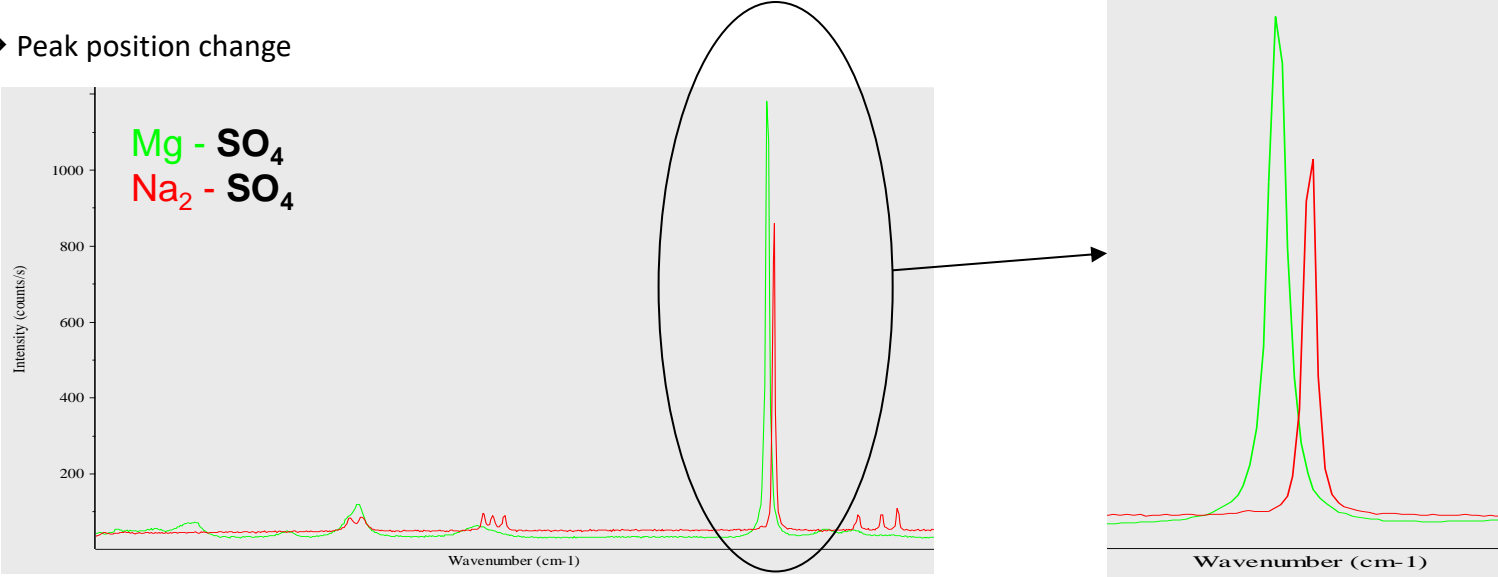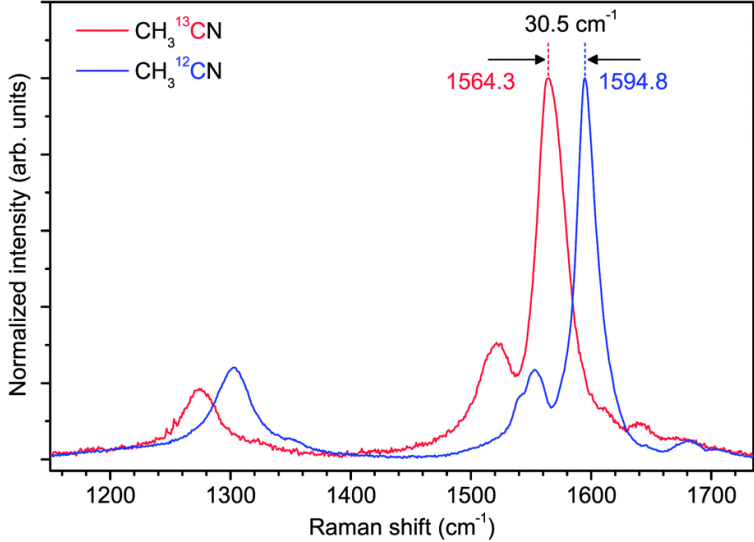
Raman spectroscopy
Interpretation of spectra
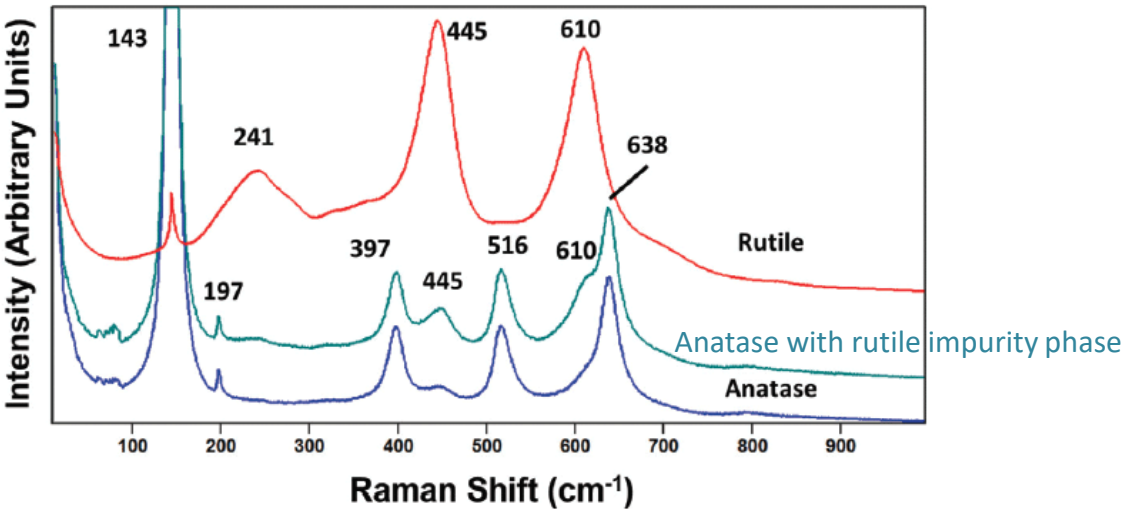
Isomers (diasteromers)

Ephedrine

Pseudoephedrine

Polymorphs (different crystalline structure)

