Fourier Transform Infrared Spectroscopy: A Practical Application of the Fourier Transform

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The fourier transform is an operation that transforms one function of a real variable into a different variable. A common application of fourier transforms in the sciences is the use of Fourier Transform Infrared Spectroscopy (FTIR). In this technique, a Michelson interferometer is used to expose a chemical compound to a wide range of light and determine its composition based on its vibrational selection rules. A detector produces an interferogram of time verses intensity and a fourier transform is used to deconvolute the linearly superimposed frequencies into a graph of frequency verses intensity.

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I. INTRODUCTION

When collecting data in a scientific experiment, a signal represents a certain piece of information. Collected signals can be easily manipulated by representing data as linear combinations of simple and well defined functions. Fourier analysis represents signals in terms of sinusoidal waves. By using sinusoidal waves, it is simpler to manipulate large sets of signals, as in data collection, for practical applications. Signals mostly occur in the time-domain representation and often the signal amplitude, *x(t)*, is given as a function of time, *t*. If the signal is constantly defined at all times, with some constant interval between instants of time, the signal is considered a discreet signal. Fourier transforms are able to deconvolute overlapping signals and determine the frequencies present.[1]

The Fourier transform changes a function, *f(t)*, from a function with respect to time to a function that is given as a function of frequency, which is generically defined as $g(\omega)$. The exponential form of the transform is the most common type of Fourier transform.[2]

$$g(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \exp(i\omega t) dt \tag{1}$$

It is possible to use this relation to determine the inverse relationship.

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(\omega) \exp(-i\omega t) d\omega \tag{2}$$

These equations both have physical significance. We can also move these relations to three dimensional space.[2]

$$g(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int f(\mathbf{r}) \exp(i \cdot \mathbf{k} \cdot \mathbf{r}) d^3 r \tag{3}$$

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3/2} \int g(\mathbf{k}) \exp(-i \cdot \mathbf{k} \cdot \mathbf{r}) d^3 r \tag{4}$$

If the function *f(t)* is odd or even, it is possible to sine and cosine functions rather than an exponential. For an even function such that *f(t)=f(-t)*, one can write the exponential of equation (1) in its trigonometric form.[2]

$$g(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t)(cos\omega t + isin\omega t) dt \tag{5}$$

$$g(\omega) = \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} f(t) cos\omega t dt \tag{6}$$

The inverse Fourier transform can also be written using the cosine function.

$$f(t) = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} g(\omega) cos\omega t d\omega \tag{7}$$

If the original exponential function is odd, *f(t)=-f(-t)*, then the sine function can be used to describe the original exponential function as well as the inverse Fourier relationship.[2]

$$g(\omega) = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(t) sin\omega t dt \tag{8}$$

$$f(t) = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} g(\omega\omega) sin\omega t d\omega \tag{9}$$

Note that for both the Fourier cosine transform and the Fourier sine transform that only positive zeros of the arguments.

An important first step in developing the theory for Fourier Transform Infrared Spectroscopy is the ability to use Fourier transforms to resolve a finite pulse into sinusoidal waves. The transformation of a sine wave into its frequency component is shown pictorally in Figure one. The waves are given by sinω_o t.[3]

$$f(t) = sin\omega_o t \tag{10}$$

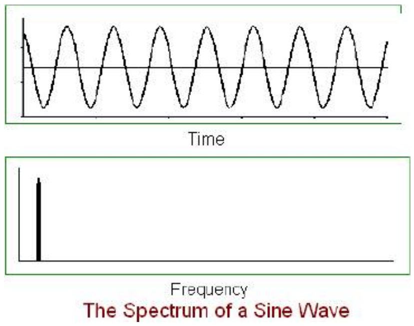

FIG. 1: A finite sine wave and its resulting Fourier transform, illustrated as a function of frequency.

