CHEM-E4205 Crystallography Basics and Structural Characterization

Infrared spectroscopy (IR)

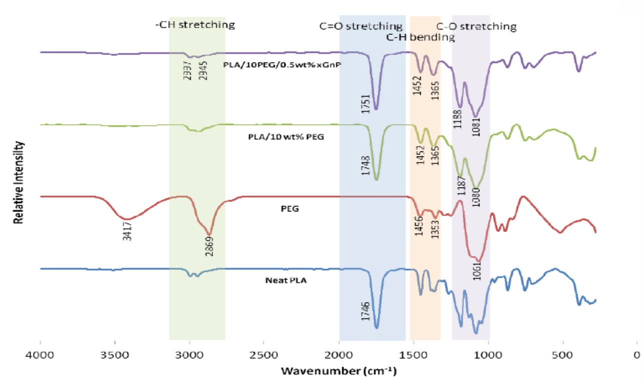
Aalto University
School of Chemical
Engineering

Freya Huck & Anni Virta

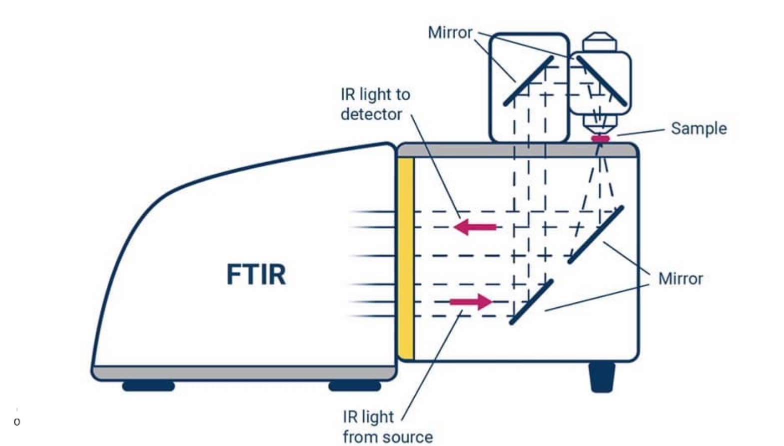
29.05.2024

Contents

1. **Theory and principle**
2. **Samples and information gained**
3. **Interpretation of data**
4. **Advantages and limitations**
5. **Research examples**



Chieng, B.W. et al. Effects of Graphene Nanopletelets on Poly(Lactic Acid)/Poly(Ethylene Glycol) Polymer Nanocomposites, Polymers 6 (2013) 93-104.



https://www.agilent.com/en/product/molecular-spectroscopy/ftir-spectroscopy/transmission-ftir-mode