Rutile

TiO$_2$

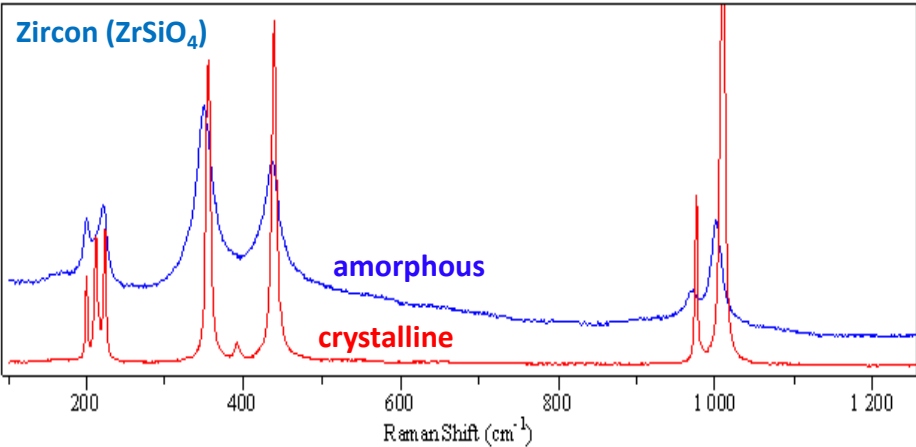**Anatase**

Rutile

Anatase with rutile impurity phase

Anatase
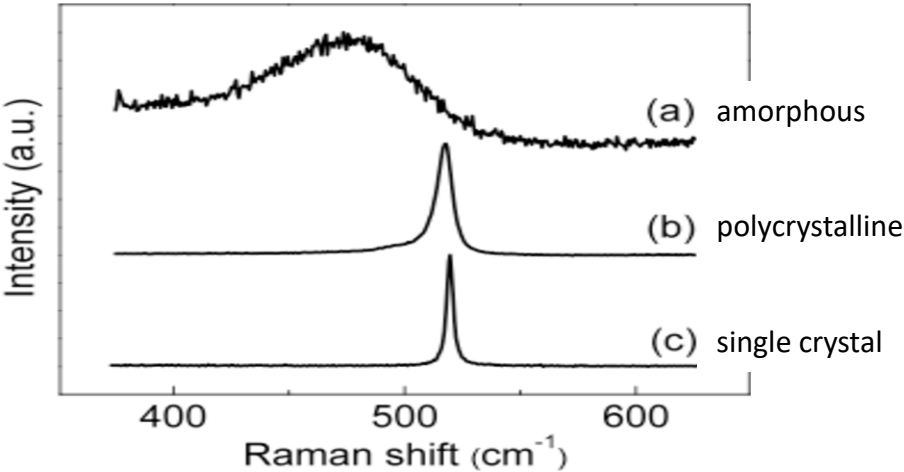
Raman spectroscopy
Interpretation of spectra

Structural order / disorder

Zircon ($ZrSiO_4$)

amorphous

crystalline

Silicon

(a) amorphous

(b) polycrystalline

(c) single crystal
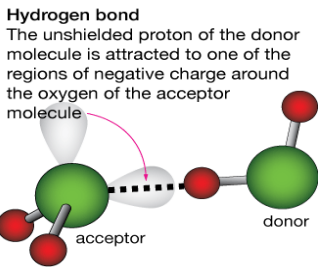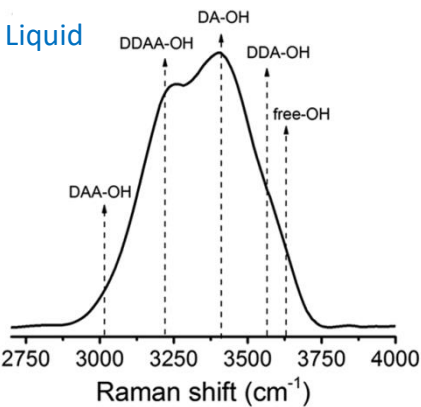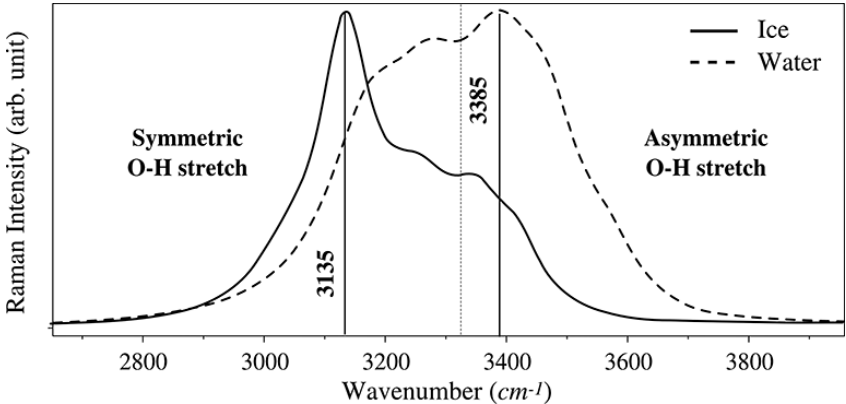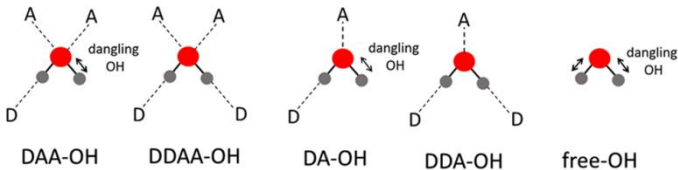
Structural order – networking

Water – different types of hydrogen bonding environments

Liquid

Hydrogen bond
The unshielded proton of the donor molecule is attracted to one of the regions of negative charge around the oxygen of the acceptor molecule

acceptor

donor

A ... acceptor
D ... donor

DAA-OH   DDAA-OH   DA-OH   DDA-OH   free-OH

Symmetric O-H stretch
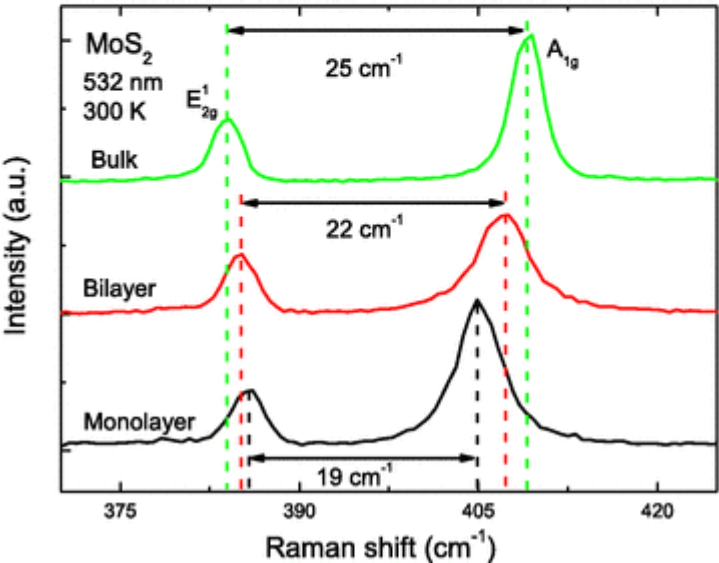
Asymmetric O-H stretch
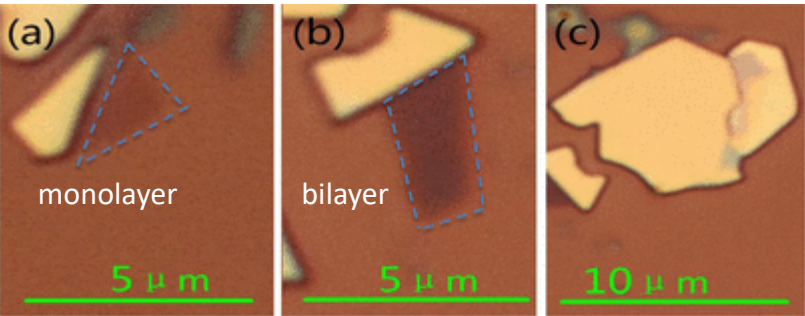
3135   3385

