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Understanding FT-IR Data Processing

Part 1: Data Acquisition and Fourier Transformation

1 Introduction

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Although Infrared spectroscopy is one of the most powerful tools available to the analytical chemist and is routinely used in research and application labs and for process control, the most advanced form of IR-spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), still holds some secrets for the chemist who is trained to work with conventional grating instruments. One reason is surely that the generation of the spectral trace is not straightforwardly controlled by setting appropriate knobs controlling slit widths, scanning speed, etc. but involves a certain amount of mathematical manipulations such as Fourier transformation, phase correction, and apodization, which may introduce a barrier to understanding the FT-IR technique. Despite this difficulty, moderately and low priced FT-IR instruments are now entering even routine labs, because of their clear advantages compared to grating spectrometers. Even in lower-??ed FT-IR spectrometers, а laboratory-o« dedicated computer is the most important component apart from the optics. As the quality of its software directly determines the accuracy of the spectra, it is recommended that the user be familiar with the principles of FT-IR data collection and manipulation. Unfortunately, there still seems to be a lack of literature on FT-IR at an introductory level. Therefore, this series of articles attempts to compile the essential facts in a, hopefully, lucid way without too many mathematical and technical details and thus provide an insight into the interrelation between FT-IR hardware, the data manipulations involved, and the final spectrum.

This is the first of a series of three articles, describing the data acquisition and mathematics performed by the minicomputer Inside an FT-IR spectrometer. Special emphasis is placed on operations and artifacts relating to the Fourier transformation and on methods dealing directly with the interferogram. Part 1 covers the measurement process and the conversion of the raw data (the Interferogram) Into a spectrum.



Or. Werner Herres and Dr. Joern Groohote Bojker Analytische Messtechnik GmbH, WlkIngstr. Figure 1: A) Schematics of a Michelson Interferometer. S: source. D: detector. M1: fixed mirror. M2: movable mirror. X: mirror displacement. B) Signal measured by detector D. This Is the Interferogram. C) Interference pattern of a laser source. Its zero crossings define the positions where the Interferogram Is sampled (dashed lines).

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Series



The essential piece of optical hardware in a FT-IR spectrometer is the interferometer. The basic scheme of an idealized Michelson interferometer is shown in Figure 1.

Infrared light emitted by a source (Globar, metal wire, Nernst bar...) is directed to a device called the beam splitter, because it ideally allows half of the light to pass through while it reflects the other half.

The reflected part of the beam travels to the fixed mirror M1 through a distance L, is reflected there and hits the beam splitter again after a total path length of 2 L The same happens to the transmitted part of the beam. However, as the reflecting mirror M2 for this interferometer arm is not fixed at the same position L but can be moved very precisely back and forth around L by a distance x, the total path length of this beam is accordingly 2^* (L + x). Thus when the two halves of the beam recombine again on the beam splitter they exhibit a path length difference or optical retardation of 2 * x, /. i.e. the partial beams are spatially coherent and will interfere when they recombine.

The beam leaving the interferometer is passed through the sample compartment and is finally focused on the detector D. The quantity actually measured by the detector is thus the intensity / (x) of the combined IR beams as a function of the moving mirror displacement x, the so-called inter-ferogram (Figure 18).

The interference pattern as seen by the detector is shown in Figure 2A for the case of a single, sharp spectral line. The interferometer produces and recombines two wave trains with a relative phase difference, depending on the mirror displacement. These partial waves interfere constructively, yielding maximum detector signal, if their optical retardation is an exact multiple of the wavelength A, /. e. if

$$2 * x - n^* l(n = 0, 1, 2...).$$
 (1)

Minimum detector signal and destructive interference occur if 2 * x is an odd multiple

of A/2. The complete dependence of / (x) on x is given by a cosine function:

(2)

 $I(x) = S(\nu) * \cos(2\pi \cdot \nu \cdot x)$

where we have introduced the wavenumber $v \ll 1/A$, which is more common in FT-IR spectroscopy, and S (v) is the intensity of the monochromatic line located at wavenumber v.

Equation (2) is extremely useful for practical measurements, because it allows very precise tracking of the movable mirror. In fact, all modem FT-IR spectrometers use interference pattern of the the monochromatic light of a He-Ne laser to control the change in optical path difference. This is the reason why we included the interference pattern of the He-Ne laser in Figure 1C. This demonstrates how the IR interferogram is digitized precisely at the zero crossings of the laser interferogram. The accuracy of the sample spacing Δx between two zero crossings is solely determined by the precision of the laser wavelength itself. As the sample spacing Δv in the spectrum is inversely proportional to Δx , the error in Dv is of the same order as in Δx. Thus, FT-IR spectrometers have a builtin wavenumber calibration of high precision (practically about 0.01 cm"¹). This advantage is known as the Connes advantage.

3 Advantages of FT-IR

Besides its high wavenumber accuracy, FT-IR has other features which make it superior to conventional IR.