Aalto University
School of Chemical Engineering

Theory and principle

Theory

What is IR-Spectroscopy

- Interaction between matter and IR

What is IR

- Electromagnetic radiation
- 4000-600 cm^{-1}

Principle

- Molecules absorb IR
  - Transformation into molecular vibrations

Molecular vibrations

Principle

- Molecules absorb IR
    - Transformation into molecular vibrations

Radial

Symmetrical stretching
Asymmetrical stretching

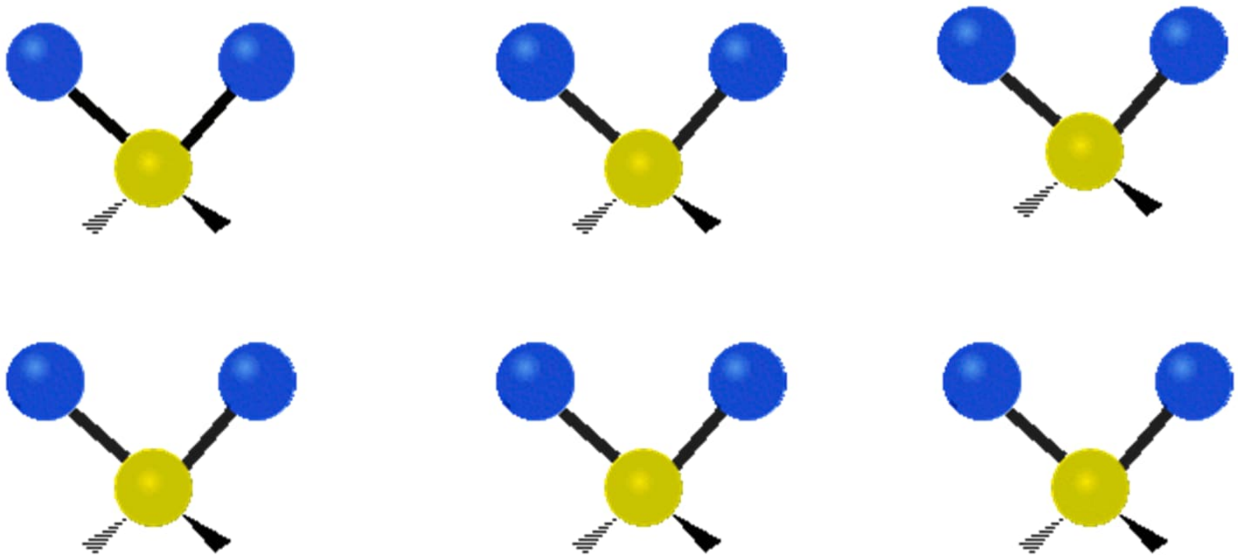
Latitudinal

Scissoring
Rocking

Longitudinal

Wagging
Twisting

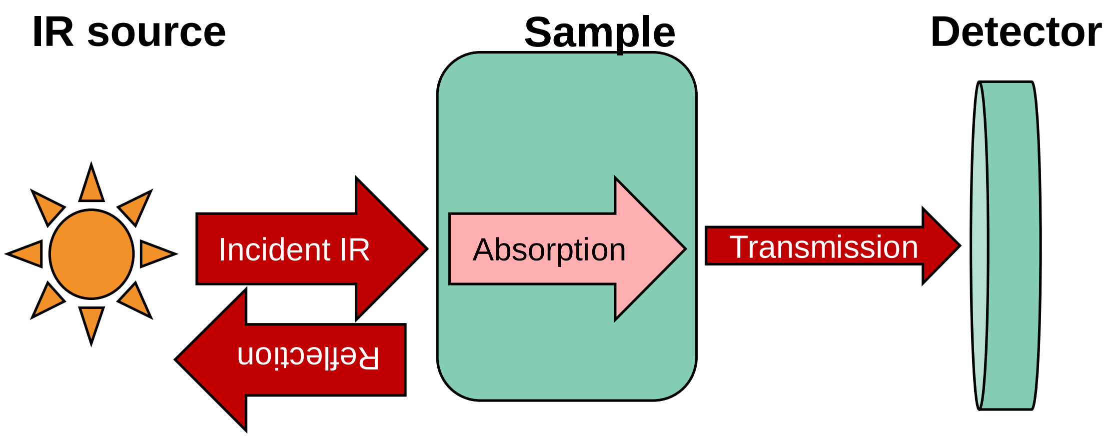
Molecular vibrations



FTIR

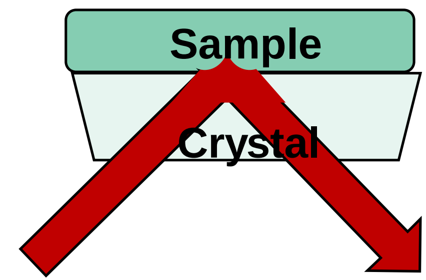
Transmission

- Transmitted light collected by detector



Attenuated Total Reflectance

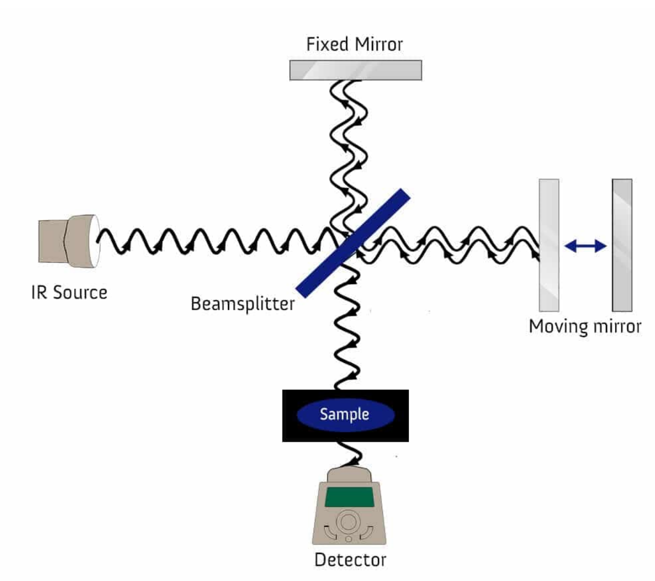
-internally reflected IR



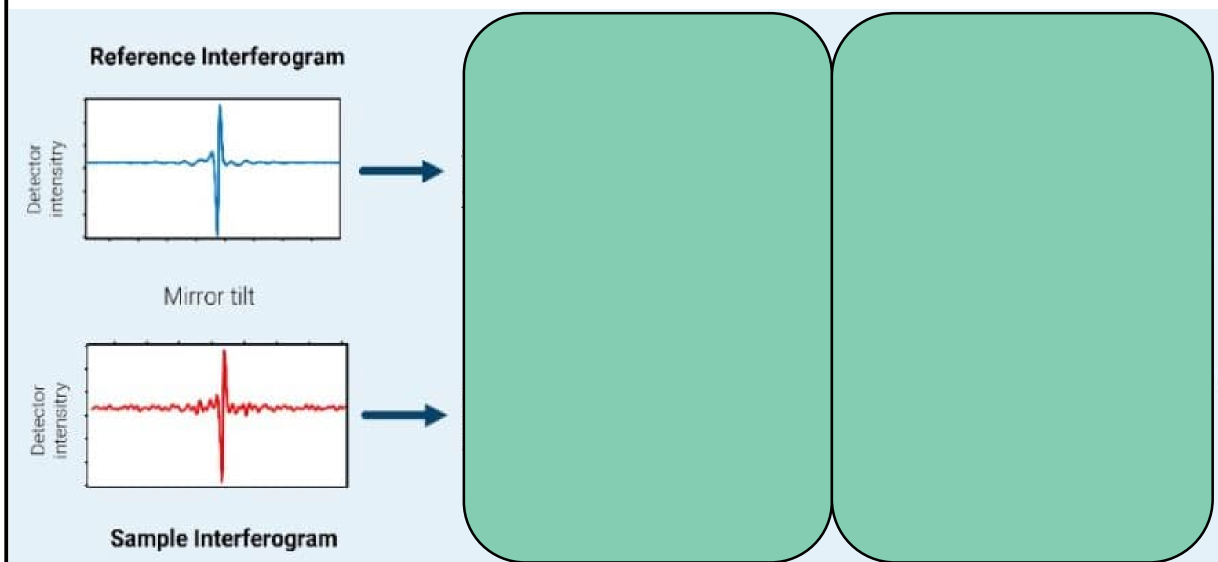
Aalto University
School of Chemical
Engineering

https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/alpha-ii-compact-ft-ir-spectrometer.html

