TECHNICAL NOTE

Infrared Spectroscopy

Atmospheric Vapor Compensation on Spectrum Two and Frontier FT-IR Spectrometers

Summary

The Atmospheric Vapor Compensation (AVC) function on the Spectrum™ Two and Frontier Series addresses the difficult task of reducing the effects of unwanted atmospheric absorptions in sample spectra. The algorithm automatically performs this task in real time, improving spectral quality and consistency, enhancing convenience, and saving time and money for the user.

Introduction

A traditional problem in FT-IR spectroscopy is the effect that the measured ratio spectrum of a sample may be contaminated by small features from atmospheric absorptions. One reason is that FT-IR spectrometers are single beam instruments. They must first measure a background spectrum without the sample and then run a sample spectrum with the sample in the beam in order ratio spectrum. Atmospheric non-compensations can be observed if the absorptions of water vapor and carbon dioxide between the sample and background measurements change. This happens, for example, if the concentration of water vapor and carbon dioxide changes between the two measurements (simply breathing into the sample compartment while loading the sample can cause this) or if the sample alters the length of the optical path in the sample compartment. Another reason for these artifacts may be small changes of the beam geometry by the sample itself or by accessories that influence the shape of the water vapor bands, resulting in derivative-like residuals. In addition to introducing variations that are not related to the chemical composition of the sample, these unwanted artifacts can obscure the underlying details in the sample spectrum and disturb qualitative and quantitative spectral information.

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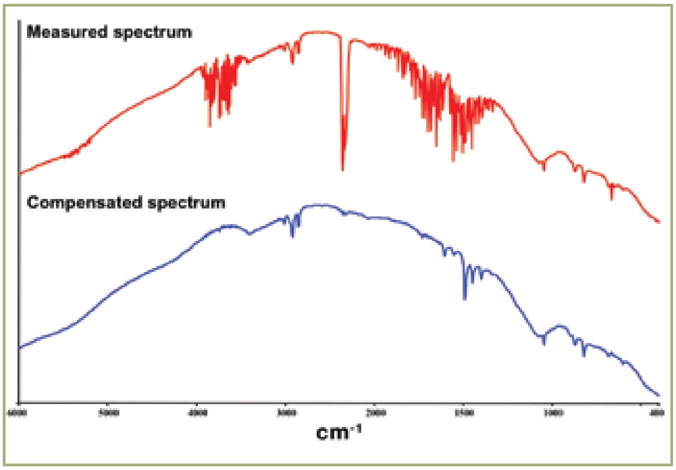

Figure 1: Atmospheric Vapor Compensation of a single beam spectrum. With AVC, the compensated spectrum is displayed in real time.

Standard approaches to the problem

Various means have been adopted to reduce this contamination to acceptable levels. For example, the optical bench and sample area might be purged with dry air or nitrogen, which is rather inconvenient and time-consuming. In addition, it is extremely difficult in practice to maintain a constant level of purge during background and sample data collection, which is required to achieve proper atmospheric compensation. The situation can be improved significantly by using sealed and desiccated optics, as used in the Spectrum Two and Frontier instruments. But this leaves the problem with the sample compartment, which usually has to be open to the atmosphere to allow sample introduction. Another solution is to use a sample shuttle that automatically moves the sample in and out of the beam and measures background and sample spectra in an interleaved mode. However, this is only applicable to simple transmission samples and does not work with larger accessories. A stored water vapor and carbon dioxide reference spectrum can also be subtracted from the contaminated sample spectrum. Unfortunately, this is not an easy task as it requires that the water vapor reference spectrum to be subtracted fits the atmospheric bands in the sample spectrum perfectly. In practice, this is seldom the case even if this reference spectrum is measured under very similar conditions as the sample spectrum. Thus, the results of this approach are often not very successful.

Difficulty in subtracting a water vapor reference spectrum

Successful removal of the interfering water vapor by automatic subtraction has two prerequisites:

- The detailed shape of the water vapor spectrum to be subtracted must be known
- The subtraction factor must be determined accurately to prevent under- or over-subtraction.

