Materials design & selection for Circular Economy

Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

Lecturer: **Paolo Dolcet**

Vibrational spectroscopies

- In polyatomic species, along with electronic levels, vibrational and rotational levels are also present
- Similar to electronic states, vibrational and rotational states are quantized
- Infrared radiation can promote transition of electrons between vibrational and rotational states

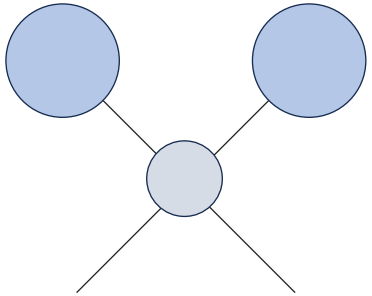
Region	Wavelength λ (μm)	Wavenumber $\bar{\nu}$ (cm^{-1})	Frequency ν (Hz)
Near	0.78 – 2.5	12800 – 4000	$3.8 * 10^{14} – 1.2 * 10^{14}$
Middle	2.5 – 50	4000 – 200	$1.2 * 10^{14} – 6.0 * 10^{12}$
Far	50 – 10000	200 – 10	$6.0 * 10^{12} – 3.0 * 10^{11}$
Typical range	2.5 – 15	4000 – 670	$1.2 * 10^{14} – 2.0 * 10^{13}$

Vibrational spectroscopies are usually discussed in terms of wavenumber, mainly for convenience

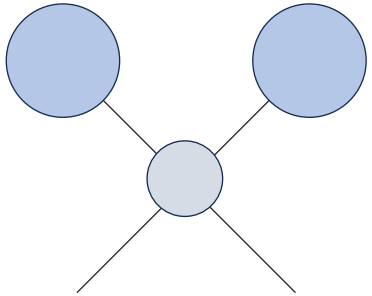
Infrared ranges

Region	Wavenumber $\bar{\nu}$ (cm^{-1})	Measurement type	Kind of analysis	Applicable samples
Near	12800 – 4000	Diffuse reflectance	Quantitative	Solid or liquid commercial materials
		Absorption	Quantitative	Gaseous mixtures
Middle	4000 – 200	Absorption	Qualitative	Pure solid, liquid or gases
			Quantitative	Complex liquid, solid or gaseous mix.
			Chromatographic	Complex liquid, solid or gaseous mix.
Far	200 – 10	Reflectance	Qualitative	Pure solids or liquids
		Emission	Quantitative	Atmospheric samples
		Absorption	Qualitative	Pure inorganic or organometallic species

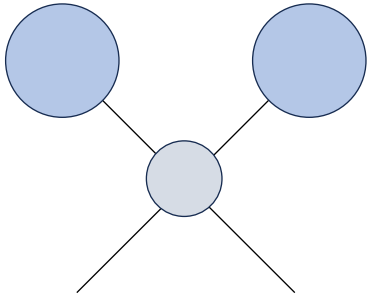
Vibrations and rotations



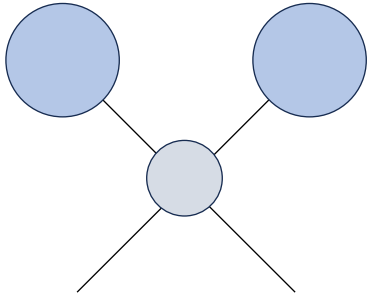
Symmetric
stretching



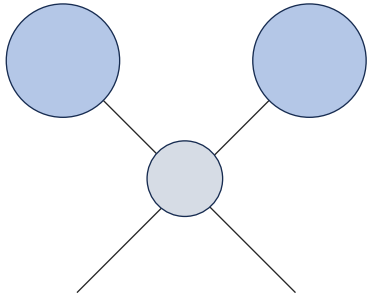
Asymmetric
stretching



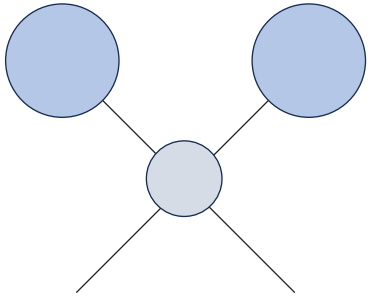
In-plane
rocking



In-plane
scissoring

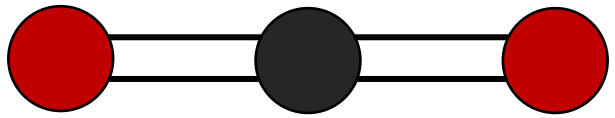


Out-of-plane
wagging

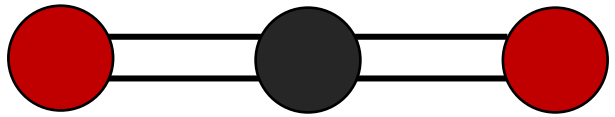


Out-of-plane
twisting

Are all vibrations visible?



IR **inactive**



IR **active**

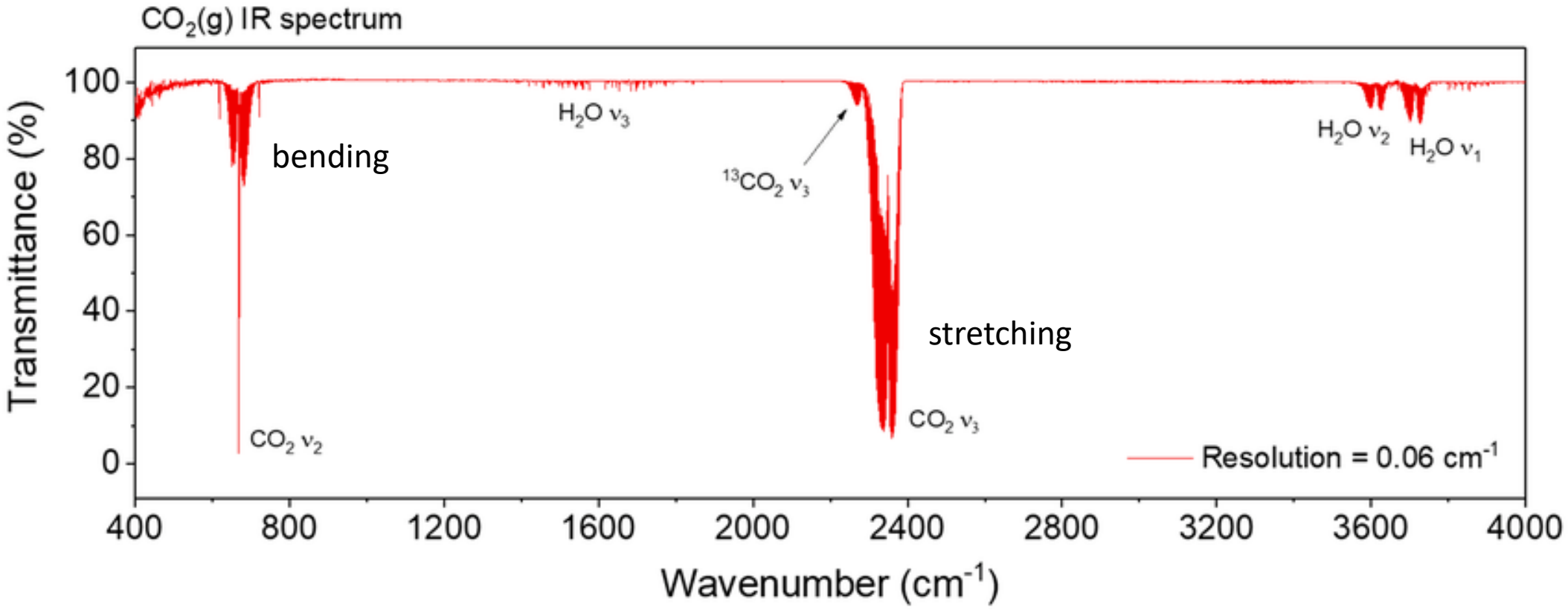
In the infrared spectra of CO_2, I can see two stretching signals, one for symmetric and one for the asymmetric modes, correct?

- A molecule can absorb infrared radiation **only if** a **net change in dipole moment** occurs

