

REVIEW ARTICLE

Fourier Transform Infrared Spectroscopy

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ABSTRACT

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FT-IR CAN provide;

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

Key words: FT-IR, source of noise, super position, Michaelson Interferometer, FT-IR, SPECTROSCOPY, Interference, IR and laser interferograms.

INTRODUCTION

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. In Qualitative Analysis FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common

materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

Draw backs of conventional spectroscopy

- Low intensity of available source
- Low energy of IR photon
- Signal to noise ratio is low
- Limited slit width (light reaching the detector is small)
- Provide information of spectral element serially (one information at any one time)
- Time consuming
- A typical spectrum consist of a few sharp peaks with long stretches of noisy base line i.e. most of the measuring time wastes in recording base line

To over come

1. Multichannel spectrometer
2. Fourier Transfer method

Noise:

Signal has the information of the analyte.

Noise is the extraneous information in the information due to electronics, spurious response, and random events.

Signal to noise ratio (S/N)

Noise is generally constant and independent of the signal.

The impact of noise is greatest on the lowest

signal.

The ratio of signal to noise is useful in evaluating data.

You might want to start with first understanding what measurement Noise is.

Let's say I'm trying to measure the average volume (power) of sound produced inside a room inhabited by some specified number of teenaged girls on cell phones. I've got a mic located at some point in the room that recording the complex jumble of "how cute"s and "and she's like"s. Now, the mic (and associated instrumentation) converts the audio input into an electric signal, which ultimately can be stored as an array of numbers.

Now the circuit that converts the audio signal to a voltage is not ideal. The resistors in the circuit, for instance, do not maintain a perfectly constant resistance. Their resistance fluctuates ever so slightly, due to thermal effects. This introduces "noise" into the voltage signal. This noise turns out to be white; as it has no specific frequency dependence (this may become more clear after the next bit). The ratio of signal to noise is useful in evaluating data.

In addition to the noise from the circuitry, another source of noise may be, say noise from a nearby construction site, with a jackhammer going off at 100Hz. This type of noise is not considered white, because it happens more at certain frequencies (in this case, around 100Hz) than others, and so, can be identified and eliminated mathematically.

So, if you looked at your data as total sound power vs time, you'll see that it has fluctuations about some average value. These fluctuations will include among other things, the 100Hz input from the jackhammer. If this (jackhammer) signal is small compared to the total size of the voice, you won't easily notice it, just by looking at signal vs time. However, if you decompose your noise into "bins" of different frequencies, you'll notice that while much of it has no preferred frequency (and is hence called white), there's a clear peak at around 100Hz that tells you about the jackhammer.

Signal to Noise: Value of the signal to noise can vary – Values less than 3 make it hard to detect

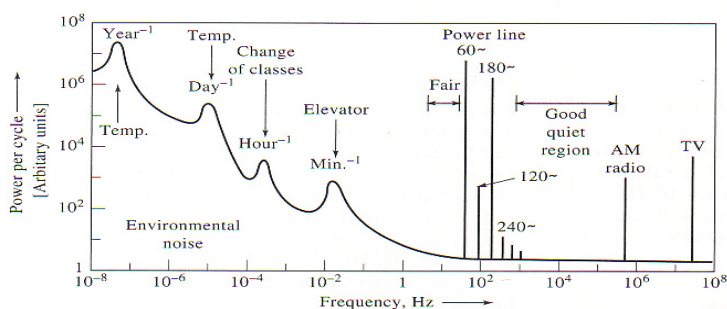


Figure 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. (From T. Coor, J. Chem. Educ., 1968, 45, A540. With permission.)

signal.

SOURCE OF NOISE:

• Chemical Noise

– Uncontrollable variables affecting chemistry of system under investigation

• Change in equilibria due to variations

-Temperature Pressure

-Sample variation

- Humidity

• Instrumental Noise:

-Thermal noise

-Shot noise

-Flicker

– Environmental noise

• Thermal noise:

Thermal agitation of electrons in electronics

• Boltzmann's equation

$$f_{eq}(r, v) = n(r) \left(\frac{2\pi k_B T_0}{m^*} \right)^{-3/2} \exp \left(-\frac{m^* |v|^2}{2k_B T_0} \right) \quad (3)$$

Instrument Noise

• Based on Boltzmann:

$$\bar{v}_{rms} = \sqrt{4kTR\Delta f}$$

- R is resistance

- k is Boltzmann's constant

• 1.38E-23J/K

- T inK

- f is frequency band width (1/3*rise time)

