Molecular Spectroscopy Glossary of Terms: Three Techniques of MidIR, NIR & Raman Spectroscopy

General

FT (Fourier Transform)
A technique utilising an interferometer and mathematical algorithm to convert data from time to frequency domain, can be used for Mid-IR (known as FTIR), Raman (FT-Raman) and NIR (FTNIR).

Dispersive
Type of spectrometer where radiation is split by a diffraction grating, prism, or other device into discrete wavelengths. Pre-dispersive is where the process described above is performed prior to light interaction with the sample, whereas post-dispersive is performed after.

Wavenumber
The reciprocal of wavelength (in cm^{-1}); and is the x-axis unit commonly used in Mid-IR and Raman vibrational spectroscopy. It is proportional to energy, larger wavenumber value = higher energy, smaller wavenumber value = lower energy.

Wavelength
The period of a wave or the distance required for a wave to repeat; and is the x-axis unit commonly used in Near Infrared (NIR) vibrational spectroscopy.

Spectral Resolution
The ability to resolve two peaks in a spectrum: the minimum difference between two lines in a spectrum that can be distinguished. It can also be defined as the full width at half height (FWHH) of an infinitely sharp peak as measured by a particular spectrometer.

Spatial Resolution
The smallest physical distance between measured positions on the sample.

Absorbance:
Absorbance = $A = - \log_{10} (I_T/I_0)$
Where I_0 is the incident radiation and I_T is the transmitted radiation.

Transmission
The process whereby radiation enters and leaves a sample: Transmittance of a sample is defined as $T = (I_T/I_0)$. Often applied as %T.

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Reflectance
Mathematically identical to transmission, but applicable to reflected radiation. Often applied as %R.

Transflection
A reflection absorption measurement in the mid or NIR range using a mirror (mid) or ceramic disk (NIR).

Pathlength
The distance of sample (in a cuvette or film for example) the radiation passes through.

Signal to Noise (S/N)
Usually calculated as the ratio of the average signal divided by the standard deviation of the noise (known as root-mean-square RMS noise).

Photometric Noise
Prevents the detection of very small absorbances as they are not differentiated from noise.

Stray Light
Light of a wavelength other than that required which reaches the detector without having been in contact with the sample and reduces the linearity of a detector.

Technique 1: Mid-IR spectroscopy

Mid-IR Spectroscopy
Measurement of the absorption of light by a sample across the wavelength range 4000 – 400 cm-1 / 2500 – 25000 nm / 2.5 – 25 micron to probe the fundamental vibrations and rotational/vibration structure of a molecule. A change in the dipole moment of the molecule must occur during the absorption of light for it to be infrared active.

DRIFT(S)
Diffuse Reflectance Infrared Fourier Transform Spectroscopy is an analysis technique used for low reflectance samples such as fine powders. IR radiation incident on the sample can be immediately reflected (and lost) or transmitted through a particle and reflected from the next, or indeed transmitted through the next and so on. This effectively increases the pathlength of the sample and as absorbance can occur during the process an absorbance/reflectance spectrum can be calculated from the collected radiation.

ATR
Attenuated Total Reflectance is a reflectance accessory used for samples too thick or strongly absorbing for transmission IR work, or alternatively to probe a sample surface. IR radiation is passed

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through an IR transmitting crystal with a high refractive index (such as ZnSe or Ge) in intimate contact with the material. There can be multiple bounces of radiation within the crystal and interaction of light and sample at each bounce therefore the effective pathlength of the sample can be increased using ATR.

Specular Reflection

Accessory used for the analysis of films and coatings on reflective metal surfaces such as aluminum or steel. The angle of incidence and reflection is the same. The infrared energy passes through the film, reflects off the metal substrate and passes back through the film to the detector.

Technique 2: Near Infrared spectroscopy

Near Infrared (NIR) Spectroscopy

Measurement of the absorption of light of a sample across the wavelength range 12500 – 4000 cm-1 / 800 – 2500 nm / 0.8 – 2.5 micron to probe overtones or harmonic vibrations of a molecule.

SWIR

The short wave NIR from 1000 to 2500 nm.

Chemometrics

The application of maths or statistics to chemical data.

Multivariate Data Analysis

Analysis of a property affected by multiple variables. For example using many spectral wavelengths in a NIR indirect analysis of property A. The chosen spectral wavelengths must 'carry' the information you require about property A.

Prediction

By finding a relationship between a set of measured variables and the property, indirect predictions about the property can be made.

Calibration Model

The mechanism which relates measured variables to the property.

Technique 3: Raman spectroscopy

Raman Spectroscopy

Measurement of the inelastic scattering of light from a sample (more commonly gaining energy) to probe vibrational/rotational structure of a molecule. During the scattering process collisions occur

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and energy is exchanged between photon and molecule. This energy change is consistent with changes in the vibrational and rotational state of the molecule (therefore equivalent in spectral range to Mid-IR (0 to 4000 cm-1). A change in polarisability of the molecule must occur during the light scattering process for it to be Raman active.

Rayleigh scattering

Light scattered from a sample at the same frequency as the incident radiation, known as elastic scattering.

Fluorescence

Interference in a Raman spectrum caused by coincidence with an electronic transition resulting in absorbance of the incident radiation, this is re-emitted as fluorescence. Can obscure your Raman spectrum entirely. If your sample fluoresces try automatic baseline correction (a common software function) or photobleaching. Alternatively, you can change your excitation wavelength away from the electronic transition, usually from the visible to the NIR.

Photobleaching

The fluorescence background caused by impurities in a sample may be removed by laser irradiation to physically break down the impurities.

Excitation Wavelength

Wavelength of laser used in the Raman experiment. Typically 1064 nm, 785 nm, 633 nm or 532 nm.

Raman Shift

Raman bands are measured as changes in energy from the wavelength of incident laser light. They are shifted from the laser wavelength which is set as 0 in the Raman experiment.

Stokes and Anti-Stokes

Inelastic scatter can result above and below the wavelength of incident radiation. Radiation scattered with a higher wavelength (lower frequency) is known as Stokes, radiation scattered with a lower wavelength (higher frequency) is called anti-Stokes. The Raman experiment considered here deals only with Stokes radiation since anti-Stokes requires the molecule to be in an excited state before scatter takes place.

SERS

Surface Enhanced Raman Scattering (SERS) is a method to increase the sensitivity of Raman by attaching molecules to roughened metal surfaces or metal colloidal particles prior to analysis.

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RRS

Resonance Raman Scattering (RRS) is a method to increase sensitivity of Raman by selection of laser wavelength. The resonant condition exists when the laser wavelength coincides with an absorption band in the sample.

Mutual exclusion

For molecules containing a centre of symmetry Raman active vibrations are also IR active and vice versa. For molecules without a centre of symmetry some vibrations can be both Raman and IR active.

Spectral Library

Collection of spectra (NIR, FTIR or Raman) of a range of substances of interest. Each substance is first identified and verified, then a single spectrum or mean spectrum is collected under specific conditions. This spectrum can then be used as a comparison with spectra of other materials or other batches of the same material. (See below)

Discrimination analysis

Separation of groups of data. An entry in a spectral library (above) can be comprised of a cluster of data/samples all representing allowable or known variation rather than just a single sample.

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