

Vibrational Spectroscopy (IR, Raman)

Vibrational spectroscopy is an energy sensitive method. It is based on periodic **changes** of **dipolmoments (IR)** or **polarizabilities (Raman)** caused by molecular vibrations of molecules or groups of atoms and the combined **discrete energy transitions** and changes of frequencies during **absorption (IR)** or **scattering (Raman)** of electromagnetic radiation of wavelengths from 1 to 300 μm (**selection rules**).

One can get/detect:

- the presence of known compounds (finger print)
- the components of an unknown compound (functional groups)
- and thus a likely structure of a compound
- changes in the concentration of a species during a reaction
- the properties of bonds (bond strength, force constants)
- state and order parameters of phase transitions

Vibrational Spectroscopy (IR, Raman)

In order to describe the $3N-6$ or $3N-5$ different possibilities how non-linear and linear molecules containing N atoms can vibrate, the models of the harmonic and anharmonic oscillators are used.

These modes of vibration (normal modes) give rise to

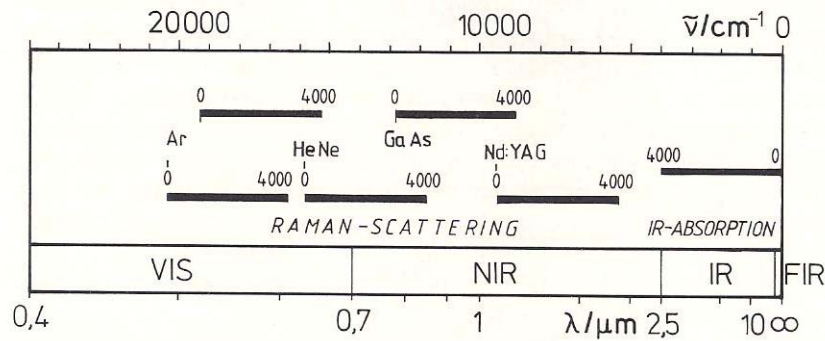
- **absorption bands (IR)** if the sample is irradiated with **polychromatic light** of suitable wavelengths upon **changes of the dipole moment** $\mu = \alpha \cdot \mathbf{E} + \beta \cdot \mathbf{E}^2 + \dots$
- **scattered light (Raman)** if the sample is irradiated with **monochromatic light** of a suitable wavelength upon **changes of the polarizabilities** α

with characteristic **energies/frequencies/wavenumbers**, **intensities** and **Fwhm's** to be determined and analyzed.

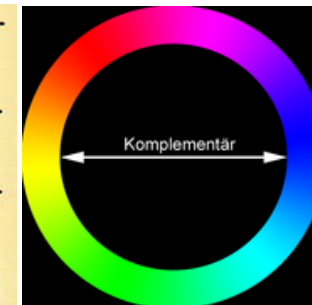
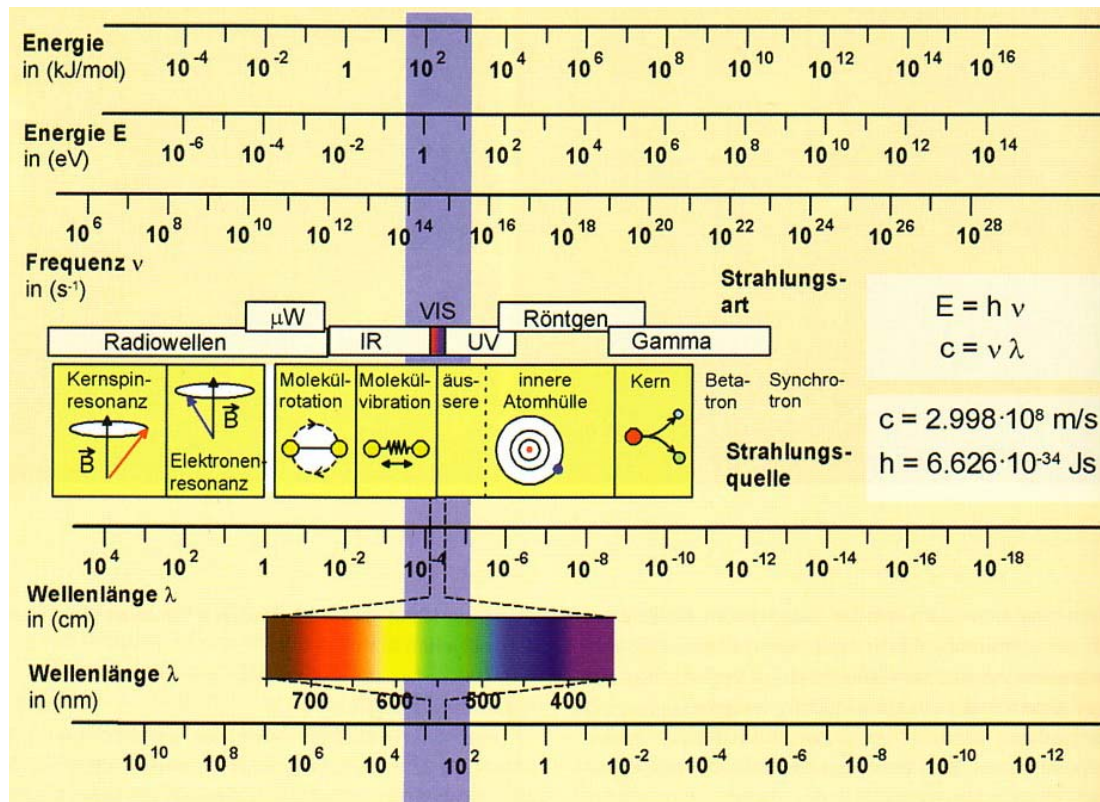
The frequencies are in the range of 10^{12} to $3 \cdot 10^{14}$ Hz with vibrational energies from 0.4 to 120 kJ/mole ($4 \cdot 10^{-3}$ - 1.24 eV), wavenumbers from 33 to 10^4 cm^{-1} , and wavelengths from 300 to 1 μm .

The intensities are proportional to the square of the changes of the dipole moments and polarizabilities.

Wavelengths and energies in vibrational spectroscopy



Vis, IR, and Raman areas drawn in a scale of linear wavenumbers and some lasers sources

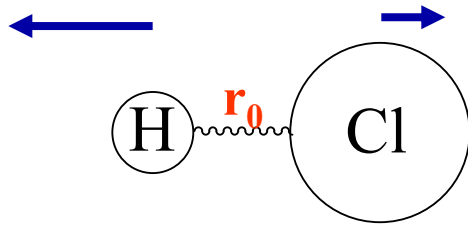


Wavenumber reciprocal of λ : $1/\lambda \text{ (cm}^{-1}\text{)}$

rot	$\approx 790\text{--}630$
orange	$\approx 630\text{--}580$
gelb	$\approx 580\text{--}560$
grün	$\approx 560\text{--}480$
blau	$\approx 480\text{--}420$
violett	$\approx 420\text{--}390$

Wavelength in nm

Vibrational Spectroscopy - the main principle



Extension from r_0 (equilibrium distance)

→ Absorption of energy E

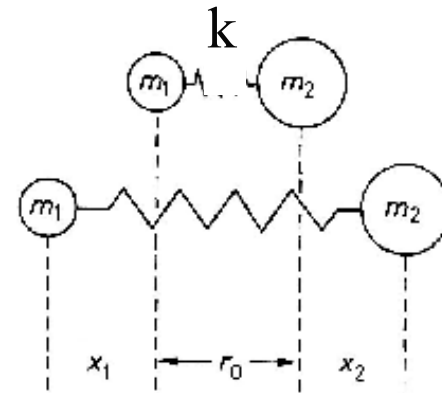
→ Relaxation to r_0

→ **Vibration**

*Center of mass is not allowed
to shift during the vibration*

→ *Hooke's law*

Spring with rate/spring constant k



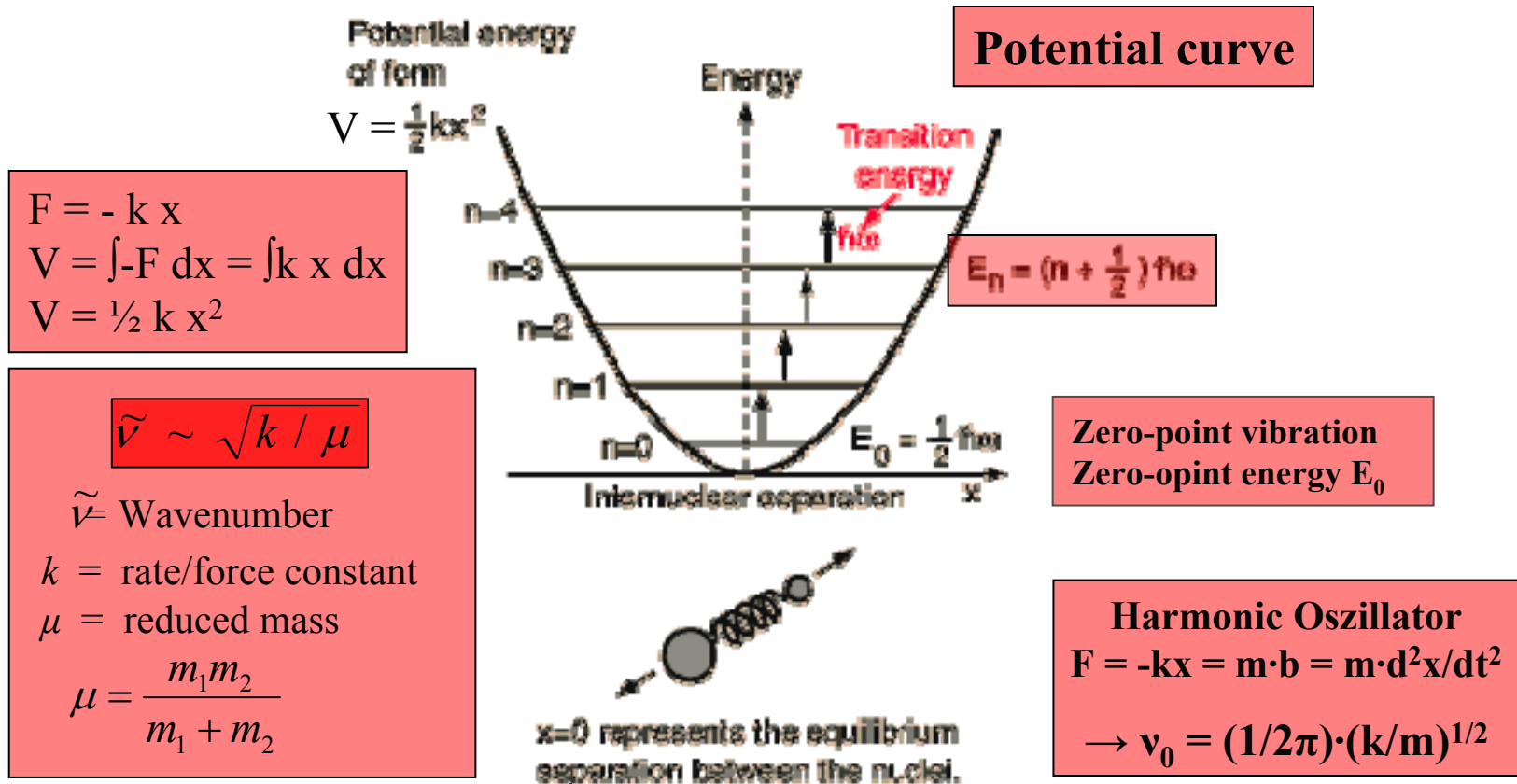
$$F = -k x$$

$$V = \int -F dx = \int k x dx$$

$$V = \frac{1}{2} k x^2$$

Together with molecular vibrations also molecular rotations are excited as well since rotational energies are much smaller ($\sim 0.01 \cdot E_{\text{vib.}}$)!

