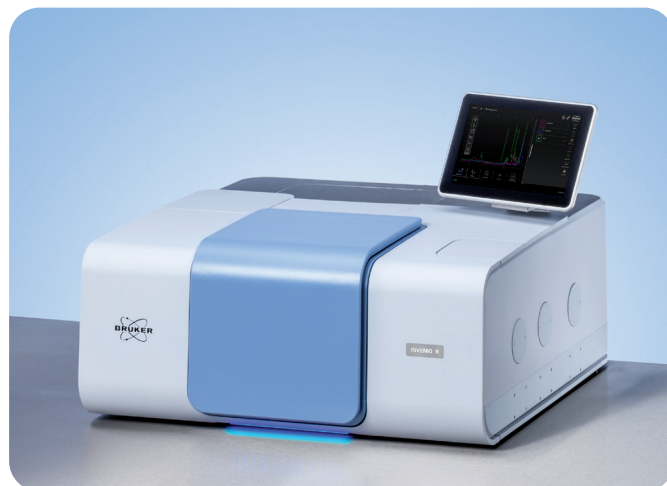


Product Note T26-10/19

Spectral resolution in FTIR spectroscopy



Spectral resolution is one of the most important attributes of spectrometers, since it defines the ability of instrument to resolve the bands of close proximity. The highest achievable resolution for a FTIR instrument is calculated as a Full-Width at Half Height (FWHH) of a low-pressure gas phase spectrum molecule, where the Doppler bandwidth is more narrow than the achievable resolution of the spectrometer. Bruker uses carbon monoxide at 5 mbar for this purpose. Table I summarizes the achievable spectral resolution for various Bruker FTIR spectrometers. All Bruker FTIRs allow a continuous (not discrete) selection of resolution values that provides greater more flexibility for spectral recording.

Table 1

	standard, cm^{-1}	optional, cm^{-1}
ALPHA II	2.0	0.75
INVENIO S	0.4	0.16
INVENIO R	0.16	0.16
INVENIO X	0.09	0.09
VERTEX 70v	0.4	0.16
VERTEX 80/80v	0.2	0.06
IFS125HR	0.007	0.0009

Achievable spectral resolution for Bruker FTIR spectrometers

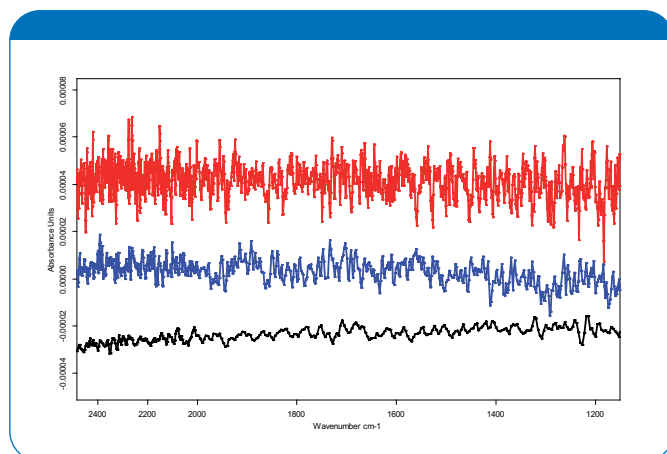


Figure 1: 1 minute zero absorbance open beam measurements at different resolutions. Spectra measured at 2cm^{-1} (top) resolution show a higher noise level in comparison to spectra collected at 4 (middle) and 8cm^{-1} (bottom) resolution (Vertex 80v, DTGS detector).

Selection of the correct resolution is a crucial point in FTIR spectrometry. A resolution that is too low will not resolve the bands and a resolution that is too high introduces more noise without improving band separation, as shown in Figure 1. If the resolution is increased by a factor of 2, the noise will be twice as high. The noise decreases as the square root of acquisition time. For example, it will take 16 times longer to collect a spectrum of equivalent signal-to-noise, when the spectral resolution is increased by four.

Resolution better than 4cm^{-1} requires the use of smaller apertures in the spectrometer that reduce the beam intensity and lead to higher noise. The purpose of the aperture is to achieve the necessary degree of beam collimation in the interferometer. The OPUS software automatically advises user about selecting the right aperture for a given resolution.

