Molecular Spectroscopy: Infrared

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Overview

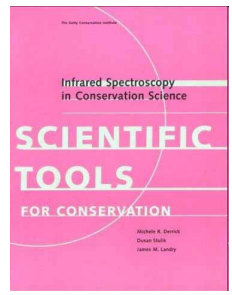
- Molecular Spectroscopy: Theory, Electromagnetic Spectrum Vibrational Energy Levels
- Vibrational Spectroscopy: Phenomena of Infrared Absorbtion, Overtones and Combinations
- Instrumentation: Michelson Interfermoter (Fourier Transform Infrared Spectroscopy)

Applications

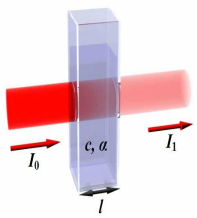
- Applications of Infrared Spectroscopy and Micro-FTIR: Different set-ups
- Interpretation of IR spectra
- Analysis of Minerals, Degradation and Organic materials
- Applications of Near Infrared Spectroscopy

Introduction to IR Spetroscopy

- Common technique used for the analysis or organic and inorganic materials
- Semiquantitative analysis of a range of cultural heritage materials
- A very powerful tools for the assessment of degradation, and identification of pigments, classes of binders
- In IR absorption, frequencies which match the natural vibrational frequencies of molecules will be absorbed



Absorbtion: Beer Lambert Law

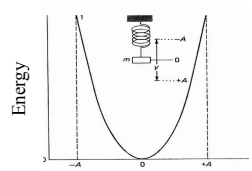


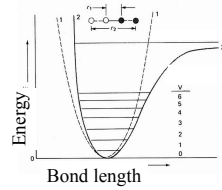
$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon \ell c}$$

FTIR sensitivity: approximately 1 %*

Simple model of infrared absorption

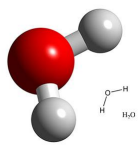
- In molecules, the chemical bond exerts an elastic force between atoms
- Absorption takes place only for discrete frequencies that correspond to the energy separation of vibrational levels

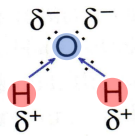




Simple model of infrared absorption

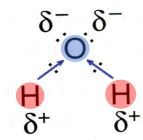
- In molecules, the chemical bond exerts an elastic force between atoms
- If the barycentre of the positive charge + does not match that of the negative charge – the molecule can absorb IR radiation and vibrate
- The greater the dipole moment, the stronger the absorption





Simple model of infrared absorption

- Absorption takes place only for discrete frequencies that correspond to the energy separation of vibrational levels



In the same way the rotation of a molecule can be triggered by the absorption of infrared radiation (this effect mainly takes place in gases)
Homonuclear molecules do not show any charge separation +/- and do not absorb infrared radiation

Dipole Moments of Specific Molecules

Molecule	μ (debye)
H_2O	1.85
HF	1.91
HCl	1.08
HBr	0.80
HI	0.42
CO	0.12
CO_2	0
NH_3	1.47
PH_3	0.58
AsH_3	0.20
CH_4	0
NaCl	9.00

Molecular vibrations - Mathematics

- Molecular vibrations can be divided in two basic types
  - Stretching
  - Bending
- For a molecule made of two atoms having masses m_1 e m_2

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

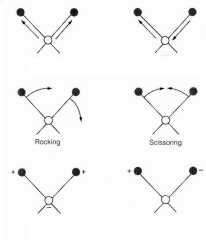
- The energetic separation between 2 vibrational levels is:

$$\Delta E = h\nu = \hbar\sqrt{k/\mu} \quad \Rightarrow \quad \hbar\frac{c}{\lambda} = \frac{\hbar}{2\pi}\sqrt{\frac{k}{\mu}}$$

- In terms of wave numbers

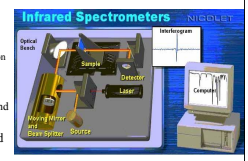
$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

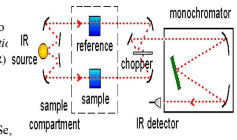
- The strength constant k depends on the bond type (simple, double,..)
- Equations above allows us to estimate the spectral band for IR absorption
- **Beyond the "fundamental band", other absorption bands corresponding to higher harmonics (2^{ν_5}, 3^{ρ_5}, …) are present, even if they show lower intensity**