Harmonic vibrational levels



Warning: Molecular vibrations are essentially *anharmonic*!

Vibrational energy levels in harmonic/anharmonic approximation

condition for IR $d\mu \neq 0$, condition for Raman: $d\alpha \neq 0$
Selection rules!

$$E_{\text{VIB}} = h\nu_{\text{osc}} \left(n + \frac{1}{2} \right) = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right)$$

$$n = 0, 1, 2, \dots \quad \Delta n = \pm 1$$

$$\Delta E_{\text{VIB}} = E_{n+1} - E_n = h\nu_{\text{osc}}$$

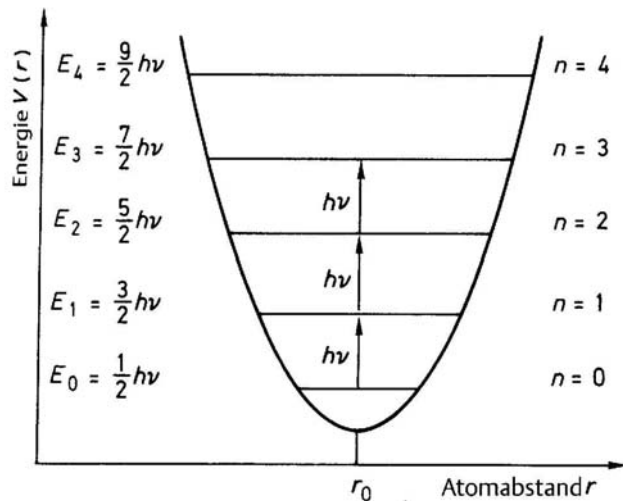
n Schwingungsquantenzahl

h Planck-Wirkungsquantum

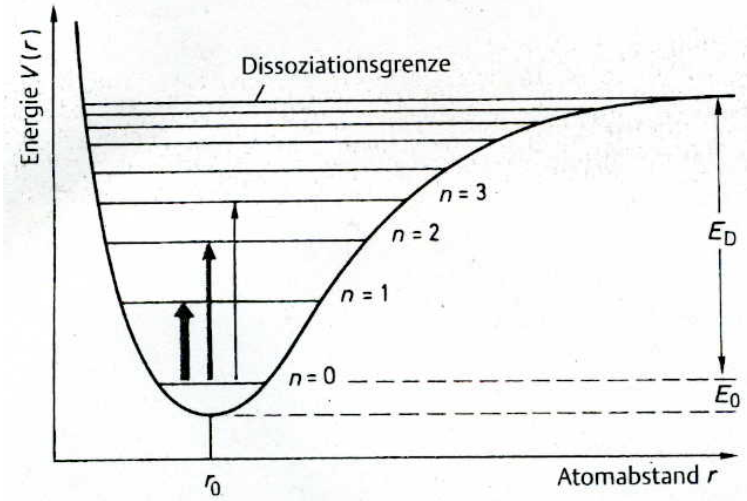
E_{VIB} Schwingungsenergie (VIB von Vibration)

$$E_{\text{VIB}} = h\nu_{\text{osc}} \left(n + \frac{1}{2} \right) - \frac{h^2\nu^2}{4E_D} \cdot \left(n + \frac{1}{2} \right)^2 \quad (\Delta n = \pm 1, \pm 2, \dots)$$

For *anharmonic* vibrations the distances of neighboring vibrational levels decrease with increasing n (the thickness of the arrows stand for the transition probabilities and intensities respectively).

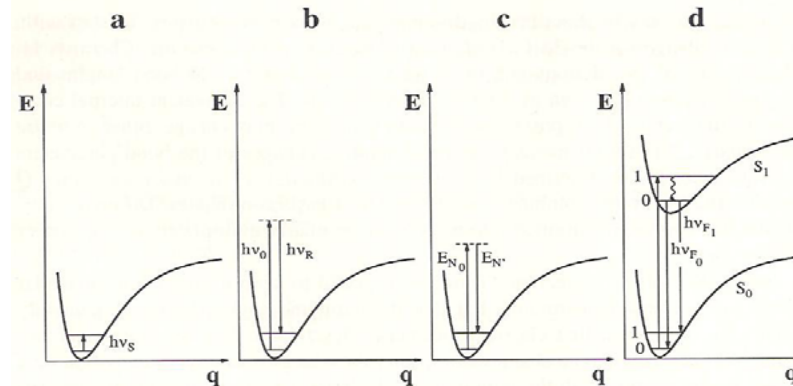


Potential curve of the *harmonic* oscillator
 (E_n : Vibrational levels, E_0 : Zero-point energy)

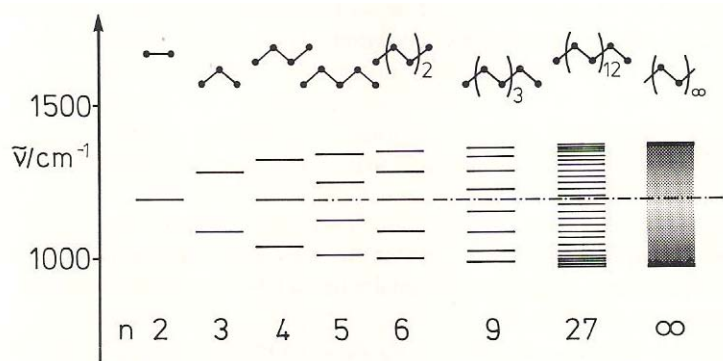


Potential curve of the *anharmonic* oscillator
 (E_0 : Zero-point energy, E_D : Dissociation energy)

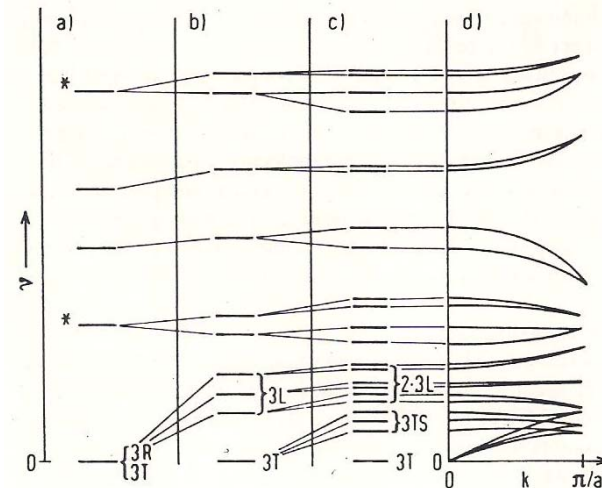
Vibrational states and frequencies



Excitation of a vibrational state in the electronic ground state S_0 by
 a: infrared absorption, b: Raman scattering, c: inelastic neutron scattering, d: fluorescence.



Vibrational coupling in zig-zag chains
 of different lengths



Variation of frequencies in case of a free molecule (a),
 static (b) and dynamical (c) coupling in a crystal lattice,
 and dependence on the wave vector k for all unit cells 7

Normal modes

Each atom of a molecule (structure) has three degrees of freedom (dof) with respect to displacements, resulting in $3N$ dof for N atoms. Subtracting the dof for translations (3) and rotations (3 or 2), $3N-6$ and $3N-5$ degrees of freedom are expected for non-linear and linear N -atomic molecules, respectively.

The corresponding vibrations are called normal modes. It is valid that:

1. All atoms of a molecule move with the same frequency and in phase, and they move simultaneously through the points of maximum elongation and equilibrium displacement r_0 while the mass center remains unchanged.
2. The amplitudes of the different particles can be different.
3. The normal vibrations (typically) do not interfere with each other (orthogonality principle).
4. The number of normal vibrations (vibrational degree of freedom) is
 - $3N-6$ for non-linear molecules
 - $3N-5$ for linear molecules

Normal modes

Every vibrational mode exhibits its **own “pattern** (vector, matrix)” for the atomic displacements ($\pm\Delta x$, $\pm\Delta y$, $\pm\Delta z$), leading to normal coordinates, but the **vibrational modes** are usually **not known**:

Assignment of the vibrational modes via symmetry properties of the molecules (point group, irreducible representation, character, character tables).

→ Symmetry of vibrations (symmetry species = *Rassen*, types of vibration)

Symmetry species (Rassen) of the modes are denoted after Mulliken:

A = symmetric, B = antisymmetric with respect to C_n ;

E, F, G, H = 2-, 3-, 4-, 5-fold degenerate with respect to C_n ;

g = symmetric with respect to i (from German *gerade*);

u = antisymmetric with respect to i (from German *ungerade*);

Index subscripts of A or B: 1 = symmetric, 2 = antisymmetric with respect to C_n or S_n (a mirror plane);

Example: A_{2g} is a vibration that is symmetric with respect to C_n and i (character = 1) and antisymmetric with respect to S_n or σ (character = -1).

Normal modes

Point group Symmetry operations

Symbol

Active vibrations in

C_{3v}	E	$2C_3$	$3\sigma_v$	IR	Raman
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

Symmetry species
(*Rassen*)

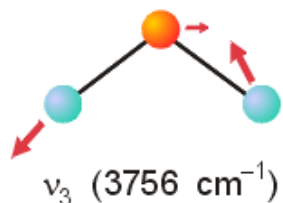
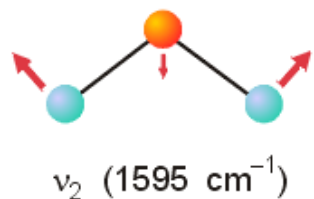
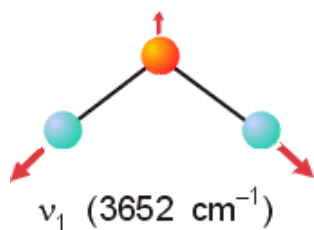
Group characters

Combinations of the symbols x, y, z, R_x , R_y and R_z , the first three of which represent the coordinates x, y and z, and the last three of which stand for rotations about these axes. These are related to transformation properties and basis representations of the group.

Character table for space group C_{3v}

Normal modes (Examples)

$3N - 6$ Modes ($3N - 5$, if linear)



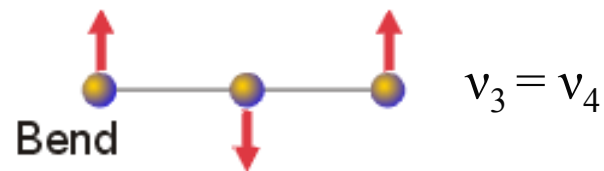
$$\tilde{\nu} \sim \sqrt{k / \mu}$$

ν = Wavenumber

k = Force constant

μ = Reduced mass

Three normal vibrations of H_2O
and their wavenumbers



Four normal vibrations of
 CO_2 (linear)

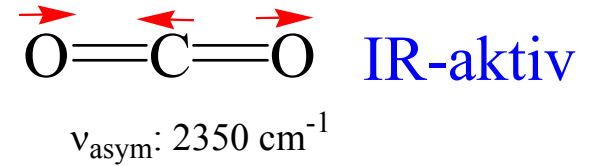
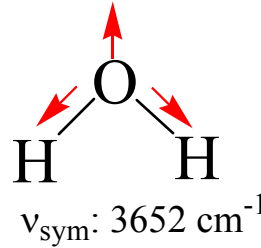
Normal modes of vibration (IR-) activity

Dipole moment changes during the vibration!

