CH205: Spectroscopy

3 lectures leading to ~12 MCQ questions

- Texts:
  - 2nd year Physical Chemistry Spectroscopy Notes.
- Many different analytical text books:
  - Harris: Quantitative Chemical Analysis.
    - Chapters: 19 & 20.
  - Higson: Analytical Chemistry.
    - Chapters: 5, 6, & 12.
  - Willard, Merritt, Dean & Settle: Instrumental Methods of Analysis, 7th ed.
    - Chapters: 6, 7, 11, & 12.
  - Various Specialist texts in Hardiman Library
- Notes & Links available on my website.
  - http://www.nuigalway.ie/chem/AlanR/
  - http://www.nuigalway.ie/nanoscale/undergraduate.html

2Y Spectroscopy: Topic 1

- Spectrometers:
  - Absorption spectroscopy (Beer-Lambert etc.)
  - Spectrometers (design, components etc.).
  - Fibre Optic probes & sampling
- Know the fundamentals of spectroscopy, spectrometer design, and fibre optics.

Wavenumber (cm\(^{-1}\))

Inverse of the wavelength in cm: \( \bar{\nu} = 1 / \lambda \)

Directly related to energy (\(\varepsilon\)): \(\varepsilon = h\nu = hc / \lambda = hc\bar{\nu}\)

- 500 nm = 0.5 x 10\(^{-4}\) cm = 20,000 cm\(^{-1}\) — Visible (high energy)
- 1000 nm = 1 x 10\(^{-4}\) cm = 10,000 cm\(^{-1}\)
- 2000 nm = 2 x 10\(^{-4}\) cm = 5,000 cm\(^{-1}\) — Near IR
- 5000 nm = 5 x 10\(^{-4}\) cm = 2000 cm\(^{-1}\) — IR (low energy)

Absorption spectroscopy

- Can refer to the absorption of any frequency of radiation, most common are:
  - UV-visible absorption (electronic).
  - IR absorption (vibrational).
  - NIR absorption (vibrational).
  - Microwave absorption (rotational).
- These are all types of molecular spectroscopy.
- Transition from Low to High energy states.
- Energy of the radiation \(\equiv\) energy of transition.
UV-Spectra

- Usually displayed:
  - Wavelength (nm) vs. absorbance (A), peaks up the page.
  - Not much detail for accurate identification & qualitative analysis.

Molar absorption coefficient ($\varepsilon$)

- Measure of how much light a molecule will absorb:
  - Larger value...more light absorption.
- Central to any quantitative analysis.
- Varies with wavelength.

Exponential Decrease with conc.

- Limits sample types:
  - Need relatively low absorbances
  - Lowish conc.'s (<0.01 M)
- Best Range:
  - Absorbance of 0.2 to 0.7
  - ~70% to 20% transmittance.

Solvents for UV-Visible absorption

- Polar solvents "blur" vibrational features more than nonpolar.
- Polar solvents more likely to shift absorption maxima.
- Shifts of $\lambda_{\text{max}}$ with solvent polarity
  - hypsochromic/blue shift
  - bathochromic/red shift
Cuvette materials:

- Cuvettes (also Lenses, Prisms, gratings, filters):
  - Silica/quartz 200-3000 nm (UV-near IR).
  - Glass 400-3000 nm (vis-near IR)
  - Plastic PS: 350 nm – 1100 nm
  - Plastic PMMA: 300 nm – 1100 nm
  - NaCl 200-15,000 nm (UV-far IR)

Cuvette types:

- Select according to application:
  - Micro cells: small volumes, microlitres.
  - Flow: follow kinetics of a reaction.
  - Thermal: follow temp. dependances.
  - 1 mm cells: highly absorbing samples.

How to sample & measure

- Top down:
  - The spectroscopic techniques (selection rules, 2Y PChem).
  - The measurement instrumentation
    » what spectral information can be collected.
  - Sampling methods (how to collect spectra).
- Bottom Up:
  - What am I? Solid, liquid, gas.
  - Bulk, Trace, Big, Small
  - Complex, or single molecular entity.

Type of Analysis

- Quantitative:
  - Concentration: how much of a specific component is present.
  - Quality: How good is a material.
- Qualitative:
  - Identification: what is the material?
  - Classification: what class does the material belong to?
  - Analysis of variance: has the material/spectra changed?

