An Audio Analogy To FT-NMR and FT-IR Spectroscopy

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Abstract: The principles behind the operation of a nuclear magnetic resonance spectrometer and an infrared spectrophotometer were fairly easy to explain to students fifteen years ago. As NMR and IR instruments became FTIR and FTNMR instruments, students understanding of these important chemical tools became vague to nonexistent. Furthermore, the task of a teacher to explain them to the students became more difficult. The audio-frequency analogy presented here is offered as a plausible technique for presenting these difficult ideas to chemistry students.

Introduction

The principles behind the operation of a nuclear magnetic resonance spectrometer and an infrared spectrophotometer were fairly easy to explain to students fifteen years ago. The IR instrument was based on em-radiation dispersion, much like the light prism demonstrations students had seen all their lives. The sources and detectors were different from those used in the visible region, but students could fit these devices into their largely analog instrument paradigm without much difficulty. Their comprehension of continuous wave NMR was probably more vague than that of IR devices because chemistry students often have a meager knowledge of electronics. This prevents them from understanding radio frequency generation and absorption circuitry and from really understanding how the magnetic field in which the sample is immersed can be swept linearly over a small range.

Still, if they accept that such circuitry can exist, they can make analogies that are reasonably valid to the visible absorption instruments;. thus, they can understand a continuous wave NMR as a low frequency (and thus with closely spaced energy levels) absorption instrument. The fact that these energy levels don't exist without the magnet creating them is a little hard to understand, but NMR can be understood sufficiently to allow its use for solving chemical problems.

And Then There Was FFT, The Fast Fourier Transform

As NMR and IR instruments became FT-IR and FT-NMR instruments, the understanding of these important chemical tools became vague to nonexistent. Furthermore, the task of the teacher to explain them became more difficult. The audio-frequency analogy presented here is offered as a plausible technique for presenting these difficult ideas to chemistry students.

Session 1: The Analogy

I have chosen to present my analogy as a dialog between professor and student. The student in this scenario is a chemistry major, junior or senior, who has an understanding of the electromagnetic spectrum, dispersive visible UV and IR instrumentation, and some experience with analog and digital audio (audio cassette versus CD music). The professor is, of course, myself, sitting at a PC running audio spectral analysis software. I use SpectraPlus FFT [1], but any similar software package will do.

Professor: Let's talk about sound waves first. To capture a specific example, would you please say, "moo!" into this microphone that is connected to the computer's sound card?

Student: moo!

Professor: Thank you. As you see on the screen, the computer recorded that sound and is now displaying it as a squiggly-looking wave. Think about this wave. It is a plot of sound amplitude versus time. The amplitude, or loudness, of the sound is an arbitrary scale, but the time is listed on the *x* axis as about half a second. The computer deceives us a little bit with this graph. It looks like a continuous line (a voltage) varying up and down as the sound varies. It looks, in other words, like an analog signal.

It was an analog signal when it came from the microphone into the sound card. But, the sound-card electronics immediately converted this voltage variation with time into a bunch of numbers; that is, it sampled the wave many times per second faster than the length of one wave. In this case, as you can see here below the graph, the sampling rate was 11,025 Hz. So, this sound has been converted by the microphone to a voltage variation, one that is analogous to the pressure fluctuations in the air (analog signal). Then the computer replaced this analog signal with a digital signal. The digital signal is really just a list. This list consists of two columns of numbers, one the amplitude at one instant, the other the time at that instant. Then, to make it seem analog to our eyes, the computer has drawn a line between the points. Let's ask the computer to show us the data points in the vicinity of 0.4 seconds.

We can also expand the plot and see this region close up (Figure 3).

I think you can see that the signal is now digital, just an array of numbers. This is the important first step to using the FFT technique to find spectral information. If you can't digitize the squiggles, you can't use FFT. Remember that the frequencies that make up this squiggle of moo! are audio frequencies. Most of them are frequencies from 100 to 5000 Hz. It would be nice if we could do this digitizing to infrared frequencies or even optical and ultraviolet light frequencies, but we can't do this directly because we don't have