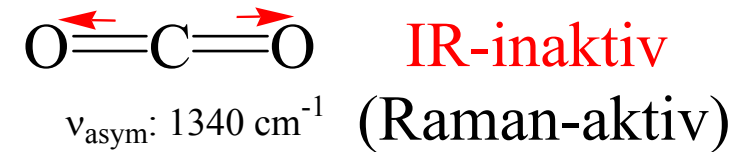
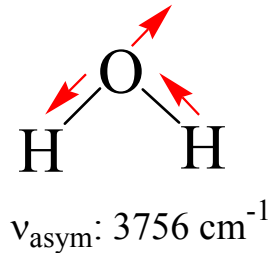
Stretching vibration

Changes of bond lengths

IR-aktiv



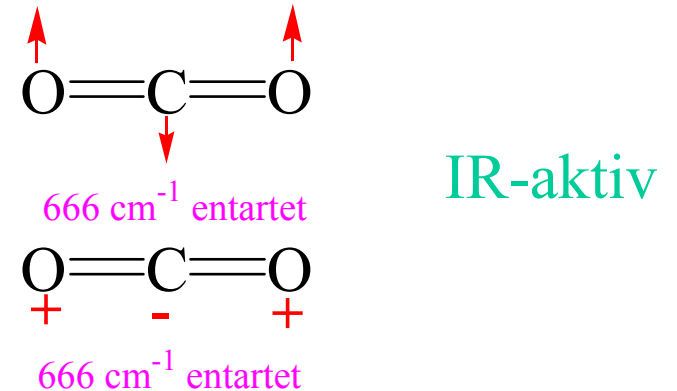
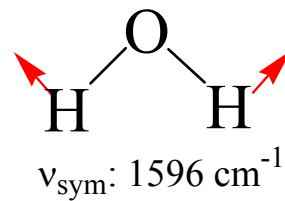
IR-aktiv



Bending vibration

Changes of bond angles

IR-aktiv



Normal modes (Examples)

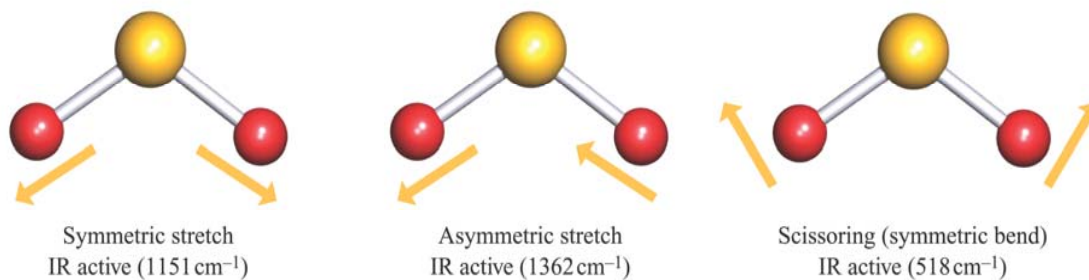
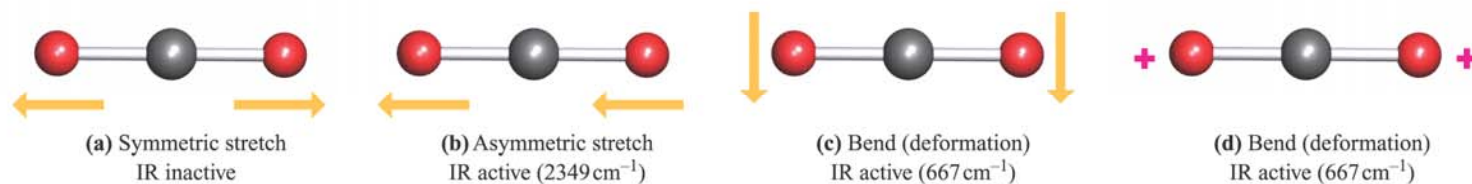


Fig. 3.12 The vibrational modes of SO_2 (C_{2v}).

Normal modes (Examples)

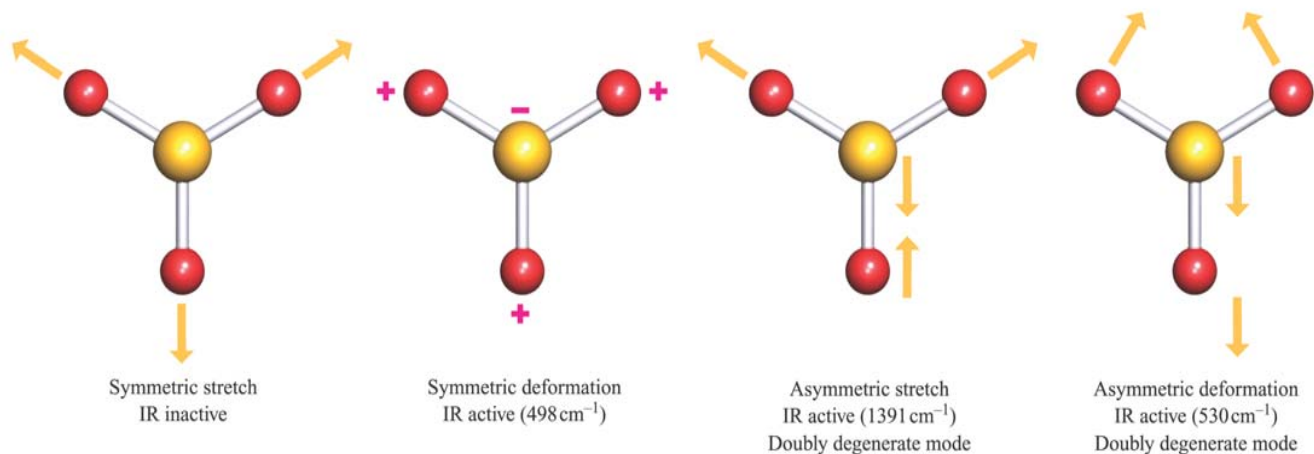


Fig. 3.13 The vibrational modes of SO_3 (D_{3h}); only three are IR active. The + and - notation is used to show the 'up' and 'down' motion of the atoms during the mode of vibration. [*Exercise*: Two of the modes are labelled as being degenerate: why is this?]

Catherine E. Housecroft and Alan G. Sharpe: *Inorganic Chemistry 2e* © Pearson Education 2005

Normal modes (Examples)

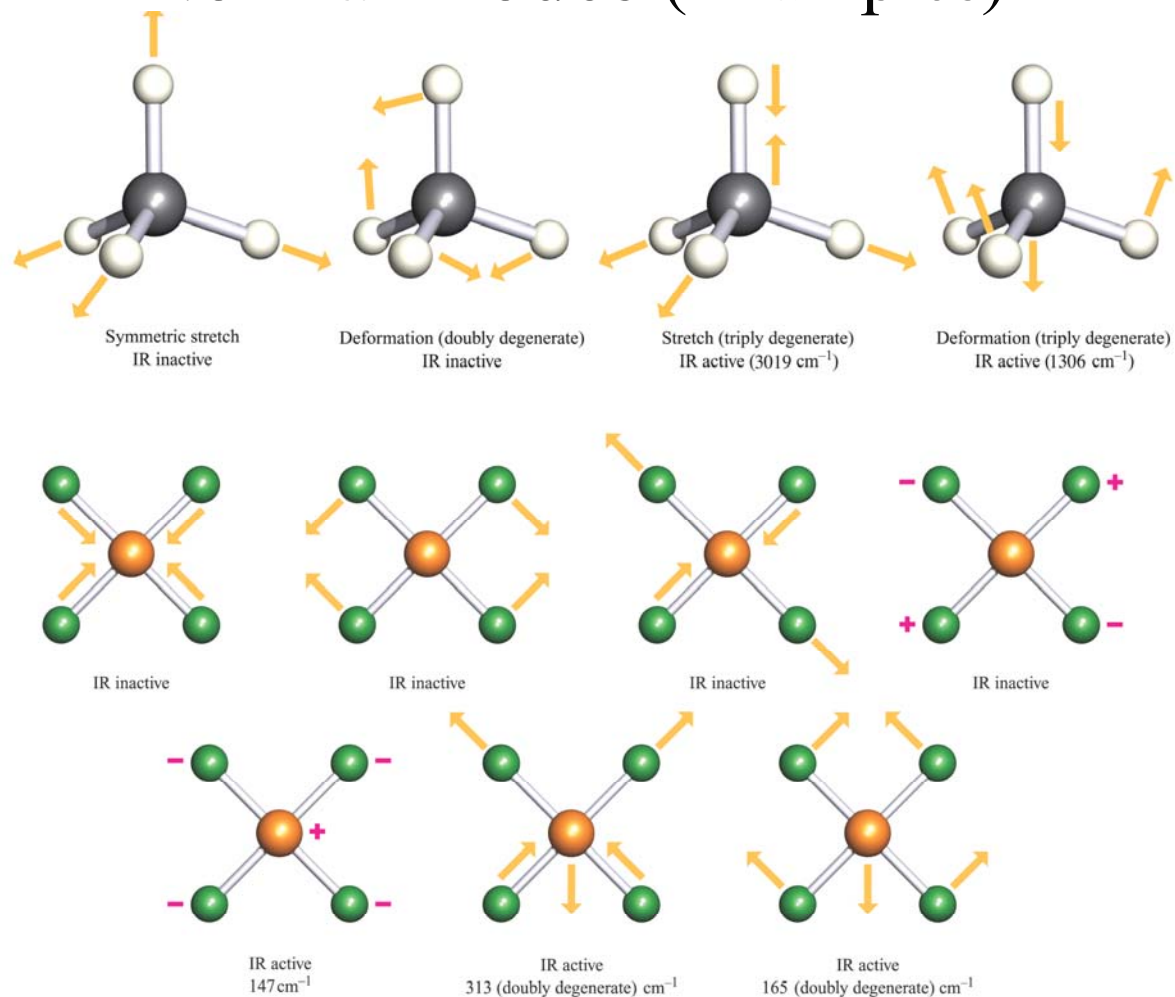
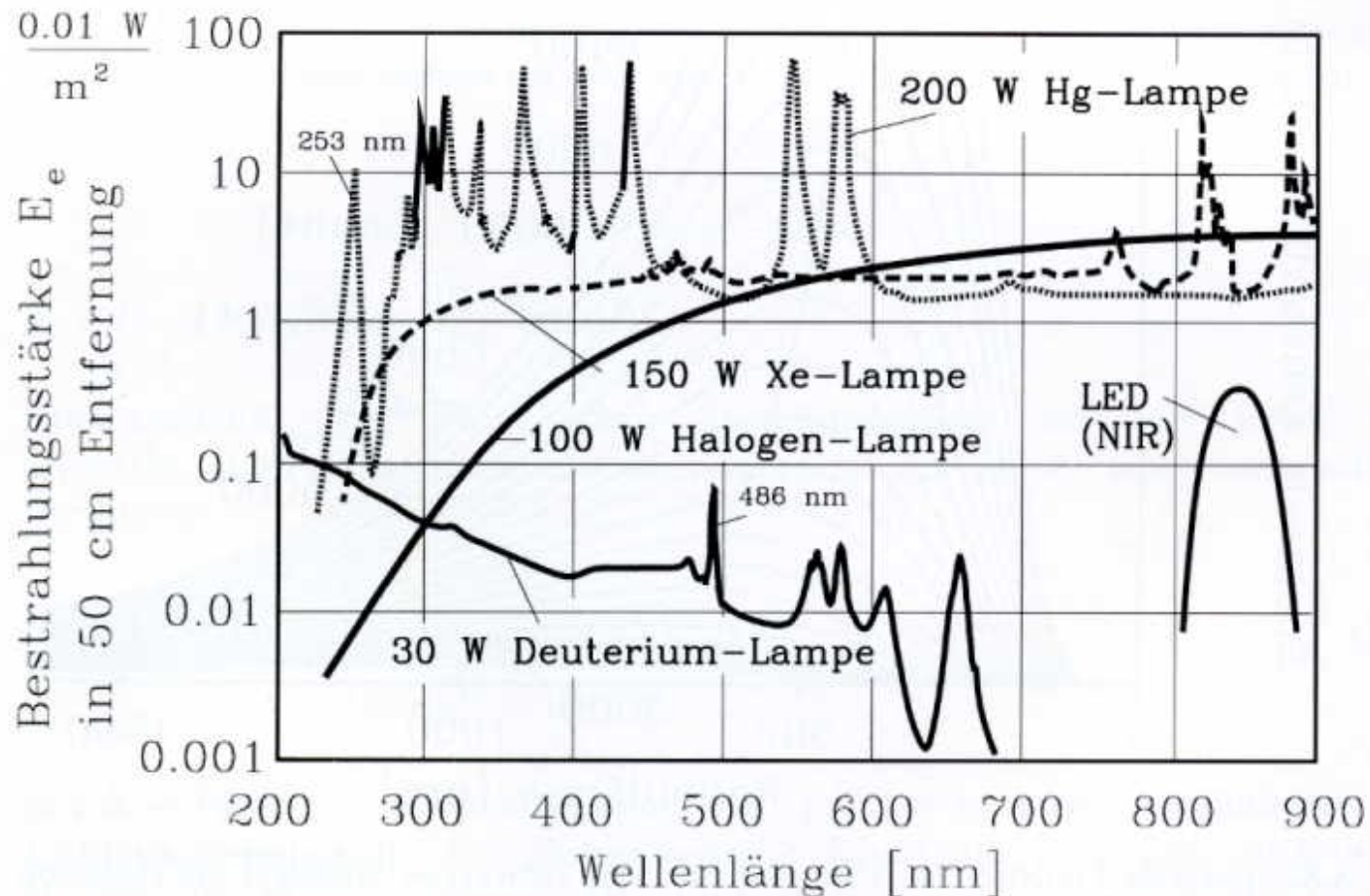


