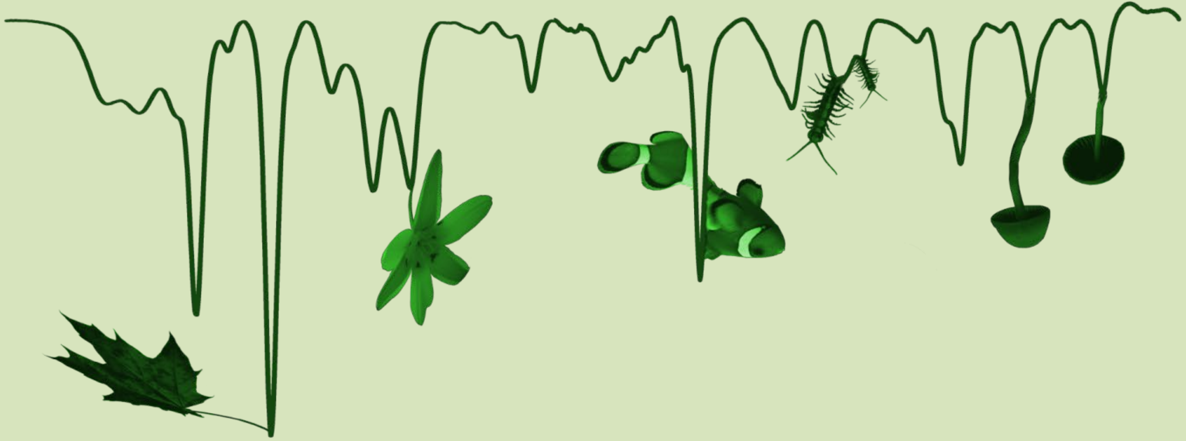
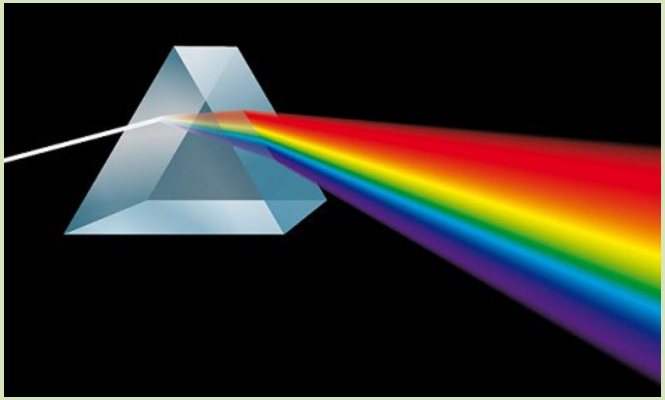


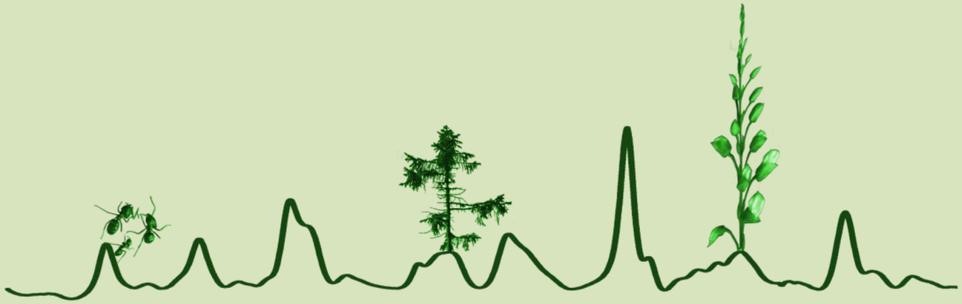
NICOLET CZ
MOLECULAR SPECTROSCOPY

Infrared and Raman spectroscopy basics

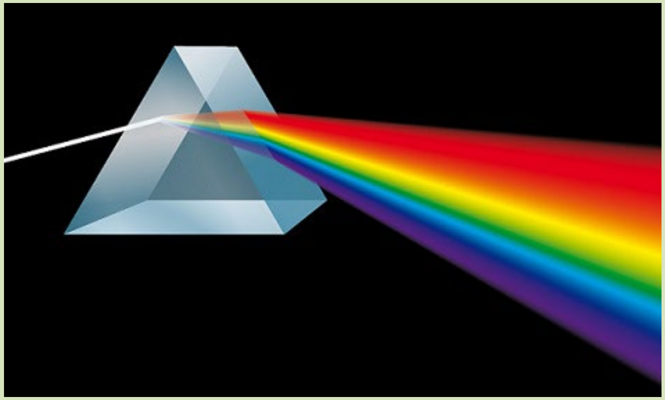


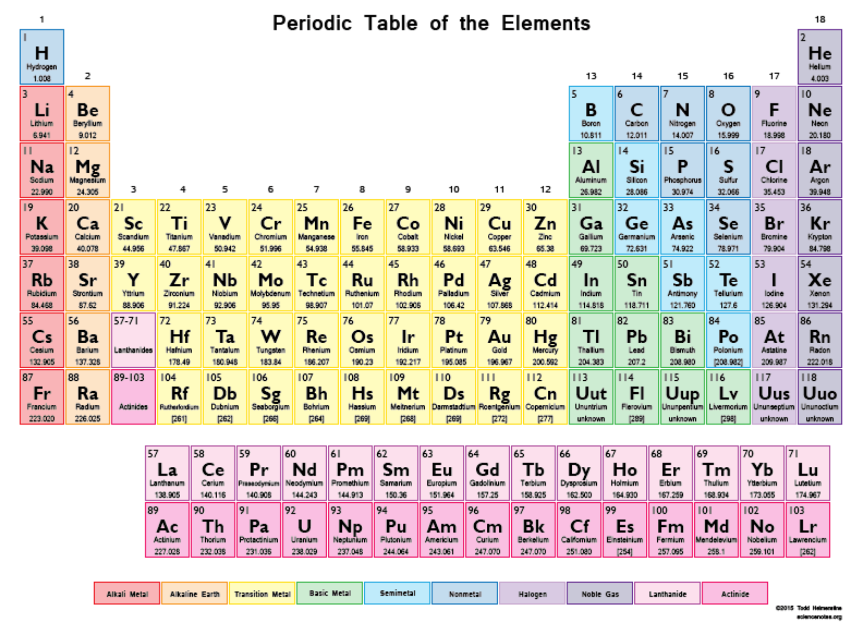
Ing. Karel Šec, PhD.
sec@nicoletcz.cz

Baptism of Fire, Brno 2023



What is spectroscopy?





Periodic Table of the Elements

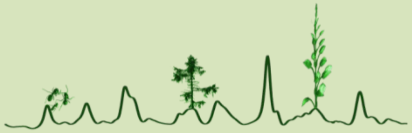
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.631	33 **As** Arsenic 74.922	34 **Se** Selenium 78.971	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.798
37 **Rb** Rubidium 84.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.414	49 **In** Indium 114.818	50 **Sn** Tin 118.711	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.294
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.328	57-71 Lanthanides	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103 Actinides	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Uut** Ununtrium unknown	114 **Fl** Flerovium [289]	115 **Uup** Ununpentium unknown	116 **Lv** Livermorium [298]	117 **Uus** Ununseptium unknown	118 **Uuo** Ununoctium unknown
		57 **La** Lanthanum 138.905	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.243	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.055	71 **Lu** Lutetium 174.967	
		89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]	

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetal | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide

Light = electromagnetic radiation

Study of interaction of light with matter (sample) with resulting aim of obtaining an optical "spectrum" that "reflects" the properties of the sample in a defined way......

Matter: elements versus molecules



Molecular spectroscopy

Monitoring the interaction of different types of radiation with an unknown substance - molecule.

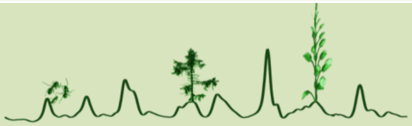
Use of observed phenomena in order to:

- **Identification**
- **Study of molecules structure and behavior**
- **Determination of concentration of different components - molecules**

Important note: molecular versus atomic spectroscopy

WHY?

Atomic	Molecular
Interaction between atoms and electromagnetic light	Interaction between molecules and electromagnetic light
Line spectra	**Complicated band spectra**
Electron transitions in elements / atoms	Vibrational, rotational and electronic transitions in molecules

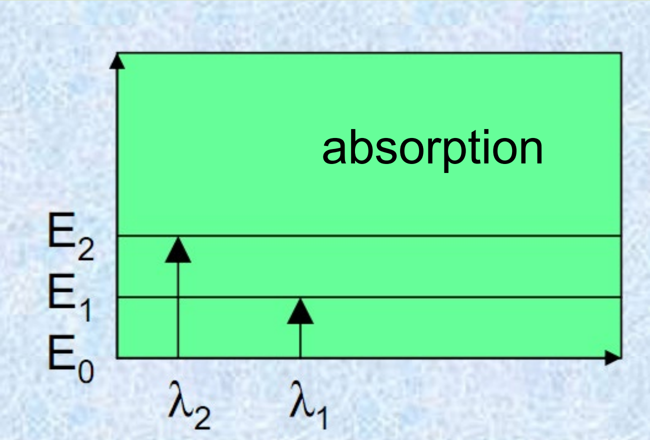


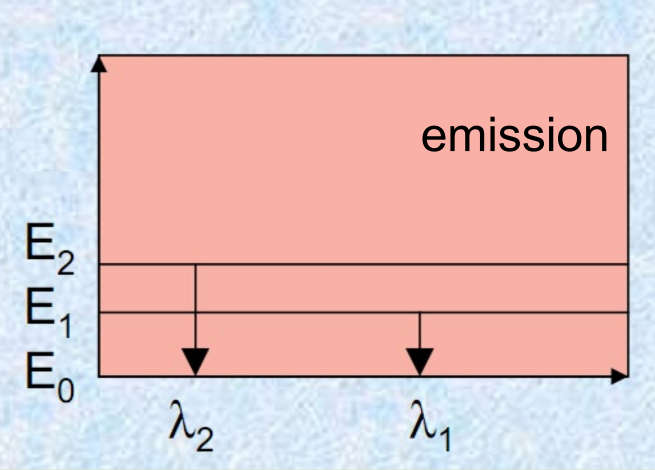
Molecular spectroscopy

WHY? ⟷

Atomic spectroscopy	Molecular spectroscopy
Line spectra	**Complicated band spectra**

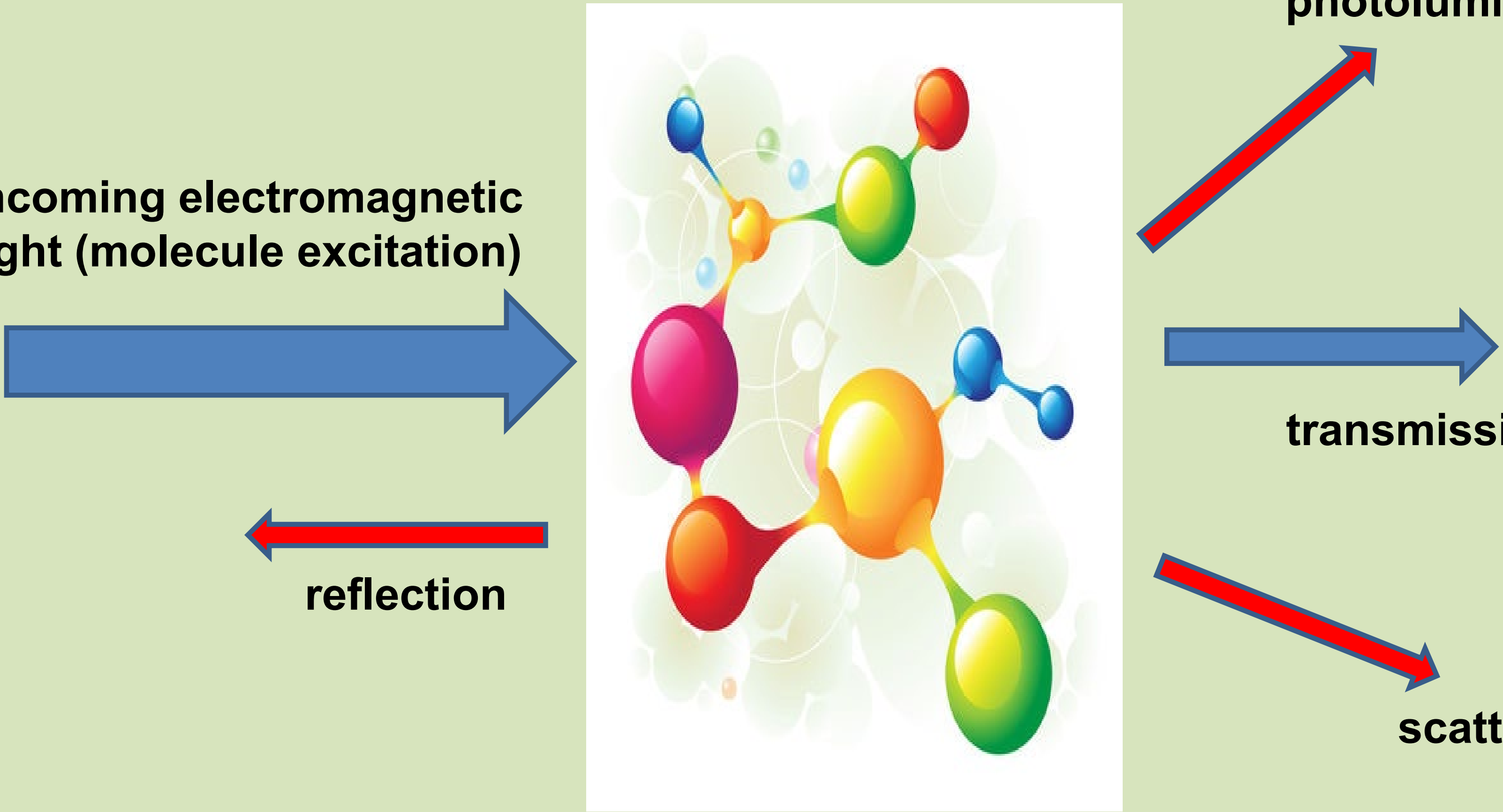
Electrons in an atomic orbital can acquire only certain (different) energies, and the transition of an electron from one orbital to another by receiving (absorption) or giving up (emission) a photon with an energy corresponding to the difference between the energy levels