- Homonuclear molecules cannot absorb IR radiation

FTIR spectrum of CO_2

$$E = hc\bar{\nu}$$



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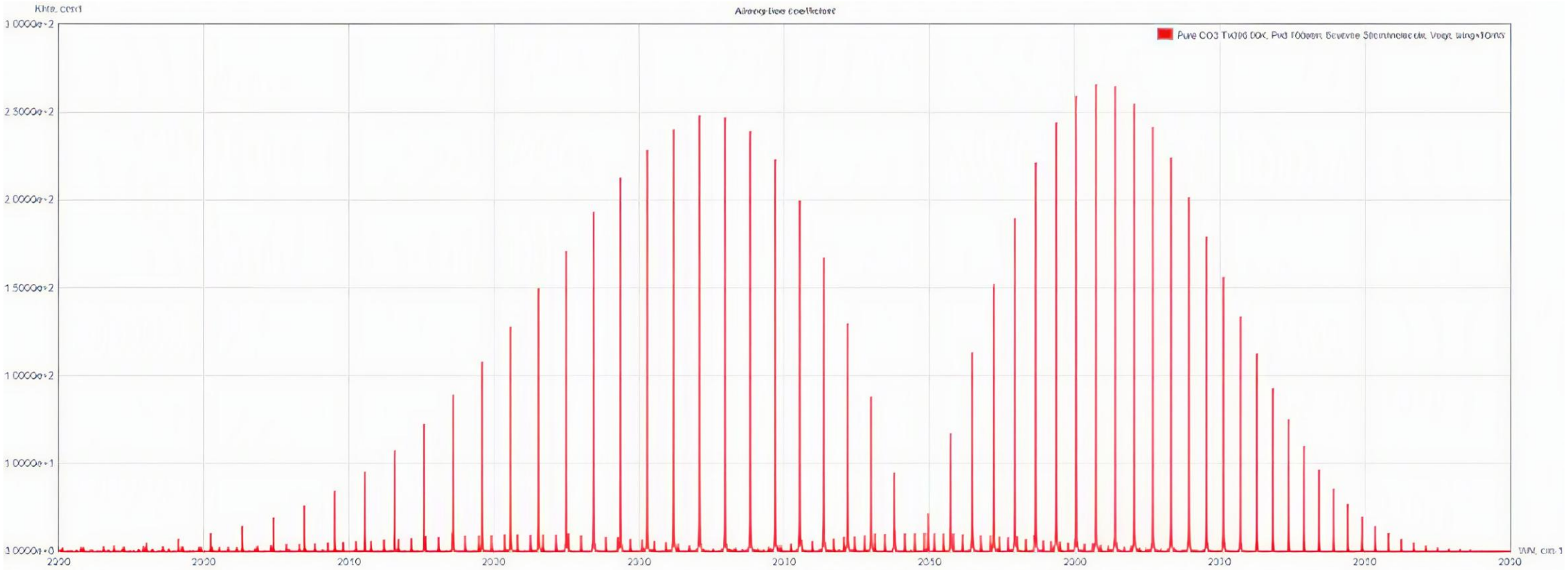
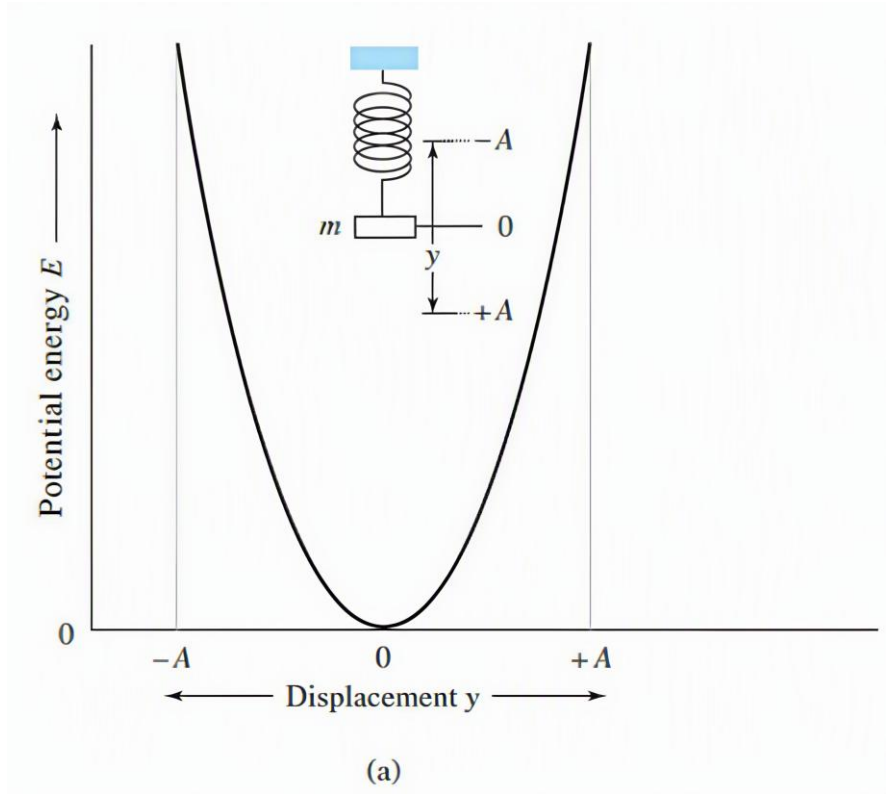


In gas-phase, rotational fine structure is visible
Two branches due to transition selection rules

Harmonic oscillator



The molecular vibrations can be interpreted with a harmonic oscillator model

- Hooke's law (restoring force):

$$F = -ky$$

k = spring constant

- Potential energy of the spring:

$$E = \frac{1}{2}ky^2$$

- Weight trajectory:

$$y = A\cos(2\pi\nu_m t)$$

A = oscill. amplitude

ν_m = oscill. frequency

- Our aim, **frequency $\boldsymbol{\nu_m}$** *:*

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The frequency depends **only** on the **force constant *k*** and **mass *m***

Harmonic oscillator

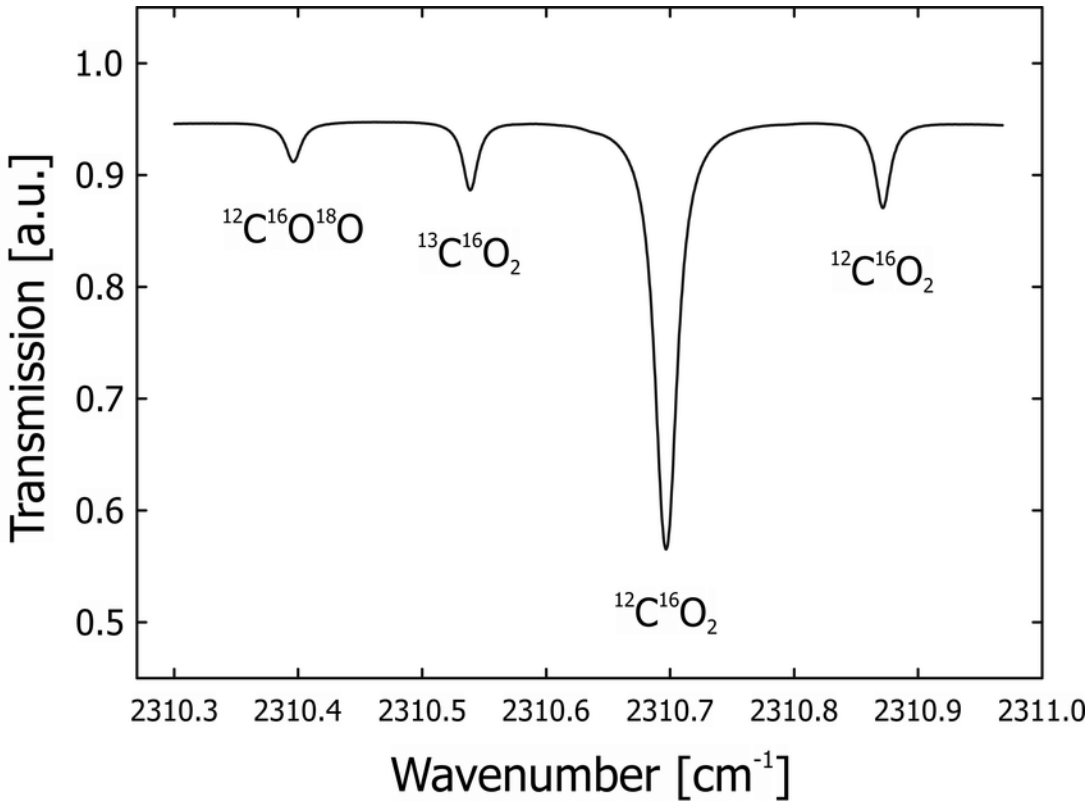
- In a molecule, we have two masses oscillating → reduced mass μ

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- The fundamental vibration frequency becomes:

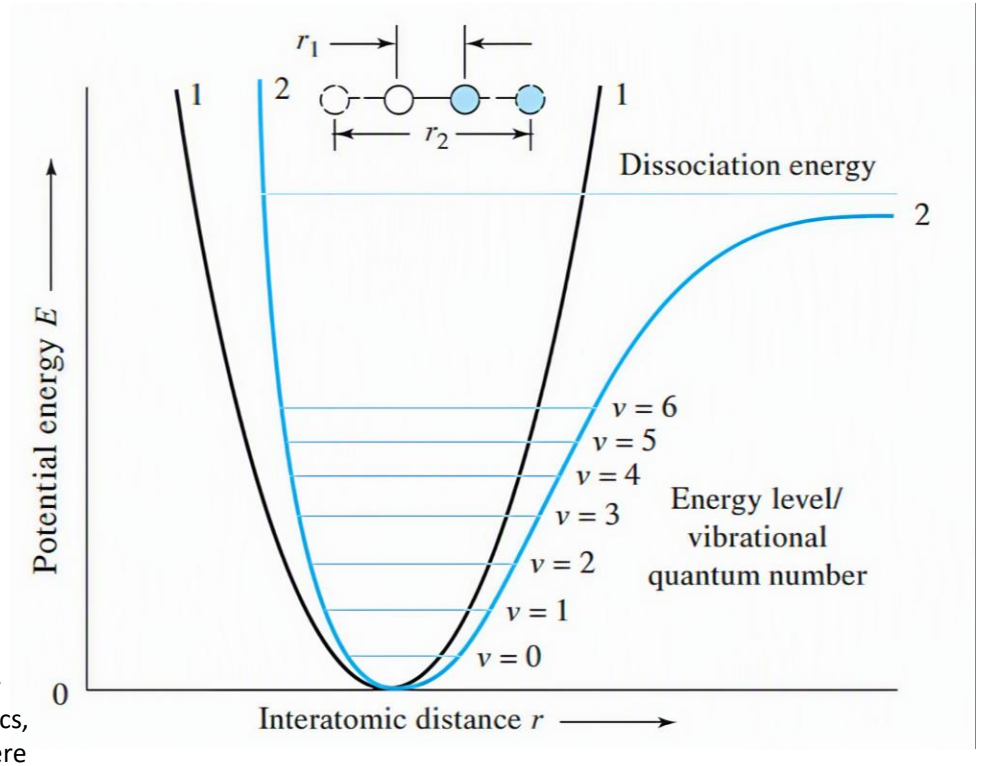
$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

- Infrared spectroscopy is sensitive to isotopes!



https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/rcm.7859

Real molecules: anharmonic oscillator



$E_0 = \frac{1}{2} h\nu_m$

Zero-Point Energy
In quantomechanics, even at T = 0 K there can be vibration

- In molecules, vibrational levels are quantized

$$E = \left(v + \frac{1}{2}\right) h\nu_m = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

v = vibrational quantum number

- **Selection rule** for vibr. transition: $\boldsymbol{\Delta v = \pm 1}$

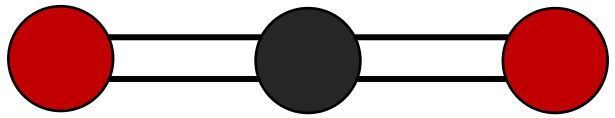
$$\Delta E = E_1 - E_0 = \frac{3}{2} h\nu_m - \frac{1}{2} h\nu_m = h\nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

- Real molecules behave like **anharmonic oscillators** → ΔE between successive levels decreases with increasing v
- Transitions with $\Delta v = \pm 2, \pm 3, \ldots$ become possible (overtones & combinations, weak signals)

IR measurements are quantifying the force constant of bonds

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \approx 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}$$

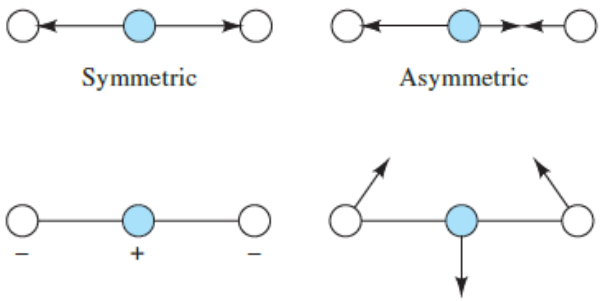
Vibrational modes

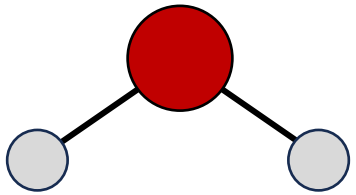


- How many vibrational modes does CO_2 have?