Fig. 3.15 The vibrational modes of $[\text{PtCl}_4]^{2-}$ (D_{4h}); only the three modes (two of which are degenerate) shown in the lower row are IR active. The + and - notation is used to show the 'up' and 'down' motion of the atoms during the mode of vibration

Typical values for stretching and bending vibrations

“Molecule“	stretching	bending
C - H	2800 - 3000	
N - N	3300 - 3500	
H ₂ O	3600 - 3000	1600
C = O	1700	
C = C	1600	
SO ₃ ²⁻	970 (ν _s) 930 (ν _{as})	620 (γ) 470 (δ)

Sources for IR- (and Raman-) radiation



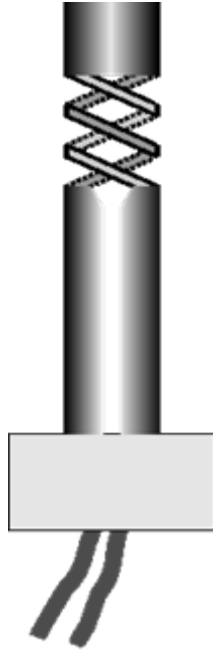
Conventional lamps are not adequate, because
 near IR: ~ 700 to 1400 nm; mid-wavelength/far IR: > 1400 nm

IR-Source (Globar, Nernst-Lamp)



new

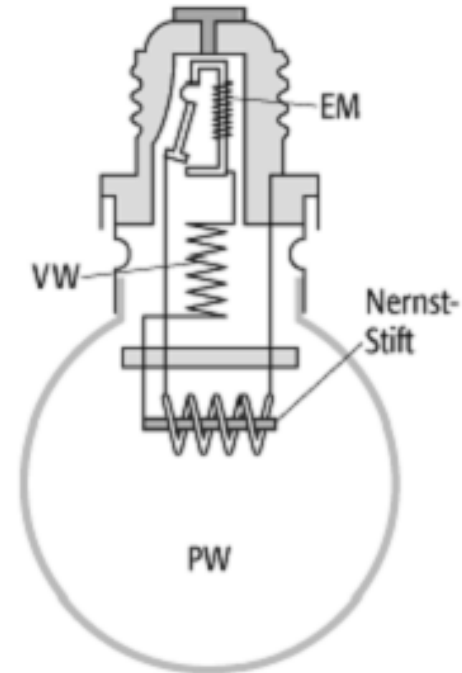
Globar (SiC, ~1.500 K)



schematic



used



Nernst lamp with Nernst rod
 $\text{ZrO}_2/\text{Y}_2\text{O}_3$ ionic conductor, 1.900 K

All heated materials emit infrared radiation

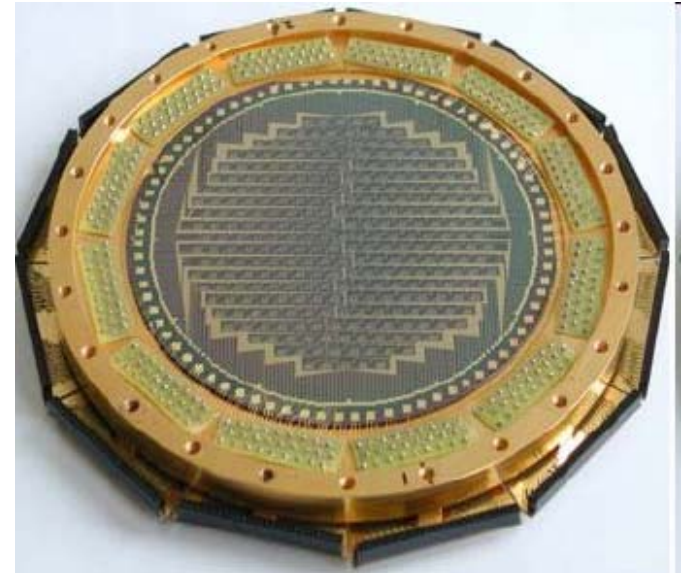
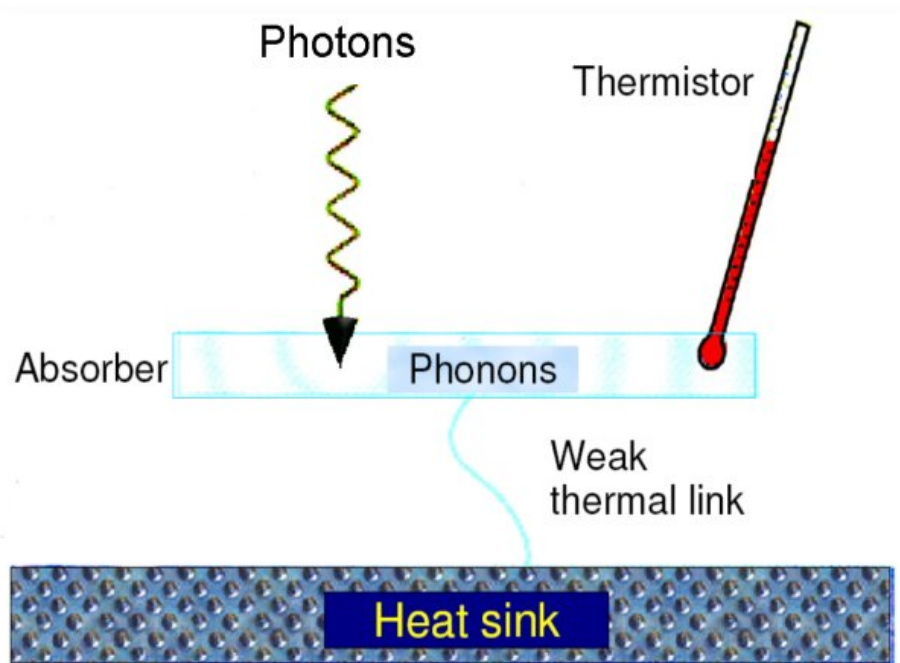
IR-sources, monochromators and detectors

Range	Source	Monochromator	Detector
Far IR	Nernst rod (ceramic rod with heating coil)	CsI-prism; grating	Bolometer
Mid IR		LiF-prism; grating	Bolometer
Near IR	Light-bulb	quartz-prism	PbS-Cell; Se-Cell

Nernst rod: cub. ZrO_2 stabilized by rare earth elements (e.g.. Y^{3+})

Near IR: ~ 700 bis 1400 nm; Mid-wavelength/Far IR: > 1400 nm

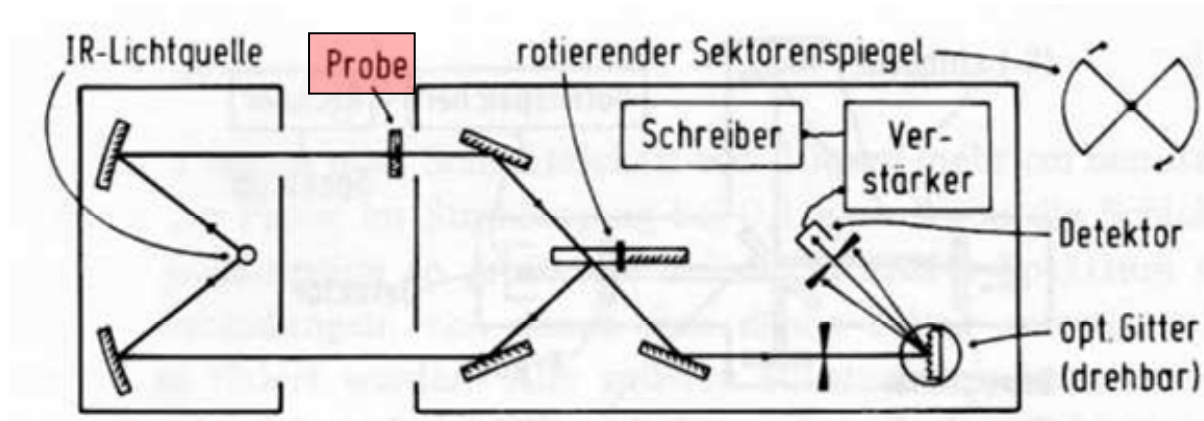
IR-Detectors



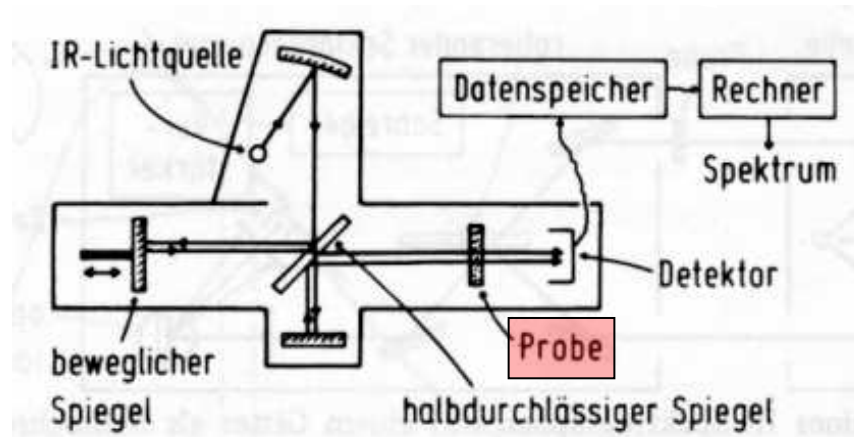
Main principle and a picture of a bolometer:

A cooled metal foil (Pt, Au) absorbs IR radiation. The resulting rise of the temperature is detected by a resistor-type thermometer.

