

Introduction to infrared absorption spectroscopy

Basics

Molecules and solids are not composed of stationary elementary particles that are constantly at given distances from each other. Instead, they are in constant movement, much like a system of springs (chemical bonds) connecting balls (atoms, ions) oscillating around their equilibrium positions. In the case of dissolved or gaseous molecules, rotation around two or three axes also carries energy. Though the motion of atoms in polyatomic systems due to vibration and rotation appears to be extremely complex, it can be decomposed into elementary movements, the so-called fundamental or normal modes (spinning around an axis, stretching vibration and bending vibration). All normal modes carry a certain, quantized amount of energy. Appropriate energies may induce transitions between ground and excited vibrational states. These transitions carry important information about the material.

Infrared (IR) is the name given to the range in the electromagnetic spectrum between visible light and microwave radiation, conventionally from ca. 0.8 μm to 1 mm wavelength ($12,500\text{--}10\text{ cm}^{-1}$). The far (1 mm–25 μm ; $10\text{--}400\text{ cm}^{-1}$) to mid-IR (25 μm –2.5 μm ; $400\text{--}4000\text{ cm}^{-1}$) range coincides with the energies needed to excite fundamental modes of rotation and vibration in gases, liquids or solids. In this short description we will focus only on solids (no rotational energy) and the mid-IR range (stretching and bending normal modes of vibration).

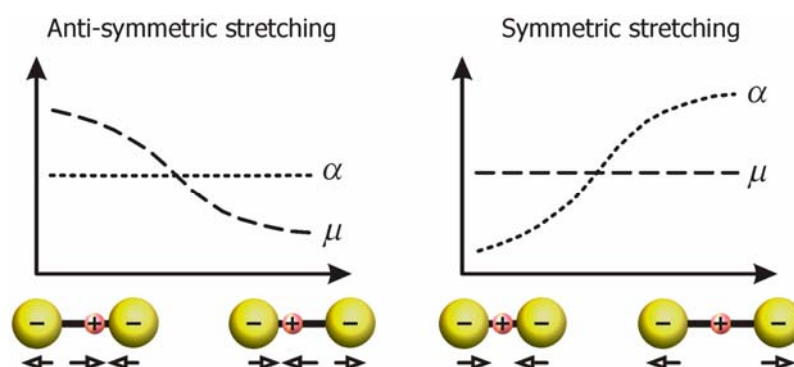


Fig. 1. A comparison of infrared and Raman-active vibrations. A vibration is IR-active (left) if the dipole momentum (μ) changes due to the oscillation. If the dipole momentum is constant in time, the vibration is IR-inactive. If, however, there is a change in polarisability (α) during the vibration (right), the vibration is Raman-active. Image redrawn after Schmidt (1994).

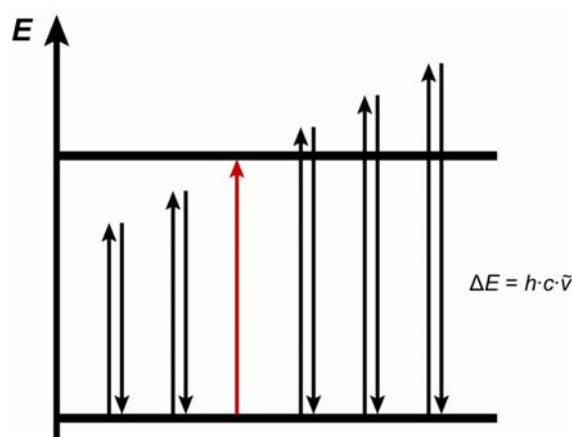


Fig. 2. Schematic energy diagram of IR absorption. An absorption of IR radiation occurs only if the energy (frequency) of the incident photon coincides exactly with the energy difference between vibrational states.

