

Fourier Transform-Infrared (FT-IR) and Raman Spectroscopies

Principles and Applications

Prepared by

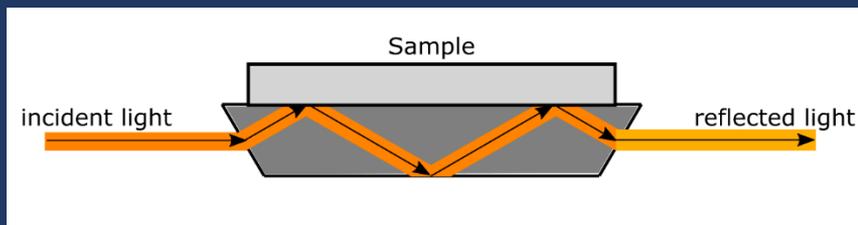
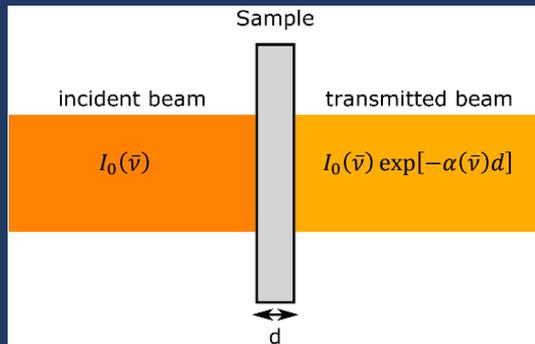
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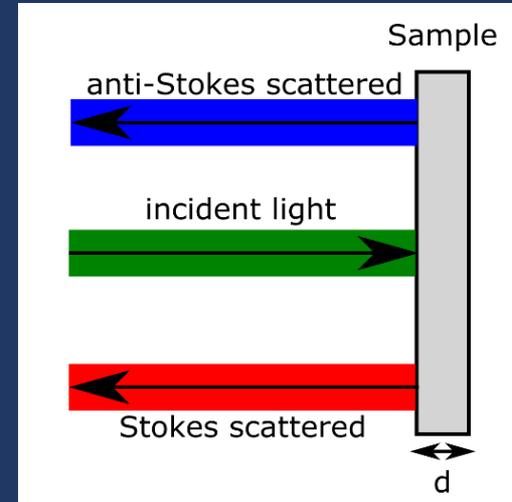
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This tutorial will address two types of optical spectroscopy.

Part 1: Fourier Transform-Infrared (FT-IR) spectroscopy



Part 2: Raman spectroscopy

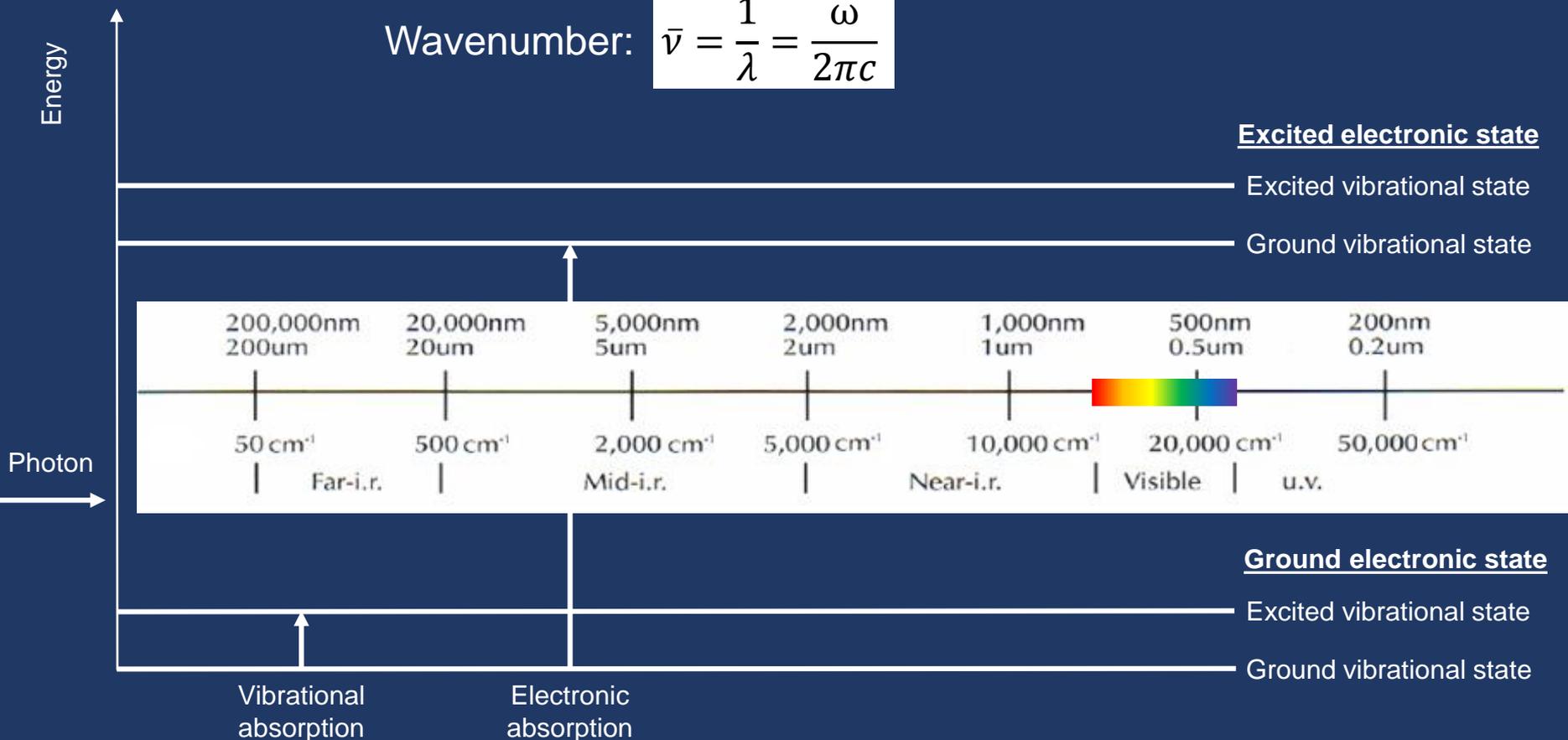


- The principles behind FT-IR and Raman spectroscopy.
- How modern instruments implement these techniques.
- Complementary aspects of IR and Raman spectroscopy.

Infrared spectroscopy

Vibrational and electronic absorption occur in the IR and visible spectral regions.

Wavenumber: $\bar{\nu} = \frac{1}{\lambda} = \frac{\omega}{2\pi c}$



$$E = \frac{hc}{\lambda} = \frac{1239.8 \text{ eV-nm}}{\lambda}$$

$$E = hc\bar{\nu} = (0.12398 \text{ meV-cm})\bar{\nu}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 1.240 \mu\text{m} = 8066 \text{ cm}^{-1}$$

Atomic dipole oscillator (harmonic approximation) is used to model vibrational transitions.

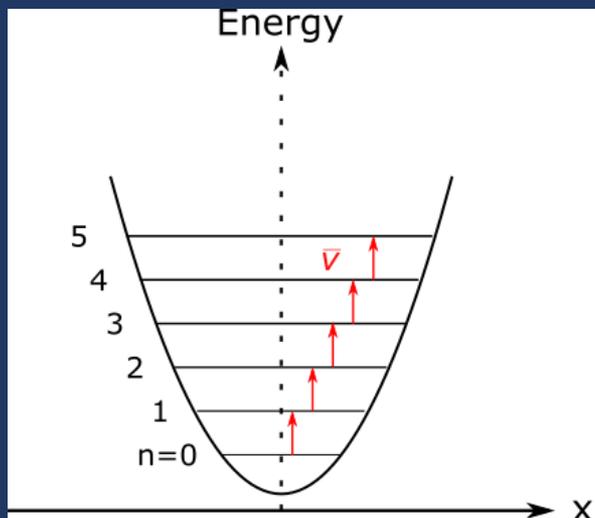
Point masses = atoms

Chemical bond = spring



$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}; \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Quantum Mechanics



Observations

$$E_{\text{har}} [\text{cm}^{-1}] = \left(n + \frac{1}{2}\right) \bar{\nu}$$

Quantized levels

$$\Delta E_{\text{har}}(n \rightarrow n + 1) [\text{cm}^{-1}] = \bar{\nu}$$

Equal spacing

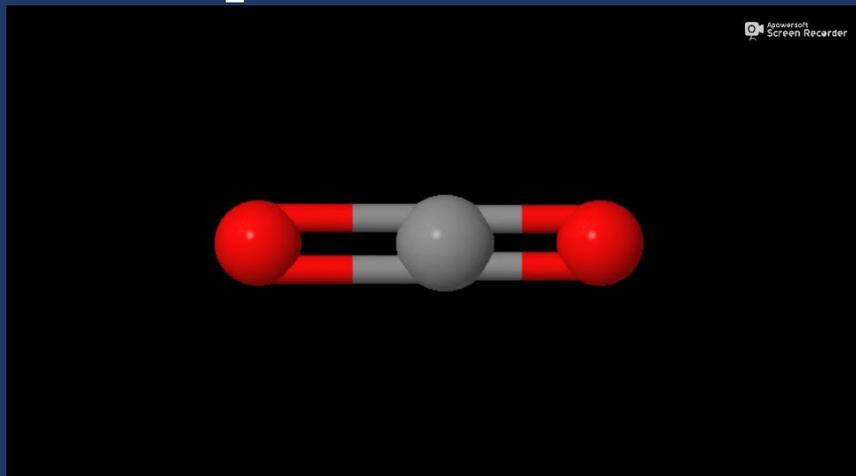
$$\Delta n = 1$$

Selection rule

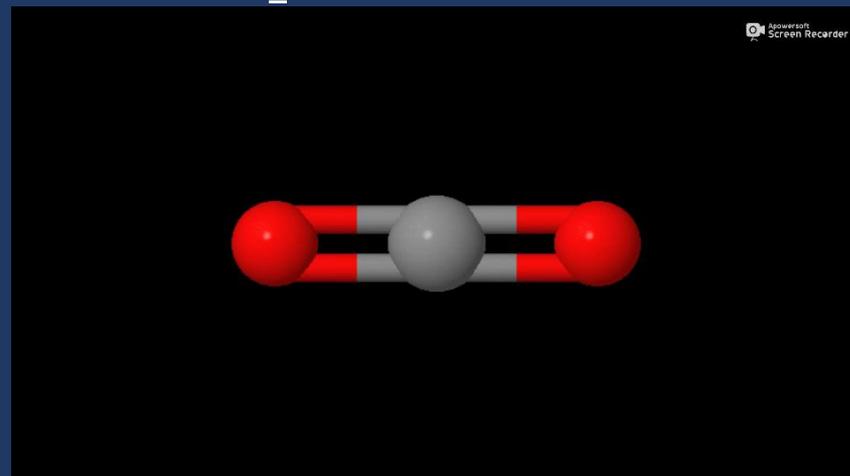
At 295 K and below, most molecules are in the $n = 0$ ground state.

IR-active vibrations require a **non-zero** change in the net electric dipole moment.