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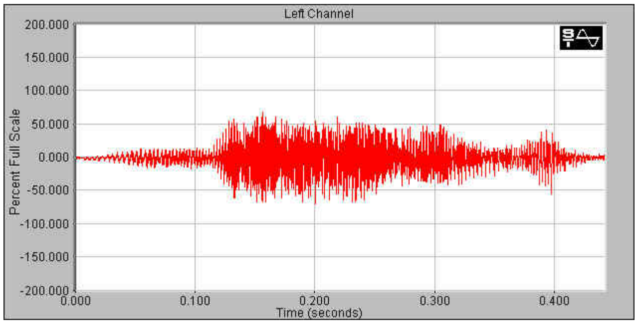
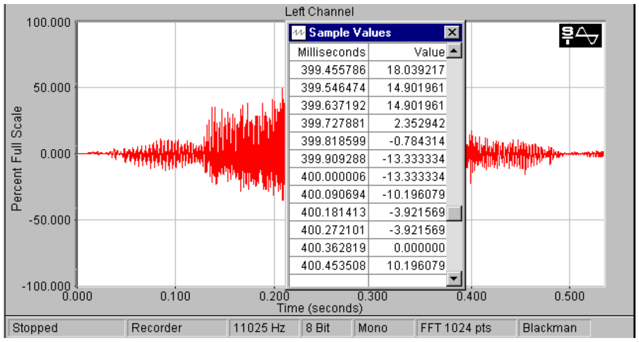


Figure 1. What moo! looks like to the computer



Sample Values

Milliseconds	Value
399.455786	18.039217
399.546474	14.901961
399.637192	14.901961
399.727881	2.352942
399.818599	-0.784314
399.909288	-13.333334
400.000006	-13.333334
400.090694	-10.196079
400.181413	-3.921569
400.272101	-3.921569
400.362819	0.000000
400.453508	10.196079

Figure 2. The digital nature of the power versus time recording.

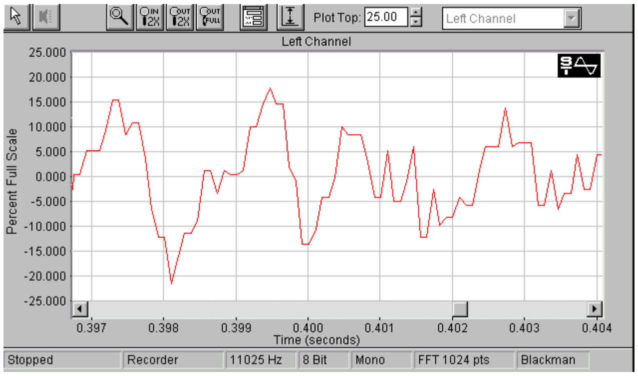


Figure 3. Expanded portion of Figure 1 to show digital segments.

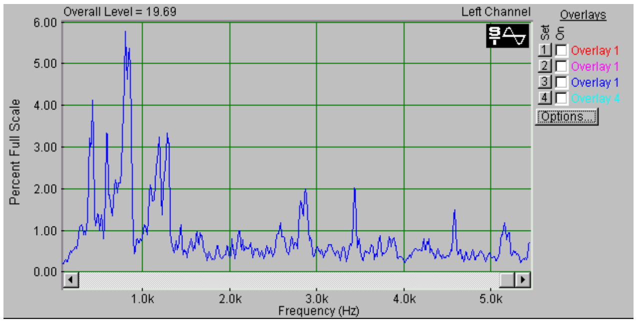


Figure 4. The spectrum of moo!

transducers (like the microphone here) to convert the light waves into voltage variations. Another problem is that the computer cannot sample fast enough to digitize such incredibly high frequencies; so, as I shall show you later, we must do sneaky tricks to make FT-IR and FT-NMR instruments.

Student: I see that this audio moo! has been digitized, but what has that got to do with Fourier transforms?

Professor: We are almost there. Be patient. Let me ask you to guess what the frequency of this "boo!" Signal is.

Student: I don't understand. How am I to know?

Professor: Look at this close-up we just generated. If there was a complete wave up and down and back to zero that you could find, you can estimate the time for that cycle. The reciprocal of the time for one cycle is the frequency.

Student: O.K. It looks like one cycle takes about two milliseconds. That's $1/(2 \times 10^{-3})$ equals 0.5 kHz; so, I guess 500 for one of the frequencies.

Professor: Excellent! Now, look at some of the faster squiggles and find another frequency.

Student: Well, there seems to be a kind of cycle of about 0.0004 seconds between successive peaks. That would be 0.4 milliseconds, reciprocal about 2.5 kilosomethings. Oh, yes. 2.5 kHz. Am I right?

Professor: It sounds reasonable. What you can now appreciate is that this complex squiggle is made up of a mixture of lots of frequencies generated by your larynx. What the FFT can do is what you just tried to do, find these frequencies and their contribution to the overall squiggle.

