Techniques of measurement and interpretation of IR and Raman spectra

(introduction to vibrational spectroscopy)

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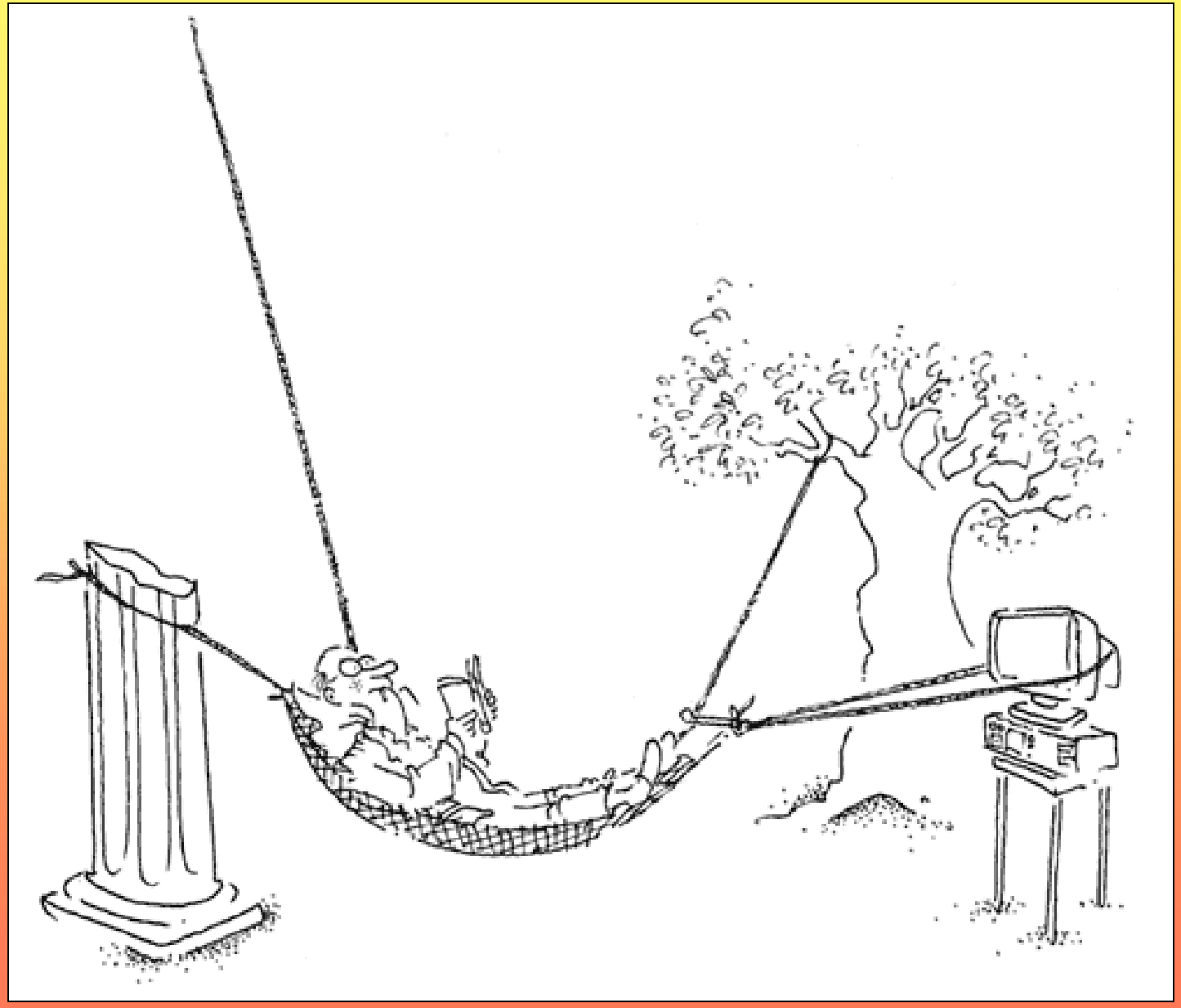
Introduction
- dependence of spectra on periodical motion

The properties of every line of a vibrational (IR, Raman) spectrum depends on a number and mass of collectively oscillating atoms of a molecule, on their spatial arrangement and on a molecular force field.

Prof. Dr. Arnošt Okáč
Výklad k základním operacím v chemické analyse
JČMF 1948

APPROXIMATIVE CLASSICAL MODEL
- a network of balls connected with springs

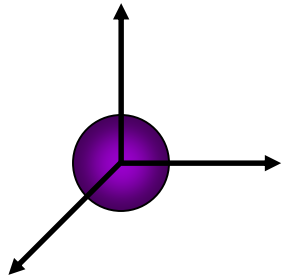
Movement in space



Movement in space

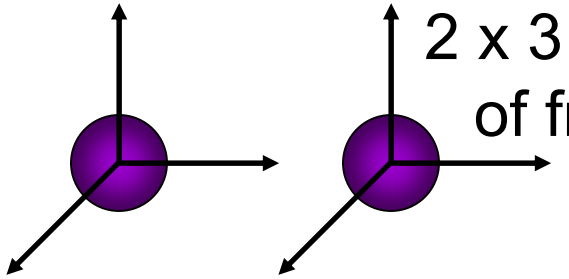
free particle – translational motion

1 atom

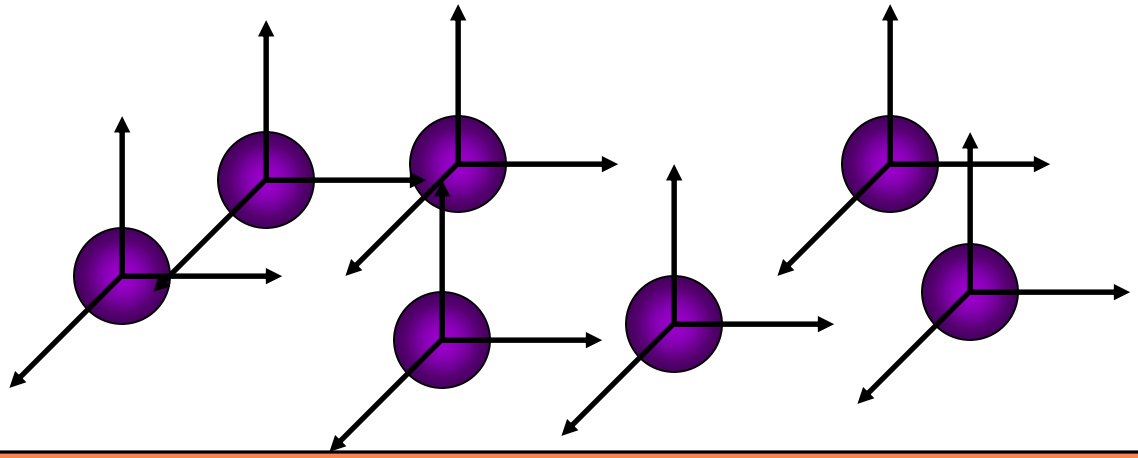


3 degree
of freedom

2 atoms



2 x 3 degree
of freedom

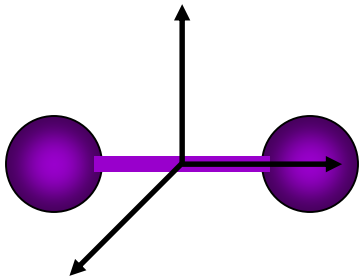


N atoms

N x 3 degree
of freedom

Movement in space

mutual bonded particles



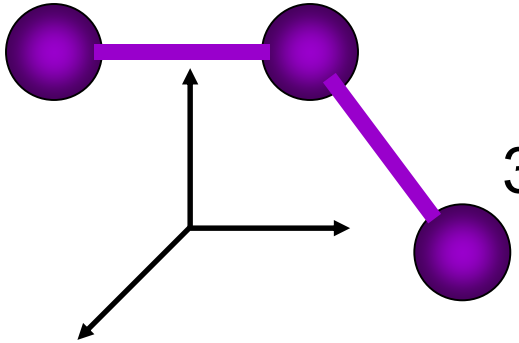
2 atoms bonded - LINEAR MOLECULE

2 x 3 degree of freedom ~ 6

ONLY 3 translation of gravity centre

2 degree of freedom - rotation of a molecule

1 degree of freedom – vibration – periodical motion



3 atoms bonded – NON-LINEAR MOLECULE

3 x 3 degree of freedom ~ 9

ONLY 3 translation of gravity centre

3 degree of freedom - rotation of a molecule

3 degree of freedom – vibration

Movement in space

bonded particles

N atoms bonded - LINEAR MOLECULE

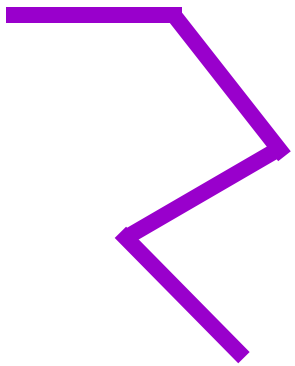
N x 3 degree of freedom ~ 3 N

ONLY 3 translation of gravity centre

2 degree of freedom - rotation of a molecule

3 N - 5 degree of freedom - vibration

N atoms bonded - NON-LINEAR MOLECULE



N x 3 degree of freedom ~ 3 N

ONLY 3 translation of gravity centre

3 degree of freedom - rotation of a molecule

3 N - 6 degree of freedom - vibration

Motion of atoms in a molecule
VIBRATION

TYPES of VIBRATIONS

- **STRETCHING** - change of bond(s) length
- **DEFORMATION** - change of angles (bond angles, torsion angles)
- bending, scissoring, umbrella, rocking, wagging, twisting

» **SYMMETRIC**
» **ANTISYMMETRIC**

» in-plane
» out-of-plane – oop modes

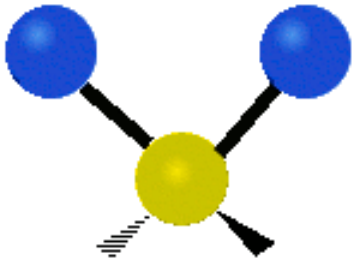
Motion of atoms in a molecule
VIBRATION

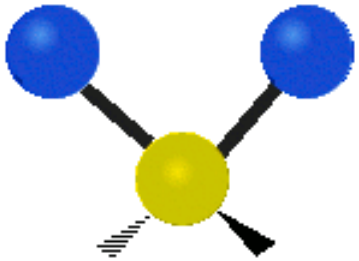
TYPES of VIBRATIONS

- **STRETCHING** - change of bond(s) length

» SYMMETRIC

» ANTISYMMETRIC

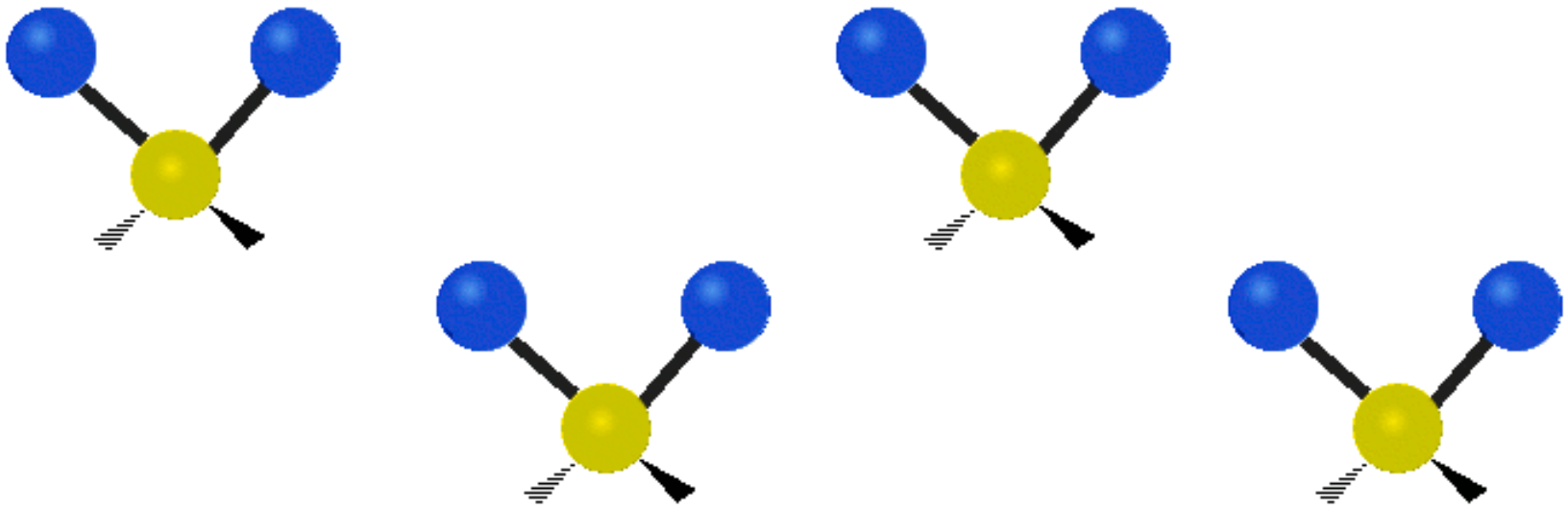




Motion of atoms in a molecule
VIBRATION

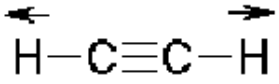
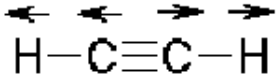
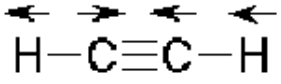
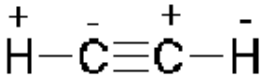
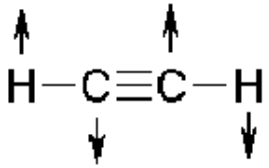
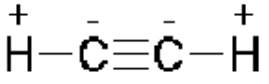
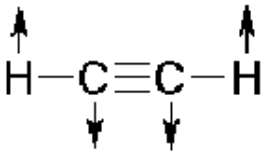
TYPES of VIBRATIONS

- **DEFORMATION** - change of angles (bond angles, torsion angles)
- scissoring, rocking, wagging, twisting



Motion of atoms in a molecule

VIBRATION

Normal mode		Symmetry	Description	Activity	Wavenumber (cm^{-1})	
					C_2H_2	C_2D_2
	ν_1	Σ_g^+	CH stretching symmetric	R*p*	3373	2705
	ν_2	Σ_g^+	CC stretching (sym)	R*p*	1974	1765
	ν_3	Σ_u^+	CH stretching antisymmetric	IR	3295	2439
		ν_4	Π_g	Deformation symmetric	R*dp*	613	512
		ν_5	Π_u	Deformation antisymmetric	IR	730	539

Motion of atoms in a molecule

VIBRATION

DESCRIPTION OF VIBRATION

- **FREQUENCY**
  - **- key information for STRUCTURE ANALYSIS**
    - * MASS of ATOMS, STRENGTH of BONDS
- **TOTAL AMPLITUDE – "DISPLACEMENT"**
- **POTENTIAL ENERGY CURVE**
  - › **HARMONIC OSCILLATOR**
  - › **ANHARMONIC OSCILLATOR**
    - » STRETCHING VIBRATION
    - » DEFORMATION VIBRATION
- **SET of LEVELS - ENERGY EIGENSTATES**

Motion of atoms in a molecule

VIBRATION

THEORETICAL CALCULATIONS of VIBRATIONAL MODES

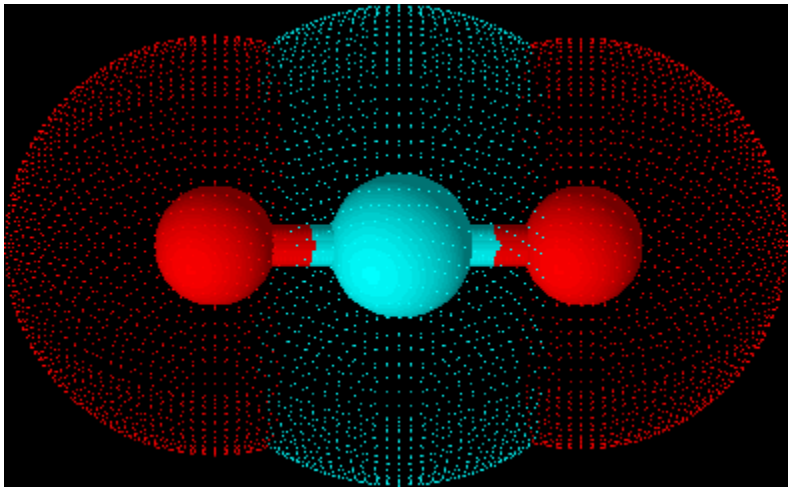
- **QUANTUM CHEMICAL CALCULATIONS**
  - ***ab initio***
  - ***empirical***
    - * EQUILIBRIUM COORDINATES of ATOMS
    - * MASS of ATOMS
    - * MOLECULAR FORCE FIELD (force constant matrix)
- **APPROXIMATIONS MADE by CALCULATIONS**
  - model of isolated molecules, special methods to consider the effects of surroundings (non-covalent interaction, etc.)

Motion of atoms in a molecule

VIBRATION

THEORETICAL CALCULATIONS of VIBRATIONAL MODES

IR/Raman Spectra of CO_2

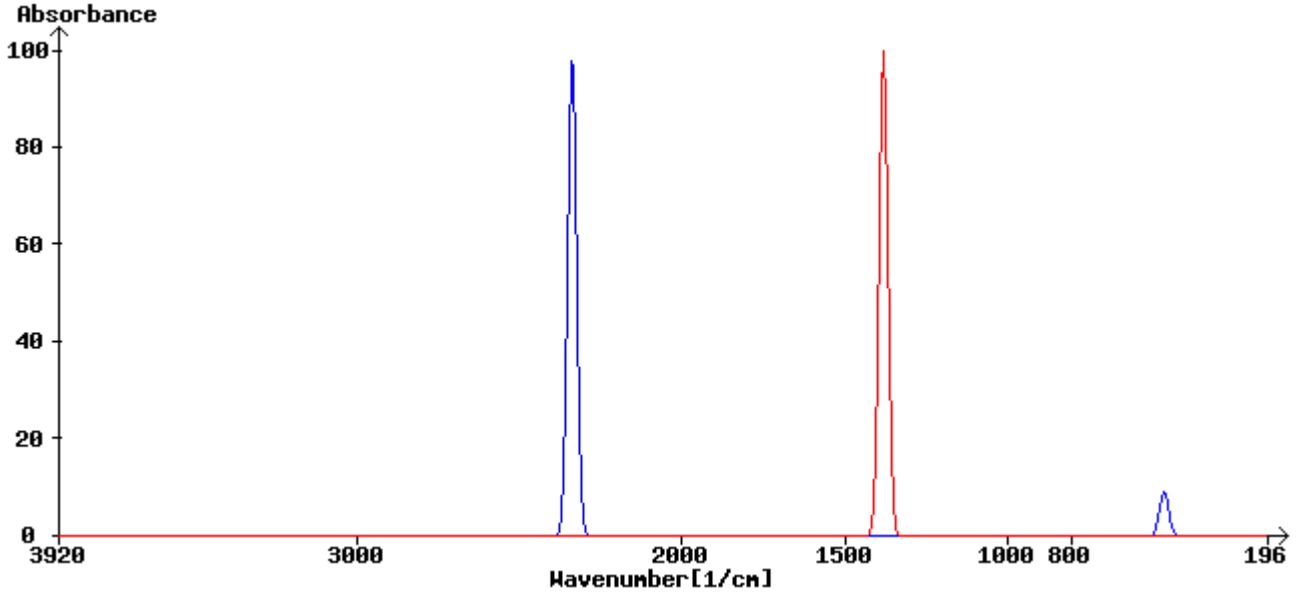


(3 x 3) – 5 = 4

Motion of atoms in a molecule

VIBRATION

THEORETICAL CALCULATIONS of VIBRATIONAL MODES *IR/Raman Spectra of CO_2*



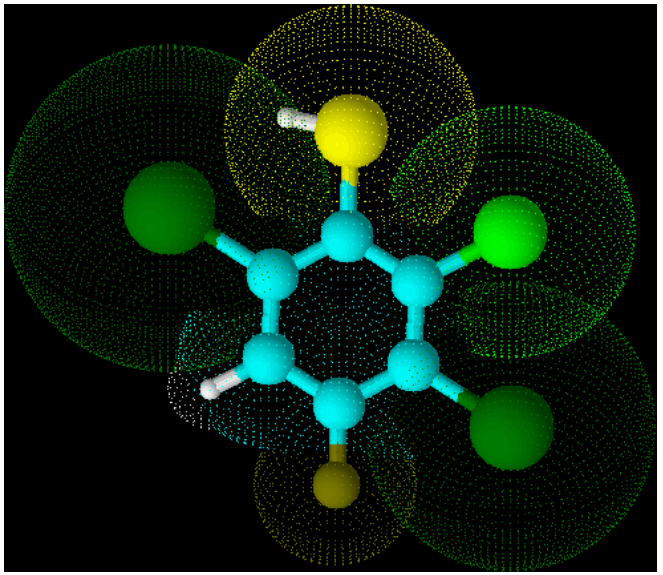
IR:	calculated (3557 data points)	Structure:	CO_2
Origin:	Vamp7.0	Method:	PM3
Author:	WWW daemon apache	Date:	2005-09-05 14:38:02
From:	3920.0 [1/cm]	To:	196.0 [1/cm]
Xunit:	[1/cm]	Yunit:	Absorbance

Motion of atoms in a molecule

THEORETICAL CALCULATIONS of VIBRATIONAL MODES

IR/Raman Spectra of $C_6H_2BrClFIS$

- some examples



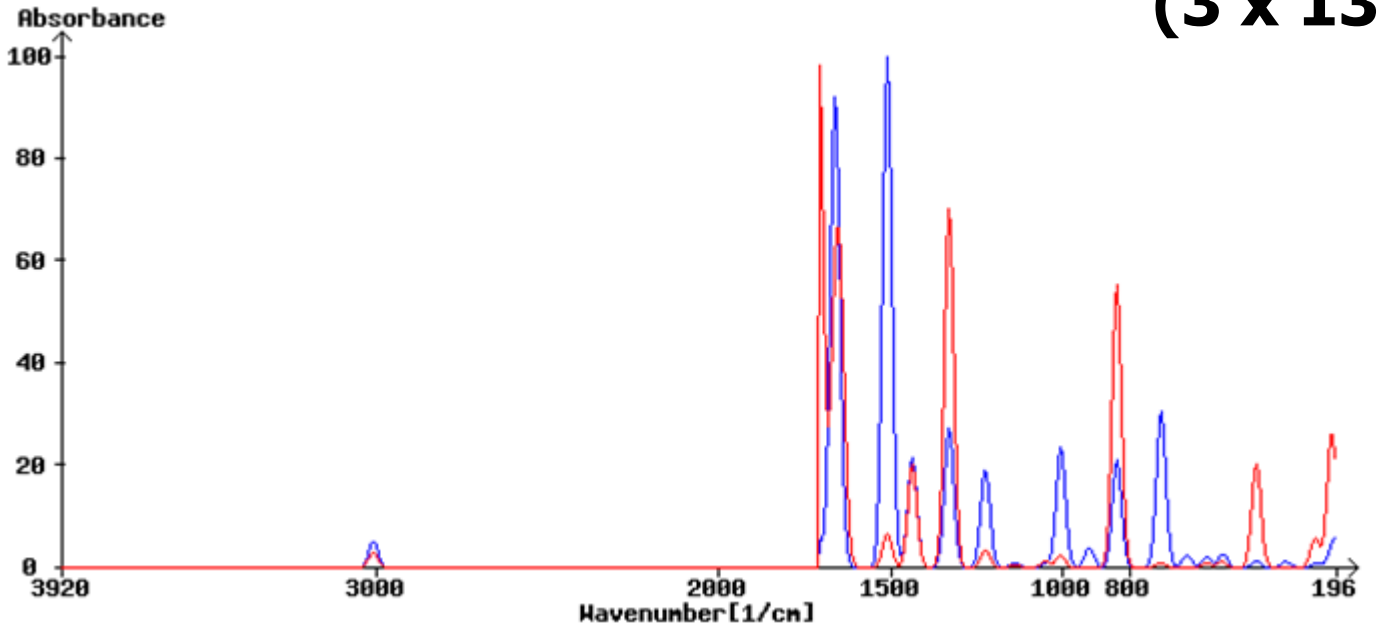
(3 x 13) – 6 = 33

Motion of atoms in a molecule

CALCULATIONS of VIBRATIONAL MODES

IR/Raman Spectra of $C_6H_2BrClFIS$

(3 x 13) – 6 = 33



IR:	calculated (3557 data points)	Structure:	$C_6H_2BrClFIS$
Origin:	Vamp7.0	Method:	PM3
Author:	WWW daemon apache	Date:	2005-09-05 16:15:10
From:	3920.0 [1/cm]	To:	196.0 [1/cm]
Xunit:	[1/cm]	Yunit:	Absorbance