Ice —
Water ---

Raman spectroscopy
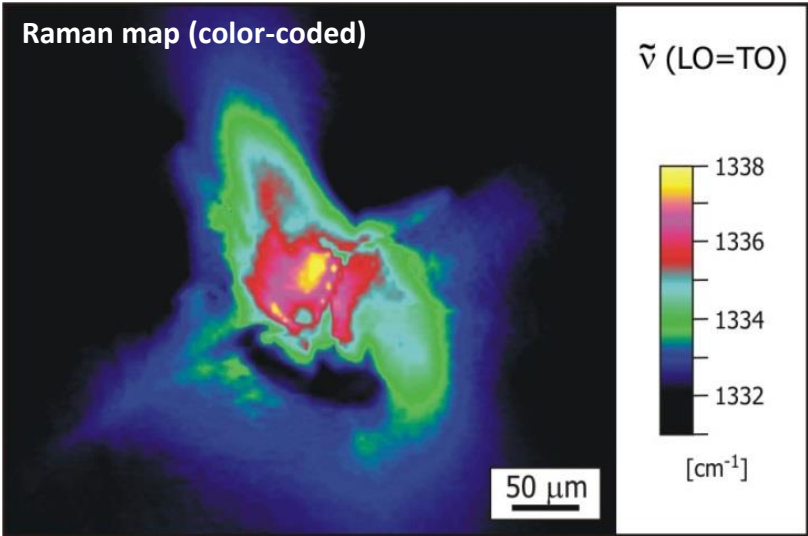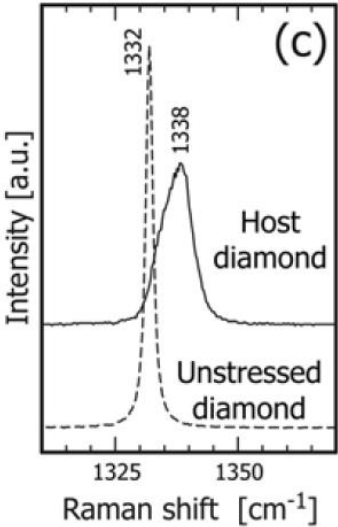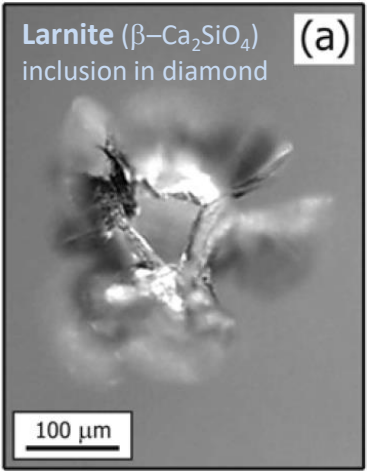## Interpretation of spectra

Dimension

MoS$_2$ thin film on SiO$_2$


Raman spectroscopy → contrast method in microscopy

Stress and strain

Surface vibrational spectroscopies & hybrid methods (spectromicroscopies)
Povrchové vibrační spektroskopie a hybridní metody (spektromikroskopie)

- Reflection Absorption Infrared Spectroscopy
- High Resolution Electron Energy Loss Spectroscopy
- Surface & Tip Enhanced Raman Scattering
- High Resolution Electron Energy Loss Spectroscopy
- Inelastic Electron Tunneling Spectroscopy
- Infrared Scanning Tunneling Microscopy
- Atomic Force Microscopy-based IR Spectroscopy
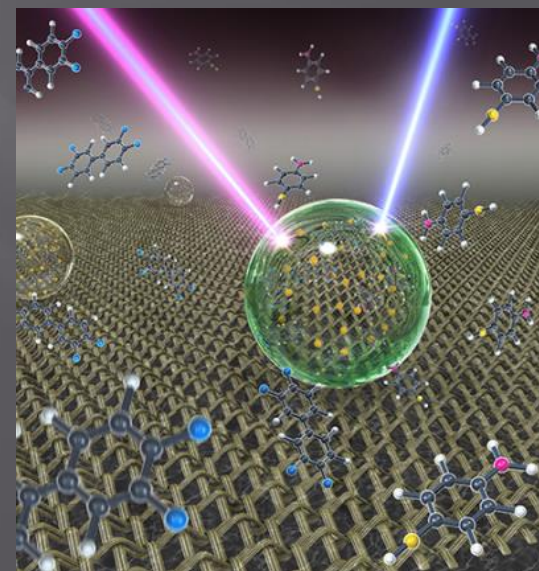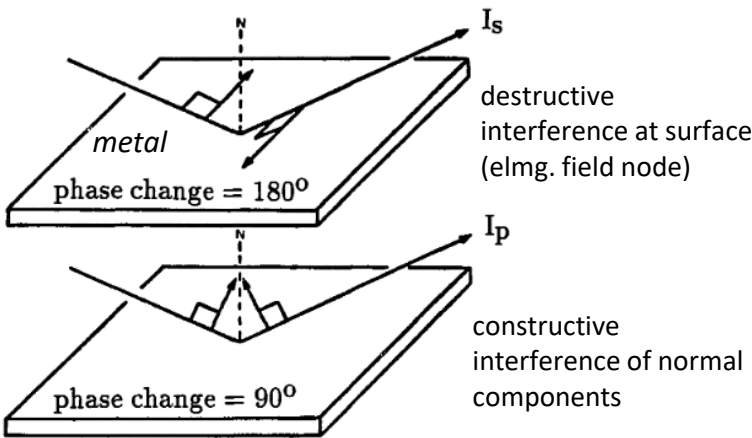
Reflection-Absorption IR Spectroscopy
Fundamentals

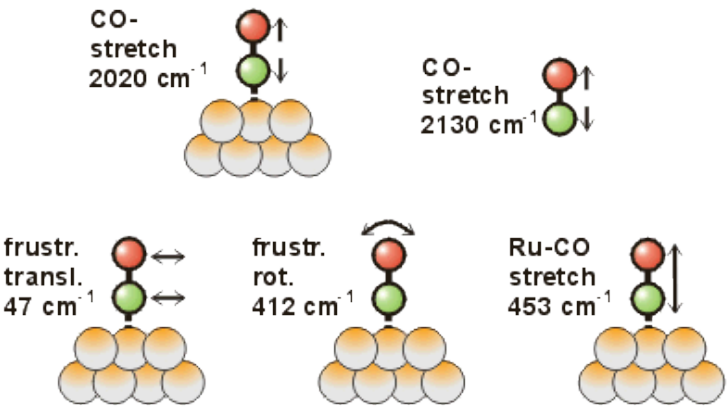**Reflection-Absorption IR Spectroscopy (RAIRS, IRAS, IRRAS)**