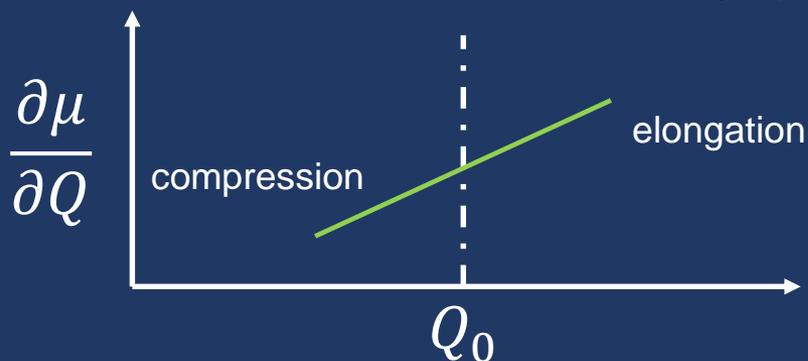
CO₂ antisymmetric stretch



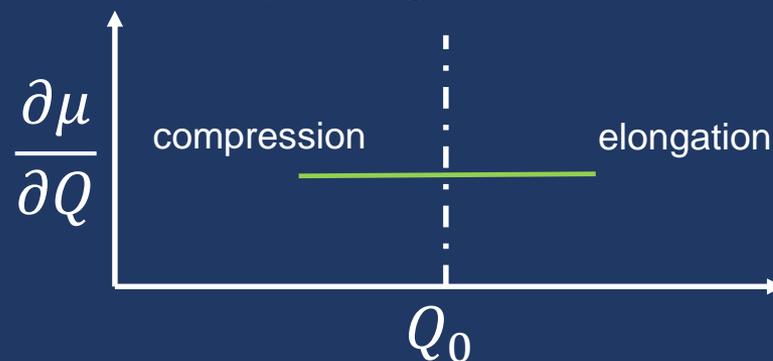
CO₂ symmetric stretch



Follow normal coordinate Q (e.g., position of one O atom) during the vibration.

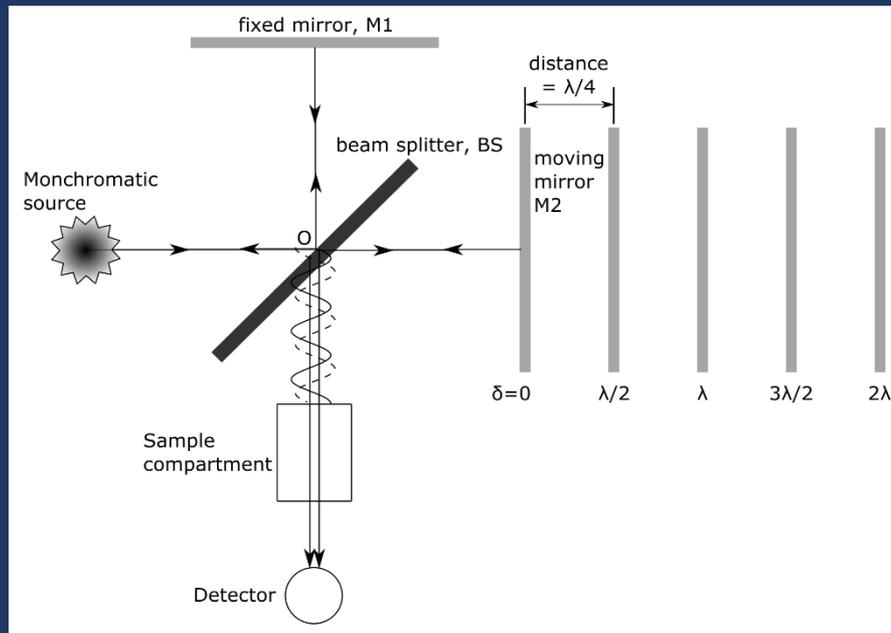


IR active

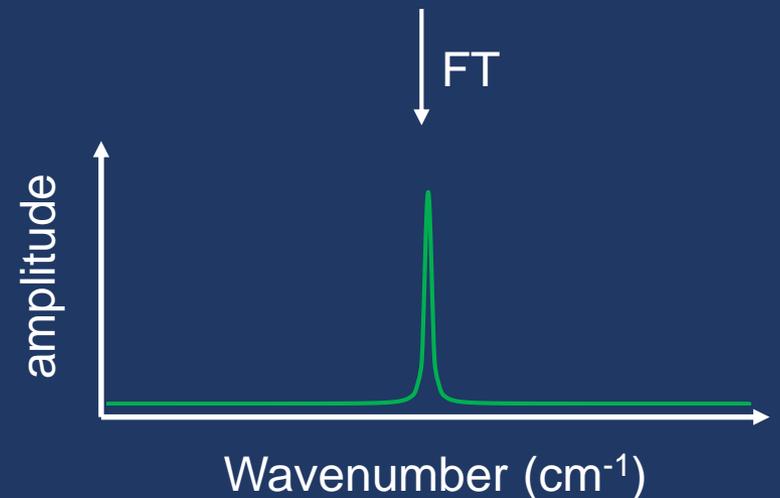
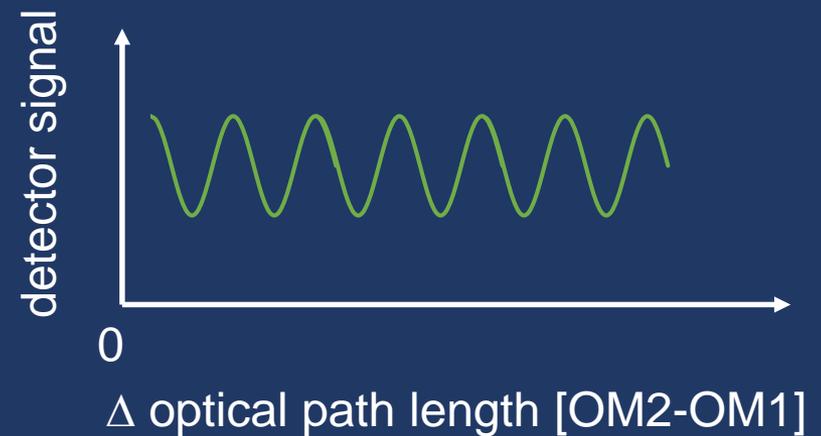


IR inactive

Fourier Transform technique uses a Michelson inteferometer to modulate the amplitude of the incident light on the detector.

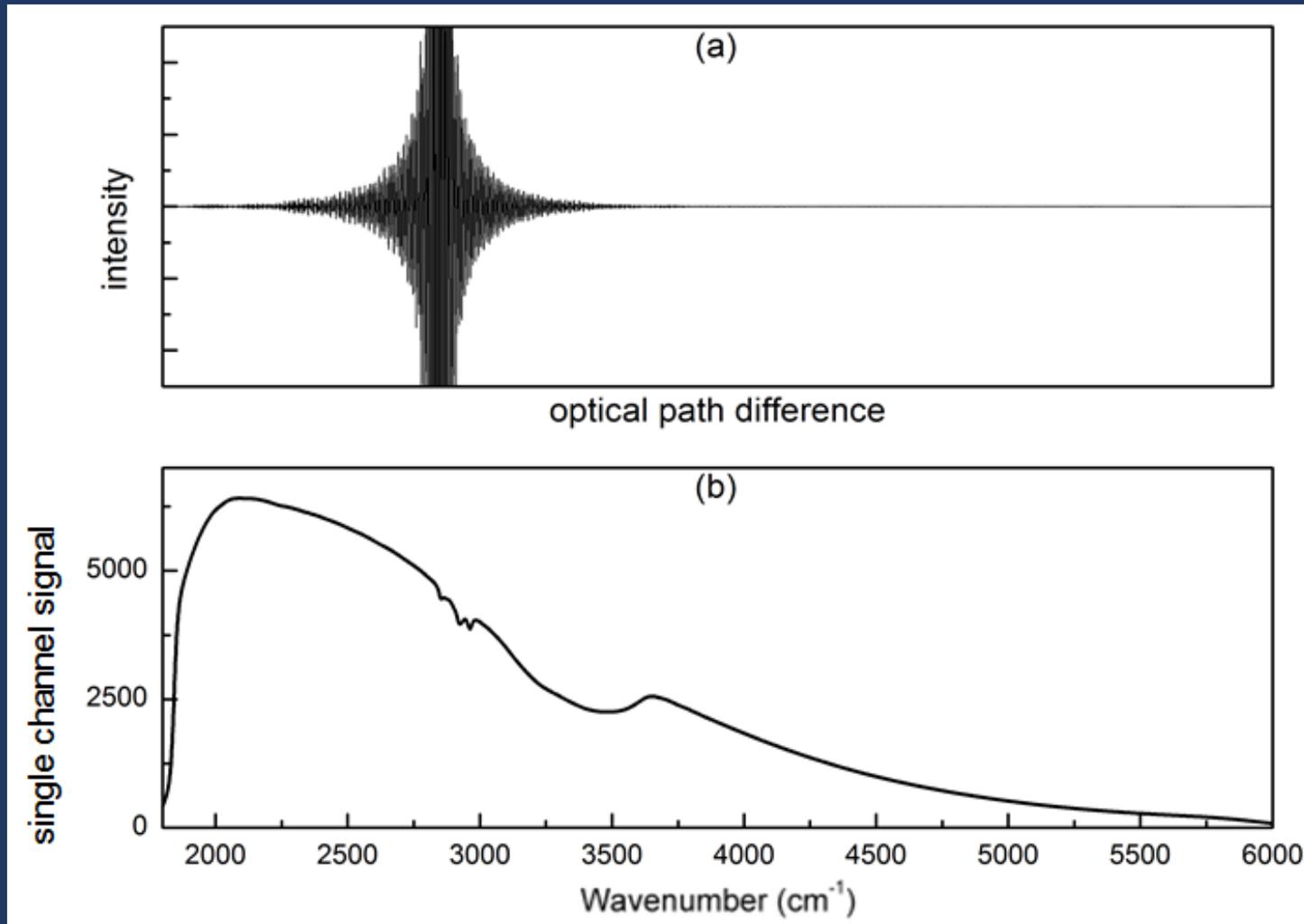


- Translation of M2 yields alternating constructive and destructive interference.
- Interferogram: detector signal vs. Δ OPL



Fourier transform recovers frequencies and amplitudes of contributions.

The Fourier Transform allows the spectrum of a broad light source to be measured **without** dispersing the light.



FT-IR spectroscopy requires **two** measurements: background + sample.

