

# A Comparison of FTNMR and FTIR Techniques

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Nuclear magnetic resonance (NMR) and infrared (IR) are two spectroscopic methods that commonly use the Fourier transform (FT) technique (1, 2). Spectroscopy is a study of the interaction of an electromagnetic (EM) wave with a sample. Traditionally, a description of spectroscopy emphasized quantum mechanical molecular energy levels of the sample. Noting that a spectrum is a record of intensities of the EM wave resulting from the interaction, we present here a spectroscopic description based on the examination of the EM wave. This approach provides a basis for discussing similarities and differences of FTNMR and FTIR.

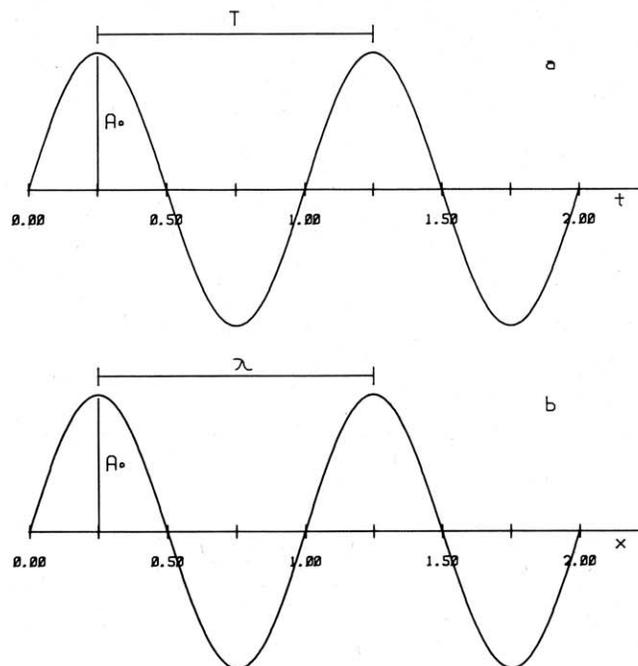
FT spectroscopy was first developed in NMR. In an FTNMR the spectral intensities are detected by using a pulsed NMR spectrometer operating at a resonance frequency (3). Although the pulsed NMR technique is as old as the NMR itself (4, 5), even the largest of first generation computers have been inadequate to carry out the numerical integration in FT to be of practical use until the development of Cooley-Tukey algorithm in 1965 (6). This algorithm has revolutionized the computational process to the extent that it is now possible for even a small personal computer to do FT in a matter of few minutes. Since then there has been explosive development in FTNMR and FTIR use. Moreover, the FT technique is increasingly used in ion cyclotron resonance, and electron spectroscopy for chemical analysis (1, 2, 7). For an FTNMR spectrometer with a superconducting magnet, the advantages outweigh the relatively high cost to the point that it is becoming increasingly difficult to find a commercial manufacturer of a conventional continuous wave (CW) NMR spectrometer. Instrumental descriptions have been published in *this Journal* for the FTNMR (8) as well as the pulsed NMR (9) and FTIR (10) spectrometers. Mathematical properties of FT integrals have been recently published also (11). These previous papers adequately discuss the advantages of using the FT technique. In this paper we re-examine both FTNMR and FTIR from the fundamental spectroscopic point of view. First we discuss the four variables involved in spectroscopy and then point out the similarities and differences of FTNMR and FTIR.