Set up

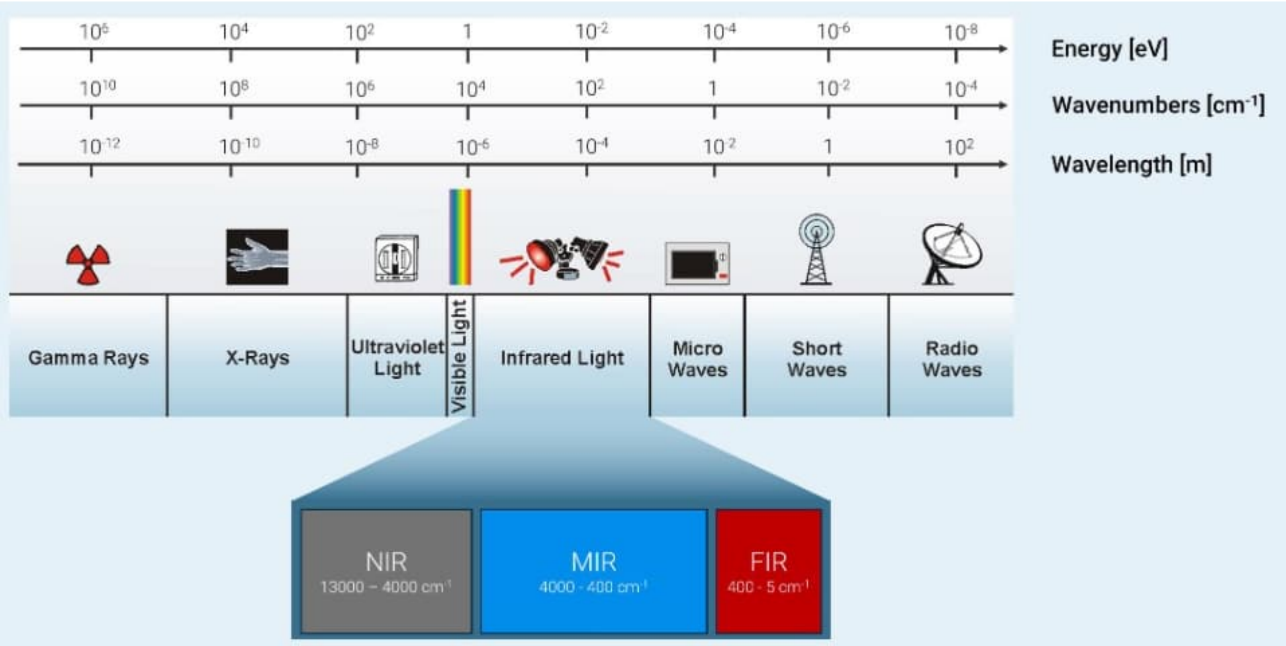


Fourier transformation



Aalto University
School of Chemical
Engineering

Different IR regions



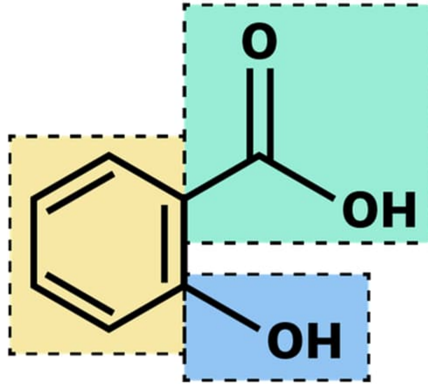
MIR

→most commonly used

→Coincides with vibration

Samples and information gained

Information gained



1) Characterizing unknown substances
2) Studying the composition of known substances
3) Comparing samples and the changes in them

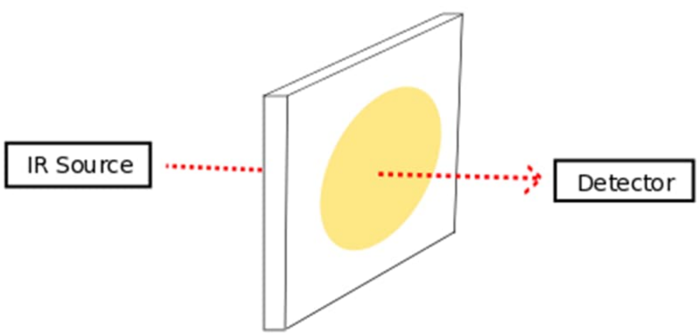
Information on the sample's:

- Chemical composition (functional groups)
- Molecular structure (bonds)
- Purity (comparison with pure substances)
- Concentration (quantitative analysis on intensities)
- Phases and structure (crystal forms)

Samples

Transmission FTIR

- Thin films and coatings
- Pellets
- Liquids (on quartz or glass cells)
- Solids transparent to IR radiation