In an atom, as a result of the emission or absorption of electromagnetic radiation, only the distribution of electrons in the respective atomic orbitals changes, not the rotational and vibrational states...!

Molecular spectroscopy: Measurements (spectrometers) according to (observed) behavior of radiation



Incoming electromagnetic light (molecule excitation)

reflection

photoluminescence

transmission

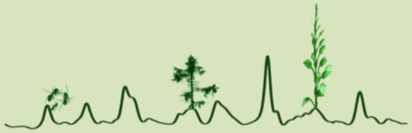
scattering

Absorption

Spectrometry techniques, generally……

- Measures how much electromagnetic radiation (light) is absorbed, emitted, or diffusely reflected by a sample
  - intensity and wavelength of the light is controlled and subsequently measured by measurement device - spectrometer
  - results of the measurements – the spectra – are highly characteristic for the sample, sometimes one can even speak about fingerprint.

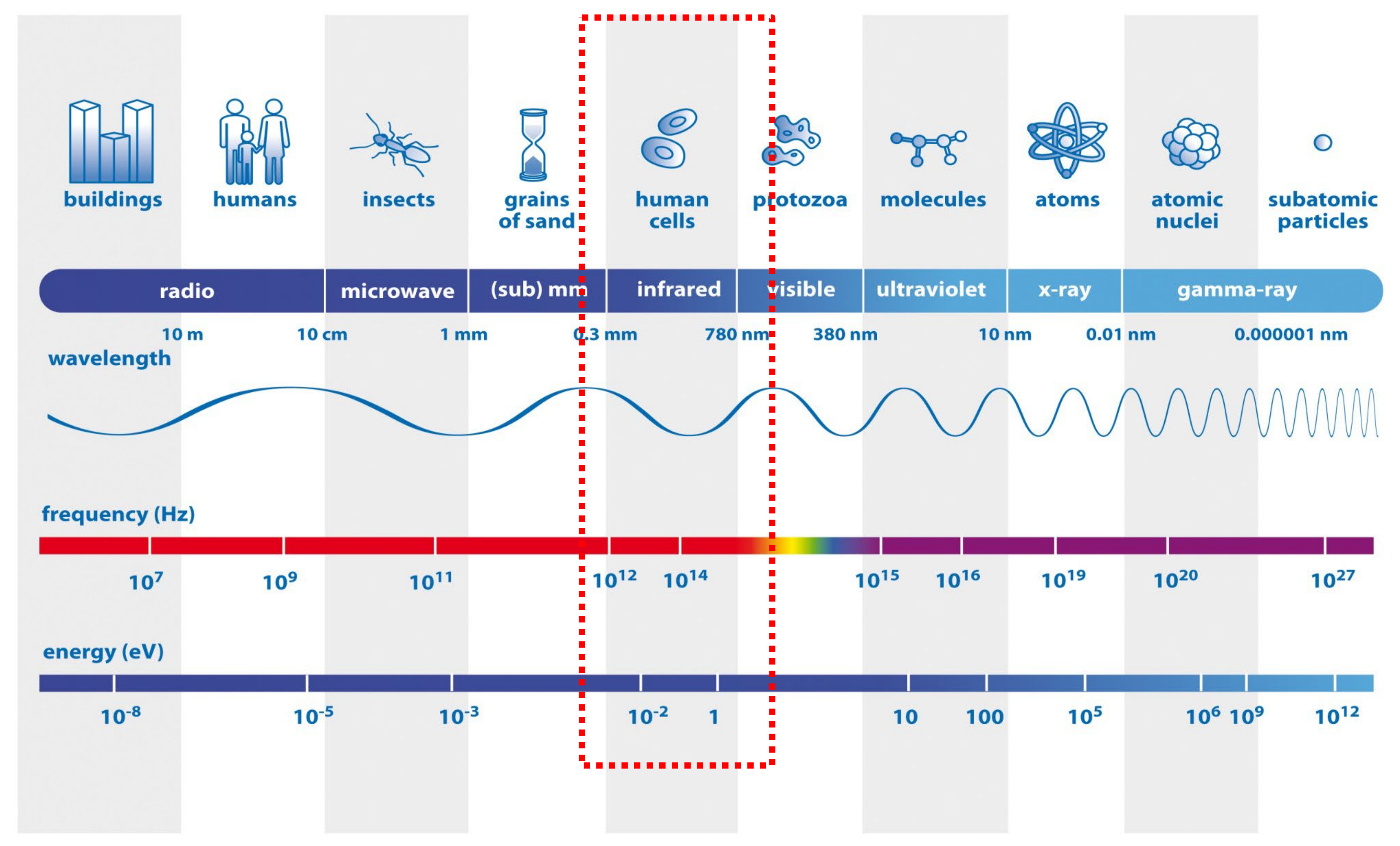
- Main measurements principles
  - **Absorption** – how much of electromagnetic light was absorbed by sample and on what frequency? F.e. **Infrared spectroscopy**
  - **Fluorescence and Emission** – sample is emitting new kind of radiation after excitation of molecule by light, heat, electricity etc. F.e. **Raman spectroscopy**



Molecular spectroscopy types

Technique	What we measure	App examples
Ultraviolet and Visible spectroscopy: UV-VIS	Electron molecular absorption	Quantitative analysis of unsaturated inorganic substances and some colored inorganic substances
Fluorimetry	Fotoluminiscence. Absorbed radiation emitted by higher (longer) wavelengths	Routine quantitative organic analysis, often more sensitive than UV-VIS. Biochemistry / bioimaging
Infrared spectroscopy: IR, FTIR	Vibrational-rotational molecular spectroscopy	Identification, quantification and study of organic and inorganic molecules
Raman spectroscopy	Vibrational-rotational molecular spectroscopy	Identification, quantification and study of organic and inorganic molecules
Nuclear magnetic resonance: NMR	Nukleární absorption: change of the spin state of atomic nuclei by a magnetic field	Identification, quantification and study of mostly organic molecules
Mass spectroscopy	Ionization and fragmentation of molecules	Identification, quantification and structural study of mostly organic molecules

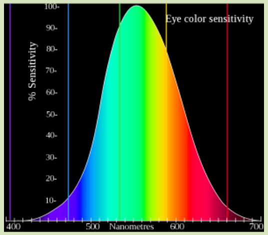
Molecular spectroscopy



http://solar-center.stanford.edu

NICOLET CZ
MOLECULAR SPECTROSCOPY

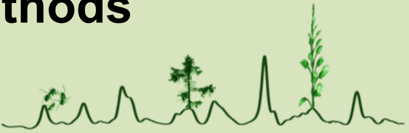
Molecular spectroscopy



"Anthropocentric" division: nomenclature according to proximity to what the human eye can see……

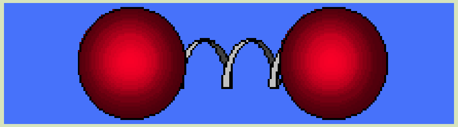
	λ (micrometers)	Wavelength (cm^{-1})	Note
UV – VIS area	0,19 – 0,8	53 000 – 12 500	Electron absorption
Near infrared area: NIR, FT-NIR spectroscopy	0,8 – 2,5	12 500 – 4 000	Higher absorption harmonic transitions
Mid infrared area MIR, FT-IR spectroscopy	2,5 – 25	4 000 – 350	Normal vibration transitions
Far infrared area: FIR, FT-FAR spectroscopy	25 - 1000	350 – 10	Lattice vibrations, inorganic mostly

Raman spectroscopy: approx. 8 000 – 2 cm^{-1}, usually systems 3 500 – 40 cm^{-1}
Compatibility with IR, FT-IR spectra – complementary methods



The physical nature of molecular spectroscopy

✓ Chemical bonds can be represented like oscillating springs connecting atoms.



✓ Absorption of infrared radiation leads to a change in the rate of oscillation.

✓ Absorption of radiation occurs only when it induces a permissible change in the rate of vibration for the measured molecule.

✓ Position of absorption peaks in spectra is determined via: atomic mass, bond strength, surrounding bonds in the molecule

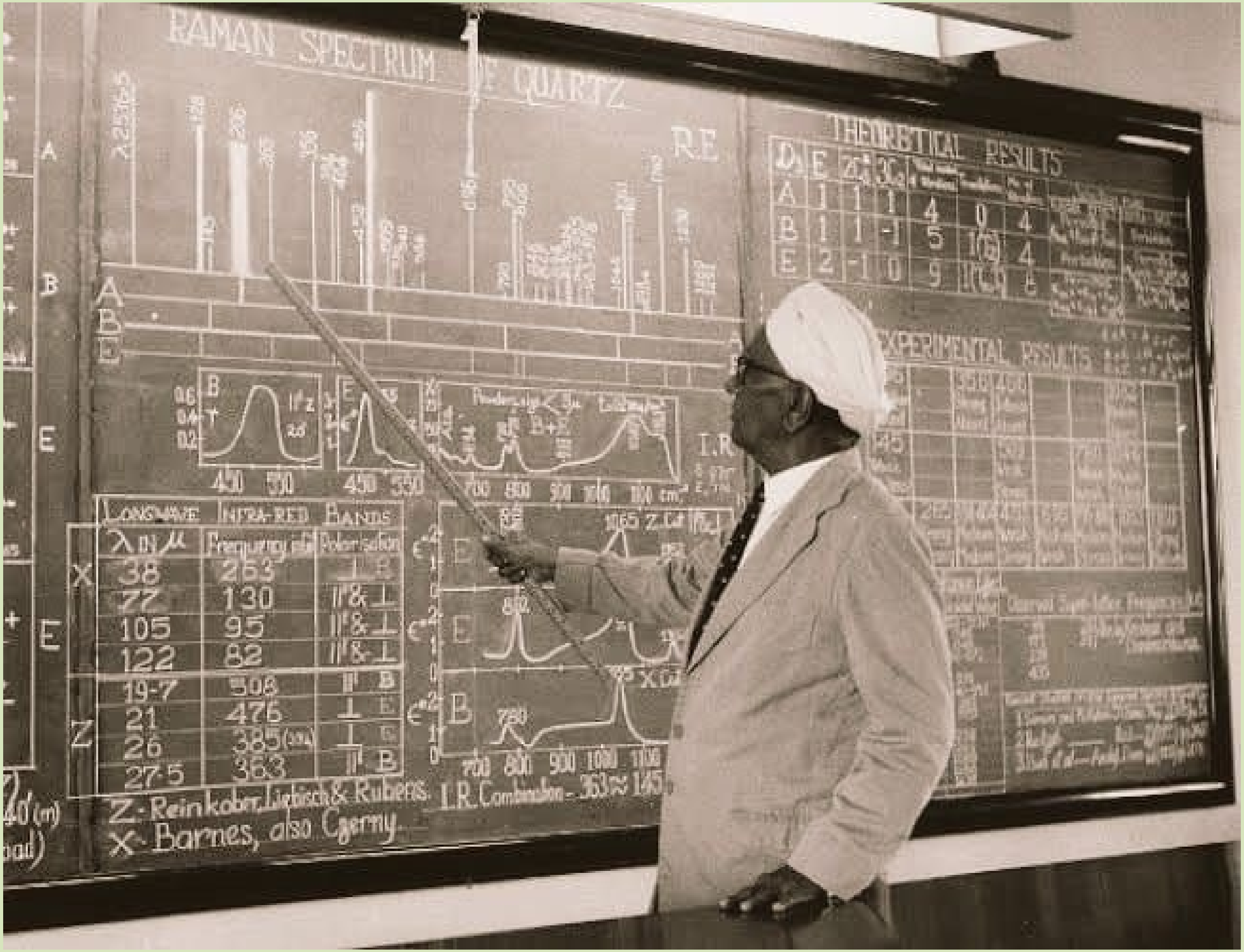
Sir Chandrasekhara Venkata Raman
1888 – 1970