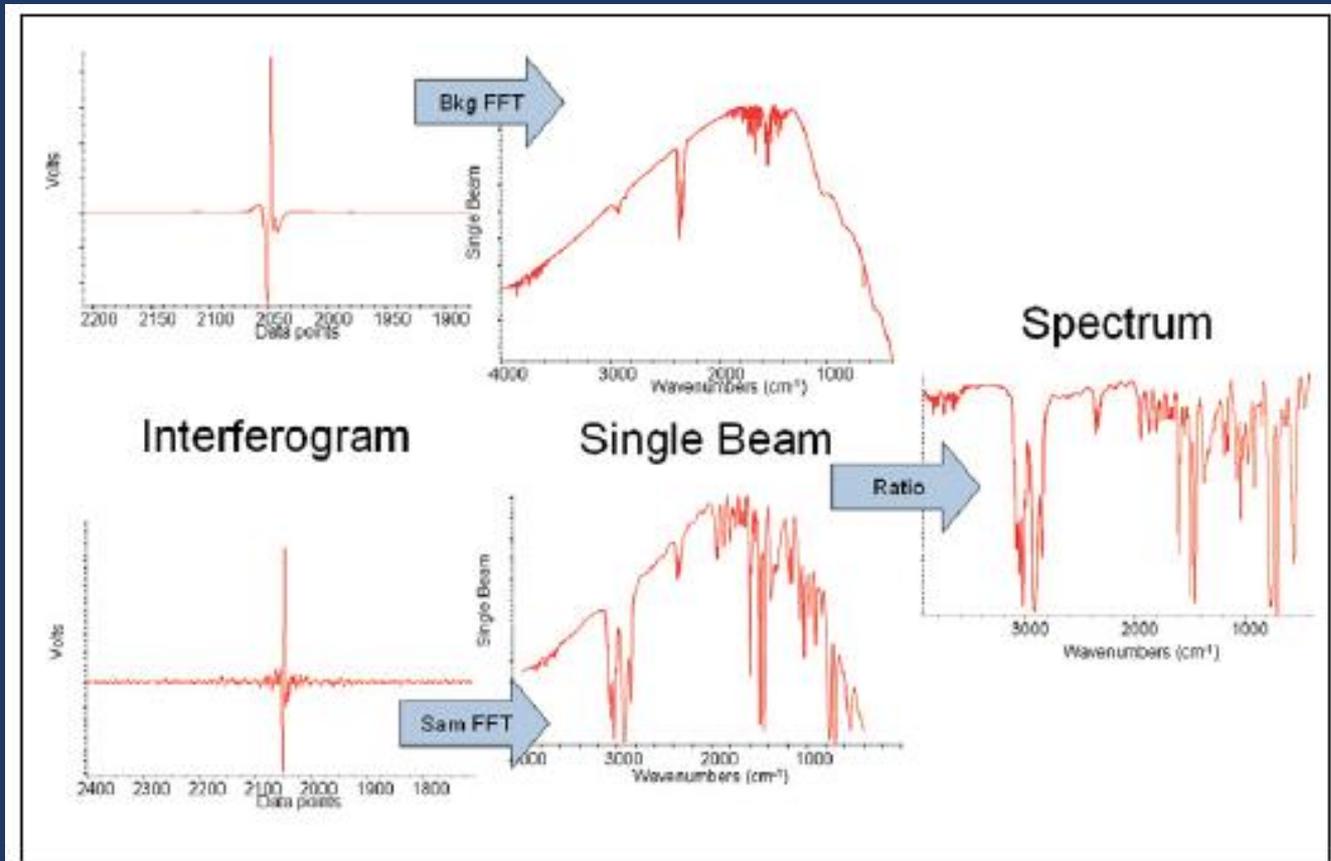


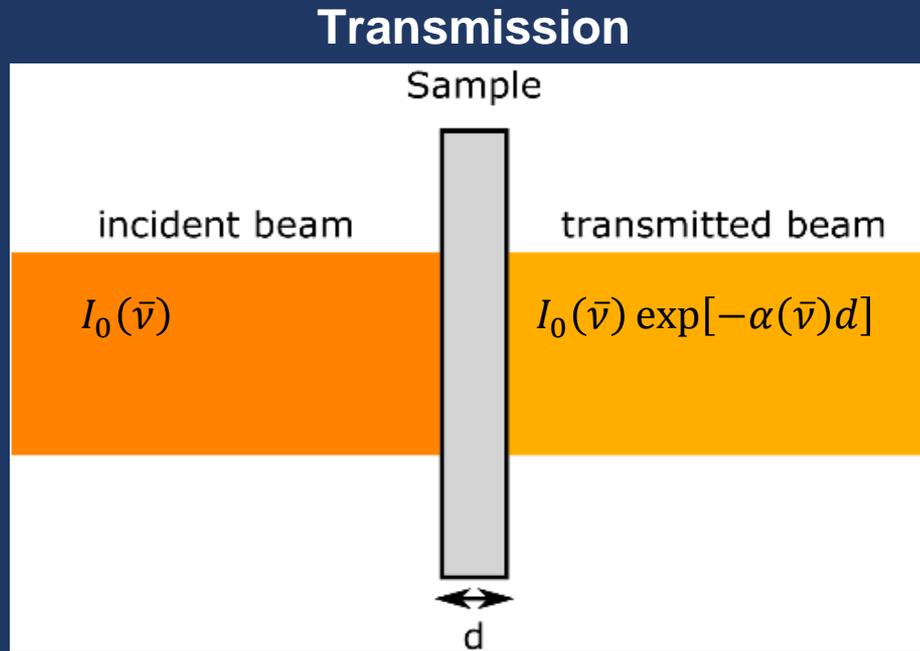
Figure credit: Thermo Nicolet TN-00128 «FT-IR vs. Dispersive Infrared»

Background: spectrometer components + ambient

Sample: spectrometer components + ambient + **sample**

Ratio of sample to background yields desired spectrum.

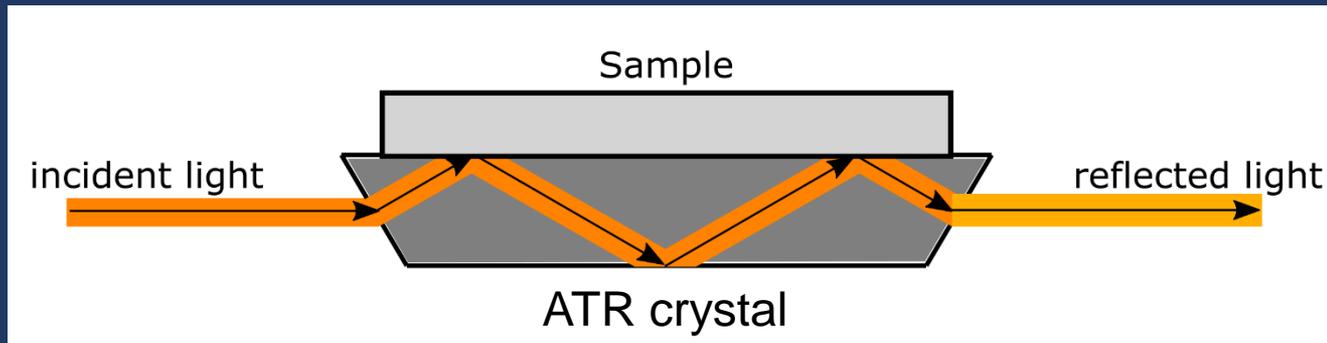
Different sampling geometries used for a wide class of materials.



- Simple: light in, light out.
- Samples: bulk single crystals, liquids and gases.
- Sample preparation + mounting can be time-consuming.

Different sampling geometries used for a wide class of materials.

Attenuated Total Reflectance (ATR)



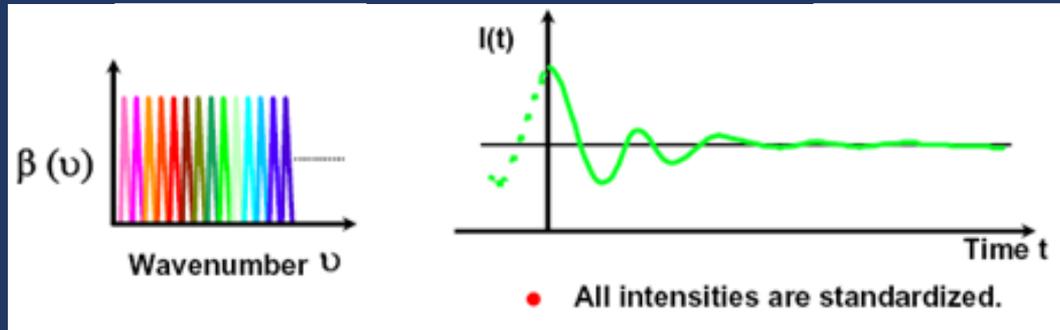
- Complex: total internal reflection + evanescent wave
- Samples: anything except gas phase (thin films and powders)
- Almost no sample preparation -> **most popular form of FT-IR**

ATR Crystals: *diamond, ZnSe, Ge, Si*

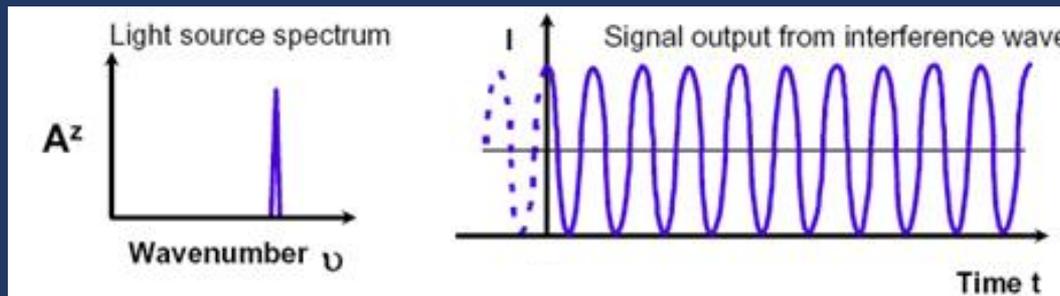
- Need good contact between the sample and the crystal
- Tradeoff between spectral range, penetration depth, and \$\$\$

FT-IR technique offers significant advantages over older, dispersive techniques.

- **Multiplex advantage** - single scan measures entire spectral range.



- **Throughput advantage** – higher optical throughput (circular aperture) increases the signal-to-noise ratio. $S/N \sim \sqrt{n}$
- **Precision Advantage** – He-Ne laser interferogram used to digitize spectrum, acts as a secondary standard.

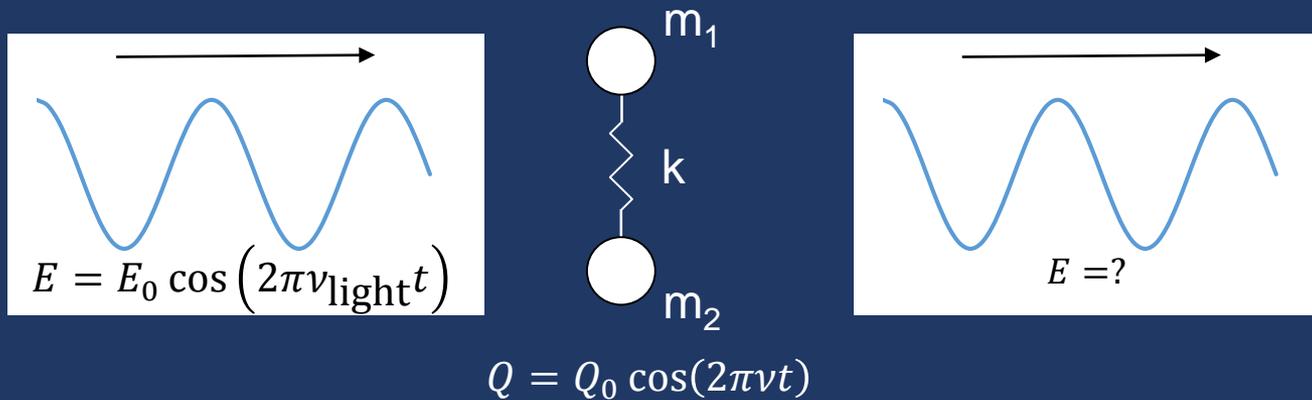


FT-IR Limitations

- **Single channel technique** - sample and reference are not measured at the same time.
- **Beer's Law (signal \propto species concentration)** – limit of detection of 10^{14} atoms/cm³ (1 cm thick) or 10^{18} cm⁻³ (1 μ m thick) .
- **Quantitative Analysis** – require calibration factor from another technique (e.g., secondary ion mass spectrometry).
- **Competing Absorption Mechanisms** – signal of interest may overlap or be completely masked by other absorption mechanisms.