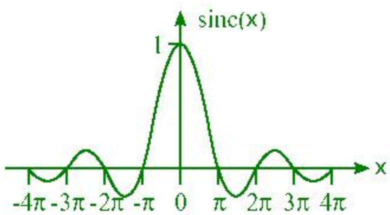

FIG. 2: Fourier transform about a central point.

Where t < $\frac{N\pi}{\omega_o}$.

This corresponds to N cycles of our original wave train. Because *f(t)* is odd, it is possible to use the Fourier sine transform.[3]

$$g(\omega) = \sqrt{\frac{2}{\pi}} \int_0^{N\pi/\omega_o} sin\omega_o t sin\omega t dt \tag{11}$$

Integrating equation (11) gives the amplitude of the original sine wave. The Fourier transform of this function shows a high amplitude at $\omega{=}\omega_o$. The amplitude of this central peak depends on the value of N and is shown in Figure two.

A common and very useful application of Fourier Transforms in chemistry is the use of Fourier Transform Infrared Spectrometry (FTIR). This technique is used to analyze the group frequencies of various chemical compounds based on their vibrational selection rules. Vibrational transitions are well defined and when exposed to light of a corresponding frequency, a vibrational level transition occurs and can be observed in a spectrum. This can either be done by exposing the molecule to one frequency at a time by using a diffraction grating or grating spectrometer, or the molecule can be exposed to a wide range of frequencies at one pass, such as with a Michelson interferometer, and the absorption frequencies can be deconvoluted later using Fourier techniques. The latter is preferred technique since a larger range of frequencies may be scanned in a single sweep rather than scanning through frequencies individually. In FTIR, data is collected as amplitude verse time and Fourier transforms are used to transform the data to an amplitude verse frequency spectrum. In other words, spectral information is encoded such that the intensity distribution at all frequencies is measured simultaneously by a single detector, producing an interferogram. The Fourier transform describes the resolution of a time-varying wave into its constituent frequencies. This process is known as the Fourier decomposition of waves. We can "pick out" the frequencies hidden in the superimposed time spectra.[4] Figure three shows the addition of two sine waves and the ability of a Fourier transform to determine each individual frequency.

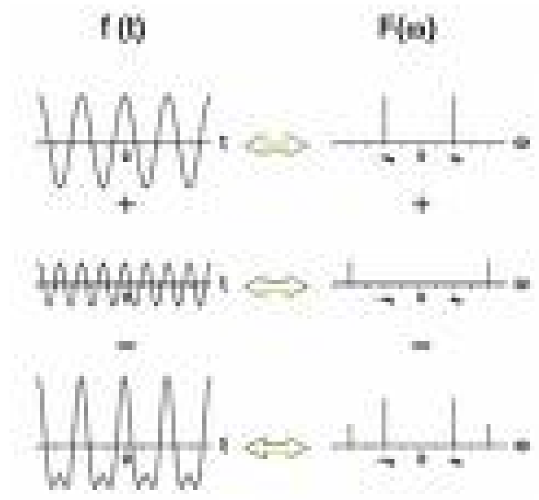

FIG. 3: A Fourier transform is able to determine the frequencies present in a constructive interfering sine wave. The bottom wave is the addition of the first two waves and its resulting Fourier transform shows both frequencies.

II. APPLICATIONS

In FTIR, a broadband light source is exposed to a chemical compound. Therefore, the signal at the detector is a linear combination of excitation at different wavelengths of light. Because these are independent of one other the principle of superposition, where the presence of one excitation does not affect the response of a system to another excitation, holds for FTIR.[4]

$$f(t) + g(t) \to F(t) + G(t) \tag{12}$$

Where *f(t)* and *g(t)* are the original time functions and *F(t)* and *G(t)* are the independent outputs of the Fourier transform. The linear systems present in Fourier transform infrared spectroscopy are not only linear, but homogeneous in that the excitation can be scaled linearly and the corresponding Fourier response will also scale linearly.[4]

$$Cf(t) \to CF(t) \tag{13}$$

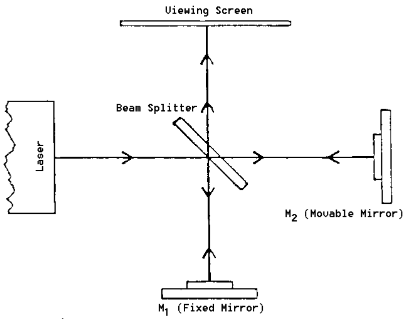

FIG. 4: A typical Michelson interferometer.

