



Application Note AN M71

Spectral Resolution in FTIR Spectroscopy

Spectral resolution is one of the most important attributes of spectrometers, since it defines the ability of the instrument to resolve bands of close proximity. The highest achievable resolution for an FTIR instrument is determined as the Full-Width at Half-Height (FWHH) for a specified spectral band measured for a low pressure gas sample in which the Doppler bandwidth is narrower than the achievable resolution of the spectrometer. Bruker uses carbon monoxide at 5 mbar for this purpose. Table 1 summarizes the achievable spectral resolution for various Bruker FTIR spectrometers. All Bruker FTIR spectrometers allow a continuous (not discrete) selection of resolution values that provides greater flexibility for spectral recording.

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 approximately twice as high for the same acquisition time. The noise decreases as the square root of acquisition time.[1] Allowing for the separate background and sample measurements, it will take 8 times longer to collect a spectrum of equivalent signal-to-noise, when the spectral resolution is increased by two. Resolution better than 2 cm^{-1} requires the use of smaller apertures in the

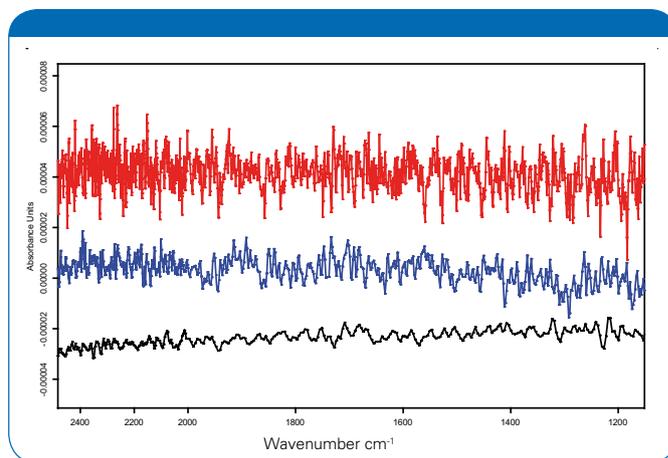


Figure 1: 1 minute zero absorbance open beam measurements at different resolutions offset for clarity. Spectra measured at 2 cm^{-1} (top) resolution show a higher noise level in comparison to spectra collected at 4 cm^{-1} (middle) and 8 cm^{-1} (bottom) resolution (VERTEX 80v, DTGS detector).

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 the user about selecting the right aperture for a given resolution and wavenumber range.

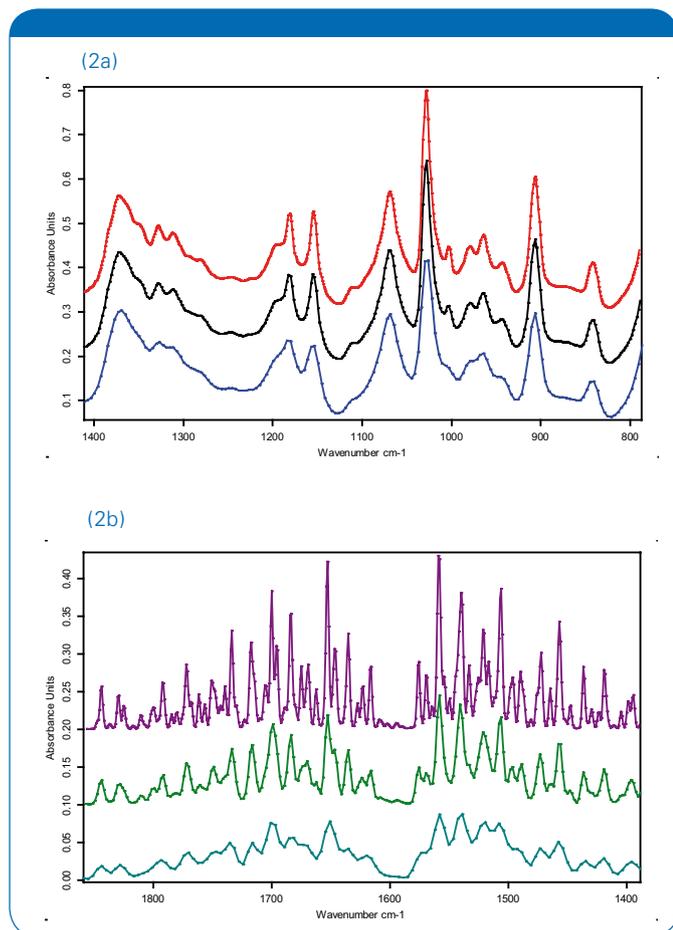


Figure 2a+b: Spectra of polystyrene (2a) and water vapor (2b) measured with 2 (top), 4 (middle) and 8 cm⁻¹ (bottom) resolution. 4 cm⁻¹ resolution is adequate to measure spectra of polystyrene, but not high enough to resolve fine ro-vibrational bands of the water molecule in the gas phase. In the case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

According to the 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.[2] In practical terms, the correct spectral resolution for a spectrum of a condensed phase material should be set to FWHH/2.5. For the majority of liquids, polymers and non-crystalline solids where the typical band width in the Mid-IR spectrum (4000-400 cm⁻¹) is about 10-12 cm⁻¹ the appropriate resolution will be 4 cm⁻¹, as shown in Figure 2. Bands in the Near-IR spectral range (10000 – 4000 cm⁻¹) are broader in comparison to Mid-IR bands and a resolution of 8 or 12 cm⁻¹ is usually sufficient.