Infrared light interacts only with those vibrations whose dipole moment (μ) periodically changes due to the oscillation of the atoms (Fig. 1, left). If the oscillating electromagnetic field of the incident photon couples with the dipole oscillating at the same frequency, it is absorbed (Fig. 2). Those vibrations that are not accompanied by a change in the dipole moment are IR-inactive, but may be Raman-active if the polarisability (α) of the electron configuration changes in the course of an oscillation period (Fig. 1, right).

Infrared absorption spectroscopy is one of the methods used to probe the vibrational properties of matter. The absorption bands in the IR spectra (Fig. 3) correspond to the photon energies used to excite lattice vibrations (phonons). Structure (bond lengths, symmetry) and composition determine which vibration energies are present in a solid, therefore each material has its unique IR absorption spectra that may be used as a “fingerprint” for identification. A sampling of vibrations between neighbouring atoms means that IR spectroscopy is sensitive only to the short-range order.

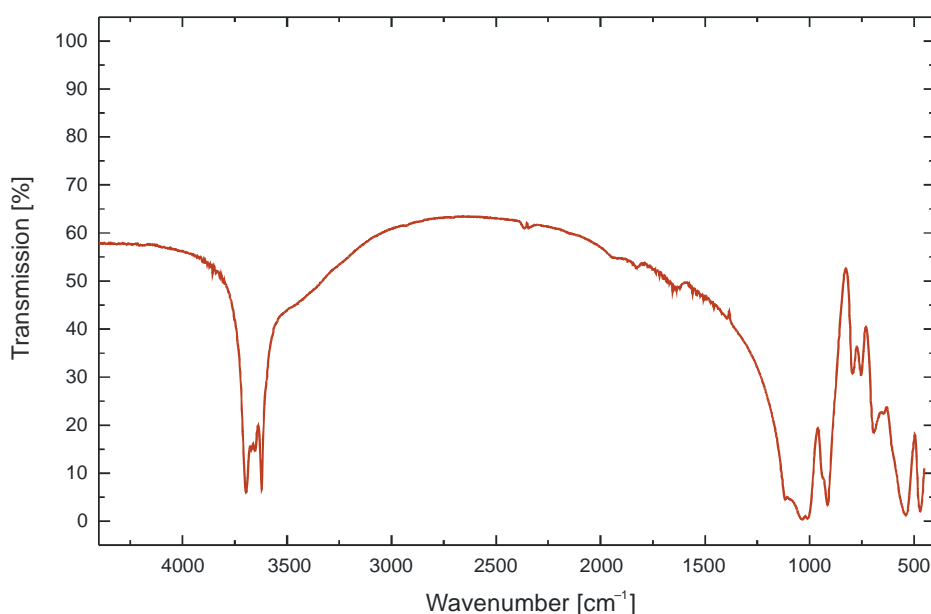


Fig. 3. IR absorption spectrum of the mineral kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (KBr pellet, powdered sample). The range below $\sim 1200 \text{ cm}^{-1}$ is the so-called fingerprint region that is most often used for phase identification. The absorption bands around 3600 cm^{-1} appear due to the O–H stretching vibrations. (Spectral data: Caltech Mineral Spectroscopy Server, <http://minerals.gps.caltech.edu>)

Experimental

In IR absorption spectroscopic experiments a polychromatic (“white”) IR radiation, usually from an incandescent source, interacts with the sample. Collecting of spectra may occur in two different ways. Dispersive spectrometers employ the dispersion of IR light on a grating, and spectra are recorded by a sequential registration of intensities in the desired energy range by turning the grating or the detector. The IR beam is shone through the sample and a reference object (most often an empty sample holder or pure pellet) simultaneously and the difference. Note that the dispersive method in IR absorption spectroscopy is effectively outdated today; all modern IR spectrometers are so-called Fourier transform (FT) instruments. The most distinctive component in FT-IR devices is an interferometer, in which the combination of a beam splitter, a stationary mirror and a moving mirror produces interference in the IR beam. Two so-called interferograms are recorded, one without and one with a sample in the beam path. The collected interferograms are then converted into spectra (wavenumber vs. transmission plots) using a mathematical method called Fourier transform. The difference between a reference spectrum (no sample) and a sample spectrum (with sample) gives us the IR absorption spectrum: the “missing” intensities at specific energies give us the information on the vibrational properties of the sample.