Nobel price in physics 1930

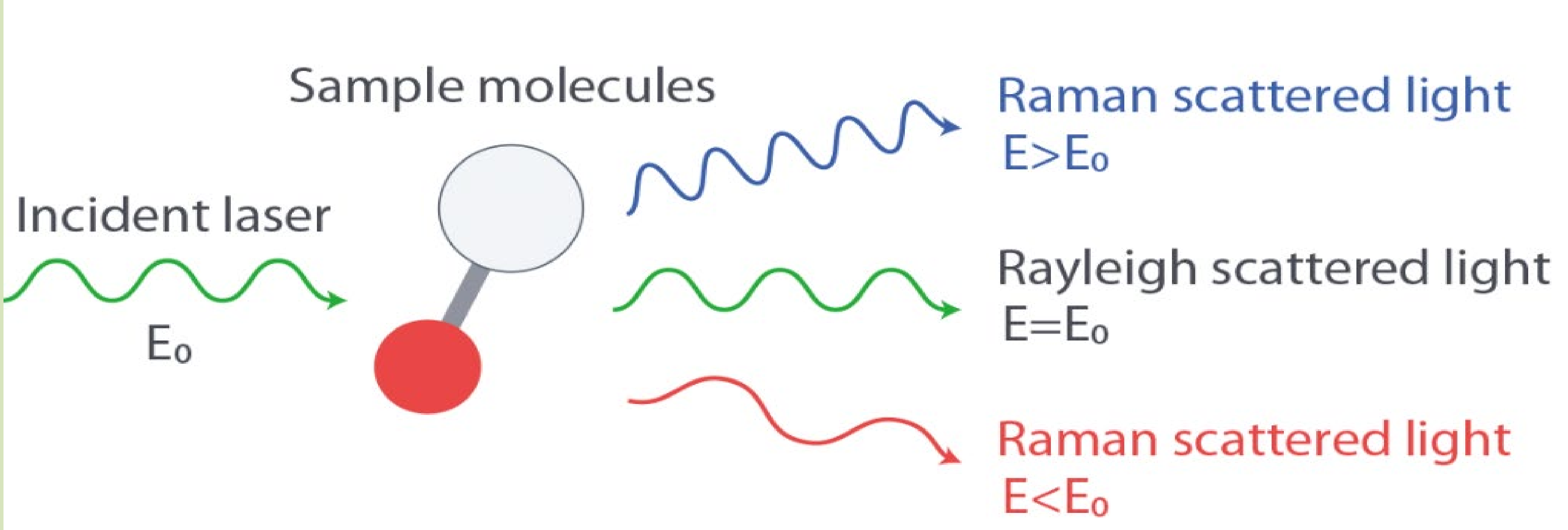
A New Type of Secondary Radiation

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 wavelength as the incident beam, is accompanied **<u>by a modified scattered radiation of degraded frequency</u>**.


RAMAN SPECTRUM OF QUARTZ
R.E.
THEORETICAL RESULTS
EXPERIMENTAL RESULTS
I.R.
LONGWAVE INFRA-RED BANDS
λ IN μ
Frequency
Polarisation
38 263
77 130
105 95
122 82
19·7 508
21 476
26 385
27·5 363
Z- Reinkober, Liebisch & Rubens.
X- Barnes, also Czerny
I.R. Combination

The physical nature of Raman spectroscopy



Sample molecules

Incident laser

E_0

Raman scattered light

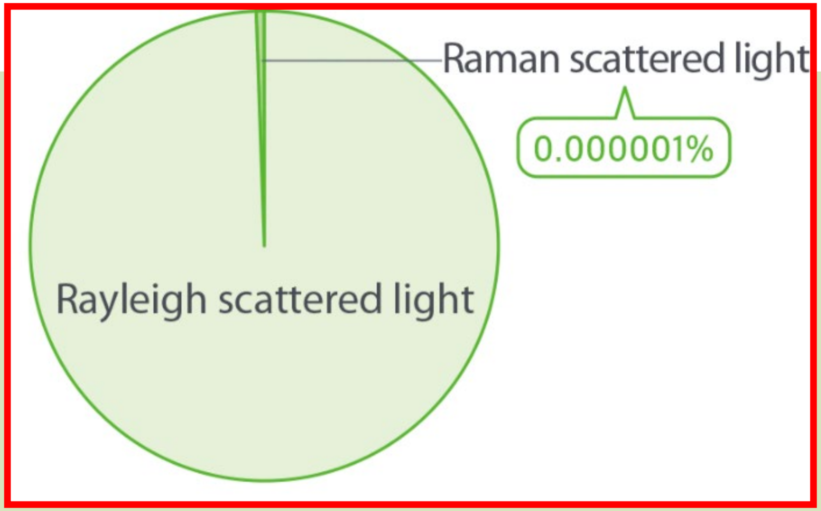
$E>E_0$

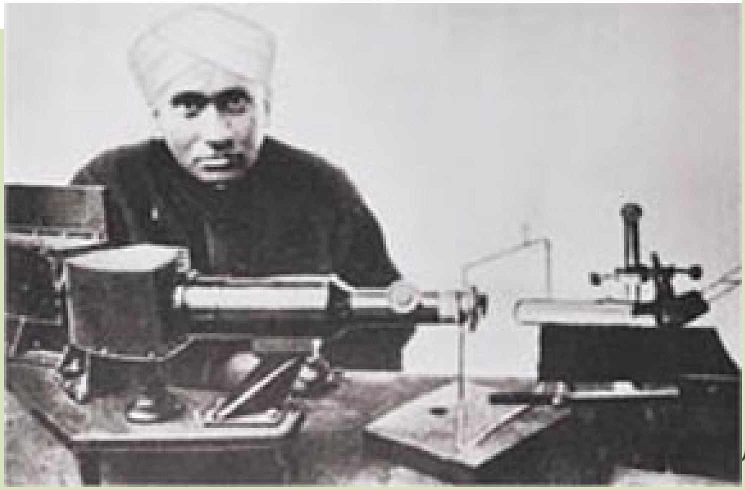
Rayleigh scattered light

$E=E_0$

Raman scattered light

$E<E_0$



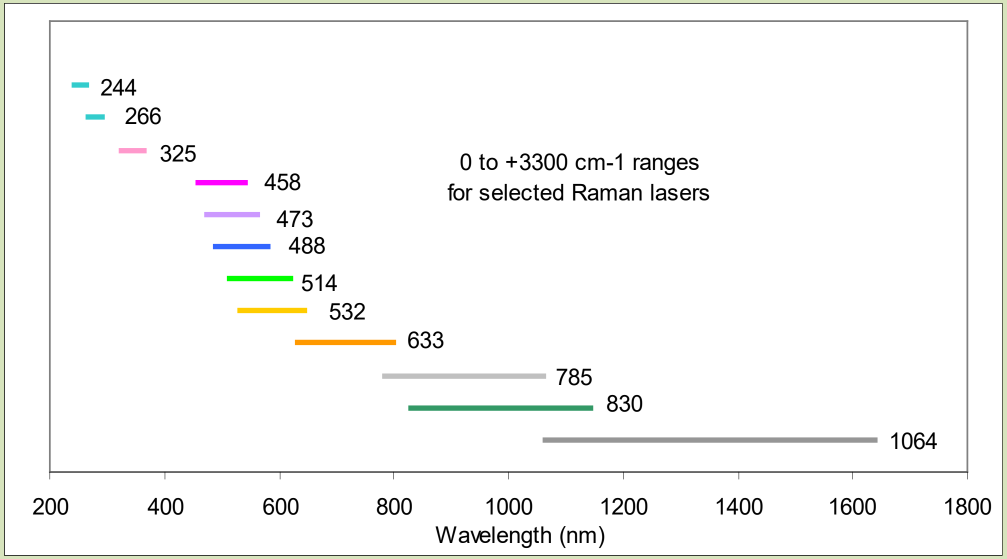


The physical nature of Raman spectroscopy

The vibrational frequencies of molecules are independent of whether we study them with infrared or Raman spectroscopy, but the intensities of the spectral lines will be for both spectroscopic techniques distinctly different.

One of the main difference is type of light forcing on sample:

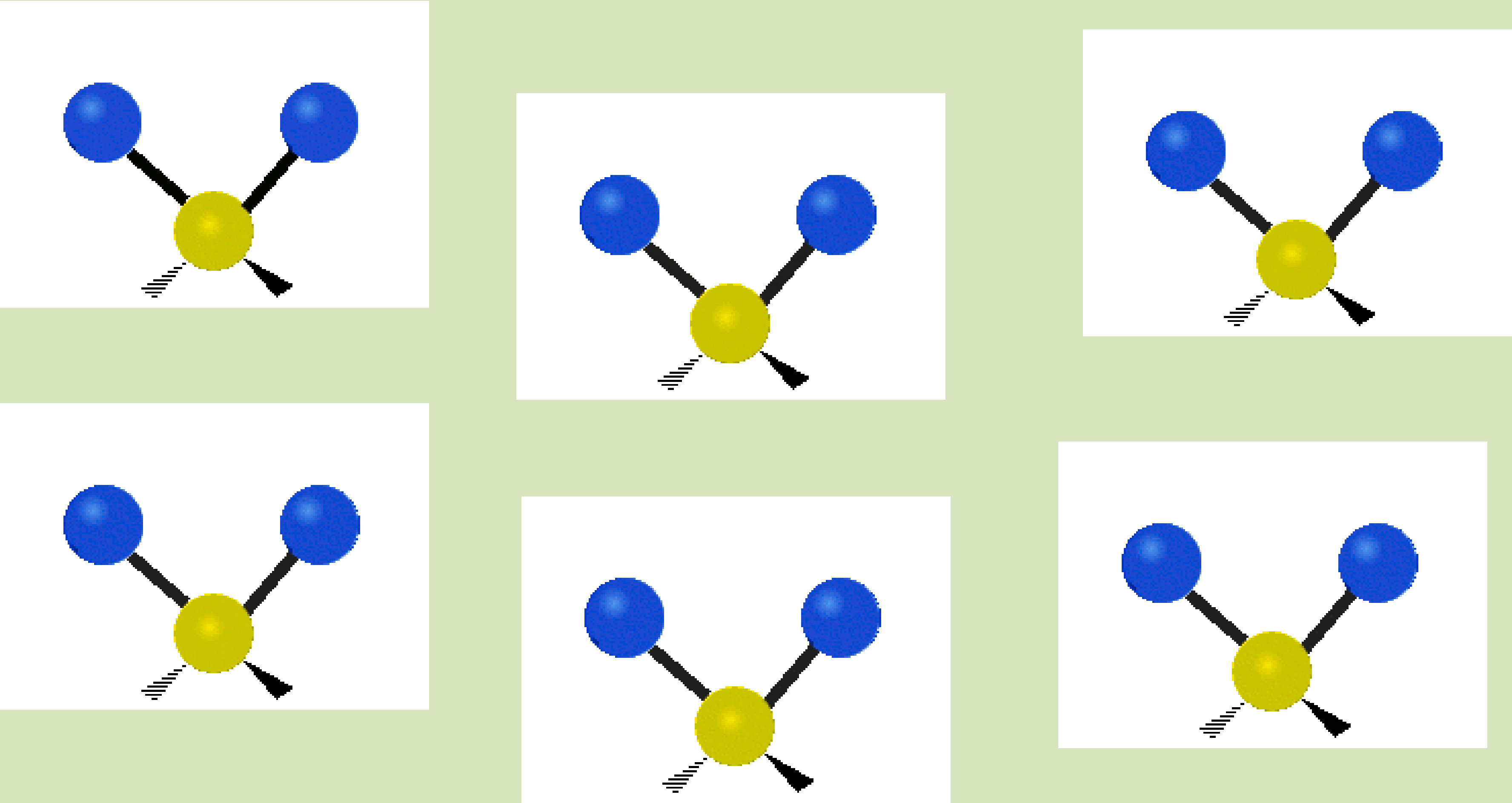
- **FTIR = polychromatic light (heated ceramics, diodes etc.)**
- **Raman = monochromatic light - LASERS**