The FWHH/2.5 rule is not applicable for selecting the resolution for low pressure gas phase spectra, since vapor phase bands are typically more narrow than the instrument

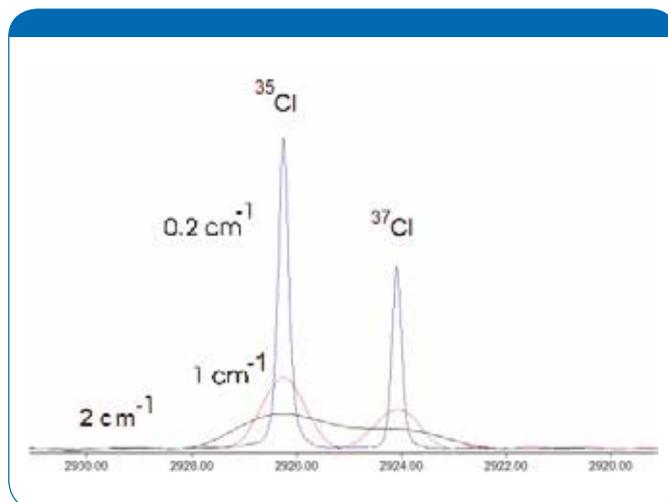


Figure 3: 1 cm⁻¹ resolution is sufficient to resolve isotopic splitting in the gas phase infrared spectrum of HCl at 5 mbar pressure.

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 H³⁵Cl and H³⁷Cl isotopes. Based on the IR spectrum, students can calculate the vibrational band origins and moments of inertia for both isotopes and knowing the reduced masses can further determine the (theoretically same) force constants and bond lengths. Figure 3 clearly shows that 1 cm⁻¹ resolution is enough to separate the spacing between the isotopic peaks of HCl down to the baseline. The TENSOR II and ALPHA II are therefore good choices for performing such experiments. These instruments can also be used in analytical laboratories for routine gas analysis, where a spectral resolution better than 0.5 cm⁻¹ is rarely needed.

Resolution	Standard	Optional
ALPHA	2.0 cm ⁻¹	0.8 cm ⁻¹
TENSOR II	0.4 cm ⁻¹	
INVENIO R	0.16 cm ⁻¹	
VERTEX 70v	0.4 cm ⁻¹	< 0.16 cm ⁻¹
VERTEX 80/80v	0.2 cm ⁻¹	< 0.06 cm ⁻¹
ISF 125 HR	0.0063 cm ⁻¹	< 0.0007 cm ⁻¹

Table 1: Achievable spectral resolution for Bruker FTIR spectrometers.

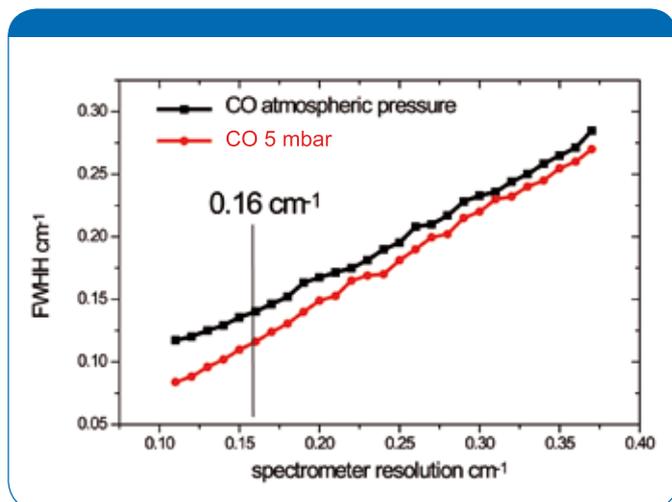


Figure 4: The FWHM of a single CO vapor phase ro-vibrational band at 5 mbar (red) and at atmospheric pressure (black) shows broadening with the higher pressure. Although this effect is more pronounced at higher resolution, it is not necessary to use the highest resolution to study it. Band broadening is observable at 0.16 cm^{-1} resolution, which can be measured with the INVENIO R.

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 0.16 cm^{-1} , as shown in Figure 4. For these measurements, the INVENIO R can be used.

