

Week 2

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2.1 Lecture 3: Time, Frequency, and Fourier Transforms

1/10:

- Frequency- and time-domain spectroscopy.
 - Two ways of extracting the same information.
 1. Absorption spectrum (frequency domain).
 - Vary frequency of driving field or disperse white light after passing through the sample and look at each frequency component.
 - Measure the power absorbed for different frequencies.
 - Tells us the resonance frequency, how strongly the light interacts with the matter, and damping times or relaxation processes.
 2. Pulsed excitation (time domain).
 - Apply a pulsed driving force.
 - Measure resultant periodic oscillation and relaxation.
 - This is the basis for modern NMR and FTIR instruments.
 - Both represent the time-dependent behavior of a molecule.
- A powerful reason to use the time domain is the formal relationship between time and frequency data, the **Fourier transform**.
- **Fourier transform:** A formal relationship between the time domain and the frequency domain.
 - Underlying idea: Any function can be expressed as a sum of sines and cosines, i.e.,

$$F(t) = \sum_{n=1}^{\infty} [a_n \cos(n\bar{\omega}t) + b_n \sin(n\bar{\omega}t)]$$

- In practice, sample N points over a period T .
 - The values of time at which we sample are $t = n\delta t$ for $n = 1, \dots, m$.
 - Numerical analysis: Expand in harmonics of base frequency, i.e., we let $\bar{\omega} = \pi/T$ be 1/2 cycle of T . The harmonics are $n\bar{\omega}$ for $n = 1$ to N . We thus have as many harmonics as we do data points.
 - Then we plot the expansion coefficients vs. the frequency, and that is the spectrum in the series of expansion coefficients.
 - There's more to it than this, but this is the basic concept.
 - Also, this is only a discrete data set.
- **Fourier analysis:** Determining the coefficients a_n, b_n .

- Fourier transform relations.

- For continuous functions, we use Fourier transform integrals.

- Note that although both of the following integrals are sine transforms, there also exist cosine and complex $e^{-i\omega t}$ transforms.

- Sine and cosine transforms are used for real data; the complex form is more general.

- To convert to the time domain $S(t)$, we write

$$S(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{S}(\omega) \sin \omega t d\omega$$

- To convert to the frequency domain $\tilde{S}(\omega)$, we write

$$\tilde{S}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S(t) \sin \omega t dt$$

- Example: Damped harmonic oscillator.

$$S(t) \propto e^{-\gamma t} \sin \omega_0 t \quad \Longleftrightarrow \quad \tilde{S}(\omega) \propto \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$

- Parameters in the time and frequency domains.

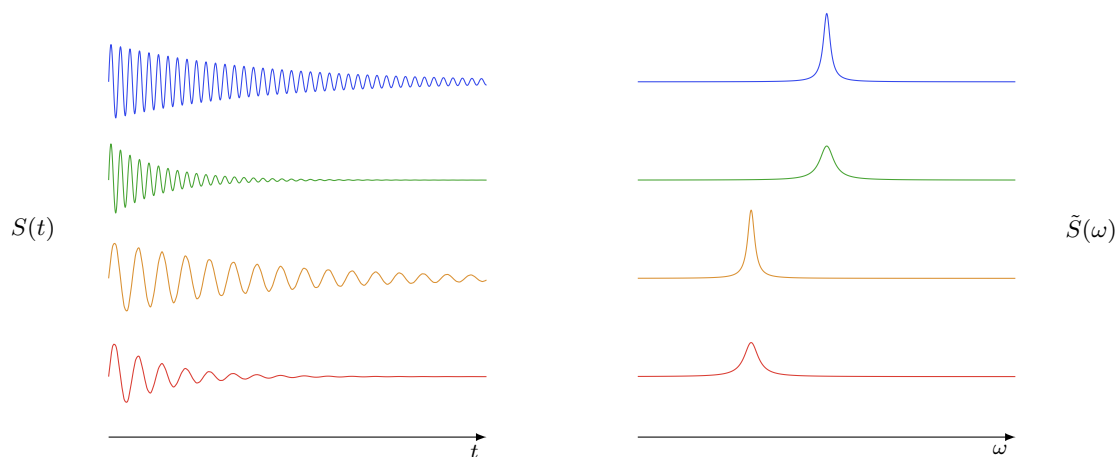


Figure 2.1: Parameters in the time and frequency domains.

