TECHNICAL NOTE

Infrared Spectroscopy

A Combined Mid-IR/Far-IR Spectrometer for Analytical Research Applications

Introduction

The long wavelength range of Mid-IR FT-IR spectrometers may be extended to ca 200 cm^{-1} by substituting the KBr beamsplitter and associated optical components with caesium iodide (CsI) counterparts. However, this arrangement is not optimal for demanding Far-IR (FIR) measurements, especially in the ca 220 cm^{-1} region.

Considerably better performance may be achieved by using a specialized FIR beamsplitter that has much higher throughput and efficiency in this region. By combining a specialized FIR beamsplitter with the standard high-performance Mid-IR (MIR) beamsplitter on a single changeover mechanism, with additional FIR detector, a high performance Mid-Far IR system is available on a single optical bench. This more effectively extends the useable range of the system into the far infrared than use of a single CsI beamsplitter. Using an automatic beamsplitter changer and motorized beam switching between Mid- and Far-IR detectors, with automatic software reconfiguration, simplifies the practical task of obtaining FIR spectra. This enables high quality FIR spectra to be obtained in shorter timeframes.

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The PerkinElmer Frontier IR/FIR system incorporates this design; offering a single instrument platform covering the range ca 7800-30 cm^{-1} with exceptional performance in the regions around 2000 and 200 cm^{-1} in the Mid- and Far-IR regions respectively.

Far infrared measurements

In contrast to the Mid-IR region where spectral features arise mainly from intramolecular vibrational modes, Far-IR spectral features can be due to a number of different types of transitions. In addition to the low frequency vibrational modes (these may involve heavy metal atoms if present), other underlying mechanisms include torsional and ring-puckering modes, intermolecular modes involving hydrogen bonds and charge-transfer species. In the solid state, lattice modes may give rise to strong FIR features, and certain impurity 'photo-ionization' mechanisms can be observed in semiconductors. In the gaseous state, pure rotation spectra are also observed in the FIR region. For these and practical reasons outlined below, most FIR measurements tend to be performed in academic or industrial research environments.

From a practical perspective, FIR spectroscopy can present some more challenges than most MIR measurements. Reasons for this include:

1) The inherent relative weakness of the source in the FIR region and low efficiency of FIR beamsplitters result in lower signal to noise than the corresponding MIR region.

2) Water vapor shows strong FIR absorption and spectral features can be distorted by water vapor interference unless special precautions are taken during measurement.

3) Sampling techniques may need to be slightly more specialized in the FIR. For example in transmission, KBr discs are no longer suitable for measurement beyond about 350 cm^{-1}, and an alternative matrix such as low density polyethylene may need to be used. In ATR measurements, which are increasingly popular in MIR measurement, common IR optical materials such as ZnSe and germanium are no longer suitable for FIR.

While the sampling issues pertaining to FIR are a separate discussion area, the Frontier IR/FIR system does incorporate a number of important features that are particularly advantageous to FIR measurements.

- A high performance interferometer with dedicated multilayer FIR beamsplitter and FIR DTGS detector with polyethylene window providing high performance in the ca 700-30 cm^{-1} region, in addition to the dedicated MIR beamsplitter and detectors(s).

- High efficiency independent interferometer and sample compartment purge systems allowing both rapid attainment of low water vapor concentration in the beampath and purge stability during the FIR measurement.

- Automatic switchover of beamsplitters and detectors. Combined with the efficient purge system, this provides more rapid and trouble-free system switchover from MIR to FIR operation.

- Optional sample-shuttle accessory allowing transmission measurements to be obtained by interleaving background and sample measurements throughout the scan cycle to minimize the effects of residual water vapor interference.

For the exceptional cases where the highest levels of performance are required, it has been customary to replace the detector and even source components. In the source area for example, where the standard MIR/FIR source is located, it is possible to add an optional auxiliary input beam device allowing an external source to be injected into the Frontier interferometer. High-pressure mercury lamps or even synchrotron sources have been used for FIR in the past, although it is generally considered that the mercury lamps are only really advantageous (if at all) at the extreme FIR range at the edge of the microwave region, <50 cm^{-1}. On the detector side, the use of a helium-cooled bolometer can dramatically increase sensitivity, especially at longest wavelengths, and the Frontier incorporates an optional external General Purpose Optical Bench (GPOB) which could accommodate such a device. This is also useful if the sample needs to be cooled to liquid helium temperatures as it is sometimes possible to locate the sample inside the bolometer next to the detector position, obviating the need for a separate sample cryostat.

However, a very large proportion of FIR measurements can be well-addressed without the need for such specialized additional components, and some examples of FIR measurements are shown here using the factory-supplied MIR/FIR source, FIR beamsplitter and FIR DTGS detector combination.