IR/Raman Spectra of $C_6H_2BrClFIS$

Peakname	[1/cm]	IR Intensity	Raman Intensity	Peakname	[1/cm]	IR Intensity	Raman Intensity
33 A	3010.89	5.214	2.861	16 A	576.98	2.183	0.938
32 A	1800.38	45.395	65.419	15 A	531.99	1.578	1.153
31 A	1709.01	5.227	100.000	14 A	524.55	1.039	0.000
30 A	1662.21	91.305	46.787	13 A	431.24	1.407	20.471
29 A	1643.51	4.218	39.684	12 A	346.34	1.080	0.001
28 A	1509.32	100.000	6.542	11 A	324.58	0.229	0.069
27 A	1436.06	21.370	20.223	10 A	259.80	0.699	5.791
26 A	1328.75	27.595	70.763	9 A	233.78	0.260	0.001
25 A	1222.94	19.341	3.487	8 A	211.48	1.546	26.381
24 A	1135.48	1.029	0.452	7 A	201.60	3.966	0.000
23 A	1046.47	0.864	1.370	6 A	188.00	1.191	2.001
22 A	1002.52	23.849	2.397	5 A	154.21	0.235	3.066
21 A	919.24	3.910	0.001	4 A	153.38	0.549	0.008
20 A	838.63	21.114	55.658	3 A	118.75	0.411	1.463
19 A	758.30	0.113	0.000	2 A	67.89	0.156	0.000
18 A	709.39	30.864	0.984	1 A	54.91	0.228	0.000
17 A	633.68	2.353	0.004				

Motion of atoms in a molecule

VIBRATION

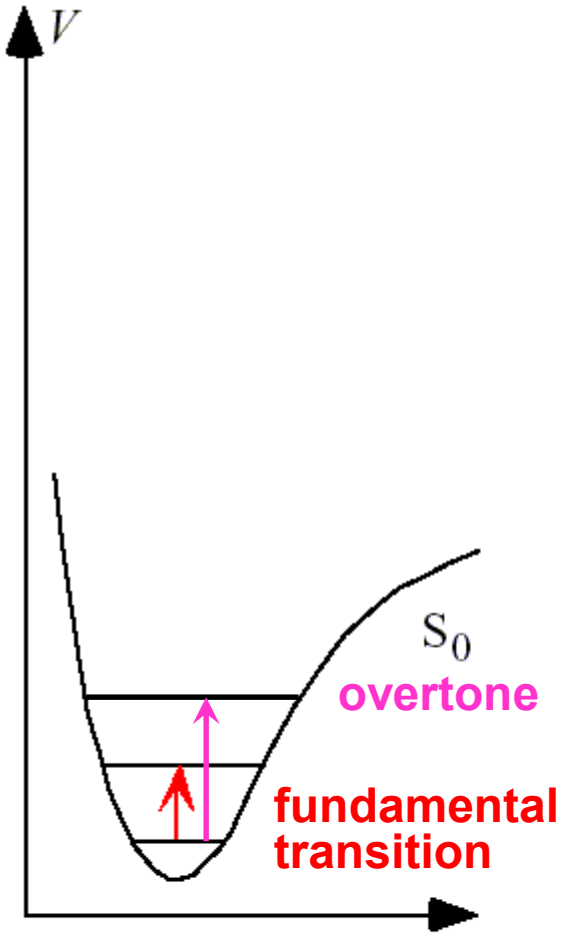
EXPERIMENTAL APPROACH

measurement of VIBRATIONAL SPECTRA

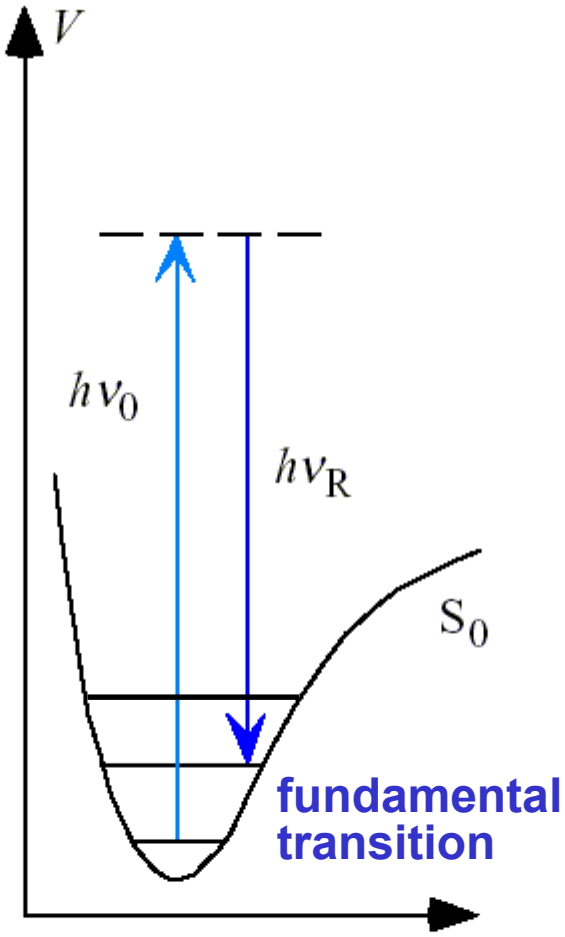
- GENERATION of VIBRATIONALLY EXCITED STATES
- ENERGY of VIBRATION TRANSITION is related directly to VIBRATION FREQUENCY

- **INFRARED SPECTRA**
  - EXCITATION via ABSORPTION of INFRARED RADIATION
- **RAMAN SPECTRA**
  - INELASTIC LIGHT SCATTERING

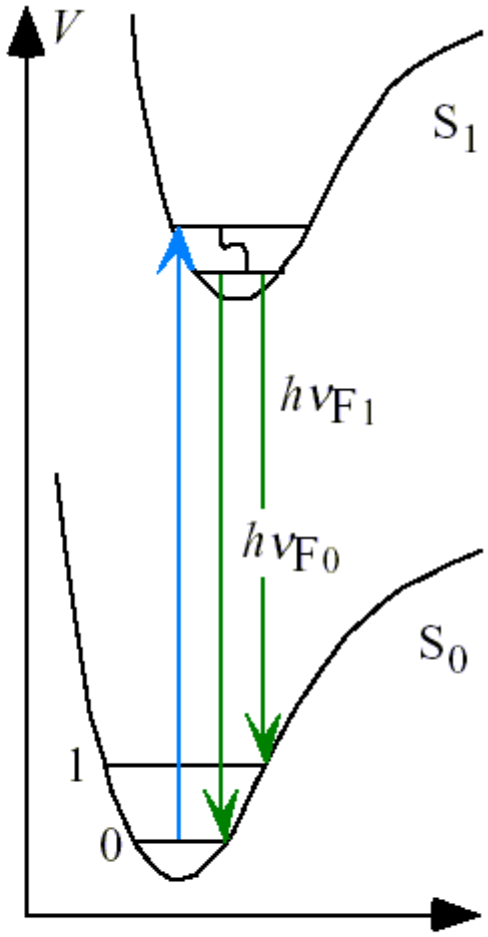
Scheme of levels



IR absorption



Raman scattering



Fluorescence

InfraRED spectrometry

PRINCIPLE of infrared absorption

one-photon transition
between two
vibrational (vibration-rotational)
states of molecule,
characterized by energies E_1 and E_2,
caused by interaction with photon
of incident radiation

$$h\nu_{abs} = |E_2 - E_1|$$

$$h\nu_{vib} = |E_2 - E_1|$$

only for fundamental transitions

Infrared spectrometry

Principal of infrared absorption

transitions between

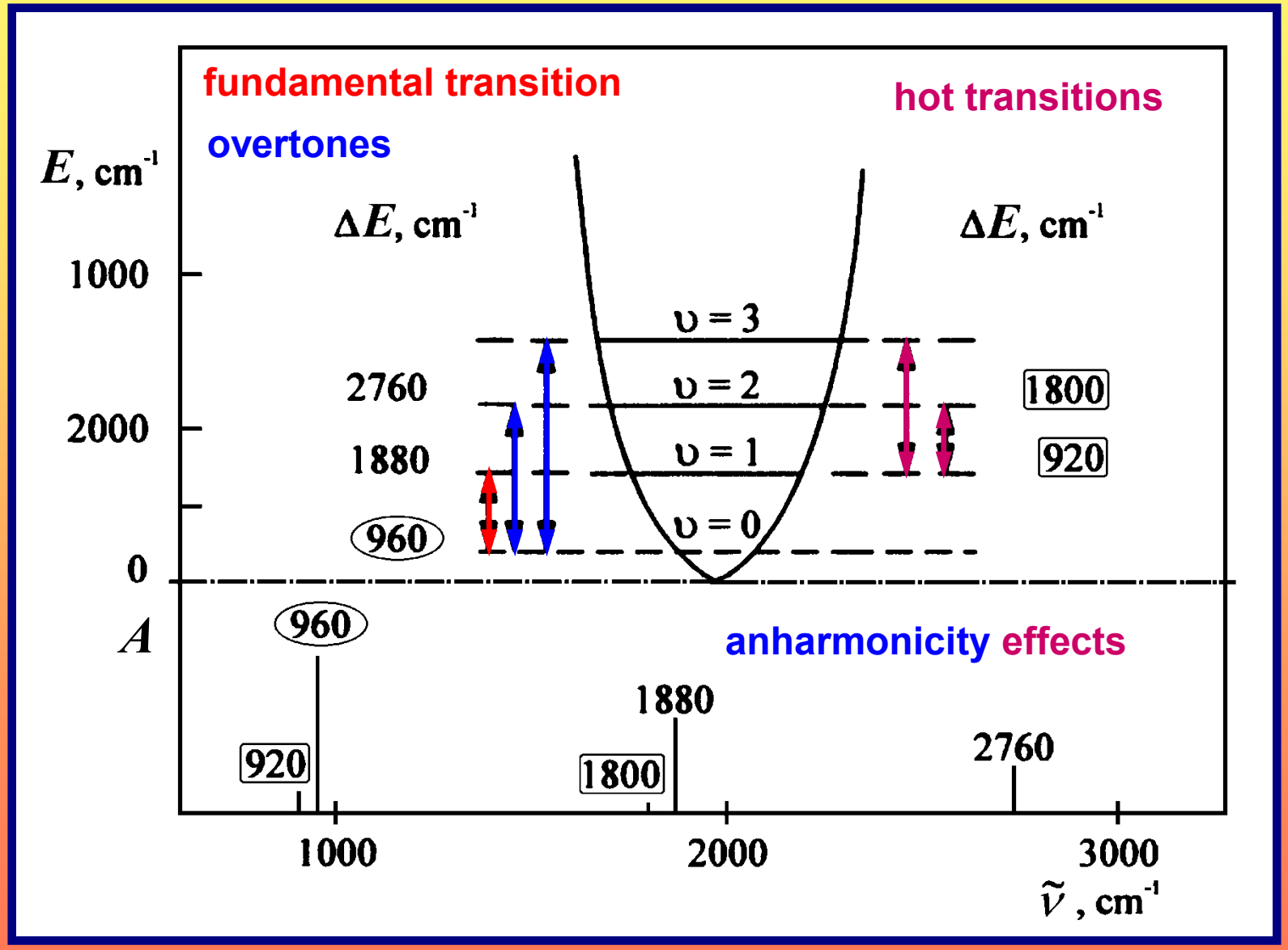
vibrational (vibration-rotational) states

- types of allowed transitions via IR absorption
  - concerning single vibrational mode
    - fundamental (0←1), hot (1 ← 2, 2 ← 3 …)

      (change of quantum number +1)
    - high(-order) harmonic – overtones,

      (0 ← 2, 0 ← 3, 0 ← 4, …), hot overtones
  - more vibrational modes involved
    - combination (0 ← 1 + 0 ← 1')

Infrared spectrometry



Infrared spectrometry

Oscillating dipole moment

motion of a molecule accompanied by a change of an electric dipole moment is related to absorption (or emission) of radiation

$$p = p_0 + \left(\frac{\partial p}{\partial q}\right)_0 q$$

p - actual dipole moment

p_0 - dipole moment at an equilibrium position

q - normal coordinate of vibration mode

Infrared spectrometry

Fundamental selection rule of infrared absorption

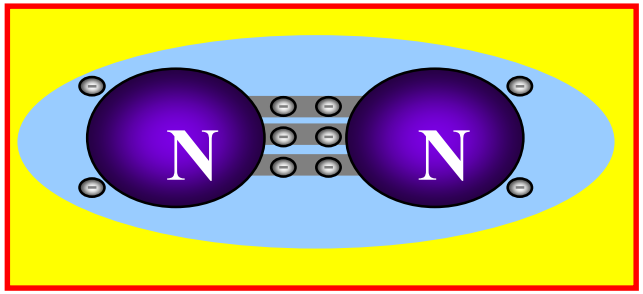
$$\frac{\partial p}{\partial q} \neq 0$$

BAND INTENSITIES PROPORTIONAL TO CHANGES of DIPOLE MOMENT in the course of VIBRATIONAL MOTION

Infrared spectrometry

$$\frac{\partial p}{\partial q} = 0$$

SPECIES
NON-ABSORBING
IR radiation



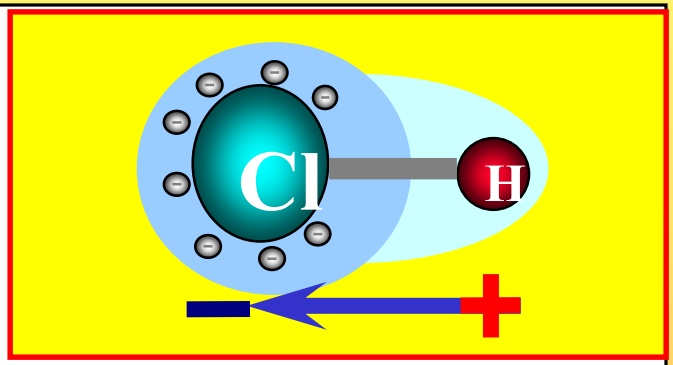
O_2, N_2, H_2, O_3
powdered sulfur
silicon
carbon - graphite, diamond

species, non-absorbing IR radiation,
can reflect it,
can scatter it

Infrared spectrometry

$$\frac{\partial p}{\partial q} \neq 0$$

SPECIES STRONGLY ABSORBING IR radiation



HCl, H_2O, CO_2, SO_2, N_xO_y – greenhouse gases

alcohols, carbonyl and carboxyl derivatives

nitro-, sulfo- compounds

halogen-derivatives

inorganic salts and co-ordination compounds

Symmetry selection rules

- Fundamental transitions - **active in IR spectrum** (an absorption band is observed), when the normal vibrationa coordinate is attributed to the same reperesentation as any of the Cartesian coordinates (***x***, ***y***, and ***z***). *(dipole moment is a vector)*
- Fundamental transitions - **active in Raman spectrum** (an scattering band is observed), when the normal vibrationa coordinate is attributed to the same reperesentation as any of the products of Cartesian coordinates (***x²***, ***xy***, ***xz***, ***y²***, ***yz*** a ***z²***). *(polarizibility is a tensor)*

C_i	E	i	_	_
A_g	1	1	R_x; R_y; R_z	x^2; y^2; z^2; xy; xz; yz
A_u	1	-1	x; y; z	

Table of characters

Point group

Operation of symmetry

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

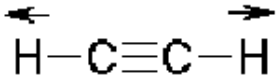
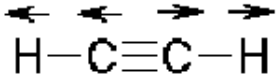
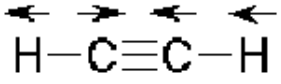
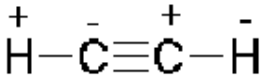
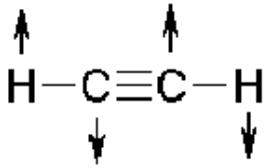
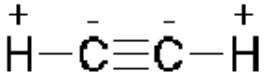
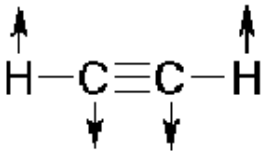
Mülliken symbols

Characters
+1 symmetric behaviour
-1 antisymmetric

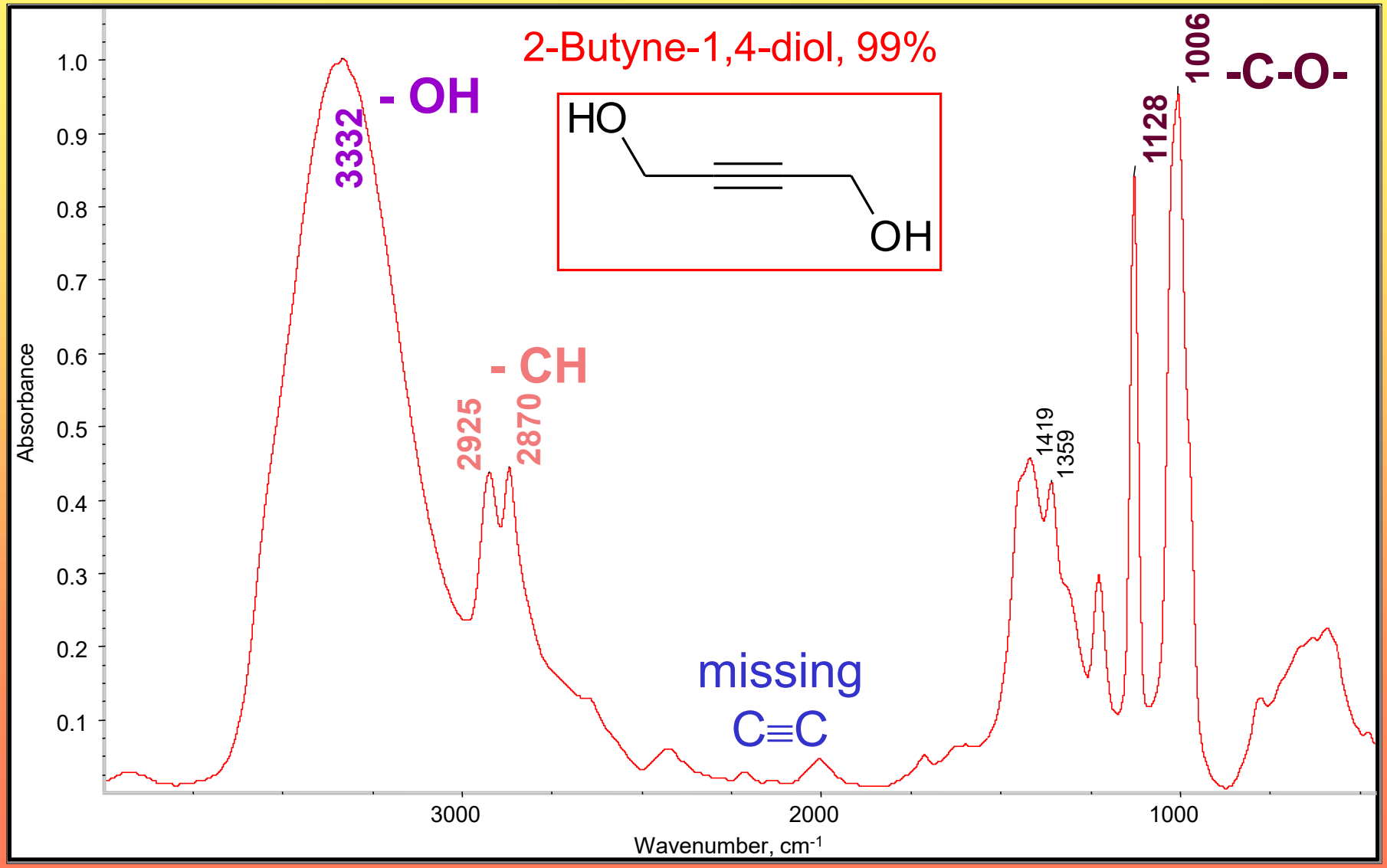
One row – one irreducible representation – one type of symmetry behaviour
Vibration mode can be assigned to one row.

Motion of atoms in a molecule

VIBRATION

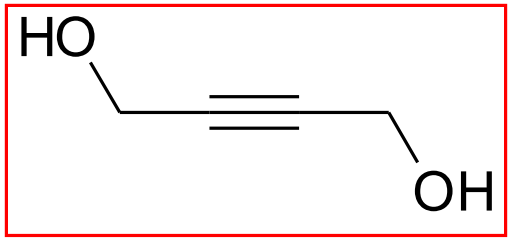
Normal mode		Symmetry	Description	Activity	Wavenumber (cm^{-1})	
					C_2H_2	C_2D_2
	ν_1	Σ_g^+	CH stretching symmetric	R*p*	3373	2705
	ν_2	Σ_g^+	CC stretching (sym)	R*p*	1974	1765
	ν_3	Σ_u^+	CH stretching antisymmetric	IR	3295	2439
		ν_4	Π_g	Deformation symmetric	R*dp*	613	512
		ν_5	Π_u	Deformation antisymmetric	IR	730	539

Infrared spectrometry

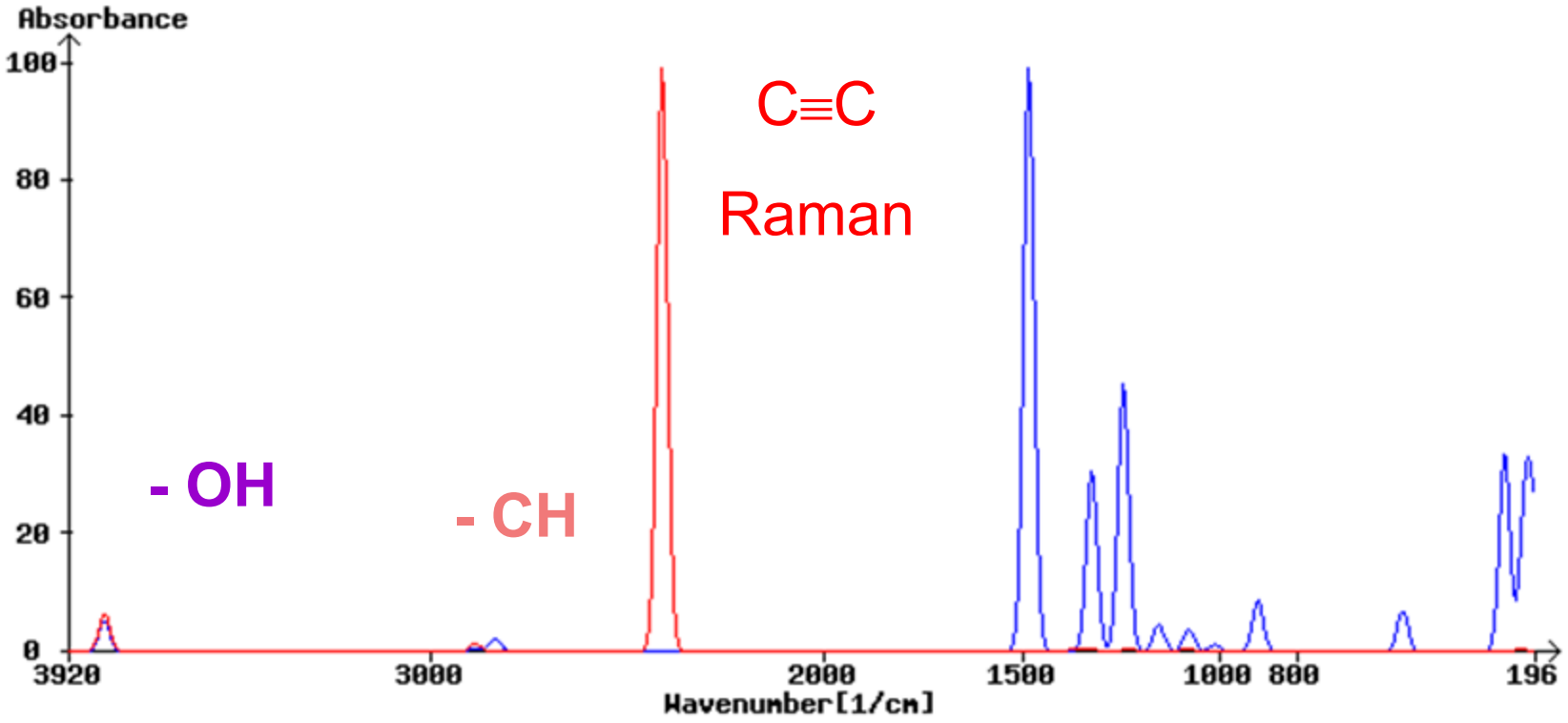


Infrared spectrometry

2-Butyne-1,4-diol, 99%



IR:	calculated (3557 data points)	Structure:	$C_4H_6O_2$
Origin:	Vamp7.0	Method:	PM3
Author:	WWW daemon apache	Date:	2005-09-05 15:01:13
From:	3920.0 [1/cm]	To:	196.0 [1/cm]
Xunit:	[1/cm]	Yunit:	Absorbance