In the transmission geometry of IR absorption experiments, powdered as well as single crystal samples may be studied. The sample powder is mixed (usually strongly diluted) with KBr powder, a

material having no IR-active vibrations in the mid-IR range. The mixture can be pressed into a transparent disk and inserted in the beam path. In this case, a sum of vibrational properties is recorded; this method is most used for “fingerprint” identification of materials (Fig. 3).

Examples, applications

In a single crystal, lattice bonds are highly directional. Polarised IR measurements on oriented single-crystal sections contain information on the orientation of vibrational modes as well. From three different sections the orientation of vibrations may be reconstructed.

Infrared absorption spectroscopy is very often used for the study of hydrous species in solids. With oriented single-crystal measurements, even the crystallographic properties (orientation, bond lengths) of H₂O or OH groups may be determined. The length of hydrogen bonds, for instance, has a strong influence on the energy of the stretching vibration of the OH group. It is possible to calibrate O–H stretching wavenumbers from IR absorption and O···O distances from diffraction experiments (Fig. 4; Libowitzky, 1999). Owing to the extremely high sensitivity of the method to the O–H stretching vibration, hydrous species in nominally anhydrous materials may be investigated even at µg/g levels. With a proper calibration, IR spectroscopy may even be applied to measuring concentrations of hydrous species (Libowitzky & Rossman, 1997).

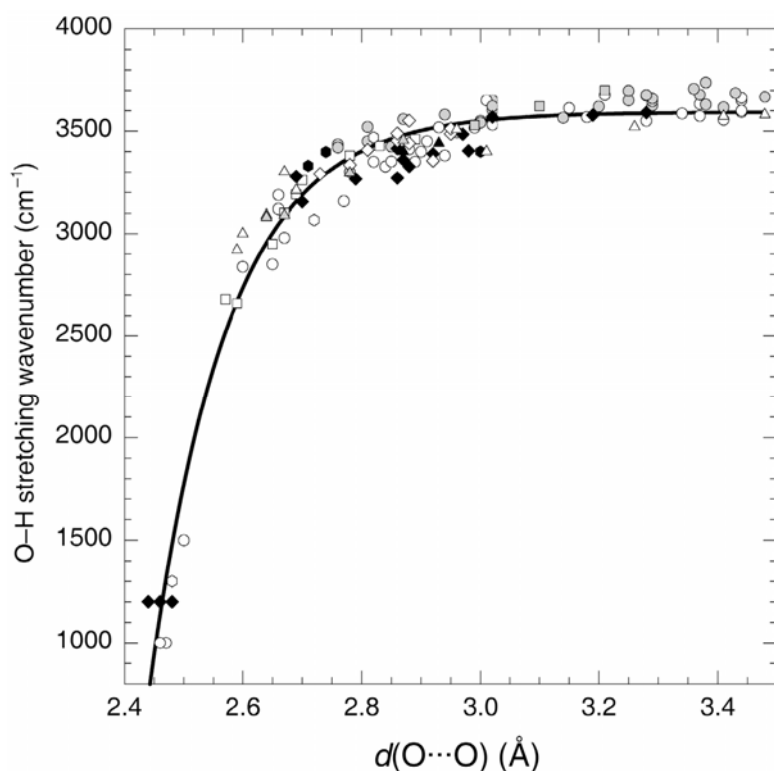


Fig. 4. Plot showing the effect of hydrogen bonding on the O–H stretching wavenumber. The O–H vibration is more energetic with weak hydrogen bonds (long O···O but short O–H distances). As hydrogen bonds get stronger, the O–H distance increases and a shift to lower energies is observed (after Libowitzky & Beran, 2004).