The first step in Fourier transform infrared spectrometry is to pass light from a light source through a Michelson interferometer, as shown in Figure four. The light is split at a beam splitter and takes two different paths. One light path goes towards a fixed mirror, bounces back to the beam splitter and on towards the sample or towards a detector, while the second path moves towards a movable mirror. When the mirrors are both the same distance from the beam splitter , there is constructive interference. There is also constructive when the two light paths differ by an integer of the light wavelength. If the path lengths are not whole integer wavelengths apart, then destructive interference occurs.

The total Fourier transform gives a way to sum over many frequencies, resulting in a total observed interference given by *I(t)*. The cosine Fourier transform is used because the resulting interferogram is an even function.

$$I(t) = \int_0^{\infty} B(\omega) cos(2\pi\omega t) d\omega \tag{14}$$

where each frequency ω has a spectral intensity B(ω) at position t. Because *I(t)* is a continuous function, it can be decomposed into the sum of even and odd functions, represented by *e(t)* and*o(t)*.[4]

$$I(t) = \frac{I(t) + I(-t)}{2} + \frac{I(t) - I(-t)}{2} = e(t) + o(t) \tag{15}$$

It is possible to relate the even and odd functions by the fact that *e(x)* is an even function defined by *I(t)=I(-t)* and *o(t)* is defined as *I(t)=-I(-t)*. We can then construct even and odd functions as a combinations of sines and cosines.[4]

$$e(t) = \int_{-\infty}^{\infty} B_e(\omega) \cos(2\pi\omega x) d\omega \tag{16}$$

$$o(t) = \int_{-\infty}^{\infty} B_o(\omega) \sin(2\pi\omega t) d\omega \tag{17}$$

But, by definition, odd integrals disappear when integrated over all space so we are left with a function of our observed intensity to be:

$$I(t) = \int_{-\infty}^{\infty} B(\omega) \exp(i2\pi\omega t) d\omega \tag{18}$$

It is possible to manipulate equation (19) to give an equation for the frequency distribution, *B(ω)*, for an observed interferogram, *I(t)*. Multiplying each side of equation (19) by [cos($2\pi\omega$ t)-isin($2\pi\omega$ t)] and integrating over t we obtain:

$$\int_{-\infty}^{\infty} I(t)[\cos(2\pi\omega t) - i\sin(2\pi\omega t)]dt =$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} B(\omega)[\cos(2\pi\omega t)+i\sin(2\pi\omega t)][\cos(2\pi\omega t)-i\sin(2\pi\omega t)]d\omega \tag{19}$$

This can be simplified as:

$$B(\omega) = \int_{-\infty}^{\infty} I(t) \exp(-i2\pi\omega t) dt \tag{20}$$

In reality, the interferogram is not a symmetric function due to instrumental limitations, and therefore, the resulting spectrum is also not symmetric. A practical interferometer has a finite optical path difference and the optics have a finite size and reflectivity.[4]

III. CONCLUSION

Fourier transforms provide a pathway to transform a function in one set of variables to a function in another set of variables. One popular application of Fourier transforms in science is the use of Fourier Transform Infrared Spectroscopy (FTIR). By using a large range of infrared frequencies at once to excite a chemical compound, it is possible to deconstruct the interferogram into its component frequencies. This allows for identification of vibrational energy levels of the molecule, and therefore the ability to determine the functional groups of the molecule and the ultimate chemical structure.

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