IR - Spectrometer



Double beam, optical grating



Fourier-Transform (FT)

Fourier-transform spectroscopy

“Classical” (grating, prism) IR spectroscopy has been replaced by the much faster FTIR spectroscopy. In the case of the “classical” (i.e. non FT) infrared spectroscopy the different wavelengths had to be measured successively. In the case of the FTIR technique the complete range of interest is measured at once. The fundamental instrument for FTIR is the **Michelson interferometer** that replaces the monochromator. The sample is irradiated by polychromatic light and a movable mirror produces a time dependent signal that is transformed by Fourier transformation into a frequency spectrum.

Fouriertransform (FT) spectrometry

a) Michelson Interferometer

S radiation source, Sa sample chamber, D detector,
A amplifier, M1 fixed, M2 movable mirror,
BS beam splitter, x mirror deflection, L distance

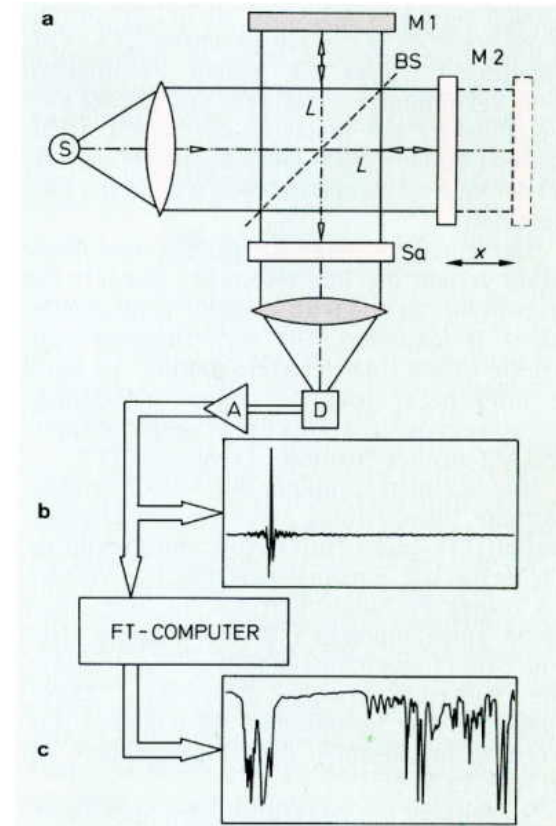
b) Interferogram

Signal recorded by the detector

c) Spectrum

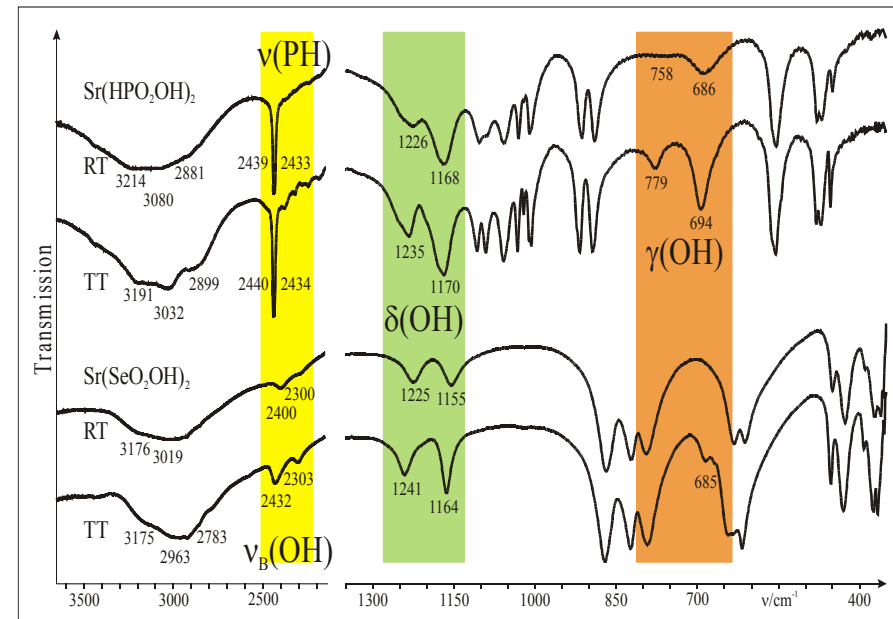
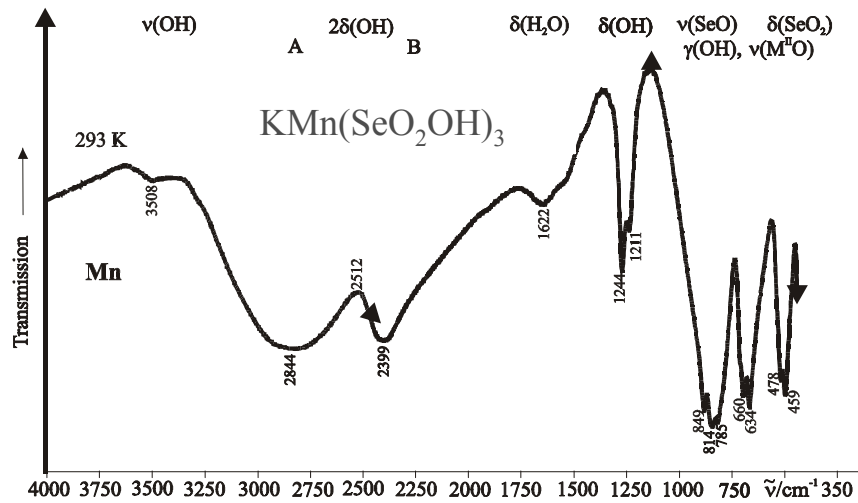
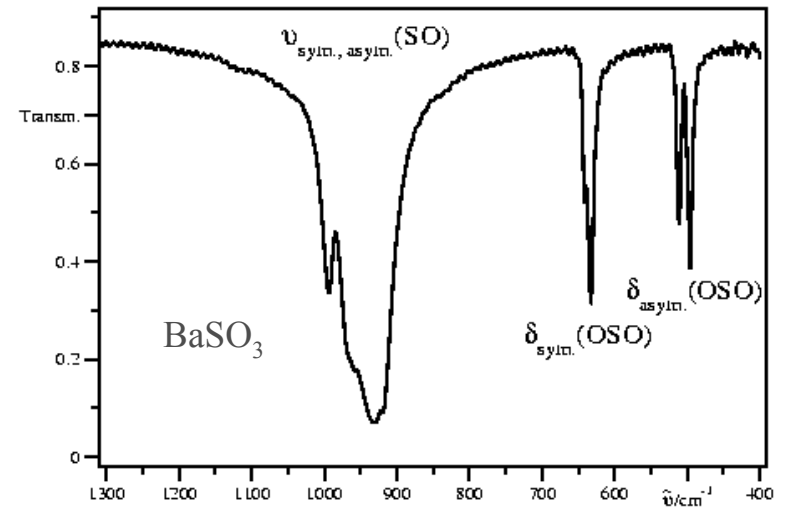
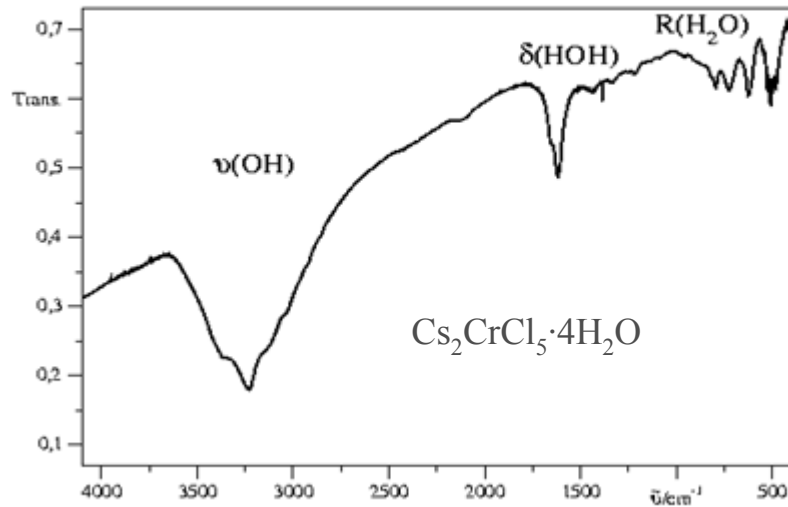
Obtained by Fourier transform (FT)

From the interferogram



Schematic representation of a Michelson interferometer (a) with interferogram (b) and spectrum (c) obtained by Fourier transform.

Examples from current research activities



Raman spectroscopy

Irradiation of a sample with monochromatic light of a suitable wave length may force oscillations of the electrons.

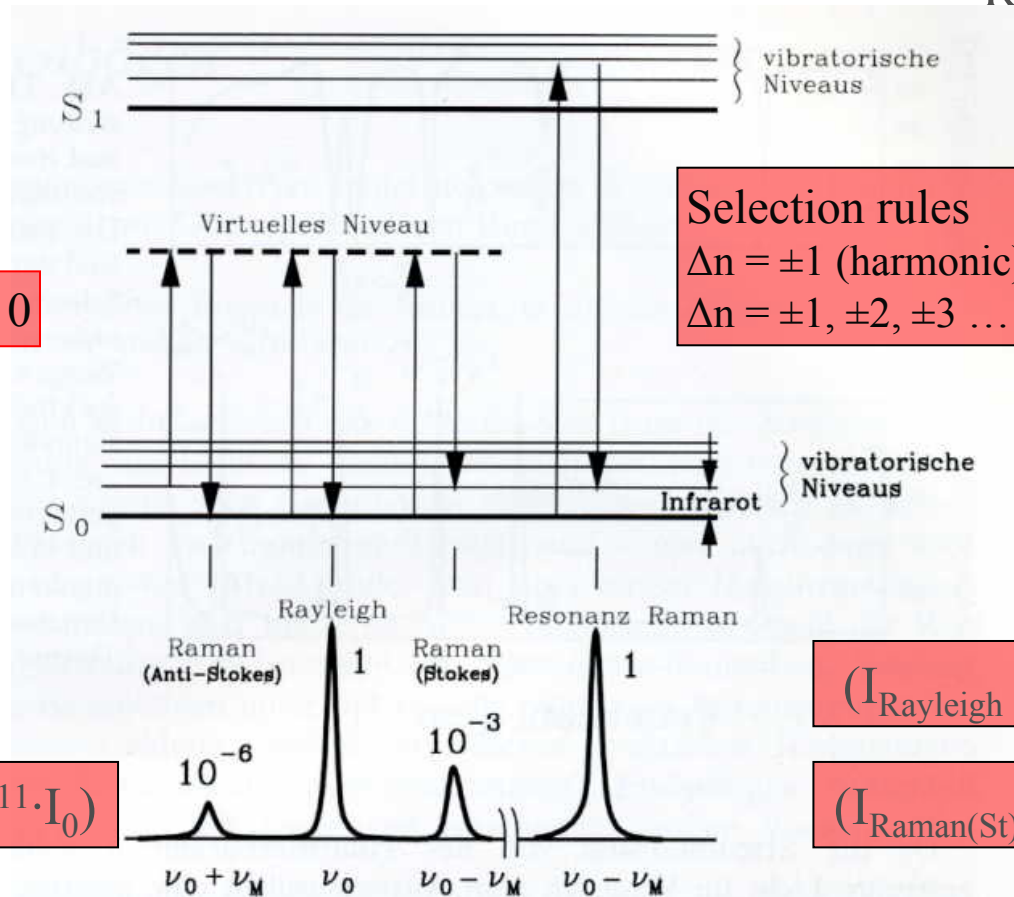
A small portion ($I_{\text{Rayleigh}}/I_0 \sim 10^{-5}$) of the absorbed radiation energy is scattered with the same frequency as the incident light into all directions of space (**elastic, Rayleigh scattering**).