Have to ask yourself, what do I want to know & with what precision.
**Which Spectroscopy?**

- Good for Qualitative:
  - Mid IR (FT-IR).
  - Raman spectroscopy.
  - Lots of spectral detail.
  - Functional group & structural analysis possible.

- Good for Quantitative:
  - UV-visible absorption.
  - NIR spectroscopy.
  - Broader bands, less spectral detail.

Chemometrics can be used to:
- Make mid-IR & Raman good for quantitative.
- Make NIR good for qualitative (ID & variance)

---

**Light - Matter Interactions**

- Have to look at instrument design carefully.

---

**Spectrometers:**

- Basic Design:
  - Light source.
  - Sampling system.
  - Wavelength selection.
  - Detection.

- Filter, Single or Dual Beam.
- Single Channel or multi-channel.

---

**Absorption spectrometer**

- Light source:
  - Need the right photon energies.
- Sample holder or sampling system:
  - Need to get the light into & out of the sample.
- Light selector:
  - Need to separate wavelength of light to see spectral detail.
- Light detector: have to measure the light, different detectors needed for different photon energies.
**Light Sources**

- Depends on the spectroscopy:
  - UV-visible:
    - Tungsten (300/350-1000 nm, )
    - Deuterium (200-400 nm)
  - NIR:
    - Incandescent / Quartz-Halogen.
  - Mid IR: 200 – 4000 cm\(^{-1}\)
    - Globar source: silicon carbide rod, heated to ~1500K.

**Wavelength selection:**

- Filters: mainly UV-visible
  - Inexpensive & very simple.
- Dispersive: all kinds of spectroscopy.
  - Very versatile.
- Fourier-Transform: mainly mid-IR & NIR
  - Found in most laboratories.

**Filter Spectrometers**

- Inexpensive
- Use glass (interference)
- AOTF:
  - Acoustic-optical tuneable filter

**Filters (1): selecting wavelengths.**

- Bandpass filters: allow light through, small wavelength range.
- Absorption filters: stop light getting through.

http://www.olympusmicro.com/primer/lightandcolor/filter.html
AOTF:

- A piezoelectric material (E) is attached to one end of the TeO2 crystal which, under excitation from an external radio frequency signal (RF), produces a mechanical (acoustic) wave which propagates through the crystal.
- The acoustic wave produces a periodic variation of the refractive index of the crystal in a frequency determined by the RF signal, in the range of 50 to 120 MHz.
- The interaction of the EM wave (A) and the acoustic wave causes the crystal to refract selectively a narrow wavelength band (B).


AOTF based instruments

- This device made of a birefringent crystal of TeO2, cut in a special angle. The characteristics of TeO2 are suitable for the UV-vis & NIR regions.
- Instruments based on Acousto-Optical Tuneable Filters (AOTF) are:
  - Scanning spectrophotometers with no moving parts.
  - Perfectly suited for fibre optics.
  - Are capable of reaching very high scan speeds.
  - Suitable for a broad range in the UV-visible & NIR spectral regions.
  - Scan speed is usually limited by the detector response time.

Pros & Cons of filter spectrometers

- PROS:
  - Can be inexpensive.
  - No moving parts.
  - Can be very compact.
  - Can be very accurate for selected applications.

- CONS:
  - Filters not available for all wavelength ranges.
  - Sometimes need full spectrum.

Dispersive optics-based instruments

- Uses diffraction gratings & monochromators:
- Diffraction grating:
  - Large number of narrow closely spaced lines on a reflective substrate.

\[ n\lambda = d(\sin \theta - \sin \phi) \]

- d = groove separation.
- \( \lambda \) = wavelength of incoming light.
- n = an integer, \( \theta \) = angle of incident light.
- \( \phi \) = angle of reflected light.
**Dual Beam spectrometer**
- Reference & sample beam.
- Good accuracy.
- Complex optics.
- Lots of moving parts.

**Basic Diode Array Spectrometer**
- Multiple detector elements, fast.
- No moving parts (200-1100 nm in one shot).
- Can be very small.