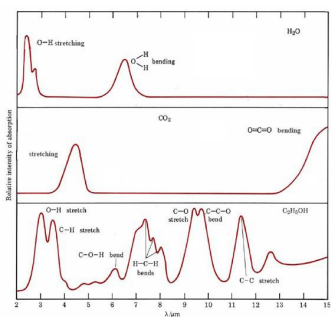
FTIR Absorption: Inside an instrument

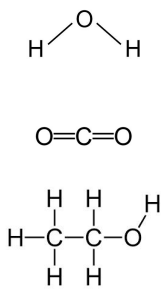
- A spectrometer (or spectrophotometer) is made of:
  - radiation source, a dispersive element (e.g. diffraction grating), detection subsystem
- Source
  - Usually a blackbody emitter with temperature between 1500 and 2200 K
    - tungsten lamp for normal measurements (**NIR** and **MID-IR**)
    - special lamps for **far infrared** measurements
- Dispersive element
  - based on a diffraction grating as in UV/VIS spectrometers
    - Usually the double beam configuration is used to *compensate for water vapour and e CO_2 absorpti*
  - based on interferometric methods in Fourier transform (FTIR) spectrometers
- Detectors
  - Photoconductive detectors
    - Thin slabs of semiconductor materials: PbS, PbSe, HgCdTe (77 K)
    - HgCdTe (MCT) detectors for imaging
  - Thermal detectors





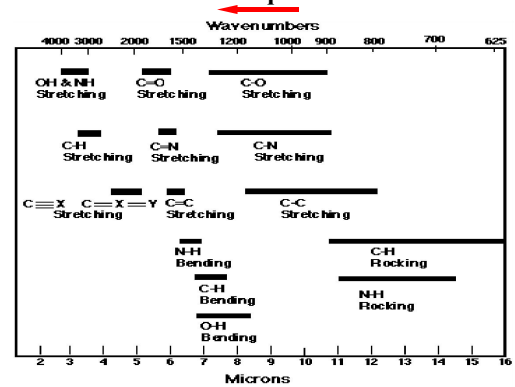
FTIR spectroscopy of simple molecules



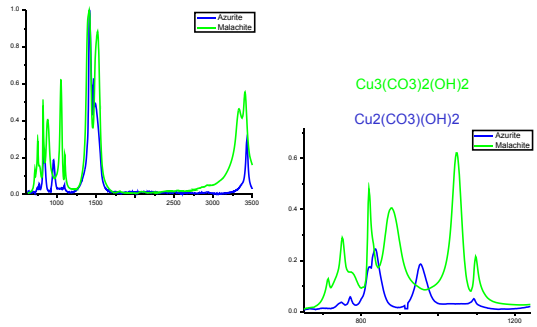


Functional Groups are key to spectral **interpretation**

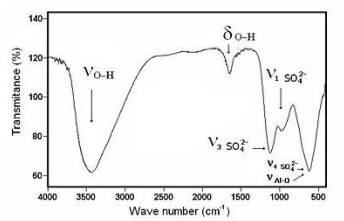
IR Vibrational Frequencies for FTIR



FTIR spectra of Copper Carbonate minerals: Malachite vs. Azurite



How to Examine a FTIR spectrum



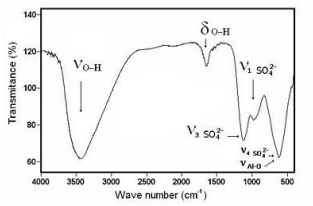
Trasmittance vs. Wavenumber (cm^{-1})
Absorbance vs. Wavenumber (cm^{-1})
Reflectance vs. Wavenumber (cm^{-1})

Crucial differences in applicability and results

Spectral properties

Bands

- **Position/frequency**
  - Depends on the bonds
- **Shape**
  - Reflects the purity of the sample, and the presence of similar bonds in a sample
- **Relative intensity**
  - Number of molecules in a sample (concentration)



Applications of FTIR

- How do we prepare samples?
  - Usually FTIR is used in Transmittance
    - KBr, Nujol, thin films on NaCl
  - Requires sample preparation and careful isolation of material
- Non-destructive alternatives
  1. Reflectance FTIR (for IR Reflective materials)
  2. Attenuated Total Reflectance
  3. Near Infrared Reflectance

Reflectance Analysis

- Specular Reflection (smooth surfaces)
  - measurement of thin layers or monolayers
  - coatings on metals, surface characterization
- Diffuse Reflection (DRIFTs) (rough surfaces)
  - structural information is from the bulk matrix

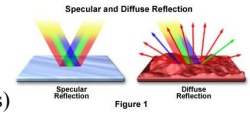


Figure 1

Reflectance FTIR

- Collect IR radiation which reflects from a surface
  - Fibre optic or directly in air
- **Distortions** to spectrum due to the distortion of reflectance bands
- Specular reflectance can result in distortions of absorption bands
  - mathematically correct (Kramers Kronig)
- Diffuse reflectance:
  - correct scattering (Kubelka Munk)

Calcite in transmission vs. reflectance Restrahlen bands

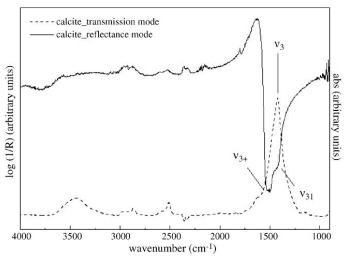


Fig. 1. Mode distribution and selection rules for calcite structures.

