

A Tutorial on Spectral Resolution for the Nicolet iS5 FT-IR Spectrometer

Key Words

Fourier Transform Infrared Spectroscopy, Gas Phase Molecules, Physical Chemistry Laboratory

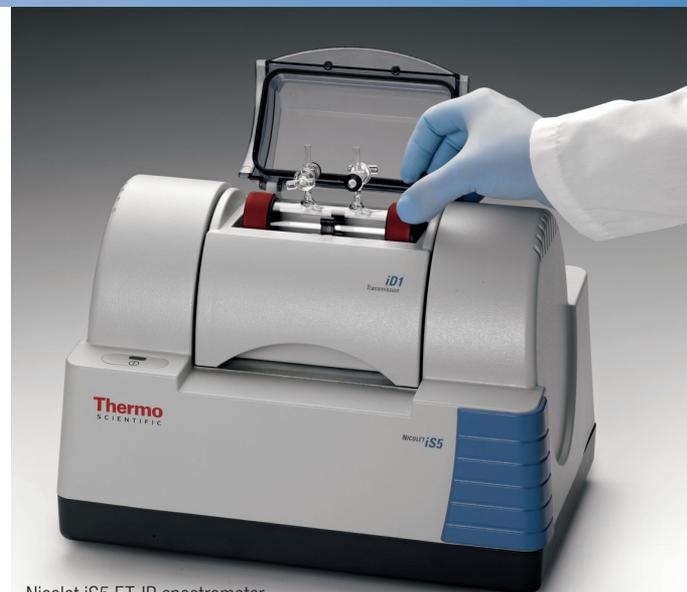
Introduction

The same characteristics that make the Thermo Scientific™ Nicolet™ iS™5 FT-IR spectrometer ideal for industrial applications – ruggedness, humidity resistance and simplicity – make it equally suited for the teaching laboratory. One additional requirement, met by the Nicolet iS5 FT-IR spectrometer, is the need for high spectral resolution for gas analysis in the physical chemistry laboratory. In this technical note, we describe some fundamental characteristics of Fourier transform spectrometers that affect spectral resolution and how to optimize the Nicolet iS5 system to produce spectra at better than 0.5 cm^{-1} spectral resolution.

Theory

Spectral line shapes are affected by many factors.¹ Gas phase spectra tend to have very narrow and sharp peaks. Natural physical effects, like pressure and temperature as well as strong intermolecular forces, can broaden and shift these peaks. The study of these phenomena is a standard item in the physical chemistry curriculum. The spectrometer used must obtain spectra at sufficiently high resolution to permit diagnostic laboratory studies, but only rarely are more expensive units with resolutions better than 0.4 cm^{-1} needed. The Nicolet iS5 FT-IR spectrometer is completely capable of performing these undergraduate physical chemistry laboratory experiments.

The key optical component in the Nicolet iS5 FT-IR spectrometer is a high-precision Michelson interferometer. Spectral resolution in a Michelson interferometer is largely controlled by the optical path difference between the fixed and moving mirror, which is called the



Nicolet iS5 FT-IR spectrometer with 10 cm gas cell

retardation.² The maximum retardation the interferometer can obtain while maintaining optical coherence determines the highest resolution possible on the instrument. This capability is controlled by the mechanical design of the interferometer with higher resolution requiring the moving mirror to travel a greater distance. However, moving the mirror a longer distance increases the acquisition time.

Retardation is twice the mirror travel distance and is the reciprocal of the nominal resolution setting. Thus a retardation of 1.0 cm is equivalent to a spectral resolution of 1.0 cm^{-1} , 0.5 cm equals 2.0 cm^{-1} and so on. Figure 1 shows the effect of increasing optical retardation on the resolution of a carbon dioxide spectrum. At small retardations, the rotational peaks of carbon dioxide are not observed. Increasing the mirror travel in stages

shows the improving resolution of the instrument which eventually reveals the fine spectral details. For many gas phase spectra the natural band shape is very narrow, owing to the rotational peaks, which require higher retardation and spectral resolution to be seen. For condensed phase samples, the band shapes are naturally broad and a spectral resolution of 4.0 cm^{-1} is generally adequate for most analysis.