Linear molecules
3N-5 vibrational modes

- CO_2 has 3*3-5 = **4** vibrational modes

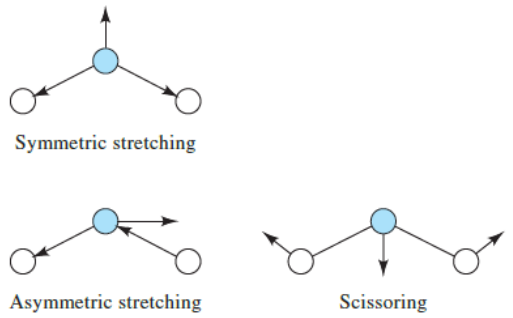




- How many vibrational modes does H_2O have?

Bent molecules
3N-6 vibrational modes

- H_2O has 3*3-6 = **3** vibrational modes



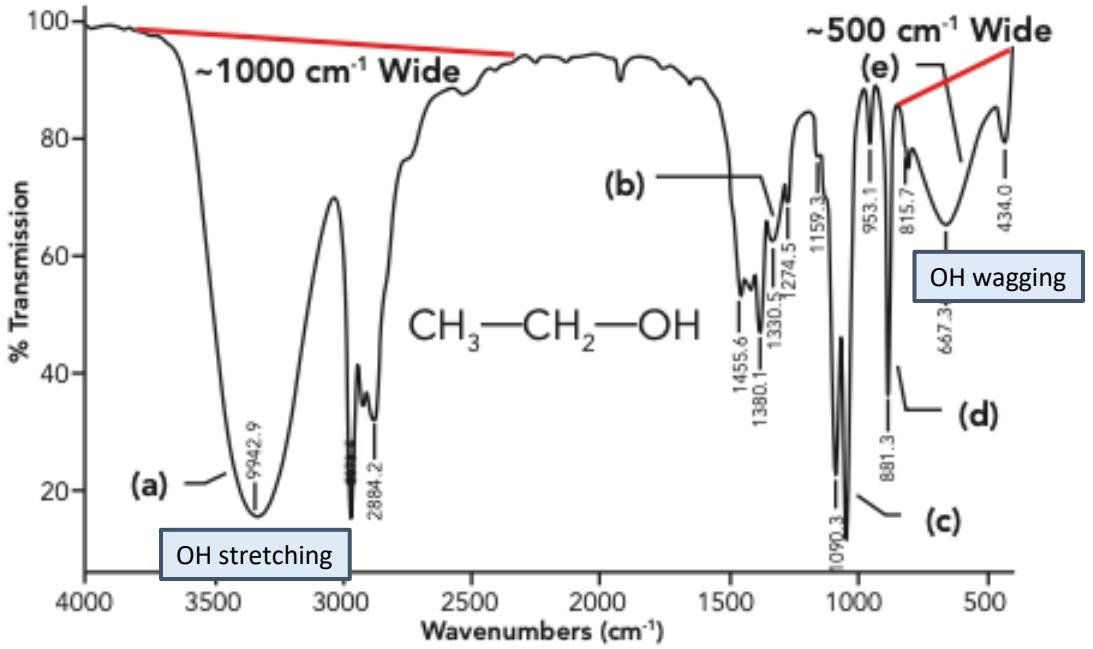
Remember!
Not all vibr. nodes are **necessarily IR active**

Vibrational modes

- Knowing the number **N** of **active IR modes**, does **not necessarily** mean we will see **N peaks** in the spectrum

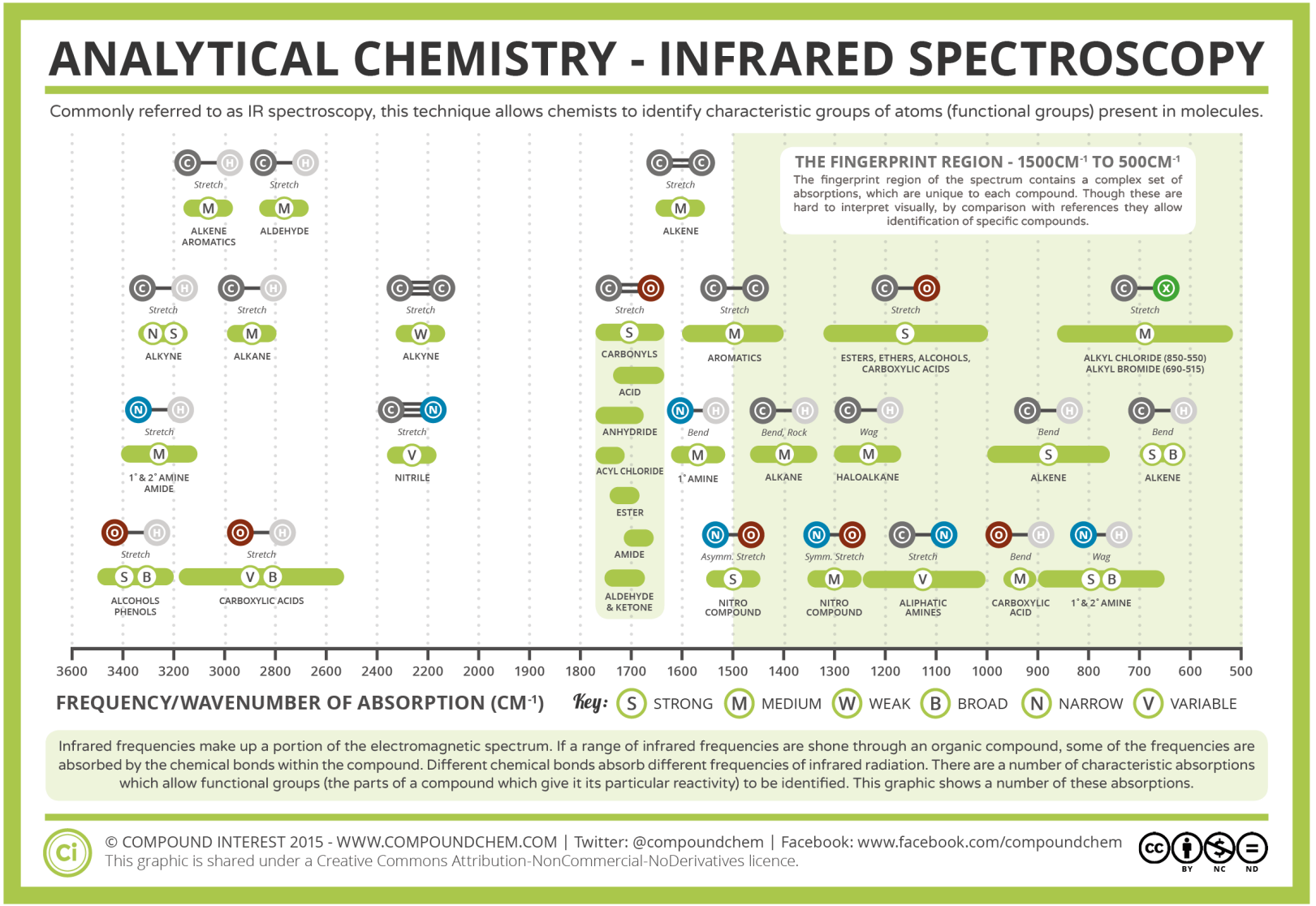
- Factor decreasing the number of peaks:
  - Vibrations having similar energies
  - High molecular symmetry
  - Sensitivity issues
  - Energy outside the operational range of the instrument

- Other factors affecting the intensity /width of the infrared peaks:
  - Temperature
  - Hydrogen bonding
  - Crystallinity



Infrared correlation table

Functional group region (4000 – 1500 cm^{-1})
Distinct, easily identifiable peaks
Stretching modes



Fingerprint region (1500 – 500 cm^{-1})
Overlap of several **bending** modes
Representing the skeleton of the organic molecule

Remember

$$\bar{\nu} = \approx 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}}$$

https://i0.wp.com/www.compoundchem.com/wp-content/uploads/2015/02/Analytical-Chemistry-Infrared-Spectroscopy.png?ssl=1

Sample preparation

- Only rarely samples are measured as pure materials (in transmission mode)
- No solvent/dispersant is completely transparent to IR