**Dispersive Multi-channel**
- Spectrographs:
  - sensor array (D) allows to scan an entire spectra in a few milliseconds, OR,
  - Use fixed grating for robust spectral data collection.

**PE λ950 versus Ocean optics**
- Multichannel vs. Scanning dual beam:
  - Much smaller.
  - No moving parts.
  - Inexpensive.
  - Is portable.
  - Is rugged.
Pros & Cons of dispersive systems

PROS:
- Mature & relatively inexpensive technology.
- Suitable for a wide range of spectroscopies.
- Large spectral ranges.

CONS:
- Slow scan speed.
- Lack of wavelength precision.
- Reproducibility.
- Precision moving parts: limits the use of dispersive instruments in the field and in more aggressive environments.

Detectors: measure the light

The Ideal Detector for Spectroscopy:
- 100% efficient at all wavelengths:
  - Measure/count every incoming photon.
- High sensitivity:
  - Give a strong signal for each photon.
- Fast:
  - Take a spectrum/measurement every microsecond (or faster).
- Low noise:
  - Able to measure very small differences in signals.
- Inexpensive...i.e. very cheap.
- Hardwearing & Robust: student proof.
- Can get some but not all...trade off.

UV-Visible Spectrometers: detectors

- PMT: photomultiplier tube.
  - Used in single & dual beam spectrometers.
  - Very mature technology.
  - Not very robust, easily broken.
  - Very sensitive & good S/N.
- Silicon Photodiodes:
  - Used in inexpensive single & dual beam spectrometers.
  - Very mature & robust technology.
  - Low sensitivity & relatively poor S/N.
- CCD: Charge coupled devices
  - Used in multichannel spectrometers.
  - Now a mature & fairly robust technology.
  - Good sensitivity & good S/N (can be very good but expensive EMCCD)

Photomultiplier Tube: single channel

- Incoming photon of light strikes photocathode.
  - Ejects electrons, high voltage moves e’s towards dynodes.
  - Every time electron hits a dynode, ejects more electrons.
  - Eventually a large amount of electrons reach anode and are registered as a current.
  - More Photons → Larger current: Domino effect.
  - Different photocathodes give different wavelength sensitivity.
CCD detector: multichannel.

- Charge Coupled Device (CCD): silicon based.
- Photon creates a free electron & “hole”...
- Free electron collected in a potential well...then read out.
- Used for Raman, UV-VIS, Fluor, X-Ray, etc. applications.

http://www.andor.com/learn/digital_cameras/

Fibre Optic Probes: in-situ sampling

- Very Flexible:
  - Probe into…bodies, oceans, cells, reactor vessels, etc.

www.hellma-worldwide.com

Total Internal Reflection

- Ray of light strikes boundary between two media:
  - Refraction ($\theta_1$)
  - Reflection ($\theta_2$)
- Critical Angle ($\theta_C$):
  - Angle above which reflection occurs.

$$\theta_c = \arcsin \frac{n_2}{n_1}$$

Fibre Optics: How it works

- Total Internal Reflection:
  - Refractive Index.
  - Core $n_1 >$ cladding $n_2$
  - Acceptance angle ($\alpha$): angular aperture.
    - Bigger $\alpha$, more light collected.
  - Fibre core: varying core sizes
    - 8 - 10 µm (single mode, communications).
    - 50 – 1000 µm (multi-mode, spectroscopy).
Probe designs: transmission

- Glass or quartz fibres:
- Defined path length.
- Different tip designs.
- Not good for corrosive environments.

Probe designs: reflection

- Can use single or multiple fibres.
  - Used for Raman & Fluorescence measurements.
  - Exciting & Sample light along same path.
  - Window made out of:
    - Quartz: good transmission
    - Sapphire: chemical protection

Reflection Probes:

- One excitation Fibre.
- Six collection Fibres.
- Separately coupled.

- Raman & Fluorescence spectroscopy.
- Better light collection efficiency than single fibre.

Specular vs. Diffuse reflectance:

- Specular: Mirror like reflection.
  - Not always good for spectroscopy.
- Diffuse: scattered at lots of different angles.
  - Used widely in spectroscopy.
**Pros & Cons of Fibre optics**

- **PROS:**
  - Flexible sampling.
  - Lots of different types.
  - Relatively inexpensive.
  - Can be sterilised...