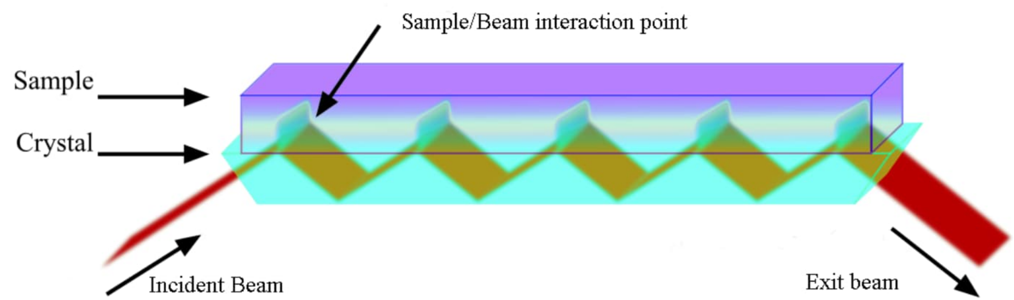


https://en.m.wikipedia.org/wiki/File:Transmission_FTIR_Spectroscopy.png

ATR (Attenuated total reflectance)-FTIR

- Powders and fibers
- Soft and non-uniform surfaces (polymers)
- Liquid and semi-solid samples (gels, creams)

→ Eliminating the need for sample preparation

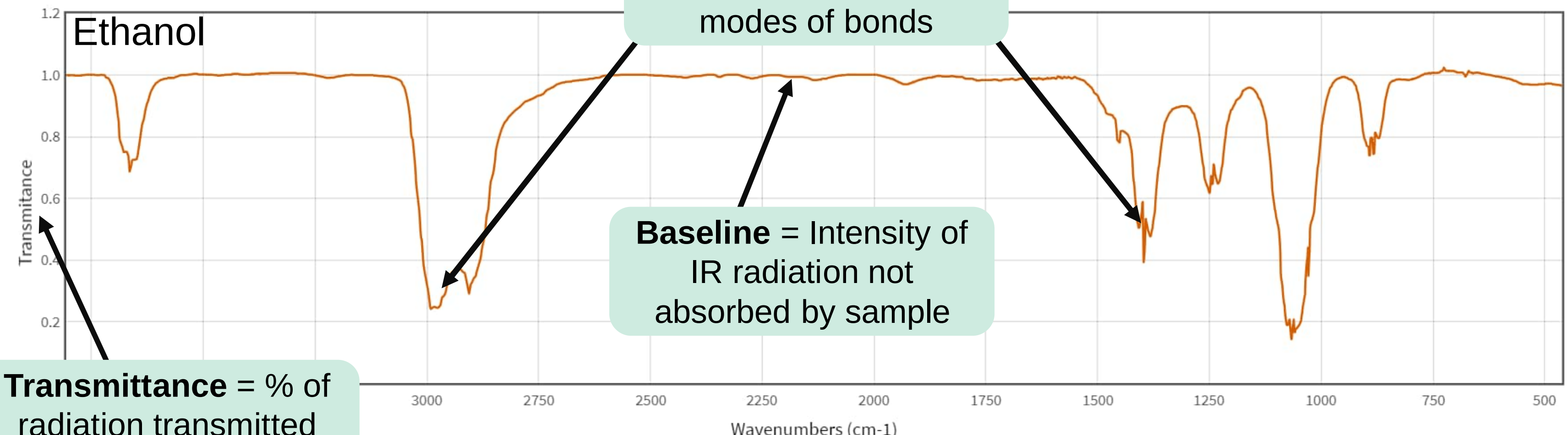


https://rtilab.com/techniques/ftir-analysis/

Interpretation of data

Spectrum

- Intensity as a function of wavenumber
  - Intensity → Transmittance or absorbance
  - Wavenumber → reciprocal centimetres from high to low