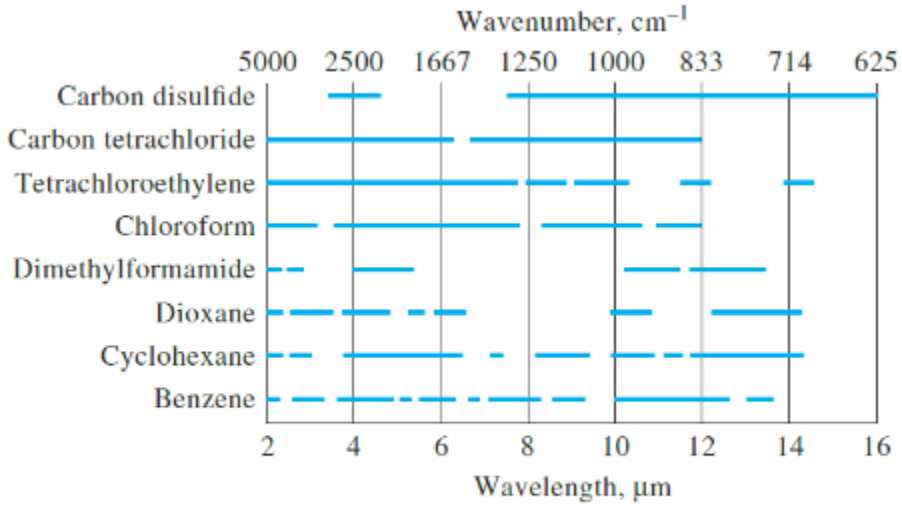
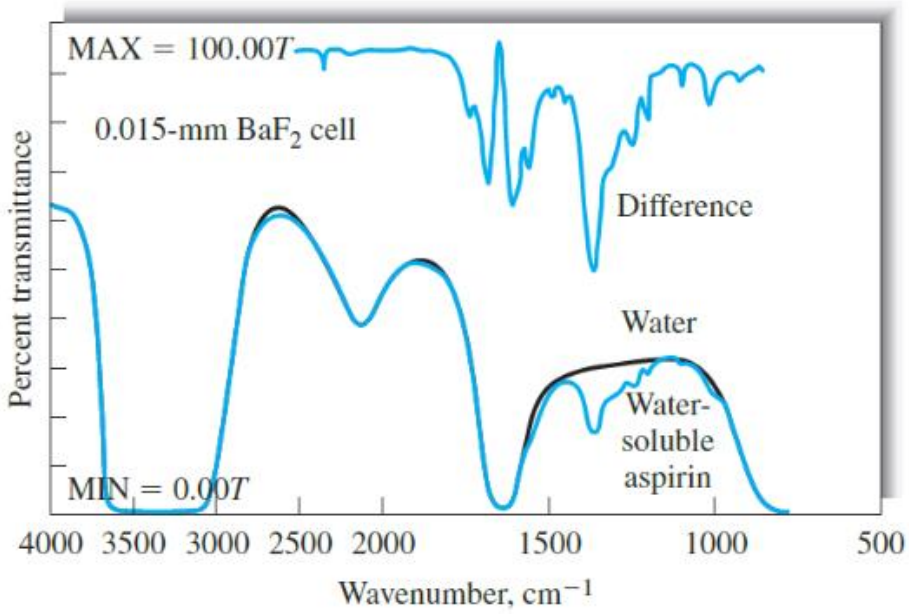


FIGURE 17-1 Solvents for IR spectroscopy. Horizontal lines indicate useful regions.



- For solids, common dispersants are **KBr** (no infrared active modes) or **Nujol** (mixture of alkanes)

Common materials and cell designs

TABLE 17-2 Common IR Window Materials

Window Material	Applicable Range, cm^{-1}	Water Solubility, g/100 g H_2O, 20°C
Sodium chloride	40,000–625	36.0
Potassium bromide	40,000–385	65.2
Potassium chloride	40,000–500	34.7
Cesium iodide	40,000–200	160.0
Fused silica	50,000–2,500	Insoluble
Calcium fluoride	50,000–1,100	1.51×10^{-3}
Barium fluoride	50,000–770	0.12 (25°C)
Thallium bromide iodide, KRS-5	16,600–250	<0.0476
Silver bromide	20,000–285	1.2×10^{-7}
Zinc sulfide, Irtran-2	10,000–715	Insoluble
Zinc selenide, Irtran-4	10,000–515	Insoluble
Polyethylene	625–30	Insoluble

From *Practical Sampling Techniques for Infrared Analysis*, P. B. Coleman, ed., Boca Raton, FL: CRC Press, 1993.

CaF_2 or **BaF_2** common water-insoluble windows

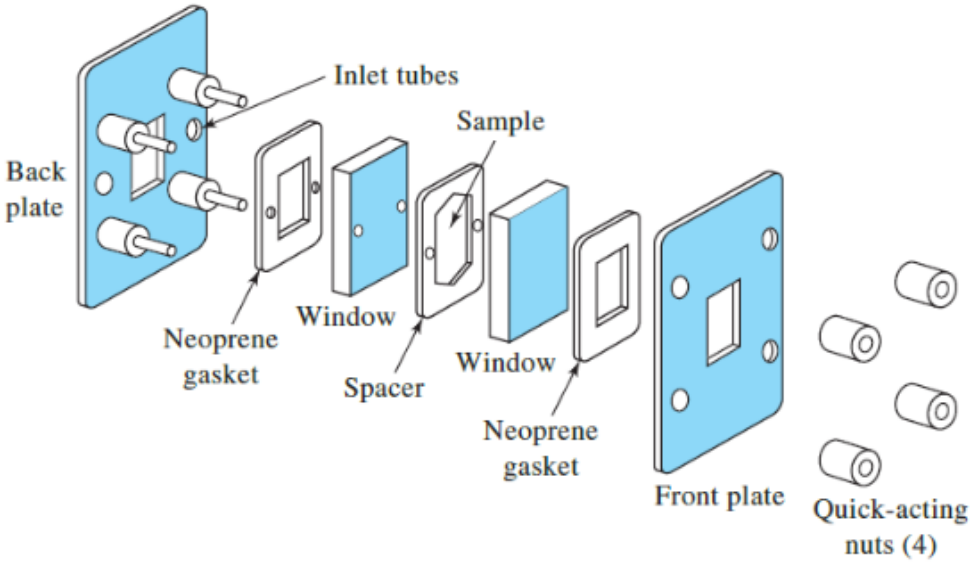
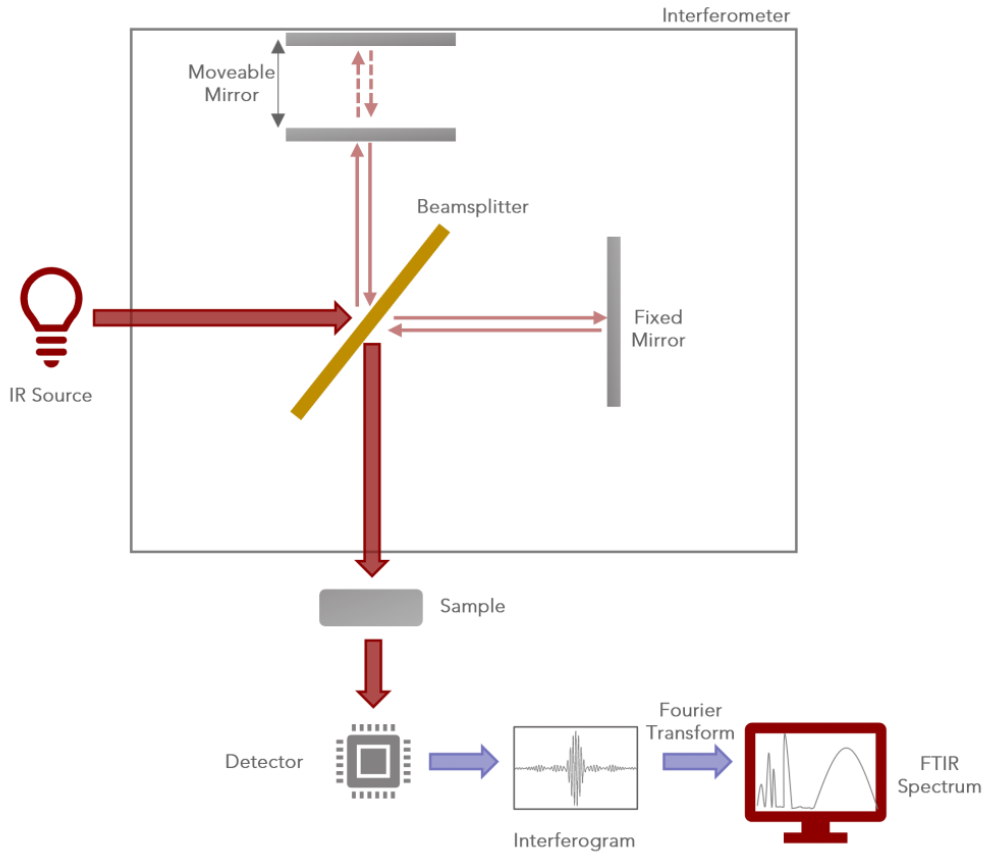


FIGURE 17-3 Expanded view of a demountable IR cell for liquid samples. Teflon spacers ranging from 0.015 to 1 mm thick are available. (Courtesy of Perkin-Elmer Corp., Norwalk, CT.)

- Optical path should be **short**
  - Liquids: **10 – 50 µm** for pure liquids, **0.1 – 1 mm** for solutions
  - Solids: **10 – 100 µm**
  - Gas: **5 – 10 cm** (the exception)

Fast Fourier transform IR spectrometer



- Standard measurements are done in transmission

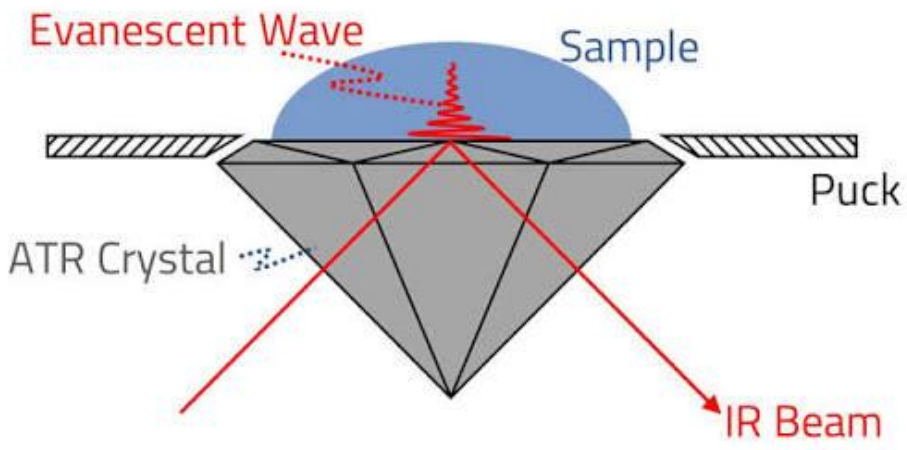
1. IR source emits multiwavelength beam
2. Interferometer creates an interferogram

$$I = f(cm)$$

3. Sample absorbs specific frequencies → modification of interferogram
4. The FT transform converts the interferogram to a spectrum