- **CONS:**
  - Lose a lot of light compared to free space optics.
  - Fibres can be destroyed by bending.
  - Only certain wavelength ranges available.
  - Immersion probes can be:
    - Fouled by growth.
    - Corroded by chemicals.

**CH205 Spectroscopy: Topic 2**

- Sampling for FT-IR: spectroscopy:
  - Instrumental factors: windows etc.
  - Nujol mulls, KBr disc, Solution cells,
  - Attenuated Total Reflection
  - Microscopy & chemical imaging
  - Forensic case study: fingerprints & paint.

- Understand and be able to explain the different modes of sampling:

**IR-absorption spectroscopy**

- Light absorbed by molecule:
  - passes light through the sample.
  - Measure how much absorbed.

- Vibrational transitions (lowish energy)
  - IR radiation (2 µm to 1000 µm)
  - (5000 cm\(^{-1}\) to 10 cm\(^{-1}\))

- Spectra from ~400-600 cm\(^{-1}\) to 4000 cm\(^{-1}\)

- Obeys Beer-Lambert (linear with conc., dilute systems.

**Typical IR spectrum**

Plot of % Transmittance Versus Wavenumber

<table>
<thead>
<tr>
<th>Vibration type</th>
<th>cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>2850–2960</td>
</tr>
<tr>
<td>C–H</td>
<td>3000–3050</td>
</tr>
<tr>
<td>C–C stretch, band</td>
<td>700–1250</td>
</tr>
<tr>
<td>C–O stretch</td>
<td>1640–1760</td>
</tr>
<tr>
<td>O–H stretch</td>
<td>3300–3650</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1600–1700</td>
</tr>
<tr>
<td>C=N stretch</td>
<td>2215–2275</td>
</tr>
<tr>
<td>N–H stretch</td>
<td>3200–3570</td>
</tr>
</tbody>
</table>

Hydrogen bonds: 3200–3570
IR spectrometer: DISPERSIVE

- Dispersive, wavelength separation using grating scan across different wavelengths to make spectrum. Use slits to make small wavelength steps for resolution (loses light).
- Not very common now / Mainly research systems.
- Difficult alignment, lots of mirrors.

http://www.chemistry.adelaide.edu.au/external/soc-rel/content/ir-instr.htm

Fourier Transform Spectrometer

- Most modern IR spectrometers are Fourier-Transform (FT) based and use a Michelson Interferometer.
- All light frequencies at once.
- Faster than scanning

FT-IR advantages:

- **Multiplex:** Each point in the interferogram contains information from each wavelength of light being measured.
- **Throughput:** No slits, fewer mirror surfaces (lower reflection losses) than in a dispersive spectrometer. Overall, more light reaches detector.
- **Precision:** laser used to control mirror & wavelength calibrate, very precise.

Windows For IR sampling

- IR low frequency cut-off cm⁻¹
- Normal cell windows
  - NaCl (650), KBr (350), AgCl (350)*, CsI (200)
  - *=insoluble in H₂O
Background Spectra:
- CO₂ band very strong.
- Cutoff ~400 cm⁻¹ due to KBr windows.
- Weak bands due to thin polymer coating on windows.

FT-IR Gas Cells:
- Use NaCl or KBr end windows.
- Needs long pathlength.
- Low concentration.
- High resolution.
- More in 3rd Year.

FT-IR solution cells
- Organic solvents: generally non-aqueous / non-polar
- NaCl windows.
- Variable pathlength: Teflon shims (0.1-1 mm)

Solvents for IR absorption
- Try & avoid polar solvents:
  - strong absorptions, have to be dry, & hydrogen bonding.
  - Difficult to see sample peaks.
- Hydrocarbons & chlorinated HCs:
Pros & Cons of solution cells

**PROS:**
- Can observe solvent-solute interactions.
- Can look at dilute solutions.
- Gives narrow bands for analysis.
- Relatively simple method.

**CONS:**
- Extensive sample prep. & specialist sample holder needed.
- Changes sample.
- Have to use very pure & specific solvents.
- Have to use very dry solvents & sample.
- Cannot scan below 400 cm⁻¹.
- Can't do in-situ sampling.