An even smaller portion ($I_{\text{Raman(Stokes)}}/I_0 \sim 10^{-8}$) of the irradiated energy will be transformed into molecular vibrations (with a corresponding **change of the polarizability tensor α**) and thus leads to an absorption of vibrational energy from the scattered light. The scattered light therefore has a lower frequency than the irradiated light (**inelastic, Raman scattering, Stokes**).

If the radiation interacts with a vibrational excited molecule then the scattering process may result in an emission of energy to the scattered light. Thus the scattered light has a larger frequency compared to the irradiated light (**inelastic, Raman scattering, anti-Stokes, $I_{\text{Raman(anti-Stokes)}}/I_0 \sim 10^{-11}$**).

Raman scattering requires a change of the **polarizability α** . The intensity of the scattered light is proportional to the square of the change of the polarizability.

Condition: $d\alpha \neq 0$



Selection rules

$\Delta n = \pm 1$ (harmonic)

$\Delta n = \pm 1, \pm 2, \pm 3 \dots$ (anharmonic)

$(I_{\text{Ra(anti-St)}} \sim 10^{-11} \cdot I_0)$

$(I_{\text{Rayleigh}} \sim 10^{-5} \cdot I_0)$

$(I_{\text{Raman(St)}} \sim 10^{-8} \cdot I_0)$

Schematic representation of the energy levels

Raman scattering, anti-Stokes; Rayleigh scattering; Raman scattering, Stokes

(ν_0 = Frequency of the irradiated light, ν_M = vibrational frequency of the molecule)

Resonance Raman bands with high intensity occur if instead of a forced oscillation an electronically excited state is generated (absorption).

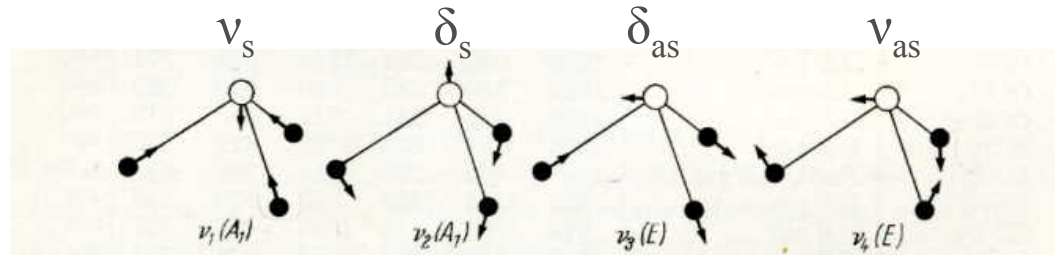
Molecular vibrations of PCl_3 and comparable moleculesc) XY_3 , pyramidenförmig (C_{3v})

Diese Moleküle enthalten als Symmetrieelemente eine dreizählige Achse und drei Symmetrieebenen, in welchen die Bindungen X—Y liegen. Die zugehörige Punktgruppe ist C_{3v} ; Abzählung der Normal-schwingungen und ihre Symmetrieeigenschaften zeigt Tab. 22.

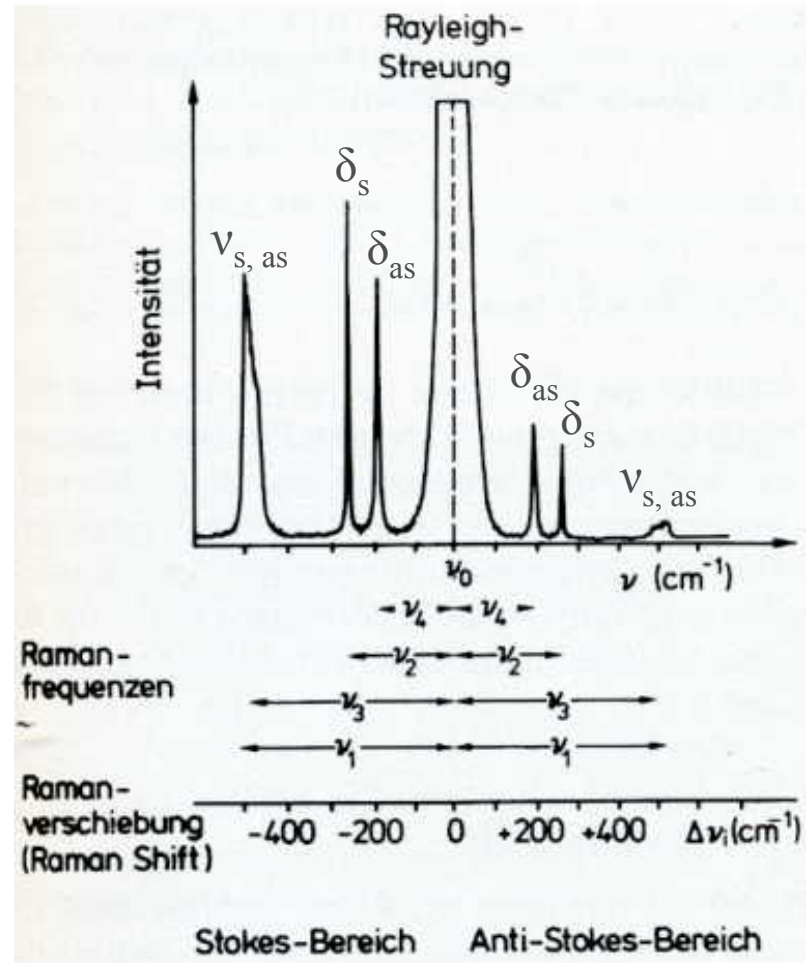
Tabelle 22. Punktgruppe C_{3v} . Symmetrieelemente: C_{3z} , σ_x , $2\sigma_v$

Klas- se	C_{3z}	σ_x	Ra	UR	Abzählung					
					XY_3 Pyramide	ZXY_3 Tetraeder	CH_3CN	H_3SiNCS	P_4S_3	$\text{NH}_3 \cdot \text{BF}_3$
A_1	s	s	p	\mathfrak{M}_z	$2\nu, 1\delta$	$2\nu, 1\delta$	$3\nu, 1\delta$	$4\nu, 1\delta$	$3\nu, 1\delta$	$3\nu, 2\delta$
A_2	s	as	$-$	$-$	$-$	$-$	$-$	$-$	1τ	1τ
E	e	e	dp	\mathfrak{M}_\perp	$1\nu, 1\delta$	$1\nu, 2\delta$	$1\nu, 3\delta$	$1\nu, 4\delta$	$3\nu, 2\delta$	$2\nu, 4\delta t$

Die Zuordnung ergibt sich aus den Polarisationsverhältnissen im Raman-Effekt und aus der Rotationsstruktur der UR -Banden (symmetrische Kreisel). Ferner ist ν_1 im Ra im allgemeinen stark, ν_3 schwach. Im UR -Spektrum liegen die Verhältnisse umgekehrt. Die Schwingungsformen zeigt Abb. 19, die Frequenzen der untersuchten Moleküle Tab. 23.

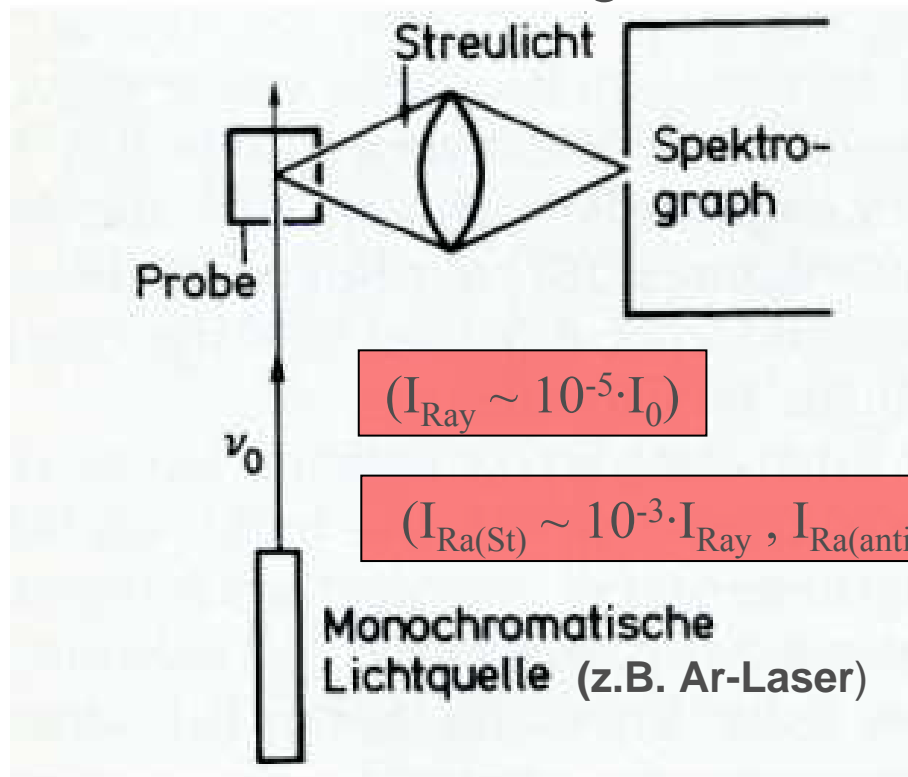


PCl_3 is a tetra-atomic molecule with C_{3v} symmetry



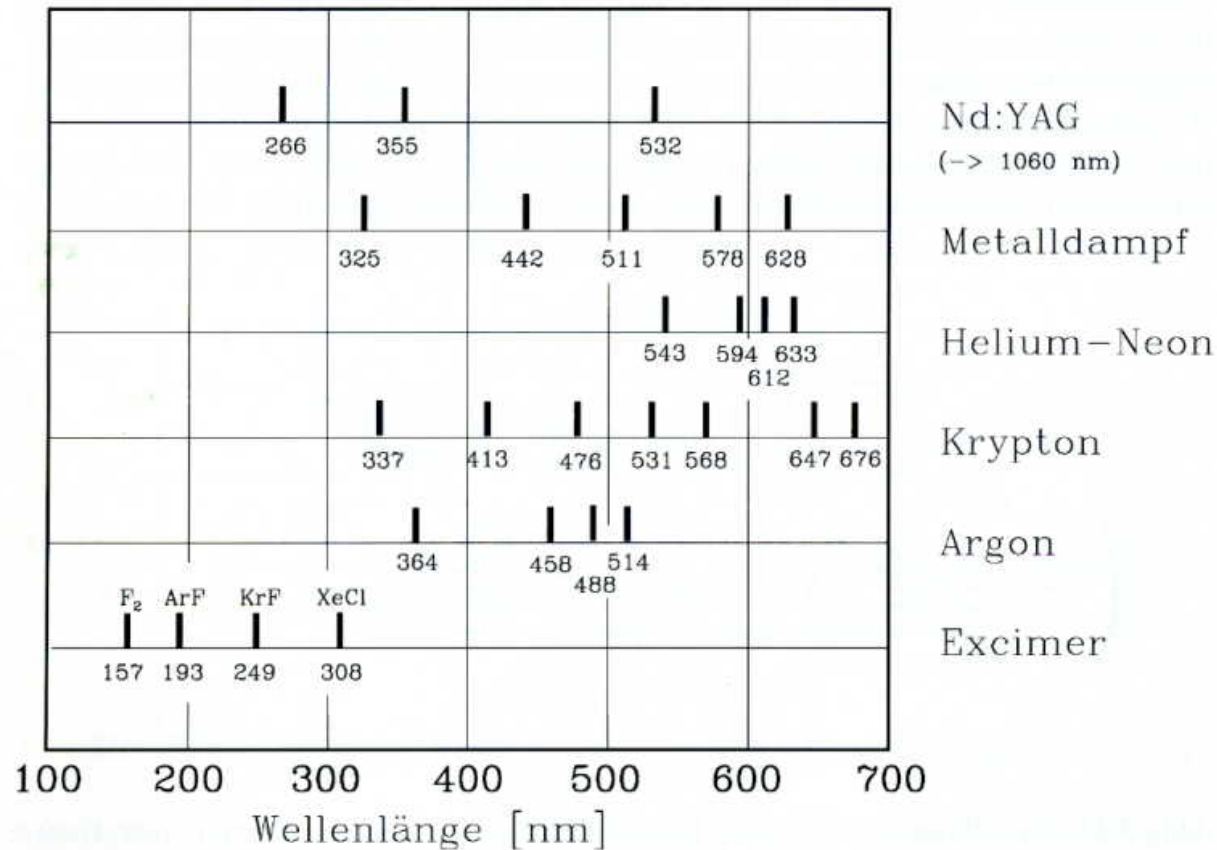
Raman spectrum of PCl_3 (liquid) in the *Stokes*- and *anti-Stokes* range
exciting line $514,5 \text{ nm} \equiv 19436 \text{ cm}^{-1}$ (Ar Laser)