• Relates to response time in instrument

• Shot Noise

$$i_{rms} = \sqrt{2Ie\Delta f}$$

- Electrons crossing a junction

• pn junction, anode and cathode

• Random events

• $e=1.6e-19C$

Instrument Noise:

• Flicker Noise

➤ Inverse of signal frequency

• Important below 100 Hz

• Drift in instruments

➤ Environmental Noise

- Emanates from surroundings

• Electromagnetic radiation

Signal to Noise Enhancement:

1. Hardware and software methods:
 - Hardware is based on instrument design
 - Filters, choppers, shields, detectors, modulators
 - Software allows data manipulation
2. Grounding and Shielding:
 - Absorb electromagnetic radiation
 - Prevent transmission to the equipment
 - Protect circuit with conduction material and ground
 - Important for amplification

Hardware:**Difference and Instrumentation Amplifiers:**

- Subtraction of noise from a circuit
- Controlled by a single resistor
- Second stage subtracts noise
- Used for low level signal

Analog filtering:

- Uses a filter circuit
- Restricts frequency

Modulation:

- Changes low frequency signal to higher frequency
- Signal amplified, filter with a high pass filter, demodulation, low pass filter

Signal Chopping:

- Input signal converted to square wave by electronic or mechanical chopper
- Square wave normalizes signal.
- **Software methods:**
 - Ensemble Average
 - Average of spectra
 - Average can also be sum of collected spectra
 - Boxcar average:
 - Average of points in a Spectra

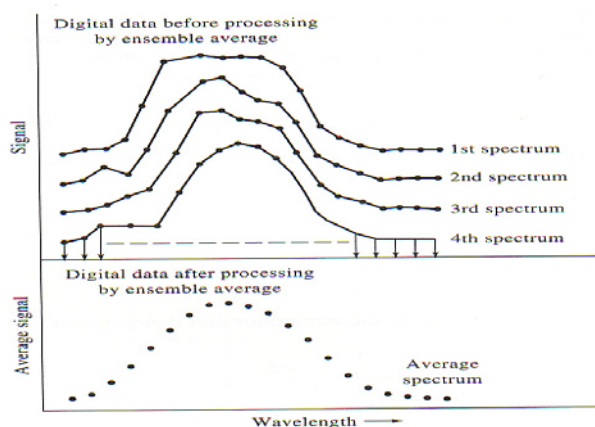


Figure 5-9 Ensemble averaging of a spectrum. (From D. Binkley and R. Dessy, *J. Chem. Educ.*, 1979, 6, 150. With permission.)

S/N RATIO:

To get more accurate result repeat the measurement many times. The signal (peak)

will accumulate as the number of spectral scans, N , but the noise at any particular point (frequency) in spectrum is random. The noise amplitude at that frequency may be treated simply as a random walk about zero (the average noise level) which is proportional to $\sim\sqrt{N}$ after N steps. Thus the true measure of precision of repeated measurement, the S/N, is proportional to $\sqrt{N}/\sqrt{N} = 1$.

Digital Filtering:

- Numerical methods
 - Fourier transform
 - Time collected data converted to frequency
 - NMR, IR
 - Least squares smoothing
 - Similar to boxcar
- Uses polynomial for fit
- Correlation
- Electromagnetic Radiation:
 - Interaction with matter
 - Quantum mechanical properties
 - Electromagnetic radiation
 - orthogonal in phase oscillations

SINE WAVES ($y = \sin x$) are ubiquitous. They represent the behavior of a simple oscillator. This animation illustrates the relationship between a circle (the wheel in this movie) and the phase (stage) of the sine wave. As the wheel rotates the attached horizontal pointer traces out a sine wave on the purplish screen. The maximum amplitude of the wave is the same as the diameter of the circle (wheel in this case). The height of the wave at any point depends on the sine of the angle that the radius of the circle (yellow line) makes with a horizontal plane (not shown). The labeled diagram explains the relationship between the angle, the sine and the resulting sine wave.

COSINE WAVES:-COSINE WAVES ($y = \cos x$) are identical to sine waves but are shifted by $1/2 \pi$ with respect to the sine wave. In this animation the cosine wave (yellowish green undulation) is shown traced out on the lower greenish screen by the vertical pointer. The height (value) of the cosine wave at any point depends on the cosine of the yellow radial arm. At the beginning of the animation notice how the sine wave has a value of zero and the cosine wave a value of one (we assume the diameter of the wheel is one). The two arms projecting from the wheel are at

right angles to each other (i.e. 90° or $1/2 \pi$) apart and this helps you to visualize the phase difference of $1/2 \pi$ between the sine and cosine curves. RADIANS are a fundamental way of describing angles. We are used to angles like 90° for a right angle but radians use the arc of a circle to describe a degree of rotation. The length of this arc is measured in terms of the radius of the circle. The circumference of a circle is equal to the radius multiplied by two (gives the diameter) multiplied by a constant called pi (π) which has a value of about 3.141. Consequently a complete circle contains 2π radians. This helps to explain why a graph of a sine wave is measured in fragments of π .