FT-IR Nujol mull Cell

- Organic Liquids or mulls.
  - Liquids
  - Thin layer (one drop).
- Halide salt windows:
  - ~25 mm diameter.
  - NaCl cheapest.
  - CsI for low wavenumber studies.
- Have to clean carefully.
- Have to re-polish.
- Very fragile

Nujol mulls:

- The large refractive index change on going from solid to air bends the IR beam and most of the beam is scattered.
- The refractive index of Nujol is closer to that of a solid. There is less bending of the IR beam and the sample has better optical properties.

Nujol

- Nujol: heavy paraffin oil...all alkanes.
  - Peaks in well defined areas.
  - Good for carbonyl analysis.
- Always aim for transmittance above ~25%.
- Want sharp peaks.
- Square ends are bad: means out of range.
**Nujol Mull method**

- Dry grind sample to reduce the crystal size:
  - ~5 mg of sample will be enough.
  - Use agate mortar & pestle:
- Add mulling liquid (one drop) and mix:
  - Need well dispersed mull.
- Wet grind
- Transfer to NaCl flats and squeeze out
- Examine & analyse


---

**Sample Nujol Mull spectra**

- Always aim for transmittance above ~25%.
  - Takes practice.
- Want sharp peaks.
- Square ends are bad: means out of range.

**Pros & Cons of Nujol mull sampling**

**PROS:**
- Relatively simple method.
- Relatively inexpensive.
- Suitable for a wide range of compounds.

**CONS:**
- Nujol peaks obscure sample bands.
- Extensive sample preparation & skill required.
- Physically destructive of sample.
- Contaminates sample.
- Have to use very pure Nujol.
- Cannot scan below 200 cm$^{-1}$.
- Can't do *in-situ* sampling.

**KBr Discs**

- Grind up in mortar & pestle:
  - 1-2 mgs of sample
  - 250 mgs dry KBr.
- Fine dispersion.
- Use very dry & good KBr.
- Use hydraulic press & die kit to make thin disc.
- Have to keep in desiccators.
Spectroscopy handout

Sample KBr disc spectra

- No useable detail: peaks smeared together, too intense.

Dilution effects:

- Dilution, reduces amount light absorbed.
- Peaks, are sharper, easier to see & analyse.

Pros & Cons of KBr sampling

- PROS:
  - Relatively simple method.
  - Gives spectra of solid form.
  - Useful for removing heterogeneity effects (large sample area)

- CONS:
  - Extensive sample prep. & skill required.
  - Destructive of sample.
  - Have to use very pure KBr.
  - Have to use very dry KBr & sample.
  - Cannot scan below 400 cm\(^{-1}\).
  - Can’t do in-situ sampling.

ATR improvement in spectra:
**Evanescent Wave**

- Total Internal reflection:
  - Same as for fibres.

- Penetration of light into lower RI medium:
  - FIR ~700 µM

**ATR: Schematic**

**ATR materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>Cut off (cm(^{-1}))</th>
<th>Refractive Index</th>
<th>pH Range</th>
<th>Hardness (Kg/mm(^2))</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>525</td>
<td>2.42</td>
<td>5-9</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>780</td>
<td>4.0 (0.65 µm)</td>
<td>1-14</td>
<td>550</td>
<td>More Chemically resistant than ZnS &amp; KRS-5</td>
</tr>
<tr>
<td>Si</td>
<td>1500</td>
<td>3.4</td>
<td>1-12</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Diamond/ZnSe</td>
<td>524</td>
<td>2.4 (1.66 µm)</td>
<td>1-14</td>
<td>5,700</td>
<td></td>
</tr>
<tr>
<td>KRS-5:</td>
<td>250</td>
<td>2.37 (1.73 µm)</td>
<td>5-8</td>
<td>40</td>
<td>Slightly soluble in H(_2)O</td>
</tr>
</tbody>
</table>

Advantages of ATR sampling
- Minimal Sample preparation
- Can use liquids or solids.
- Can adapt with reaction & temperature cells.
- Small sample size: microsampling, single xtals. & fibres.

Disadvantages of ATR sampling
- Sample needs to be in contact with surface:
  - Deform sample using pressure.
  - Not great for big samples.
  - Difficult to analyse precisely very small particles.
- Can’t use for some chemicals:
  - Conc. H₂SO₄ would digest ZnS
  - Chemical reactions will damage xtal etc.
- Can’t be used for very low wavenumbers:
- Only very small sample size.

