Ways of Knowing in Chemistry

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Science Circle, Sept. 29, 2017

An abstract.

How do we know what we say we know? In synthetic chemistry, there are tools we use which give us data from which we can deduce details of a molecule's structure. Many of these tools are spectroscopic in nature and some rely on changes in how a molecule rotates, vibrates, how its electrons are distributed, or even how individual types of nuclei spin. There are also methods based on diffraction that can yield a "snapshot" of a molecule's structure. This talk will be from a synthetic perspective, i.e. how do we make sure that what we tried to make is what we actually made, and what sort of purity did we achieve?

Catalyzes the transformation of

cat food into cat

So What is a "Way of Knowing"?

- How we ascertain that what we think we know has some truth to it.

- My intro is based on a great statement from the Union of Concerned Scientists.

- There are many "Ways of Knowing" but my talk is going to focus on science… specifically chemistry.

http://www.ucsusa.org/scientific_integrity/what_you_can_do/science-as-a-way-of-knowing.html

Statement from the Union of Concerned Scientists (UCS):

- Ways of knowing used in society include the following:
  - *Authority*
  - *Belief*
  - *Logic*
  - *Scientific Inquiry*

Not an exclusive list!

http://www.ucsusa.org/scientific_integrity/what_you_can_do/evolution-and-id-footnotes.html#1-1

UCS Definitions

- **Authority**: Parents, teachers, community leaders, and physicians are all figures of authority. The level of trust we have in them depends on our personal experiences and access to knowledge about them.
- **Belief**: God or gods, or other external or internal supernatural powers can impart or support beliefs. There are numerous deities and levels and types of belief within any society.
- **Logic**: Logic includes tests and rules that help to identify what is true and false. It is an important element of scientific inquiry but is limited by its lack of reference to the natural world.
- **Scientific Inquiry**: Science provides knowledge based on empirical evidence from the natural world. Science is the only way of knowing that provides explanations that are testable and verifiable. Ideas in science accumulate over time and are subject to revision and change.

http://www.ucsusa.org/scientific_integrity/what_you_can_do/evolution-and-id-footnotes.html#1-1