Let's ask the computer to do what I asked you to do, guess the mixture of frequencies that make up this squiggle. Incidentally, the computer can do it faster than you can. We select the whole squiggle like selecting a word in word processing: right click, choose average spectrum, and behold!

Notice that there **is** an approximately 500-Hz component (actually 429 Hz) and a 1280-Hz peak corresponding to your second guess. I guess that makes you a SAAFT, a slow and approximate Fourier transform.

Student: Very funny, but how does the computer do it?

Professor: It does it by using some mathematical methods that have been known for over a century, but before we get into that (skip ahead to Session 4 if you can't wait), I have something else to show you about graphing our moo! data. You have seen that this data contains information about the amplitude, the frequency, and the time. I am going to ask the program to display this data as a three-dimensional graph for us. Of course, it can't really make a three-dimensional graph on a flat screen, but it will try very hard, and we can use our imaginations for the perspective. Watch this!

On this graph, the frequency is obviously the left to right axis. The amplitude (actually, the power) is the vertical axis, and time is the axis perpendicular to these. Think of the time axis as an arrow starting at the upper-left blue portion and extending to the lower-left corner of the graph. The time, 51 ms, is at the back of the representation, and time, 462 milliseconds, is at the lower-left front.

Now, any plane parallel to the frequency–power axis will be a spectrum plot of the frequencies present at that moment in time. A person looking at this from the front (power-versus-frequency side) would see a series of spectra, which, if averaged, would be the spectrum we displayed earlier (Figure 4). A person standing to the left side of this 3-D plot would see a series of power-versus-time plots, which, if averaged, would be the squiggle plot we began with (Figure 1).

Student: It's hard to imagine, but I guess so.

Professor: The viewer on the left is seeing the signal "in the time domain," as we say in the industry. The viewer in the

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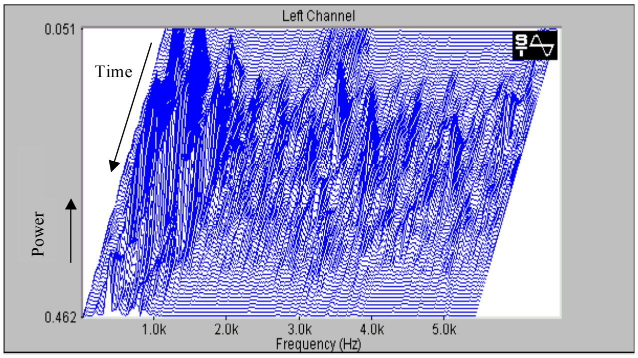

Figure 5. A three dimensional graph of the two domains

front is seeing the signal "in the frequency domain." The FFT operation switches you from one view to the other.

Student: I have heard those terms before, but they never made sense; but, why are there so many slices of the frequency domain, not all the same?

Professor: That is because these are audio frequencies, quite low frequencies. Our computers have become so fast that they can do an FFT operation in a very short time. During the 411-ms duration of this moo!, the computer can do over 100 FFT operations. These are stacked one behind the other in the 3-D chart. When I showed you the frequency domain graph before (the spectrum), I had asked the program to average the spectrum over the time of the moo. The spectrum is actually different during different moments of the moo.

Student: I suppose this speed of processing, impressive at audio frequencies, is not going to be fast enough when we extend this to infrared frequencies!

Professor: Very true! The sampling rate of the computer has to be at least twice the frequency of the highest frequency in the spectrum. Because infrared frequencies are about 10^{13} Hz, we can't do the digitizing anywhere near that fast; so, we resort to a trick to move the IR frequencies down to a workable range. In the case of the radio frequencies of NMR (90–500 MHz) we do, still, a different trick. But, let's take a break and look at FFT for these regions later.

Student: I'll have milk instead of coffee...to improve my moos.

Session 2: FT-IR

Professor: How was your milk?

Student: Moo!

Professor: Excellent. Now, for the infrared trick I spoke about earlier. What do you know about radios and how they work?

Student: Radio waves come into them from somewhere far away, and the radio circuits convert these frequencies to rock music.

Professor: Close, but the point I want to make here has to do with frequency conversion. Give me the frequency of your favorite FM station.

Student: One oh three rock, of course.