- Grazing incidence => **p-polarized** light reflected, s-polarized almost cancelled
- Excellent resolution – different adsorption sites resolved
- Good for metals (metal cannot be measured in transmission)
- Not in-situ and UHV restriction → operando spectroscopy

metal

phase change = 180°

destructive interference at surface (elmg. field node)

phase change = 90°

constructive interference of normal components

Surface vs. bulk IR spectrum

Symmetry of the system changes
=> shifts, new active modes, missing modes

Frustrated ro-vibrational modes

CO-stretch
2020 cm^{-1}

CO-stretch
2130 cm^{-1}

frustr. transl.
47 cm^{-1}

frustr. rot.
412 cm^{-1}

Ru-CO stretch
453 cm^{-1}

Effect of thermal excitation of the CO-stretch vibration:
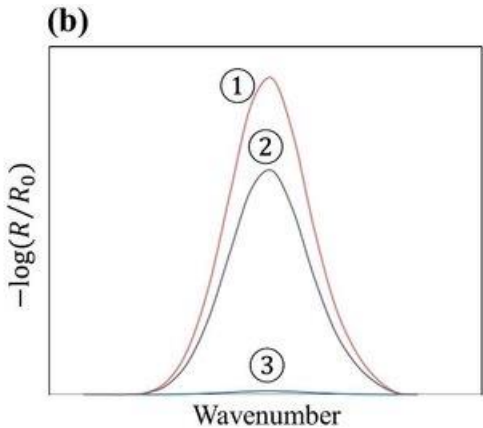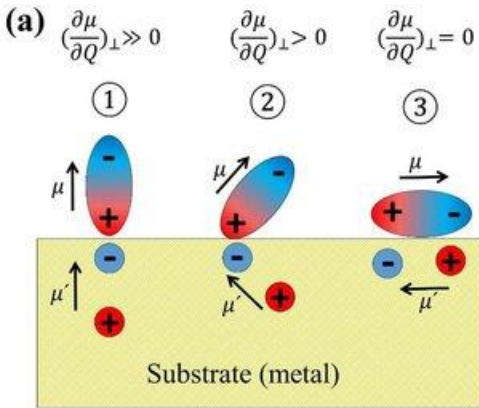
Redshift   Redshift ?   Blueshift

Surface dipole selection rule

– on metals
– only vibrational modes with dipole perpendicular to surface IR active

(a) $(\frac{\partial\mu}{\partial Q})_\perp \gg 0$ $(\frac{\partial\mu}{\partial Q})_\perp > 0$ $(\frac{\partial\mu}{\partial Q})_\perp = 0$ (b)

① ② ③

Substrate (metal)

$-\log(R/R_0)$

Wavenumber

Vibrational spectroscopy
RAIRS – examples

Site Identification: NO/Pd/Al₂O₃
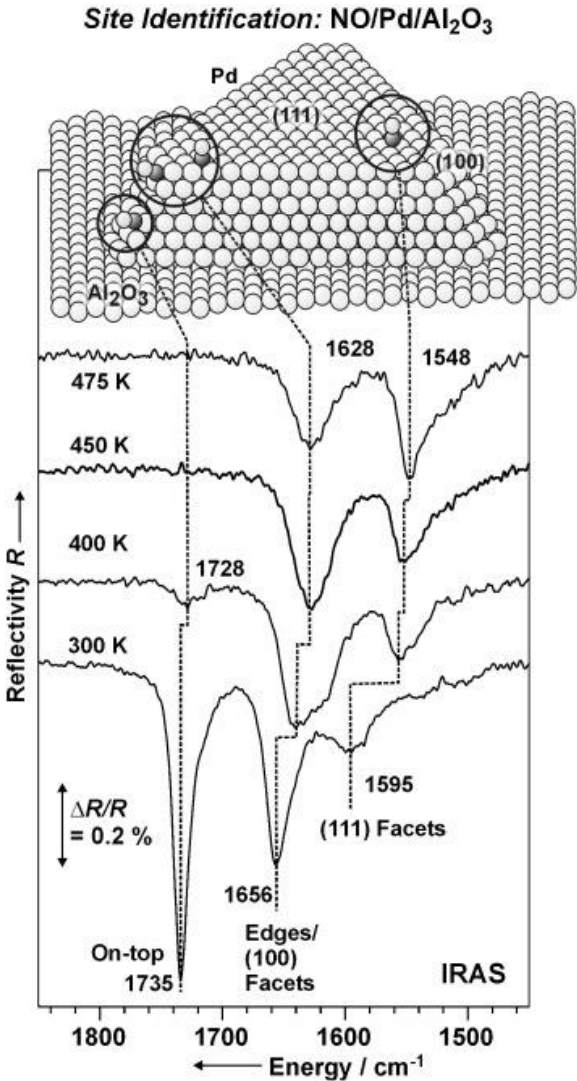
Transient experiment (TR-RAIRS): kinetics of NO decomposition on NP catalyst
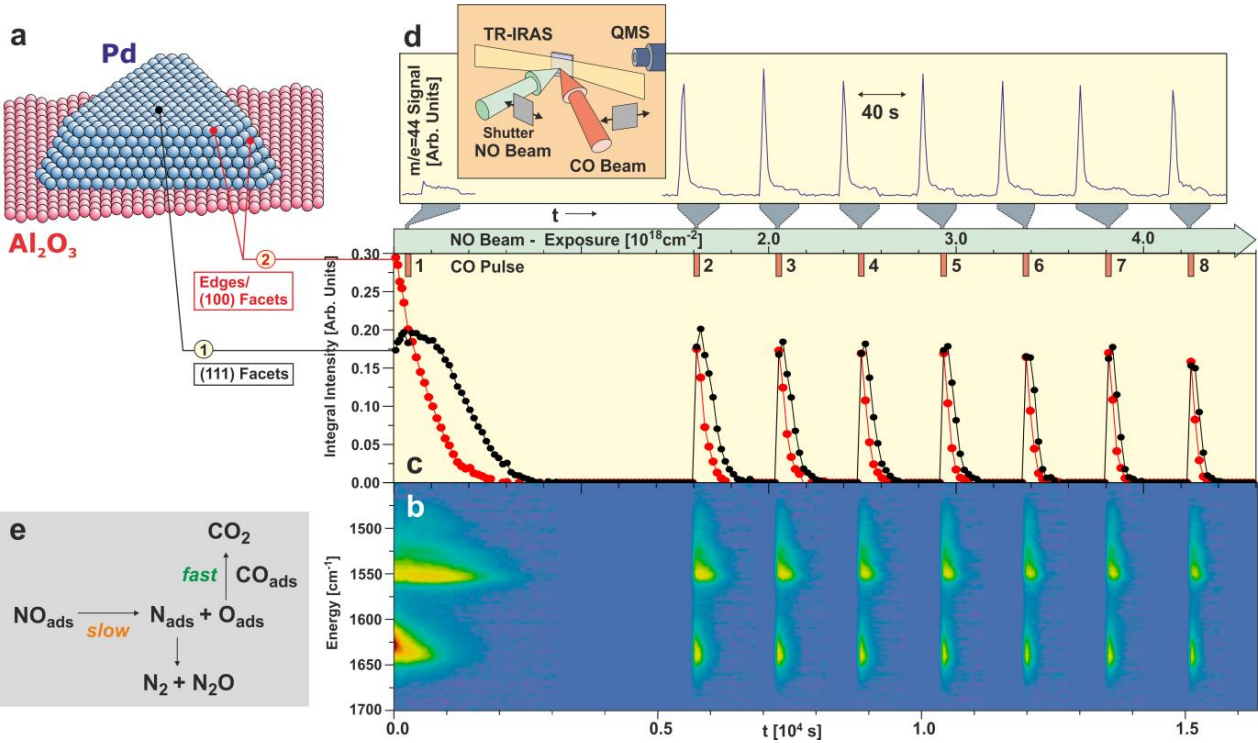
Lower coordinated sites = preferential reaction centers