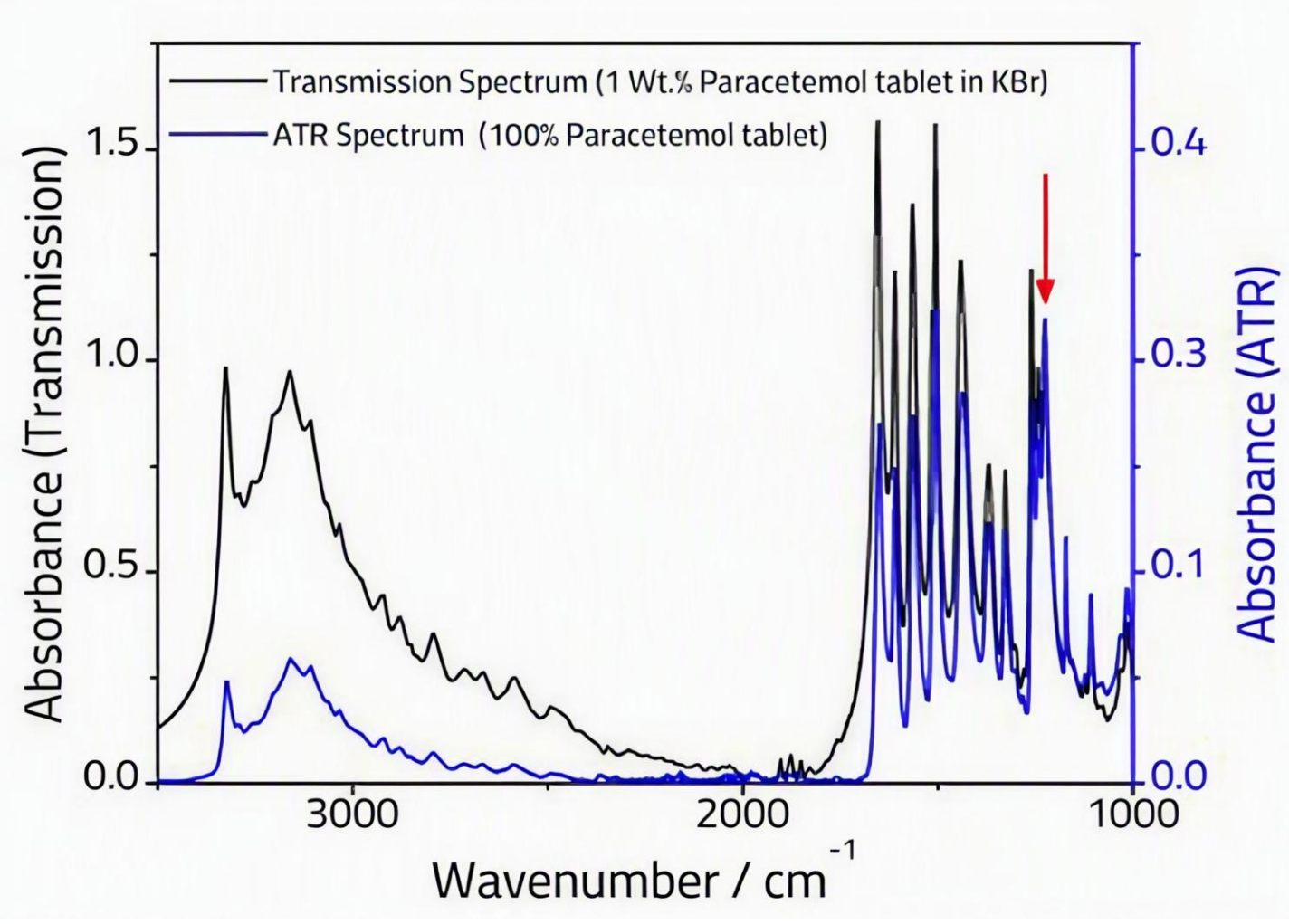
$$I = f(cm^{-1})$$

Attenuated Total Reflectance (ATR)



- Preparing KBr pellets not always possible (or convenient)
- ATR requires little to no preparation, can be used for solids and liquids
- Exploitation of crystal with very high refraction index (n = 2.4 – 4) >> sample
- IR beam hits the sample at $\theta > \theta_c$ → total internal reflection
- At the interface, evanescence wave is created
- Interaction evan. wave ↔ sample leads to specific frequencies absorption

ATR vs FTIR

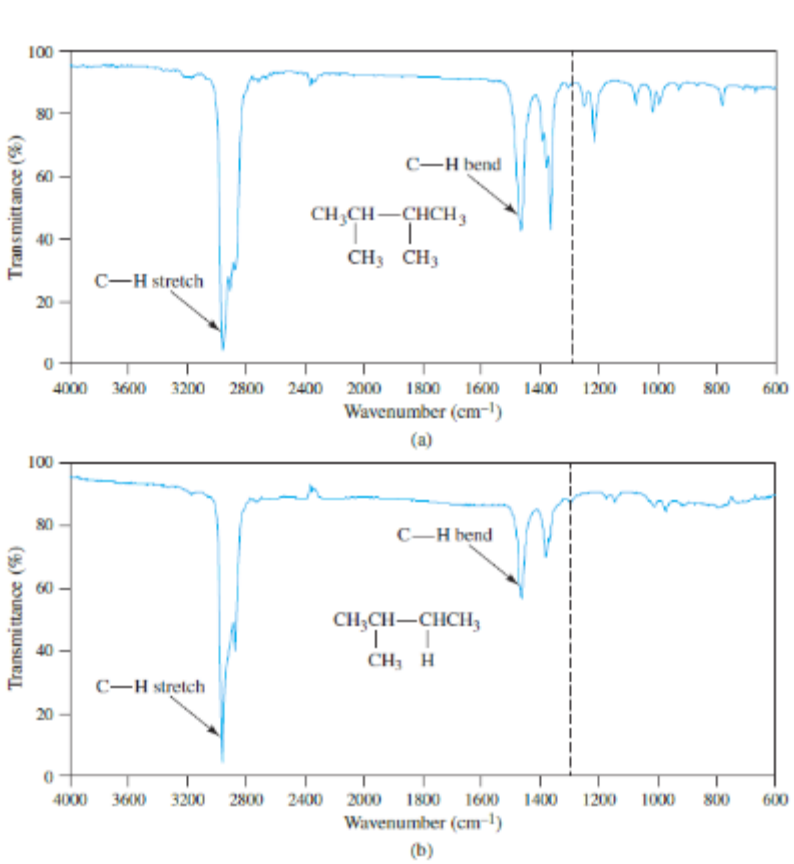


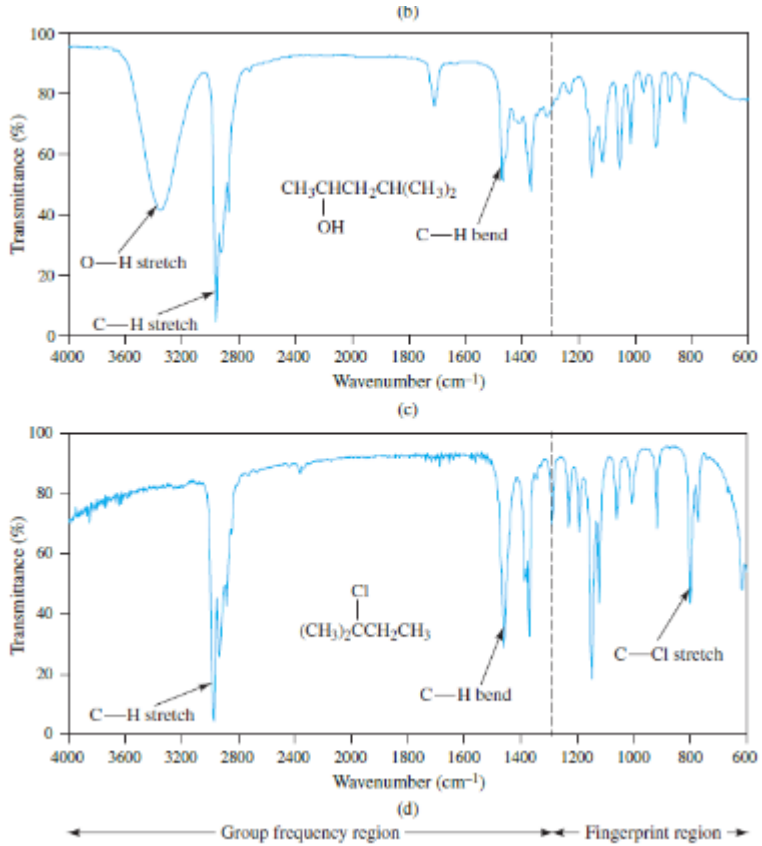
ATR penetration depth

$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}$$

FTIR and ATR spectra provide the same information, but in ATR peaks at higher wavenumber have lower intensity (penetration depth smaller)

Qualitative comparison





The fingerprint region amplifies tiny differences in the chemical backbone

Quantitative analysis

- Quantitative analysis similar to UV/Vis approach, but:
  - Spectra are more complex
  - Bands are narrower
- Standard with known concentration must be used for calibration
- Comparison with background necessary
- ATR quantification trickier:
  - Optical path might vary
  - Penetration depth is λ-dependent and *n*-dependent