Raman spectroscopy

Atomic dipole scatterers (harmonic approximation) are used to model scattering of light.



Incident light (non-resonant) induces oscillating dipole moment.

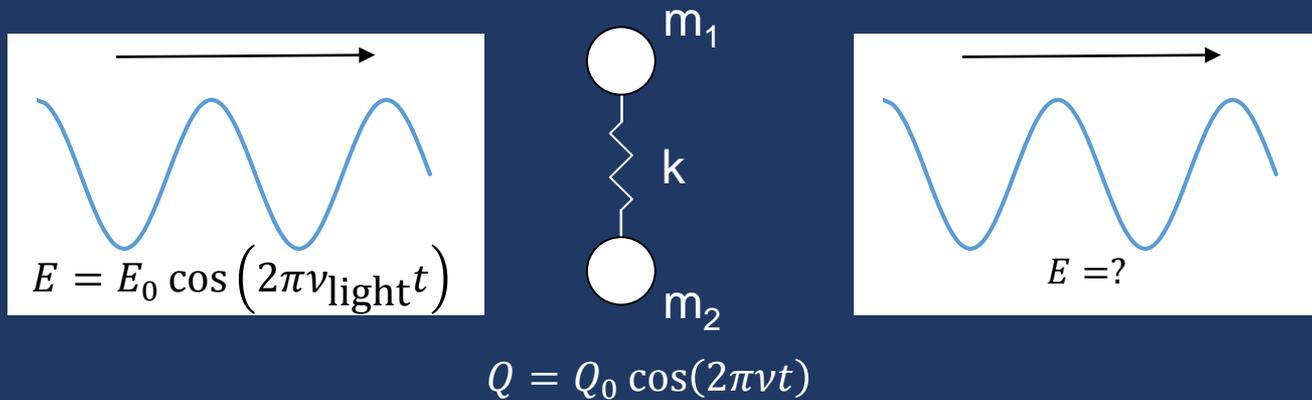
$$\mu = \alpha E = \alpha E_0 \cos(2\pi\nu_{\text{light}}t)$$

α = polarizability (ease to distort electron cloud)

For small amplitude vibrations (harmonic approximation),

$$\alpha \cong \alpha_0 + \frac{\partial \alpha}{\partial Q} Q = \alpha_0 + \frac{\partial \alpha}{\partial Q} Q_0 \cos(2\pi\nu t)$$

Atomic dipole scatterers (harmonic approximation) are used to model scattering of light.



Expression for the oscillating dipole moment becomes,

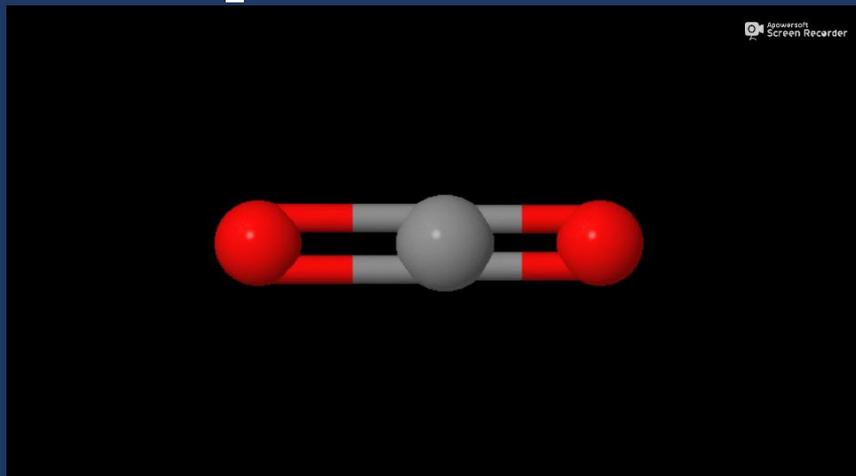
$$\mu = \alpha E = \underbrace{\alpha_0 E_0 \cos(2\pi\nu_{\text{light}} t)}_{\text{Rayleigh}} + \underbrace{\frac{\partial \alpha}{\partial Q} E_0 Q_0 \cos(2\pi\nu t) \cos(2\pi\nu_{\text{light}} t)}_{\text{Rewrite}}$$

$$\cos(2\pi\nu t) \cos(2\pi\nu_{\text{light}} t) = \underbrace{\cos(2\pi [\nu_{\text{light}} - \nu] t)}_{\text{Raman Stokes}} + \underbrace{\cos(2\pi [\nu_{\text{light}} + \nu] t)}_{\text{Raman anti-Stokes}}$$

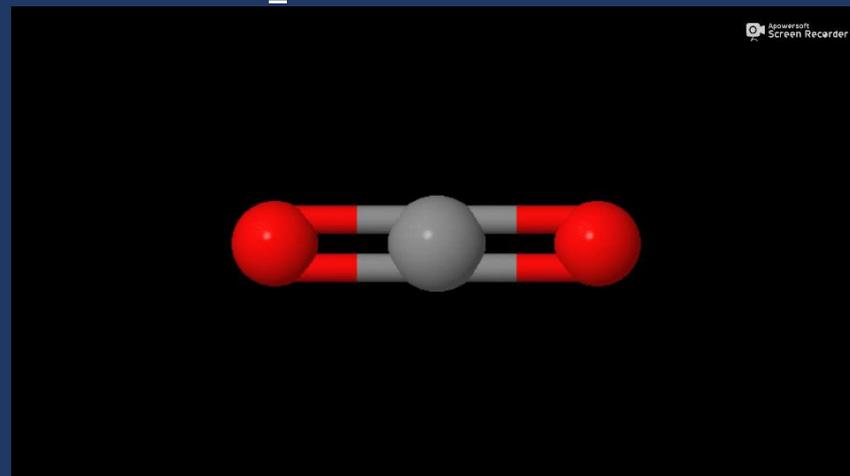
Raman effect: inelastic scattering of light yields info about vibrations.

Raman-active vibrations require a **non zero** change in the polarizability of a molecule.

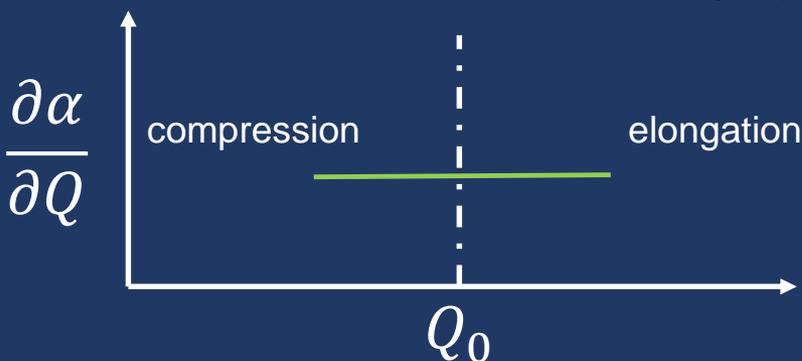
CO₂ antisymmetric stretch



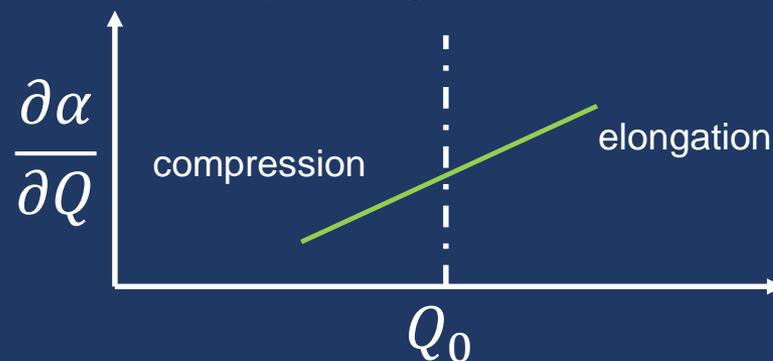
CO₂ symmetric stretch



Follow normal coordinate Q (e.g., position of one O atom) during the vibration.