Professor: I'll try to avoid that region of the dial, but that means 103 MHz is the carrier frequency that enters the radio antenna coil. This frequency is not so great that it cannot be amplified and manipulated by modern transistorized circuits, but, for reasons we won't go into, FM radios convert this frequency to 10.7 MHz by a circuit called a mixer circuit. Then the rest of the radio manipulates this approximately ten-times-lower frequency. The lower frequency (approximately 10 MHz) "carries on its back," so to speak, all the audio information that was carried by the 103 MHz signal from the station. The mixer circuit just has shifted it to a lower and more easily managed signal. Are you with me?

Student: I've been to a few mixers myself.

Professor: Hmmm. The point is that the infrared being too high a frequency to digitize needs to be converted to a lower, more manageable frequency so that we can perform the Fourier transform mathematics on it. Still, we can't do the conversion electronically because we don't have the proper infrared transducer, so the trick is to use an interferometer.

This device causes the infrared waves to reflect back upon themselves in a way that makes them either interfere with themselves constructively (bigger wave) or destructively (smaller wave). One of the mirrors that do the reflecting of the waves is moveable. If this mirror is mechanically moved back and forth at a known rate, the result is that the detector detects infrared frequencies varying in time at a much lower rate than their true variations. The amplitude fluctuations of the detector signal are proportional to what the detector would see if it could follow the variations of infrared itself. The factor by which the frequencies are mixed and shifted down are much greater than the ten-times shift of the FM radio we mentioned earlier. The interferometer shifts the frequencies down by a factor of 10^{10}. This shifts them into the audio range. From there, they are analyzed by Fourier transform software exactly as we have analyzed the moo! signal.

Student: So the "trick" you mentioned is to shift the frequencies using an interferometer so that IR becomes audio. Then use FFT to convert this time-domain signal to a frequency-domain signal. The spectrum will be, I suppose, just like the spectrum obtained using an older dispersive IR instrument?

Professor: Yes, very much like the old IR spectrum, but better.

Student: Why better?

Professor: For two reasons: One, the energy in the IR beam is never spread out. The full IR energy falls on the sample at all times. Even more importantly, the time-domain signal is repeated over and over many times per minute. Each of the generated time-domain signals (squiggles) presumably would give identical spectra. Because of noise, they won't be identical, but it is simple for a fast computer to average the data from many squiggles and print out a time-averaged spectrum. This improves the signal-to-noise ratio of the spectrum by a factor of the square root of the number of repetitions that are averaged; thus, FT-IR spectra are (in general) superior to older IR spectra.

Student: I'm convinced. I'll buy one. How does their cost compare with the older dispersive models?

Professor: In 1985 they cost ten times more. Today they are about the same price, and tomorrow they will, no doubt, be even lower. The dispersive IR instruments will become part of the history of chemistry. But if you ever buy a new FFT one be sure it has a helium–neon laser in it.

Student: A red light laser? Why. Can it analyze laser light? Hey, the laser would only be one frequency. A pretty dull spectrum.

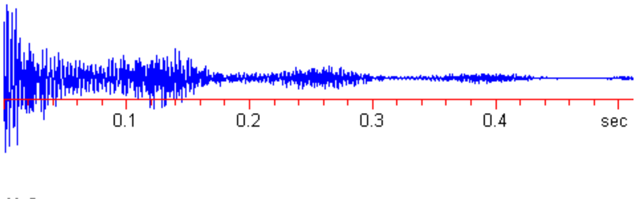

Figure 6. A typical free-induction-decay signal.

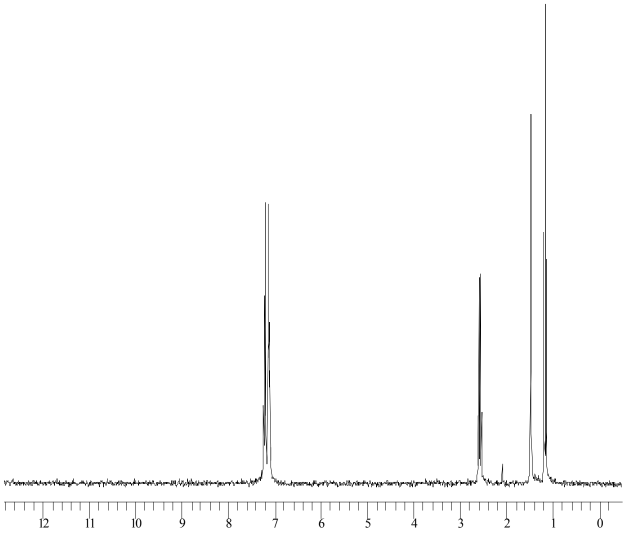

Figure 7. The FID after being transformed to a spectrum.

