

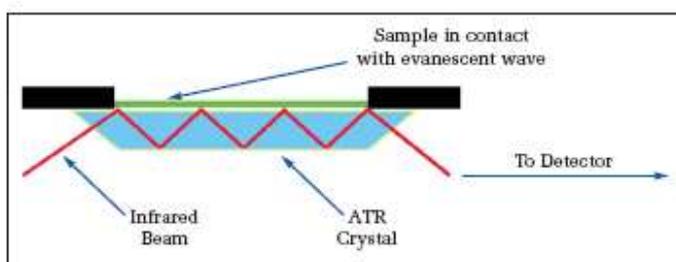
Practical

Infrared Spectroscopy

Please familiarise yourself with the theory of Infrared Spectroscopy from any suitable textbook or the Analytical Chemistry lecture course.

Attenuated total reflectance (ATR) is a sampling technique used, which enables samples to be examined directly in the solid, liquid or gas state without any sample preparation.

ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed.^[2] The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometers can be converted to characterise samples via ATR by mounting the ATR accessory in the spectrometer's sample compartment.



Scheme 1: principle of ATR-IR.

This evanescent effect only works if the crystal is made of an optical material with a higher refractive index than the sample being studied. Otherwise light is lost to the sample. In the case of a liquid sample, pouring a shallow amount over the surface of the crystal is sufficient. In the case of a solid sample, it is pressed into direct contact with the crystal. Because the evanescent wave into the solid sample is improved with a more intimate contact, solid samples are usually firmly clamped against the ATR crystal, so

that trapped air is not the medium through which the evanescent wave travels, as that would distort the results.

Typical materials for ATR crystals include germanium, KRS-5 and zinc selenide, while silicon is ideal for use in the Far-IR region of the electromagnetic spectrum. The excellent mechanical properties of diamond make it an ideal material for ATR, particularly when studying very hard solids, but its much higher cost means it is less widely used. The shape of the crystal depends on the type of spectrometer and nature of the sample. With dispersive spectrometers, the crystal is a rectangular slab with chamfered edges, seen in cross-section in the illustrations. With FTIR cylindrical crystals are used with liquid samples.

Experiment 1: Identification of functional groups

At the beginning of the practical you have been handed two unknown substances. Please record the IR spectra of these two substances.

Identify functional groups present in your sample by identification of characteristic IR absorption frequencies.

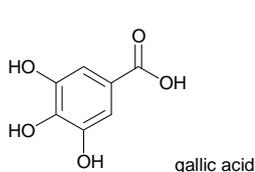
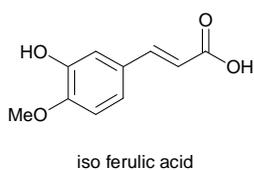
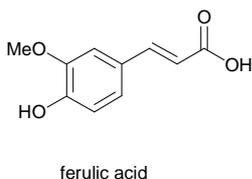
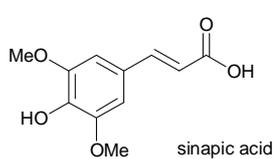
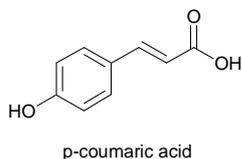
The TA lab demonstrator will give you an introduction into the basic operation of the instrument including sample preparation, hardware, software and instrument cleaning.

Experiment 2: Identification of compounds using the fingerprint region

The aim of the experiment is to identify an unknown compound based on its IR fingerprint region.

You will be handed copies of six IR spectra of reference compounds containing the identical set of functional groups (structures see below). Additionally you will be handed one unknown sample. Record its IR spectrum and identify the characteristic functional group absorptions and by comparison of the fingerprint region the identity your sample.

Argue which signals in the fingerprint region allow identification of your sample.



Experiment 3: Isotope effects

The wavenumber of IR absorptions depends on the value of the force constant k of the bond under investigation and on the reduced mass.

The aim of this experiment is to appreciate the effect of isotopic substitution on the appearance of an IR spectrum.

Obtain an IR spectrum from a sample of acetone and of D6-acetone (fully deuterated acetone).

Compare the two spectra and identify all peaks which have been shifted by isotopic substitution.

Questions

1. From the reduced masses in the C-H and C-D stretching mode calculate the force constant k of the two modes of vibration.
2. Show that the experimental C-D stretching frequency in acetone corresponds to the theoretically expected value by assuming a different reduced mass.
3. Estimate from the experimental IR spectrum of D6-acetone the degree of deuteration.
4. In all previous spectra you have recorded peaks corresponding to isotope substitution should in theory be visible as well (eg 1 % ^{13}C in C=O or 1 % ^2H in C-H absorptions). Identify two such examples in your spectra.