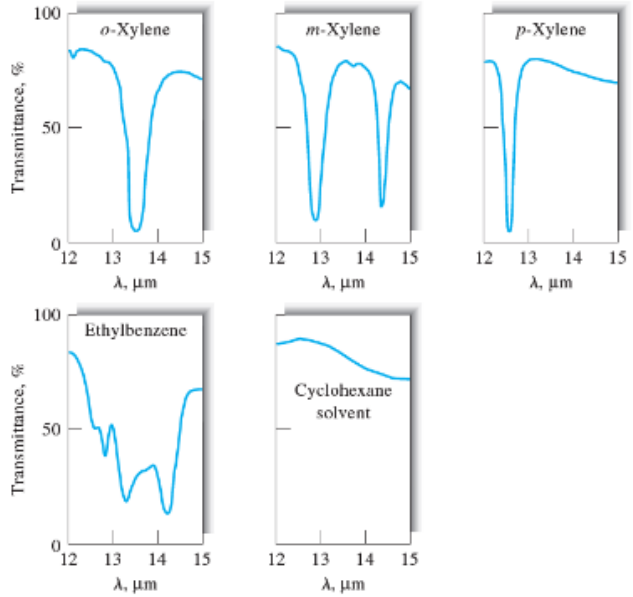
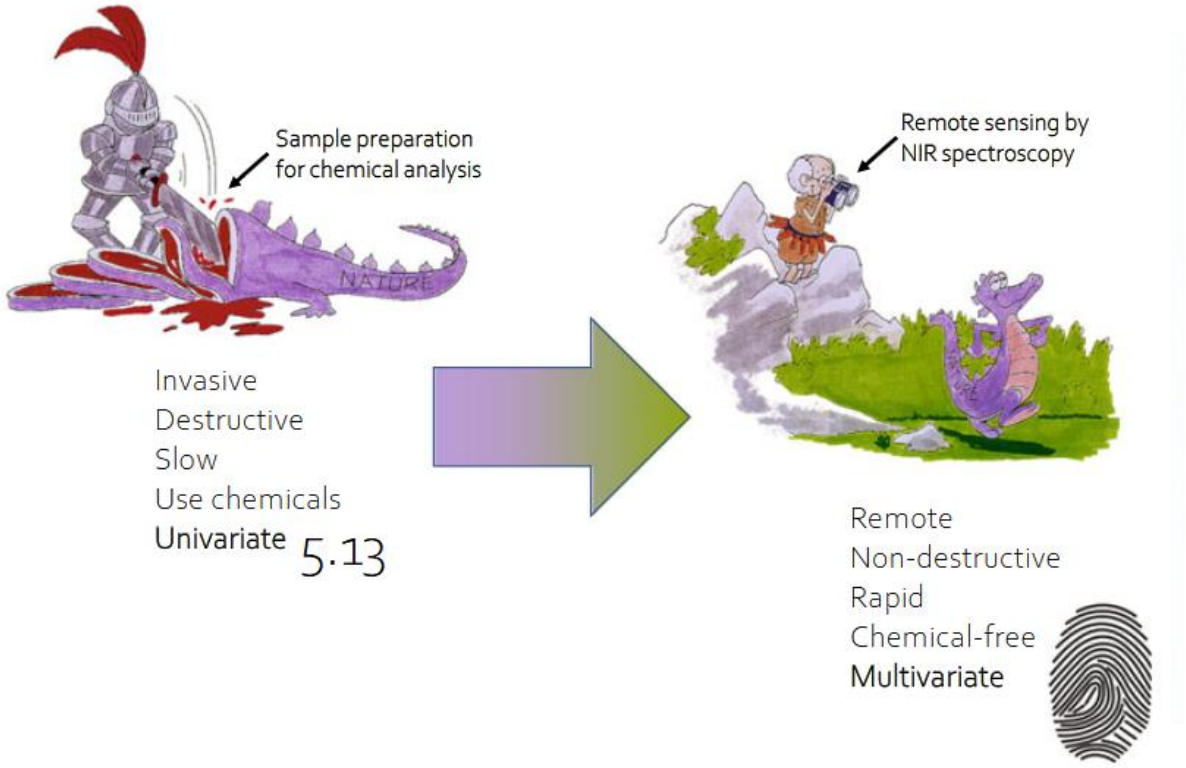


FIGURE 17-10 Spectra of C_8H_{10} isomers in cyclohexane.



Near infrared spectroscopy

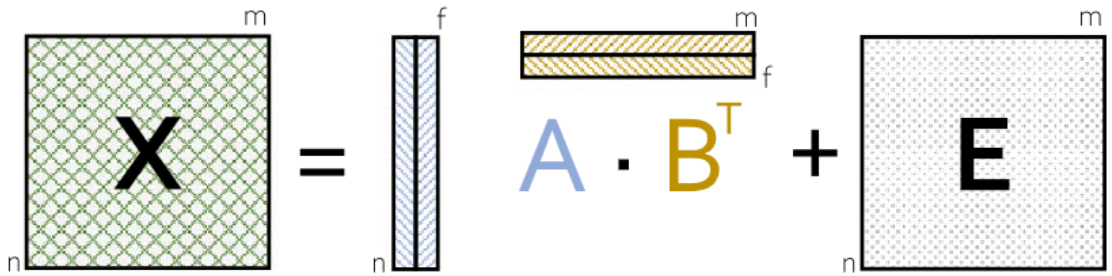
- Near infrared (12800 – 4000 cm^{-1}) range covers mostly **overtone** and **combination vibrations** + **electronic transitions**
- Signals **10 – 100 weaker** than mid-IR
- Not sensitive, but **higher penetration depth** → possible to investigate bulk materials, **no sample preparation**
- Broader, overlapping signals → **direct assignation difficult**
- NIR spectra normally analyzed using multivariate approaches

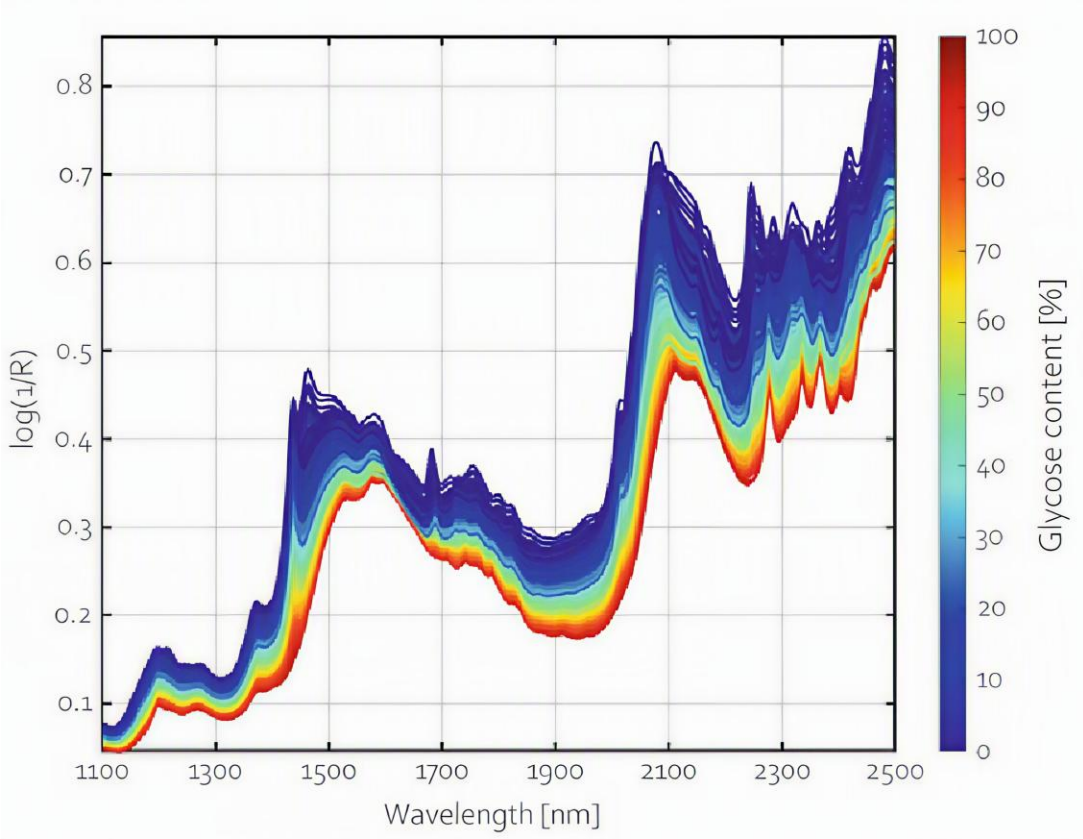


Y. Ozaki *et al.*, Near-Inrfared Spectroscopy: Theory, Spectral Analysis, Instrumentation and Applications, Springer

Chemometrics

- Chemometrics:
  - Reduction of complex dataset into a dataset of principle variables
  - P. V. used to classify, identify outliers and suggest trends.





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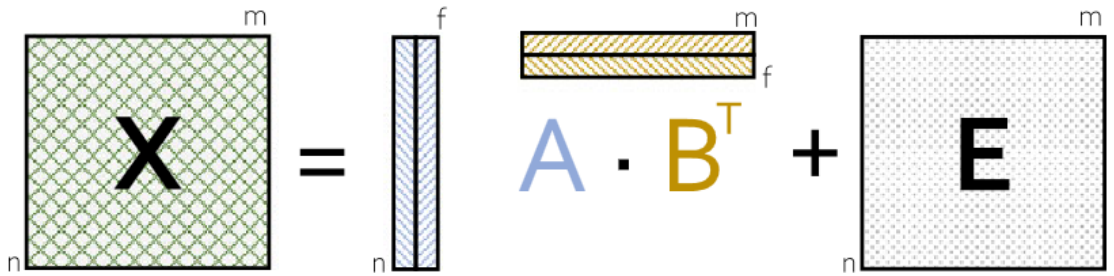
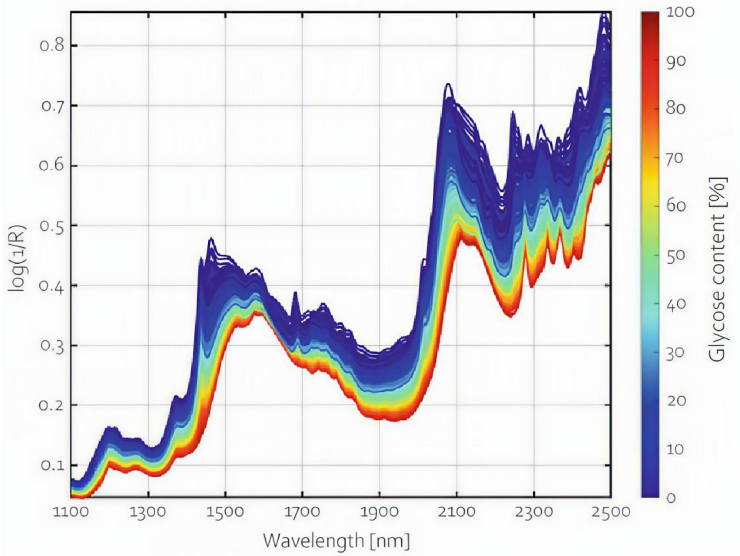
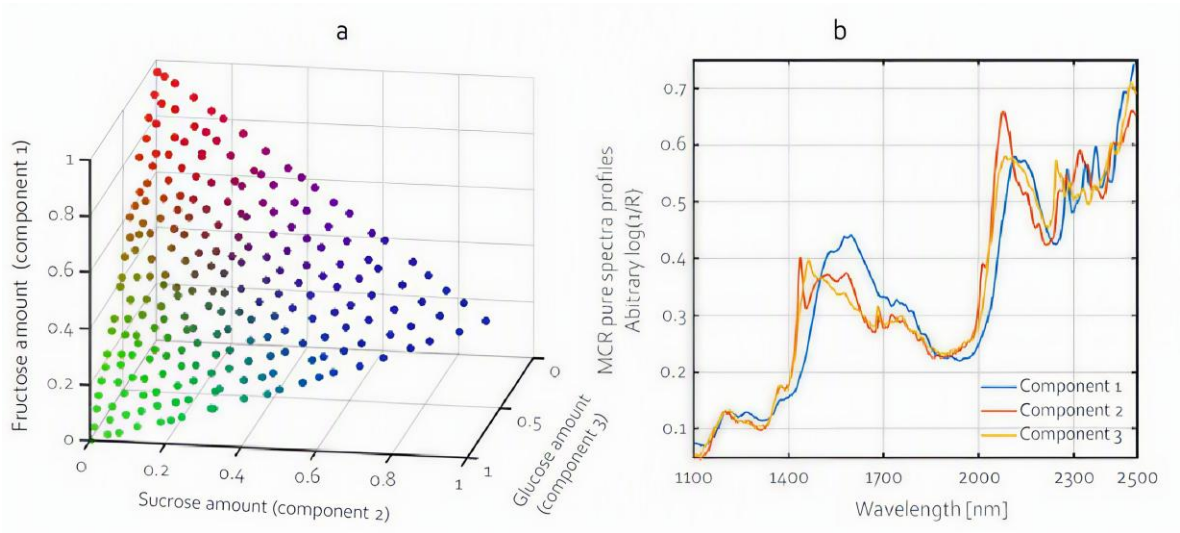