Vibrational spectroscopy
PM-RAIRS – examples

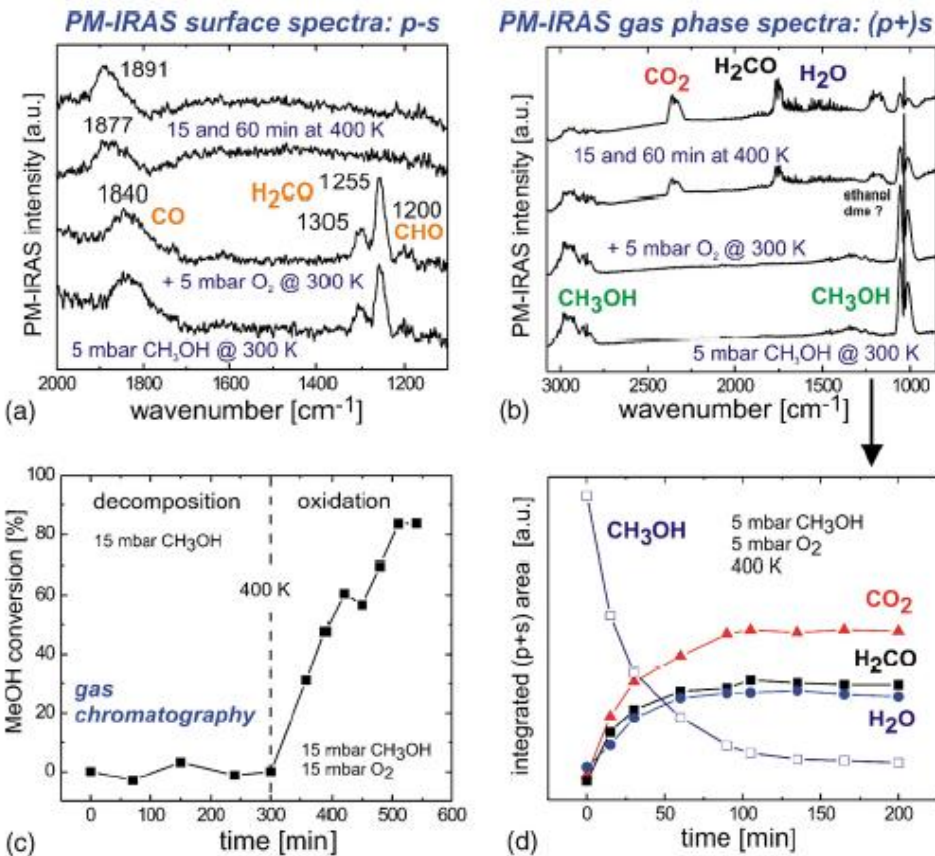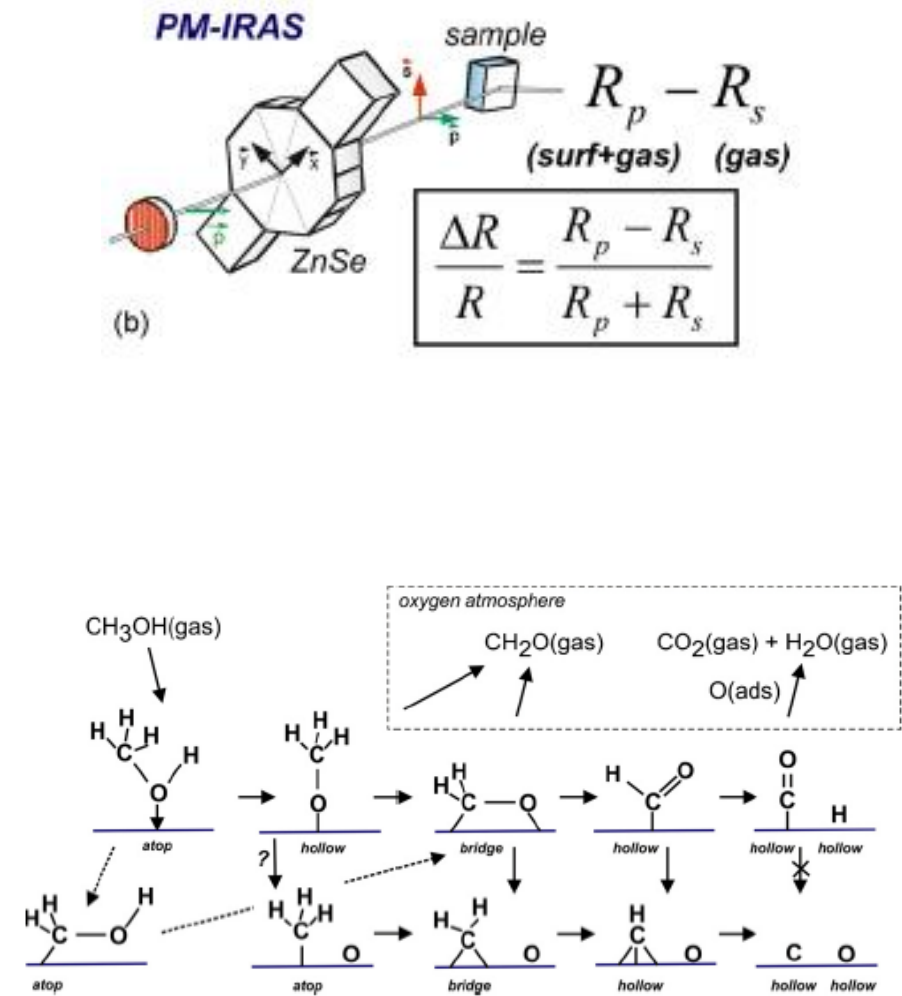**Polarization modulation RAIRS (IRAS)**

Fig. 7. Suggested mechanism of CH_3OH decomposition and oxidation on Pd catalysts.