Infrared spectrometry

2-Butyne-1,4-diol, 99% - 12 atoms

Normal Vibrations:

Click on the wave number to see corresponding 3D normal vibration

Peakname	[1/cm]	IR Intensity	Raman Intensity	Peakname	[1/cm]	IR Intensity	Raman Intensity
30 A	3830.30	3.452	2.118	16 A	1078.01	0.000	0.532
29 A	3830.27	1.641	4.440	15 A	1075.70	3.665	0.000
28 A	2887.79	0.507	0.040	13 A	1010.01	1.134	0.000
27 A	2887.47	0.015	1.279	11 A	901.26	8.723	0.000
26 A	2837.91	2.054	0.000	10 A	815.80	0.000	0.188
25 A	2837.68	0.114	0.000	9 A	622.15	0.000	0.160
24 A	2413.72	0.000	100.000	8 A	533.46	6.858	0.000
23 A	1482.66	100.000	0.000	7 A	471.99	0.000	0.000
22 A	1364.99	0.000	0.444	6 A	274.10	33.914	0.000
21 A	1323.06	30.805	0.000	5 A	235.36	0.159	0.419
20 A	1322.73	0.005	0.393	4 A	222.13	25.474	0.000
19 A	1242.50	45.661	0.000	3 A	200.94	19.550	0.000
18 A	1228.56	0.030	0.533	2 A	114.09	13.314	0.000
17 A	1152.97	4.665	0.000	1 A	-18.45	8.758	0.000

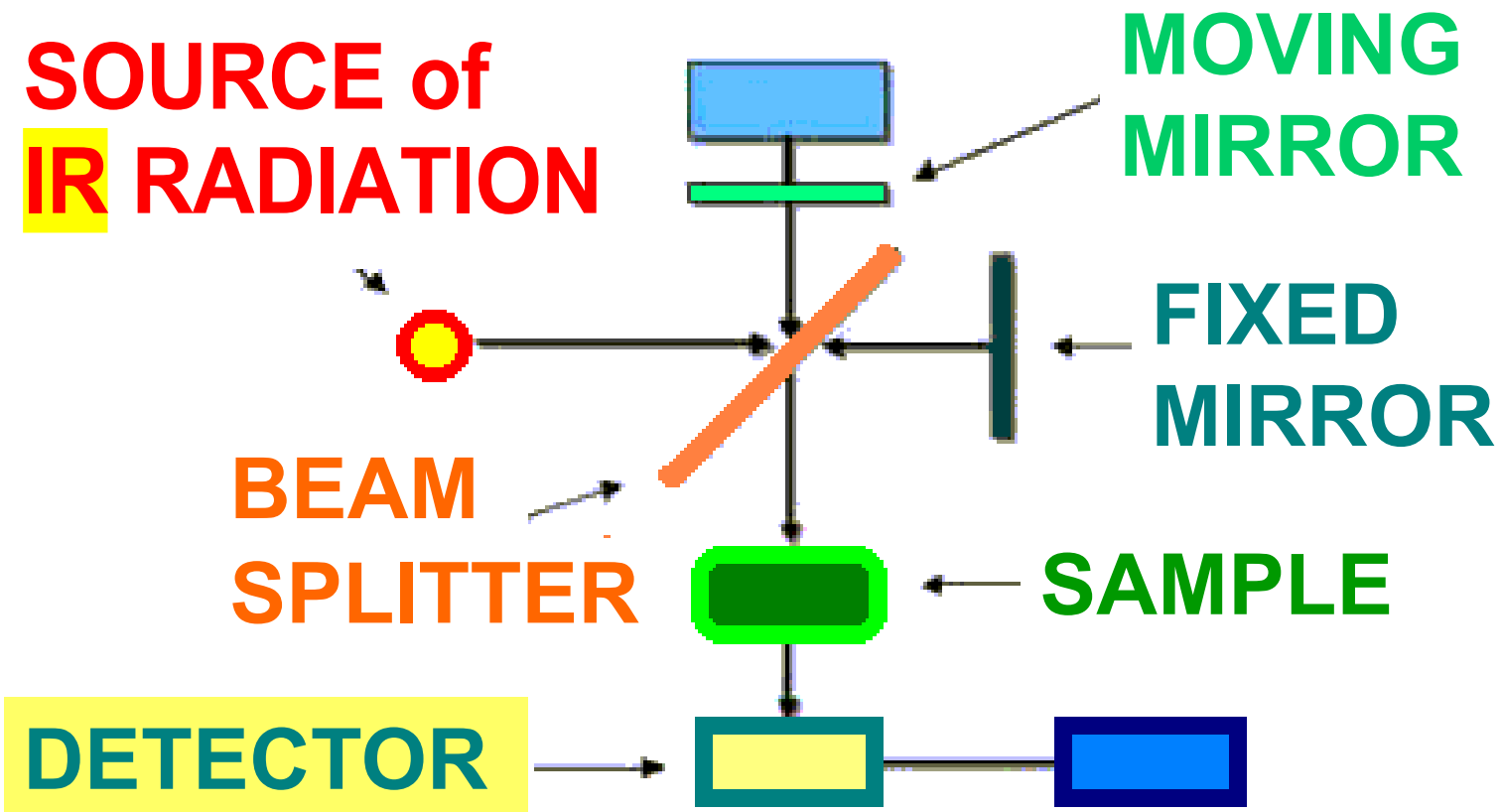
Infrared spectrometry

TYPES of MATERIALS ANALYZED

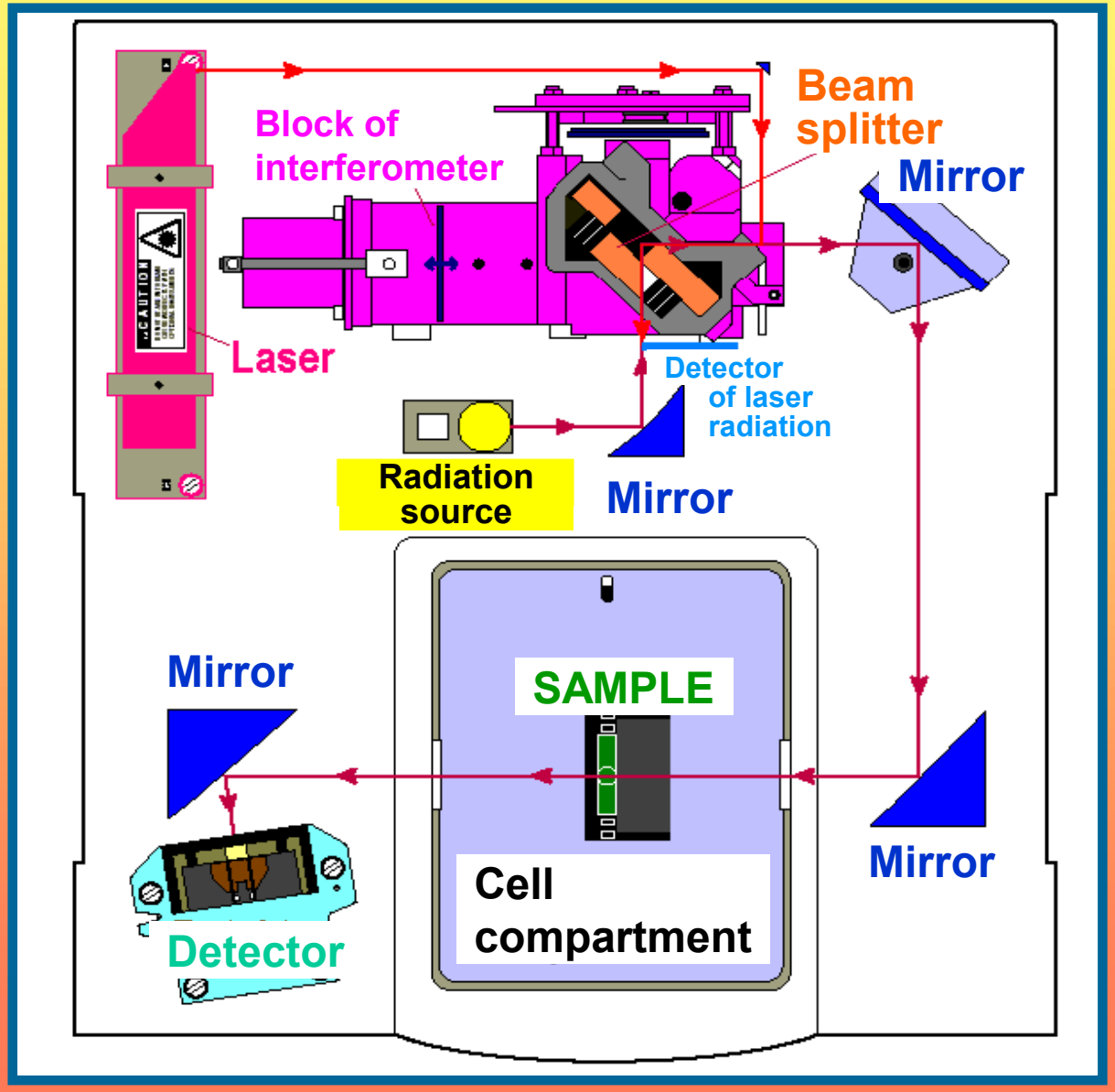
- gases - analysis of natural gas composition
  - monitoring of air pollutants
- liquids, solutions - analysis of oils
  - analysis of water (waste, drinking)
  - analysis of milk
- powdered samples - analysis of drugs, chemicals, explosives
  - analysis of ores, fertilisers
- interface of phases - surface analysis

Infrared spectrometry
- instrumentation

FTIR spectrometer



Infrared spectrometry - instrumentation



Infrared spectrometry
- instrumentation

PARTS of FTIR SPECTROMETER

- **RADIATION SOURCE**

MIR, FIR – thermal light source – heated rod
uo to 1000 - 1600°C - SiC, Globar
FIR – mercury vapour lamp
NIR - bulb - tungsten, tungsten-halogen

- **BEAM SPLITTER**

MIR – Ge-coated KBr, ZnSe, CsI
NIR - Si coated CaF_2, or quartz
FIR - metal screen, PET-Mylar, plastic films

Infrared spectrometry
- instrumentation

PARTS of FTIR SPECTROMETER

- **DETECTOR of RADIATION**

MIR - DTGS (deuteriumtriglycine sulphate)
- MCT (mercury-cadmium-telluride)

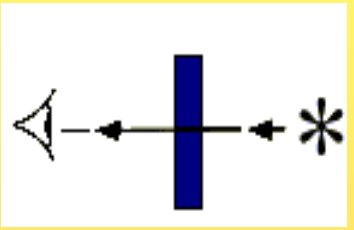
NIR - PbSe, PbS, InSb, Ge, MCT

FIR - DTGS, GaAs-Zn

- **other parts – windows, crystals, etc.**

NaCl, KBr, ZnSe, CaF_2, CsI, silicon, diamond

Differences Between Transmission and Reflection FT-IR Techniques

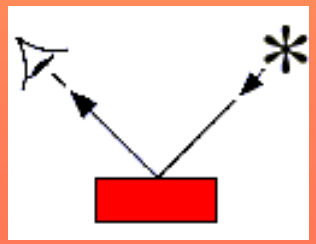


Transmission:

- Excellent for solids, liquids and gases
- The reference method for quantitative analysis
- Sample preparation can be difficult

Reflection:

- Collect light reflected from an interface
  air/sample, solid/sample, liquid/sample
- Analyze liquids, solids, gels or coatings
- Minimal sample preparation
- Convenient for qualitative analysis, frequently used for quantitative analysis



Infrared spectrometry

- **TRANSMISSION MEASUREMENT**

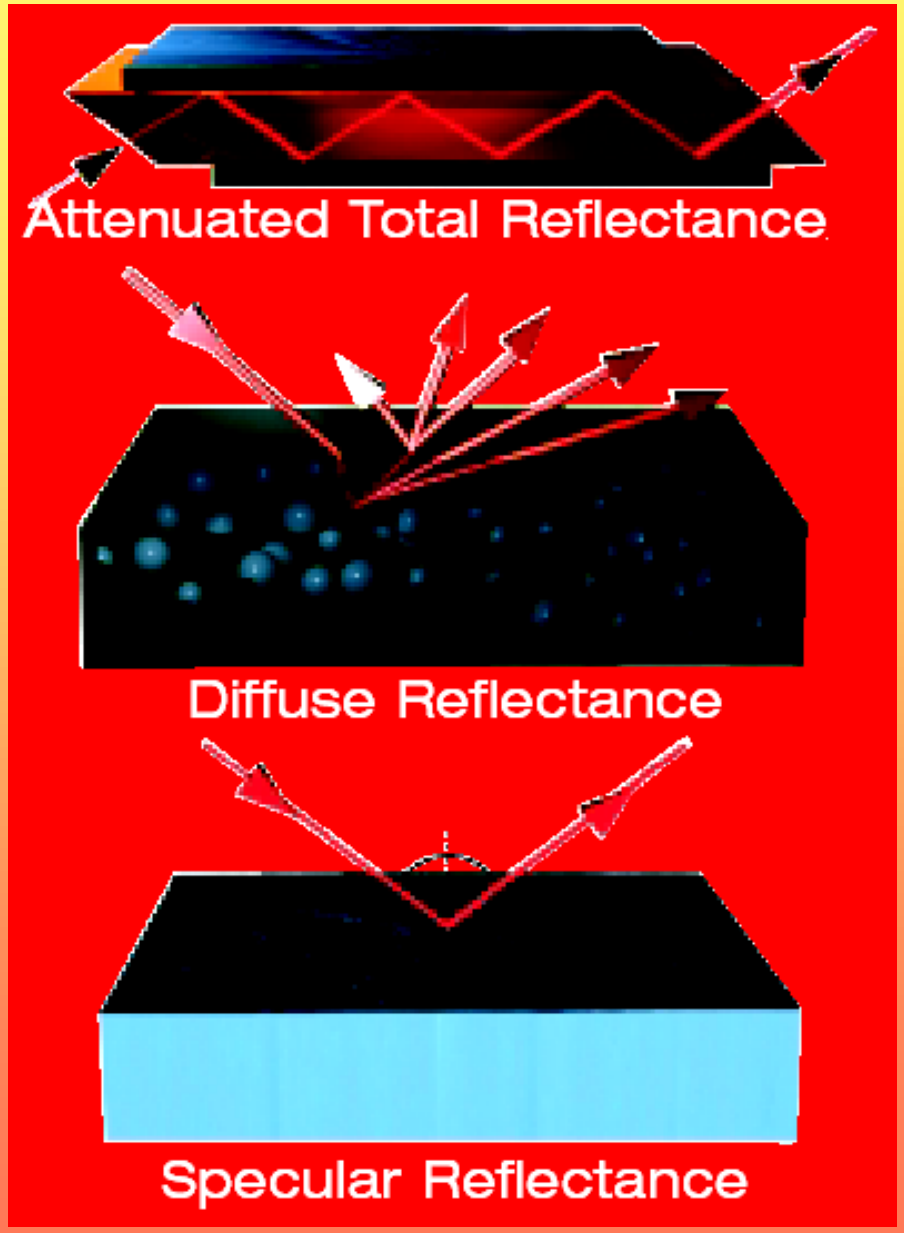
- gases - gas cells - pathlength 1 cm - 10 m

- solutions – cells for liquids - 0,01 mm - 10 mm

- liquids - cells for liquids - 0,002 mm - 0,05 mm

- solid materials - suspension with Nujol,
  Fluorolube - cells for liquids
  - pellets with KBr as matrix

FT-IR Reflection Techniques



- Infrared beam reflects from a interface via total internal reflectance
- Sample must be in optical contact with the crystal
- Collected information is from the **surface**

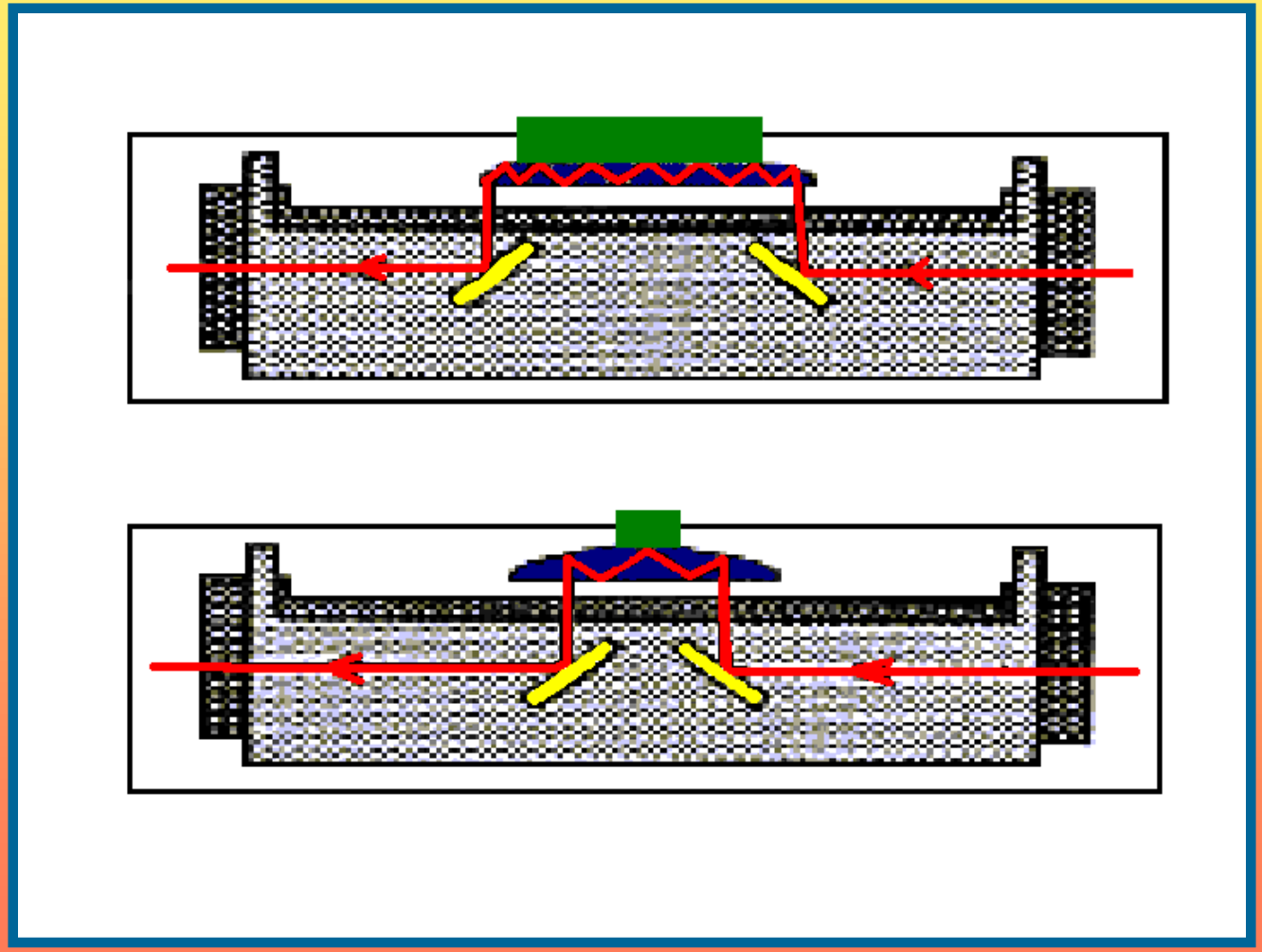
- Solids and powders, diluted in a IR transparent matrix if needed
- Information provided is from the **bulk matrix**

- Sample must be reflective or on a reflective surface
- Information provided is from the **thin layers**

Infrared spectrometry

- **Reflection techniques**

ATR

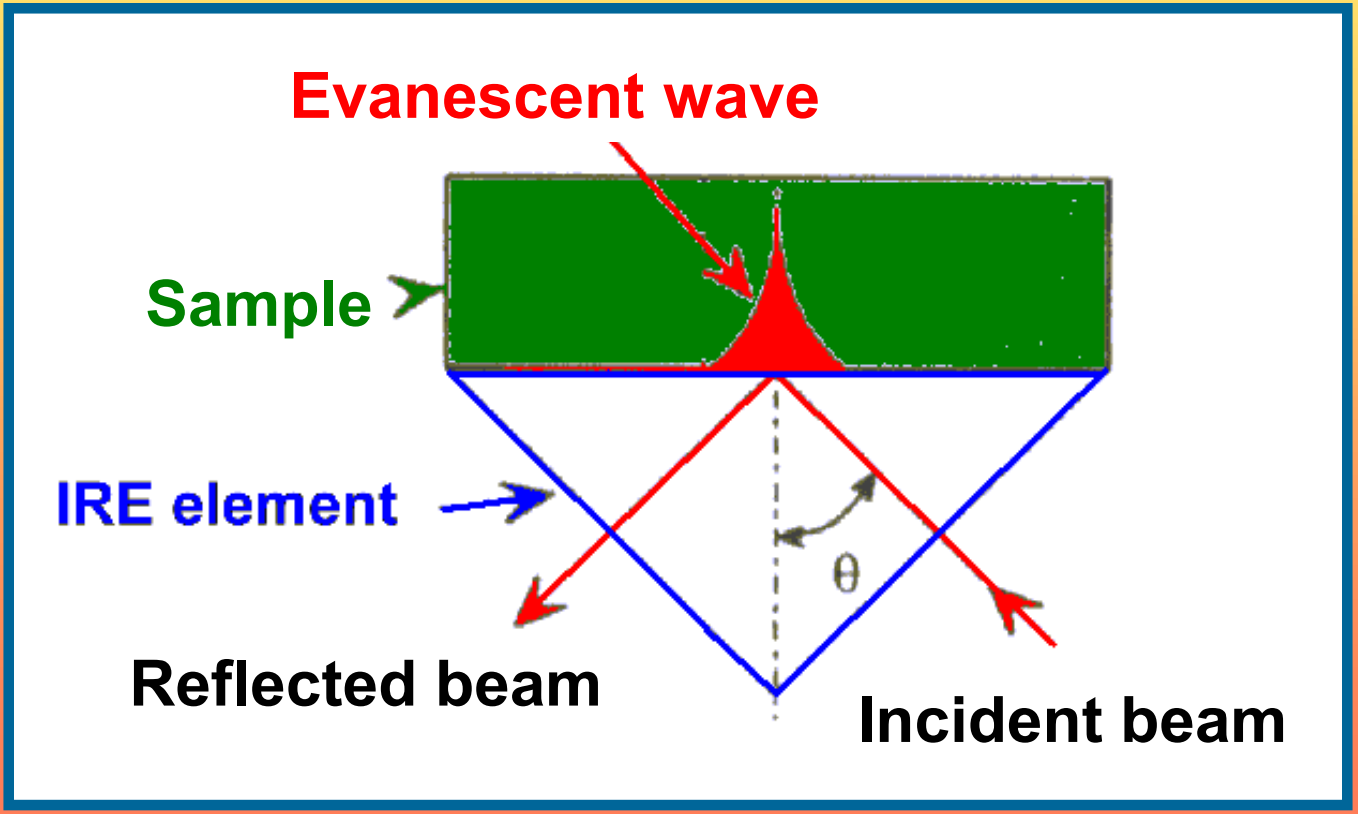


Infrared spectrometry

- Reflection techniques

ATR - attenuated total reflection

IRE – internal reflection element – ATR crystal



Infrared spectrometry

Contact of the sample and IRE

Evanescent wave

nearfield standing wave exhibiting exponential decay with distance from surface (interface),
i.e. it is very **important** to ensure
perfect optical contact of the sample with the IRE