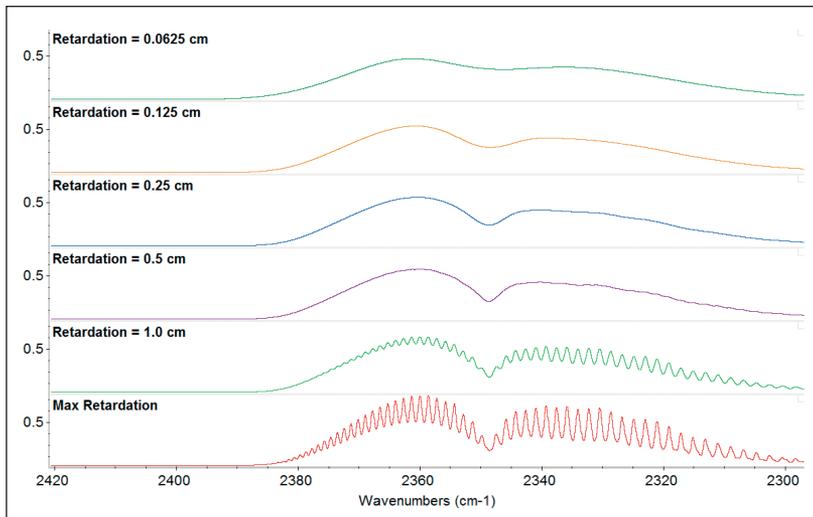


Figure 1: Affect of retardation on the resolution of peaks in carbon dioxide spectra

Retardation is the most important consideration in determining resolution, but several other parameters affect peak shapes. An excellent discussion of theoretical resolution and the effects of various parameters can be found in the first chapter of the book *Fourier Transform Infrared Spectroscopy* by Griffiths and de Haseth.²

Perhaps the least understood parameter with a significant impact on spectral resolution is beam divergence. If an infrared light source could be an infinitesimal point the beam through the interferometer could be perfectly collimated. An actual infrared source is not a point, it has dimension and emits light at many angles. To maximize sensitivity you want as many photons to impinge on the detector as possible. This is done by using an open aperture to allow as much light to travel through the instrument as is practical. However, when this is done the solid angle of the beam (the cone of light emerging from the source) limits the maximum resolution since there are a significant number of light rays traveling off the main axis. As an outcome of this a limit is reached beyond which increased mirror retardation will not improve resolution. This limit can only be overcome by using a reduced aperture to limit the solid angle of light as it travels to the detector. The trade-off between open aperture for better sensitivity and small aperture for better resolution is an important consideration in any experiment. On high-resolution instruments, such as the Nicolet iS50 FT-IR spectrometer, an automated aperture is present permitting fine balance control of the resolution and throughput.

The Nicolet iS5 FT-IR spectrometer was designed for routine educational teaching labs and QA/QC applications. For these applications most analysis is done using condensed phase samples which exhibit natural band widths not requiring control of the resolution. The fixed aperture design of the system was optimized for maximum sensitivity at 4 cm^{-1} resolution. Even so, the Nicolet iS5 FT-IR spectrometer easily achieves a resolution less than 0.8 cm^{-1} which is sufficient for many experiments commonly used in undergraduate p-chem laboratories. However, the inherent resolution of the Nicolet iS5 FT-IR spectrometer can be further improved by inserting an aperture card into the sample compartment just in front of the sample. The narrowing of spectral band widths and improvement in observed spectral resolution resulting from the use of an aperture card can be observed in Figure 2. Note the sharpening and improved separation of many peaks that are close together as well as the appearance of shoulders that are not obvious without the aperture, especially around 1701 and 1684 cm^{-1} .

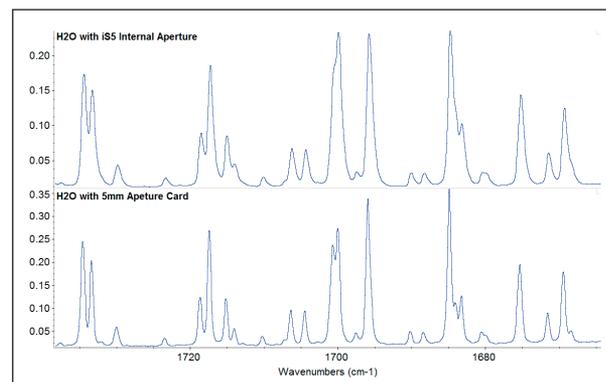


Figure 2: Improvement in line shapes by inserting a 5 mm aperture card in a Nicolet iS5 FT-IR spectrometer

As previously discussed, retardation and divergence are key physical attributes of the spectrometer related to spectral resolution. Another important aspect is digital data processing, which also directly affects the observed resolution. Theoretically, the interferogram should extend infinitely. In reality, the mirror can only travel a finite distance, which results in spectral artifacts created mathematically during the Fourier transform calculation. These artifacts, called “pods”, which typically appear as waves in the spectrum are unrelated to the molecular features of the sample. These are normally eliminated by the “apodization” function where a digital, post-collect, weighting function dampens out the wings of the recorded interferogram. This is generally a desirable effect; however, the apodization function increases the widths of the spectral lines. The best resolution is obtained with no apodization, often called Boxcar apodization because the weighting function is one (no change applied) over the entire interferogram. Figure 3 shows five spectra created from a sample of carbon monoxide using the same interferogram with different apodization functions. The unapodized (Boxcar) peak shows a sharp, symmetric single peak

with obvious “ringing” present. As stronger apodization functions are applied, the “pods” disappear and the peak clearly broadens. Using full-width at half-height to measure resolution of these spectra gives a range from less than 0.4 cm^{-1} with Boxcar apodization to about 0.6 cm^{-1} using the “heavy” Blackman-Harris apodization. The selection of apodization function depends on the information desired from the spectrum with the trade-off being between narrowest peaks (highest observed resolution) and minimum baseline noise (highest signal-to-noise).