Electron Energy Loss Spectroscopy
Fundamentals

Electron Energy Loss Spectroscopy

Scattering mechanisms:

Dipole scattering
– electron scattered at long range (~100 Å) by oscillating electric field of a vibrational mode
– strong maximum near specular direction

Impact scattering
– electron „kinematically" scattered at short range (few Å) by atomic core potentials of surface, modulated by nuclear motion (vibration)
– electron scattered over wide range of angles
– not restricted to perpendicular modes
– much lower cross section than dipole scattering

HREELS and RAIRS comparison

	RAIRS	HREELS
Spectral range	>100 meV (internal stretches)	>5 meV
Resolution	0.05 meV	>1 meV
Sensitivity	0.1% ML (strong dipoles)	0.1% ML
Substrate	crystals	conductors
Pressure range	< 1 atm	UHV

HREELS spectrum of CO on Rh(111)

C-metal stretching vibration

C-O stretches

G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis,* Wiley Interscience, New York (1994)
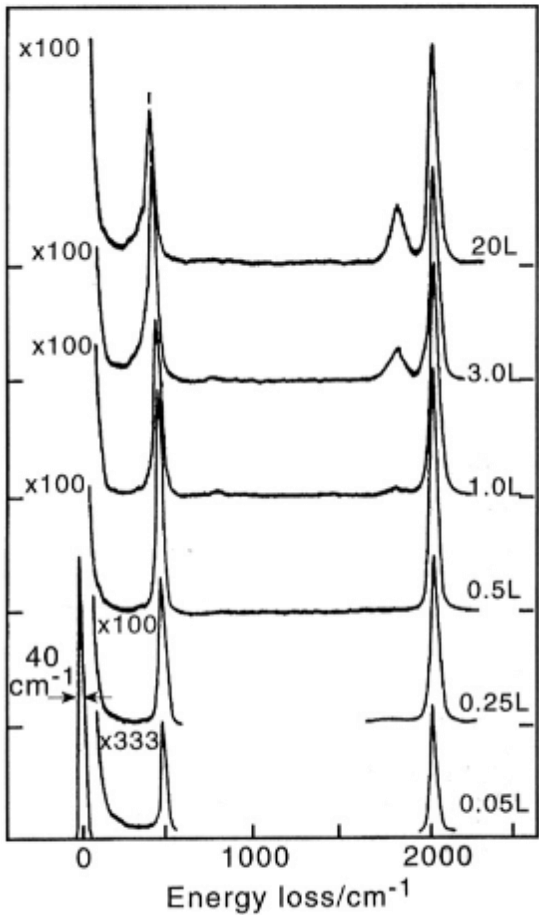
Surface Enhanced Raman Spectroscopy
Fundamentals

Surface Enhanced Raman Spectroscopy (SERS)
(Surface Enhanced Raman Scattering)
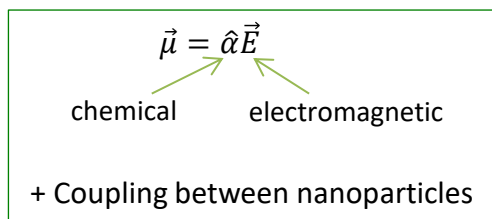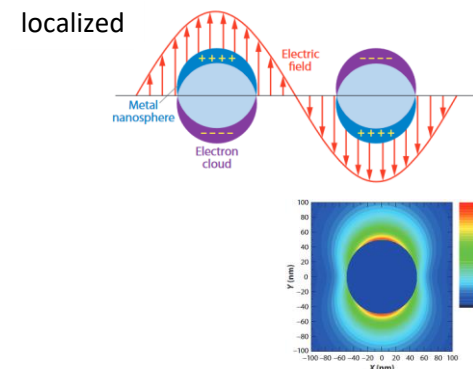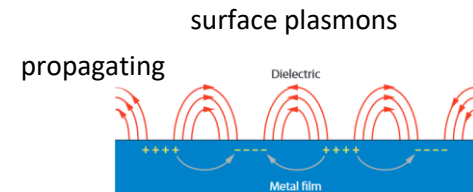
- On rough metal surfaces or nanostructures
- Strong signal enhancement ~10^6–10^{10} => single molecules observable

Possible mechanisms:
1) electromagnetic: strong EM field generated by plasmon resonance
   - **localized** surface plasmons – **perpendicular** to surface => rough surfaces, nanoparticles
   - double enhancement – incident light, Raman scattered light
   - enhancement maximized at $\omega_{plasmon}$ in resonance with source
   (*spherical particles*: $\omega_{src} = \omega_{plasmon}/\sqrt{3}$)
   => enhancement smaller for larger Raman shifts

2) chemical: due to bonding between target molecule and substrate
   - formation of charge-transfer complexes → resonance Raman
   - dominant for clusters with band gap