Materials of crystals (IRE elements)

ZnSe, AMTIR (Se, Ge, As), Si, Ge, saphire

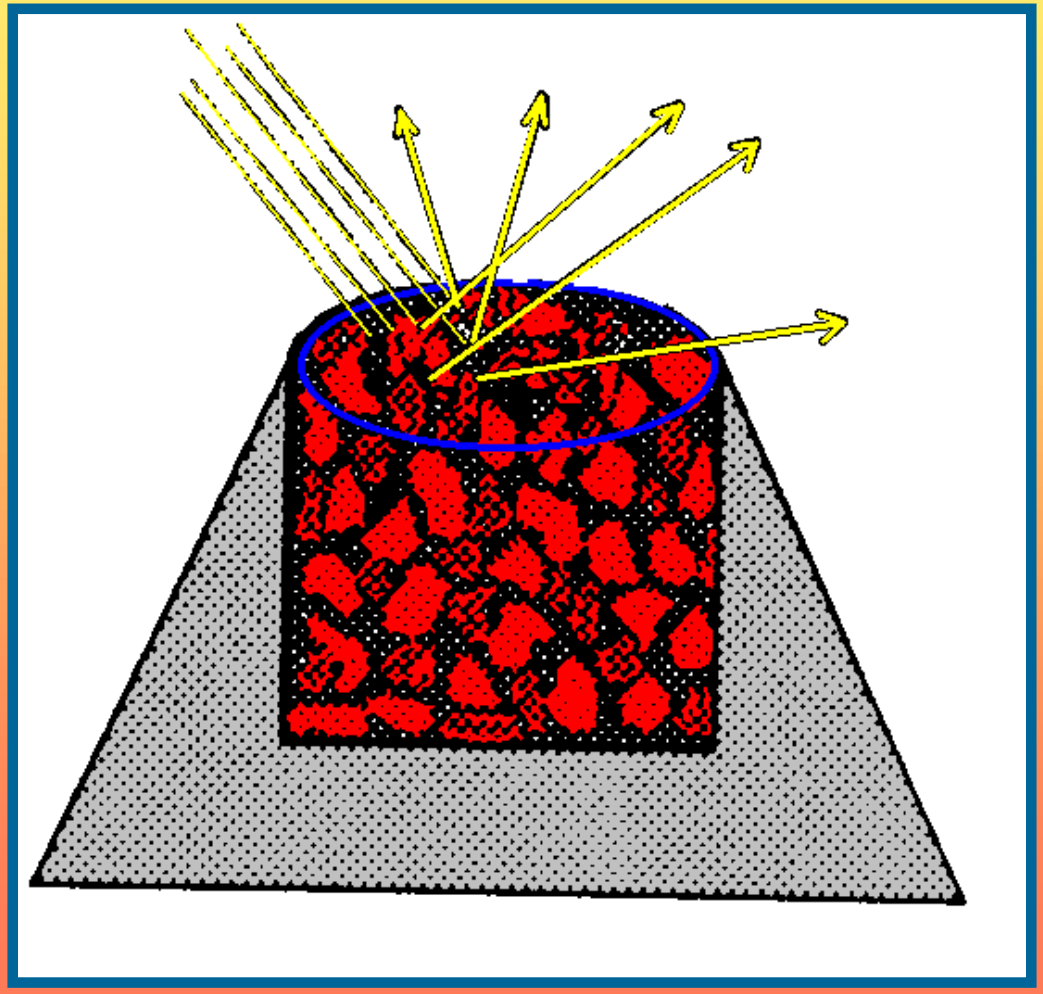
Samples

liquids, surface layers on soft material, soft solid materials, samples after evaporation of a solvent

Infrared spectrometry

- Reflection techniques

DRIFT



Infrared spectrometry

- **Reflection techniques**

DRIFT

- fast measurement of powdered samples

- low repeatability of spectral data

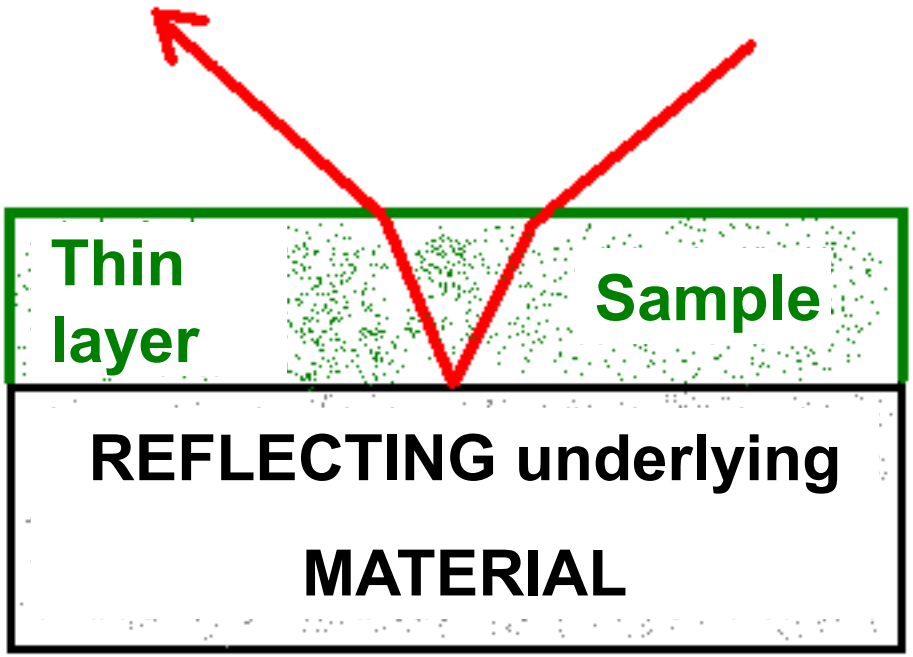
- complicated physical description of the effect

shape of particles, compactness of samples
refractive index of particles
reflectivity and absorption characteristics of particles

Infrared spectrometry

- Reflection techniques

SPECULAR REFLECTION



Infrared spectrometry

- Reflection techniques

SPECULAR REFLECTION

- measurement of thin layers up to monomolecular - monolayer

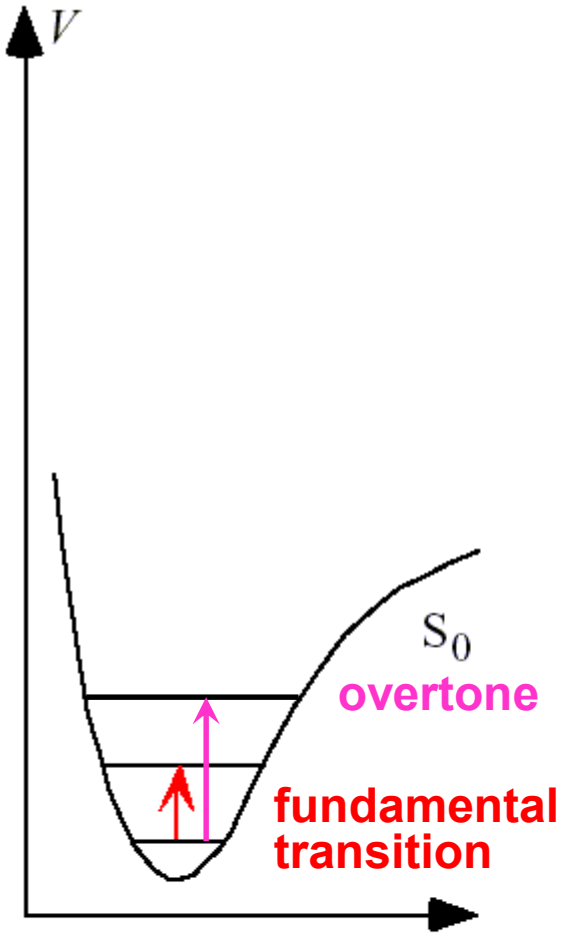
- specular reflection on reflecting underlay

- selection of incident angle

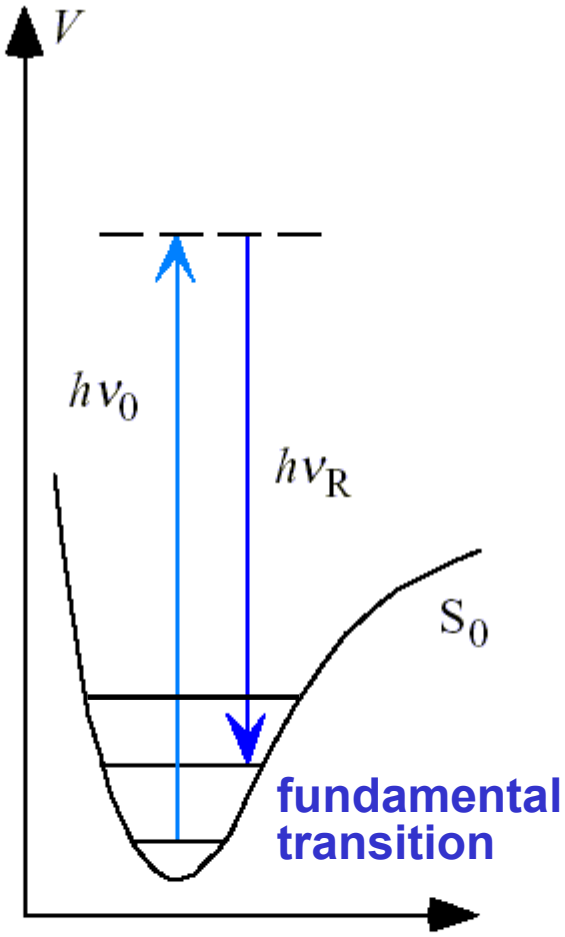
- path-length of radiation through layer

- refractive index of layer

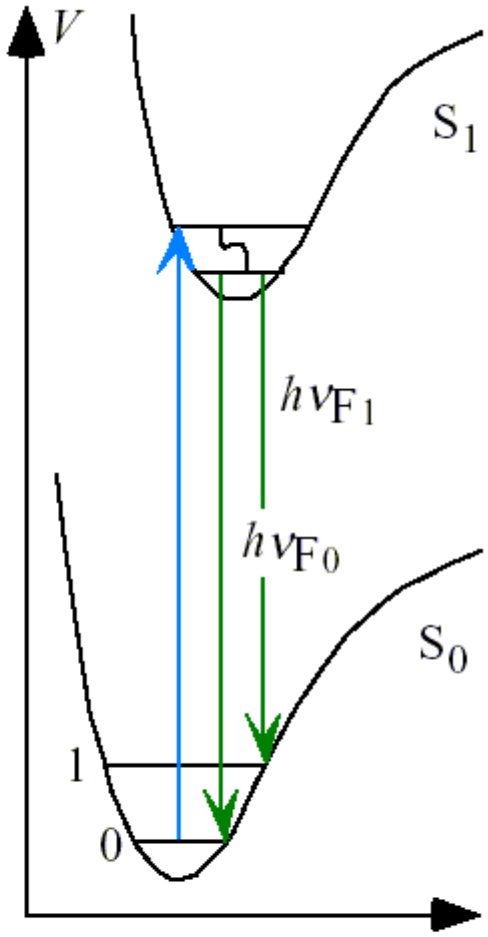
Scheme of levels



IR absorption

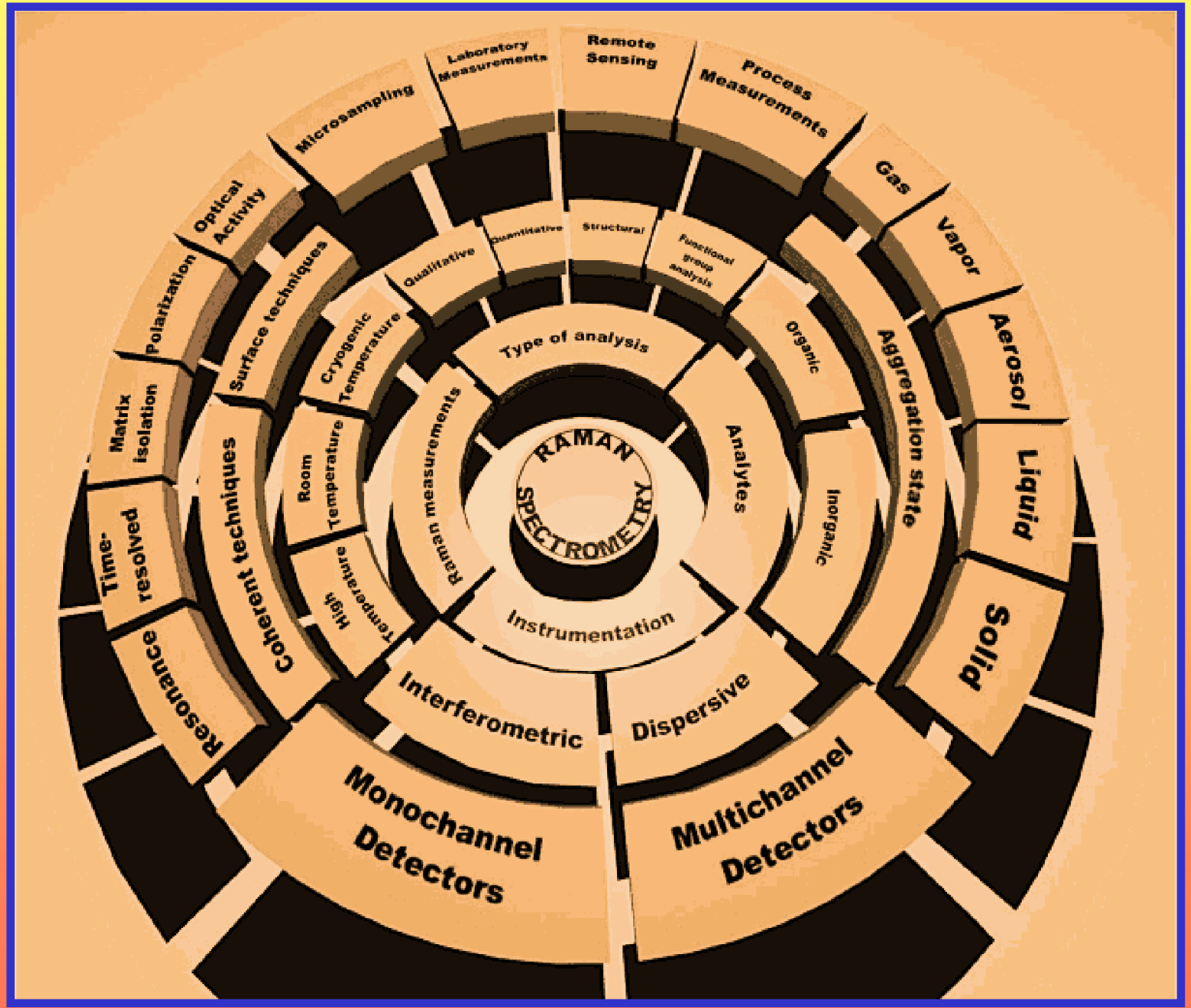


Raman scattering



Fluorescence

Raman spectrometry



Raman spectrometry

Sir Chandrasekhara Venkata Raman
1888 – 1970

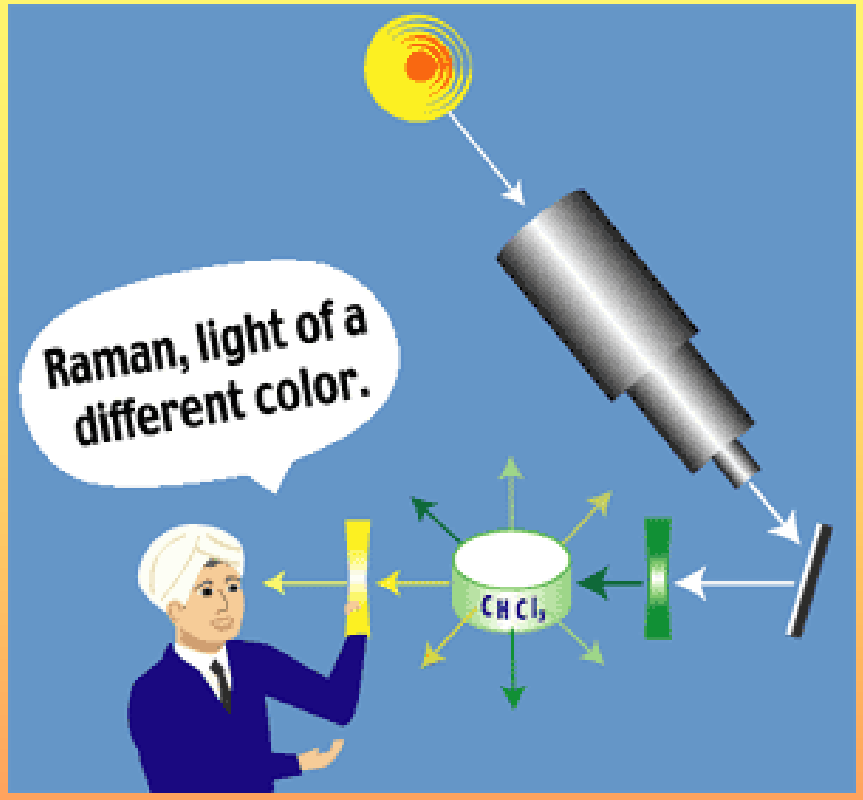
Nobel Prize in Physics 1930

A New Type of Secondary Radiation

C. V. Raman and K. S. Krishnan, Nature, *121(3048)*, 501, March 31, 1928

The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

Raman spectrometry



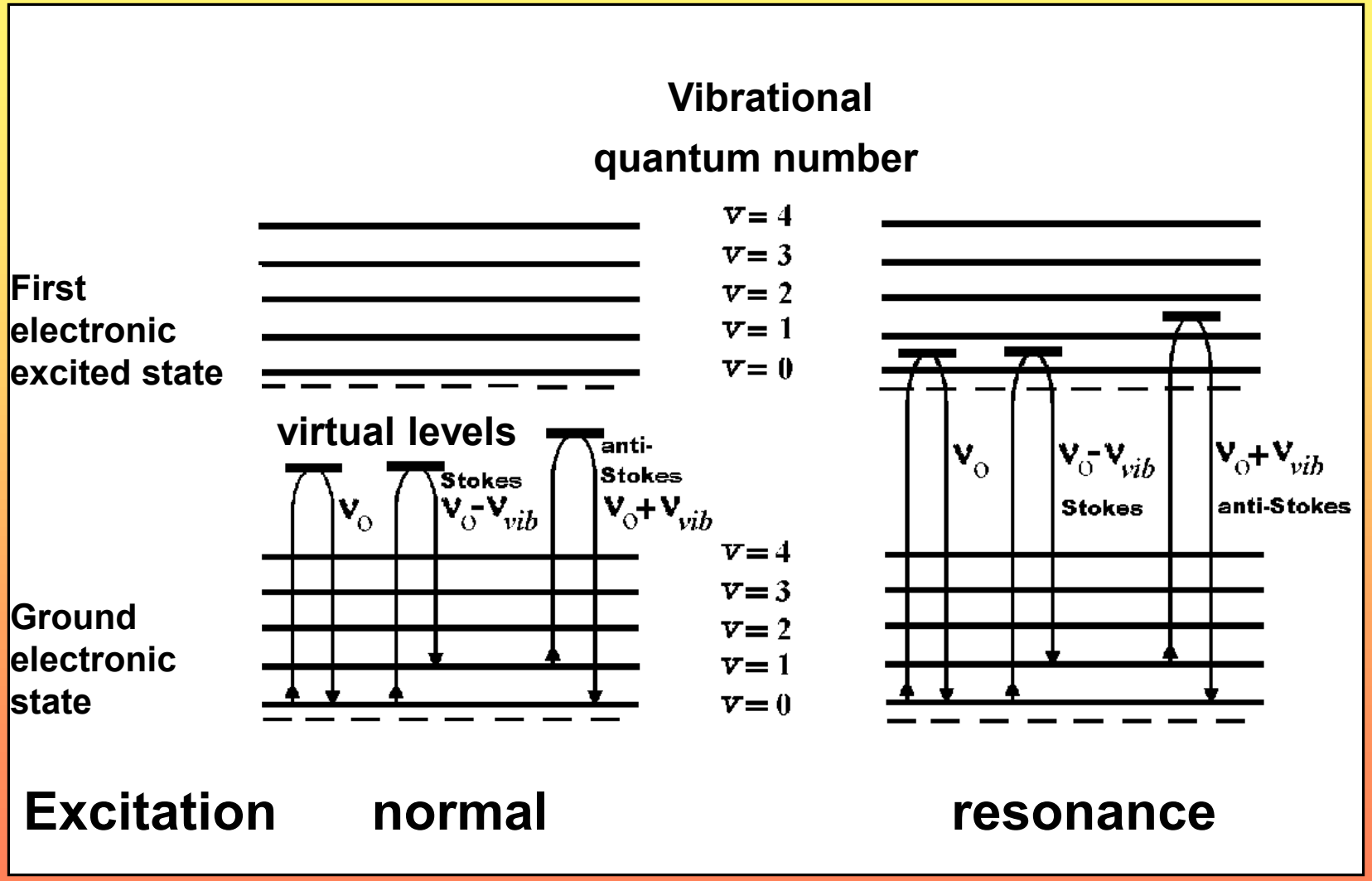
Light source

- sun and filters
- mercury arc
- LASERS
  - monochromatic
  - coherent

Light detection

- eyes
- photographic plates
- photomultipliers
- CCD chips

Raman spectrometry



Scheme of two-photon transitions

Raman and Rayleigh scattering by normal and resonance excitation

Principles of Raman and FT Raman spectroscopy

Principle of Raman effect

LIGHT SCATTERING

- scattered photon exhibit different energy compared to incident one

radiative two-photon transition

between two stationary vibration states of a molecule,

the corresponding energies are E_1 and E_2,

caused by interaction with a photon of incident radiation

with frequency $\nu_0 > |E_2 - E_1| / h$,

accompanied by "emission" of a scattered photon

of energy $h\nu_R = h\nu_0 \pm (E_2 - E_1)$,

where $h\nu_{vib} = E_2 - E_1$

Comparison of IR and Raman spectrometry

Vibration frequencies of individual modes of any molecule are independent on technique used to study them, either IR or Raman spectroscopy, but intensities of spectral lines will be significantly different for both spectroscopic techniques.

Raman scattering – additional information from polarization/depolarization of scattered radiation and from excitation profiles (resonance effect).

