SPECTRAL INSTRUMENTATION

The typical setup of an IR experiment includes a light source, a sample, (a microscope), the spectral apparatus, a detector and a computer.

IR experiment

A light source emits polychromatic IR light, which is focused on a sample. The light is partially absorbed by the sample when it is passing through it. Molecules in the sample interact with the light, they take up energy and use this energy to vibrate, with the condition that the dipole moment changes. A detector registers how much light is transmitted through the sample. The result is a characteristic spectrum showing the transmittance (absorbance) of electromagnetic radiation as function of wavelength (wavenumber).

Radiation Sources

The most frequently used light source is the **Globar**, which is silicon carbide in form of rods or helixes. A globar can be directly ignited, and has a burning temperature of 1500 K, which needs to be water-cooled. The globar has the advantage of a relatively high emissivity to about 100 cm^{-1}, so it can be used into the far IR region. Another source is the **Nernst rod**, which works at a temperature of 1900 K and is used for the MIR region.

It consists of zirconium oxide rods with additives of yttrium oxides or oxides of other REE. The Nernst rod is a non-conductor at room temperature, initial heating is required for ignition. It has following disadvantages: sensitive, deforms easily, oxide mix has negative temperature coefficient of the electrical resistance, i.e. electrical conductivity increases with temperature. **Metallic helices**, i.e., chromium nickel alloys or tungsten with operating temperatures of about 1300K, are usually air-cooled and used in NIR. For NIR you can also use **tungsten-halogen lamps**. For FIR, below 100 cm^{-1}, you can use **mercury high-pressure lamps**. It's plasma emission surpasses the spectral radiation power of a black radiator of the same temperature. They must be started by a high-voltage pulse. **Lasers** can be used as radiation sources, too. Gas lasers scan rather narrow spectral regions (CO_2 laser 1100 - 900 cm^{-1}, CO laser 2000-1800 cm^{-1}, NO_2 laser 900-910 cm^{-1}, He-Ne laser (632, 1.152 and 3.391 μm)). Semi-conductor diode lasers are larger tunable, and can cover almost the whole MIR region, e.g., PbSnSe-type lasers. A disadvantage is their low operation temperature of 15 - 90 K. Other examples, such as the gallium arsenide -, or gallium aluminium arsenide lasers work in the IR region, and can be operated at room temperature.

Microscope

Infrared microscopes use reflecting optics such as Cassegrain objectives with 15fold or 36 fold magnification instead of glass or quartz. Using a microscope makes it possible to select a distinct measurement area on the sample and exclude contaminations from the measurement.

Spectrometers

There are various types of spectrometers, non-dispersive (no variable wavelength selection possible), dispersive (variable wavelength selection using gratings or series of filters) and Fourier Transform (FT) spectrometers (spectral splitting via interferometer allows wavelength-dependent radiaton modulation). The optical system in a spectrometer is used to transmit radiation to the detector. Lens systems of glass or quartz as used in UV and VIS range are useless in the IR range, because they absorb most of the radiation below 5000 cm^{-1}. Thus, IR spectrometers are equipped with mirror optics.

Dispersive spectrometers consist of a monochromator splitting radiation into its parts, which then separately exit to the detector by turning the grating or mirrors. With the Echelle grating earlier problems of low light intensity were overcome by using specially formed grooves (in metal or glass).

The main part of a FT spectrometer is the Michelson interferometer, in which the radiation is split by a semi-permeable beamsplitter into two partial beams that are reflected back to the beamsplitter via a fixed and a movable mirror. At the beamsplitter the two beams recombine and are brought to interfere. The motion of the movable mirror changes the optical pathlength, so both partial beams have a phase difference and the interference amplitude is changing. The detector registers an intensity signal as function of the change of the optical pathlength, which is then transformed into an interferogram.

Beamsplitter

Spectral range

Quartz

15600 - 2700 cm^{-1}

CaF_2 / Fe_2O_3

12000 - 1200 cm^{-1}

KBr/Ge

6500 - 450 cm^{-1}

CsI/Ge

7000 – 220 cm^{-1}

Advantages of FT spectrometers over dispersive ones:

- wavelengths are measured simultaneously
- shorter measurement time at same signal-to-noise ratio
- higher light throughput at same spectral resolution
- wavenumber stability is higher
- scattering can be neglected, because sample is place behind the interferometer

Spectral Resolution

Spectral resolution is defined by the distance between two neighboring absorption maxima having about the same height, which are separated by an absorption minimum, the transmittance of which is approximately 20 % higher than the band maxima.

Spectral apparatus

Resolution

Dispersive spectrometer (grating monochromator)

0.2 cm^{-1}

specially designed dispersive set ups

0.02 cm^{-1}

Dispersive spectrometer (prism monochromator)

2 – 20 cm^{-1}

FT spectrometer

0.001 cm^{-1}

IR Detectors

Detectors convert the optical signal into electrical signals. There's a variety of different types, such as thermal, pneumatic, pyroelectric or photoelectric detectors. Nowadays most detectors are photoelectric detectors because of their higher sensitivity. Incident light alters the electrical conductivity in an irradiated semiconductor material. The photosignal is measured as a change in voltage via the resistance or current.

Common types

InSb: photoconductive or photodiode, 10000 – 1500 cm^{-1}, liquid-nitrogen- cooled

MCT: photoconductive, spectral range 12500 – 400 cm^{-1}, liquid-nitrogen- cooled

DTGS: pyroelectric, MIR region, works at room temperature

Polarized measurements

Polarized measurements can be very useful for the analysis of oriented minerals with IR spectroscopy. Polarized radiation is produced with a polarizer consisting of a fine grating with parallel metal wires. In oriented crystals certain dipole moment changes lie in a fixed direction during the molecular vibration and can be excited when the IR radiation is also polarized in this direction. The efficiency of a polarizer depends on its grid spacing and optical throughput. Common materials are ZnSe (MIR), KRS-5 (MIR), Ge (MIR, highest efficiency with 90% throughput), polyethylene (FIR), polyester (FIR), CaF_2 (NIR).

Source:

https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/raman_ir.html