Professor: The laser is used to provide a single spectral line from the plotted graph. This spectral line is used to make sure each spectral scan begins at the same instant in time. Otherwise, without a reproducible standard, the spectrum of one squiggle might shift relative to the spectrum of the next. If this were to happen, the time averaging would be of no use.

Student: Hey! They could make a computer with a hole in the top of it. You would just pour in a sample and see the spectrum on the screen!

Professor: Sure, go home and try it, but be sure to come back for FT-NMR, the next big trick.

Session 3: FT-NMR

Student: I poured some ethanol into my computer at home and no spectrum appeared. There goes my patentable idea.

Professor: Where did you get the ethanol? Never mind. I'm sorry I asked. Are you ready for FT-NMR?

Student: Ready, but I already know the answer. You shift the frequencies of NMR from the radio range down to audio using a mixer. Then do regular moo! FFT stuff.

Professor: That is certainly a reasonable guess, but not quite right. You will recall that the energy levels involved in NMR are very closely spaced energy levels? And further, that this means that their relative populations (protons in the upper level/protons in the lower level) are only slightly less than 1. In IR work, the energy levels are much further apart, and at room temperature the upper levels are significantly less populated than the lower levels. When you do continuous wave NMR experiments it is very easy to apply too much rf power to the sample. If you do, you "saturate" the sample with rf (radio-frequency) energy. That means that the upper-level and lower-level populations can be so similar that no absorption (or emission) takes place. In continuous wave (old-fashioned) NMR, you try to avoid this by keeping the rf power low.

But, in FTNMR you intentionally saturate the sample by irradiating it with a rather high-energy pulse. This pulse of radiation contains all the frequencies across the NMR spectrum of interest. At the end of this short pulse, the nuclei in the higher energy levels begin to relax back to their former state; that is, more (but not much more) are in the lower state than in the upper.

What eventually comes out of this decay of radio frequencies is an audio-frequency squiggle that is called the "free induction decay." Here is an example:

When an FFT is performed on this free induction decay, the result is a spectrum display.

Student: Wait. The free-induction decay does not look like our audio moo sample. Why not?

Professor: You are very observant. It does look different because of the exponential decay shape of the audio frequencies. What are exponentially decaying are really the radio frequencies that were contained in the pulse applied to the sample coil. What you see in the FID is not this decaying radio frequency, but the audio component that modulates it. You remember that after 103 Rock was converted to 10.7 MHz in your FM receiver that you didn't listen to this 10.7 MHz signal. You can't hear 10.7 MHz. You listened to the audio signal that was "riding on its back," as we put it at the time. This rock music audio signal was placed on the back of (modulated) the original 103-MHz signal at the radio station studio. It also modulated the shifted frequency, 10.7 MHz. In your radio it was extracted from the radio signal by a circuit called a detector. After that point, it was audio, amplified (probably too much) by the audio amplifier circuits, and then transduced into sound by your speaker system.

In a similar manner, the relaxation processes of the nuclear magnets modulate the radio frequency decay after the pulse ends. This radio frequency goes to a detector circuit and comes out as an audio decay, the FID.

Student: So these FID things are just like the *.wav files of audio sounds?

Professor: Not exactly. They are audio files, but are in a different format than *.wav files like our moo!; therefore, this audio analyzer we have been using will not accept them. You have to have an audio analyzer made to handle the file type produced by your NMR instrument. In the above FID the instrument was a Bruker, and the file format is called Bruker Aspect 2000. Fortunately, you can download a free FFT analyzer for these and other FID files from the Web. One such program is called MestRe-C 2.2, and is available at the URL in reference 2.

Student: So the FID can be recorded on a disk, just like my moo! and taken to anyone's computer to be converted into a spectrum by FFT, integrated, and so forth?

Professor: Exactly, the FT-NMR (and its sample) can be in one city, and the FID transmitted on the Internet to a chemist with only a computer and the required software to analyze it.

Student: This FT stuff is cool! How did you old folks ever get any spectra before FFT came along?

Professor: Like a porcupine makes love. Very carefully!

Session 4: The Mathematics of FFT

Professor: You asked me earlier how the computer does FFT. The best way to give you a feeling for what the computer is doing during a fast Fourier transform is to let you make a spreadsheet to do the same thing on a small scale. Jean Baptiste Joseph Fourier was a contemporary of Napoleon, and you may appreciate there were no spreadsheets at that time. If you want mathematical rigor you may wish to consult the library, but if you want a quick and dirty FFT spreadsheet we can do it here.