Raman spectrometry

Fundamental selection rule of Raman scattering

$$\boldsymbol{p} = \alpha \boldsymbol{E} \cos\left(2\pi \nu_0 t\right) + \frac{1}{2}\frac{\partial \alpha}{\partial q} q \boldsymbol{E} \left\{\cos\left[2\pi\left(\nu_0 - \nu_{vib}\right) t\right] + \cos\left[2\pi\left(\nu_0 + \nu_{vib}\right) t\right]\right\}$$

$$\frac{\partial \alpha}{\partial q} \neq 0$$

***BAND INTENSITIES PROPORTIONAL TO CHANGES of* POLARIZABILITY *in the course* of VIBRATIONAL MOTION**

Principles of Raman and FT Raman spectroscopy

Relation of intensities of corresponding anti-Stokes and Stokes bands

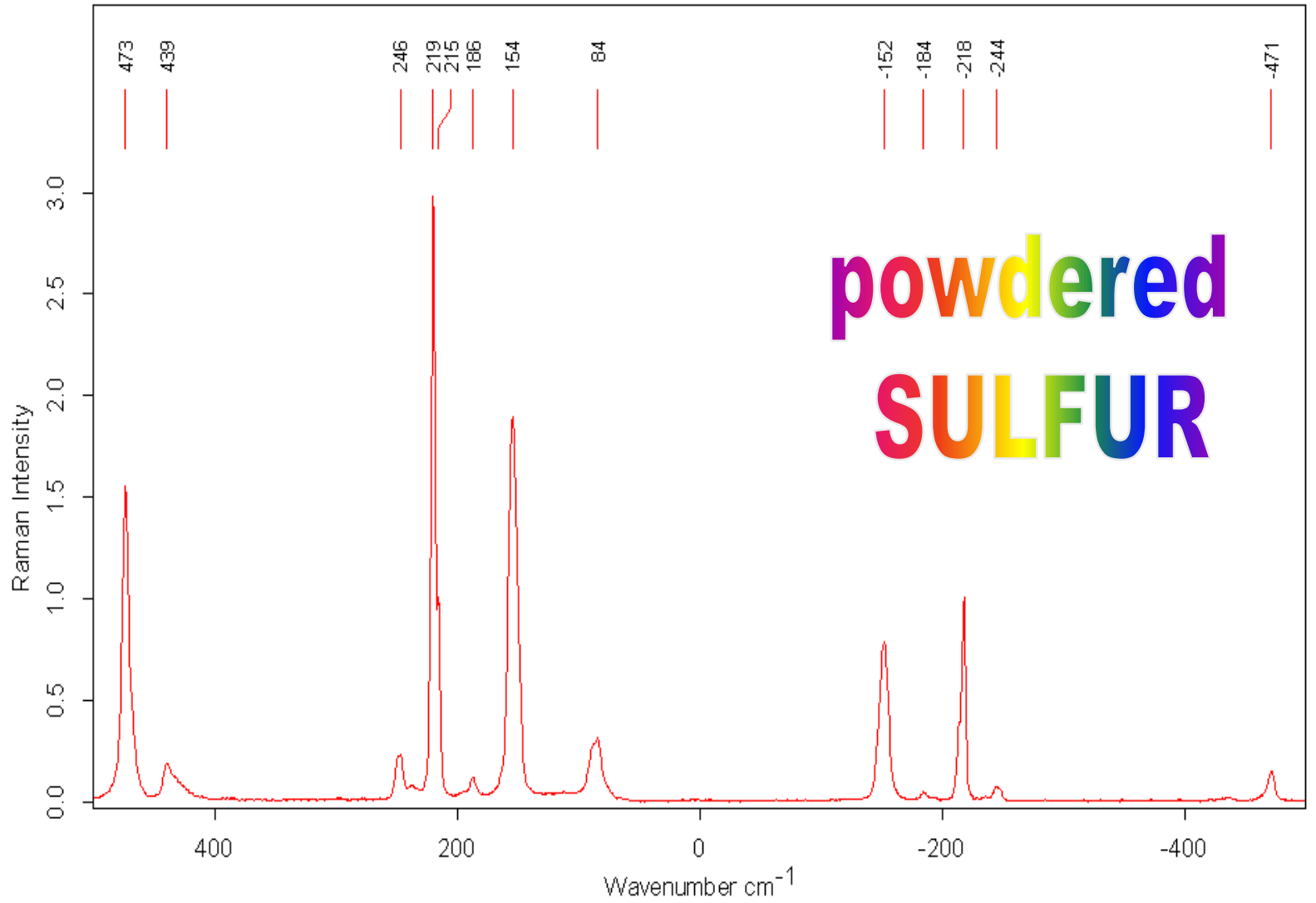
- possibility to measure temperature of a sample

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \left(\frac{\nu_0 + \nu_{vib}}{\nu_0 - \nu_{vib}} \right)^4 e^{-\frac{h\,\nu_{vib}}{k\,T}}$$

Principles of Raman and FT Raman spectroscopy

- Interpretation of spectra – structural analysis, identification of substances – spectral libraries
- Intensity of bands – quantitative analysis
- Time-resolved spectra – kinetic studies
- Temperature-dependent spectra
- Analysis of mixtures – identification of subspectra – factor analysis

Stokes and anti-Stokes scattering



Raman spectrometry

- possibility to measure in aqueous solution
  - low intensity of Raman scattering of water
  - used optical materials are not sensitive to humidity
- possibility to measure in glass vessels
  - measurement in sealed ampules – e.g. under vacuum
- easy use of glass fibre optics
- minimal requirements on preparation of solid state samples
- intense bands of -C=C-, -N=N-, -S-S- and other symmetric vibration

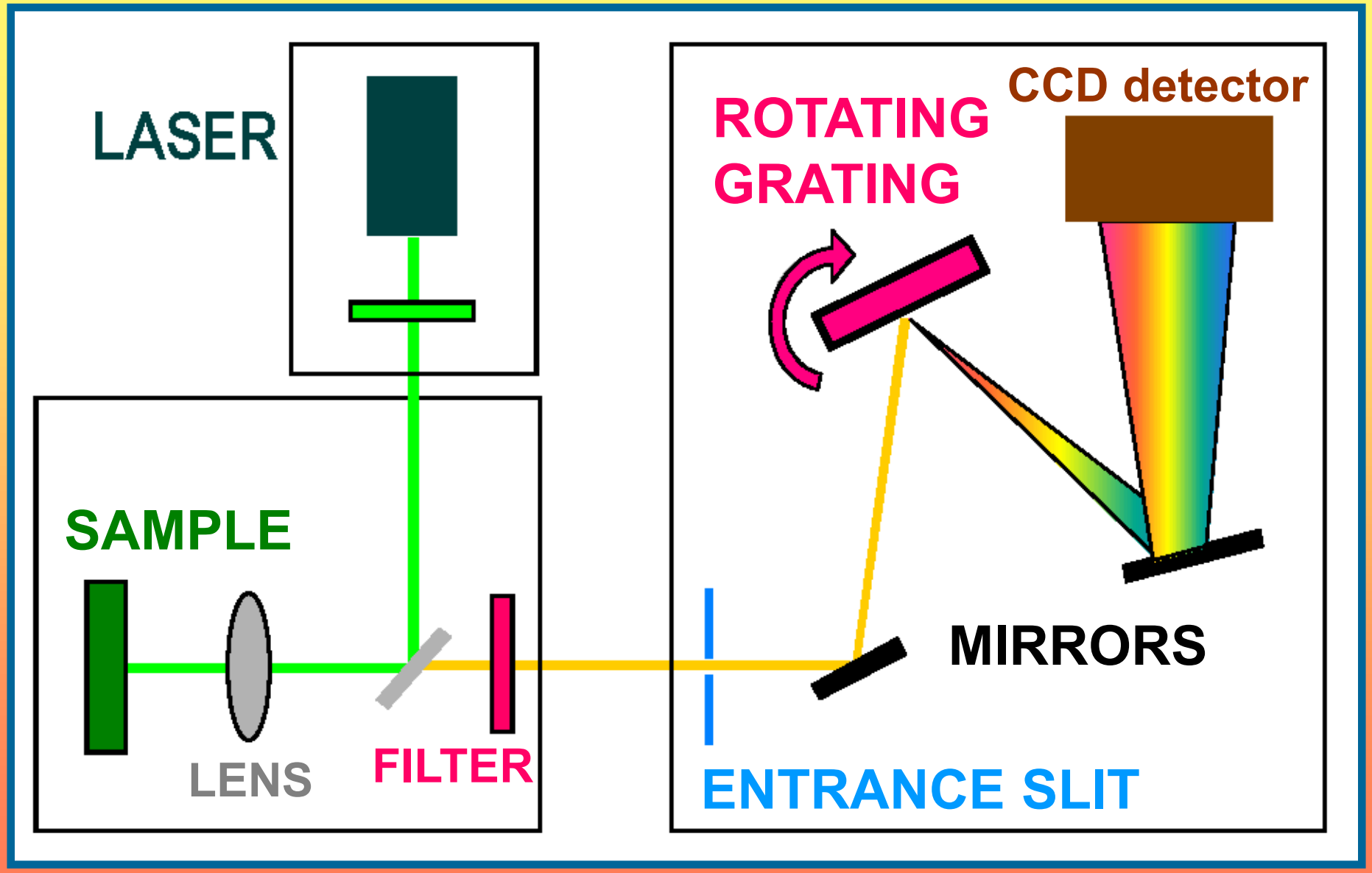
Instrumentation

The following experiment seems to us to be decisive: between the scattering quartz crystal and the spectrograph slit we placed a quartz vessel which was filled with mercury vapours and totally absorbed light with a wavelength of 2536 A. We did not obtain this line in the spectrogram, but obtained only the satellites.

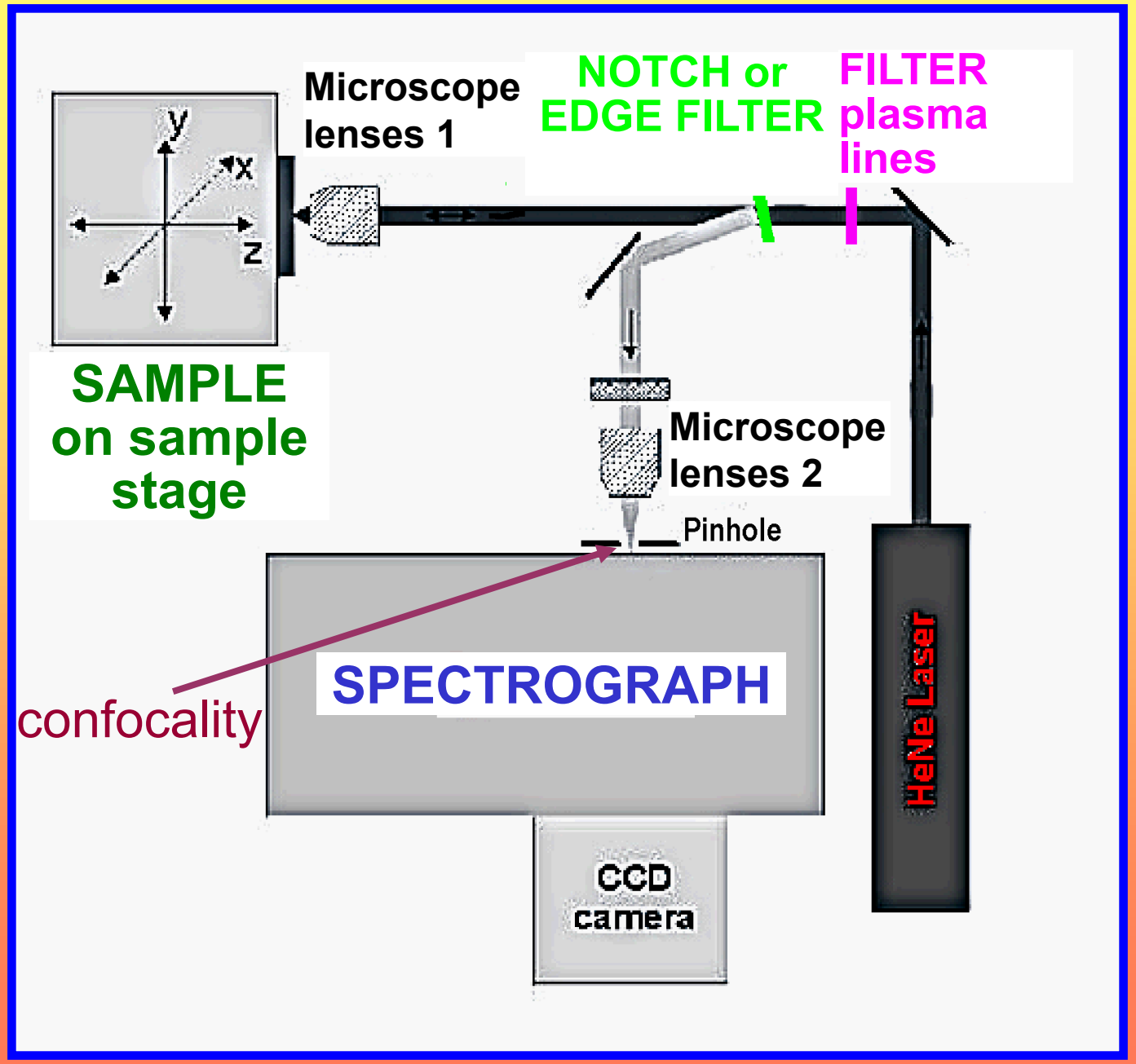
G.S. Landsberg, L.I. Mandelstam, 1928

- source of excitation radiation
- excitation optics
- sample compartment
- collection optics
- „separation“ of radiation of different energies
- detection of radiation
- acquisition electronics
- data storage and processing

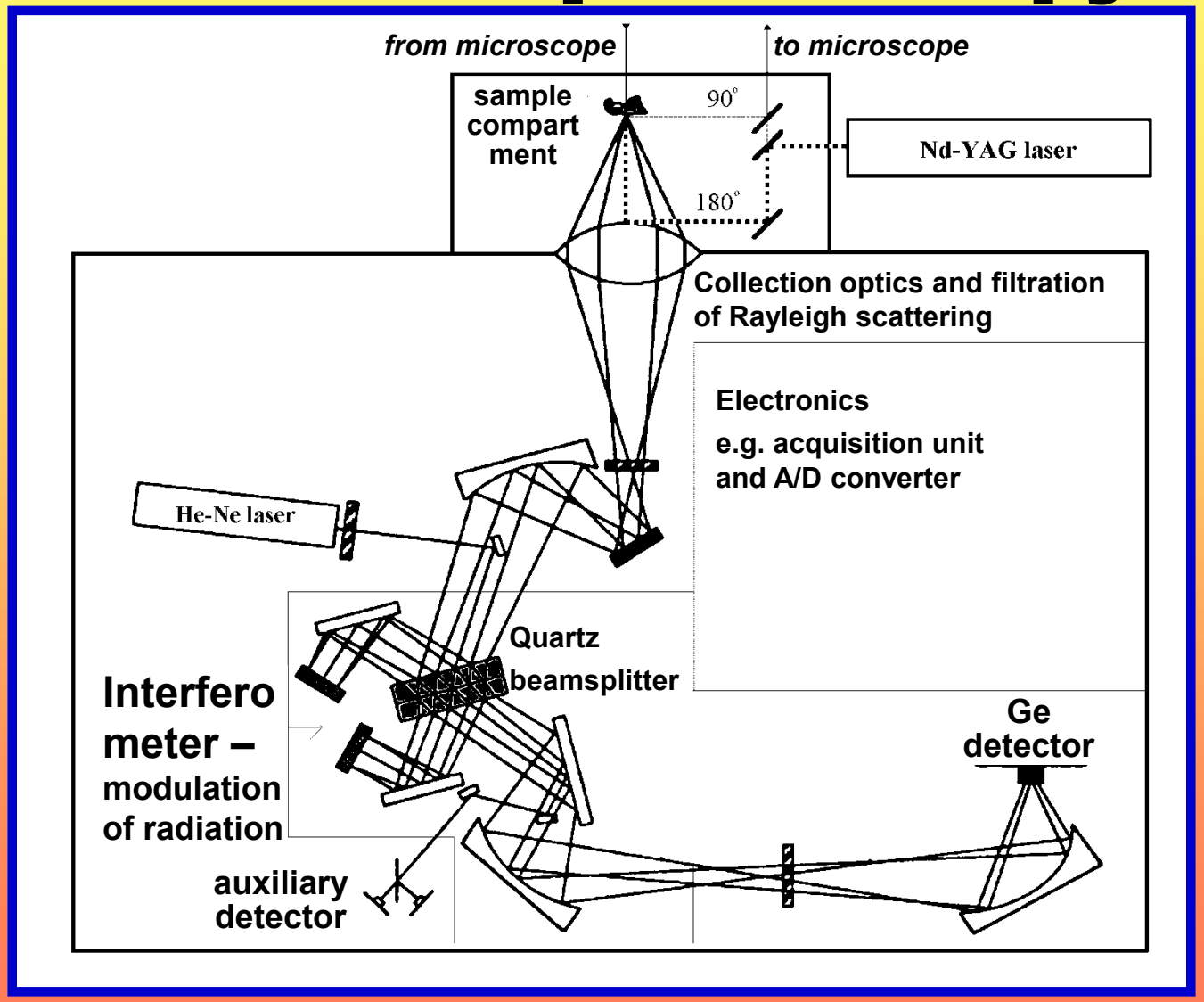
Scheme of Raman disperse instrument



Scheme of Raman microscope

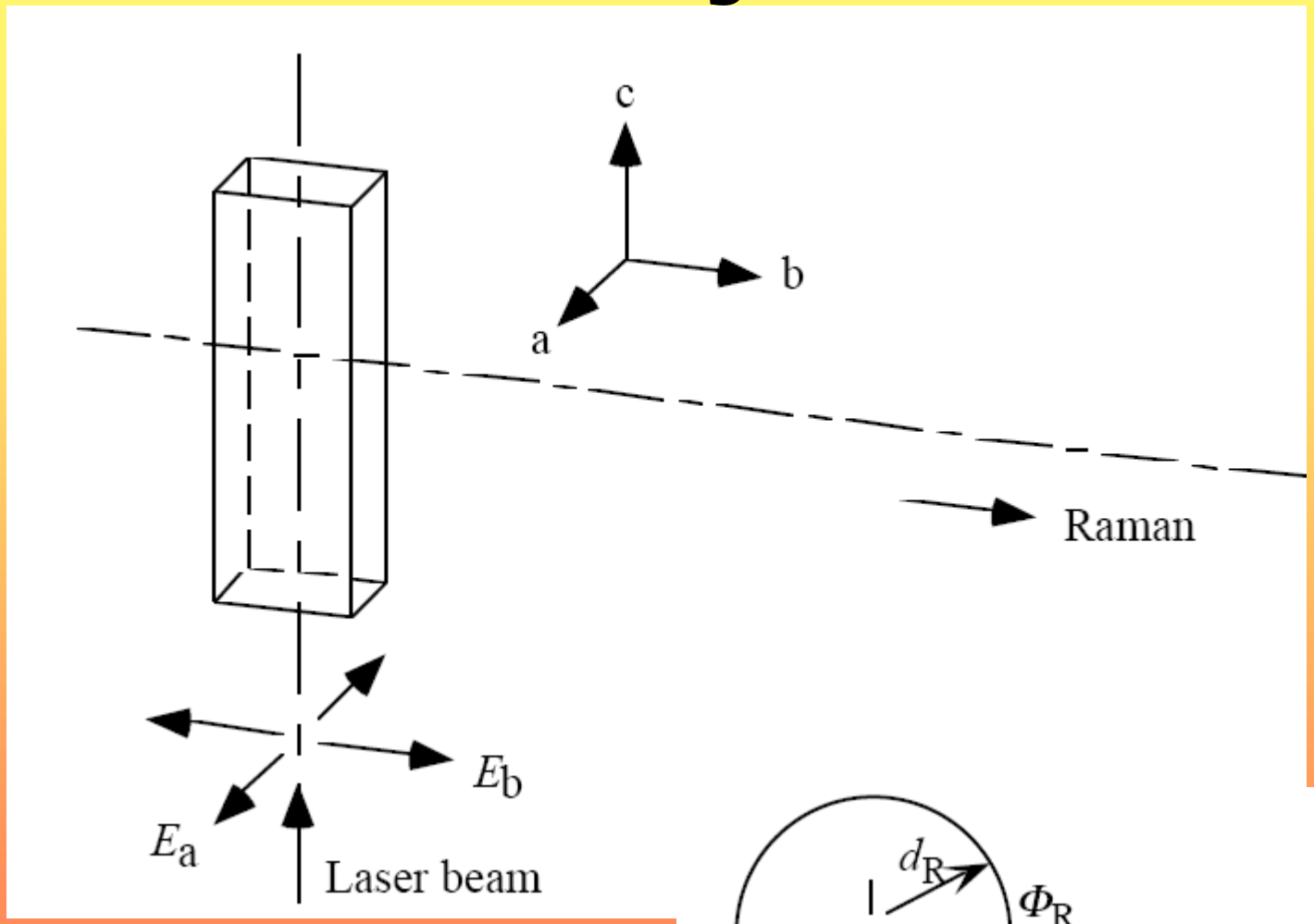


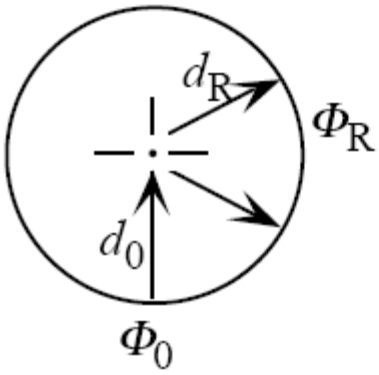
Principle of FT Raman spectroscopy

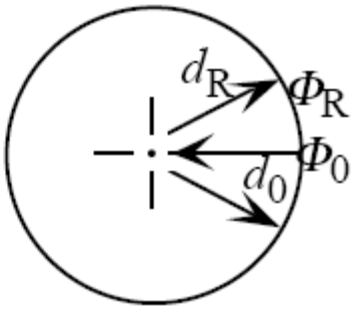


Scheme of FT Raman spectrometer with NIR excitation

Geometry of scattering



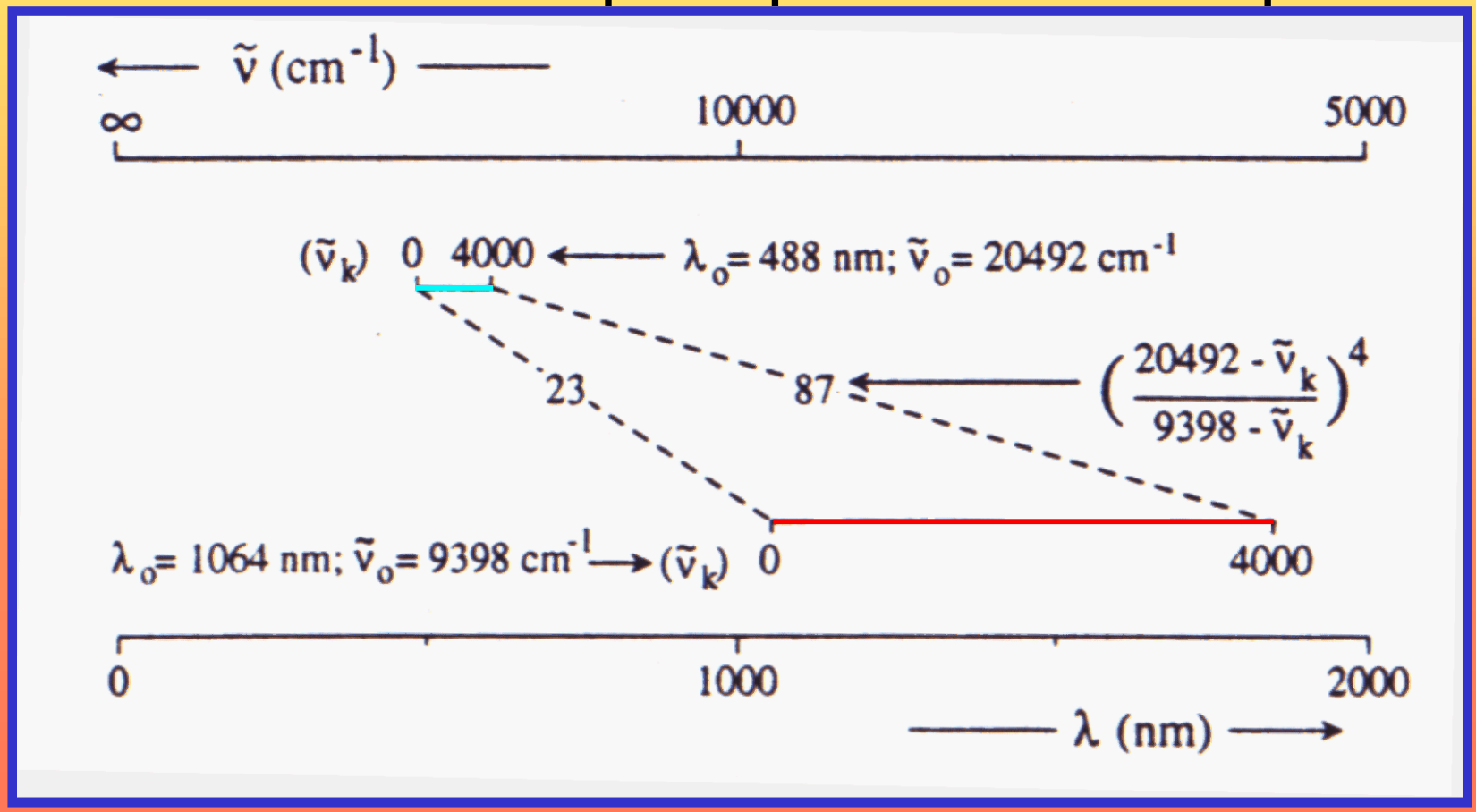




Principle of FT Raman spectroscopy

Problem of sensitivity - dependence of intensity of scattering on wavelength

Problem of resolution - disperse spectrometers vs. FT spectrometers



Instrumentation

Lasers for excitation of Raman effect

TYPe of laser	wavelength [nm]
He-Ne	632,8
Ar^+	514,5
Ar^+	488,0
Ar^+	457,9
Kr^+	568,2
Kr^+	647,1
Kr^+	676,4
Kr^+	752,6
Nd-YAG	1064
Nd-YAG - 2f	532
diode	780, 785 - NIR
dye	360 - 750 - UV, vis