Observations = Amounts · Chemical profiles + Residual

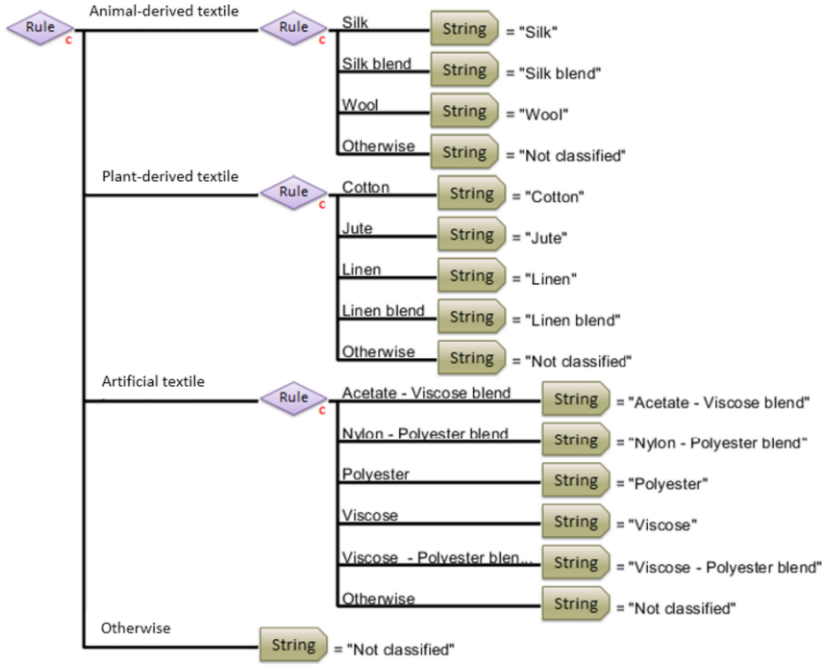
Data = Systematic information + Noise

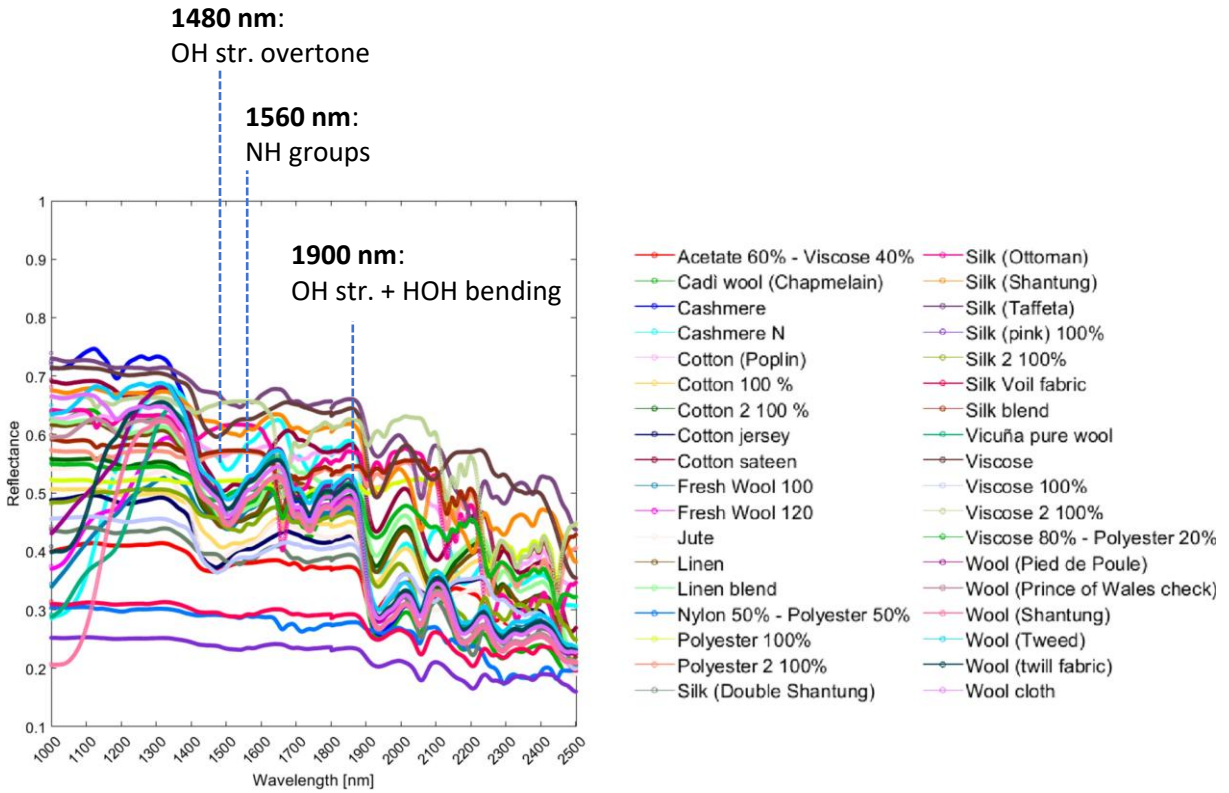




EoL Textile recovery

- 75 % textile disposed in landfills (5 % of landfill area occupied by textile)
- To improve recycle & reuse, need of fast sorting techniques





Waste Biomass Valor **15**, 1725–1738 (2024). https://doi.org/10.1007/s12649-023-02413-z

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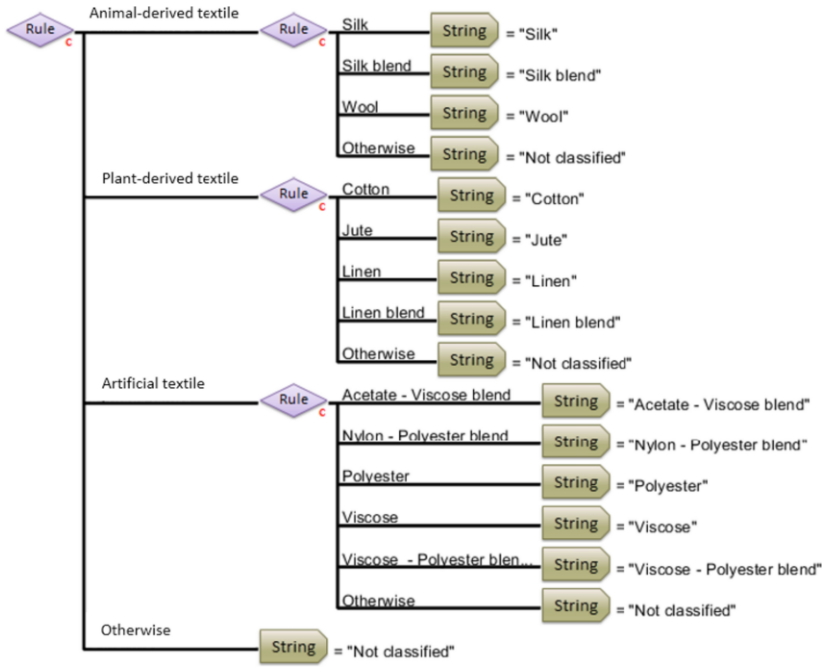

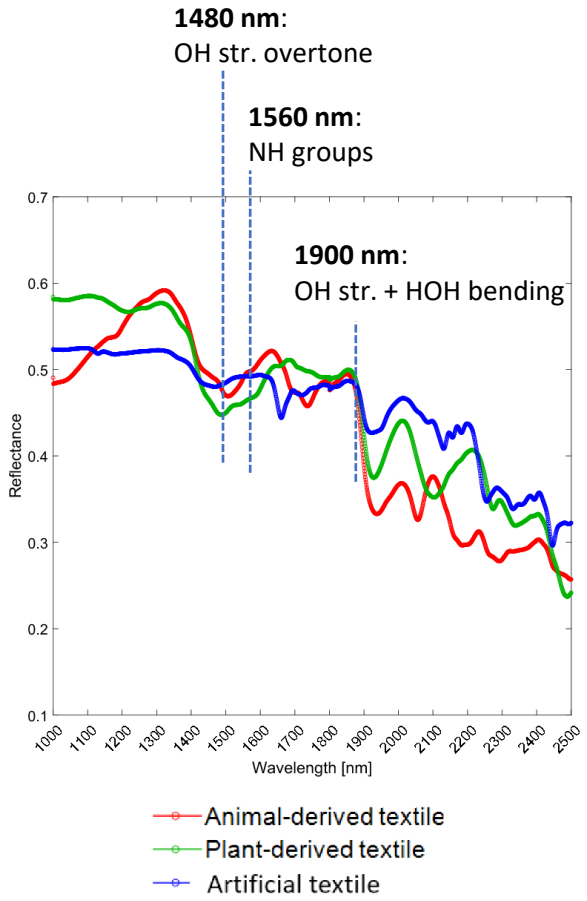

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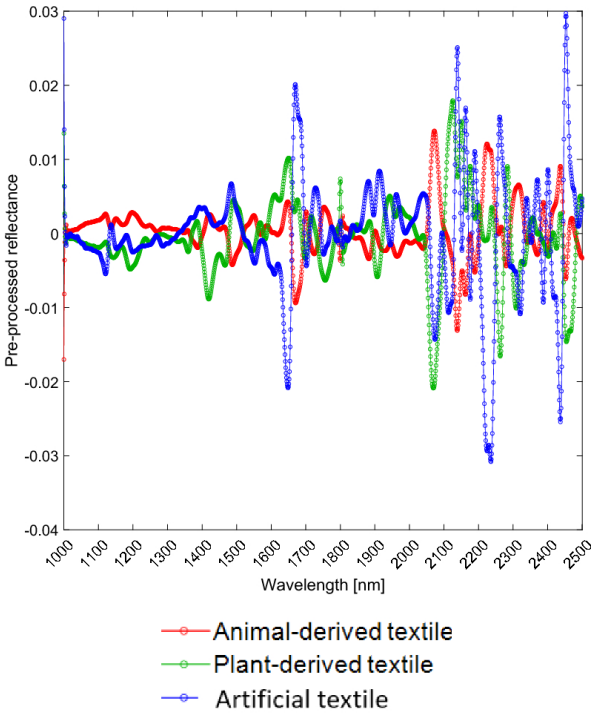