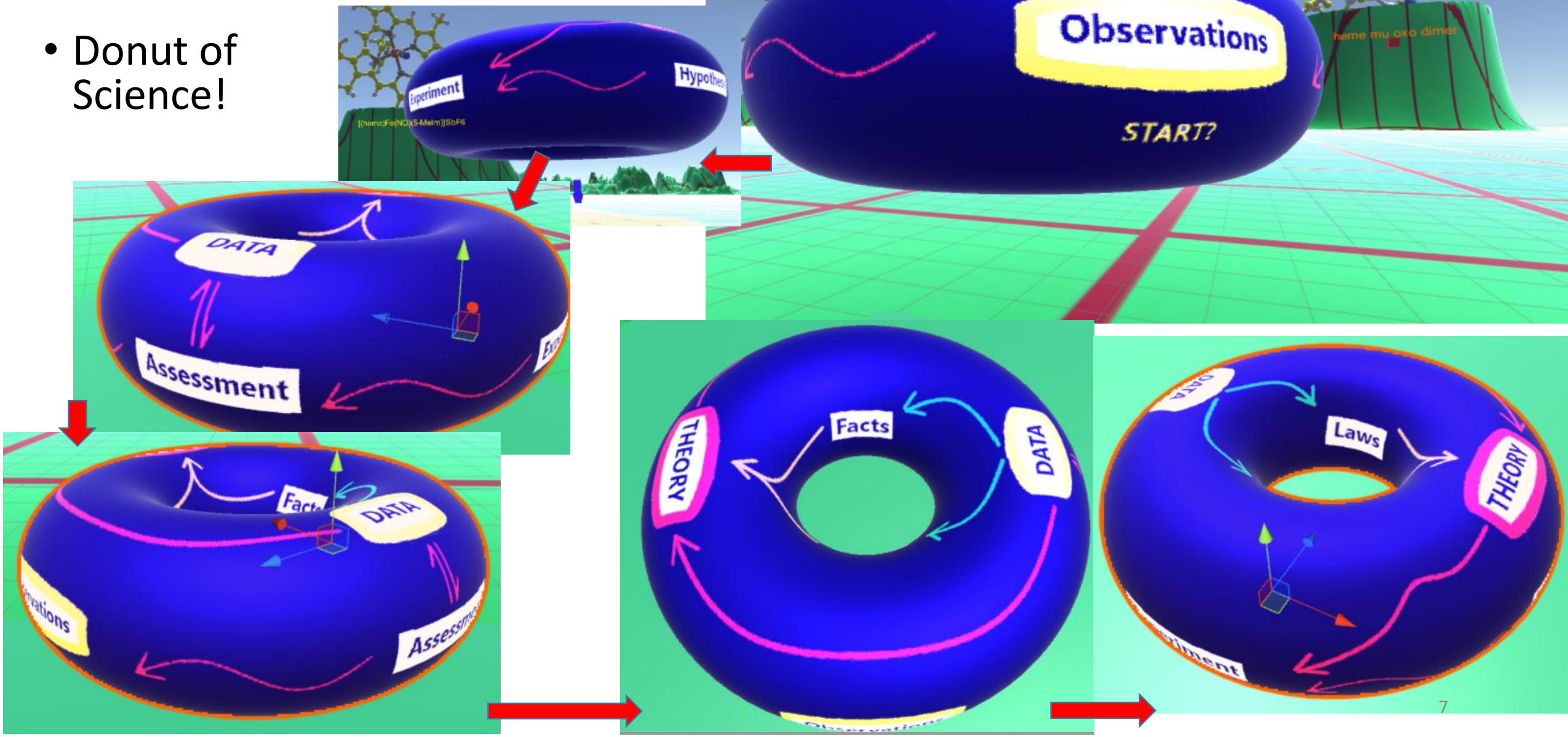
Theories (according to UCS)

- Must be tested by experimentation and observation of the natural world.
- Must be falsifiable (i.e. experiments must exist that could prove it false).
- Cannot be proven, only confirmed or disconfirmed.
- Subject to revision and change

http://www.ucsusa.org/scientific_integrity/what_you_can_do/science-as-a-way-of-knowing.html

Scientific Method

- Donut of Science!



Chemistry is science… any specific differences from other branches of science?

- Absolutely!
- Atoms are very small, so chemists tend to be detail-oriented.

- Have to rely on physical methods to garner information…
  - Until recently, could not see or manipulate individual atoms directly!
- Chemistry has developed into a HUGE science
  - Analytical, biochemistry, chem-ed, environmental, inorganic, medicinal, organic, physical
  - Crosses within Chem: Bio-X… Bio-organic, Bio-inorganic, etc
  - Cross-disciplinary fields like nanochemistry (engineering & chem)

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Artificial distinctions! All boil down to how atoms interact with each other!

Ways of Knowing…

At this point, chemists have internalized the donut of science. Hopefully with the coffee of funding….

- I see chemists as being concerned with **Form** and **Function**
- **FUNCTION**
  - **What are the starting and end points?**
  - **How do we go from one point to another?**
  - **What does it cost (think energy) to make a transformation happen?**
- **FORM**
  - **How do we establish structure?**
  - **How do we know a structural change occurred during a reaction?**
  - **Can we use what we know to build something new?**

Function?

- Spectroscopy
- Electrochemical methods
- Even temperature changes!

- Math plays a big role, too.

- Kinetics vs. Thermodynamics

Function?

- Spectroscopy
- Electrochemical methods
- Even temperature changes!

Using “thermochemical cycles, logic and math, atomic and ionic radii can be estimated…

This is using a thermometer to measure length!

- Math plays a big role, too.