Student: I want quick and dirty.

Professor: What spreadsheet are you familiar with?

Student: I use Lotus 123, but I know most of the other students use Excel.

Professor: Either will work, as would Quattro. Let's use Excel for the pop-up notes. They can be a big help in documenting the spreadsheet. In the A column we need a time base. Fill the first column from zero to 2.49 in 0.005 increments, first labeling it "time." This will be the *x* axis of the audio signal that we wish to analyze by FFT. In B1, enter "freq 1." In the B2 cell we place a cosine wave by entering =AD7*COS(AD2*$A2). This requires a little explaining.

Student: Yes please.

Professor: The AD7 is an absolute reference to a cell far to the right into which cell we shall enter the amplitude value for our first spectral peak. For example, go to cell AD7 and enter 1.

Student: Got it.

Professor: As you may have guessed, AD2 is a place to enter the *frequency* of this cosine wave. In AD2 enter 1000. The final $A2 is a partially absolute reference to the time in column A. If we copy this column to other places the A will stay, but the 2 will increment down the time axis, as we want.

Student: I save periodically. What do I call this spreadsheet?

Professor: Call it "crudefft." Now create two more columns for input frequencies. You can copy down and over from column B, then change the $AD to $AE in column C and $AD to $AF in column D. This means that the user can pick three frequencies and three amplitudes for the simulated spectrum. As a start, place 1100 and 11900 for the second and third frequencies, and 2 and 0.5 for the amplitudes. These three frequencies you just generated are shown in Figure 1 on the Excel tab. Finally, make column E be the sum of B2+C2+D2 and copy down. Column E is now our simulated moo! See Figure 2 on the Excel tab. It is a mixture of three frequencies at three amplitudes. Plotted versus time (column A), it is a signal in the time domain that is to be analyzed by our crude FFT program.

Now we shall answer the original question, "how does FFT do it?" We shall make this spreadsheet transfer this time-domain signal into a frequency-domain signal. That is to say, the spreadsheet will figure out what frequencies are hidden inside the "sum" signal. Ready?

Student: Ready.

Professor: Label each column from F through AB as frequencies from 980 through 1200 in steps of 10.

Student: I'm beginning to see. The computer is going to try each of these frequencies and see if it is there?

Professor: Absolutely. And the way it will tell if that frequency is there is by integration. In cell F2, place the formula =COS(980*$A2).

Student: But that will simply generate a cosine wave of frequency 980.

Professor: Then insert E2* before the COS. This will multiply the instantaneous value for the 0.98 signal times the time-domain "sum" signal at each time value.

Student: OK, I copied it down the column. Now what?

Professor: Total this column.

Student: If you say so. Hey, the total is small. Minus 1.38.

Professor: So you have guessed a frequency that was not included in our choice of three. Now you have multiplied one function (the sum function) by another function (the guess frequency) for each small increment of time, then summed the results. Does that sound like any mathematical operation you ever heard of?

Student: Sure. It sounds like an integration.

Professor: Go to the head of the class!

Student: But I'm the only one in the class.

Professor: Then guess what's next.

Student: I do this for all the frequencies listed on Row 1. When they are summed, there will be something different about the correct frequency sums to distinguish them from the other sums.

Student finishes the job at all listed frequencies.

Professor: Finally, plot the spectrum as a plot of integral sums versus frequency. Then, you may change the frequencies and amplitudes at will and watch the frequency domain graphs change accordingly.

Student: *Enthusiastically.* I'm placing the graphs of spectra just under the table where you enter frequencies and amplitudes. Hey, this is cool. Did you invent this?

Professor: This spreadsheet idea is not original. I found it as an example problem in Atkin's Physical Chemistry, 4th edition [3]. It is not a sophisticated FFT program, but does clearly indicate what the computer must be doing. What do you think?

Student: I think, yea, yea, yea, yea!

To the interested student:

There is an interesting and practical article in *The Chemical Educator*, Vol. 1, Issue 4 (September 30, 1996) about FTIR [4]. Also in the *Journal of Chemical Education*, there is an article about FFT that explains "aliasing," sometimes called "folded peaks" [5].

There are also many books in your library about FT-NMR, a recent one being reference [6].

Supporting Material: Readers will be able to download the spreadsheet as a Microsoft Excel file called crudefft.xls (http://dx.doi.org/10.1007/s00897990427b). The sound file moo.wav can also be downloaded should you wish to hear what is being analyzed (http://dx.doi.org/10.1007/s00897990427c).

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