

Product Note T18-07/08

Vacuum Advantages: Isolate Yourself from the Elements



Absorption by atmospheric gases such as water vapor and carbon dioxide can lead to significant noise in mid- and far-infrared spectroscopy. Figure 1 shows the areas of absorption for water vapor and carbon dioxide from 20cm^{-1} in the far infrared to 5700cm^{-1} in the near-infrared. This figure shows the amount of absorption that occurs in a typical, unpurged spectrometer optics. In the mid-infrared, the vibrational modes (the OH stretching modes around 3700cm^{-1} and the HOH bending mode around 1600cm^{-1}) of water vapor exhibit rotational splitting, giving a very large number of sharp lines. The pure rotational modes of water vapor absorb in the far-infrared, giving another set of sharp lines. Carbon dioxide also absorbs in the mid-inf-

rared, with a stretching mode at about 2350cm^{-1} and a bending mode centered at 667cm^{-1} . Both of these modes are rotationally split, but the splitting is much smaller than for water vapor and can only be seen at resolutions higher than about 1cm^{-1} . In addition to the fundamental vibrations, carbon dioxide has combination bands between 3500cm^{-1} and 4000cm^{-1} .

These atmospheric absorption bands lead to noise in two different ways:

A) First, they absorb energy and therefore degrade the signal-to-noise ratio (SNR) simply because less light reaches the detector. The magnitude of this problem is best illustrated by a

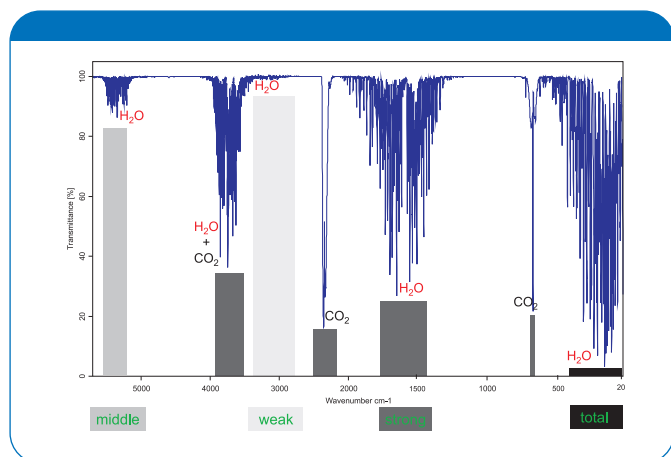


Fig.1: Regions of interference for atmospheric gases from 20cm^{-1} to 5700cm^{-1}

Vacuum Advantages

- Weak spectral features are not masked by moisture absorptions
- High spectral resolution features do not interfere with CO_2 and H_2O absorption lines
- Cast aluminum housing of the optics bench provides high stability
- Rapid evacuation by high speed, oil-free vacuum pump
- No problems caused by dry air purge supply fluctuations

simple example. If only 30% of the light is absorbed, then the SNR is 70% of that which would be obtained in the absence of atmospheric absorption. To recover this loss in SNR, the measurement time would have to be doubled.

B) The second reason why absorption bands from atmospheric interfering species lead to noise is because their concentration changes in time, which means the water vapor does not ratio out between the background and sample spectra. This problem is compounded by an effect that is more subtle, but is well known to most experienced infrared spectroscopists. A change in temperature causes a change in the relative intensities of the rotationally split lines, so that even if the concentration of the water vapor remains constant, it will not correctly ratio out. This is also the reason why it is nearly always impossible to completely subtract water vapor lines from a spectrum.

The most common method of reducing the effects of atmospheric contaminants is to purge the instrument with dry air or nitrogen. There are certain cases, however, in which it is difficult to obtain adequate results with a purged instrument. The alternative is to use a vacuum spectrometer, and eliminate the contaminants altogether. Some example applications in which a vacuum spectrometer will provide superior results are:

Fast sample turnaround

In this situation, a purge may actually be worse than nothing. Atmospheric contaminants will only ratio out if they are the same in the background and sample spectra. A purged instrument must be left for long enough that the atmosphere inside stabilizes. In contrast, the atmosphere in a vacuum spectrometer can be completely removed in less than two minutes.

Measurements of very small band intensities

Example application areas are low-level additives, dilute protein solutions, and surface science. Figure 2 shows example IRRAS spectra. Down to 10^{-3} monolayers can be measured in principle and have been published.

Long-term experiments

As the time difference between the background and sample spectra increases, it becomes increasingly difficult to obtain completely contaminants free spectra. As already discussed, changes in either the concentration of contaminants or the temperature of the atmosphere in the spectrometer can cause residual peaks to be present.

High-resolution measurements

Vapor phase lines are very narrow, with widths typically on the order of 0.2cm^{-1} or less. This means that as the spectral resolution is increased, the lines become more strongly absorbing. In addition, an unstabilized HeNe laser, which has

a long-term frequency stability of only a few ppm, is nearly always used as a reference in an FT-IR (an exception is the IFS 125HR, which uses a stabilized laser) spectrometer. At high resolution, even these very small shifts in the frequency calibration of the instrument can cause a significant misratio for very narrow lines.

Resolution enhancement techniques

If methods such as deconvolution or derivatives are used to enhance the resolution of spectra, sharp bands due to atmospheric contaminants are always amplified relative to the broader bands that are of interest.

Far-infrared measurements

The far infrared has a very large number of strongly absorbing water vapor lines. Only a vacuum spectrometer can completely remove these lines, permitting the highest quality spectra to be recorded. Figure 3 shows some example far-infrared spectra measured on a vacuum spectrometer.

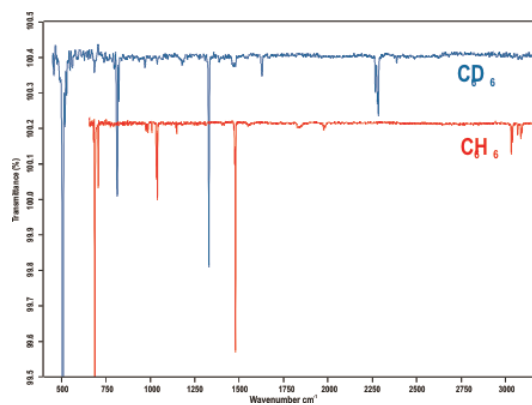


Fig. 2: Mono-layer IRRAS spectra of crystalline benzene in a UHV chamber, at 2cm^{-1} resolution. See P. Jakob and D. Menzel, *J. Chem. Phys.*, 105 (9),1996, P. 3838

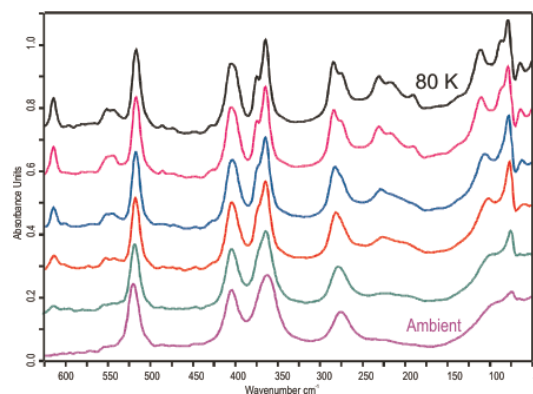


Fig. 3: FIR spectra of liquid DMTF as a function of temperature, at 4cm^{-1} resolution