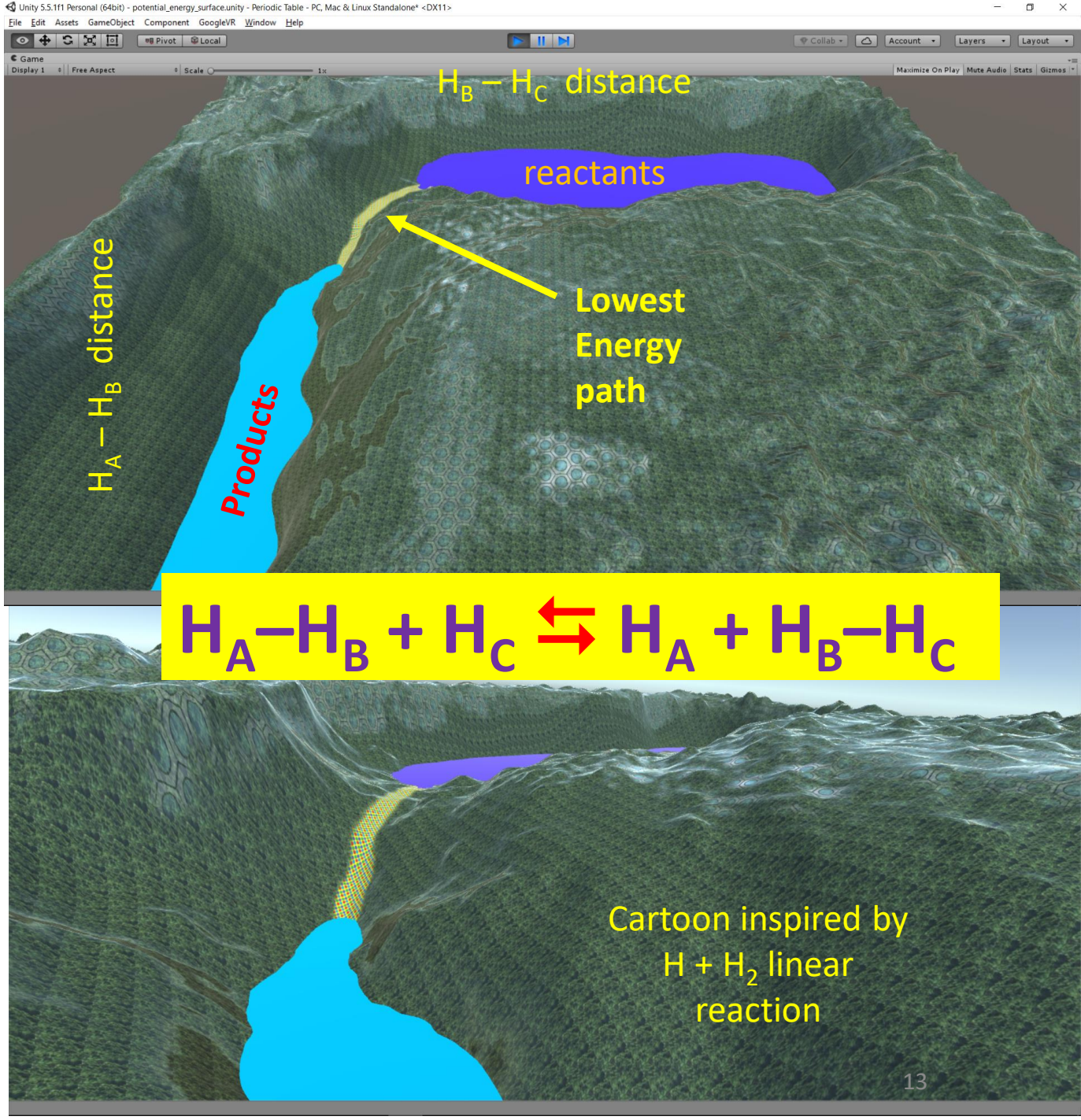
https://en.wikipedia.org/wiki/Kapustinskii_equation