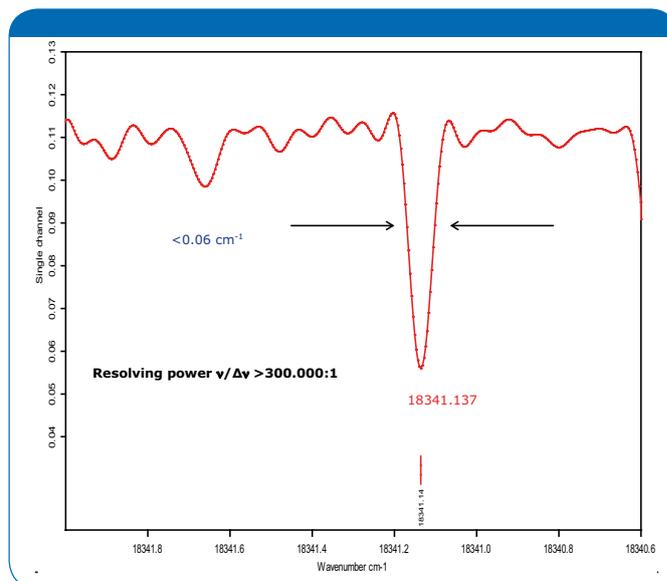


Figure 5: High resolution spectrum showing electronic band transitions of iodine vapor in the visible range (VERTEX 80v, 0.06 cm^{-1} resolution).

For fundamental molecular spectroscopy research, where the highest spectral resolution from the Far-IR to UV spectral range is required, the VERTEX 80v or IFS 125HR 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 ($v/\Delta v =$ band position divided by FWHM) of better than 300,000:1 with the VERTEX 80 and 80v.

Apodization Function	FWHM relative to resolution setting in OPUS	Application and remarks
Boxcar	0.67	High resolution gas phase spectra
Trapezoidal	0.71 for linear ramp down for last 10 % of data	High resolution gas phase spectra
Norton-Beer weak	0.76	High resolution gas phase spectra when a certain damping of the sidelobes is necessary; i.e. when the selected resolution is less than the natural linewidth
Norton-Beer medium	0.88	
Norton-Beer strong	1.0	General purpose spectroscopy. Gives better resolution than Blackman-Harris 3 term at the expense of small sidelobes
Triangular	1.0	Should be avoided in quantitative analysis because it produces all positive sidelobes
Happ-Genzel	1.0	The first sidelobe is smaller than with Norton-Beer strong, however, the roll off is only as $1/X$
Blackman-Harris, 3-term	1.3	General purpose spectroscopy. Shows virtually no sidelobes
Blackman-Harris, 4-term	1.5	Emission spectroscopy when very high dynamic range in the intensity is required

Table 2: Apodization function selection.

Apodization and Resolution

The interferogram collected with the FTIR spectrometer is finite with respect to the measured optical path difference. Fourier transform of this finite interferogram produces oscillations (sidelobes) around the bands in the spectrum when the natural band width is narrower than spectral resolution of the spectrometer. Apodization is a multiplication of the interferogram with a function which will dampen the strong sidelobes.

The apodization function also affects the resolution and the noise in the spectra. In choosing the optimum apodization a compromise must be made between the best resolution and the lowest sidelobes (Figure 6). Table 2 shows apodization functions available in OPUS and gives recommendations for the proper selection. The OPUS software warns the user if the apodization function is not in agreement with the selected resolution.

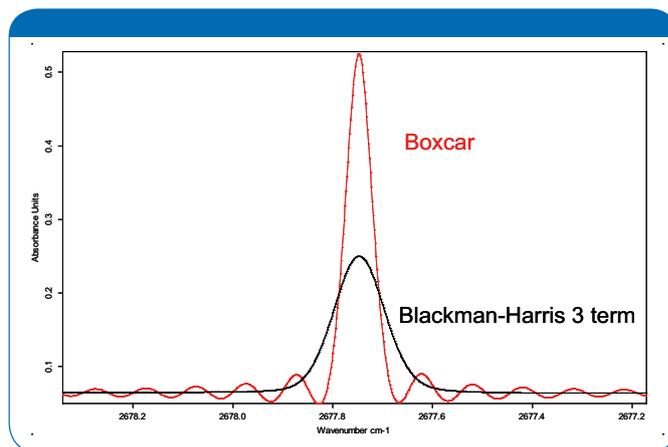


Figure 6: Boxcar apodization function produces the narrowest bandwidth but creates sidelobes around the infrared band of HCl at 5 mbar pressure. Blackman-Harris 3-term apodization removes sidelobes at the expense of the bandwidth and the band intensity. The differences in linewidth are in accordance with the FWHH values in Table 2 (the factor is 1.94).

References

- [1] P.R 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. Griffiths, Editors, Wiley, Chichester, West Sussex, England, 2002, Vol.1 , p. 241
- [3] Bruker Optic Application Note #128 Vapor Phase MIR-Spectrum of Ammonia - VERTEX 80v High Resolution Measurement Example

● Bruker Optik GmbH

Ettlingen · Deutschland
Phone +49 (7243) 504-2000
Fax +49 (7243) 504-2050
info.bopt.de@bruker.com

www.bruker.com/optics

Bruker Optics Inc.

Billerica, MA · USA
Phone +1 (978) 439-9899
Fax +1 (978) 663-9177
info.bopt.us@bruker.com

Bruker Shanghai Ltd.

Shanghai · China
Phone +86 21 51720-890
Fax +86 21 51720-899
info.bopt.cn@bruker.com