Infrared (FT-IR) versus Raman

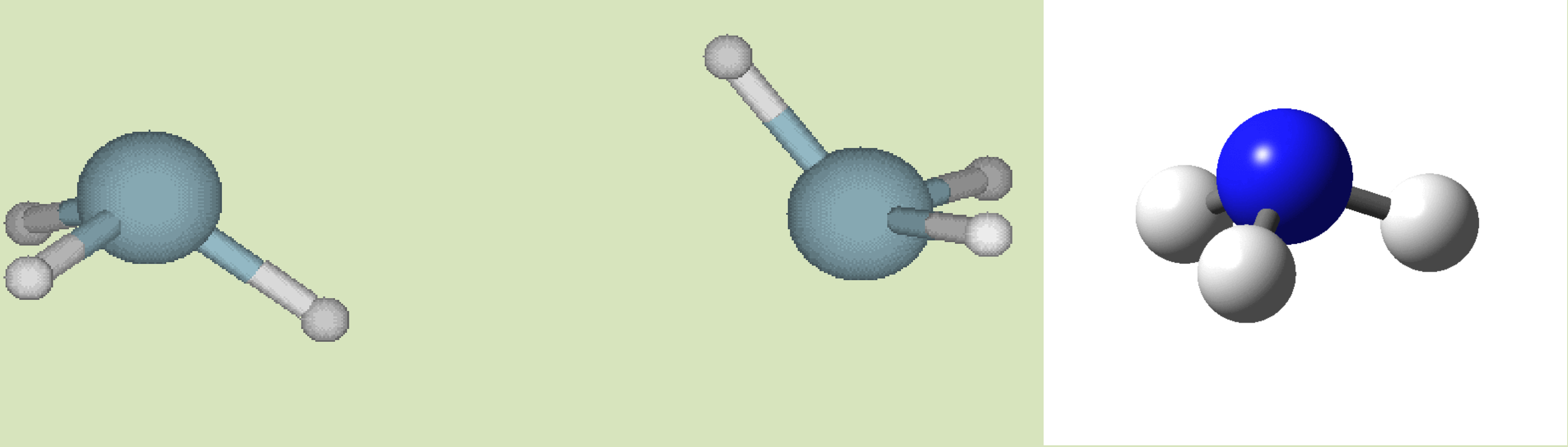
Raman	IR
Dispersion of light by vibration of molecule	Absorption of light by vibration of molecule
Molecule vibration is active in Raman spectrum only with change of polarizability	Molecule vibration is active in IR spectrum only with change of molecule dipole moment
Mikroscopy with resolution around 0,5 micrometers	Microscopy with resolution around 15 micrometers (diffraction limit)
Water is not a problem	Water have huge absorption in IR spectrum, that is problem with water as solvent
Usually no sample preparation, even possibility of measurement through different materials (packaging etc.)	Sample preparation could be challenging: KBr pellets, cutting of samples, solvents, extractions etc.
Molecular backbone is dominant -S-S-, -C-S-, -C=C- etc.	End groups of molecules – intense signal in spectrum (peaks)
Indication of covalent character of molecule	Indication of ion character of molecules
Better measurement range: FAR-IR (400 – 50 cm^{-1}) is not a problem (inorganics!)	FAR-IR is very challenging technique
Could be very expensive (lasers etc.)	Price usually lower than Raman

Classification of basic vibrations types
Vibration, rotation = peaks: IR or Raman spektrum!



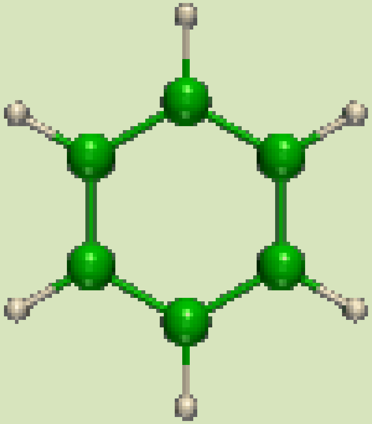
Classification of basic vibrations types

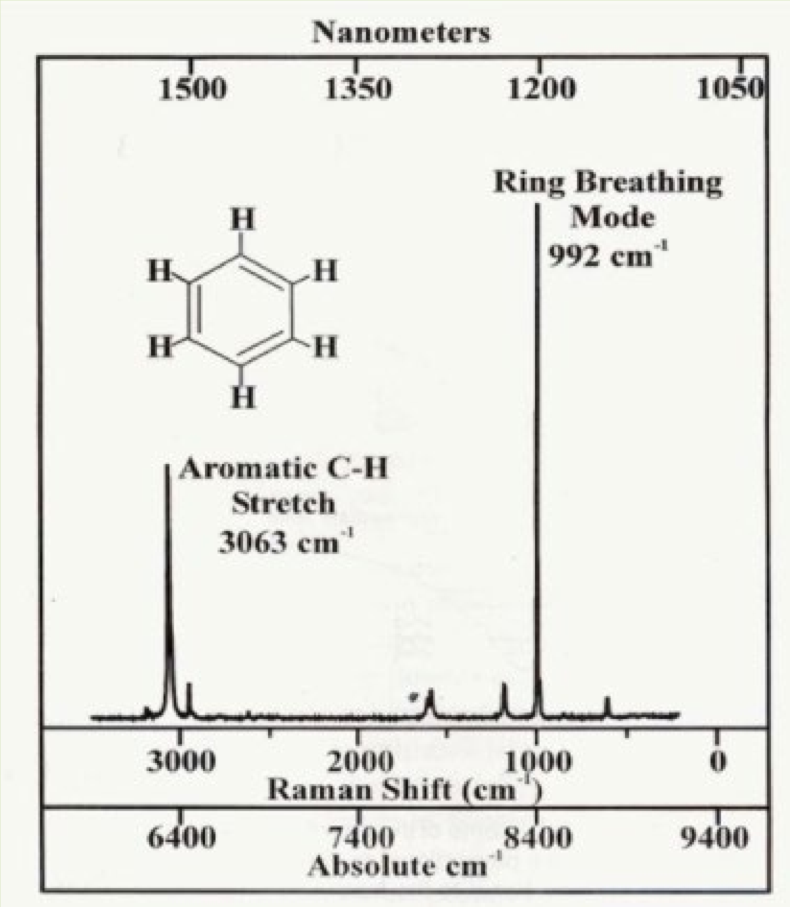
Umbrella vibration of NH_3
(out of plane bending….)



Classification of basic vibrations types

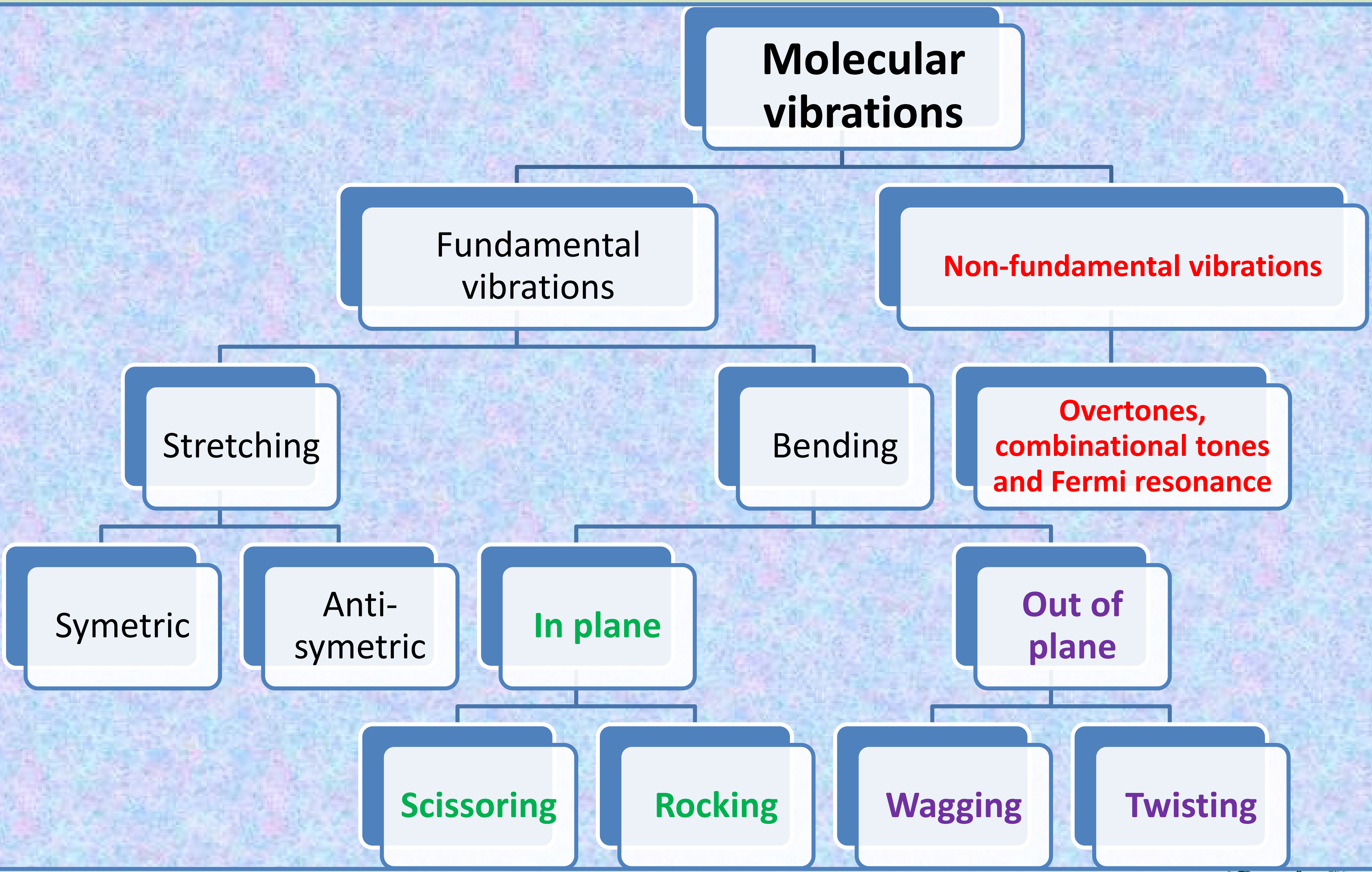
Breathing vibration of benzene





1050 – 990 cm^{-1} = breathing vibration

Classification of basic vibrations types



Molecular vibrations

Fundamental vibrations

Non-fundamental vibrations

Stretching

Bending

Overtones, combinational tones and Fermi resonance

Symetric

Anti-symetric

In plane

Out of plane

Scissoring

Rocking

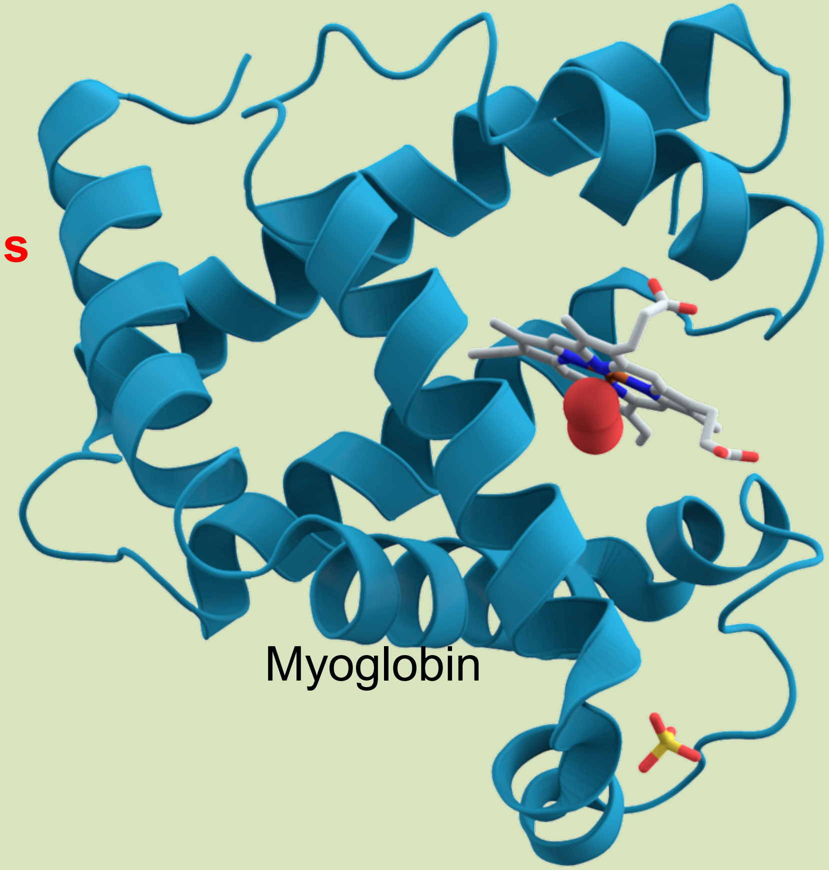
Wagging

Twisting

Classification of basic vibrations types

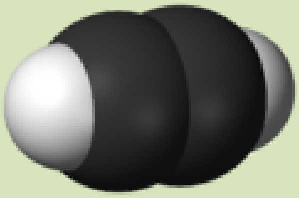
Complexity of molecule:

- Acetylene: 7 vibrations
- Benzene: 30 vibrations
- Sucralose: 129 vibrations
- Protein with 4000 atoms: **11,994 vibrations**



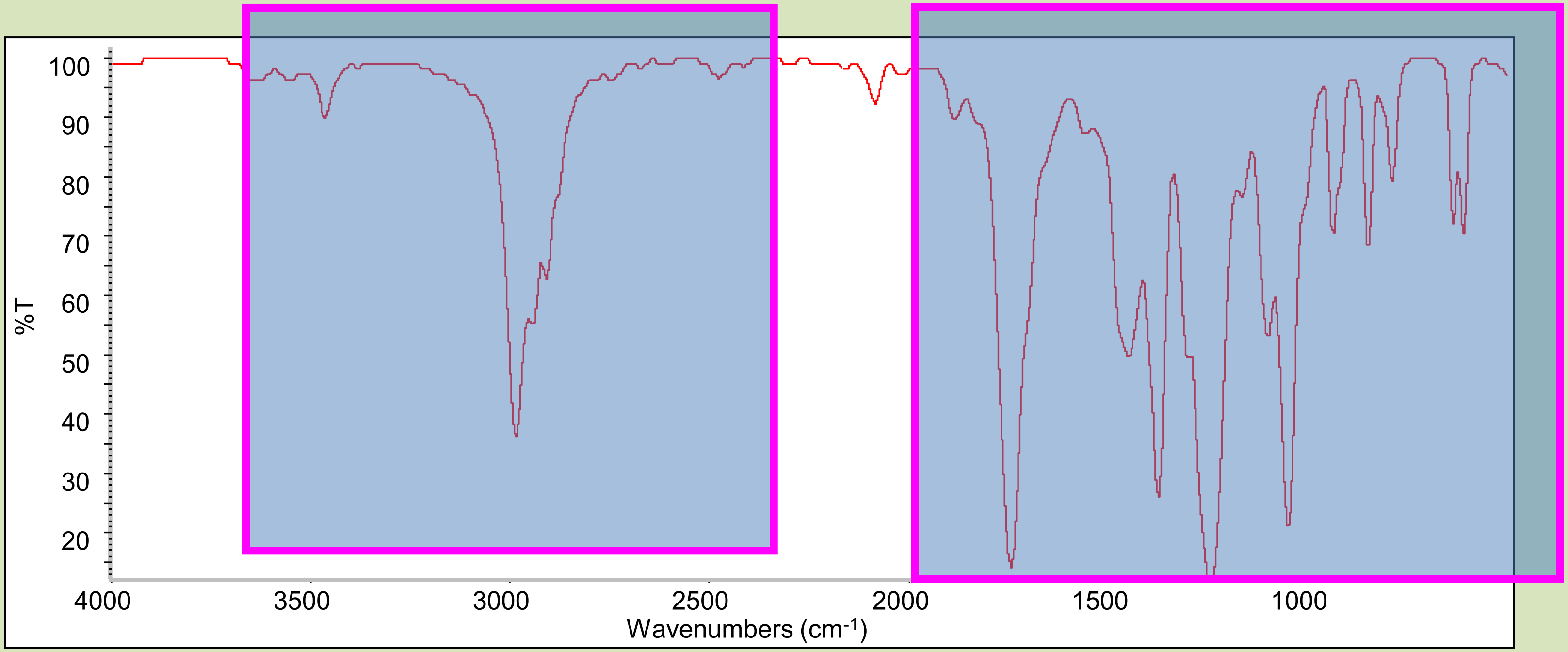
Myoglobin

$$H-C\equiv C-H$$

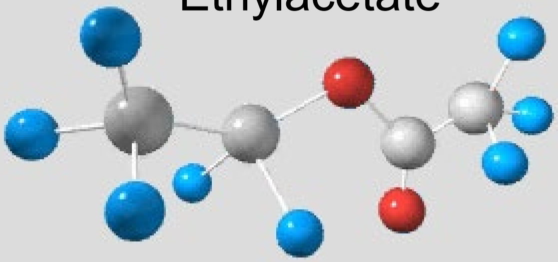


Acetylen

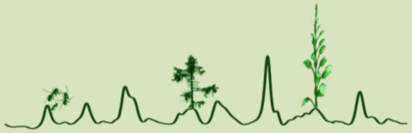
Position of peaks in spectrum are main parameter for identification!



Ethylacetate



- Direct compare with standard spectra
- Spectral libraries (commercial or prepared)
- Identification of mixtures or inpurities
- Cluster analysis (DA)
- Basic research of molecules

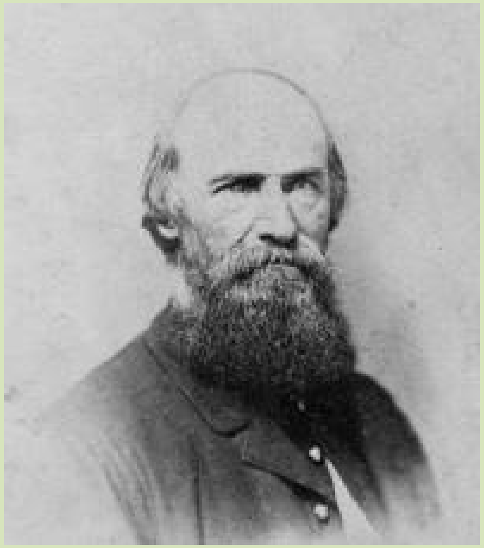


Molecular spectroscopy

Lambert-Beer law: quantitative analysis

Pierre Bouguer (1729)

Johann Heinrich Lambert (1760)



August Beer (1852)

Independently deduced that:

Light is attenuated when passing through a material, and this attenuation is material dependent

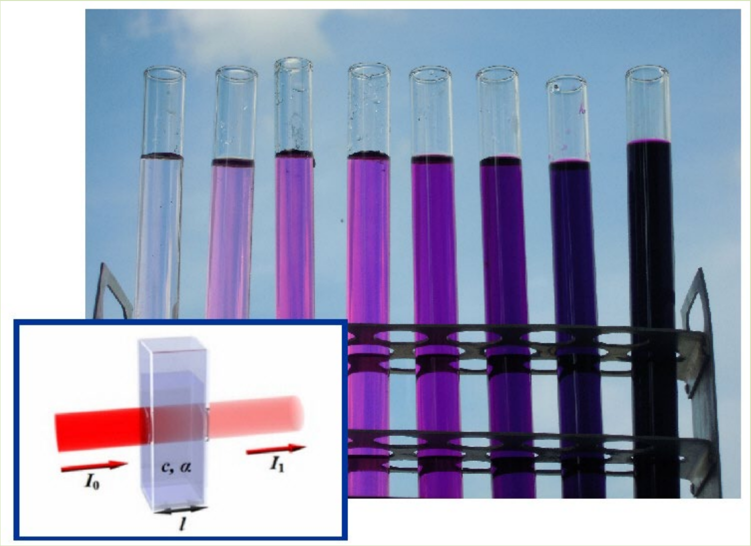
P. Bouguer discover this during drinking of red Portuguese wine

- Lambert: absorption coefficient and pathlength
- Beer: absorption coefficient and pathlength and concentration (peak height / area)

Molecular spectroscopy

Lambert-Beer law: quantitative analysis

$$A = \log(\Phi_0/\Phi) = \varepsilon_\lambda . c . l$$



A = absorbance
Φ_0 = light coming to sample
Φ = light changed by sample
ε_λ = molar absorption coefficient
c = concentration
l = pathlength

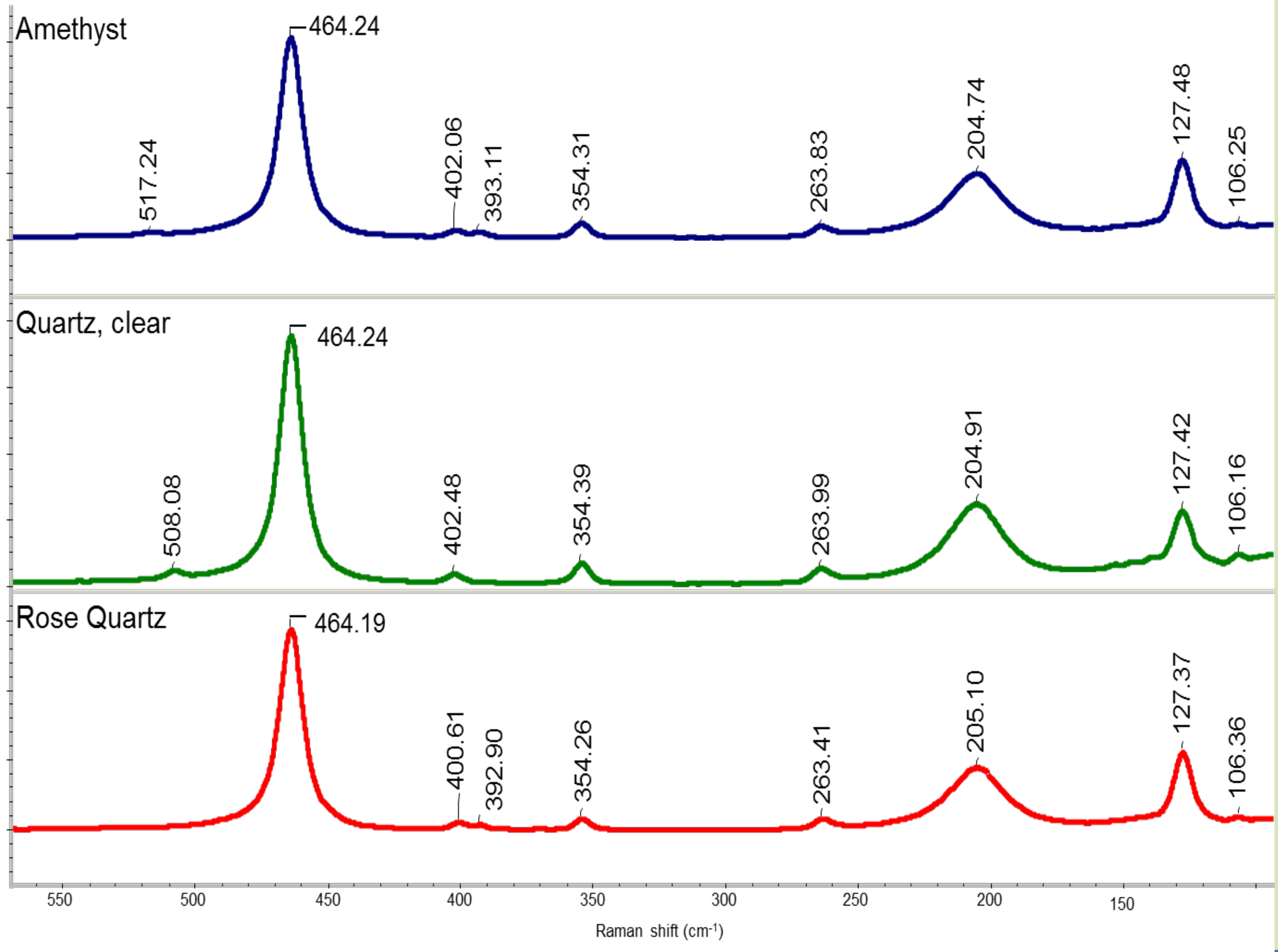
assuming a constant optical path and evaluating to one characteristic band that belongs only to the quantified component (it is not affected by another band of another component):