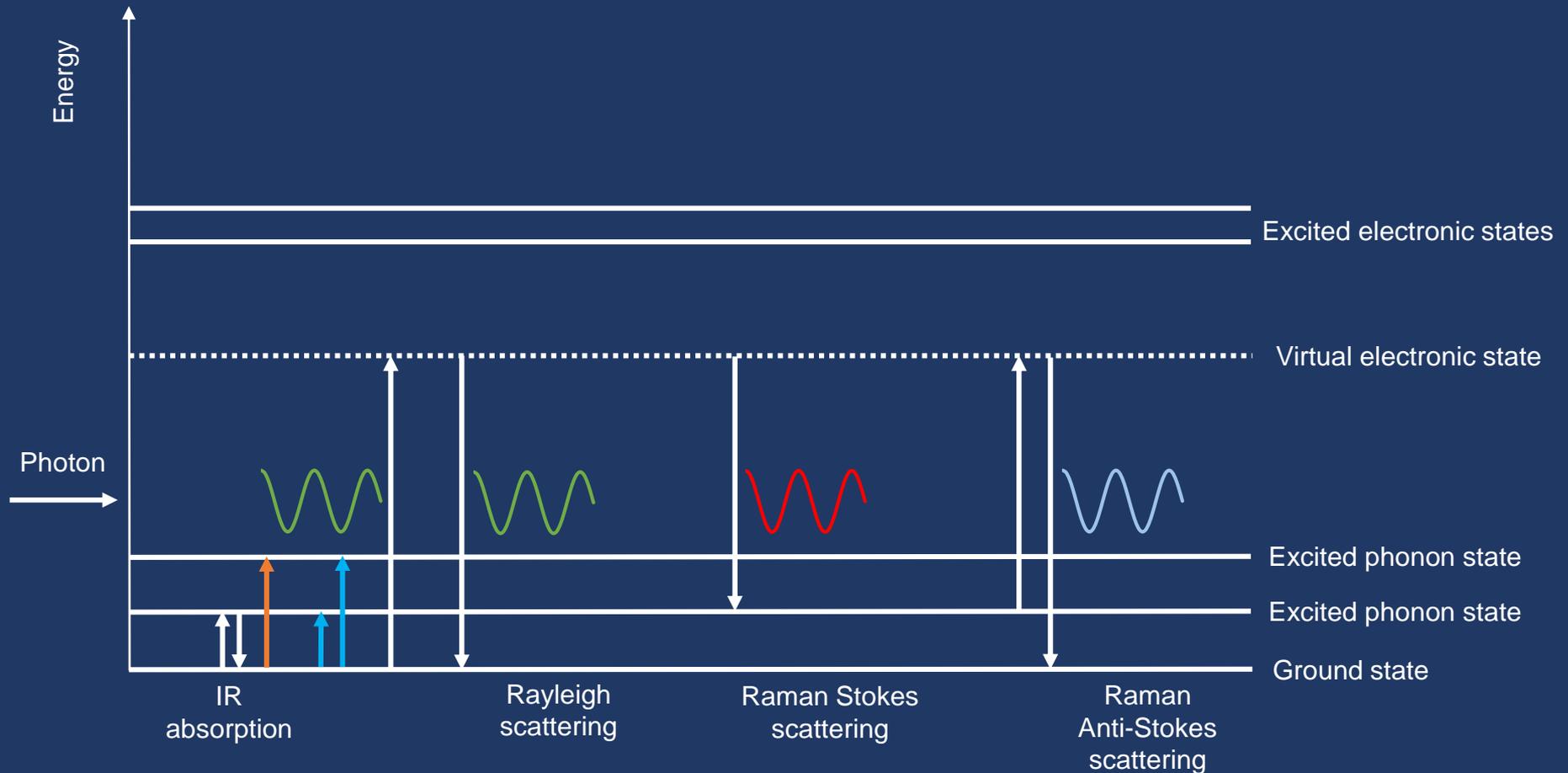


Raman inactive



Raman active

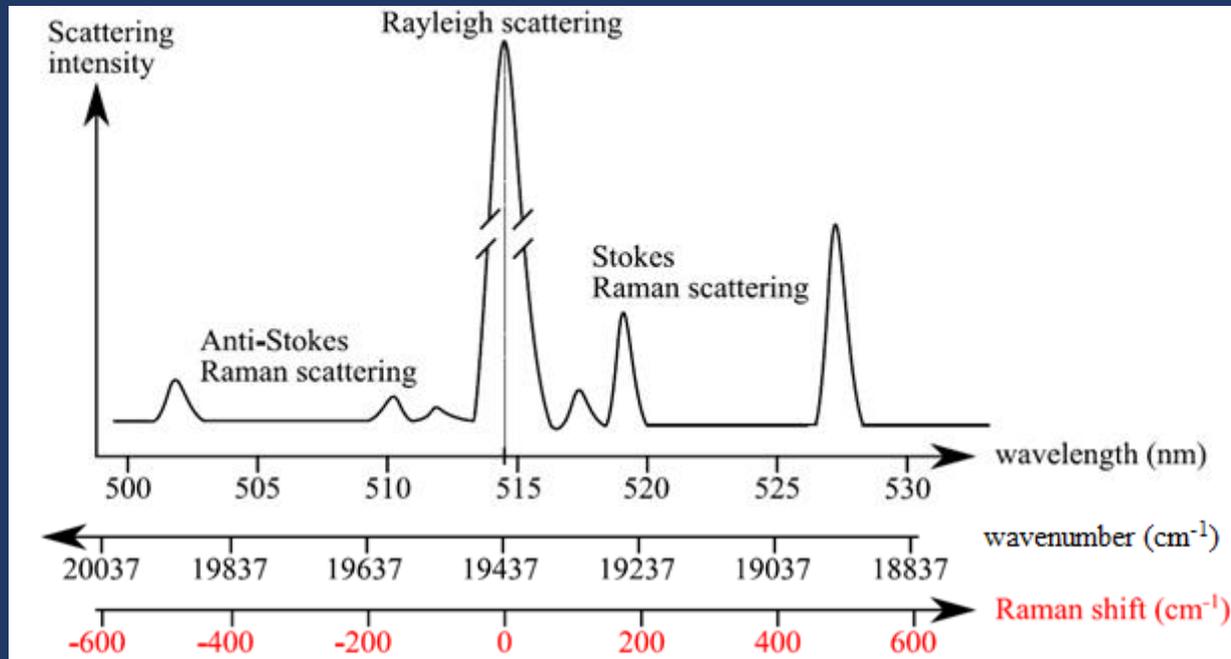
Quantum mechanical comparison of IR and Raman events.



Including anharmonicity effects leads to weakly allowed transitions of...

- Overtones
- Combination bands

Collected Raman spectrum is transformed to yield Raman shift on x-axis.



$$\bar{\nu} = \frac{1}{\lambda}$$

$$\bar{\nu}_{\text{laser}} - \bar{\nu}_{\text{spectrum}}$$

Raman shift shows the increase/decrease in energy *with respect to the material*.

- Wavenumber position => chemical identification
- Height of the peak => concentration of species
- Width of the peak => crystallinity of material

Raman spectrometers can be used for both macro- and microscopic measurements.

Macro-Raman

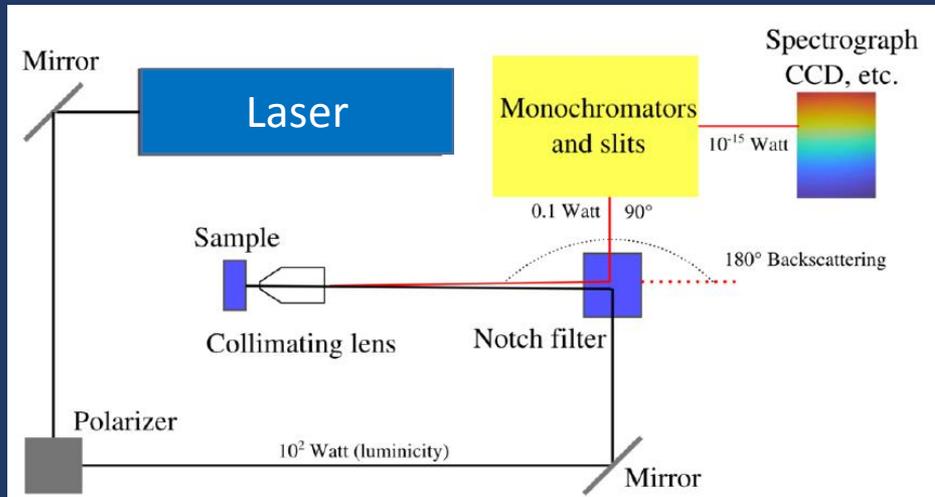


Figure credit: Dr. José A. Flores-Livas (<http://www.fysik-aztek.net/>)

Micro-Raman

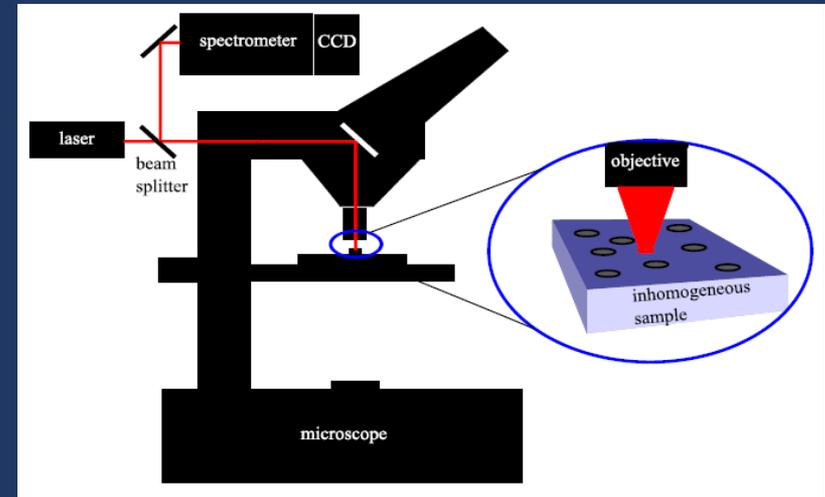
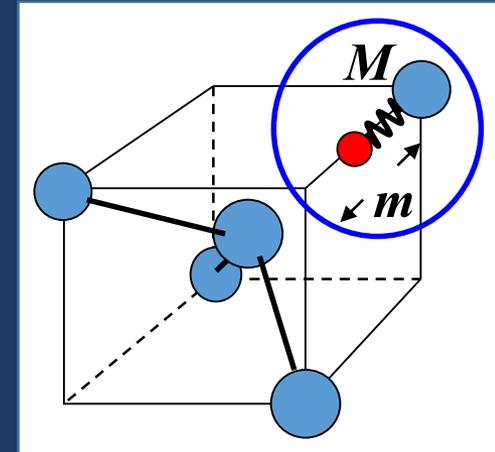
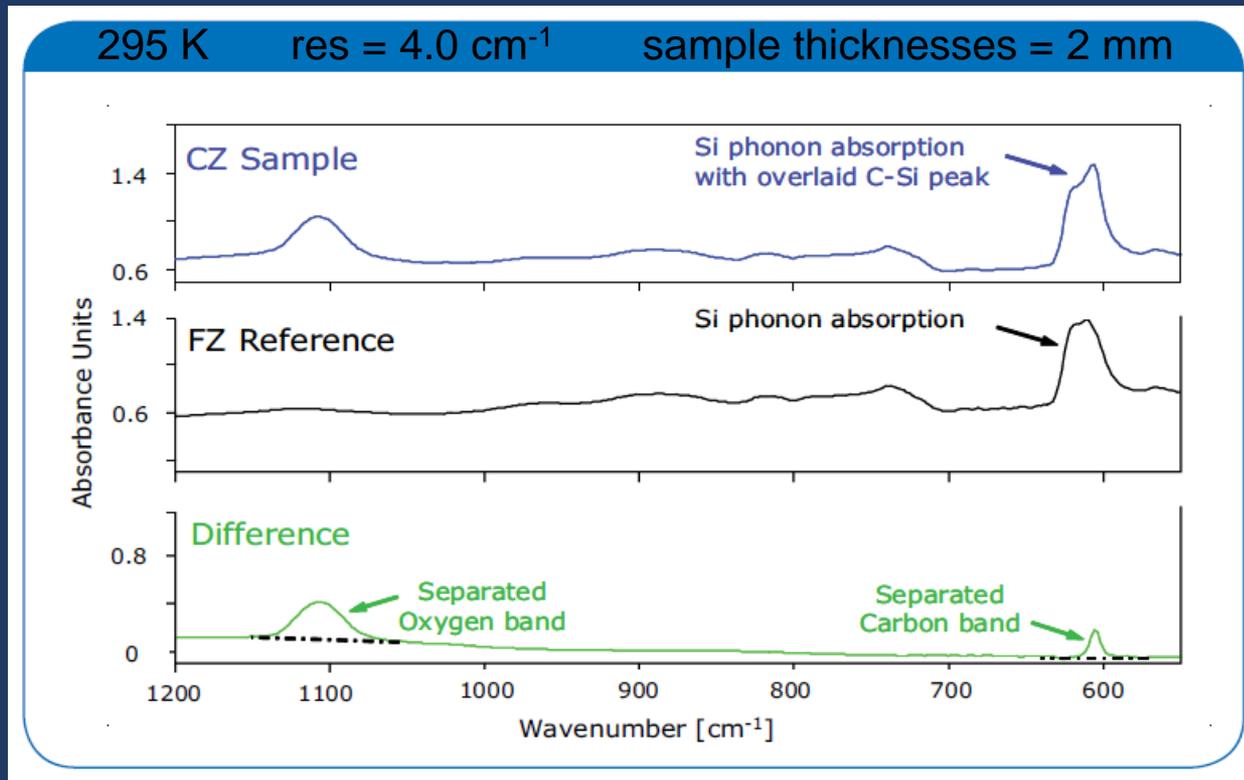


Figure credit: M. Schumm, PhD Dissertation, Julius-Maximilians-University Wurzburg (2008)

- Laser: power (intensity) and wavelength (fluorescence, penetration depth)
- Macro: Monochromator/slits determine spectral resolution
- Micro: objective lens determines spatial resolution
- Notch filters needed to suppress Rayleigh scattered laser line