Instrumentation
FT Raman

Materials of beamsplitters – NIR range

Transparent material	Semireflective coating	Spectral range [cm^{-1}]
quartz	Si (Fe_2O_3)	23 000 – 4 000
CaF_2	Si (Fe_2O_3)	10 000 – 1 000
KBr	Ge	4 700 – 350
CsI	Ge	4 000 – 200

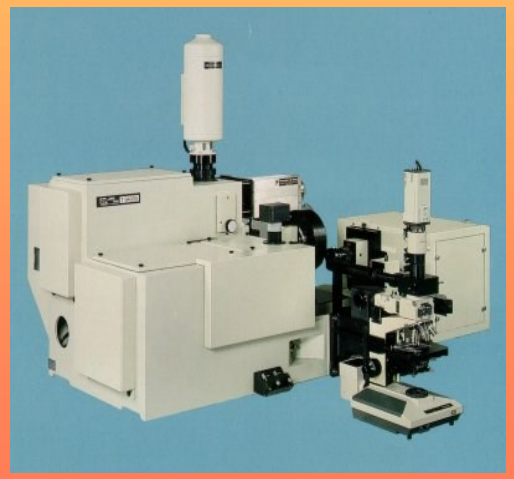
Instrumentation

Spectrometers

- **scientific systems**
- **industrial (process) systems**
- **mobile spectrometers**
- **handheld spectrometers**

RamanRxn3™
PAT Analyzer
Kaiser

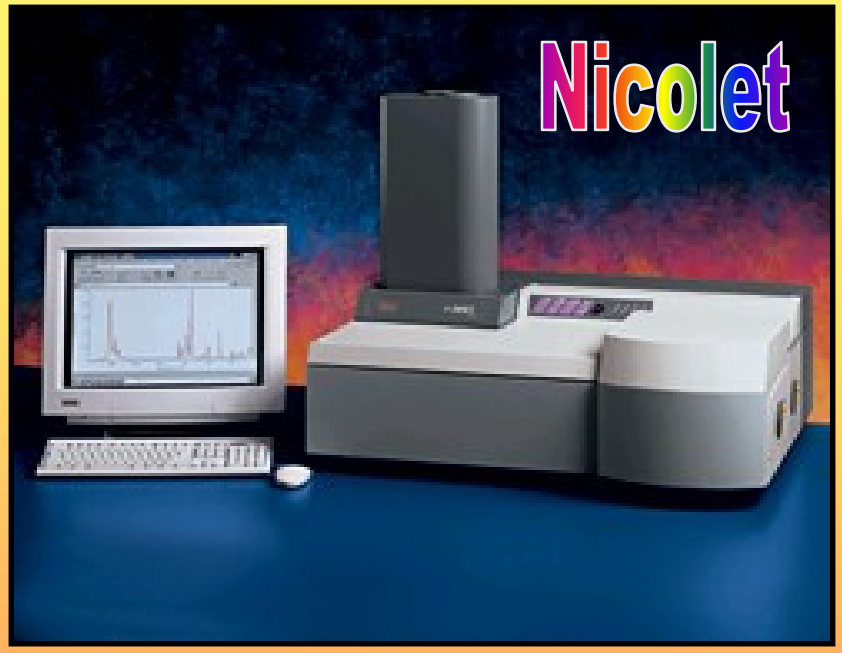
Handheld
AHURA



Research
system
T64000

InduRAM
HORIBA
Jobin Yvon

Instrumentation



Instrumentation

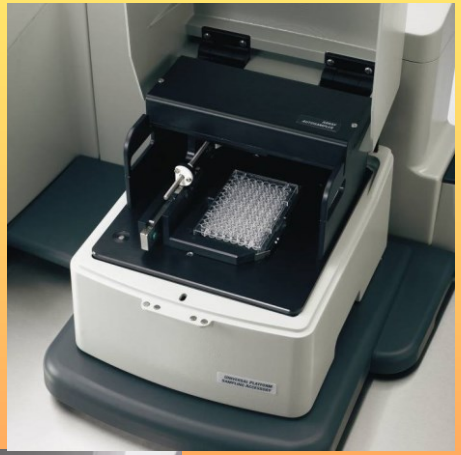
Sampling

- macroscopic – vials, glass cells (NMR, UV-vis …),
  possibility to measure samples packed using thin layer of polymers
  (bags)

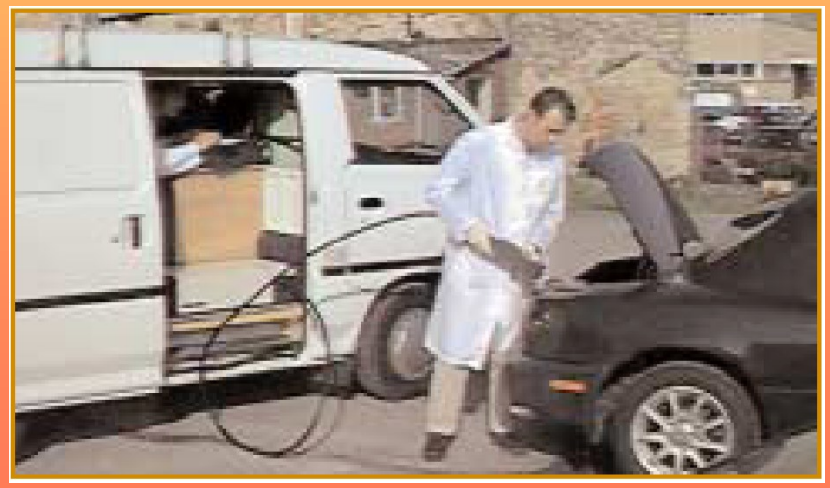
Sampling

-examples

-Nicolet



External probes – fibre optics



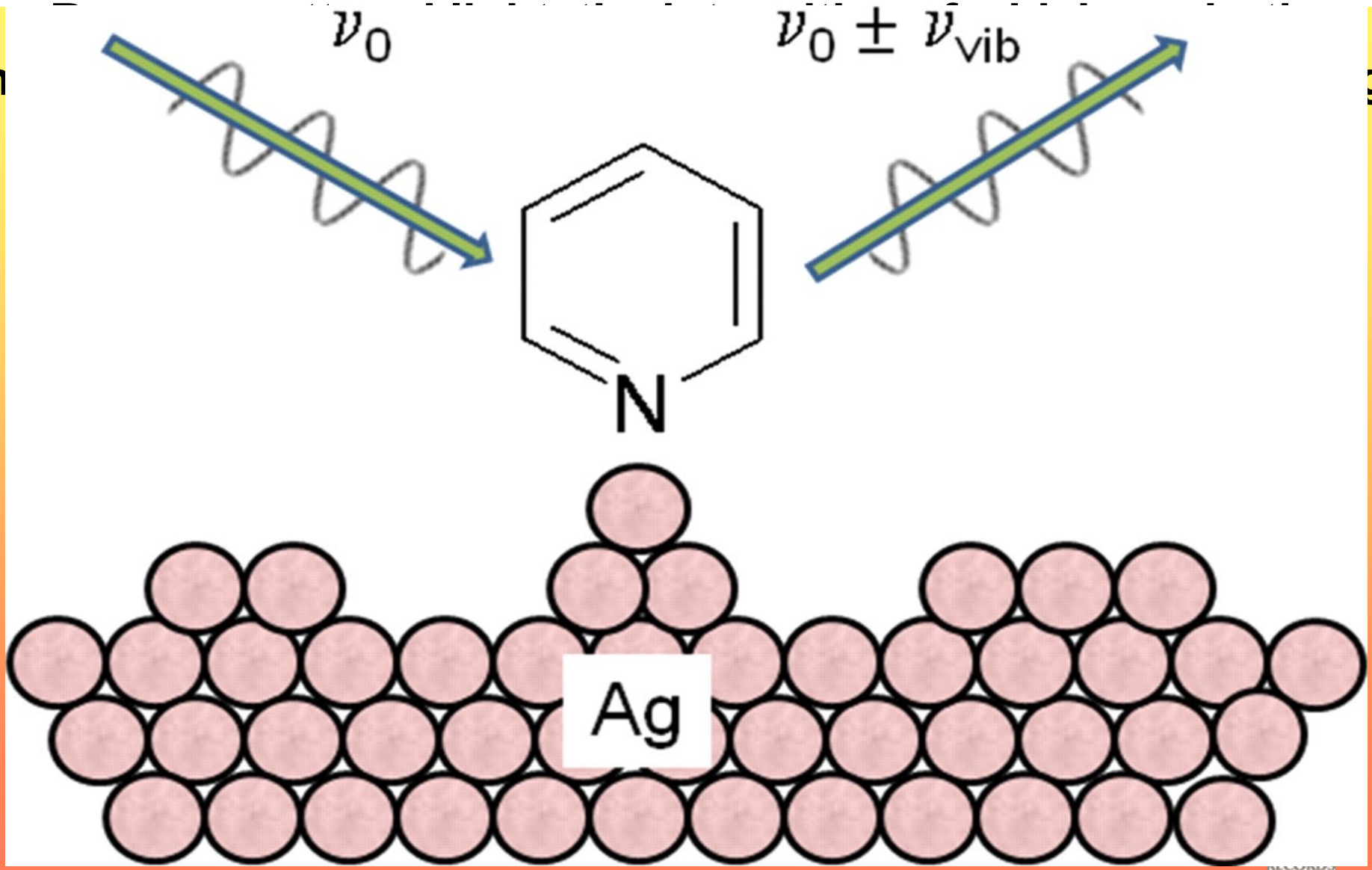
Special techniques

- resonance - RR
- surface enhanced - SERS
- resonance surface enhanced - SERRS
- photo-acoustic - PARS
- hyperRaman
- coherent anti-Stokes - CARS
- coherent Stokes - CSRS

A new field is born, apparently in full adulthood, and complete with a name. Such was the case with the Mössbauer effect and with polywater, and so, too, was the case with SERS. The first resulted in Nobel Prize, the second was shown to be spurious; SERS, I believe, has settled in the territory between.
M. Moskovits

- **surface enhanced – SERS**
  - **enhanced signal of species adsorbed on silver, copper and gold surfaces – more than 10^4,** possibility to detect individual molecules
  - **enhancement depends on surface morphology – "rough surface"**
  - **SERS-active substrates – roughened electrodes, colloidal particles, island films, interfacial films etc.**

A schematic representation of a SERS experiment with pyridine adsorbed on silver, showing the incident laser and



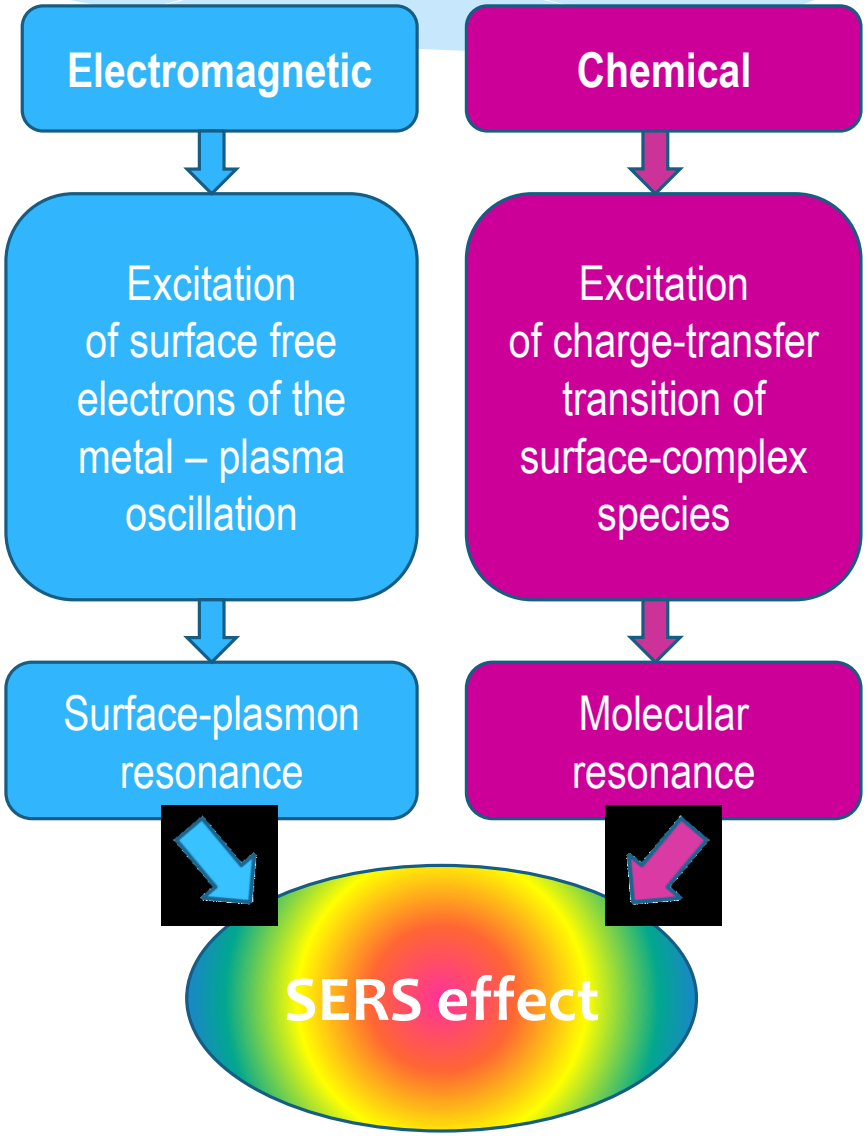
McQuillan A J Notes Rec. R. Soc. 2009;63:105-109

SERS

- surface enhanced Raman scattering
  - mechanisms of enhancement
    - electromagnetic /crucial factor/
      - effect of surface plasmon resonance on electromagnetic field near the metal surface
    - chemical
      - modification of the polarizibility of the adsorbed species – effect of chemisorption
      - charge-transfer mechanism
      - “molecular resonance” of adsorbed species

SERS

* giant enhancement of Raman signal
* two mechanisms involved
  * **electromagnetic** long range, depends on metal-substrate properties (surface plasmons are involved)
    – coin metals – Au, Ag, Cu
  * **chemical** - local, molecular structure plays an important role (formation of surface complex)



EM mechanism

Electromagnetic Mechanism of SERS

George C. Schatz, Matthew A. Young, and Richard P. Van Duyne

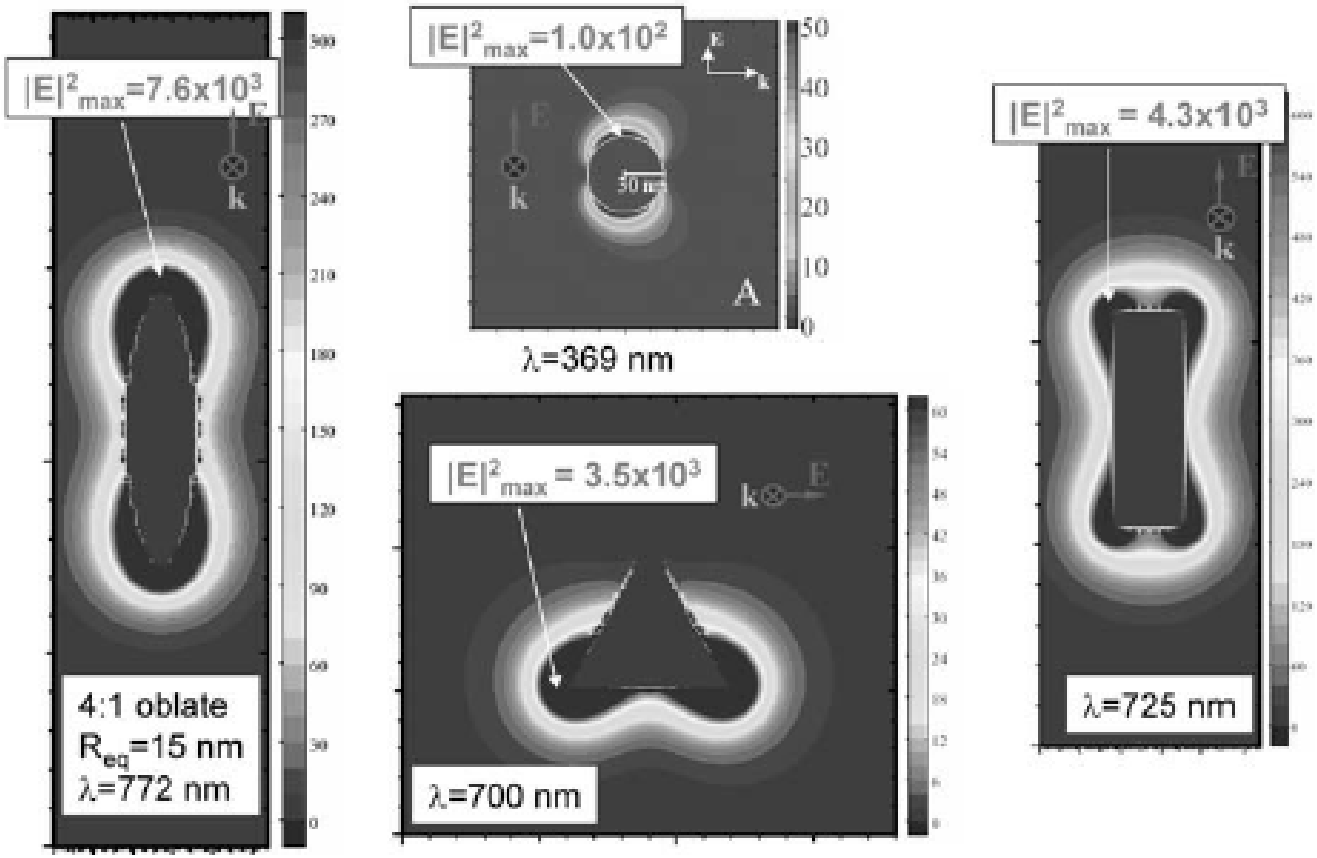


Fig. 1. Contours of the local field near silver particles at specified wavelengths, showing values of the peak field $|E|^2$

K. Kneipp, M. Moskovits, H. Kneipp (Eds.): Surface-Enhanced Raman Scattering – Physics and Applications, Topics Appl. Phys. **103**, 19–46 (2006)

EM mechanism

Electromagnetic Mechanism of SERS

George C. Schatz, Matthew A. Young, and Richard P. Van Duyne

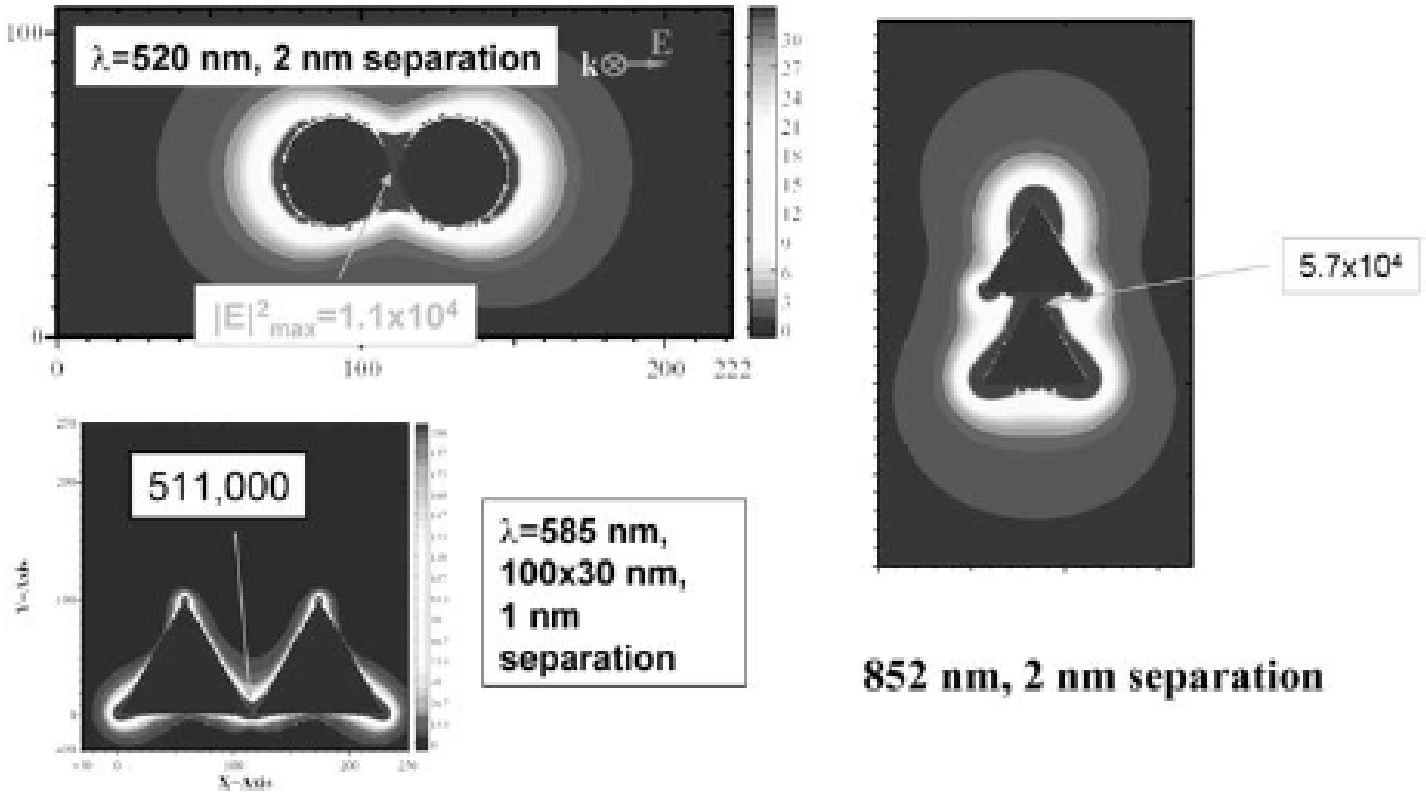


Fig. 2. Contours of the local field near dimers of silver particles at specified wavelengths, showing values of the peak field $|E|^2$

K. Kneipp, M. Moskovits, H. Kneipp (Eds.): Surface-Enhanced Raman Scattering – Physics and Applications, Topics Appl. Phys. **103**, 19–46 (2006)