- Kinetics vs. Thermodynamics

See also:
Roobottom et al, “Thermochemical Radii of Complex Ions,” J. Chemical Education, 1999, 76, 1570.
at
http://pubs.acs.org/doi/abs/10.1021/ed076p1570

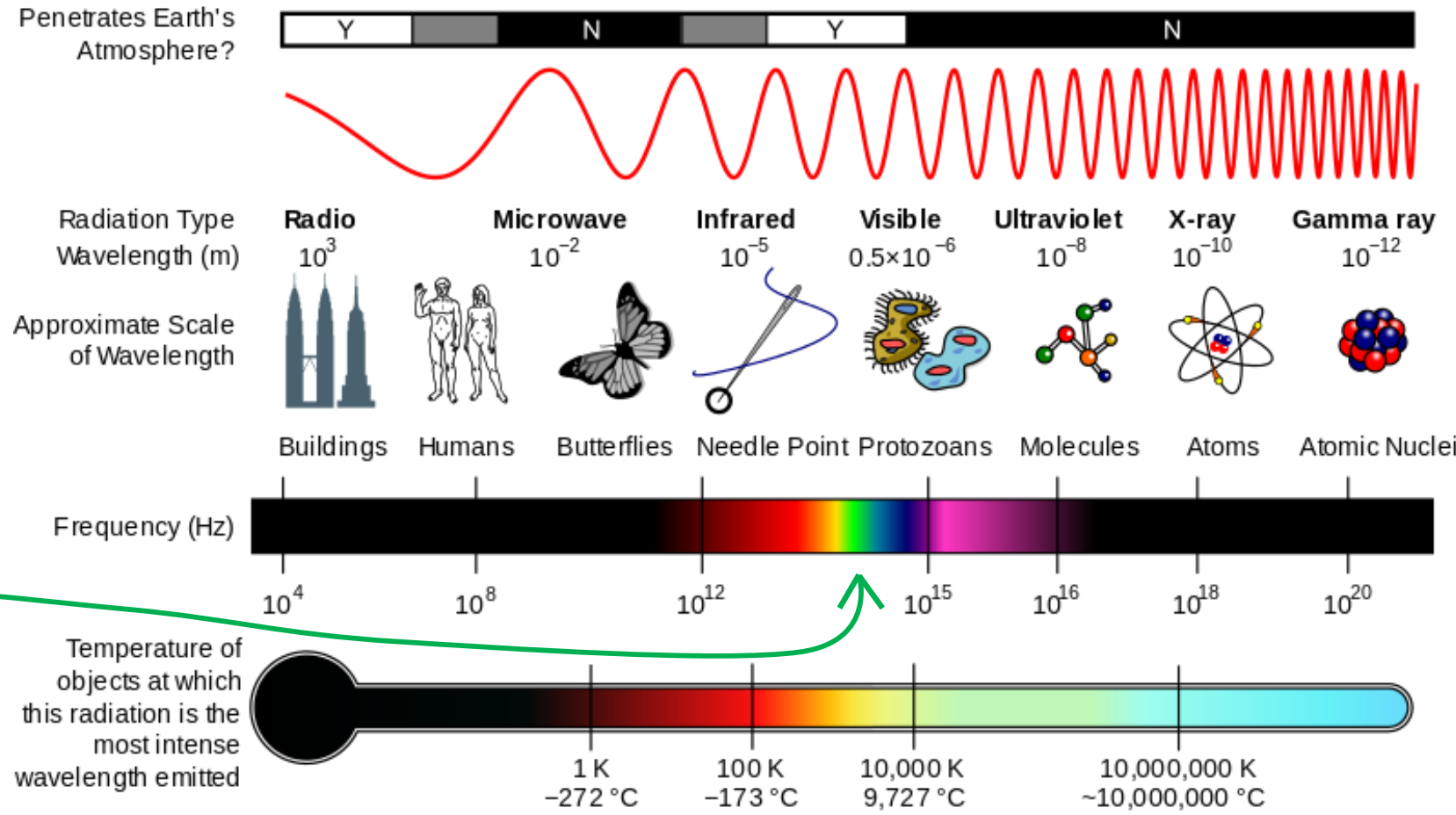
Kinetics vs. Thermodynamics

- Reaction landscapes… every point along landscape corresponds to a different structure
- Height above sea level as a metaphor for potential energy of a structure
- Difference btw pool heights related to thermodynamics
- Lowest energy path related to kinetics (reaction rates)



Form?

