Introduction to 1D and 2D NMR Spectroscopy

(1) Basics

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What you will learn from this course

- Judge if the results from your routine NMR spectra are sound
  – Challenges that modern chemists face: molecules with complex structures: block copolymers; dendrimers; amphiphilic molecules; nanogels; bottlebrush polymers; ….
- Understand several essential NMR concepts
  – Working principles of NMR experiments
  – T1 and T2 relaxations
  – Molecular dynamics
- Learn a few techniques that probe your molecules' physical behaviors (e.g., how they organize; how they move around)
  – T1/T2 measurement
  – Diffusion

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Logistics

- 9 - 10 classes
- Course slides: blogs.umass.edu/weiguoh
- Reading material: “A Brief Introduction to NMR” (also on my blog)
  - Sections about solid-state NMR can be ignored
- Homework (40%)
  - Work in a team
  - prepare your own sample, run experiments, and write reports
  - Please email your answers to me by deadlines
  - You will be given chances for revision if you make major mistakes
- Quizzes (30%): in class; ca. 10 minutes each.
- Q and A sessions: 10-10:30am after each class, or email to make appt
- Exam – ½ hour in the last class (30%)

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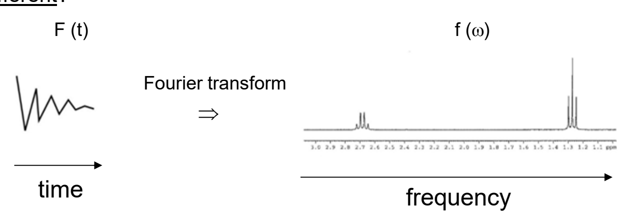
Concepts To Be Extensively Used In This Course

- Atom structure
  - nuclei are little magnets due to their spin
  - Electrons are even stronger magnets, but they are usually paired (one up and one down), so they can be considered non-magnetic
- Electromagnetic interactions
  - What happens when you put two magnets close to each other?
  - How can you produce a magnetic field without a magnet?
- Fourier transformation
  - A graph showing the frequency components is called a spectrum
  - When you strike middle C (261.6Hz) on piano, how does the spectrum of the music look like? How about a C major chord?
  - Comparing a long-lasting wave with a fast-fading one, how would their spectra look different?



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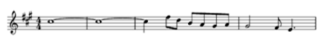
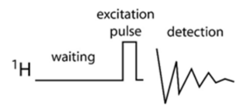
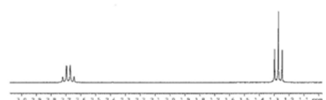
NMR – Nuclear Magnetic Resonance

<u>**Piano**</u>	<u>**NMR**</u>
Strings	Nuclei in sample
Tension on strings	Magnetic field
The knock	Pulse(s)
⇒ Music	⇒ Signal F (t)





– Fourier transform ⇒ f (ω)



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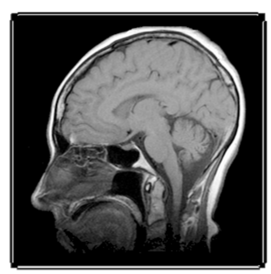
History of NMR

- Nobel Prizes:
  - 1952 Physics: Discovery of NMR phenomenon
  - 1991 Chemistry: 2D NMR
  - 2002 Chemistry: Protein 3D structure
  - 2003 Physiology: MRI
    - In the US, ca. 40 million MRI scans per year performed.



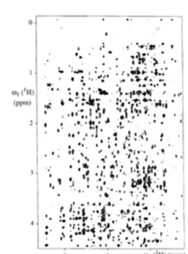
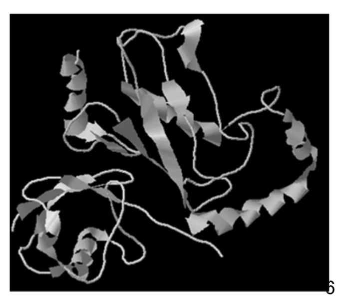


Figure 19 2D [^{1}H,^{1}H]-NOESY spectrum of the plant pathogenesis-related protein P14A (M ≈ 15000). A contour plot of the spectral region [ω_1(^{1}H) = 0–4.3 ppm, ω_2(^{1}H) = 6.3–9.5 ppm] is shown (750 MHz, 30 °C, H_2O-solution).

Wüthrich, *J. Biomol. NMR,* **27:** 13-39, 2003

2FUH



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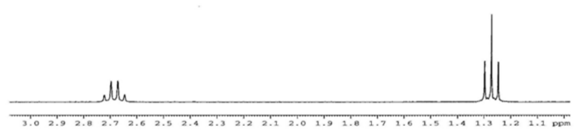
Larmor Equation

$$\omega = \gamma B$$

- ω is signal frequency of the nucleus
- γ (gyromagnetic ratio) is a property of the nucleus
  - All nuclei of the same isotope have the same γ, regardless of its chemical environment
    - γ (^{13}C) ~ ¼ of γ (^{1}H)
  - On a 400MHz spectrometer, frequency of ^{13}C ~ 100 MHz
    - A "600 NMR" means that its ^{1}H frequency is 600 MHz
    - *What is the ^{13}C frequency on a 600MHz instrument?*
- B is magnetic field strength



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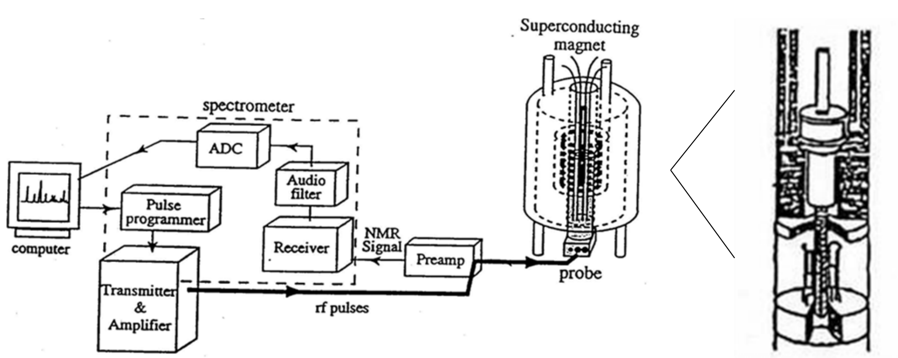
An NMR Spectrometer

- Magnet
  - Superconducting coil
  - Helium dewar
  - Nitrogen dewar
- Console
  - Pulse generation
  - Signal amplification
- Probe
  - RF coil: irradiate pulses on sample; receives signal



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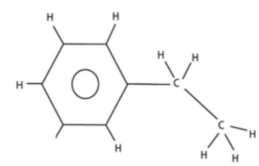
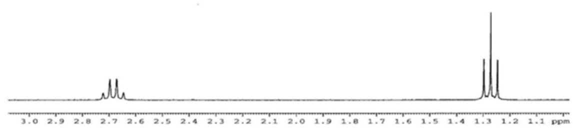
Magnets in Your Sample

- From the big environment:
  - the “big magnet” (B_0)
  - sample tube
  - insoluble particles and dirt stains
- From the small environment (molecular level)
  - electrons in the neighborhood – “shielding effect”
    - This is the physical mechanism of chemical shift
  - neighboring nuclei – “J-coupling”



$$\omega = \gamma B$$



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Summary of Important Concepts

- What are some basic components of an NMR experiment?
- What are some basic components of an NMR spectrometer?
- <u>An important equation</u>: $\omega = \gamma B_0$
  - Every peak on a proton spectrum has a different frequency. Which factor in the equation generates such a difference?
  - What kinds of magnets are present in your sample?

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