Figure 2a

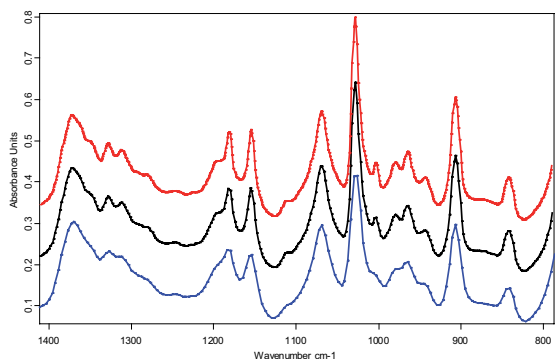


Figure 2b

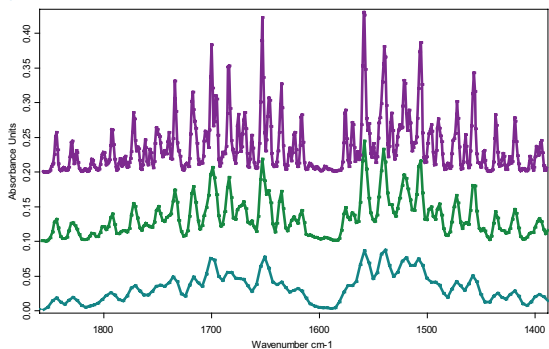


Figure 2: Spectra of polystyrene (2a) and water vapor (2b) measured with 2 (top), 4 (middle) and 8cm^{-1} (bottom) resolution. 4cm^{-1} resolution is adequate to measure spectra of polystyrene, but not high enough to resolve fine rotational bands of the water molecule in gas phase. In the case of polystyrene, 2cm^{-1} resolution does not improve band separation, while 8cm^{-1} resolution results in some smoothing of spectral features.

According to FWHH criterion, two triangular shaped lines of equal intensity and half-width are not resolved until the spacing between the lines is greater than the FWHH of either line. In practical terms, the correct spectral resolution for a spectrum of condense phase material should be set to $\text{FWHH}/2.5$. For the majority of liquids, polymers and non-crystalline solids where typical band width in Mid-IR spectrum is about $10\text{-}12\text{cm}^{-1}$ the appropriate resolution will be 4cm^{-1} , as shown in Figure 2. Near-IR bands are more broad in comparison to Mid-IR bands and a resolution of 8 or 12cm^{-1} is usually sufficient.

The $\text{FWHH}/2.5$ rule is not applicable for selecting the resolution for low pressure gas phase spectra, since vapor

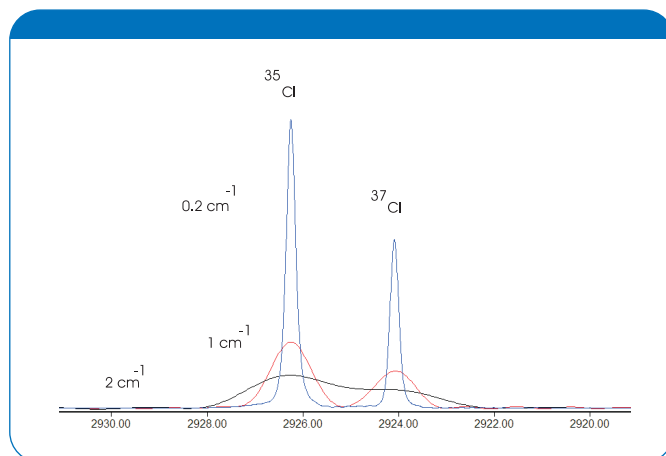


Figure 3. 1cm^{-1} resolution is sufficient to resolve isotope splitting in the gas phase infrared spectrum of HCl at 5mb pressure.

phase bands are typically more narrow than the instrument is capable of resolving.^{1,2} The appropriate resolution, in this case, depends on the specific information the researcher would like to obtain from the spectra. A classic example is the characterization of the gas spectrum of HCl, which is commonly performed in an introductory physical chemistry course. This spectrum consists of a series of sharp peaks that correspond to transitions between different rotation-vibration states in the diatomic molecule. Peaks are also split due to the presence of H^{35}Cl and H^{37}Cl isotopes. Based on the IR spectrum, students can calculate reduced masses, moments of inertia, force constants, and bond lengths for both isotopes. Figure 3 clearly shows that 1cm^{-1} resolution is enough to separate the distance from the isotope peaks of HCl to the baseline. The INVENIO S and ALPHA II are therefore good choices for performing such experiments.