Materials studied /Raman

SAMPLES – solid species, liquids,

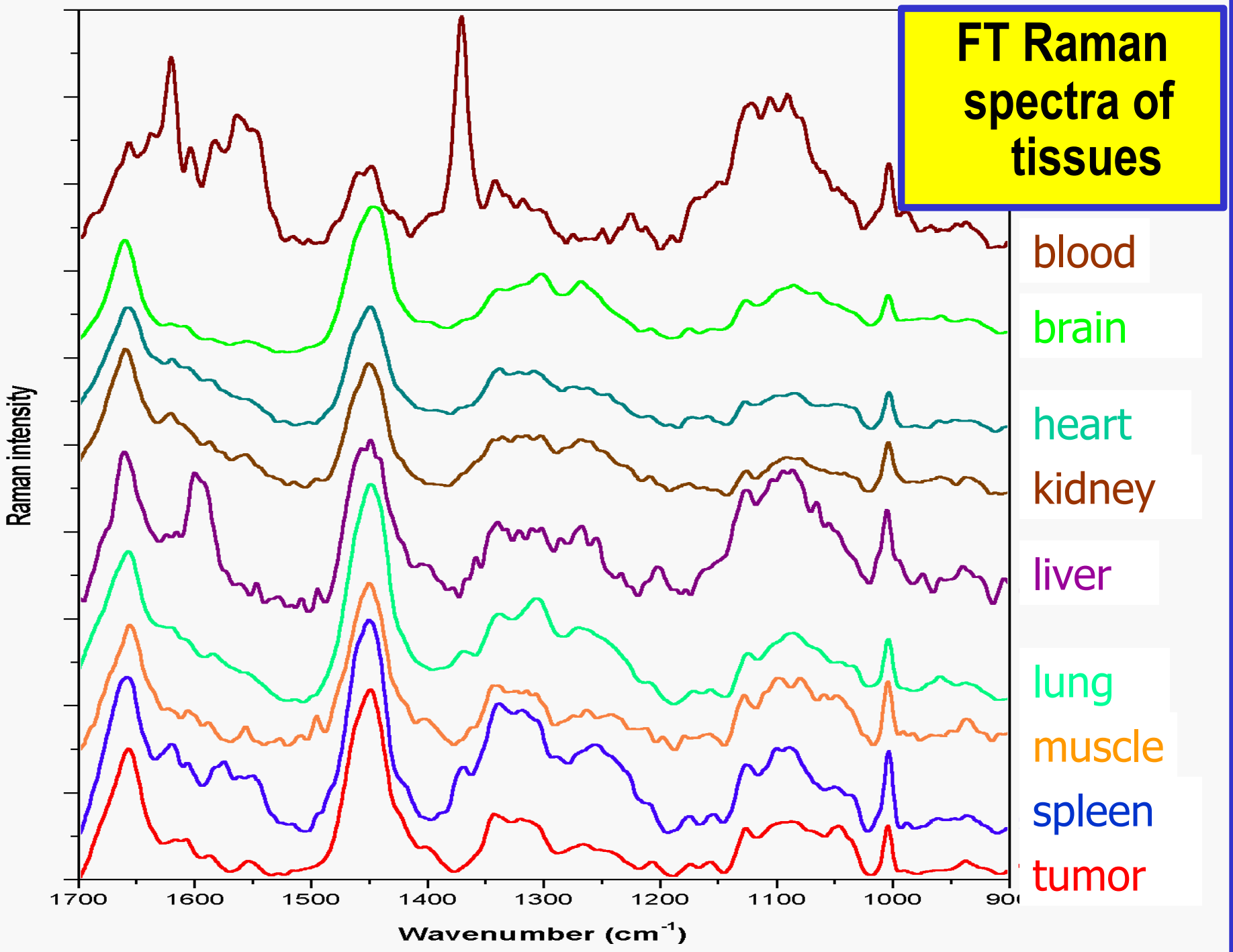
interface of phases

- EXAMPLES

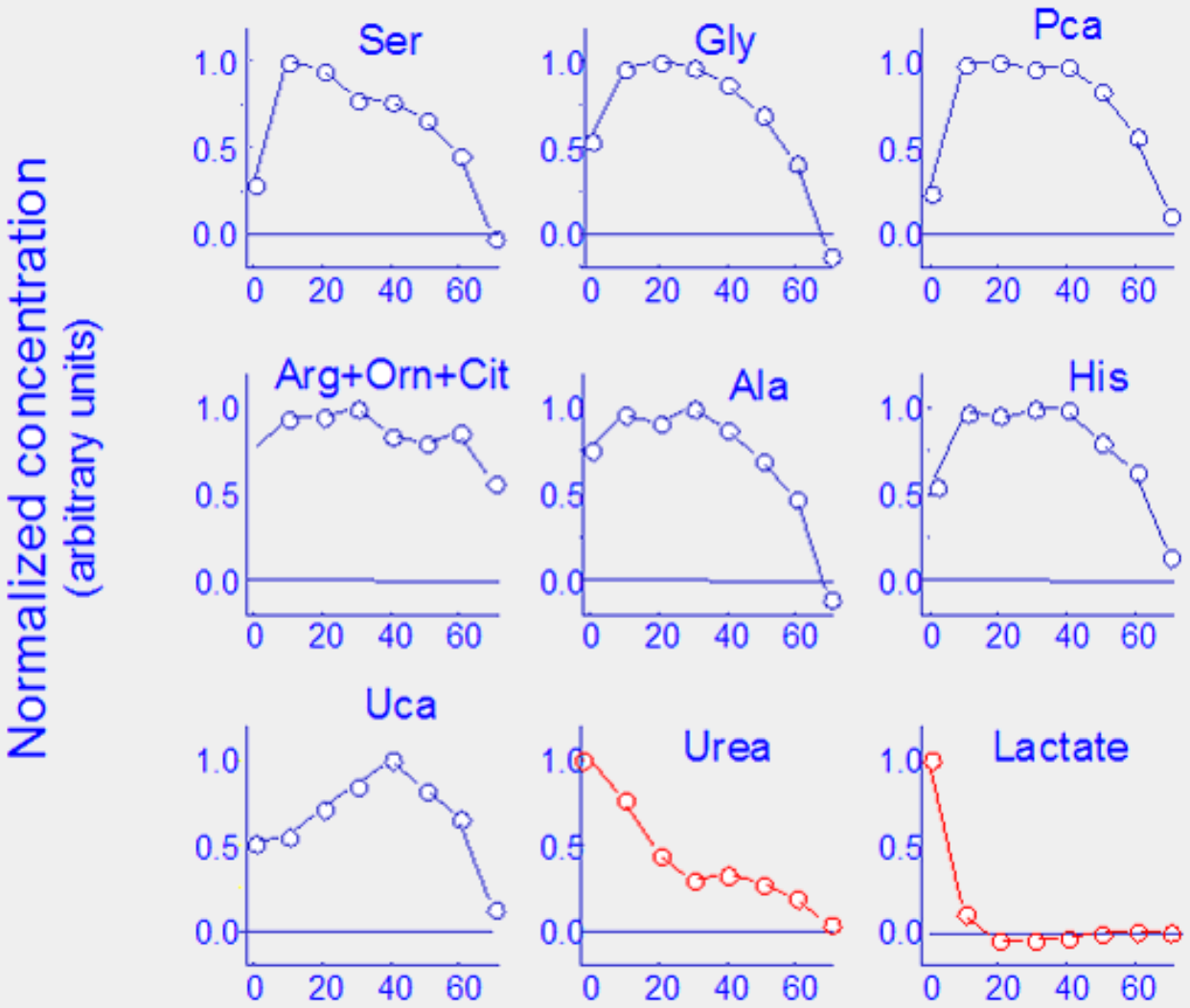
- **inorganic -** *corrosion layers, surfaces of hard discs, silicon*, *amorphous carbon, diamonds*
- **organic -** *supramolecular systems, environmental contaminants*
- **polymers –** *photo-labile materials*
- **biological** - *in vitro, in vivo*
- **geological -** *minerals, rocks*
- **archaeological -** from Paleolithic to Modern times

Materials studied

GEMMORAMAN	- 1980	gems
FRESCORAMAN	- 1980	inorganic dyes
ICONORAMAN	- 1985	organic dyes
PETRORAMAN	- 1995	stones
RESINORAMAN	- 1995	amorphous
TISSUERAMAN	- 1997	tissues
CERAMORAMAN	- 1998	ceramics
METALLORAMAN	- 1999	corrosion
VITRORAMAN	- 1999	glass samples
CLIMATORAMAN	- 1999	climatic aspects


FT Raman spectra of tissues
blood
brain
heart
kidney
liver
lung
muscle
spleen
tumor
Raman intensity
1700
1600
1500
1400
1300
1200
1100
1000
Wavenumber (cm-1)

SKIN ANALYSIS /Raman study



Caspers et al. :
Journal of Investigative Dermatology 116(3):434-442 (2001)