Quantitative Analysis by mid-IR:
- IR more difficult than UV-Vis because
  - Very sensitive to environmental conditions.
  - Weak incident beam.
  - Complex spectra.
  - Narrow bands (big variation in $\varepsilon$).
  - low transducer sensitivity.
  - Solvent absorption.
- Chemometrics can resolve some of these issues but not all.

IR Microscopy
- Can couple mid-IR spectrometers to special microscopes.
- Reflection based optics: all gold coated mirrors.
- Examples:
  - Film thickness
  - Forensic Paint
  - Narcotics.
Pros & Cons of IR microscopy

**PROS:**
- Allows analysis of very small samples ~10-20 µm in size.
- Non-destructive.
- Non-contact.
- Gives molecular fingerprint from spectra.
- Scan across surfaces.

**CONS:**
- IR radiation = long wavelength = large spot size: ~10 µm
- Can’t focus through water/glass.
- Expensive optics

Chemical Imaging

- Any technique where each pixel yields chemical information:
  - FT-IR spectrum taken @ each point.
  - Raman spectrum taken @ each point.
  - NIR spectrum taken @ each point
  - Select & plot vibrational mode intensity.

- Becoming more common:
  - Disadvantage: can be slow & generates very large amounts of data.

Analysis of paint chips: example

4-7 layers in each sample, 0.02 mm thick slices, perpendicular to the layers.
Mount on microscope & sample different layers.
Use spectra to discriminate different layers & identify the composition.

Fingerprint Analysis:

- ATR FT-IR chemical image and corresponding spectra of the protein distribution within a fingerpad surface.
- Imaged area is ~ 3.2 × 4.5 mm².
- 16 co-added scans, collection time of 13 s at a spatial resolution of ~50 µm.

www.varianinc.com
**CH205 Spectroscopy: Topic 3**

- NIR spectroscopy:
  - Theory.
  - Bands: overtones & combinations.
  - Instrumentation.
  - Sampling modes.
  - Chemometrics.
  - Measurement Examples.

- Be able to explain in detail the concept, and implementation of NIR spectroscopy.

**Introduction to NIR**

- Type of vibrational spectroscopy.
- Photon energies \((h\nu)\):
  - range of \(2.65 \times 10^{-19}\) to \(7.96 \times 10^{-20}\) J,
- Wavelength range of 750 to 2,500 nm.
- Widely used in Industry.

**Characteristics of NIR spectroscopy**

- Non-destructive: preserves samples for later analysis.
- Minimal Sample preparation:
  - in-situ measurements.
- Fast (one minute or less per sample): Allows analysis of many samples,
  - high throughput.
- Uses NIR light: inexpensive quartz optics & fibre probes, deep penetration of sample (mm):
  - flexible sampling.
- The combination of these characteristics with instrumental control & chemometrics has made it very popular for Process Analytical technologies.

**Brief History:**

- Not widely adopted until 1990's.
- Generally thought that not much info. In spectra.
- Needed computational tools to take off.
  - 2000-2009: 11,774 (6150)
  - 1990-1999: 3,551 (1,575)
  - 1980-1990: 575 (112)
  - 1970-1979: 256 (5)
**Diatomic Model: harmonic oscillator**

- Both atoms move in a vibration.
- Need to use detailed calculations:
  - Schrödinger wave equation (3rd year)
- \( v = \text{vibrational quantum number.} \)
- \( \nu = \frac{k}{2\pi\sqrt{\mu}} \), \( \mu = \text{effective mass} \)

**NIR Theory**

- Anharmonicity allows:
  - \( \Delta\nu \geq \pm 1 \): overtones: Multiple energy level jumps (overtones).
- Thus the absorptions in the NIR range are:
  - neither electronic transitions (observed in the UV and visible regions) nor fundamental vibrations.
  - NIR absorptions are due to combinations and overtones of the fundamental vibrations.
  - Thus a \( \nu(\text{C-H}) \) vibration at 3000 cm\(^{-1} \) would have an overtone at \( \approx 6000 \) cm\(^{-1} \).
  - Overtones and combinations (e.g. \( \nu(\text{C-H}) + \nu(\text{O-H}) \)) are weak because they are strictly non-allowed quantum mechanically but they can be detected.