## Electromagnetic Wave

Spectroscopy is a study of the interaction of an EM wave with a sample. A detector records intensities of the EM wave resulting from the interaction. For this reason we first examine the properties of an EM wave. An EM wave consists of mutually perpendicular, sinusoidally oscillating magnetic and electric fields. Either of the fields of a plane polarized EM wave may be represented by,

$$A = A_0 \sin(2\pi\nu t + 2\pi\bar{\nu}x) \quad (1)$$

where  $A_0$  is the amplitude,  $\nu$  is the frequency in units of hertz,  $t$  is time in seconds,  $\bar{\nu}$  is the wavenumber, and  $x$  is the position. Note that the position dependence is as important as the time dependence in an EM wave. In order to emphasize this point we plot the field intensity as a function of time at  $x = 0$ , and as a function of position at  $t = 0$ , in Figure 1a and 1b, respectively. The time plot defines the period,  $T$ , which is the inverse of the frequency ( $\nu = 1/T$ ); while the position plot defines the wavelength,  $\lambda$ , which is the inverse



Both mutually perpendicular electric and magnetic fields of a plane polarized electromagnetic wave propagating in the  $x$  direction may be represented by  $A = A_0 \sin(2\pi\nu t + 2\pi\bar{\nu}x)$ , where  $A_0$  is the amplitude. This sinusoidal wave is plotted as; (a) a function of time,  $t$ , at  $x = 0$ ; and (b) a function of position,  $x$ , at  $t = 0$ . The frequency,  $\nu$ , is the inverse of the period,  $T$ , while the wavenumber,  $\bar{\nu}$ , is the inverse of the wavelength,  $\lambda$ . Each pair of variables,  $\nu$  and  $t$ , or  $\bar{\nu}$  and  $x$ , form the conjugate pair.

of the wavenumber ( $\bar{\nu} = 1/\lambda$ ). The complementary nature of each of these pairs of variables is obvious. The pair of variables,  $\nu$  and  $t$ , are examples of conjugate variables. The variables,  $\bar{\nu}$  and  $x$ , also form a conjugate pair (12). (See figure.)

## Heisenberg Uncertainty Principle

Conjugate variables do not commute in the quantum mechanical sense; hence, they are governed by the Heisenberg uncertainty principle (UP) (13). For example, the most common form of UP is

$$\Delta p \times \Delta x = h/2\pi$$

where  $\Delta x$  is the uncertainty in position,  $\Delta p$  is the uncertainty in momentum, and  $h$  is the Planck's constant. We have written this with the equal sign to signify the minimum value of the product. The momentum of an EM wave is related to the wavenumber as  $p = h/\lambda = h\bar{\nu}$ . Therefore the UP may be rewritten as

$$\Delta\bar{\nu} \times \Delta x = 1/2\pi \quad (2)$$

We later show that this form of UP has interesting spectro-

scopic consequences. The corresponding form of UP for the other conjugate variable pair,  $\nu$  and  $t$ , is

$$\Delta\nu \times \Delta t = 1/2\pi \quad (3)$$

This equation is derivable from the more familiar form of UP in energy and time with  $h\nu$  being the energy quanta of the EM wave.

### Spectroscopic Domains

We have seen that a spectrometer measures the intensity of an EM wave resulting from the interaction of an incident wave with a sample. A brief look at eq 1 should convince the reader that a spectrum can be recorded in any domain defined by one of the four variables that appear in the EM wave expression. Historically, spectroscopy was developed by recording the intensity in the energy space as a function of frequency or in the momentum space as a function of wavenumber (or wavelength). For convenience, we denote a frequency spectrum by  $F(\nu)$ , and the wavenumber spectrum by  $G(\bar{\nu})$ .

Note that as far as the EM wave is concerned, the conjugate variables,  $\nu$  and  $t$ , are totally equivalent. This suggests that the information contained in  $F(\nu)$  should be equally obtainable by measuring the intensity,  $f(t)$ , in the time domain by specifying  $t$  as the variable. Similarly one may record the spectral intensity,  $g(x)$ , as a function of the position,  $x$ , instead of  $G(\bar{\nu})$ . The two variables,  $\nu$  and  $\bar{\nu}$ , are related through the speed of light,  $c$ , as  $\nu = c\bar{\nu}$ . When  $F(\nu)$  is measured, we are interested in the EM wave as a function of  $\nu$  and  $t$  only. For this reason the eq 1 is integrated over the sample volume with  $x$  as a variable, and we obtain the more familiar expression of the EM wave,

$$A(t) = A_0 \sin 2\pi\nu t$$

Similarly when the measurement is  $G(\bar{\nu})$ , the corresponding EM wave expression is

$$A(x) = A_0 \sin 2\pi\bar{\nu}x$$

This equation represents the EM wave as a function of  $\bar{\nu}$  and  $x$  at a given time,  $t = 0$ .