Results

The following spectra were recorded using the standard Frontier IR/FIR spectrometer, with FIR beamsplitter and detector selected, and standard polyethylene window fitted to the sample compartment. A typical single beam background measurement is shown in Figure 1. This shows the range ca 700-30 cm^{-1} is accessible with this combination, with relatively good signal throughput in the ca 200-250 cm^{-1} region.

Figure 2 shows the FIR measurement of sulfathiazole measured in transmission. This is a useful test sample for FIR, exhibiting features well below 150 cm^{-1}. The sample was prepared as a pressed polyethylene-based disk and placed at the standard sample position in the sample compartment. The sample compartment was purged only during measurement. The data was obtained using a spectral resolution of 4 cm^{-1} and scan speed (optical path difference velocity) of 1 cm/s. Data collection time was ca 1 minute.

The strong FIR absorptions of atmospheric water vapor tend to be more problematic when working at higher spectral resolution. Use of an evacuable spectrometer can help in these situations, but in addition to the practical issues of evacuating the spectrometer, problems can arise with customized sampling accessories or with the sample itself, such as sample de-gassing.

There are alternative approaches to minimize the effects of atmospheric absorption. In addition to purging, use of a sample shuttle accessory and/or mathematically subtracting the residual water vapor spectrum can have the desired effect. The reference spectrum for the mathematical subtraction can often be conveniently collected at the initial stages of purging the system for measurement. We have found the mathematical correction approach works very well provided the original spectra prior to subtraction are collected using a reasonably well purged instrument. This method has a slight advantage over use of a sample shuttle alone as use of the shuttle necessarily increases total scan time as a new background is always collected with every scan. For most situations, the high instrument stability combined with high purge stability on the Frontier instrument removes the need to collect new background spectra frequently under normal conditions.

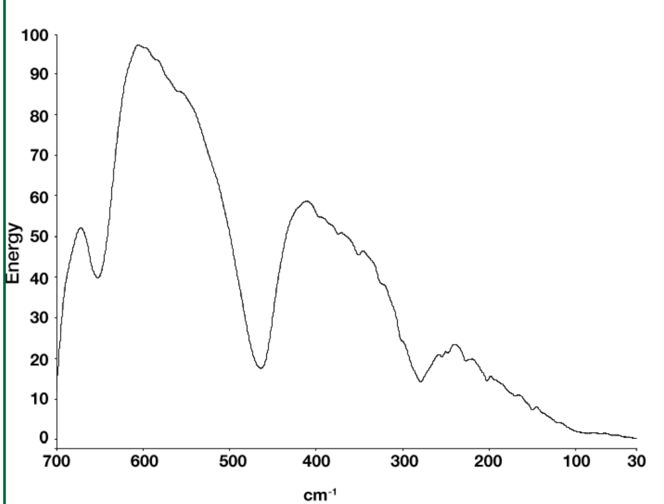

Figure 1: Single beam profile of Spectrum 400 with FIR beamsplitter and detector selected.

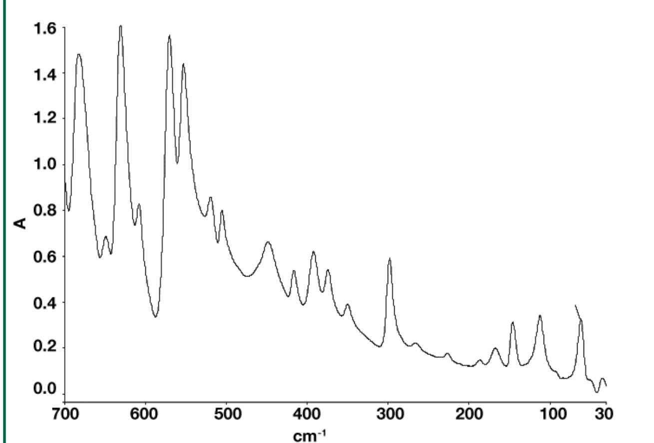

Figure 2: FIR transmission spectrum of sulfathiazole.

Summary

By use of a specialized additional wide-range FIR beamsplitter and dedicated FIR detector, it is possible to extend the high performance in the MIR well into the FIR region using a single optical bench. In terms of FIR performance, this combination is preferable to use of a single caesium iodide beamsplitter. Use of an automatic beamsplitter changer, motorized detector selection combined with high efficiency purge operation provides new levels of ease of use and convenience for FIR measurements. The added system hardware flexibility makes the Frontier IR/FIR combination an ideal choice for research environments performing more specialized experiments requiring customized components.

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008236A_02 Printed in United Kingdom