**Band Intensity:**

- Intensity of a given absorption band is:
  - associated with the magnitude of the dipole change during the vibration & with its degree of anharmonicity.
  - More polar \( \rightarrow \) Stronger absorption.
NIR bands:

http://www.foss-nirsystems.com/

The NIR advantage

- Low absorptivities of bands are compatible with moderately concentrated samples & longer path lengths:
  - Long pathlengths enable transmission thru intact materials.
  - Allows for non-destructive analysis: no sample prep.
  - Intact, opaque, samples can be analysed by diffuse reflectance.

Instrumentation

- A NIR spectrophotometer can be assembled with UV-Visible optical components:
  - Makes it less expensive & more rugged compared to mid-infrared (MIR) spectrophotometers.
  - Can be Dispersive, FT, or filter based.
- Most common Detectors for the NIR spectral region are based on:
  - Silicon, PbS.
  - InGaAs multichannel arrays.
  - Can get very high signal-to-noise ratio for NIR measurements.
Handhelds & probes

- 1000 to 1800 nm, or
- 1600 to 2400 nm
- InGaS array (multi)
- Tungsten bulb

InGaAs linear array

NIR probe systems

- Compact benchtops:
  - Multiple detectors.
  - Fibre optic probes as standard.
  - Various designs

NIR sampling modes

- Transmittance
- Transfectance
- Diffuse reflectance
- Interactance

Uses of NIR spectroscopy:

- Widely used in the analysis of:
  - Grains (moisture & protein content)
    » From the 1970’s.
  - Foodstuffs (see KVL for sample datasets & apps)
  - Pharmaceutical raw materials:
    » Identity & quality and concentration checks.
  - Biotechnology raw materials:
    » Identity & quality and concentration checks.
NIR vs mid-IR

- **NIR:**
  - ~10-100 times weaker.
  - Broad bands (50-100 nm)
  - 700 – 2500 nm
  - Glass optics.
  - Versatile sampling.
  - Good for quantitative.
  - Poor for qualitative.
  - Functional group analysis is difficult.

- **Mid-IR:**
  - Strong bands.
  - Narrow bands (10-50 cm\(^{-1}\))
  - 2000 – 10000 nm.
  - Halide salt optics.
  - Restricted sampling.
  - Poor for quantitative.
  - Good for qualitative.
  - Functional group analysis is easy.

Chemometrics: 4 steps.

- Use of mathematical & statistical techniques for extracting relevant information from analytical data:
  - **Experimental design:** what do you want to measure, how, what information do you need.
  - **Data collection:** collection of accurate, reproducible, and representative data.
  - **Data pre-treatment:** how to treat data to remove artefacts & instrumental noise.
  - **Data analysis:** mathematical analysis to extract quantitative or qualitative information and present the data/results.

Spectral Data Pre-treatment

- NIR spectral data set normally undergoes some type of pre-treatment before being used for qualitative or quantitative purposes:
  - Remove Baseline effects: can be caused by excessive scatter, normally offset & sloping effects
  - Remove noise:
- First and second derivatives of the original spectra are usually the best.

Chemometric Methods

- Most common chemometrics methods used with NIR spectroscopy are:
  - **Qualitative Analysis:**
    - Principal Component Analysis (PCA)
    - Soft Independent Modelling Correlation Analysis (SIMCA)
  - **Quantitative analysis:**
    - Multiple Linear Regression (MLR).
    - Principal Component Regression (PCR).
    - Partial Least Square Regression (PLS).

- All presuppose a linear relationship between the spectral data and the concentration or other property value to be determined.
Quantitative Analysis: PLS

• For quantitative analysis (revise Practical 6):
  • A partial least squares (PLS) calibration is built by collecting spectra on a set of known concentration samples under identical conditions.
  • The spectral data & known concentration data are input into a commercial software package, thus, creating a PLS calibration.

Forensic example

• Quantitative analysis of Ecstasy tablets:
  – Collect tablets & acquire NIR spectra.
  – Analyse concentration using HPLC.
  – Use PLS to generate model.