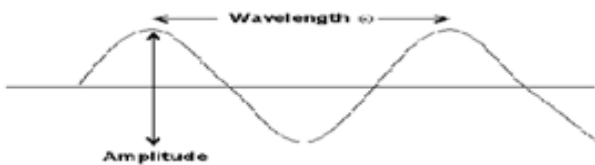
Wave Parameters:

The amplitude A of sinusoidal wave is shown as the length of electrical vector at a maximum in the wave. With time as variable, the wave can be described by the equation for a sine wave:

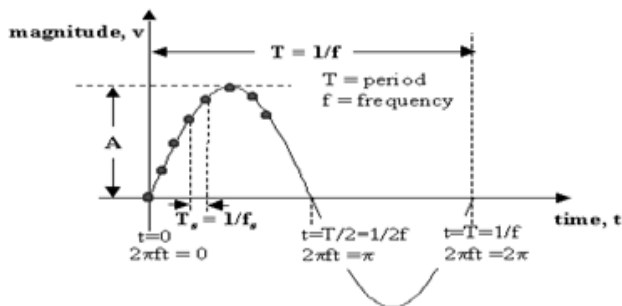
$$y = A \sin (\omega t + \phi)$$

Where y is electric field, A is the amplitude or maximum value for y, t is time and ϕ is the phase angle. The angular velocity of the vector ω is related to the frequency of the radiation ν by the equation:

$$\omega = 2\pi\nu \text{ Therefore, } y = A \sin (2\pi\nu t + \phi)$$



Amplitude and wavelength



The sine wave shown here can be described mathematically as:

$$v = A \sin 2\pi ft$$

Where A is the Amplitude (varying units), f is the frequency (Hertz) and t is the time (seconds). T is known as the time period (seconds) and $T = 1/f$. Based on the equation, When $t=0; v = A \sin 2\pi f(0) = 0$. When $t=T/4; v = A \sin 2\pi f(T/4) = A \sin 2\pi f(1/4f) = A \sin(\pi/2) = A$; when $t=T/2; v = A \sin 2\pi f(T/2) = A \sin 2\pi f(1/2f) = A \sin(\pi) = 0$; and so on.

The animation shows two sinusoidal waves travelling in the same direction. The phase

difference (called as phase angle) between the two waves increases with time so that the effects of both constructive and destructive interference may be seen. First of all, notice that the sum wave (in blue) is a travelling wave which moves from left to right. When the two gray waves are in phase the result is large amplitude. When the two gray waves become out of phase the sum wave is zero. $(\phi_1 - \phi_2)$ is 0, 360° or an integer multiple of 360° deg. maximum amplitude occur (constructive interference). A maximum destructive interference

Occurs when $(\phi_1 - \phi_2)$ is equal to 180° or $180^\circ + n$ integer multiple of 360° deg.

Superposition:

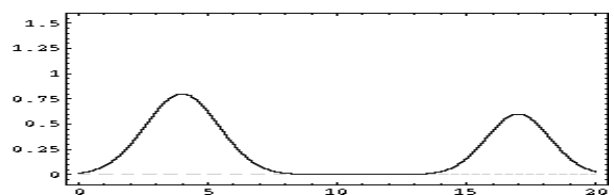
The principle of superposition states that when two or more waves traverse the same space, a disturbance occurs that is sum of the disturbances caused by the individual waves. When n electromagnetic waves differing in frequency, amplitude and phase angle pass same point in space simultaneously, then

$$y = A_1 \sin (2\pi\nu_1 t + \phi_1) + A_2 \sin (2\pi\nu_2 t + \phi_2) + \dots + A_n \sin (2\pi\nu_n t + \phi_n)$$

An important aspect of superposition is that a complex waveform can be broken down into simple component by mathematical operation called Fourier transformation.