The choice of the spectral function to be detected first in a given spectrometer depends on the design of the particular instrument. Detection in the time domain requires an accurate clocking mechanism while the detection of  $g(x)$  requires an accurate determination of distance. In the following sections we discuss FTNMR and FTIR techniques separately to see which choice is applicable.

### FTNMR: Time (t) Domain Experiment

In contrast to a CWNMR which records  $F(\nu)$  in the frequency domain, an FTNMR spectrometer records  $f(t)$ , or free induction decay (FID), in the time domain (15). An NMR intensity is proportional to the magnitude of a transverse component,  $M_y$ , of the magnetization. Here transverse denotes the direction perpendicular to the static applied magnetic field,  $H_0$ . Since the equilibrium is established when the magnetization is lined up along  $H_0$ , the NMR intensity is zero at equilibrium. The initial non-zero transverse component,  $M_y(0)$ , is prepared by a radio frequency (RF) pulse operating at the resonance frequency and designed to rotate the equilibrium magnetization by  $90^\circ$  into the transverse plane. The FID corresponds to  $M_y$  recorded as a function of time while it relaxes back to the equilibrium value of zero. If a pulse of  $10 \mu\text{s}$  duration is used, this gives  $\Delta t = 10 \mu\text{s}$ , and the UP in eq 3 tells us that the sweep width is of the order of  $\Delta\nu = 16 \text{ kHz}$ , which is wide enough to cover most chemical shifts. Since we are not familiar with  $f(t)$ , it is necessary to convert FID into a more recognizable form of  $F(\nu)$ .

The two spectral functions,  $F(\nu)$  and  $f(t)$  are mathematically related by the FT integrals as

$$F(\nu) = \int_{-\infty}^{\infty} f(t)e^{-i2\pi\nu t} dt \quad (4)$$

and the inverse transform,

$$f(t) = \int_{-\infty}^{\infty} F(\nu)e^{i2\pi\nu t} d\nu \quad (5)$$

As mentioned before the integral in eq 4 is carried out numerically by a computer using the Cooley-Tukey algorithm. The most common NMR line shape for a nonviscous liquid sample is Lorentzian centered at  $\nu_0$  (16),

$$F(\nu) = F(0) \frac{1}{1 + 4\pi^2 T_2^2 (\nu - \nu_0)^2} \quad (6)$$

where  $T_2$  is the transverse spin relaxation time. The Lorentzian half-width-at-half-height,  $\Delta\nu_{1/2}$ , is  $1/(2\pi T_2)$ . This is consistent with the UP, eq 3, in which the uncertainty in frequency,  $\Delta\nu$ , is identified with the line width and the uncertainty in  $t$  with  $T_2$ , which is related to the lifetime of spins to remain in a given spin state.

The corresponding FID is exponential with the decay constant,  $T_2$ ;

$$f(t) = f(0) \exp(-|t|/T_2) \quad (7)$$

where  $|t|$  stands for an absolute value of time. When an NMR line has  $\Delta\nu_{1/2} = 10 \text{ Hz}$ , the above discussion yields  $T_2 = 16 \text{ ms}$ , and the full spectrum is obtained by collecting  $f(t)$  data in  $0.16 \text{ s}$ , assuming that a 10-fold exponential decay brings  $f(t)$  to the baseline. For broader lines, shorter data collection time is required because of the inverse relationship. Because the convenient time scale and radio frequency are involved, NMR experiments are carried out, without exception, in the time (FT) or the frequency (CW) domains. As seen in the next section, this is not always the case in other types of spectroscopy including the FTIR.