C. Ricci et al, Non-invasive identification of surface materials on marble artifacts with fiber optic mid-FTIR reflectance spectroscopy, Talanta, 2006

Reflectance FTIR on Marble sculptures

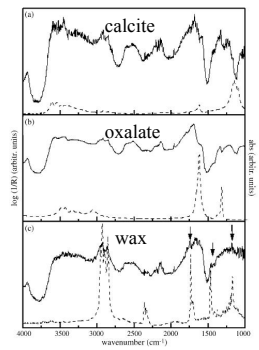


TABLE 1
Main diagnostic band for organic patinas and inorganic incrustations

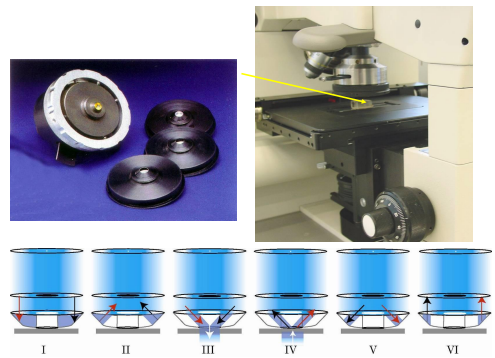
Compound	Diagnostic bands (cm^{-1})	Mode assignment
$CaCO_3$	1400 (inverted)	ν_3
	1798	$\nu_1 + \nu_4$
	2515	$\nu_1 + \nu_3$
Casein	1650	Amide I
	1545	Amide II
Beeswax	2910 and 2855 (derivative)	ν(CH)
	1740 (derivative)	ν(C=O)
	1472	δ(C—H)
	1175	ν(C—O)
Polyacrylic resin	1730	ν(C=O)
Alkyl siliconic resin	1273 and 1076	ν(Si—O)
$Ca_3(PO_4)_2$	1148, 1068 and 990 (inverted)	$\nu(PO_4^{-})$
$CaSO_4{\cdot}2H_2O$	1146 (inverted)	$\nu_3(SO_4^{-})$
$Na_2C_2O_4$	1320	ν_s(C—O) + δ(O—C=O)
	1600	ν(C=O)

C. Ricci et al, Non-invasive identification of surface materials on marble artifacts with fiber optic mid-FTIR reflectance spectroscopy, Talanta, 2006

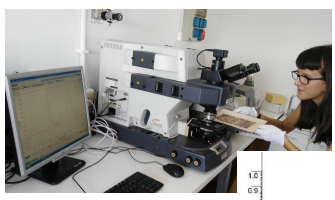
Attenuated total reflectance (ATR)

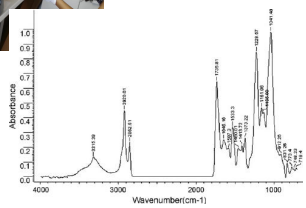
- ATR is a sampling method which requires direct contact between a material and an IR transparent crystal (eg. Diamond, Germanium, ZnSe)
- IR radiation travels through the crystal and probes only the top few micrometers of the sample
  - based on refractive index mismatch between sample and ATR crystal

ATR and Reflectance FTIR



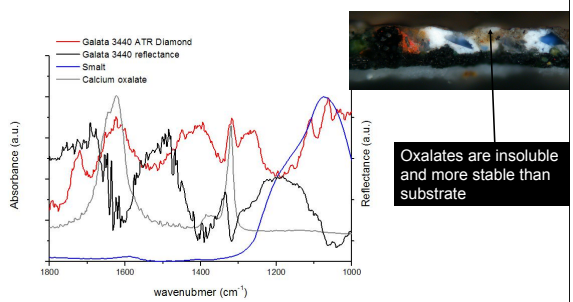
ATR applications: surface films





http://www.getty.edu/conservation/publications_resources/pdf_publications/atlas.html

ATR and Reflectance FTIR on Cross-sections

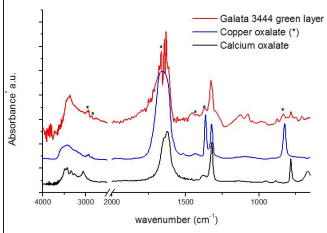


Hypotheses regarding the formation of oxalates

- degradation of binding media (proteins and other organic materials)
- attack of oxalic acid produced by lichens on calcium and other carbonates