Unfortunately the spectrum of water vapor at atmospheric pressure and temperature is very complex as it contains thousands of absorption lines that have a natural width smaller than 0.1 cm^{-1}. At 4 cm^{-1}, spectral resolution that is typically used, these lines are usually only partially resolved. In consequence, the atmospheric water vapor spectrum measured is strongly distorted compared to its natural shape, and absorption strengths of the underresolved water vapor lines are no longer a linear function of concentration and pathlength. So if we try to subtract an under-resolved water vapor spectrum from a spectrum that was measured of a water vapor sample with a different concentration or pathlength, we end up with a residual spectrum that cannot be fully compensated. This effect is illustrated in Figure 2. In addition to this high non-linearity of the water vapor spectrum, its precise shape also depends on the ambient temperature and partial pressure in the instrument. This is further complicated by the fact that changes in the beam geometry from instrument to instrument or by the sample itself also influence the water vapor spectrum. Therefore, the spectral shape of the water vapor spectrum is highly variable depending on the circumstances. Due to this complex behavior, a clean subtraction by direct computation has not been very successful – even in cases where the water vapor reference spectrum was measured in situ.

But even if the shape of water vapor spectra suitable for subtraction was known exactly, there is still the problem of determining how much to subtract. This is a difficult task to be performed automatically, especially when the sample bands of interest overlap the water vapor spectrum.

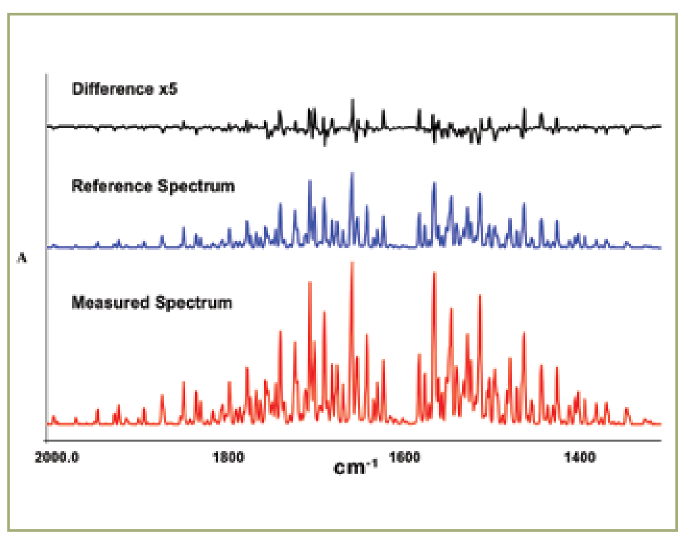

Figure 2: Attempted subtraction of two water vapor spectra with different concentrations or pressures.

Atmospheric Vapor Compensation in the Spectrum Two and Frontier FT-IR

The Spectrum Two and Frontier instruments provide a powerful solution to the water vapor subtraction problem. It is called Atmospheric Vapor Compensation. This patented algorithm is capable of successfully performing an automatic subtraction of water vapor and carbon dioxide in the sample spectrum. This occurs without any user interaction and in real time, even in the presence of strong sample features. One of the keys to this solution is to start with noise-free, high-resolution theoretical water vapor spectra that can be computed from tables and for which the coefficients for changes in concentration and pressure are known (HITRAN data). First, several spectra of these are calculated in order to model for different temperatures and pressures. In a second step, these spectra are mathematically broadened to simulate for the broadening effect by the instrument depending on the selected resolution, apodization and size of the Jacquinot stop plus small variations in line width and frequency shifts. Then, linear combinations of these candidate spectra are used to fit the sample spectrum. The problem of determining the correct difference factor for the subtraction is addressed by performing a least square fitting of the calculated water vapor spectra to the sample spectrum. This is combined with optimum filtering that concentrates on the sharper features in the sample spectrum, which are usually dominated by the water vapor bands, assuming the sample is in the condensed phase.

Having calculated the full water vapor correction spectrum, it can be used for the subtraction from the sample spectrum. The correction for the carbon dioxide non-compensations is calculated in a similar manner. This ultimately generates a corrected sample spectrum that is almost free from any atmospheric disturbances (Figure 3).

The fact that this correction succeeds by applying mathematical calculations on theoretical water vapor and carbon dioxide spectra, is also an indication of the spectral fidelity and overall performance of the Spectrum Two and Frontier instruments, with respect to line shape, wavelength stability and artifact levels. As all of these calculations are done in a sub-second timescale, the atmospheric compensation takes place in real time for every spectrum measured as long as the feature is switched on. The algorithm is also applied to the single beam spectra in order to show that the function is switched on, and the compensated spectra displayed in real time. In this case, the atmospheric absorptions are completely removed, revealing some bands of protective coatings on the instrument optics that were obscured by the water vapor spectrum. The final calculation, however, is done on the ratio spectrum.