Absorption bands (peaks) = vibrational modes of bonds

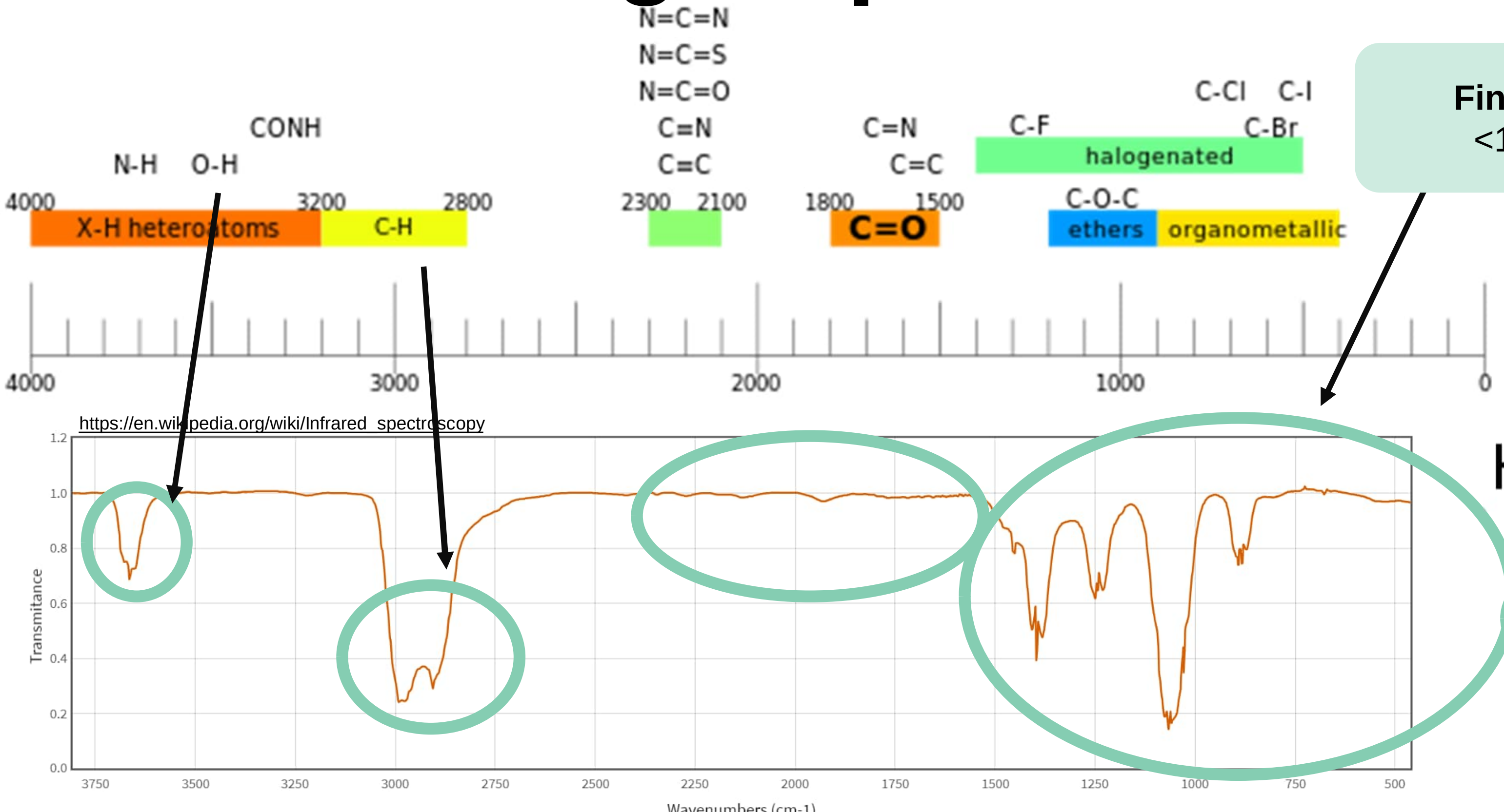
Baseline = Intensity of IR radiation not absorbed by sample

Transmittance = % of radiation transmitted trough sample

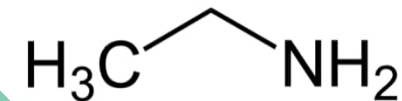
Wavenumber = proportional to the energy of IR radiation

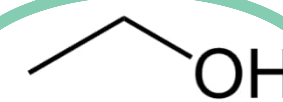
https://webbook.nist.gov/cgi/cbook.cgi?ID=C64175&Type=IR-SPEC&Index=2

Functional groups



Fingerprint=
<1500cm^{-1}



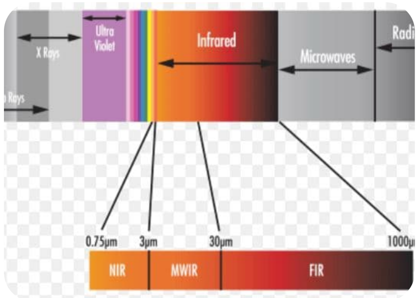


https://webbook.nist.gov/cgi/cbook.cgi?ID=C64175&Type=IR-SPEC&Index=2
https://de.wikipedia.org/wiki/Ethylamin#/media/Datei:Ethyl_Amine_Structural_Formula_V1.svg
https://en.wikipedia.org/wiki/Ethanol#/media/File:Ethanol-2D-skeletal.svg

- Specific for molecules
- Sometimes called fingerprint of molecules

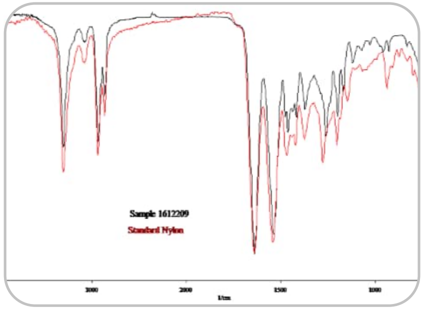
Advantages and limitations

Advantages



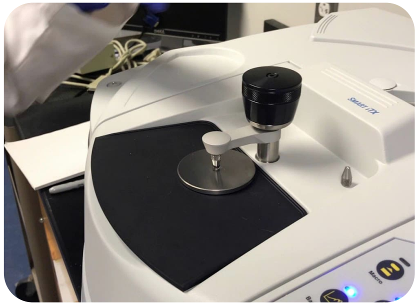
Data gathered from a large IR spectrum

https://www.tribonet.org/wiki/infrared-spectroscopy/



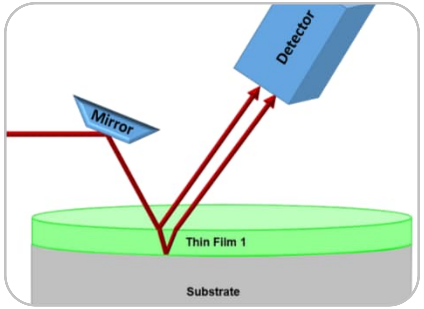
Offers both qualitative and quantitative analysis of substances