A equals c

FT-IR and Raman systems

- Portable, handheld versus laboratory systems
- microscopes

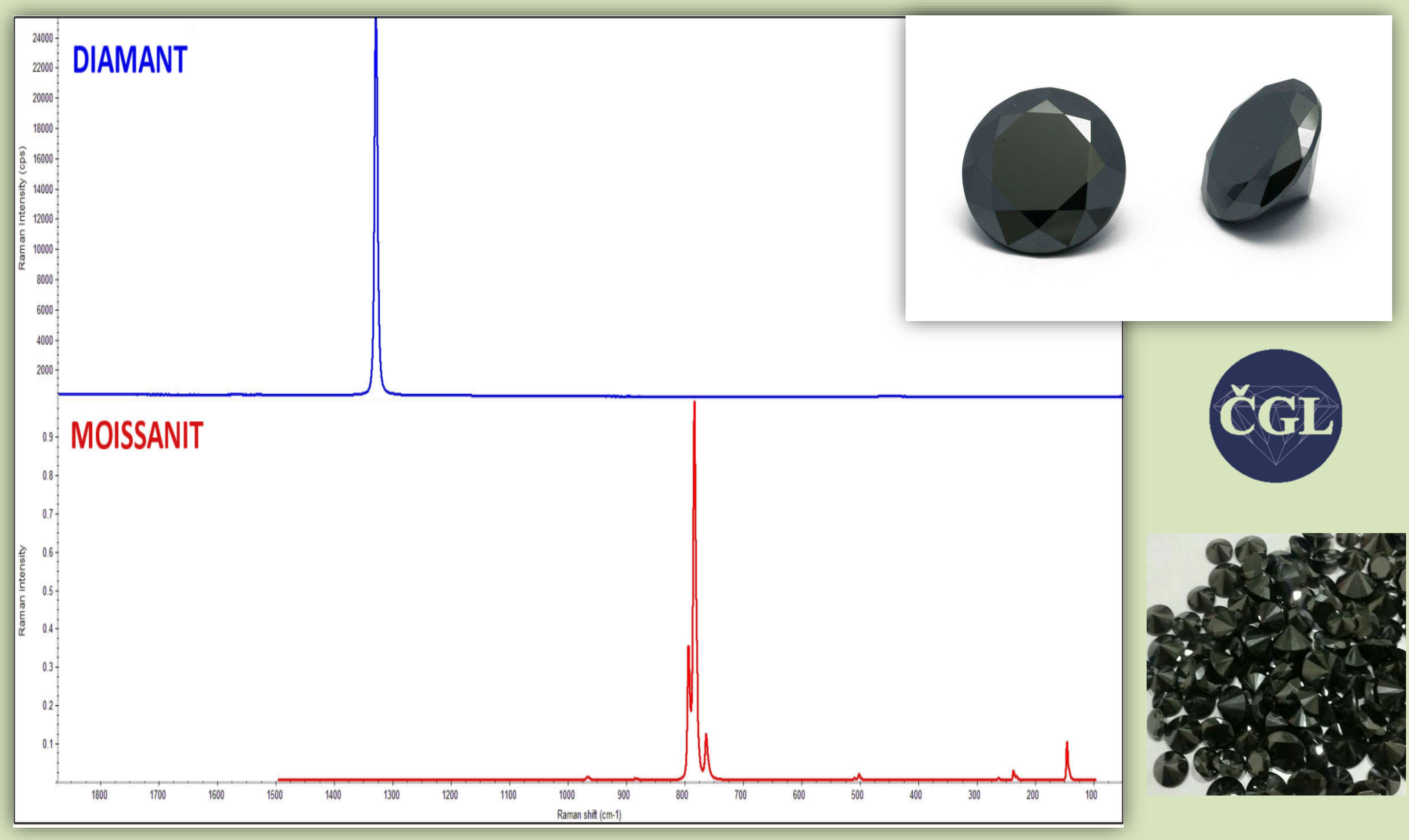
Identification of gemstones via Raman: very fast



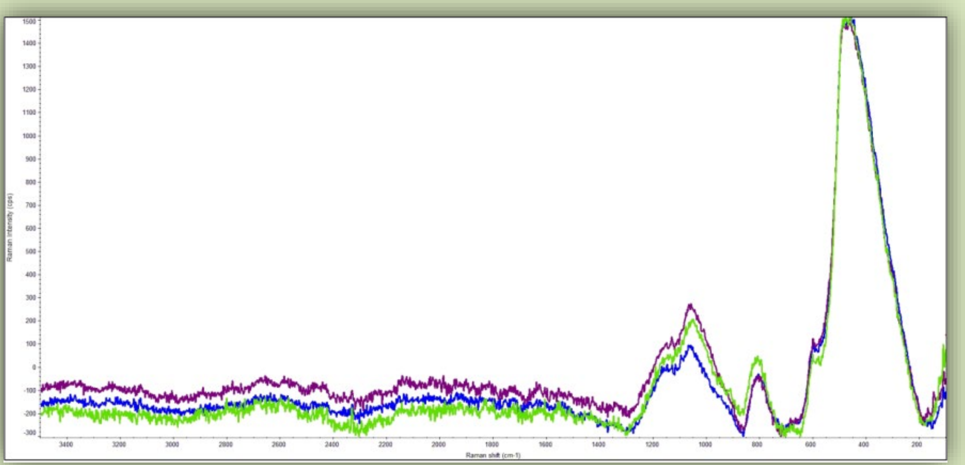
Even chemically very similar gemstones have different Raman features!

Fast ID of knock offs etc.

Moissanit (SiC) – “fake” synthetic diamonds

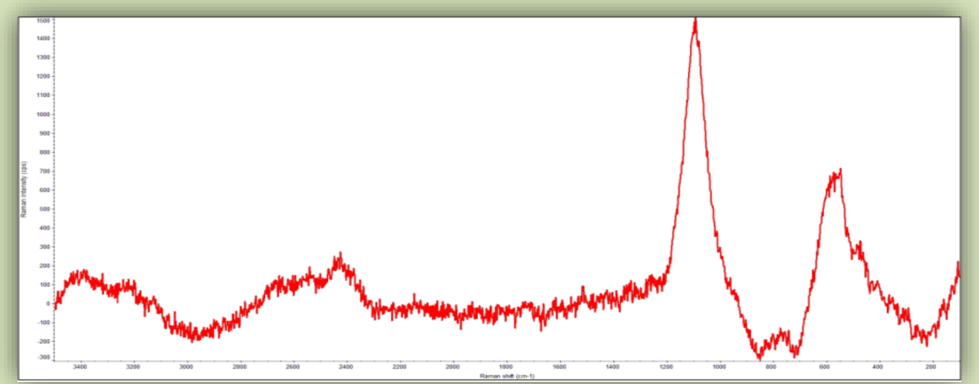


Moldavite – natural vs „china“



Tektit: $SiO_2 + Al_2O_3$

Natural: different locations



China origin

Czech garnets: quality, inclusions, purity, origin

Garnets: neosilicates with a complicated chemical formula of general shape $X_3Z_2[SiO_4]_3$, where:

- X = Ca, Mg, Fe^{2+}, Mn (bivalent cationts)
- Z = Al, Fe^{3+}, Cr, V^{3+}, Zr, Ti (trivalent cationts)

From latin *granatum malum* – pomegranate.

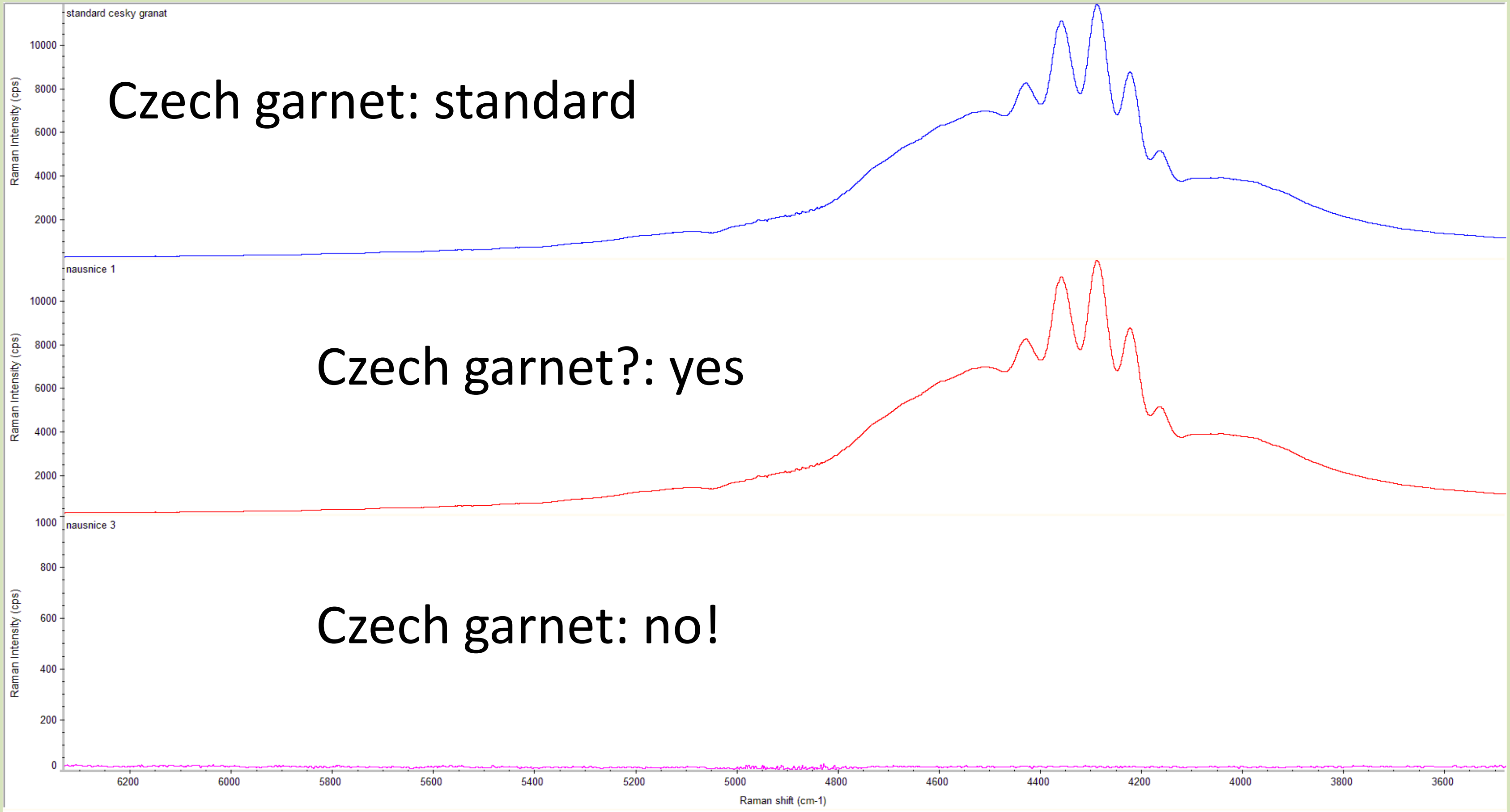
Raman spectroscopy/microscopy: garnet type determination, quality control, inclusions control (e.g. peridot), jewelry treatment control, etc…

Czech garnet (pyrop): composition is magnesium aluminum silicate $Mg_3Al_2(SiO_4)_3$, with at least 2 % Cr_2O_3.

Ideally combination of visual inspection, Raman and XRF spectroscopy. Raman immediately shows if the stone is garnet and if chromium is present!