FT-IR Application: Identifying defects in semiconductors

- Identifying O and C impurities in Cz Si



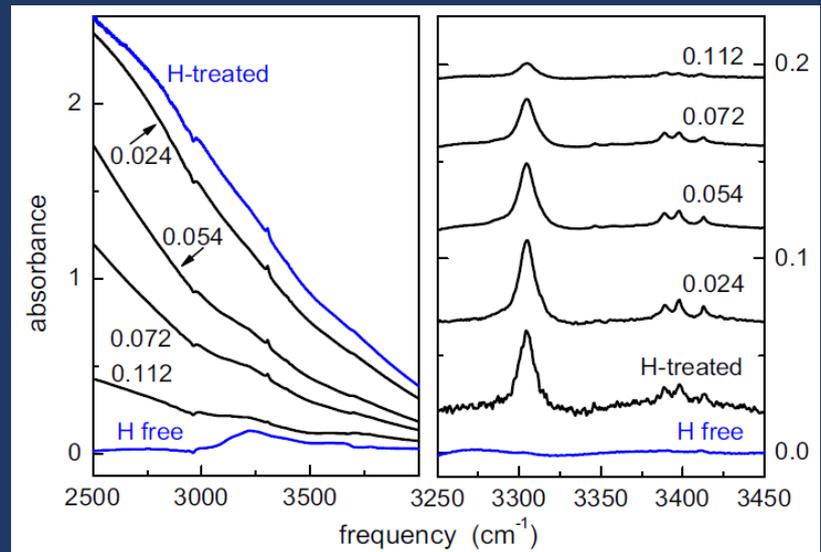
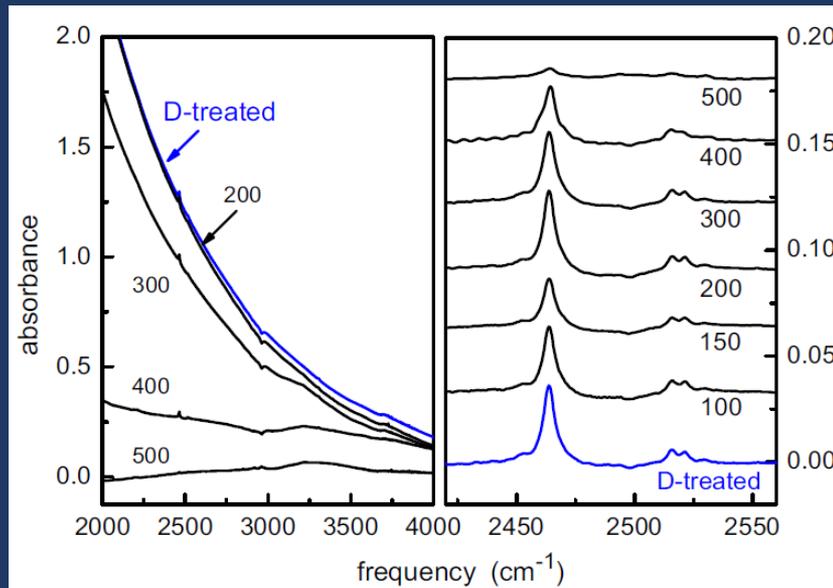
Source: Bruker, Application Note # 54, Carbon and Oxygen Quantification in Silicon.

Interstitial Oxygen – gettering sites for metallic impurities, also affect electrical conductivity.

Substitutional Carbon – affect density and electrical activity of dislocations

FT-IR Application: Identifying defects in semiconductors

- Identifying H impurities in transparent semiconducting oxides (TSOs)



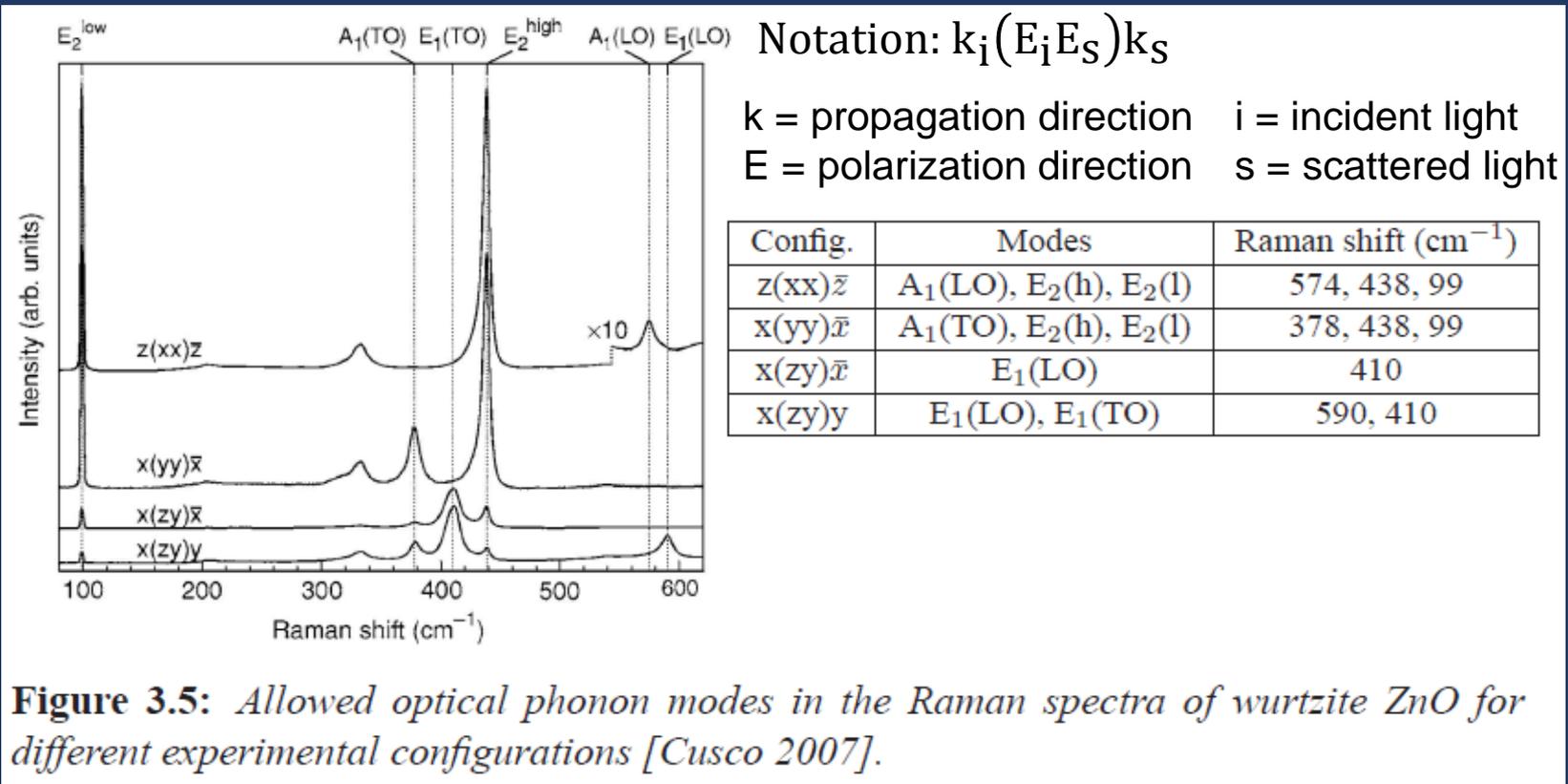
Indium oxide (In₂O₃) – dominant TSO on the market for transparent contacts on flat screen displays.

Presence of interstitial hydrogen confirmed via isotopic substitution with deuterium.

Hydrogen gives rise to unintentional *n*-type conductivity observed in as-grown samples.

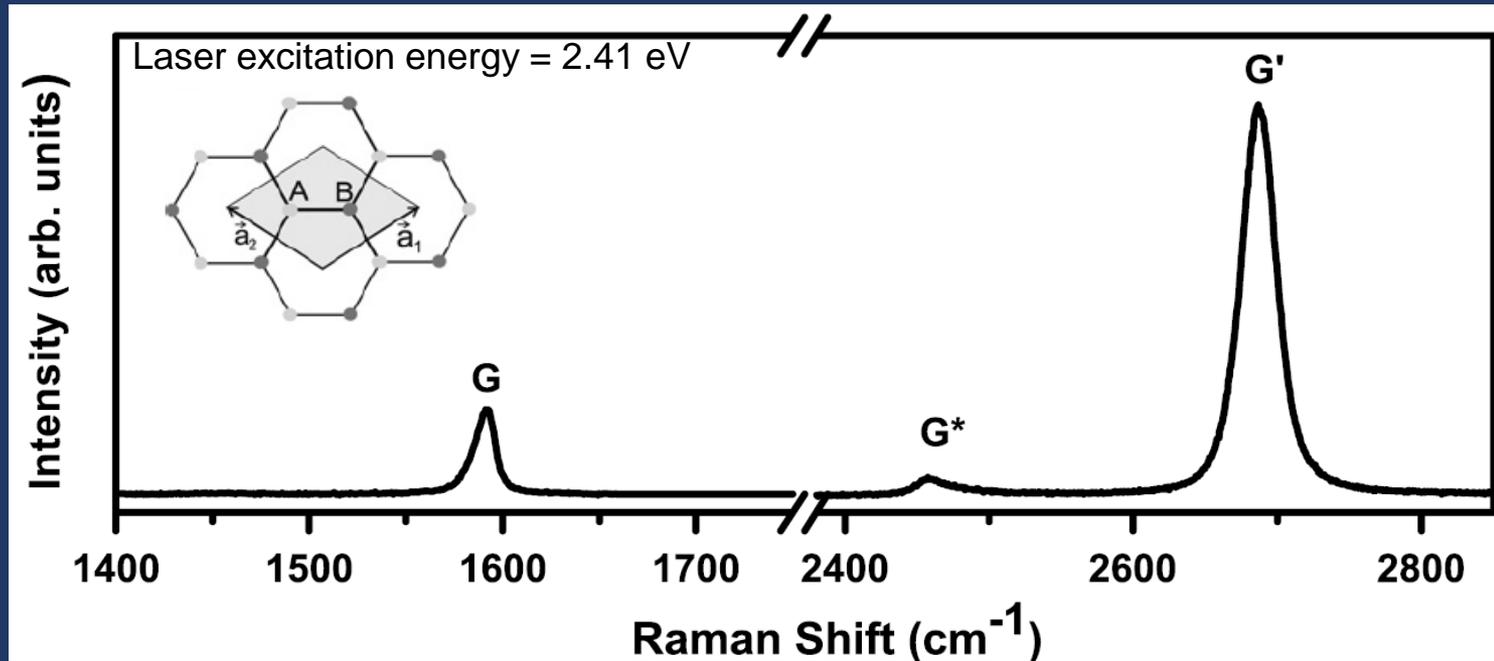
Source: W. Yin *et al.* Physical Review B **91**, 075208 (2015).

Raman Application: Optical phonon modes in zinc oxide

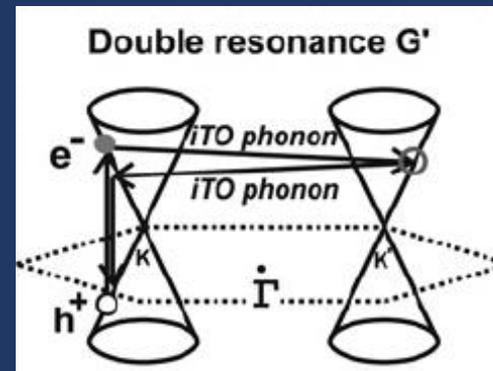
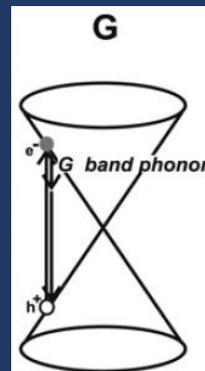


Polarized Raman spectroscopy used to compare experimentally-detected phonon modes with those predicted by theory.