The so-called Jacquinot- or throughput advantage arises from the fact that the circular apertures used in FT-IR spectrometers have a larger area than the linear slits used in grating spectrometers, thus enabling higher throughput of radiation.

In conventional spectrometers the spectrum S (r) is measured directly by recording the intensity at different monochromator settings v, one v after the other. In FT-IR, all frequencies emanating from the IR source impinge simultaneously on the detector. This accounts for the so-called multiplex- or Fellget advantage.

The measuring time in FT-IR is the time needed to move mirror M2 over a distance proportional to the desired resolution. As

the mirror can be moved very fast, complete spectra can be measured in fractions of a second. This is essential, *e.g.* in the coupling of FT-IR to capillary GC, where a time resolution of 10 - 20 spectra per second at a resolution of 8 cm⁻¹ is often necessary [1].

Finally, the Fellget- and Jacquinot advantages permit construction of interferometers having much higher resolving power than dispersive instruments.

Further advantages can be found in the IR literature, e.g. in the book by Bell [2].

4 Fourier Transformation

Data acquisition yields the digitized interferogram I(x), which must be convened into a spectrum by means of a mathematical operation called Fourier transformation (FT). Generally, the FT determines the frequency components making up a continuous waveform. However, if the waveform (the interferogram) is sampled and consists of *N* discrete, equidistant points, one has to use the discrete version of the FT, /. e. discrete FT (DFT):

$$S(k \cdot \Delta \nu) = \sum l(n \Delta x) \exp (i2 \pi nk/N)$$
(3)

n = 0

where the continuous variables x, v have been replaced by $n \cdot \Delta x$ and $k - \Delta v$, respectively. The spacing Δv in the spectrum is related to Δx by

$$\Delta \nu = 1/(N \cdot \Delta x) \tag{4}$$

The DFT expresses a given function as a sum of sine and cosine functions. The resulting new function S $(k \cdot \Delta v)$ then consist of the coefficients (called the Fourier coefficients) necessary for such a development. Alternatively, if the set S $(k - \Delta v)$ of Fourier coefficients is known, one can easily reconstruct the interferogram / $(n - \Delta x)$ by combining all cosines and sines multiplied by their Fourier coefficients S $(k \cdot \Delta v)$ and dividing the whole sum by the number of points *N*. This is stated by the formula for the inverse DFT (IDFT>;

$$l(n \cdot \Delta x) = \dots$$

$$N - 1$$

$$(1/N) \sum_{n} S(k \cdot \Delta v) \exp(-i2 \pi \cdot nk/N) \quad (5)$$

$$n = 0$$



amplitude. This illustrates the need for ADC's of high dynamic range in FT-IR measurements. Typically, FT-IR spectrometers are equipped with 15- or 16-bit ADC's.

For n = 0, the exponential in (5) is equal to unity. For this case, expression (5) states, that the intensity / (0) measured at the interferogram center-burst is equal to the sum over all *N* spectral intensities divided by *N*. This means the height of the center burst is a measure of the average spectral intensity.

In practice, eq. (3) is seldom used directly because it is highly redundant. Instead a number of so-called fast Fourier transforms (FTT^ts) are in use, the most common of which is the Cooley-Tukey algorithm. The aim of these FTTs is to reduce the number of complex multiplications and sine- and cosine calculations appreciably, leading to a substantial saving of computer time. The (small) price paid for the speed is that the number of interferogram points N cannot be chosen at will, but depends on the algorithm. In the case of the Cooley-Tukey algorithm, which is used by most FT-IR manufacturers with slight modifications, N must be a power of two. For this reason and from relation (4) it follows that spectra taken with laser-controlled FT-IR spectrometers will show a sample spacing of $\Delta v = m$ laser wavenumber/2* *N.

Figure 2: Examples of spectra (on the left) and their corresponding interferograms n the right). A) One monochromatic line. B) Two monochromatic lines. C) Lorentzian line. D) Broadband spectrum of polychromatic source.

The summation (5) is best illustrated in the simple case of a spectrum with one or two monochromatic lines, as shown in Figures 2A and 2B. For a limited number of functions like the Lorentzian in Figure 2C, the corresponding FT is known analytically and can be looked up from an integral table. However, in the general case of measured data, the DFT and IDFTmusf be calculated numerically by a computer.

Although the precise shape of a spectrum cannot be determined from the interferogram without a computer, it may nevertheless be helpful to know two simple trad-Ing rules for an approximate description of the correspondence between / $(n - \Delta x)$ and S(k Δv). From Figure 2C we can, e.g., extract the general qualitative rule that a finite spectral line width (as is always present for real samples) is due to damping in the interferogram: The broader the line the stronger the damping.