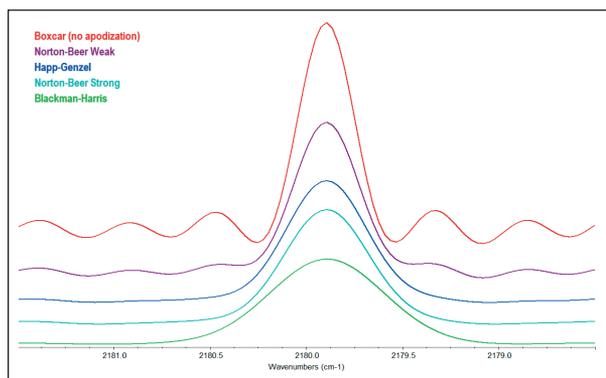


Figure 3: Bandwidth effect of apodization function on a carbon monoxide spectrum (same y-scale, but offset)

Additional digital and mechanical methods for narrowing peaks have been applied, including zero filling and deconvolution.² For the purpose of measuring resolved gas phase spectra in the educational laboratory, a basic understanding of retardation, aperturing, and apodization is sufficient.

Experimental

Studies of gas phase spectra in physical chemistry laboratories represent the largest use of high-resolution FT-IR spectroscopy in the educational teaching environment. By far, the most common experiment is the observation of vibrational-rotational fine structure of the linear hydrogen chloride molecule.³ In this experiment the infrared spectrum of hydrogen chloride gas (HCl) is collected with the main objective to determine molecular bond length. The spectrum of ^1HCl also exhibits splitting of ^{35}Cl and ^{37}Cl isotopes due to the different masses of the isotopes. Studies may also extend to a comparison of hydrogen chloride and deuterium chloride where ^1H versus ^2H (deuterium) shows the isotope effect with a much greater magnitude.

Spectra of HCl gas were collected in the Nicolet iS5 FT-IR spectrometer using a 5 cm gas cell with and without an aperture card. When used, a 6 mm aperture card was placed in the sample compartment directly adjacent to the gas cell just prior to where the incoming infrared light beam enters the cell. The maximum software resolution setting of 0.8 cm^{-1} was used in both cases.

As shown in Figure 4, the observed resolution of the spectrum with the aperture card (top) is greater than the one without the card in place (bottom). This can best be seen by viewing the expanded spectral region on the right side of the figure, which shows detail for the $2926/2924\text{ cm}^{-1}$ ^{35}Cl and ^{37}Cl isotope pair splitting. Using the full-width at half-height calculation as a measure of resolution, the 2926 cm^{-1} peak is approximately 0.4 cm^{-1} with the aperture card and 0.8 cm^{-1} without. As discussed previously, the aperture card reduces the solid angle of the infrared beam, allowing for collection of spectra that exceed the maximum resolution setting which is based solely on the retardation of the interferometer.

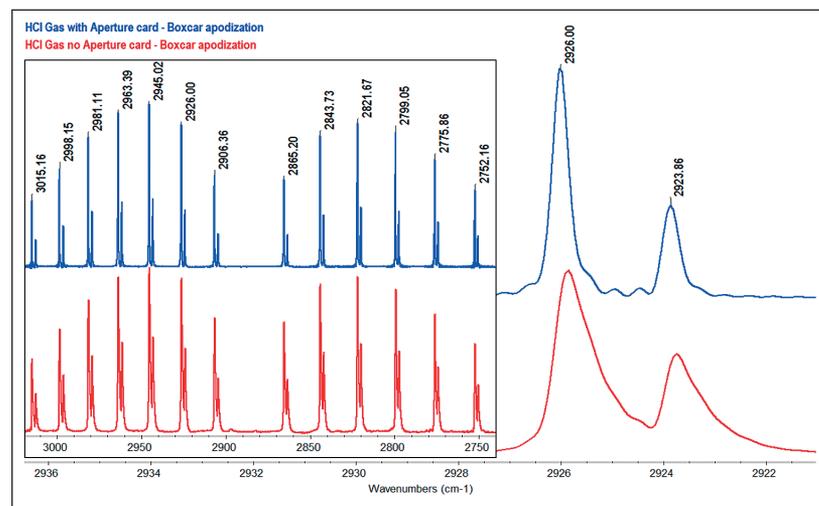


Figure 4: HCl spectra with aperture card (top) and without aperture card (bottom)

Relating this back to the HCl vibrational-rotational experiment, the labeled peaks on left side of Figure 4 (inset) represent ^{35}Cl isotope bands. These are used to calculate the P-branch and R-branch frequency separation of the rotational levels.³ The shorter peaks in each pair represent the ^{37}Cl rotations which are not needed for the bond length calculation. Whether calculating the rotational energy levels, or examining the isotope splitting effect, the inherent resolution of the Nicolet iS5 FT-IR spectrometer is sufficient and an aperture card is not required. However, as can be seen in the figure, using an aperture card does improve the observed resolution which may be of benefit by allowing students to clearly observe the isotope effect.