Raman Application: Number of layers present in graphene

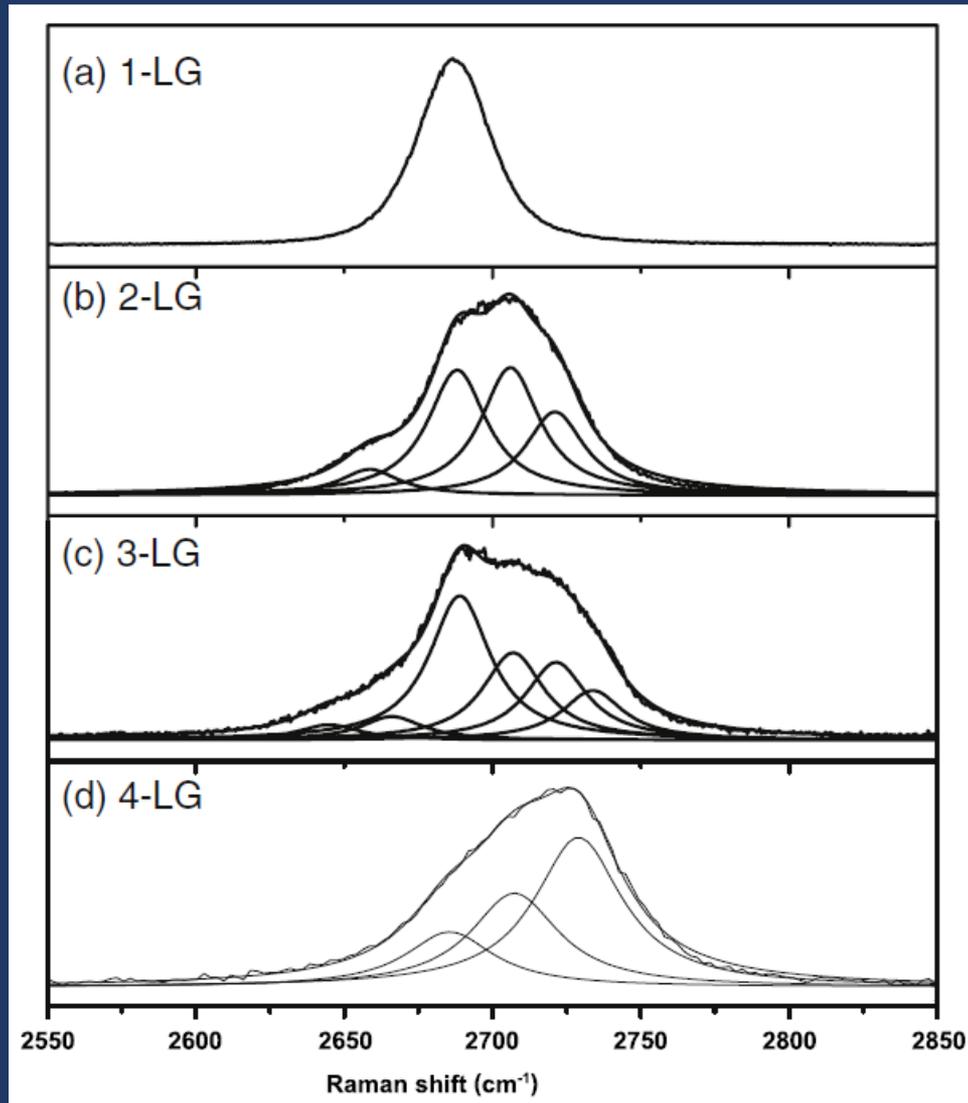


Monolayer graphene shows two characteristic Raman shifts associated with the material: G and G'.



Source: L. M. Mallard *et al.* Physics Reports **473** (2009) 51-87.

Raman Application: Number of layers present in graphene



1-LG: single Lorentzian

2-LG: four Lorentzians

3-LG: six Lorentzians

4-LG: three Lorentzians
(things get complicated...)

Source: L. M. Mallard *et al.* Physics Reports **473** (2009) 51-87.

Summary of this tutorial

- IR and Raman spectroscopies are **non-destructive** techniques and provide information about **vibrational** and **electronic** transitions in a material. (rovibronic also possible)
- Fundamental rules that determine vibrationally-active modes:
 - IR: non-zero change in the electric dipole moment
 - Raman: non-zero change in the electric polarizability
- **Complementarity** of IR and Raman permits the characterization of a broad range of materials.

Several FT-IR and Raman setups available within NNN.

FT-IR

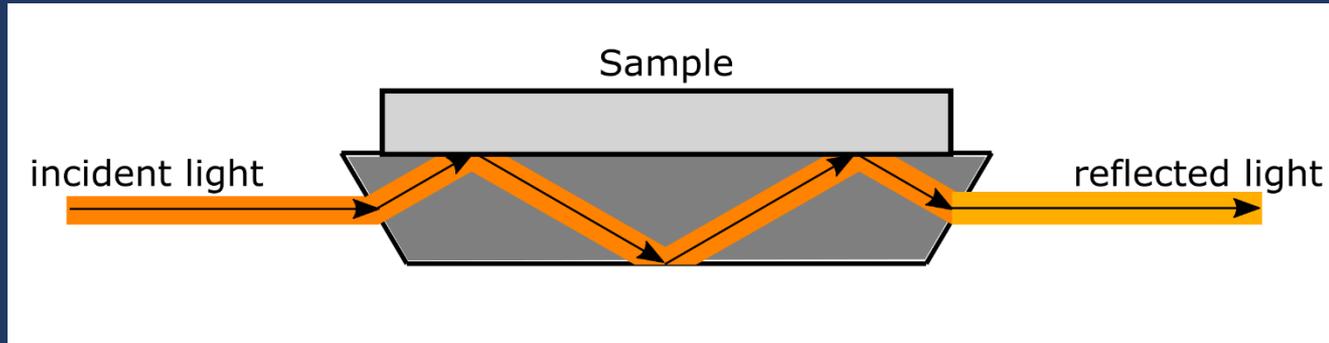
Facility	Instrument	Responsible	Contact
MiNaLAB (UiO)	Bruker IFS 125HR	Philip M. Weiser	p.m.weiser@smn.uio.no
Electrum	Nicolet iS10	Abdusalam Uheida	salam@kth.se
Electrum	Bruker Vertex 70V	Ingemar Petermann	ingemar.petermann@ri.se

Raman

Facility	Instrument	Responsible	Contact
NTNU NanoLab	Renishaw InVia Reflex	Trine Østlyng Hjertås	trine.o.hjertas@ntnu.no
Hive	Horiba XploRA	Mattias Fredriksson	mattias.fredriksson@chalmers.se
Micronova	WITec alpha300 RA+	Joonas Holmi	joonas.holmi@aalto.fi

Please check descriptions in LIMS or email above contact person for more information.

Attenuated Total Reflectance (ATR) Challenges



1. Distortion of relative peak intensities (differing penetration depths)

$$d_p = d_p(\bar{\nu}, n_{\text{sample}}, n_{\text{ATR}}, \theta_{\text{incidence}})$$

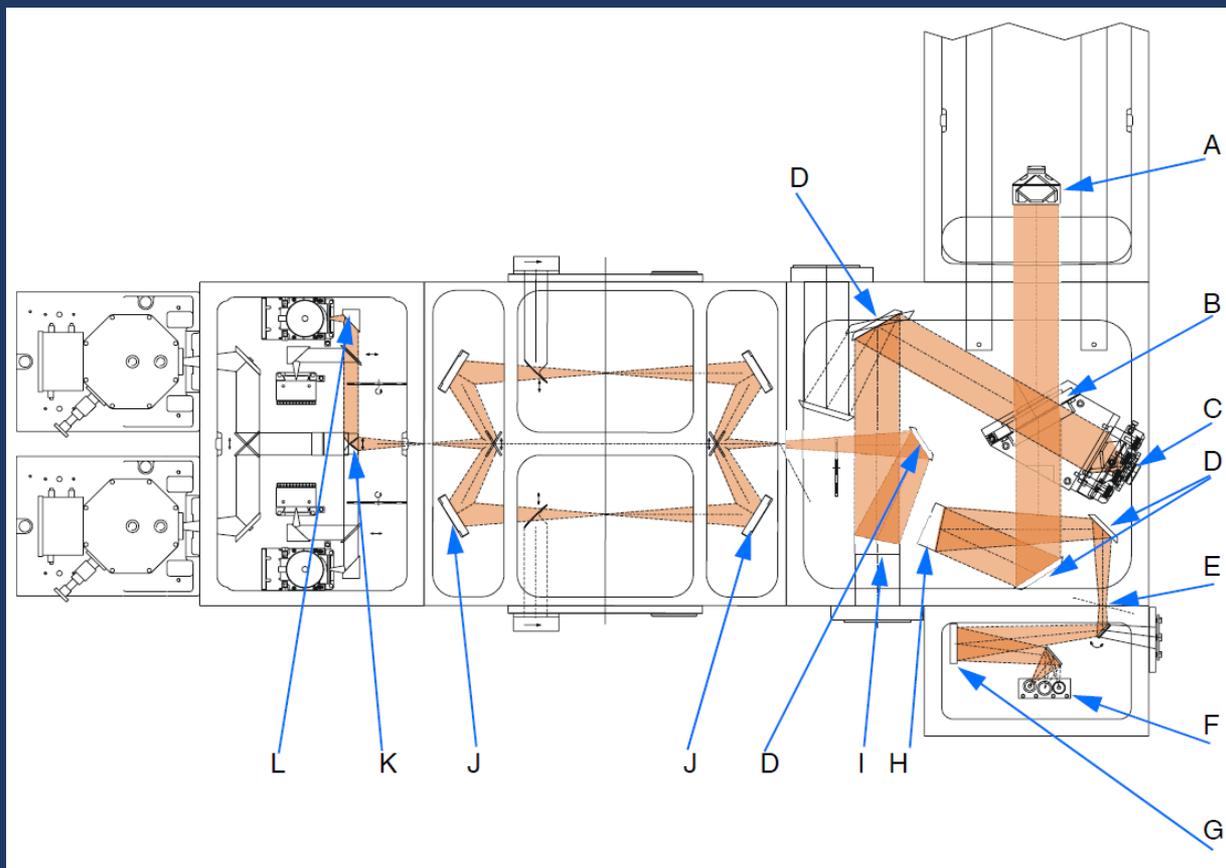
2. Shift of absorption bands to lower frequency

Absolute position of $\bar{\nu}$ depends on $n_{\text{sample}} d_p \alpha$

Anomalous dispersion associated with n_{sample} near an absorption resonance causes shift to lower wavenumber.

Most manufacturers provide software to correct these effects.