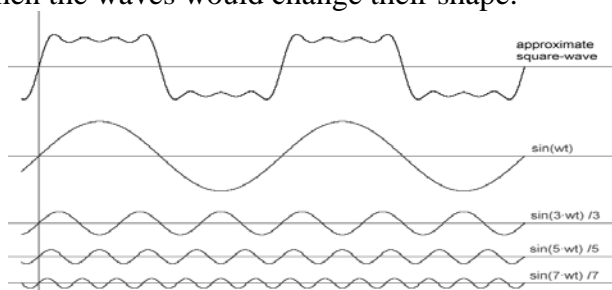
If two sinusoidal waves having the same frequency (wavelength) and the same amplitude are travelling in opposite directions in the same medium then, using superposition, the net displacement of the medium is the sum of the two waves. As the movie shows, when the two waves are 180° out-of-phase with each other they cancel, and when they are in-phase with each other they add together.

Two waves with slightly different frequencies and the same amplitude are travelling to the right. The resulting wave travels in the same direction and with the same speed as the two component waves. The "beat" wave oscillates with the average frequency, and its amplitude envelope varies according to the difference frequency.



The movie at ABOVE shows two Gaussian wave pulses are travelling on a string, one is moving to

the right, the other is moving to the left. They pass through each other without being disturbed, and the net displacement is the sum of the two individual displacements. It should also be mentioned that this string is non-dispersive (all frequencies travel at the same speed) since the Gaussian wave pulses do not change their shape as they propagate. If the medium was dispersive, then the waves would change their shape.



Square-wave synthesized using Fourier cosine coefficients

$a_n = 0$, and sine coefficients $b_n = \{ (1/n), n \text{ odd}; 0, n \text{ even} \}$

Square wave can be described by equation

$$y = A (\sin 2Svt + 1/3 \sin 6Svt + 1/5 \sin 10Svt + 1/n \sin 2nSvt)$$

Where n takes the value of 3, 5, 7, 9, 11 and so forth.

Michaelson Interferometer:

- 10^{14} Hz is too fast for the rapid changes in Power to be directly measured as a function of time.
- Cannot measure the FID signal directly
- Interferometer creates a replicate interference pattern at a frequency that is a factor of 10^{10} times slower
- 10^4 - 10^5 Hz can be measured electronically
- $f = (2v_m/c)n = 10^{-10}n$, $v_m = 1.5$ cm/s

Fourier Transform Infrared (FTIR):

- Spectrometer measures all the IR wavelengths simultaneously and produces a full spectrum.
- Any number of components (up to 50) can be analysed from single measurement and interferences are automatically resolved
- Same optical elements used for each measurement, multiple calibration checks are not necessary.

In Fourier transform infra-red spectroscopy, the source is modulated with a Michelson interferometer. This results in a signal at the detector which has a distribution of frequencies determined by the speed of the moving mirror of the interferometer. The resulting interferogram in the amplitude time

domain is then transformed via the Fourier algorithm into the appropriate amplitude-wavelength (frequency) domain, resulting in a characteristic infra-red spectrum for a particular.

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FTIR spectroscopy:

Based on the use of an optical modulator:
interferometer

Interferometer modulates radiation emitted by an IR-source, producing an interferogram that has all infrared frequencies encoded into it. Interferometer performs an optical Fourier Transform on the IR Radiation emitted by the IR source. The whole infrared spectrum is measured at high speed. Spectral range is continuously calibrated with HeNe laser. Fast, extremely accurate measurements.

Michelson interferometer:

Simplest interferometer design

- Beam splitter for dividing the incoming IR beam into two parts
- Two plane mirrors for reflecting the two beams back to the beam splitter where they interfere either constructively or destructively depending on the position of the moving mirror
- Position of moving mirror is expressed as Optical Path Difference (OPD).

Mirror movement and interference of single wavelength beam:

- When moving mirror is in the original position, the two paths are identical and interference is constructive.
- When the moving mirror moves $1/4$ of wavelength, the path difference is $1/2$ wavelength and interference is destructive.
- Mirror moves back and forth at constant velocity – the intensity of the interference signal varies as a sine wave.

Fourier transformation

- The interferogram signal is recorded as a function of optical path Difference.
- The interferogram is comparable to a time domain signal (e.g. A recorded sound) and the spectrum represents the same information in frequency domain (e.g. the frequency of the same sound).
- Fourier transformation is the mathematical relation between the interferogram and the spectrum (in general, between time domain Signal and frequency signal).
- A pure cosine wave in the interferogram transforms to a perfectly sharp narrow spike in the spectrum.

IR and laser interferograms

- IR interferogram is recorded after the IR beam passes through the interferometer and sample cell.
- IR interferogram contains the absorption of sample.
- Laser interferogram is produced by a helium-neon laser beam travelling through the interferometer into a special detector.
- Laser interferogram is a nearly ideal cosine wave A.
- Laser interferogram tells the position of moving mirror with excellent accuracy.