$$\vec{\mu} = \hat{\alpha}\vec{E}$$

chemical   electromagnetic

+ Coupling between nanoparticles

surface plasmons

propagating

localized

transverse   longitudinal

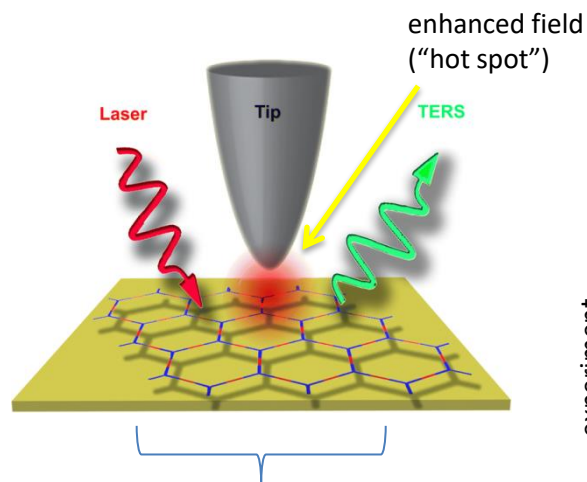T. Itoh et al.: Chem. Rev. 2023, 123, 4, 1552–1634
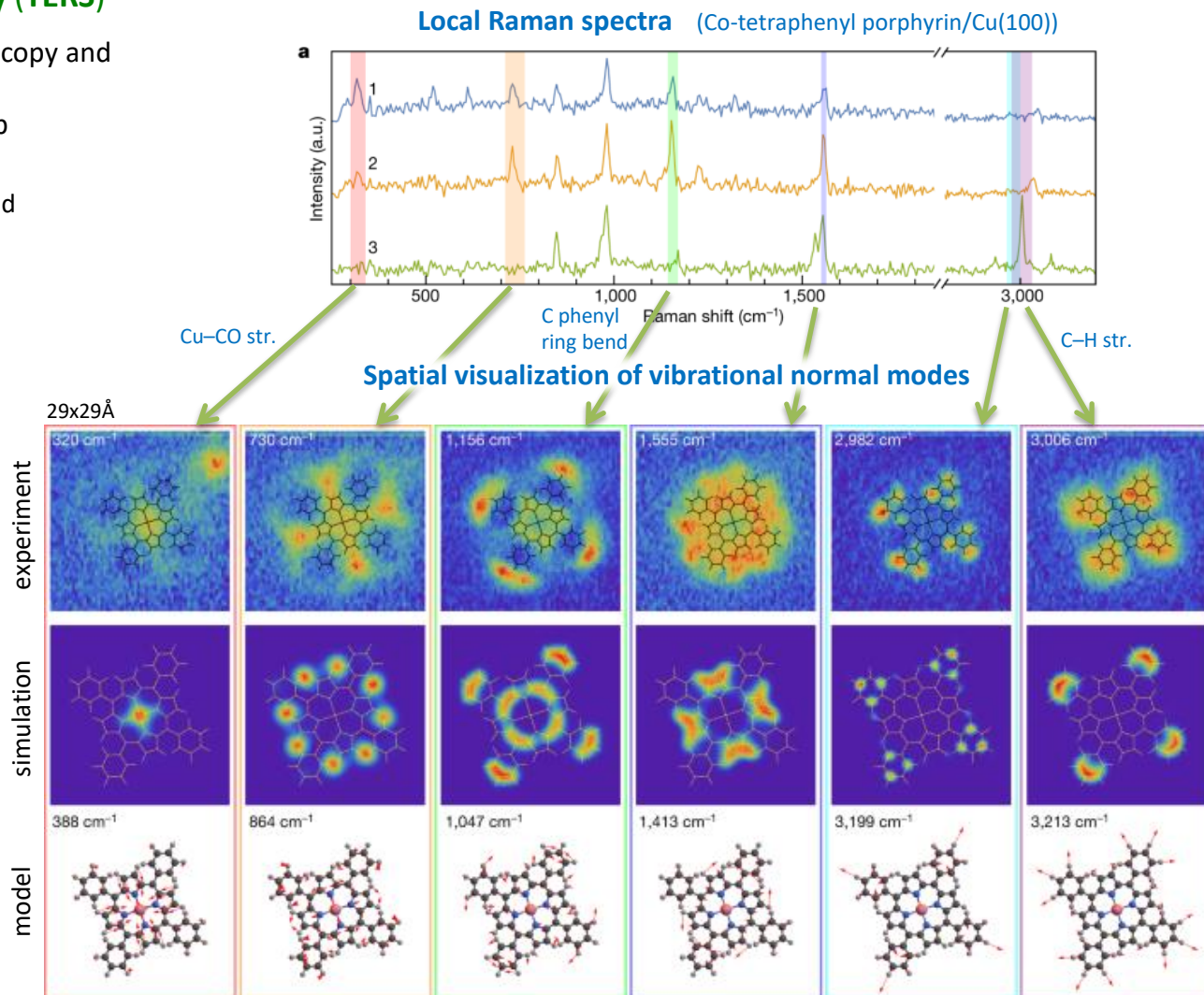
Tip Enhanced Raman Spectroscopy
Fundamentals

Tip-enhanced Raman spectroscopy (TERS)

- combination of scanning probe microscopy and Raman spectroscopy
- local Raman enhancement near the tip

enhanced field ("hot spot")

Laser   Tip   TERS

- Raman chemical sensitivity
- SERS absolute sensitivity
- SPM lateral resolution

Local Raman spectra   (Co-tetraphenyl porphyrin/Cu(100))

Cu–CO str.

C phenyl ring bend

C–H str.

Spatial visualization of vibrational normal modes

29x29Å

experiment

320 cm⁻¹   730 cm⁻¹   1,156 cm⁻¹   1,555 cm⁻¹   2,982 cm⁻¹   3,006 cm⁻¹

simulation

388 cm⁻¹   864 cm⁻¹   1,047 cm⁻¹   1,413 cm⁻¹   3,199 cm⁻¹   3,213 cm⁻¹

model

V.Ara Apkarian (UCI), 2019

T. Itoh et al.: Chem. Rev. 2023, 123, 4, 1552–1634
J. Lee et al.: Nature 568, 2019, 78–82
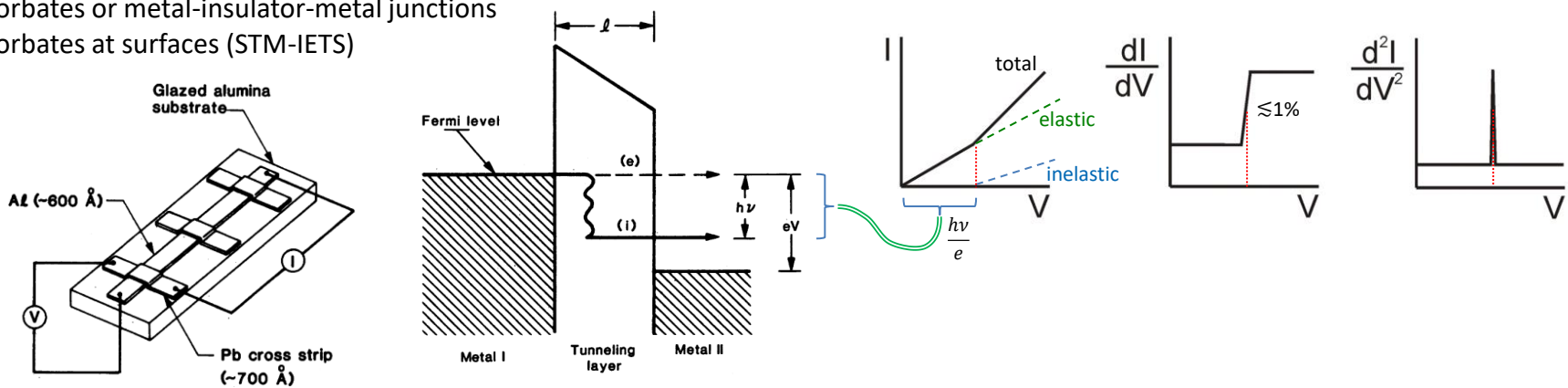
Inelastic Electron Tunneling Spectroscopy
Fundamentals

Based on inelastic interaction of a tunneling electron with adsorbed molecule
- adsorbates or metal-insulator-metal junctions
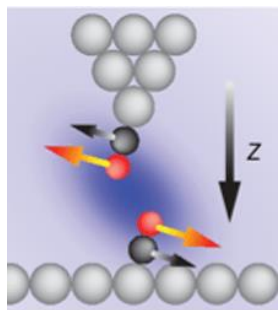- adsorbates at surfaces (STM-IETS)