Schematic representation for the observation of the Raman effect
in 90° arrangement

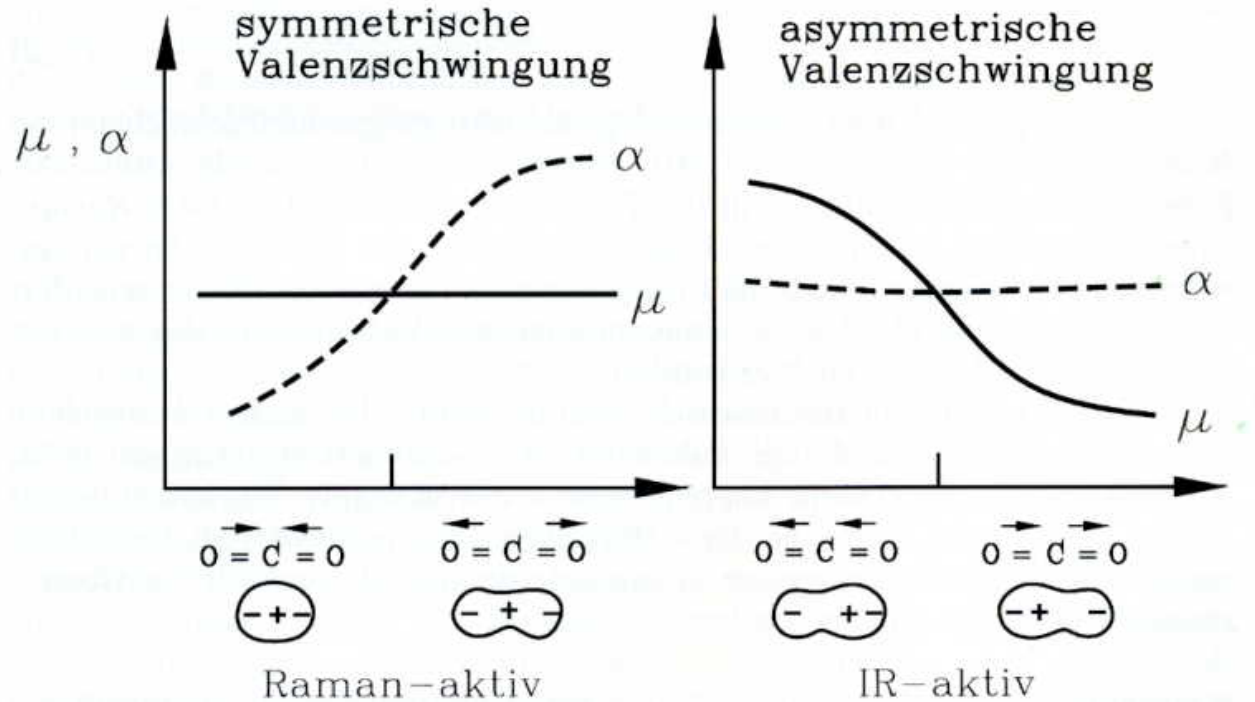


The low intensities of the scattered radiation ($I_{\text{Ra(St)}} \sim 10^{-8} \cdot I_0$, $I_{\text{Ra(anti-St)}} \sim 10^{-11} \cdot I_0$) requires the use of lasers.

Different types of lasers for the use in Raman spectroscopy (and UV-Vis)



The use of lasers is necessary because of the low intensity of the scattered light.

Raman and IR active vibrational modes of CO₂

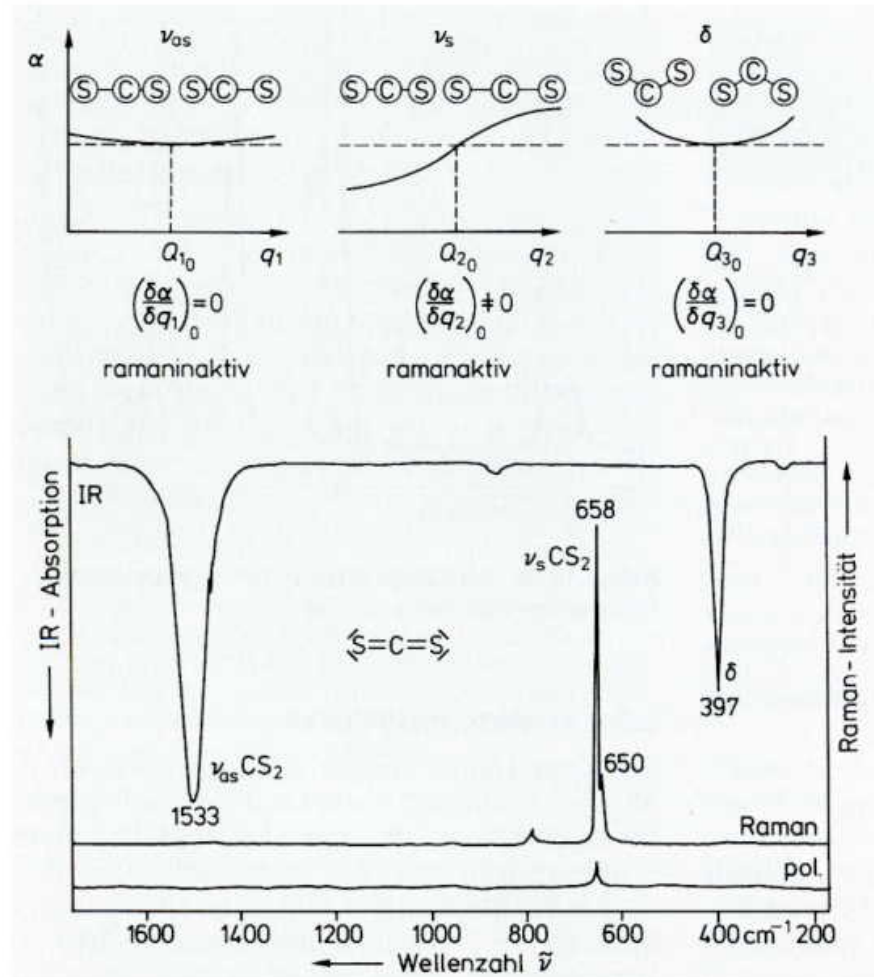
Raman active are those vibrations, at which the polarizability α changes (different in the inversion points).

$$\text{Raman condition: } d\alpha \neq 0$$

IR active are those vibrations, at which the dipole moment μ changes (different in the inversion point).

$$\text{IR condition: } d\mu \neq 0$$

Exclusion rule in IR and Raman spectra

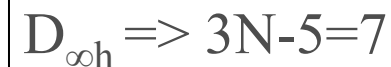
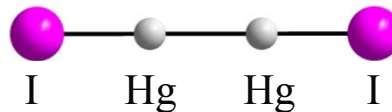
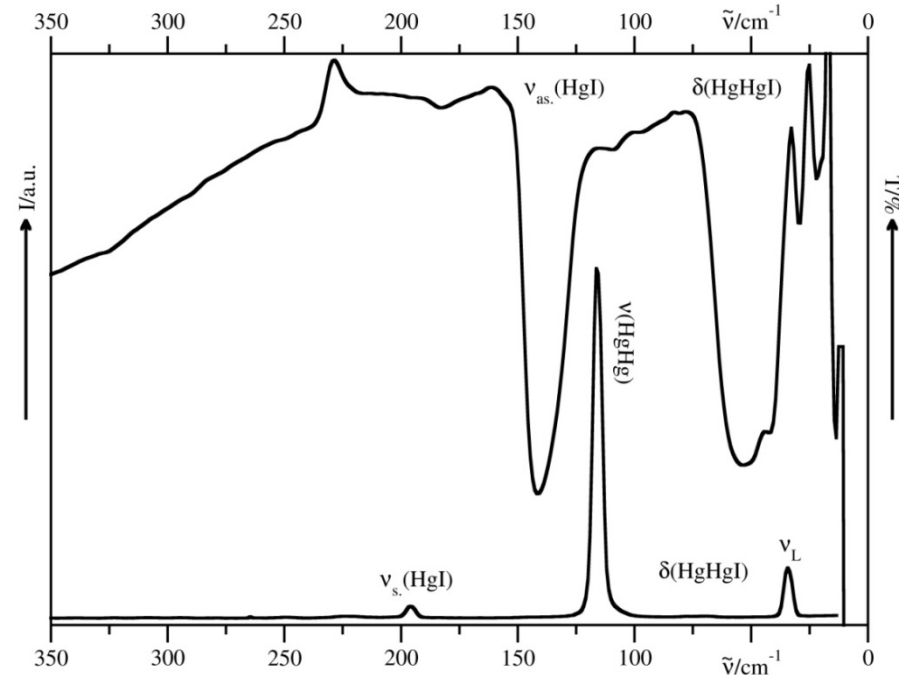


Polarizability changes ($\delta\alpha/\delta q$) of the fundamental modes (ν_{as} , ν_s , δ) and IR and Raman spectra of the CS_2 molecule

Exclusion rule in IR and Raman spectra

Vibrations symmetrical with respect to i (g) are IR inactive but Raman-ctive
 Vibrations non-symmetrical with respect to i (u) are IR active but Raman inactive