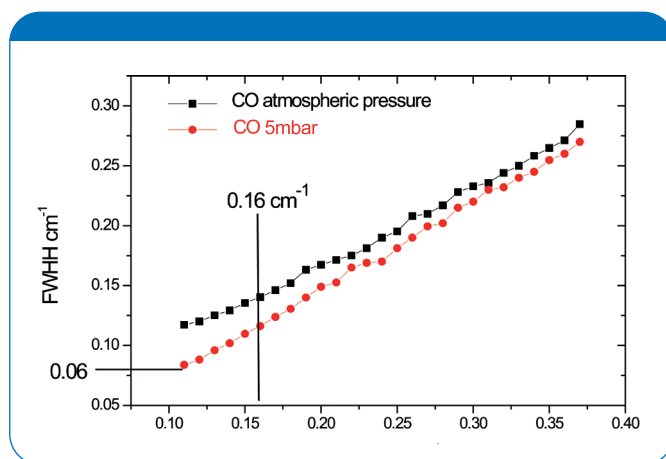


Figure 4: FWHH of a single CO gas peak at 5bar (red) and at atmospheric pressure (black) measured with the Vertex 80v shows peak broadening at high pressure. The lowest value of FWHH is 0.06cm^{-1} that corresponds to the highest resolution achievable for the Vertex 80v. Although peak broadening is more pronounced at high resolution it is not necessarily to use the highest resolution to study this effect. Band broadening is observable at 0.16cm^{-1} resolution and can be measured with the INVENIO R.

These instruments can also be used in analytical laboratories for the routine gas analysis, where a spectral resolution lower than 0.5cm^{-1} is rarely needed.

Higher spectral resolution can be required for studying peak broadening under different temperatures and pressures. Although a natural peak width is typically smaller than the instrument is capable of measuring, peak broadening is evident at resolution 0.16cm^{-1} , as shown in Figure 4. For these measurements, the INVENIO R FTIR R&D spectrometer can be used.

For fundamental molecular spectroscopy research, where the highest spectral resolution from the FIR to UV spectral range is required, the Vertex 80v or IFS125 HR are available. Figure 5 demonstrates that high spectral resolution with excellent band shape is achievable even in the short wavelength visible spectral range with a resolving power ($\nu/\Delta\nu$ band position divided by FWHH) of better than 300,000:1 with the Vertex 80v.

References

- ¹ P.G Griffiths, J.A. de Haseth "Fourier Transform Infrared Spectrometry", Wiley-Interscience, 2007
- ² P.R. Griffiths, Resolution and instrument line shape, in Handbook of Vibrational Spectroscopy, J.M. Chalmers and P.R. Eds., Wiley, Chichester, West Sussex, England, 2002, Vol.1, p. 241

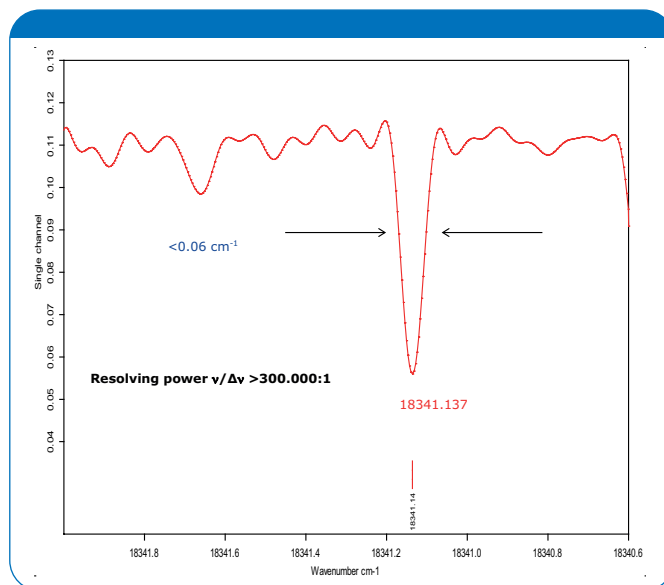


Figure 5. High resolution spectrum showing electronic band transitions of the iodine vapor in the visible range (Vertex 80v, 0.06 cm^{-1} resolution)