Main limitation of FTIR Spectroscopy: competing signals

Fourier Transform Infrared Spectroscopy – from Cross-section in Reflectance*



Band (cm-1)	Compound	Band Assignment
3423	Wheddelite	ν_s (O-H)
2962	Moolooite	ν_s (O-H)
2930	Moolooite	ν_s (O-H)
1659	Moolooite	ν_s (C=O)
1622	Wheddelite	ν_s (C=O)
1433	Moolooite	ν_a (C-O)
1360	Moolooite	ν_a (C-O)
1321	Wheddelite	ν_a (C-O)
825	Wheddelite	δ (O-C=O)
781	Moolooite	δ (O-C=O)

Presence of
Calcium and Copper Oxalates

A. Nevin et al, Journal of Cultural Heritage, 2006

Studies in Conservation

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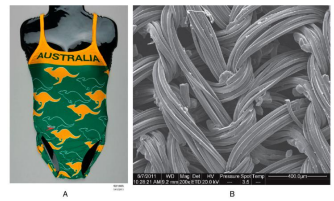
ATR-FTIR as a tool for assessing potential for chemical ageing in Spandex/Lycra®/elastane-based fabric collections

Christopher E. Marjo, Sue Gatenby, Anne M. Rich, Bin Gong & Suzanne Chee



Marjo et al. ATR-FTIR as a tool for assessing potential for chemical ageing

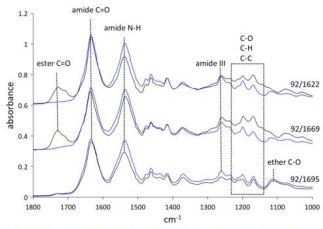
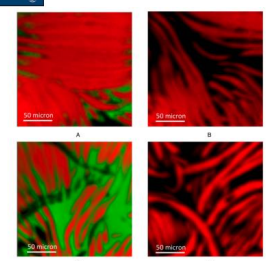


Figure 5 ATR-FTIR spectra of 92/1622, 92/1669, and 92/1695 (black) showing the effects of aqueous NaOH at 50°C for five hours (blue). Vertical axis is absorbance units and horizontal axis is in wavenumbers (cm^{-1}).



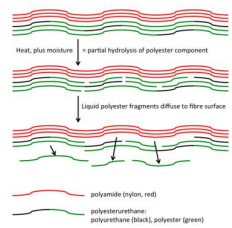
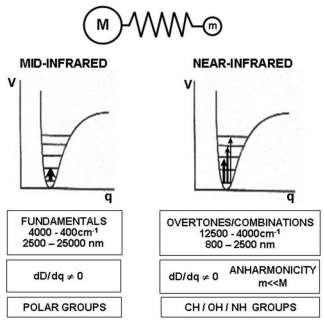


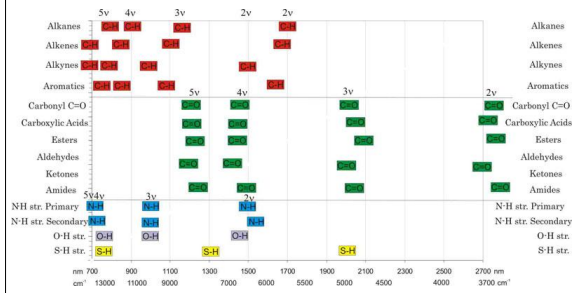
Figure 6 400 × 400 μm ATR-FTIR images of 92/1622 (A) before and (B) after treatment with NaOH at 50°C and, 92/1669 (C) before and (D) after treatment with NaOH at 50°C The red areas represent peak height of the nylon amide I peak (C=O) at 1636 cm^{-1} and the green images are the peak height of the polyesterurethane ester band at 1730 cm^{-1}.

The study demonstrates the value of ATR-FTIR for identification of elastane fabrics that may require specialized storage in a humidity-controlled environment

NIR and Mid IR Spectroscopy



Where are overtones?



A final consideration software + File formats

Different proprietary software programmes

- Origin
- Excel
- Bruker/Nicolet/Grams
- Essentialftir: http://www.essentialftir.com/

Key: useful to create a database of spectra which can be compared to unknown samples

Conclusions

- FTIR is a useful technique for analysis of organic and inorganic material
- NIR and Reflectance FTIR can be used non-destructively for rapid analysis
- NB Intrinsic limitations
  - Sensitivity
  - Resolution of Mixtures
  - Spectra Distortions
- Statistical methods are essential for NIR