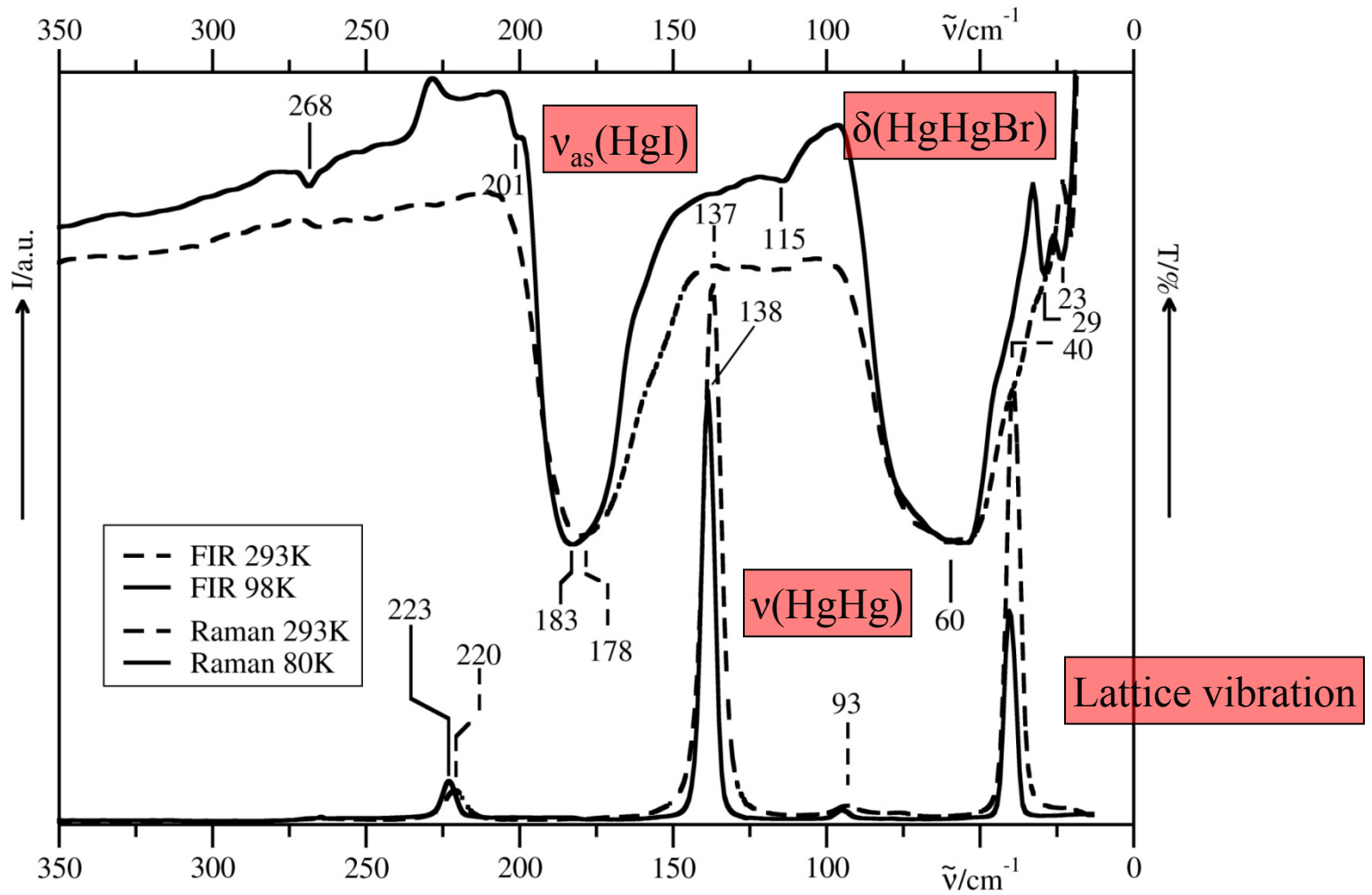
→ Exclusion rule

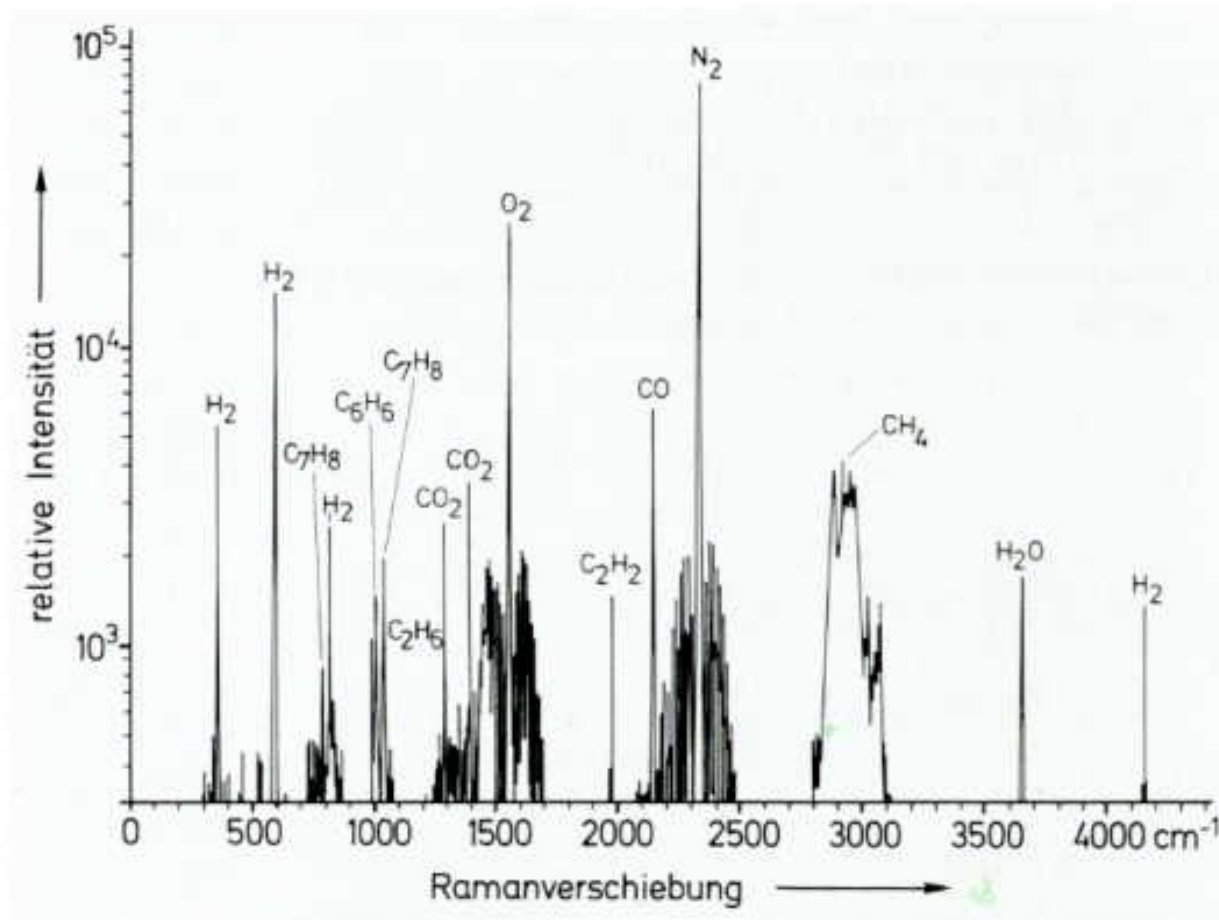


$\nu_s(\text{HgI})$	$\nu_{as}(\text{HgI})$	$\nu(\text{HgHg})$	$\delta_s(\text{HgHgI})$	$\delta_{as}(\text{HgHgI})$	ν_T
A1g	A2u	A1g	2Eg	2Eu	Eg
Ra.	IR	Ra.	Ra	IR	Ra

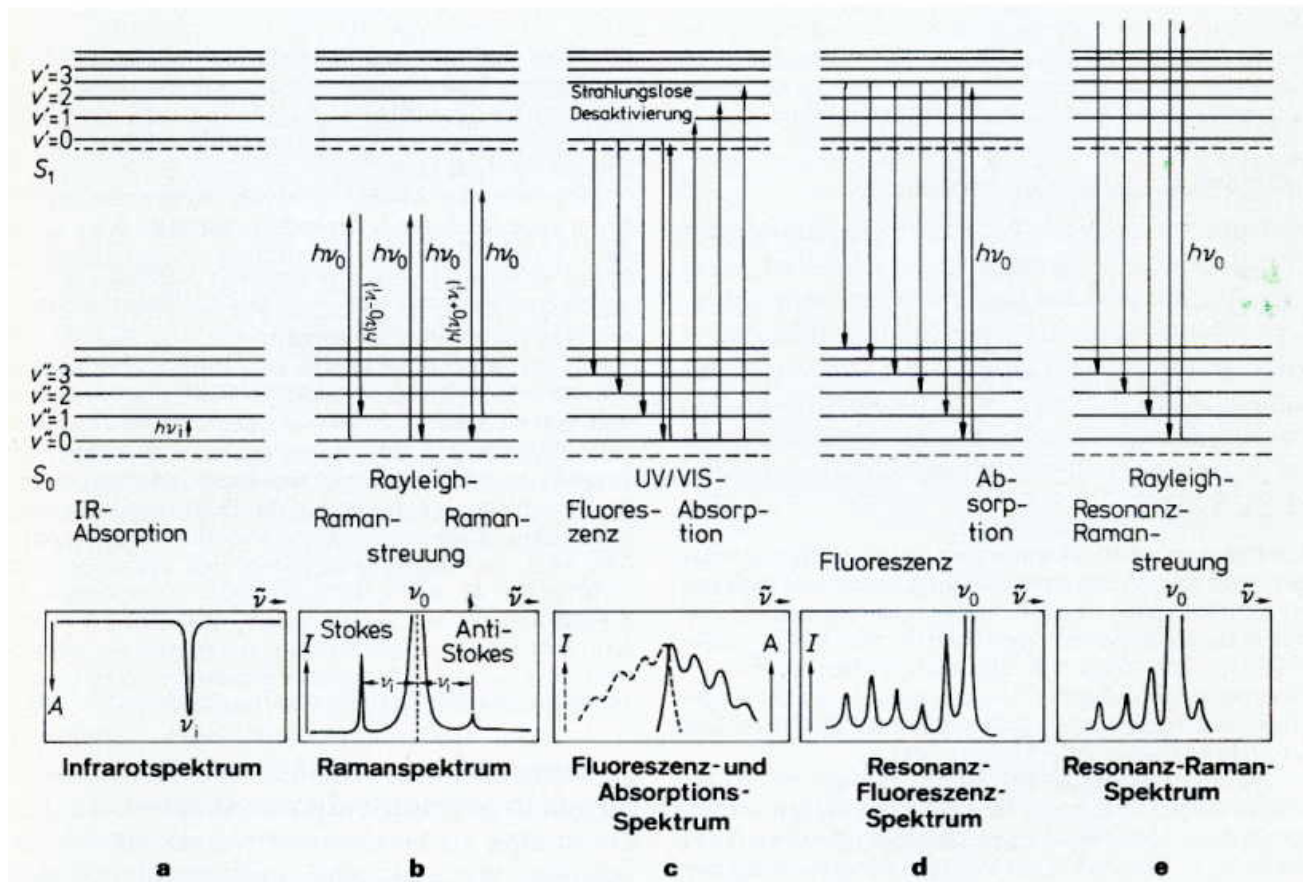
IR/Raman spectra and vibrational modes of Hg_2I_2

Temperature effects and exclusion rule

FIR and Raman spectra of Hg_2Br_2



On-line Raman spectra of the exhaust fumes of a 2 cycle engine



Schematic representation of the energy-levels and spectra of different spectroscopic transitions. The anharmonicity of a vibration is exaggerated and the distance S₁-S₀ is strongly compressed. A = Absorption, I = Intensity

Literatur

- *Untersuchungsmethoden in der Chemie – Einführung in die moderne Analytik* von **H. Naumer** und **W. Heller**, Wiley-VCH
- *Optische Spektroskopie* von **W. Schmidt**, Wiley-VCH
- *Schwingungsspektroskopie* von **J. Weidlein**, **U. Müller**, **K. Dehnike**, Georg Thieme Verlag
- *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie* von **H. Siebert**, Springer Verlag
- *Infrared and Raman Spectroscopy, Methods and Applications* by **B. Schrader**, Wiley-VCH
- *Molecular Vibrations* by **E. Bright Wilson Jr.**, **J.C. Decius**, **P.C. Cross**, McGraw-Hill