Parameter	Time Domain $S(t)$	Frequency Domain $\tilde{S}(\omega)$
Large ω_0	Fast oscillations	High frequency
Small ω_0	Slow oscillations	Low frequency
Large γ	Fast decay	Broad linewidth
Small γ	Slow decay	Narrow linewidth

Table 2.1: Parameters in the time and frequency domains.

- The area under the lines remains constant.
- Notice how the lower-frequency waves (orange and red) have frequency spikes shifted down.
- Broader Lorentzian implies more different types of frequencies are present implies destructive interference takes hold more quickly implies quicker decay.

- F.T. Example: Two resonances.
 - Consider a superposition of two oscillating decaying functions

$$C(t) = e^{-\gamma t} \sin(\omega_1 t) + e^{-\gamma t} \sin(\omega_2 t)$$
 - This implies two resonances in the spectrum.
 - In particular, they manifest as two beat frequencies, one of which is the average frequency, and the other of which is the difference.
 - The average frequency determines the regular vibrations; the difference is the bounding function.
- History of science during the French revolution.
 - Lavoisier and Fourier were both strongly influenced by their time (the French revolution).
 - Lavoisier was an elite tax collector, and was sentenced to be executed. When he asked the judge for mercy, the judge said, “the Republic has no need for scientists.”
 - Fourier got into trouble with Robespierre even though he was a revolutionary, but Robespierre’s regime was overthrown a day before his scheduled execution. Thus, we get Fourier transforms!
- Fourier transform infrared spectrometer.
 - Michelson Interferometer.
 - Named after UChicago’s first physics chair, also the first American to be awarded the Nobel prize in physics.
 - How it works: Intensity changes with pathlength-induced interference.
 - Incoming monochromatic waves get half reflected, half transmitted, allowing for phase separation.
 - Mathematically,

$$\Delta L = \frac{1}{\nu} = \frac{c}{\nu} \qquad \Delta t = \frac{\Delta L}{c}$$
 - Thus, if our light source is emitting monochromatic light (as it should be), the intensity of the light impinging on the sample changes with the pathlength.
 - In particular, if $\Delta L = n\lambda$, there is no change in intensity, but other forms see destructive interference to varying extents.
 - A Fourier transform then takes the monochromatic wave to a Fourier transform spectrum.
 - The frequency resolution for the spectrometer is given by the scan distance is $\Delta \nu = \pi/L_{\text{tot}}$.
 - Frequency resolution given by the scan surface.
 - For higher resolution, you need to scan farther??
 - We use an FTIR lamp (tungsten filament; broad bandwidth).
 - Broad bandwidth is the opposite of monochromatic; thus, it is difficult to obtain repeated peaks, and a Fourier transform yields substantial intensities over a range of frequencies, as expected.
- Measuring an FTIR spectrum.
 - Take reference and sample scans (yielding I_0 and I data) with that broadband bulb.
 - Then take an interferogram with and without the sample.
 - Then take an experimental spectrum, which is leveled and calculated from the previous work using $T = I/I_0$ and $A = -\log T$.
 - What is experimental and what is mathematical manipulations here??

- Wrap up.
 - A spectrum originates in the time-dependent behavior of molecules driven by electromagnetic radiation.
 - It is possible to perform experiments as a function of frequency or time.
 - There are practical differences, but they encode the same information.
 - These are related by a Fourier transform.
 - Fourier transform IR spectroscopy uses interferometry to relate changing optical pathlength to optical frequency.
 - More on this??

2.2 Office Hours (Tokmakoff)

- How much do we need to know about data fitting in general? Because I haven't really done data fitting since high school. Also, is what's described in the Excel tutorial enough to get us through this class, or do we need to be able to use the other tools listed in Data Fitting Exercises.pdf, understand the statistics chit-chat, etc.?
 - Just Excel will be enough for this course.
 - Tokmakoff does recommend learning some others though just because they will be useful down the line. He believes he has a video of a former TA explaining Mathematica and he will try to post it.
- Using Solver Constraints for the Fluorescence decay?
 - Yep, that was the right thing to do.
 - Necessary in Excel; in fancier softwares, you get nicer tools for such things.
- Answers to miscellaneous questions in Data Fitting Exercises.pdf?
- Are we measuring taking a spectrum of I_2 in the liquid or gas phase? Are we doing both?
 - Doing both.
 - Electronic spectroscopy will be covered in lecture next week and will not be emphasized in the short lab report; if we choose to write our long lab report on UV-VIS, though, we will be expected to discuss it in more depth.