The HCl spectrum is quite simple, with only one axis of rotation (actually two, but they are degenerate). The ammonia molecule provides a far more complex set of peaks with multiple rotation axes exhibiting different moments of inertia. Also, owing to the NH_3 trigonal pyramid molecular structure, it has an inversion doubling vibration, causing two “Q” branches to appear.⁴ The multiple vibrational-rotational bands around the different axes result in the infrared spectrum of ammonia shown in Figure 5. The spectrum was collected in the Nicolet iS5 FT-IR spectrometer using a 5 cm gas cell with a 6 mm aperture card. As in the HCl

experiment, the ability to detect and measure the two Q-branches resulting from the inversion doubling does not require the use of an aperture card. However, in the case of the ammonia spectrum the benefit of the higher resolution obtained by using an aperture card in the Nicolet iS5 FT-IR spectrometer is more evident, since the many narrow bands seen progressing on both sides of the large 967/931 cm^{-1} doublet would otherwise be obscured and overlapped. This is a phenomenally interesting gas phase spectrum with exciting educational potential, coupling a very simple infrared measurement with a quantum mechanical description covering many aspects of molecular vibration and rotation.

Further examples of experiments that provide interesting studies of molecular vibration and rotation include:

- H_2O and D_2O , multiple sets of peaks
- CO , at slightly lower frequency than CO_2
- CH_4 , which displays P, Q and R branches

Conclusion

This tutorial has demonstrated the capabilities of the Thermo Scientific Nicolet iS5 FT-IR spectrometer for performing gas phase experiments in the educational laboratory. Understanding the mechanical, optical and digital processing parameters that impact spectral resolution can play an important role in teaching students Fourier transform theory and FT-IR spectroscopy. Optimizing the unit through the use of an aperture and correct apodization functions provides both instrumental and physical insights, increasing the value of the experiment and enhancing the learning experience.

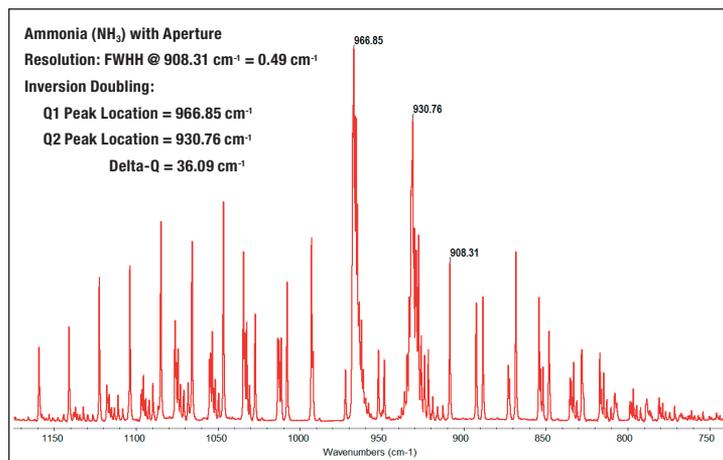


Figure 5: Ammonia spectrum exhibiting $<0.5 \text{ cm}^{-1}$ resolution on a Nicolet iS5 FT-IR spectrometer with aperture card

References

1. "Curve Fitting in Raman and IR spectroscopy: Basic Theory of Line Shapes and Applications", Thermo Fisher Scientific Application Note AN50733
2. Griffiths, P.R. and De Haseth, J.A. *Fourier Transform Infrared Spectrometry* (John Wiley & Sons, New York, 1986).
3. Garland, C.W., Nibler, J.W. and Shoemaker, D.P., *Experiments in Physical Chemistry 7th Edition*, (McGraw Hill, New York, 2003).
4. "Inversion Doubling of Ammonia", Thermo Fisher Scientific Application Note AN50753

© 2013 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries.



In the United States:

For customer service, call 1-800-766-7000
To fax an order, use 1-800-926-1166
To order online: www.fishersci.com

In Canada:

For customer service, call 1-800-234-7437
To fax an order, use 1-800-463-2996
To order online: www.fishersci.ca

Thermo
SCIENTIFIC
Part of Thermo Fisher Scientific