STM-IETS

Bias sweep at fixed position => I-V characteristics (→ STS)
   1st derivative: LDOS
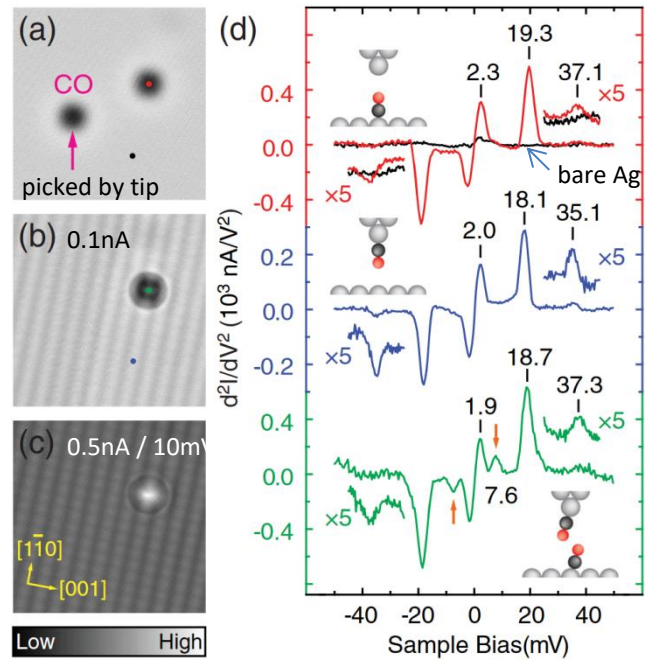   2nd derivative: vibrations

Very challenging – low temperatures, extreme stability required

Tip-enhanced IETS – resonant enhancement when energy diff. between molec. orbitals and E_F comparable to vibrational energy => much stronger peaks

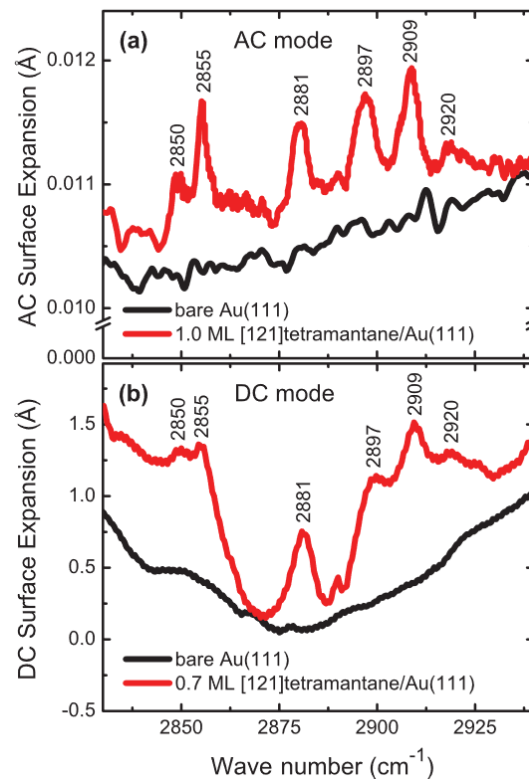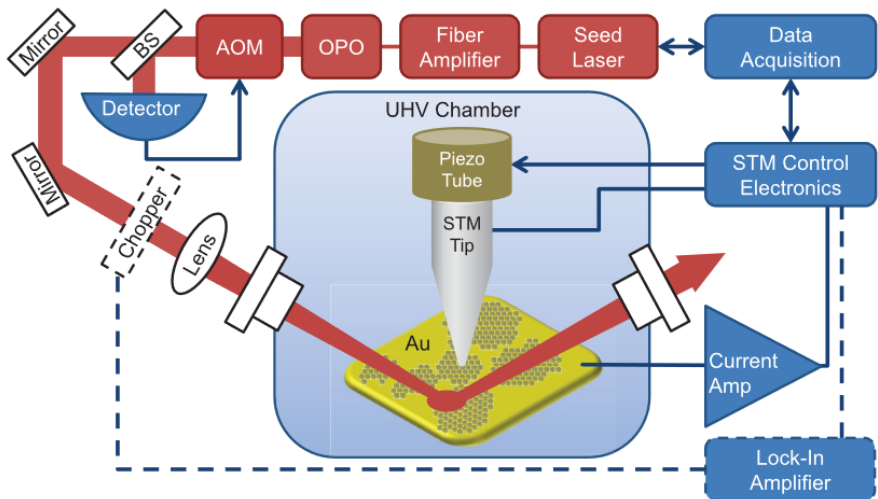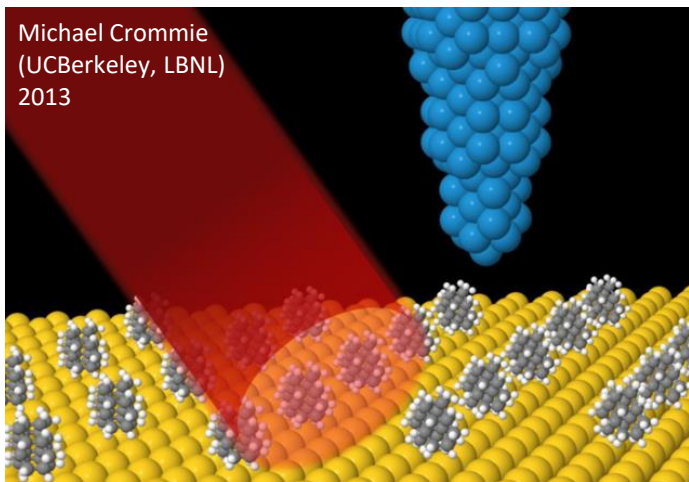Coupled vibrations – molecule adsorbed both on tip and surface

Wilson Ho (UCI), 2017

S. K. Khanna & J. Lambe: Science 220(4604), 1983, 1345–1351.
S. You et al.: Adv. Physics X, 2(3), 2017, 907-936

Infrared Scanning Tunneling Microscopy
Fundamentals

- Probing the IR response of adsorbed molecules under STM tip
- Irradiation by IR laser
- STM image of absorbing molecule changes

Michael Crommie
(UCBerkeley, LBNL)
2013

(a) AC mode

AC Surface Expansion (Å)

2850, 2855, 2881, 2897, 2909, 2920

bare Au(111)
1.0 ML [121]tetramantane/Au(111)

(b) DC mode

DC Surface Expansion (Å)

2850, 2855, 2881, 2897, 2909, 2920

bare Au(111)
0.7 ML [121]tetramantane/Au(111)

Wave number (cm^{-1})

I. V. Pechenezhskiy et al.: Phys. Rev. Lett. 111, 2013, 126101

Atomic Force Microscopy-based Infrared Spectroscopy
Fundamentals

AFM-IR

– Tunable infrared laser focused to sample at proximity of probe tip
– At λ = absorbing wavelength response detected by tip via thermal expansion
=> force impulse on tip => transient tip oscillation

Resonance enhanced AFM-IR – laser repetition rate tuned to tip resonance
=> continuous wave oscillation of cantilever
=> much more sensitive measurements

A. Dazzi & C.B. Prater: *AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging*, Chem. Rev. 2017, 117, 7, 5146–5173