Czech garnets: quality, inclusions, purity, origin

- Raman (**area 5 000 – 3 600 cm^{-1}**): luminiscence of chrome ionts! Cr^{3+} sometimes also V^{3+}



Czech garnet: standard

Czech garnet?: yes

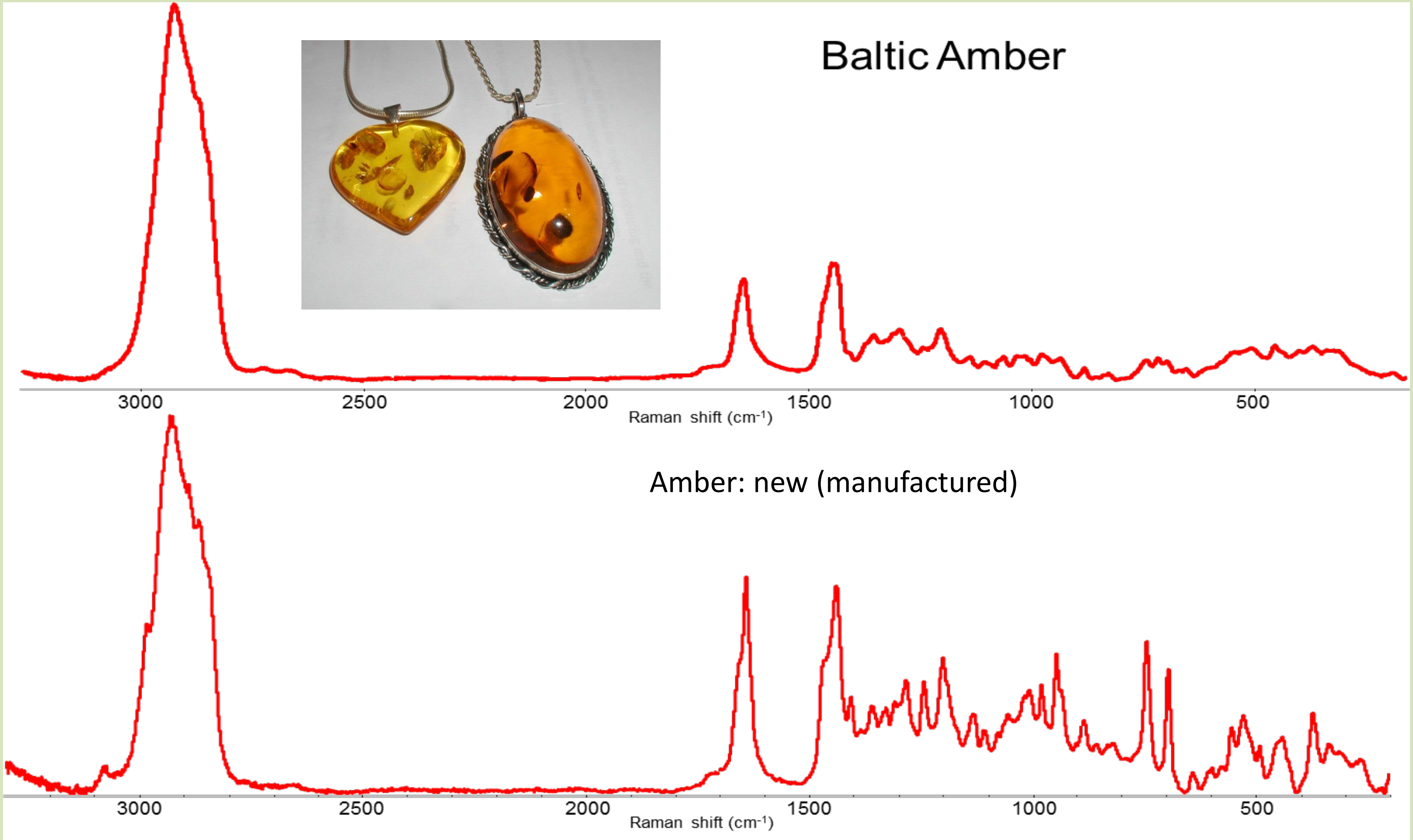
Czech garnet: no!

Renata Jasinevicius: CHARACTERIZATION OF VIBRATIONAL AND ELECTRONIC FEATURES IN THE RAMAN SPECTRA OF GEM MINERALS, THE UNIVERSITY OF ARIZONA 2009

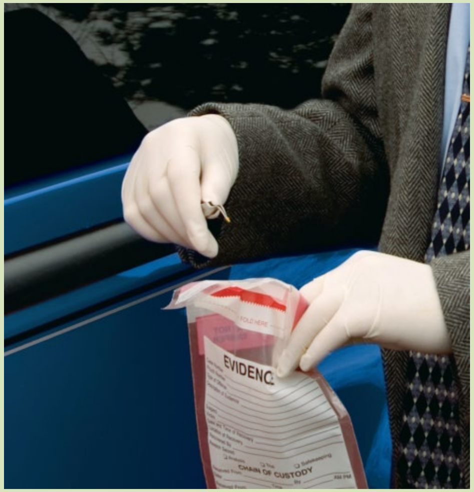
Amber: „new“ versus old

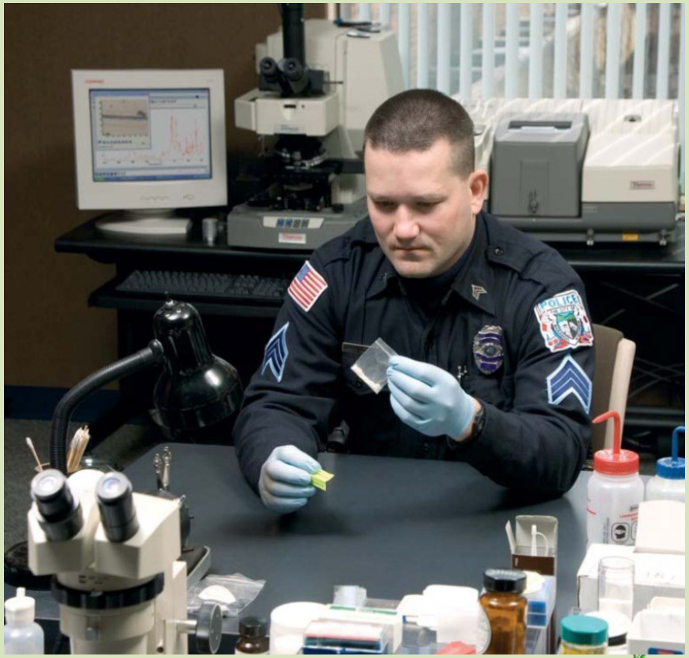
Amber: around 100 mil old (Myanmar/Barma)