Comparing the widths at half height (WHH) of / $(n - \Delta x)$ and S $(k - \Delta v)$, reveals another related rule: The WHH's of a 'hump-like' function and its FT are inversely proportional. This rule explains why in Figure 2D the Jnterferogram due to a broad band source shows a very sharp peak around the zero path difference position x - 0, while the wings of the interferogram, which contain most of the useful spectral information, have a very low

5 Final Transmittance Spectrum

To obtain a transmittance spectrum, the three steps shown in Figures 3 A, B, C are necessary (this example was taken from a GCrun):

- an interferogram measured without sample in the optical path is Fourier transformed and yields the so-called single channel reference spectrum R(v) of Fig. 3A.
- an interferogram with a sample in the optical path is measured and Fourier transformed. This yields the so-called single channel sample spectrum S(v) of Fig. 3B. S(v) looks similar to R(v) but has less intensity at those wav«numbers where the sample absorbs.

• The final transmittance spectrum T(v) is defined as the ratio $T(v) \cdot S(v) IR(v)$. This is shown in Fig. 3C. Once the transmittance spectrum has been obtained, further data processing resembles that of digitized spectra from dispersive instruments.

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: A) Single channel reference spectrum measured through an empty sample compartment. B) Single channel spectrum of absorbing sample. C) Transmittance spectrum equal to Fig. 3B divided by Fig. 3A.



Figure 4: Two closely spaced spectral lines at distance d (left) produce repeative patterns at distance 1/d In the Interferogram (right). Figure 5: A) First 2048 points of an Interferogram consisting of a total of 8196 points. Signal In the wings Is amplified 100 times. B) FT of first 512 points of inter-ferogram In Fig. 5a, corresponding to a resolution of 32 cm. C) FT of ail 8196 points of Interferogram In Fig. 5a, corresponding to a resolution of 2 cm.

6 Resolution In FT-IR

Figure 4 shows the interferogram corresponding to two sharp lines separated by a wavenumber distance *d*. Due to the separation *d* in the spectrum, the interferogram shows periodic modulation patterns repeated after a path length difference 1/rf. The closer the spectral lines are, the greater the distance between the repeated patterns. This illustrates the so-called Raleigh criterion, which states that, in order to resolve two spectral lines separated by a distance *d* one has to measure the interferogram up to a path length of at least *Md*.

For a practical measurement, which was done on a Bruker IFS-88 using a broad band MCT detector, the influence of increasing the interferogram path length on the resolution is shown in Figures 5A, B, C. The interferogram in Figure 5A represents the first 2048 points from a total of 8196. Figure 5B was obtained by transforming only the first 512 interferogram points, which corresponds to a resolution of 32 cm⁻¹. Figure 5C exhibits the full 8196 point transform. It is clearly seen that many more spectral features are resolved in the case of a longer optical path.

7 Zero Filling

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It should be noted that DFT only approximates the continuous FT, although it is a very good approximation if used with care. Blind use of eq. (3), however, can lead to three well-known spectral artifacts: the picket-fence effect, aliasing, and leakage.

The picket-fence effect becomes evident when the interferogram contains frequencies which do not coincide with the frequency sample points k * A v. If, in the worst case, a frequency component lies exactly halfway between two sample points, an erroneous signal reduction by 36 % can occur: one seems to be viewing the true spectrum through a picket-fence, thereby clipping those spectral contributions lying 'behind the pickets', *i.e.* between the sampling positions k * A v. In practice, the problem is less extreme than stated above if the spectral components are broad enough to be spread over several sampling positions.





Figure 6: Picket-fence effect in bands due to water vapor. Top: no zero filling, bands look badly clipped. Bottom: spectrum zero filled using a ZFF of 8.

The picket-fence effect can be overcome by adding zeros to the end of the interferogram before DFT is performed, thereby increasing the number of points per wave number in the spectrum. Thus, zero filling the interferogram has the effect of interpolating the spectrum, reducing the error. As a rule of thumb, one should al-> ways at least double the original interferogram size for practical measurements by zero filling it, *i.e.* one should choose a zero filling factor (ZFF) of two. In those cases, however, where the expected line width is similar to the spectral sample spacing (as *e.g.* in case of gas-phase spectra), a ZFF value of up to 8 may be appropriate.

The influence of zero filling on the appearance of water vapor bands is demonstrated in Figure 6. At the top, a spectrum with no zero filling is shown. The spectrum at the bottom is zero filled using a ZFF of 8. While the lines of the upper spectrum look badly clipped, the lines are smooth in zero filled spectrum.

It should be noted, that zero filling does" *not* introduce any errors because the in strumental line shape is not changed. It is therefore superior to polynomial interpola tion procedures working in the spectral do main.

Aliasing, leakage, apodization, and phase correction will be dealt with in the following installments.

References

- W. Herres, "Capillary GO-FTIR Analysts of Votatiles: HRGC-fTIR~ in Proceedings "Anarysis of Volatile.*", P. Schreier (editor), Walter de Gruyter &Co.. Berlin (1984).
- [2] R.J. Bell, "Introductory Fourier Transform Spectroscopy", Academic Press, New York (1972).
- [3] G.D. Bergland, IEEE Spectrum. Vol. 6. pp. 41-52(1969).