### FTIR: Spatial (x) Domain Experiment

In order to explore the feasibility of doing a time domain experiment, let us examine the time needed to record a complete  $f(t)$  for a typical IR with  $10/\text{cm}$  line widths. Converting this to the frequency unit, we obtain  $\Delta\nu_{1/2} = c\Delta\bar{\nu}_{1/2} = 3 \times 10^{11} \text{ Hz}$ . Relating this to the exponential decay constant, we obtain  $5.3 \times 10^{-13} \text{ s}$  for  $T_2$  from the UP in eq 3. Collecting enough data for a signal that decays this rapidly is not practical. To see how this difficulty is overcome, we now examine an FTIR instrumentation.

In an FTIR spectrometer, the only arbitrarily varying part is the position,  $x$ , of the moving mirror that forms one end of a Michelson interferometer (10). This suggests that the spectrum,  $g(x)$ , is recorded as a function of the position variable,  $x$ . The FT of  $g(x)$  gives a more conventional IR spectrum,  $G(\bar{\nu})$ , as a function of the wavenumber,  $\bar{\nu}$ . Mathematically, FT in this case is

$$G(\bar{\nu}) = \int_{-\infty}^{\infty} g(x)e^{-i2\pi\bar{\nu}x} dx \quad (8)$$

This equation demonstrates the fact that in FTIR the transformation is between the position and momentum domains since the wavenumber is related to the wavelength and momentum of the EM wave. Measuring  $g(x)$  requires accurate determination of the position. For a spectral line with the width of the order of  $\Delta\bar{\nu}_{1/2} = 10/\text{cm}$ , the UP in eq 2 requires the decay length of  $l = 0.16 \text{ mm}$ . If  $8k$  points of  $g(x)$  values are collected to cover the domain,  $0 < x < 10l$ , the spectrometer should be able to resolve  $x$  within  $0.20 \mu\text{m}$ . The role of a built-in He-Ne laser in FTIR instruments is to determine the value of  $x$  within the desired accuracy. The rate of movement of the mirror and the time required for it to reach a certain position are not important factors.

### Student-Constructed Pulsed NMR Spectrometer

Finally, we present a brief description of a student-built NMR spectrometer. As a project in our chemical instrumentation course, we have constructed the pulsed NMR spectrometer following the circuit diagrams published by Muller, Noble, Burnett, Harmon, and McKay (14). These authors have been helpful by providing us with a detailed list of parts. Each student in the course constructed one unit, such as a receiver, transmitter, and preamplifier. After some work putting the individual units together, the spectrometer gives satisfactory FID's and spin echoes for proton NMR of aqueous copper(II) sulfate solution, using a small electromagnet that is a part of a susceptibility measuring apparatus. This spectrometer has been used by our undergraduate research students and in a physical chemistry laboratory experiment.

### Conclusion

We have shown that spectroscopy can be performed in the domain defined by specifying any of the four variables,  $\nu$ ,  $t$ ,  $\bar{\nu}$ , and  $x$ . Although mathematically, FT formalisms in eqs 4 and 8 are identical for FTNMR and FTIR, the difference in their respective frequency scales necessitates the FTNMR to measure  $f(t)$  in the time domain while FTIR measures  $g(x)$  in the spatial domain. The former requires an accurate clocking mechanism, while the latter requires accurate determination of the position of the moving mirror. A comparison of eqs 4 and 8 shows that the numerical integration involved in carrying out the FT in both NMR and IR is identical resulting in many artificial similarities. We also note here that the FT ion cyclotron resonance technique,

which is commonly used in a mass spectrometry, is a  $\nu$  and  $t$  domain experiment, while the electron spectroscopy for chemical analysis is a  $\bar{\nu}$  and  $x$  domain experiment.

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