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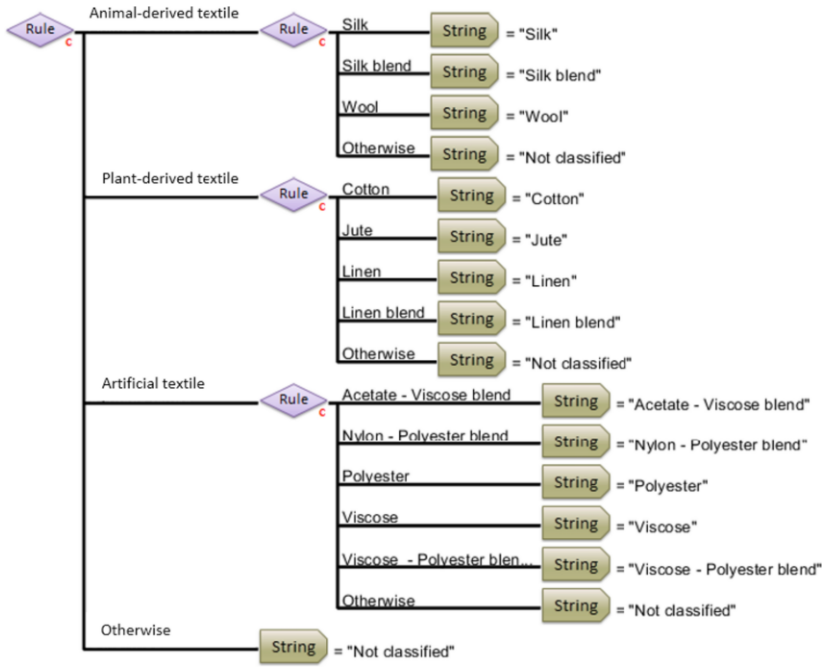

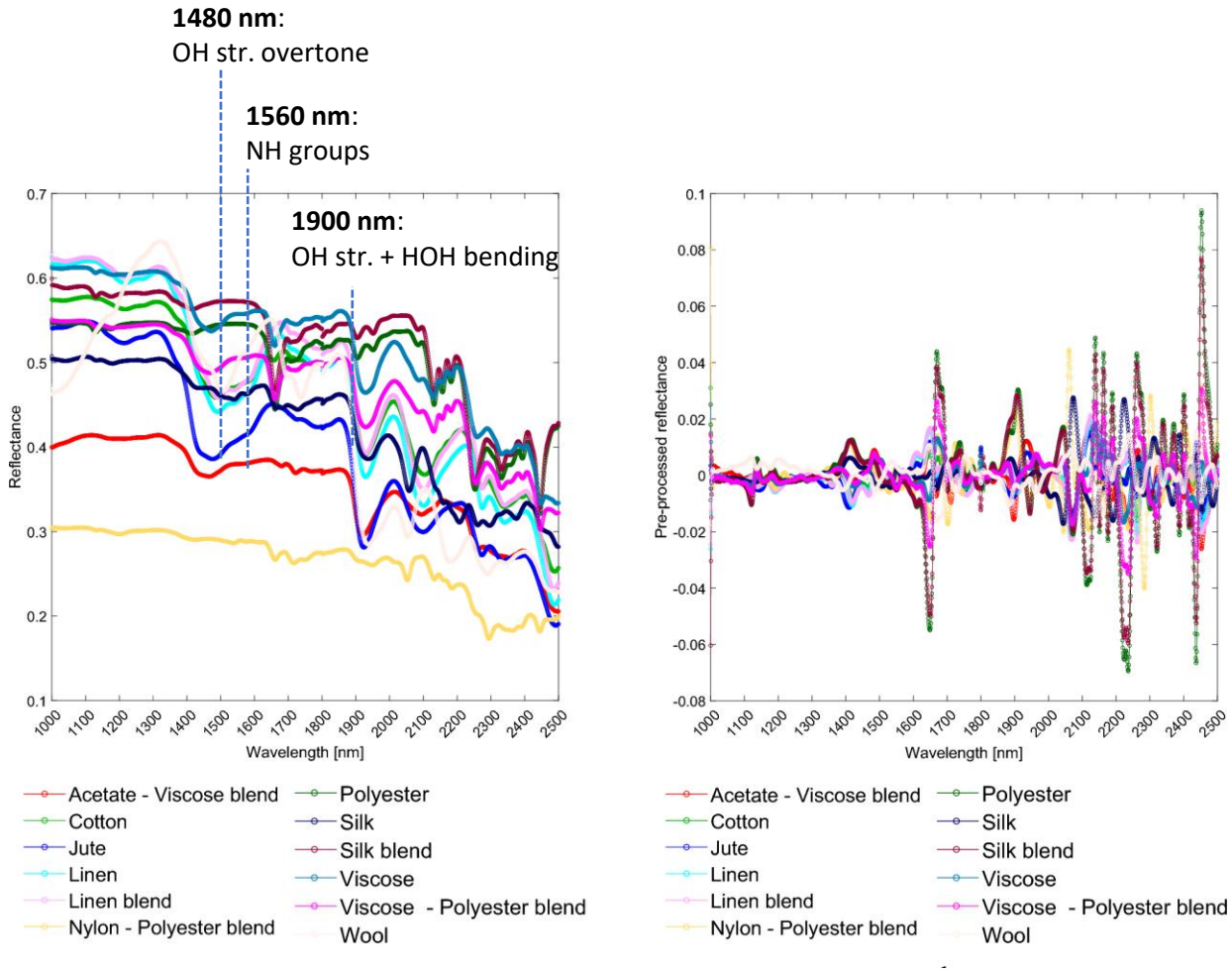

Waste Biomass Valor **15**, 1725–1738 (2024). https://doi.org/10.1007/s12649-023-02413-z

EoL Textile recovery

- 75 % textile disposed in landfills (5 % of landfill area occupied by textile)
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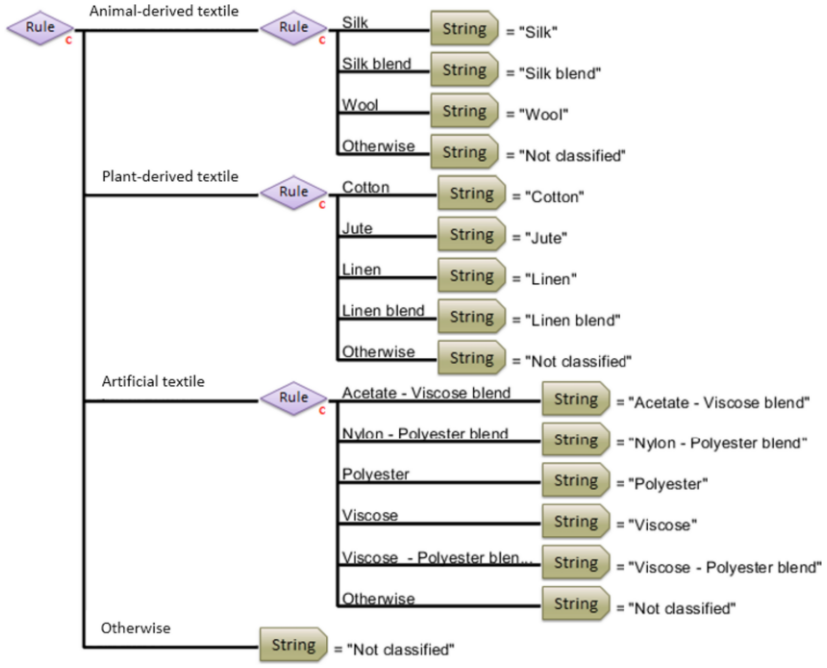

	Class	Sensitivity	Specificity	Number of spectra	Precision	Accuracy
Calibration	Animal-derived textile	0.970	1.000	100	1.000	0.983
	Plant-derived textile	0.900	1.000	40	1.000	0.978
	Artificial textile	1.000	0.950	40	0.851	0.961
Cross-validation	Animal-derived textile	0.930	1.000	100	1.000	0.961
	Plant-derived textile	0.875	0.979	40	0.921	0.956
	Artificial textile	0.950	0.921	40	0.776	0.928

Class	Sensitivity	Specificity	Precision	Accuracy
Acetate-viscose blend	1.000	1.000	1.000	1.000
Cotton	0.720	1.000	1.000	0.961
Jute	1.000	1.000	1.000	1.000
Linen	0.000	1.000	–	0.972
Linen blend	0.000	1.000	–	0.972
Nylon -polyester blend	0.400	1.000	1.000	0.983
Polyester	0.800	0.988	0.800	0.978
Silk	1.000	1.000	1.000	1.000
Silk blend	0.400	1.000	1.000	0.983
Viscose	0.067	1.000	1.000	0.922
Viscose—polyester blend	1.000	1.000	1.000	1.000
Wool	1.000	1.000	1.000	1.000
Not classified	–	0.794	0.000	0.794

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