Amber: „new“ versus old

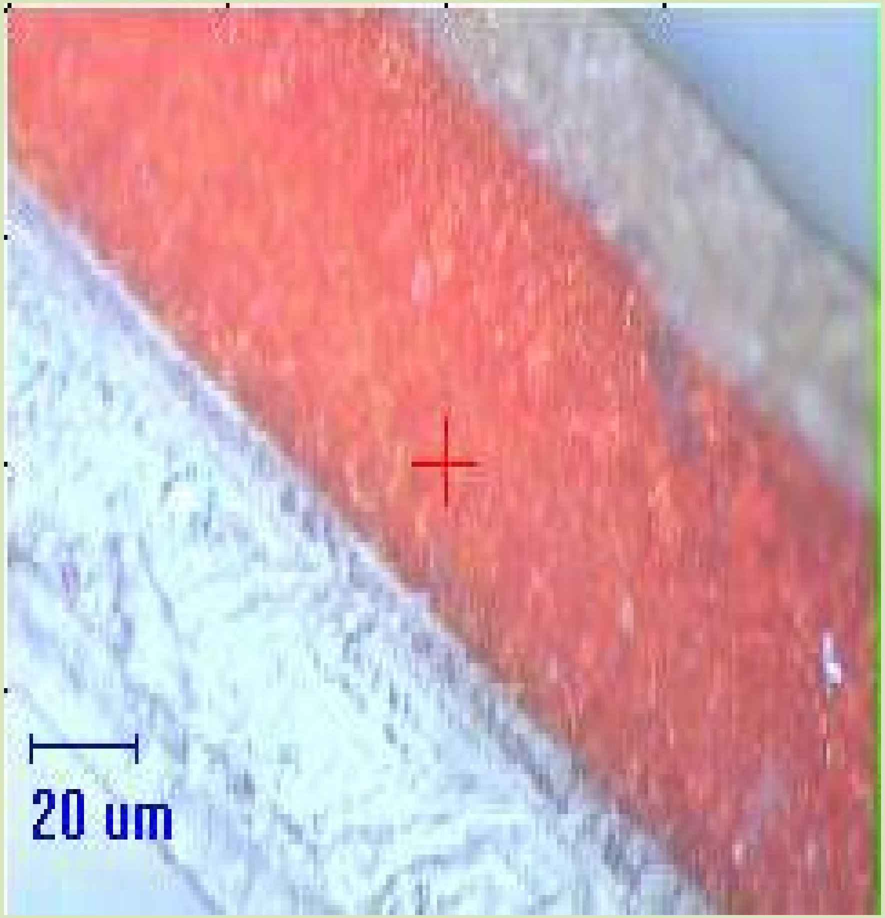


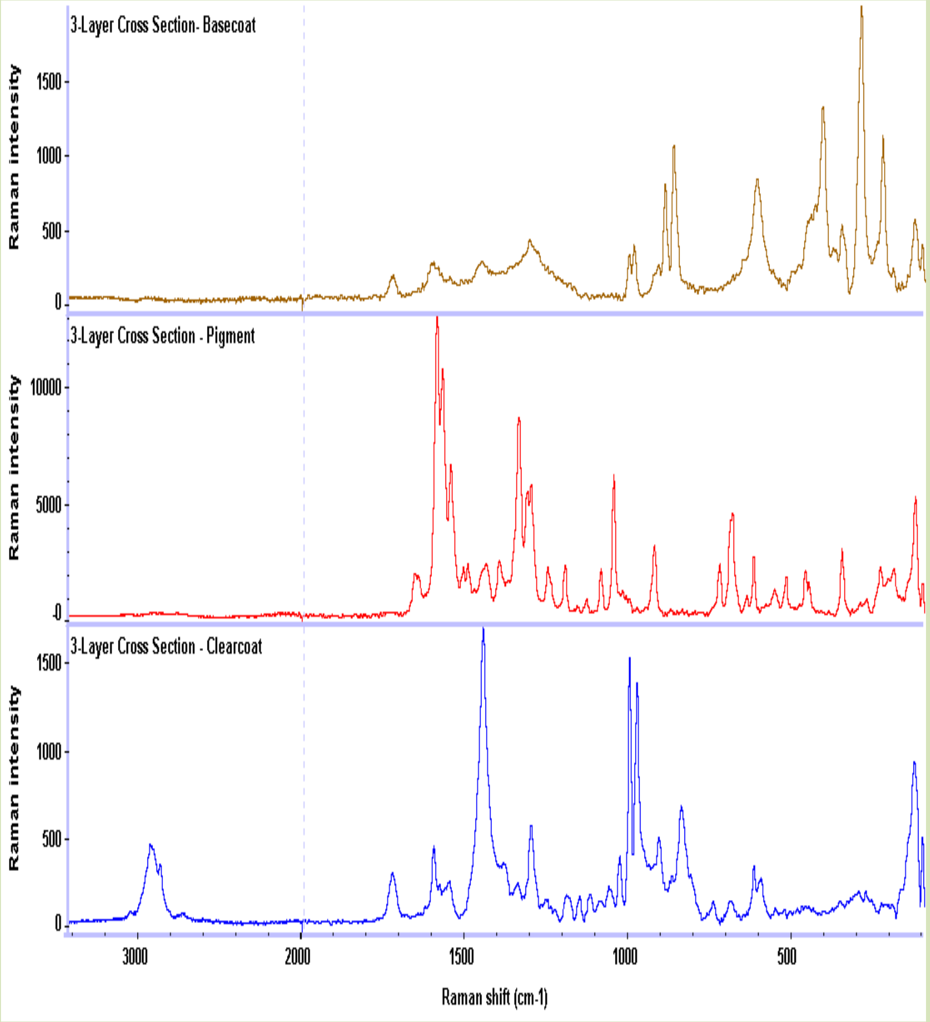
Example of forensic application





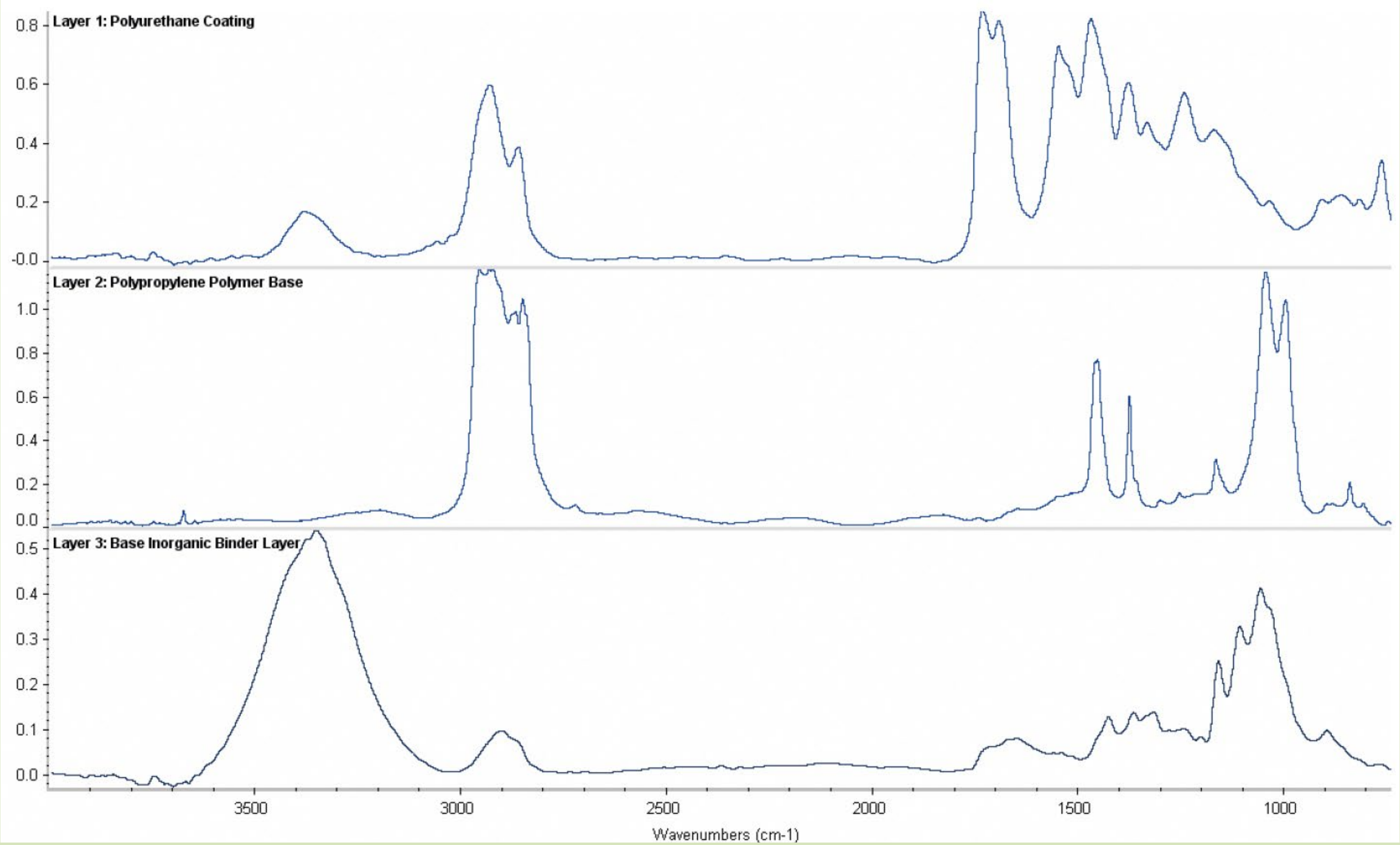
Forensic research: Car paints





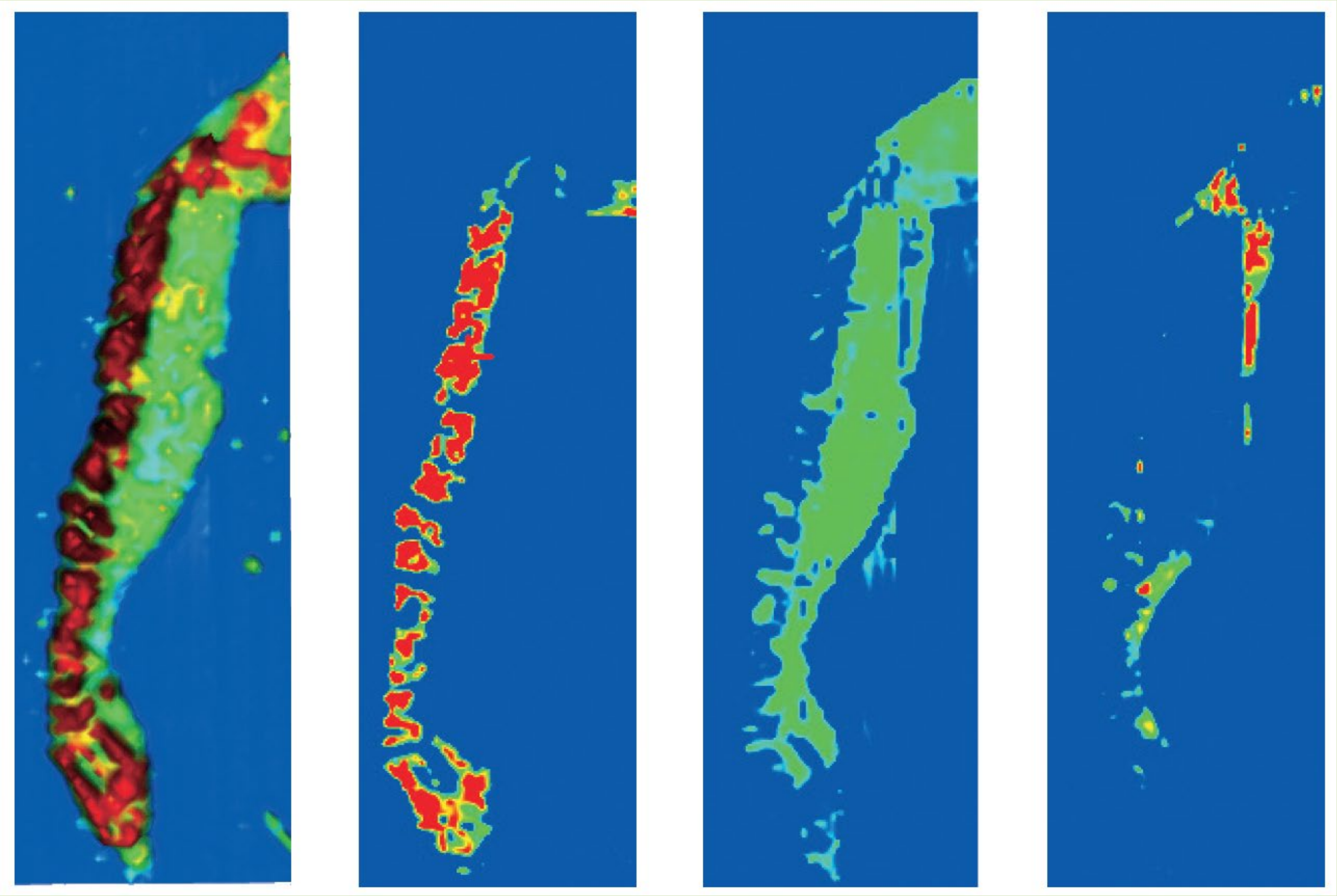
Forensic research: Car paints

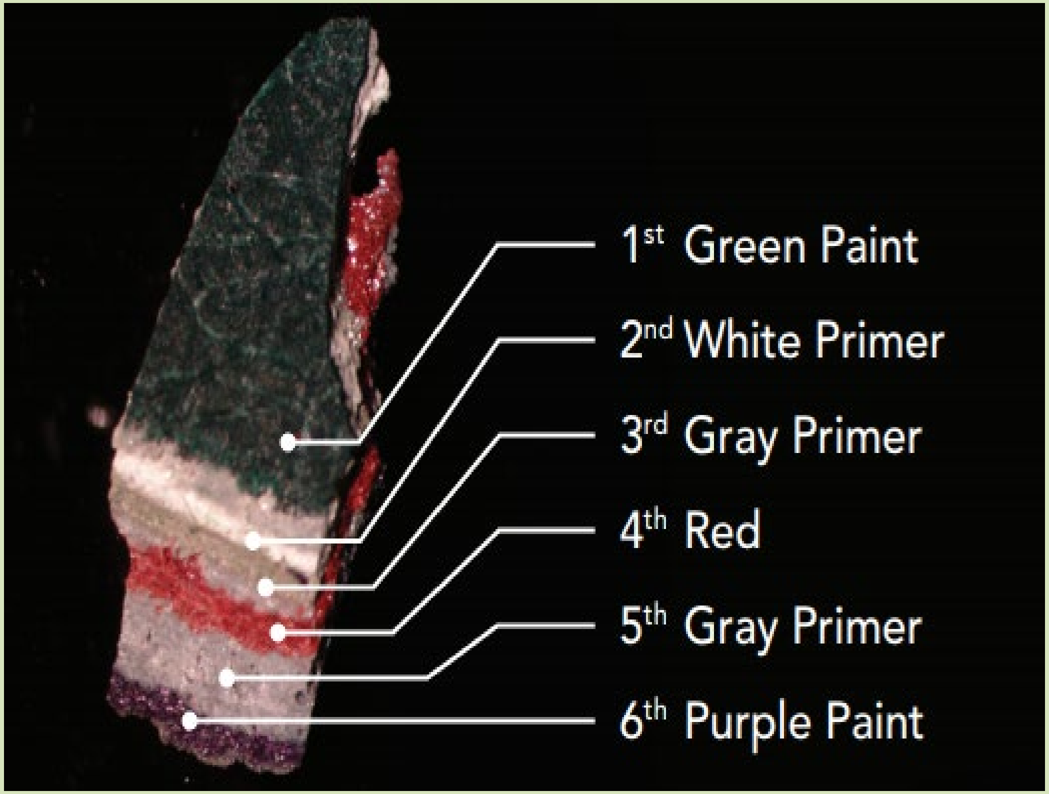
Checking with database



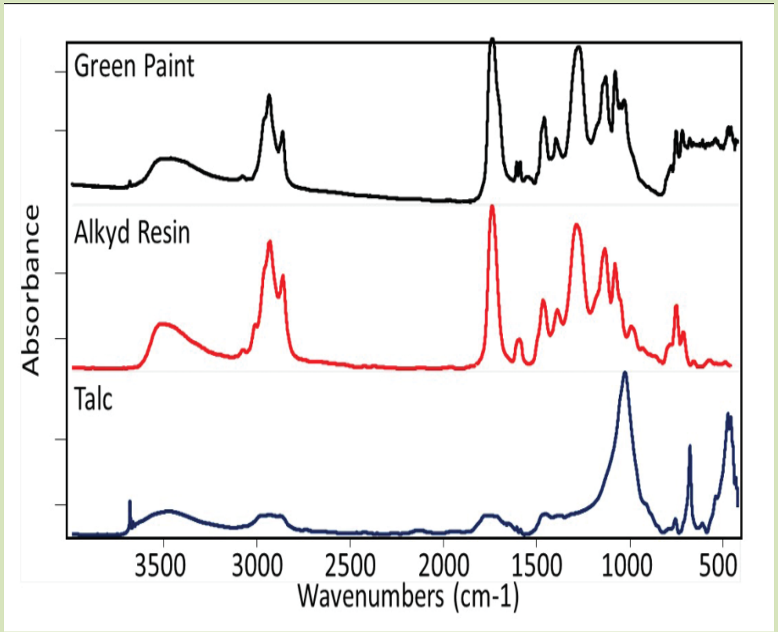
Forensic research: Car paints

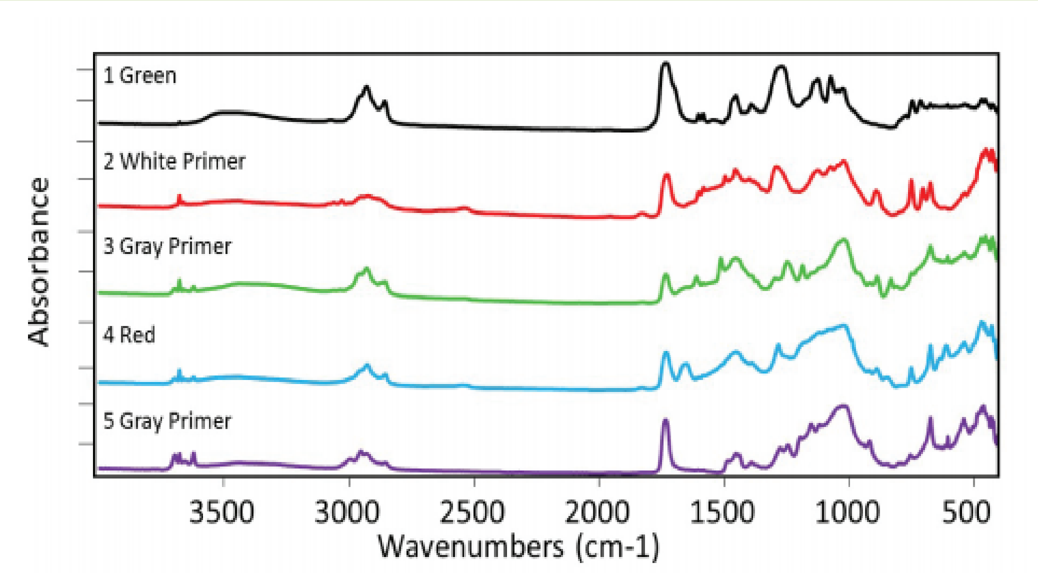
- Chemical mapping (IR) of sample from hit and run – different layers
- Mapping with spatial resolution around 5 μm





Paint chip Pontiac 79





Thank you!

sec@nicoletcz.cz