Another application of IR spectroscopy is the study of radiation damage. Figure 5 compares the spectra of natural zircon with low (sample C14) and very high (C4) level of self-irradiation damage. Little damage means a high short-range order, as seen in the 1400–2000 cm⁻¹ region. The amount of hydrous species is low (small absorption peak). In contrast, a high damage smears out sharp peaks because of the loss of short-range order. The concentration of hydrous species is strongly increased.

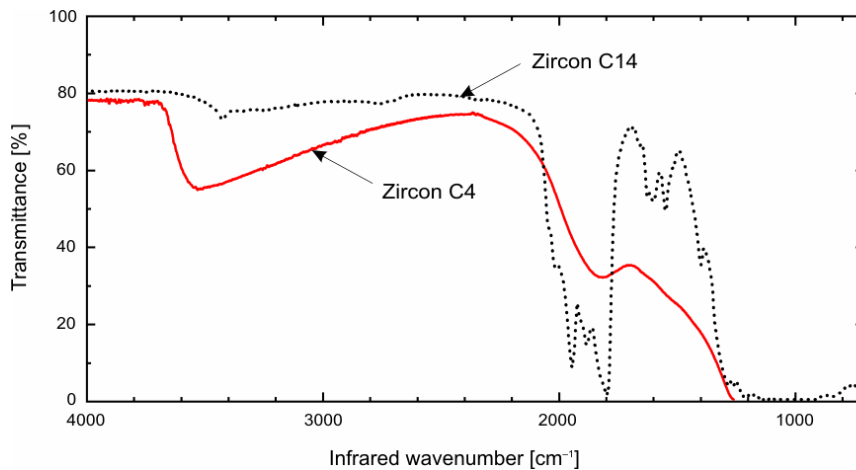


Fig. 5. IR absorption spectra of two zircon samples. Zircon C14 has low radiation damage, whereas Zircon C4 is highly damaged. The 1400–2000 cm^{-1} region shows overtones and combination modes of fundamental vibrations. Note that both spectra are saturated (opaque to IR) in the “fingerprint region”, to make other features, such as an increased concentration of hydrous species in C4, better visible (after Nasdala et al., 2001).

References, recommended reading:

- Beran, A., Voll, D. & Schneider, H. (2004): IR spectroscopy as a tool for the characterisation of ceramic precursor phases. In Beran, A. & Libowitzky, E. (eds.): *Spectroscopic Methods in Mineralogy / EMU Notes in Mineralogy*, **6/1**. Budapest: Eötvös University Press, 189–226.
- Farmer, V. C. (1974): *The infrared spectra of minerals / Mineralogical Society Monograph*, **4/1**. London: Mineralogical Society, 539 p.
- Libowitzky, E. (1999): Correlation of O–H stretching frequencies and O–H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, **130**:1047–1059.
- Libowitzky, E. & Beran, A. (2004): IR spectroscopic characterisation of hydrous species in minerals. In Beran, A. & Libowitzky, E. (eds.): *Spectroscopic Methods in Mineralogy / EMU Notes in Mineralogy*, **6/1**. Budapest: Eötvös University Press, 227–279.
- Libowitzky, E. & Rossman, G.R. (1997): An IR absorption calibration for water in minerals. *American Mineralogist*, **82/11–12**: 1111–1115.
- Nakamoto, K. (2009): *Infrared and Raman spectra of inorganic and coordination compounds. Part A: Theory and applications in inorganic chemistry* (6th ed.). New York: Wiley, 432 p.
- Nasdala, L., Beran, A., Libowitzky, E. & Wolf, D. (2001): The incorporation of hydroxyl groups and molecular water in natural zircon (ZrSiO_4). *American Journal of Science*, **301/10**: 831–857.
- Schmidt, W. (1994): *Optische Spektroskopie: Eine Einführung für Naturwissenschaftler und Techniker*. VCH Verlagsgesellschaft mbH, Weinheim.