- Physical Methods
  - Lotsa clever ways to connect electromagnetic phenomena with atomic and molecular behavior!
  - **ROYGBIV** is only the start…
  - Mass-spectrometry and related methods, too.



https://upload.wikimedia.org/wikipedia/commons/thumb/c/cf/EM_Spectrum_Properties_edit.svg/800px-EM_Spectrum_Properties_edit.svg.png

Too many to go through… so here's some of my favorites

- Vibrational spectrometry
  - Infrared (heat)
  - Raman (usually visible light)
- Magnetic resonance
  - Using radio waves to talk to nuclei
  - More on this next time…
- X-Ray Crystallography

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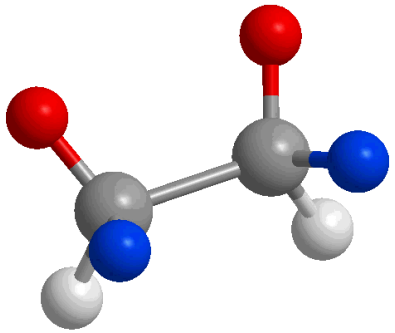
- X-Ray Crystallography

Important for sophomore-level college organic chemistry classes! And research.

Very important for basic science and health-related sciences!

Vibrational Spectroscopy: How do molecules move?

- Translation
- Rotation
- Vibration



Display panel with an ethane: http://chem123chirp2.sites.olt.ubc.ca/files/2016/02/rotate-4.gif

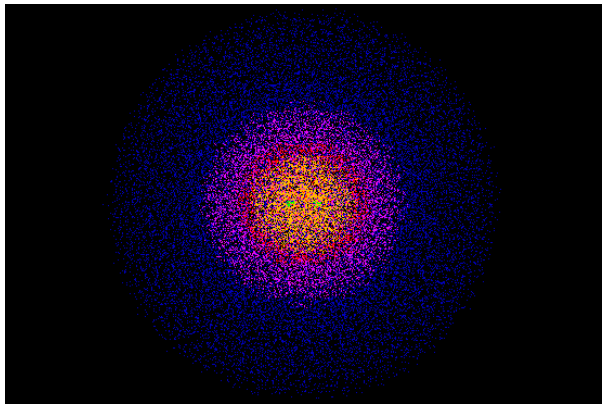
Image from http://chem123chirp.chem.ubc.ca/conformation-section/

Vibrational Spectroscopy

Vibrations are quantized… only certain frequencies allowed in any molecule. Just Hooke's Law behavior for a pendulum of a spring.

Infrared– absorption of a photon causes the molecule's vibration to change from one allowed rate/mode to another.

- Can use Group Theory to predict "normal modes" of molecules. Actually quite easy.