https://rtilab.com/techniques/ftir-analysis/



Highly sensitive and rapid analysis

https://www.youtube.com/watch?v=gEPUeUfMW4s



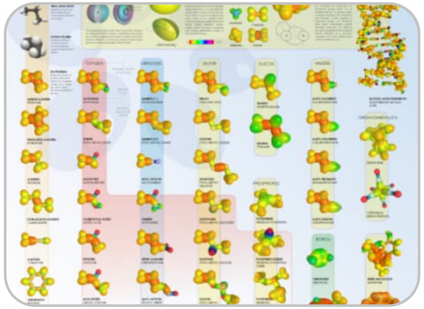
Non-destructive

Minimal preparations and a broad range of samples

https://semilab.com/category/products/ftir-reflectometry

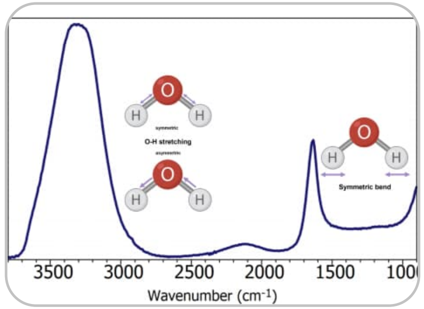
Aalto University
School of Chemical
Engineering

Limitations



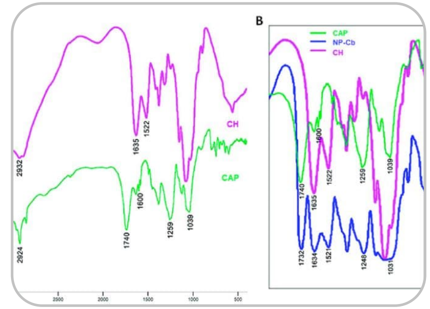
Chemical composition analysis limited to mainly functional groups

https://byjus.com/chemistry/functional-groups/



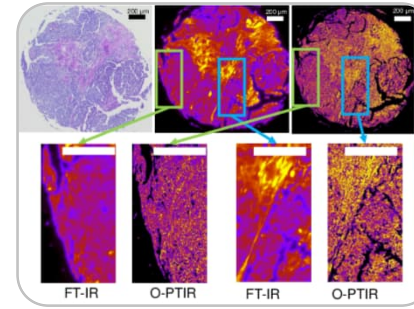
Water sensitivity can cause interference with analysis

https://www.edinst.com/atr-ftir-of-blood-serum-using-a-heated-atr-accessory/



Possibility to spectral overlaps (impurities and complex samples)

N. Nieto et al. (2022) Pharmaceuticals 15(6):662



Weak in detecting low absorbtions or detailed spatial features

C.C. Gajjela et al. (2022)

Research examples

1 - Aim

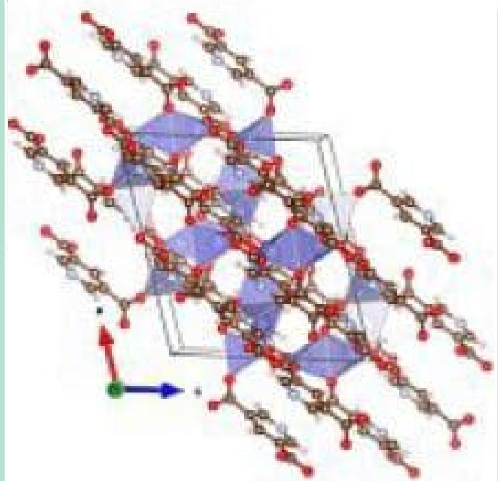
Metal–Organic Frameworks

New s-Block Metal Pyridinedicarboxylate Network Structures through Gas-Phase Thin-Film Synthesis

Jenna Penttinen, Mikko Nisula, and Maarit Karppinen*[a]

Synthesis and investigation of M-PDC materials

- Novel water-free structures were accomplished
- Insitu crystalline (Li-,Na-,K-) and amorphous(Mg-,Ca-,Sr-,Ba-) thin films
- Post-deposition water absorption behavior
- Post humidity treatment at RT followed by thermal annealing



Li_2-3,5-PDC

Experimental

- ALD/MLD
- Precursors: Metal-thd complexes (Li,Na,K,Mg,Ca,Sr,Ba)
- 3,5-PDC

1 - Why FTIR

XRR→Film thickness
SEM→morphologies
GIXRD
-confirmed the amorphous/crystalline nature
-change in structure depending on presence of water in films or not
-structure analysis

Not able to solve the crystals structure of new materials

FTIR was able to confim for unhydrated films:

1) K-3,5-PDC
   → free COOH acid groups
   → Water absorption after synthesis
2) Anhydrous films ether bidentate bridging or bidentate chelatin coordination
3) Participation of pyridyl-N in M-coordination or in H-bonding with H2O

hydrated films

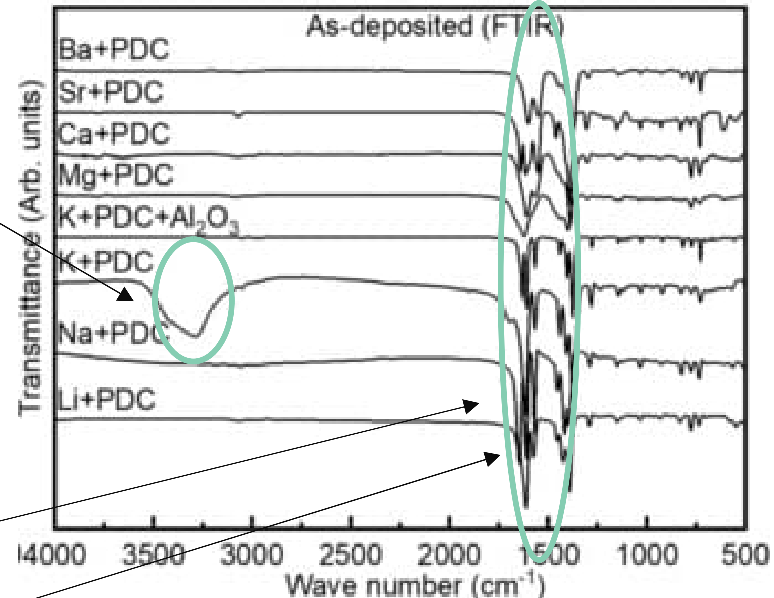
1) Presence of water
2) Reversible water in-take/release behaviour

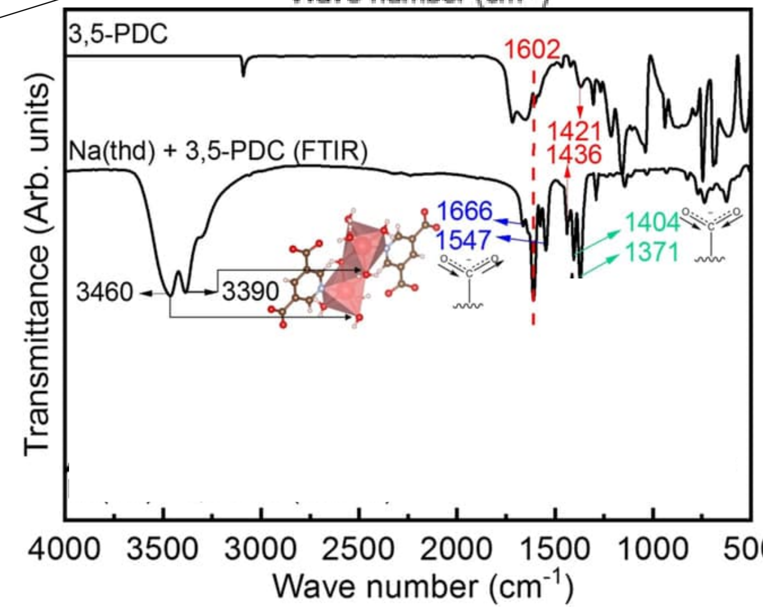
1 - Results

-OH

Table 1. Summary of the FTIR data for all thin-film samples and the 3,5-PDC precursor: symmetric and asymmetric carboxylate bands (and the corresponding Δ values) and the N-bond absorption values given in cm^{-1}; b stands for a broad peak, f for a free pyridyl nitrogen/carboxylic acid, m for a metal coordinated to the pyridyl-N or a carboxylate, and h for a water molecule having hydrogen bonding to the pyridyl-N or to a carboxylate.

Sample	Sym	Asym	Δ	N bond
3,5-PDC	1304	1720	416 (f)	1421, 1602 (f)
Li-PDC	1425	1571	146 (m)	1450, 1610 (m)
	1390	1648	258 (m)	
Na-PDC	1417	1571	154 (m)	1454, 1614 (m)
	1396	1646	250 (m)	
Na-PDC-H_2O	1404	1547	143 (m)	1436, 1602 (m)
	1371	1666	295 (h)	
K-PDC	1403	1568	165 (m)	1442, 1607 (m)
	1374	1632	258 (m)	
K-PDC-H_2O	1407	1567	160 (m)	1442, 1614 (m)
	1371	1699	328 (h)	
Mg-PDC	1398 (b)	1569 (b)	171 (m)	1442, 1618 (m)
Mg-PDC-H_2O	1382	1562	180 (m)	1446, 1610 (m)
Ca-PDC	1386 (b)	1564 (b)	136 (m)	1454, 1609 (m)
Ca-PDC-H_2O	1432	1557	125 (m)	1452, 1601 (h)
	1389	1673	284 (h)	
Sr-PDC	1380 (b)	1556 (b)	129 (m)	1448, 1608 (m)
Sr-PDC-H_2O	1423	1552	170 (m)	1454, 1596 (h)
	1382	1614	232 (h)	
Ba-PDC	1376 (b)	1549 (b)	136 (m)	1448, 1601 (m)
Ba-PDC-H_2O	1378	1547	169 (m)	1448, 1601 (h)





2 - Aim

Check for updates

Cite this: *Chem. Commun.*, 2020, **56**, 241

Received 17th September 2019, Accepted 27th November 2019

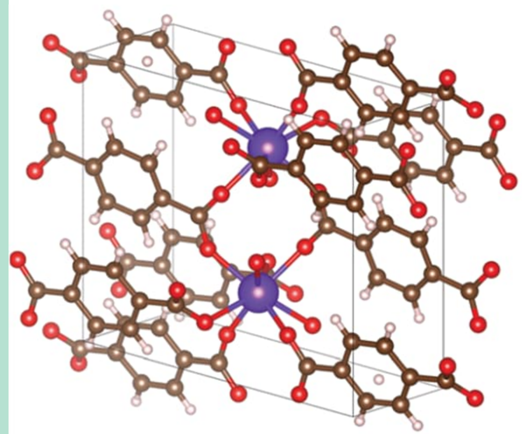
DOI: 10.1039/c9cc08904g

Amorphous-to-crystalline transition and photoluminescence switching in guest-absorbing metal–organic network thin films†