Recording an interferogram:

- Laser interferogram signal is used to digitize the IR interferogram.
- Single mode HeNe- laser provides a constant wavelength output at 632.8 nm.
- Accurate and precise digitization interval provides high wavelength accuracy in the spectrum. The data points for IR interferogram are recorded every time the mirror has moved forward by one HeNe laser wavelength.
- The digitized IR interferogram (an XY table) is transmitted to computer where the Fast Fourier Transform (FFT) algorithm computes the spectrum

X (nm)	Y (Volt)
-2531.2	4.2
-1898.4	2.1
-1265.6	-1.2
-632.8	3.6
0	7.2
632.8	3.6
1265.6	-1.2
1898.4	2.1
2531.2	4.2

Background and absorbance spectra:

Absorbance spectrum is calculated from the background and a single beam sample spectrum:

$$A = -1 \cdot \log_{10} \frac{\text{sample}}{\text{background}}$$

The absorbance peak height depends also on the concentration c of the sample, absorptivity ϵ (this is a physical constant specific to each gas and wavelength) and cell length l :

$$A = \epsilon(\tilde{\nu}) \cdot c \cdot l$$

Zero absorbance means that the amount of light arriving at the detector is the same in both sample and background. This is why the background measurement is often called a zero calibration. High absorbance means less light arriving at the detector (-1 in the formula). If the baseline (region of spectrum without peaks) is above zero, transmission of light is less than in the background.

FT-IR Advantages and Disadvantages:

1. Better sensitivity and brightness
 - Allows simultaneous measurement over the entire wave number range
 - Requires no slit device, making good use of the available beam
2. High wave number accuracy
 - Technique allows high speed sampling with the aid of laser light interference fringes
 - Requires no wave number correction
 - Provides wave number to an accuracy of 0.01 cm⁻¹
3. Resolution
 - Provides spectra of high resolution
4. Stray light
 - Fourier Transform allows only interference signals to contribute to spectrum. Background light affects greatly lowers.
 - Allows selective handling of signals limiting interference
5. Wave number range flexibility
 - Simple to alter the instrument wave number range

Disadvantage: CO₂ and H₂O sensitive

Advantages of FTIR spectroscopy:

- Speed (Fellgett advantage): All the frequencies are recorded simultaneously; a complete spectrum is measured in less than a second.
- Sensitivity (Jacquinot or Throughput advantage): In the interferometer, the radiation power transmitted on to the detector is very high which results

in high sensitivity.

- Internally Calibrated (Connes advantage): FTIR spectrometers employ a HeNe laser as an internal wavelength alibration standard, no need to be calibrated by the user.
 - Multicomponent capability: Since the whole infrared spectrum is measured continuously, all infrared active components can be identified and their concentrations determined.
- FT-IR Advantages:

reflectance or FT-IR microscopes

- High resolution experiments (as high as 0.001 cm^{-1} resolution)
- Trace analysis of raw materials or finished products
- Depth profiling and microscopic mapping of samples
- Kinetics reactions on the microsecond time-scale
- Analysis of chromatographic and thermogravimetric
- sample fractions

Fellgett's (multiplex) Advantage:

- FT-IR collects all resolution elements with a complete scan of the interferometer. Successive scans of the FT-IR instrument are co added and averaged to enhance the signal-to-noise of the spectrum.
- Theoretically, an infinitely long scan would average out all the noise in the baseline.
- The dispersive instrument collects data one wavelength at a time and collects only a single spectrum. There is no good method for increasing the signal-to-noise of the dispersive spectrum.

FT-IR Advantages (Connes Advantage):

- An FT-IR uses a HeNe laser as an internal wavelength standard. The infrared wavelengths are calculated using the laser wavelength, itself a very precise and repeatable 'standard'.
- Wavelength assignment for the FT-IR spectrum is very repeatable and reproducible and data can be compared to digital libraries for identification purposes.

FT-IR Advantages:

- Jacqui not Advantage FT-IR uses a combination of circular apertures and interferometer travel to define resolution. To improve signal-to-noise, one simply collects more scans.
- More energy is available for the normal infrared scan and various accessories can be used to solve various sample handling problems.
- The dispersive instrument uses a rectangular slit to control resolution and cannot increase the signal-to noise for high resolution scans. Accessory use is limited for a dispersive instrument.

FT-IR Application Advantages:

- Opaque or cloudy samples
- Energy limiting accessories such as diffuse

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