One of the most challenging situations for an automatic atmospheric compensation algorithm occurs when the beam geometry changes between the background and the sample measurement. In this case, the shape of the water vapor and carbon dioxide bands are different in the two single beam spectra, resulting in derivative-shaped atmospheric artifacts. This happens, for instance, when the size of the sample in the sample holder is smaller than the beam. Figure 4 shows that the AVC on the Frontier removes these distortions successfully. A simple automatic subtraction algorithm with previously measured water vapor spectra, such as is found on some current FT-IR instruments, would not have been able to remove these artifacts.

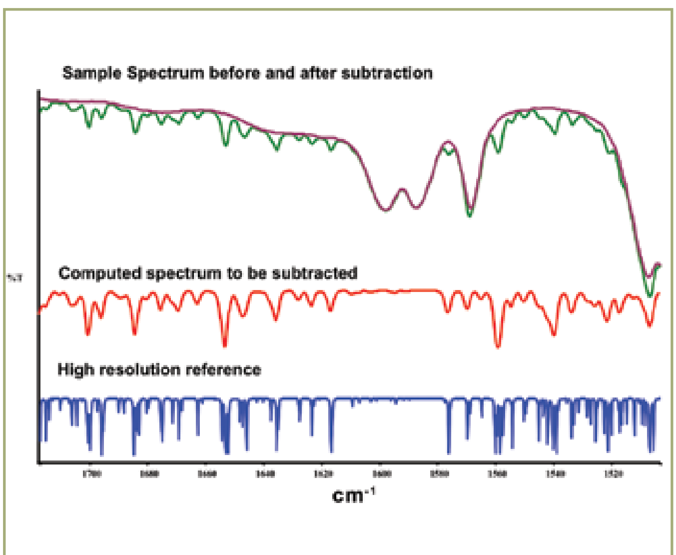

Figure 3: Spectra used in Atmospheric Vapor Compensation.

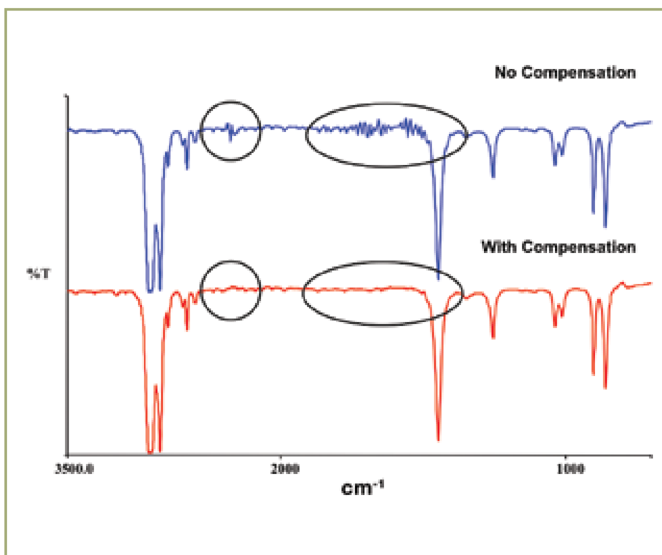

Figure 4: Atmospheric Vapor Compensation of derivative-shaped water vapor bands.

Benefits of Atmospheric Vapor Compensation

The automatic HAVC routine is very useful in many FT-IR applications with few exceptions, such as gas analysis. Its major benefits are:

- Improved spectral quality by removing unwanted atmospheric distortions and by removing variations in the data that are not related to the chemical composition of the sample.
- Significant savings of time and money by avoiding time consuming and expensive purging of instruments. It even helps if the instrument is purged.
- Convenient usage AVC is performed automatically in real time without the need to generate any reference spectra of atmospheric absorptions.
- Superior algorithm compared to simple automatic subtraction of measured reference spectra, providing lower residuals, with the further advantage that the reference spectra used for subtraction are noise-free.

Conclusion

The successful removal of unwanted atmospheric distortions in FT-IR spectra is a very difficult task. The HITRAN Atmospheric Vapor Compensation function provided with Spectrum Two and Frontier instruments performs this task automatically and in real time. It makes these instruments behave as purged instruments, without any of the disadvantages of purging. It is another example of the kind of built-in intelligence that helps the user to concentrate on his or her main tasks and get consistently high-quality data that are independent of any changes in atmospheric absorptions. This provides a further example of improving the spectral fidelity of FT-IR measurements by addressing a common problem which is inherent with all FT-IR single beam measurements.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

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