Amr Ghazy,[a] Muhammad Safdar,[a] Mika Lastusaari[b] and Maarit Karppinen*[a]

Research on novel amorphous metal-organic frameworks (aMOFs)

- No long-range order as in typical MOF materials
- Amorphous-to-crystalline transition and photoluminescence switching
- Applications on sensing, electronics, catalysis etc.



Experimental

- Neodymium terephtalate (Nd-TP) thin films deposited with ALD/MLD
- Precursors Nd(thd)3 and TPA
- Humidity and temperature treatment for the films

2 - Why FTIR

GIXRD confirmed the amorphous/crystalline nature

- As deposited films amorphous
- After humidity treatment crystalline

Not able to confirm the chemical nature

FTIR was able to confirm:

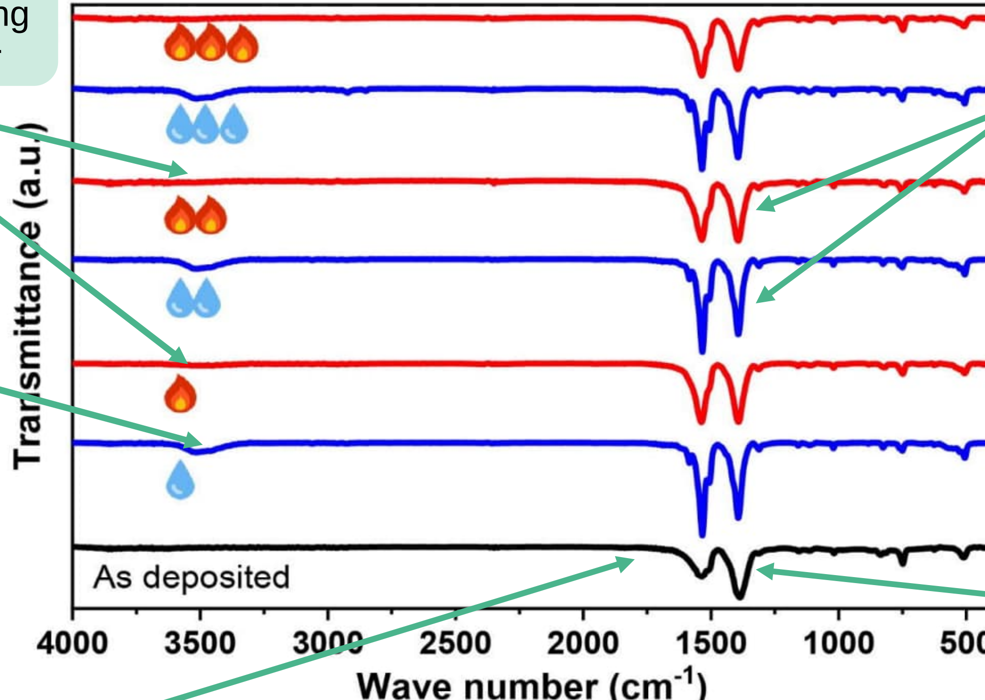
1) Nd-TP bond formation and the type of bonding mode
2) Water absorbtion in the crystal lattice after humidity treatment
3) Removal of crystal water by heating the water-containing films
4) Reversible water in-take/release behaviour

2 - Results

- Repeated humidity/heating treatments for Nd-TP films
- FTIR measured after each step

Water absorbtion peak dissapearing with heating → reversible behavior

Wide peak appearing at around 3400 cm^{-1} → Water absorbtion



Small boardening of bands with heat treatment, but bridging-type bonding remaining

Separation between carboxylate peaks →Bridging-type bonding

No carboxylic acid peak at 1700 cm^{-1} → Nd-TP bond confirmed

References

References:

1) Attenuated Total Reflectance (ATR). Available at https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/what-is-ft-ir-spectroscopy/atr-attenuated-total-reflectance.html

2) FT-IR or IR-Spectroscopy? Available at: https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer/what-is-ft-ir-spectroscopy/difference-ir-vs-ftir.html

3) Advantages and Disadvantages of FTIR Spectroscopy (2024). Available at: https://www.chemlabgenius.com/advantages-and-disadvantages-of-ftir-spectroscopy/

4) FT-IR Basics – Principles of Infrared Spectroscopy (2019). Available at: https://www.youtube.com/watch?v=KRoWMB3AR3s

Research examples:

1) J. Penttinen, M. Nisula, M. Karppinen, New s-bBlock Metal Pyridinedicarboxylate Network Structures trough Gas-Phase Thin-Film Synthesis, *Chem. Eur. J.* 25 (2019) 11466-11473.

2) A. Ghazy, M. Safdar, M. Lastusaari, M. Karppinen, Amorphous-to-crystalline transition and photoluminescence switching in guest-absorbing metal-organic network thin films, Chem. Commun. 56 (2020) 241-244.

Thank you!