Bruker IFS 125HR FT-IR spectrometer at MiNaLab

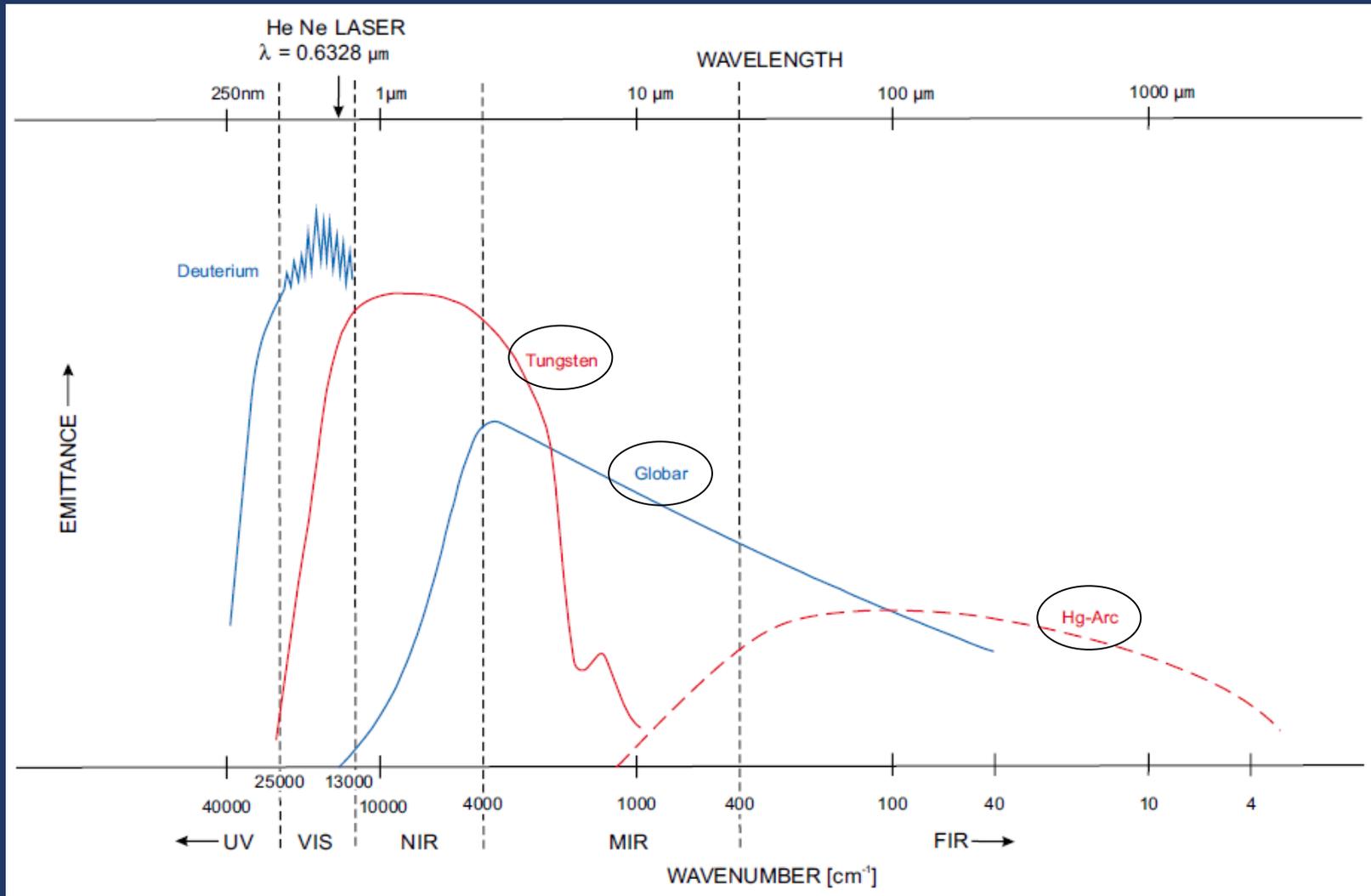


	Definition
A	Scanner with movable retroreflecting mirror
B	Beam splitter
C	Fixed retroreflecting mirror
D	Folding mirror
E	Input aperture (field stop)
F	Sources

G	Spherical mirror
H	Collimating parabolic mirror
I	Focusing parabolic mirror
J	Toroidal mirror
K	Collimating parabolic mirror
L	Focusing parabolic mirror

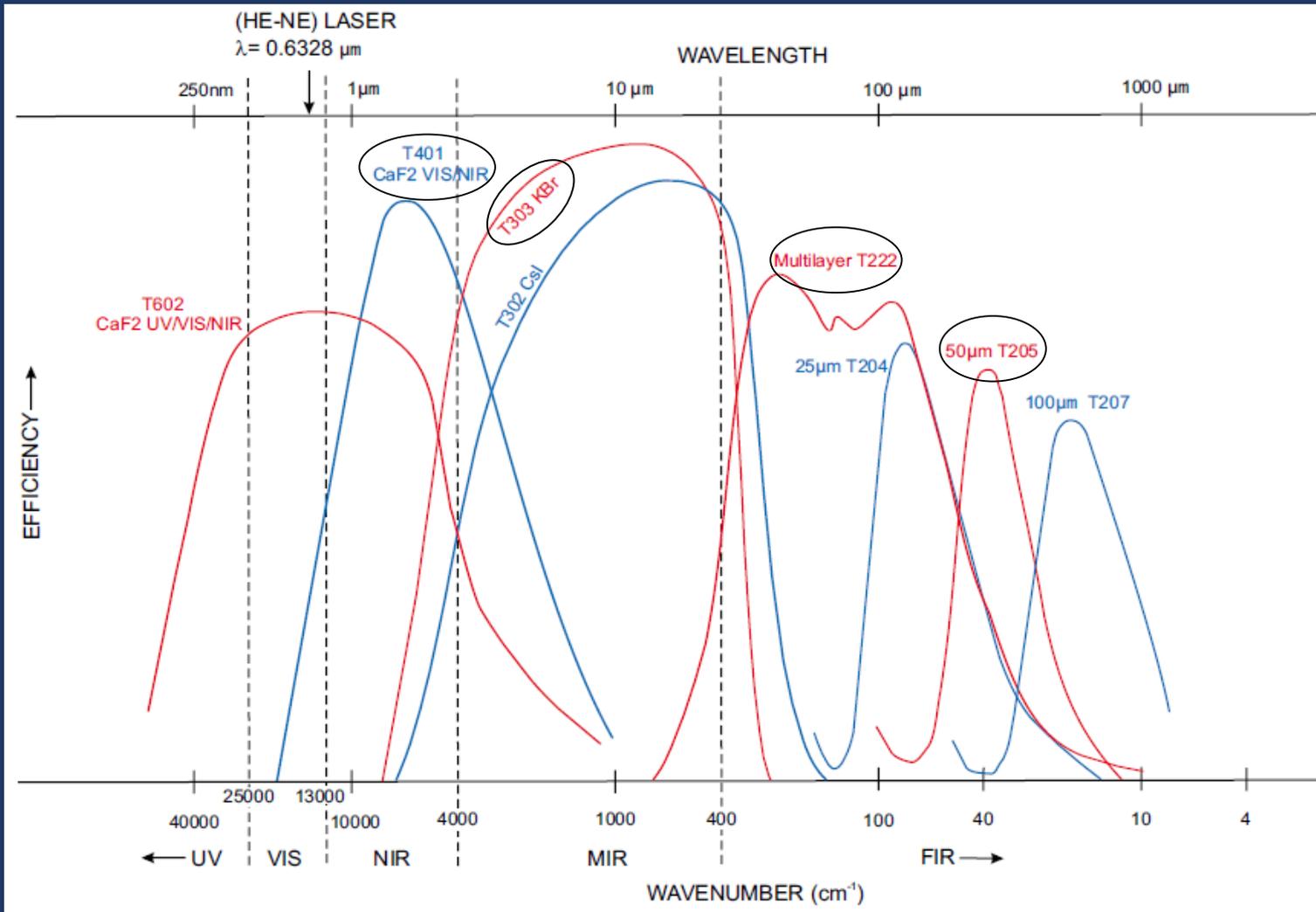
Bruker IFS 125HR FT-IR spectrometer at MiNaLab

Infrared light sources



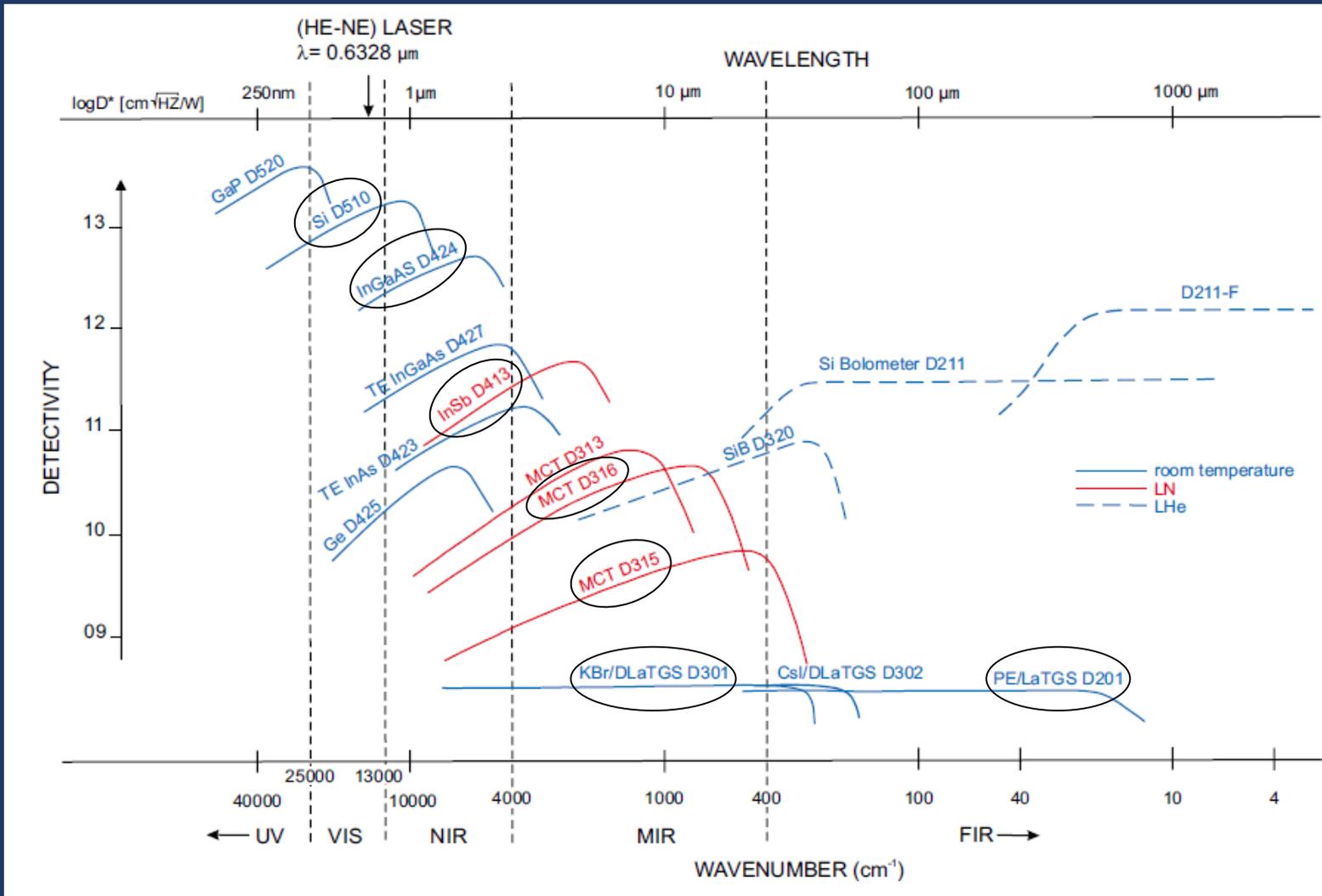
Bruker IFS 125HR FT-IR spectrometer at MiNaLab

Beamsplitters



Bruker IFS 125HR FT-IR spectrometer at MiNaLab

Detectors



Advanced pump-probe techniques can provide additional information or enhanced signals.