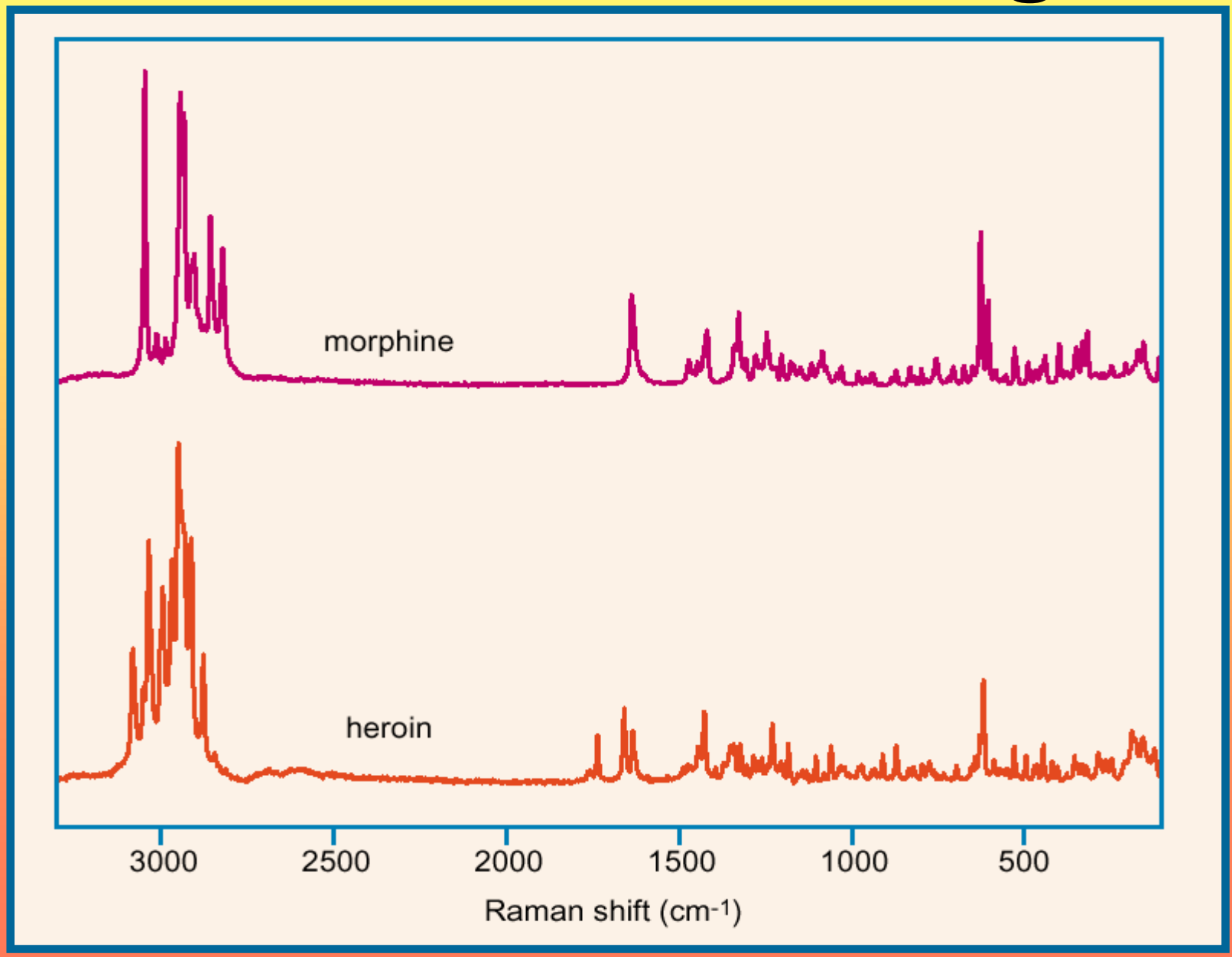
SKIN ANALYSIS /Raman study

River Diagnostics Model 3510 Skin Analyzer

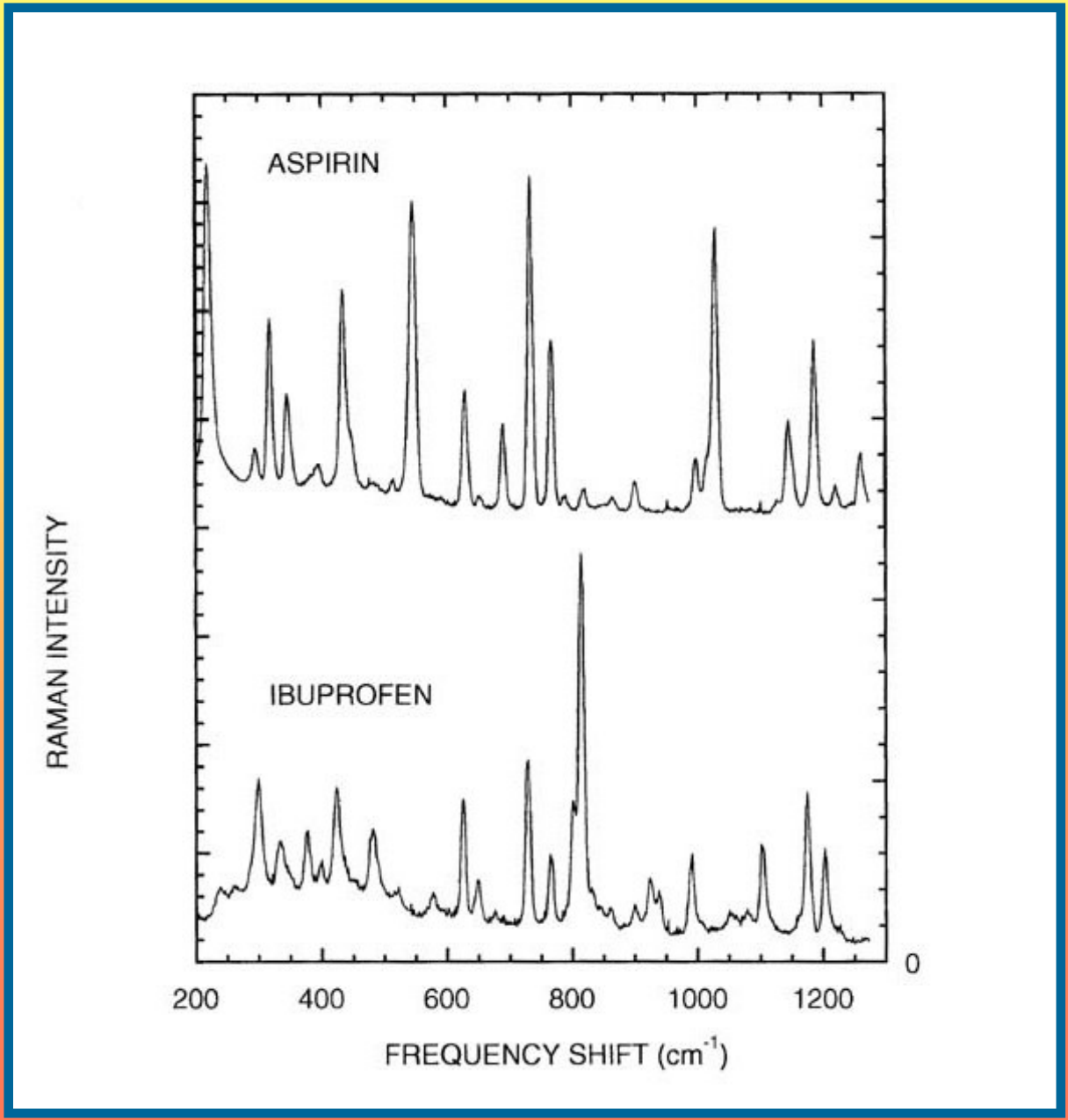
-

http://www.riverd.com/instrumentation.htm

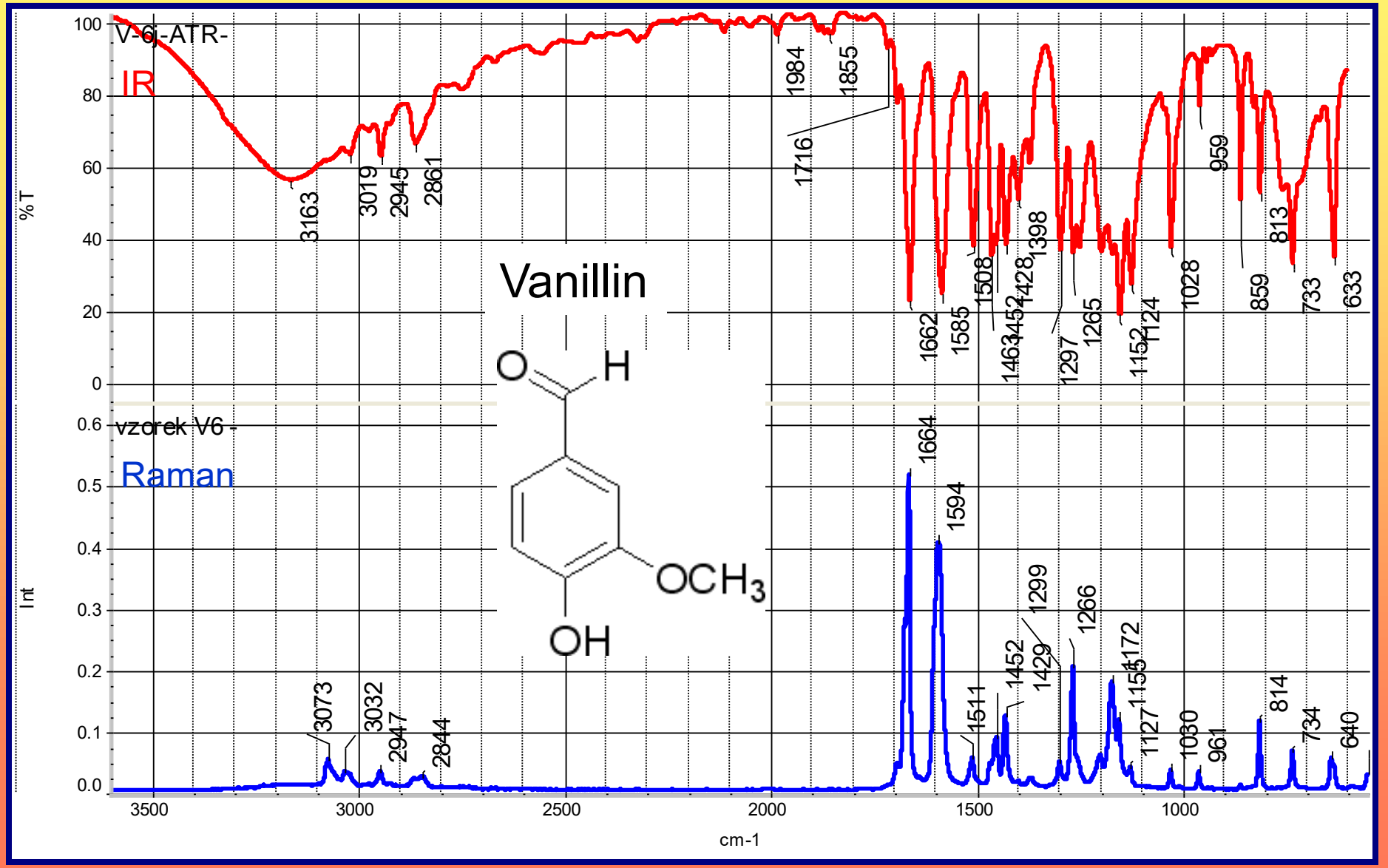
Identification of drugs



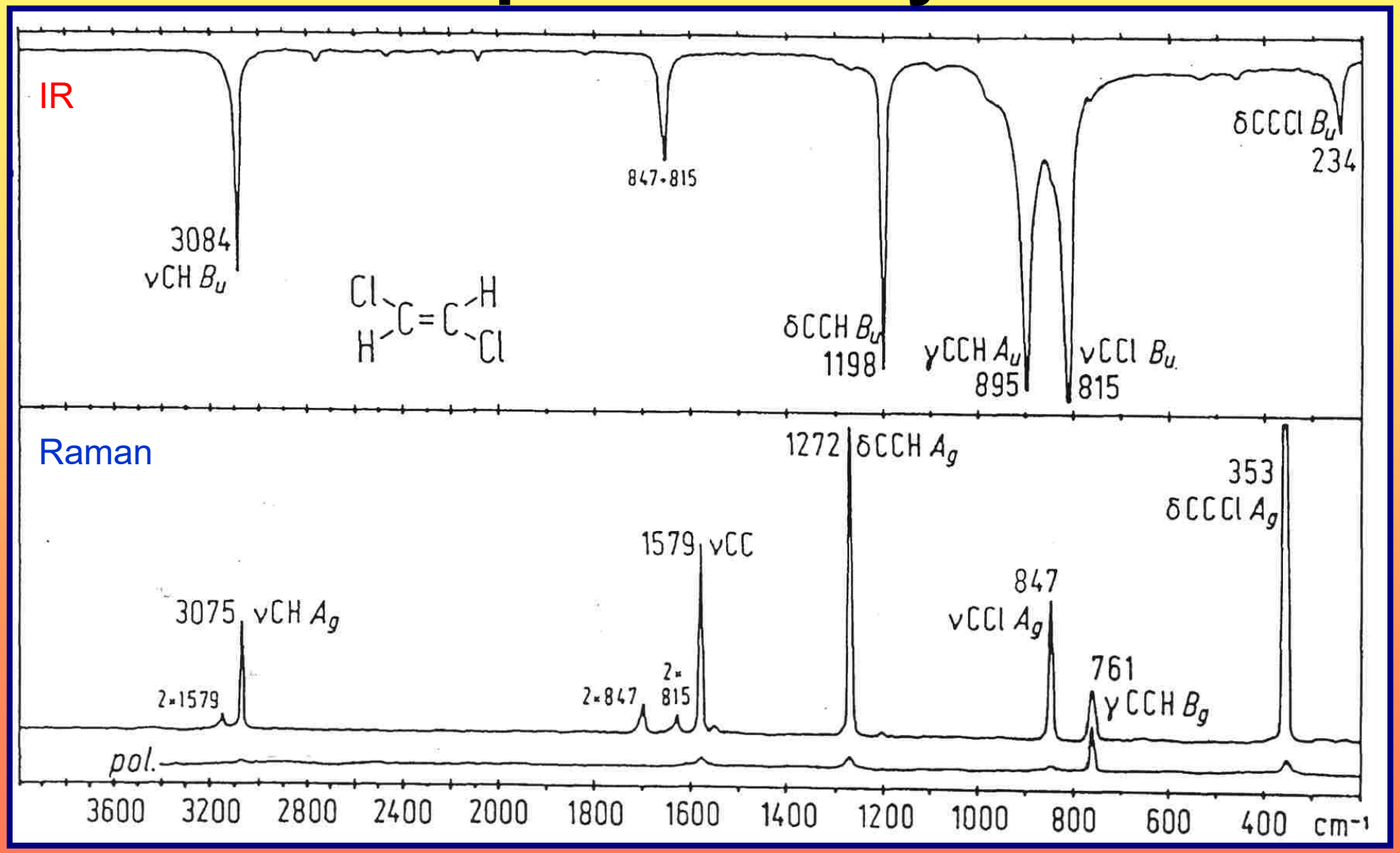
Identification of medicaments



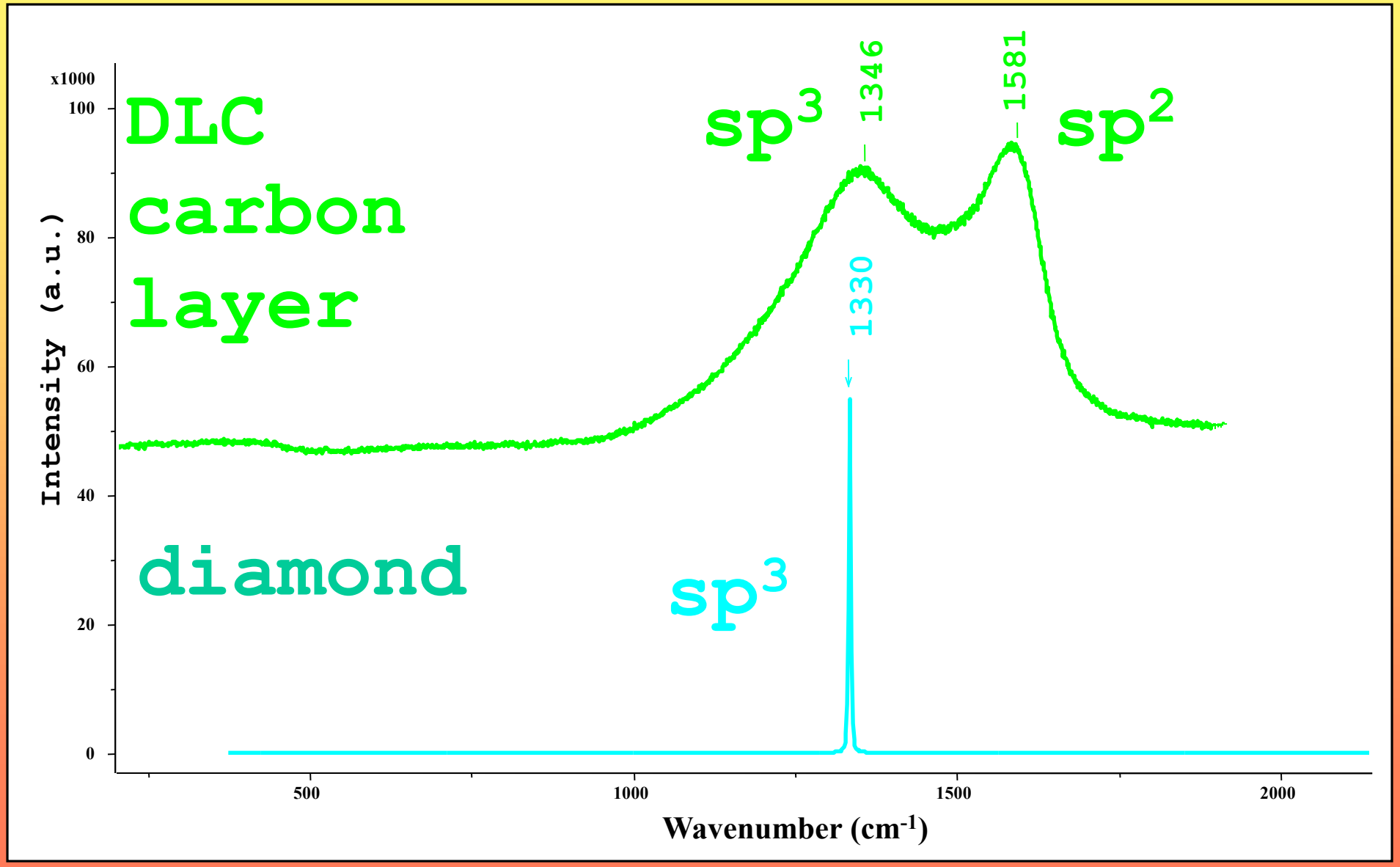
Comparison of IR and Raman spectrometry



Comparison of IR and Raman spectrometry

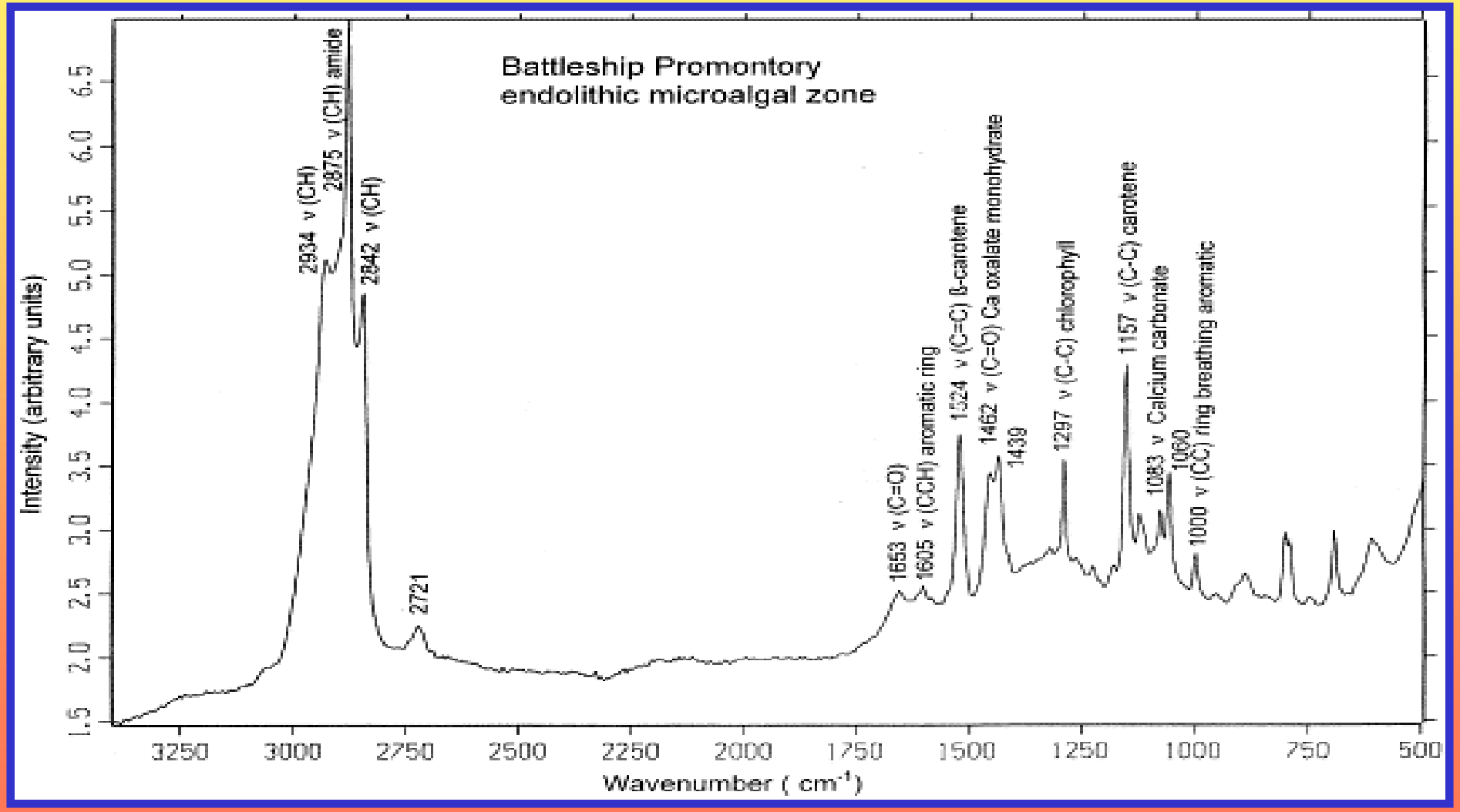


Raman spectrometry

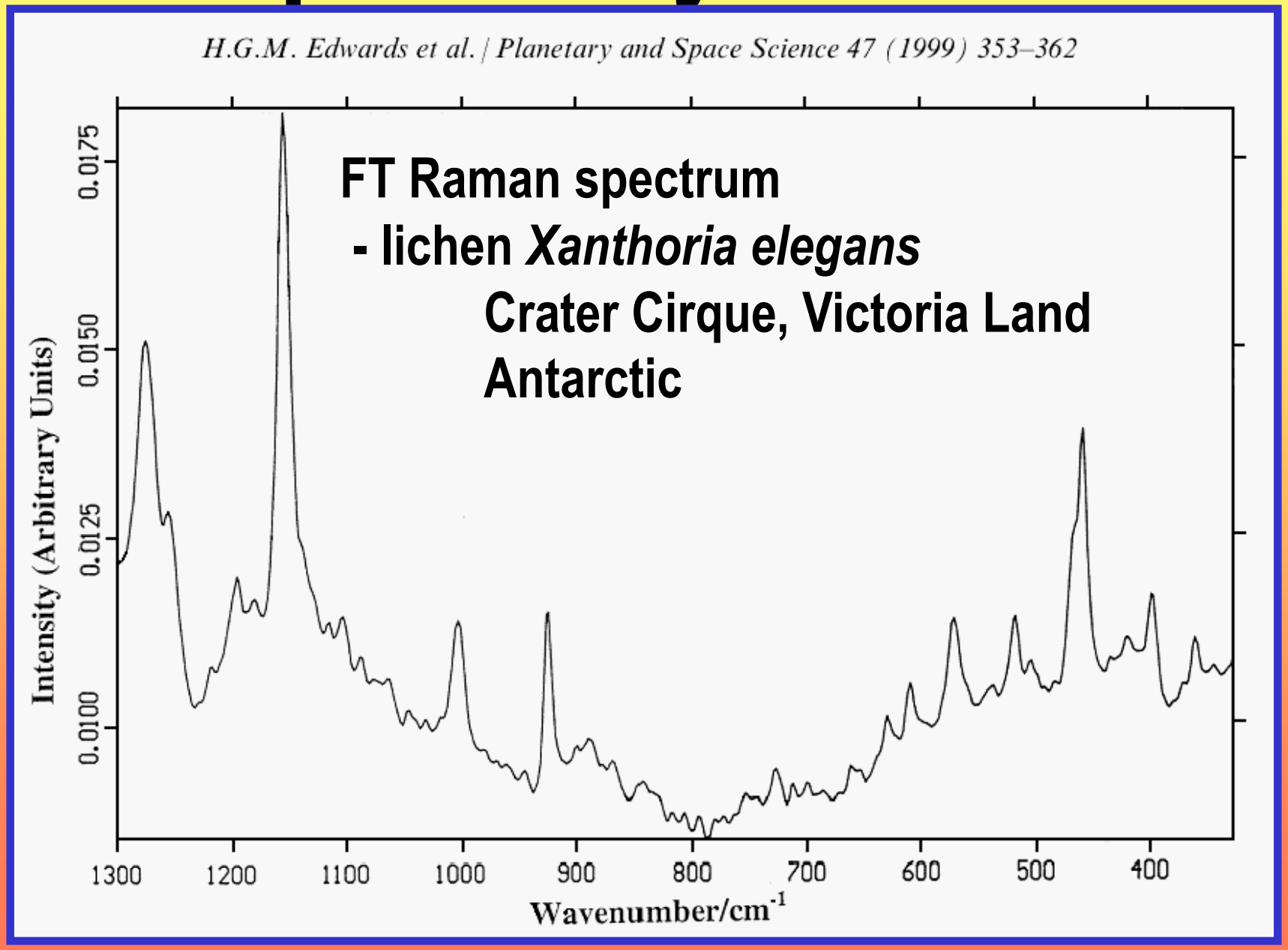


Raman spectrometry
- Antarctic studies

D.D. Wynn-Williams, H.G.M. Edwards
***Planetary and Space Science* 48 (2000) 1065.**



Raman spectrometry - Antarctic studies



Motion of atoms in a molecule
VIBRATION

INTERPRETATION
of VIBRATIONAL SPECTRA

- CHARACTERISTIC BANDS of FUNCTIONAL GROUPS

  * elucidation of type of skeleton and identification of substituents

- SPECTRUM used as „FINGERPRINT“

  * identification of PURE SUBSTANCES

    - SPECTRAL LIBRARIES

Normal vibration modes and characteristic vibration of functional groups

- **some vibrational modes are located only in a specific part of a molecule**
  - **vibration of groups with hydrogen (light atoms)**
  - **vibration of multiple bonds (bond strengths)**
  - **vibration of substituents: $-NO_2$, $-SO_2$, -P=S, (-S-S-), -C=S, -F, -Cl, -Br, -I**
  - **problem of vibrational coupling** (comparable mass of involved atoms and comparable bond strength)
  - **problem of symmetry**
  - **problem of surroundings on bond strengths** (band shifts)
  - **problem of rigidity of a structure, a question of conformers**

Normal vibration modes and characteristic vibration of functional groups

- **some vibrational modes are located only in a specified part of a molecule**

- **vibrations of groups containing hydrogen atoms**
  - **H-**C-C below 3000 cm^{-1} $-CH_3$, $-CH_2$, -CH
  - **H-**C=C 3100 – 3000 cm^{-1} $-C=CH_2$, -C=CH-, Ar
  - **H-**C≡C 3340 – 3280 cm^{-1} (3333 cm^{-1} C_2H_2, 3310 cm^{-1} $HC\equiv C-C_5H_{11}$)
  - H-O, H-N, H-S, H-B

Normal vibration modes and characteristic vibrations in Raman spectra

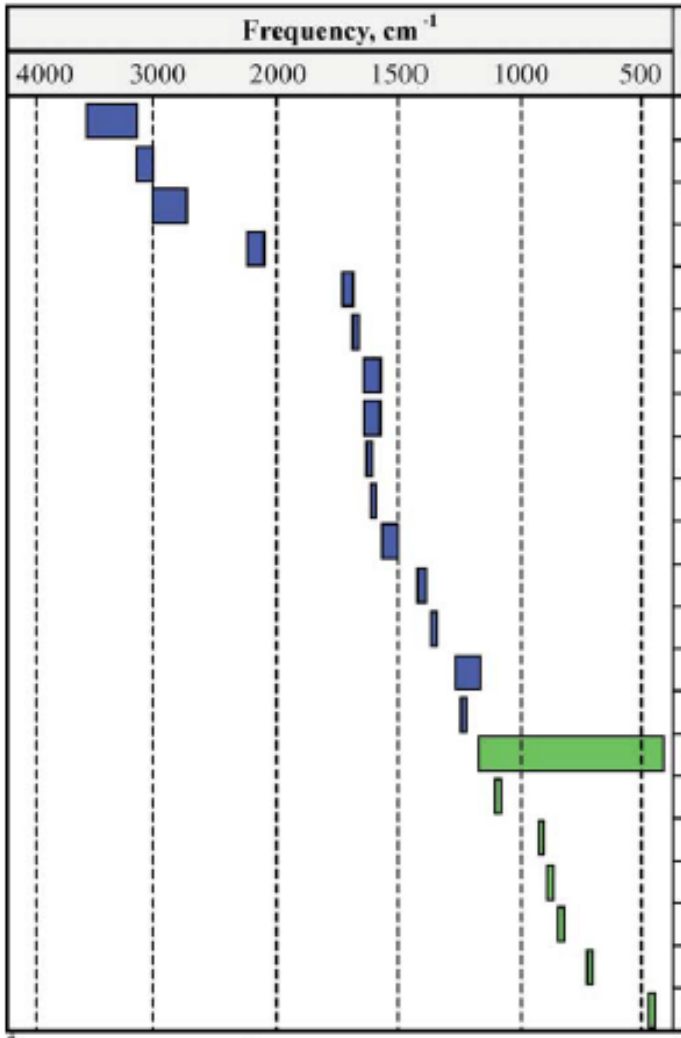
VIBRATIONS of CYCLIC SKELETONS

- **vibrations C-C – saturated cyclic hydrocarbons**
  - typical positions in Raman spectra
    - C_3H_6 1188 cm^{-1}
    - C_4H_8 1001 cm^{-1}
    - C_5H_{10} 886 cm^{-1}
    - C_6H_{12} 802 cm^{-1}
    - C_7H_{14} 732 cm^{-1}
    - C_2H_6 992 cm^{-1}

- **vibration of cycle – aromatic hydrocarbons**
  - 1050 – 990 cm^{-1} – „breathing“ vibration

(at ca. 1000 cm^{-1} typical strong band at monosubstitution, e.g. phenylalanin)

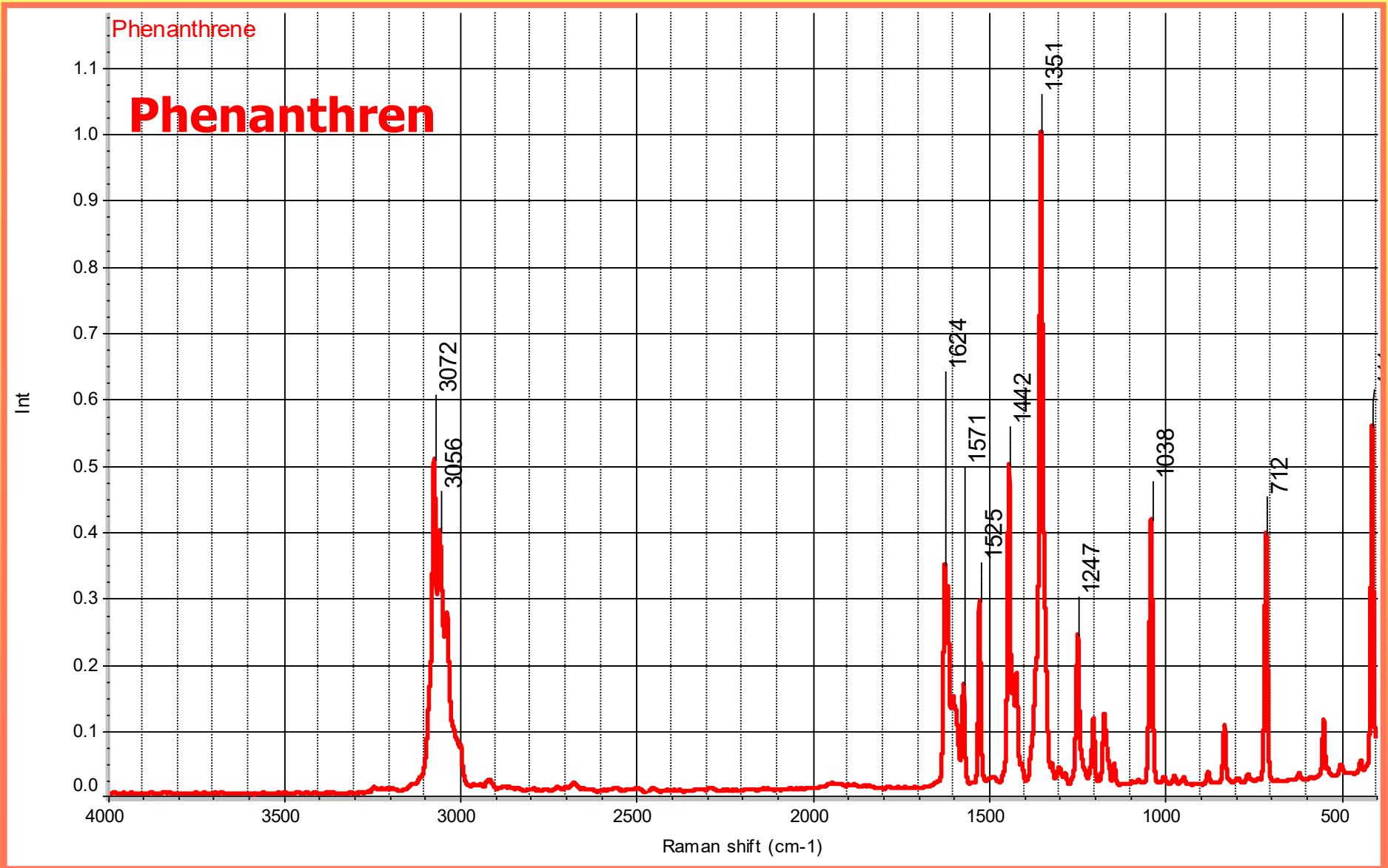
Normal vibration modes and characteristic vibrations in Raman spectra



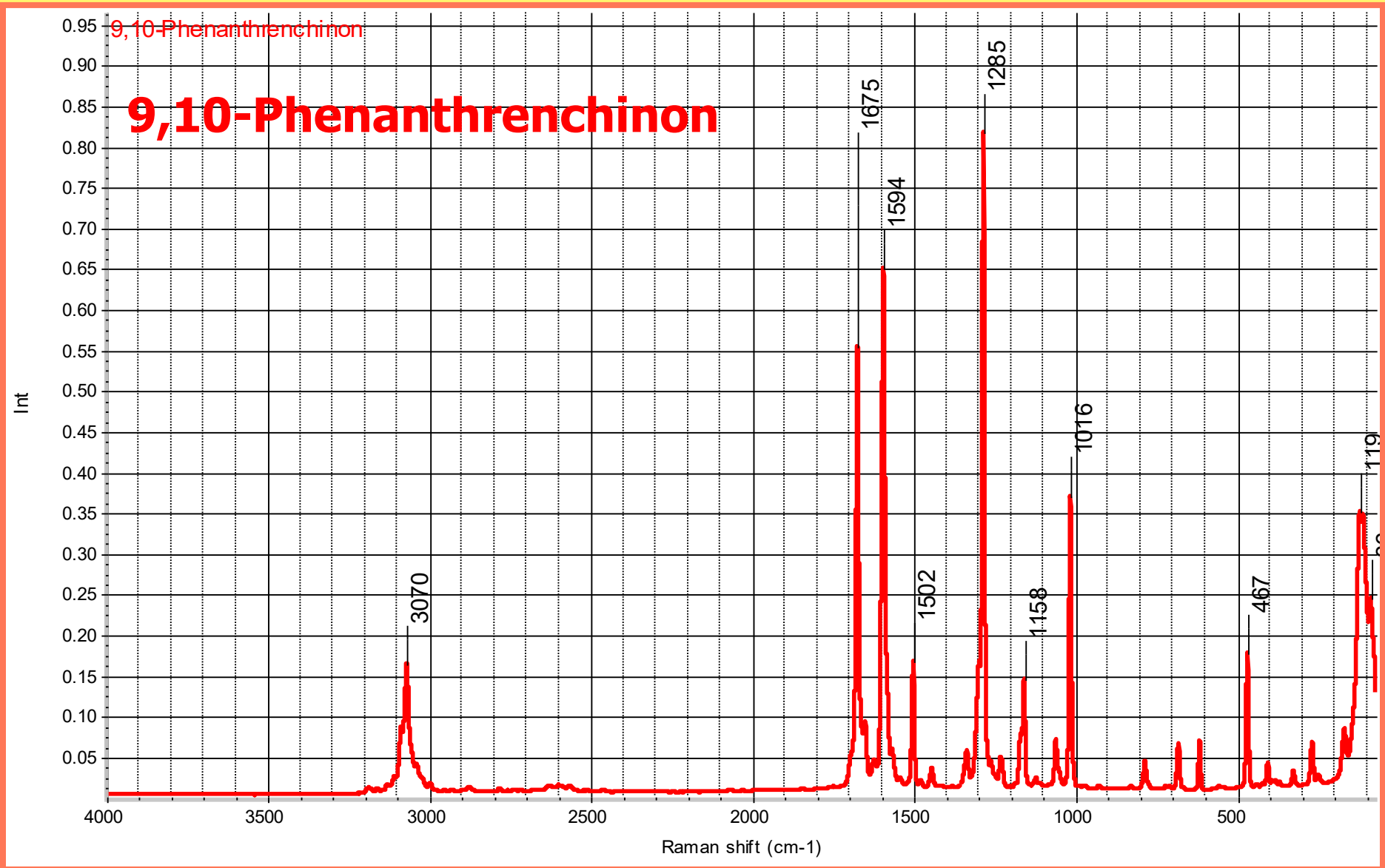
Group Vibration	Intensity#		Description	Mainly observed in
	IR	Raman		
O-H stretch	vs	vw	Hydroxyl	Liquid phase
=C-H stretch	s-m	m	Unsaturated	Lipids
-C-H stretch	s-m	m	Saturated	Lipids
-C≡N stretch	m	s	Nitrile	
C=O stretch	s	m-w	Ester	Lipids, Amino Acid
C=O stretch	s	w-m	Carboxylic acid	Lipids, Amino Acid
C=O stretch	s	m-s	Amide I	Proteins
C=C stretch	m-w	s	Not conjugated	Lipids
C=C stretch	m	s	*Trans*	Lipids
C=C stretch	m	s	*Cis*	Lipids
N-H bending	s	w	Amide II	Proteins
C-H scissoring	m	m-w	Aliphatic -CH_2	Lipids
C-O stretch	s		Carboxylates	Amino Acids, Lipids
N-H bending	w-m	var	Amide III	Proteins
P=O stretch	vs	m-w	Phosphate ester	Lipids, Nucleic Acids
	Fingerprint from skeleton			
C-O stretch	s	m-w	Ether	Carbohydrates
Skeletal mode		m	α-(1→4) linkage	Starch
C-O-C skeletal	m-w	m-w	β-configuration	Glucose, galactose, mannose
C-O-C skeletal	m-w	m	α-configuration	
C-H rocking	w-m	vw	Aliphatic -CH_2	Lipids
Skeletal mode		vs		Starch

s = strong, m = medium, vs = very strong, vw = very weak

Motion of atoms in a molecule



Motion of atoms in a molecule



IR and Raman spectra