H_2 vibration

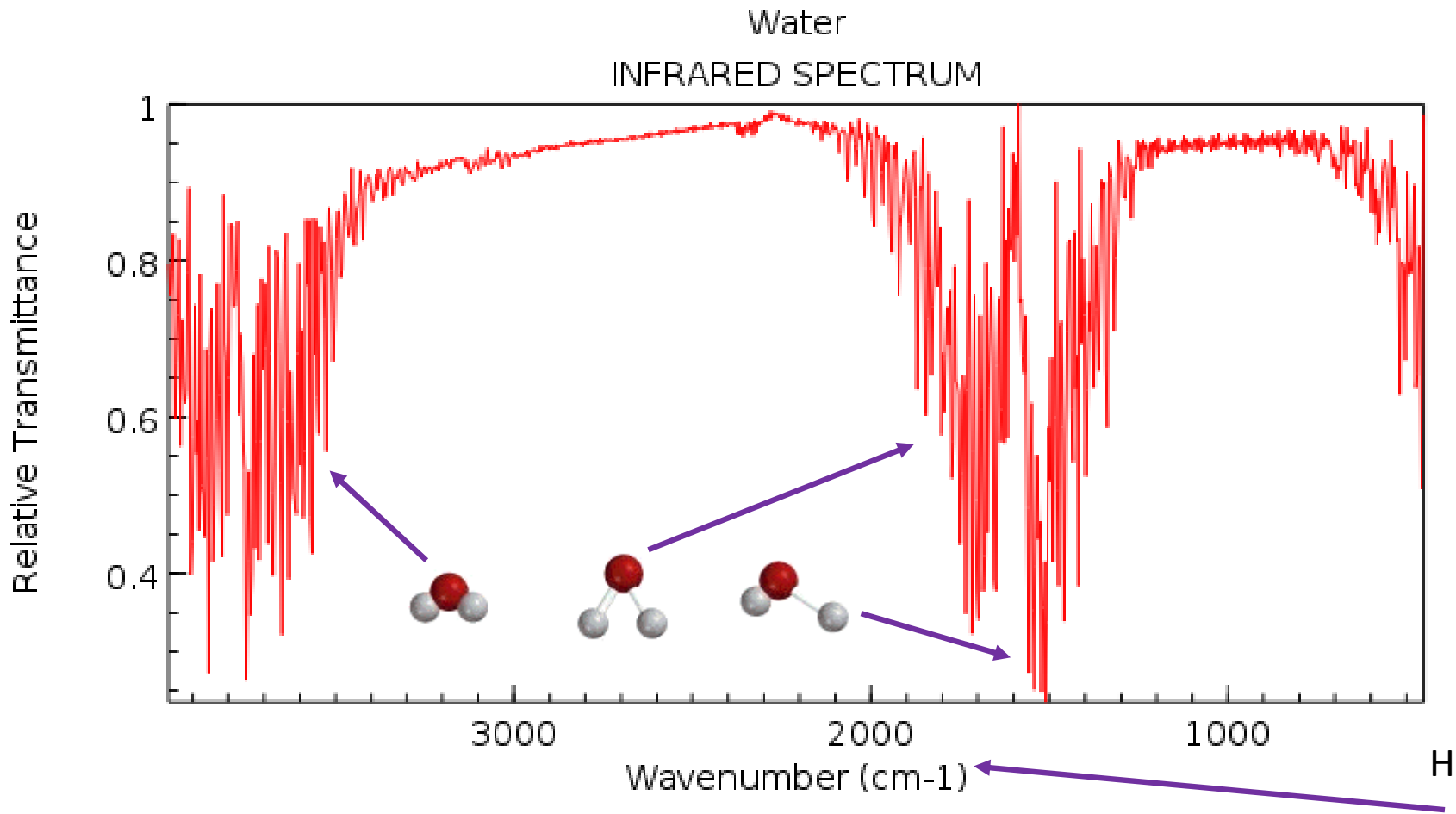
Raman – scattering of a photon (think laser) off of the electron cloud causes vibrational change.

- Photon can steal energy, so photon's frequency increases and molecule's vibration slows
- Photon usually leaves some energy
- Spectrum usually very similar to IR spectrum.

Vibration in water: from http://bestanimations.com/Science/Chemistry/molecules/3-molecules-vibrating.GIF
Vibration in H_2: http://phelafel.technion.ac.il/~orcohen/h2/h2.gif also see main page at http://phelafel.technion.ac.il/~orcohen/h2.html

Gas phase lets you see rotational fine structure….

Gas Phase Spectrum of water

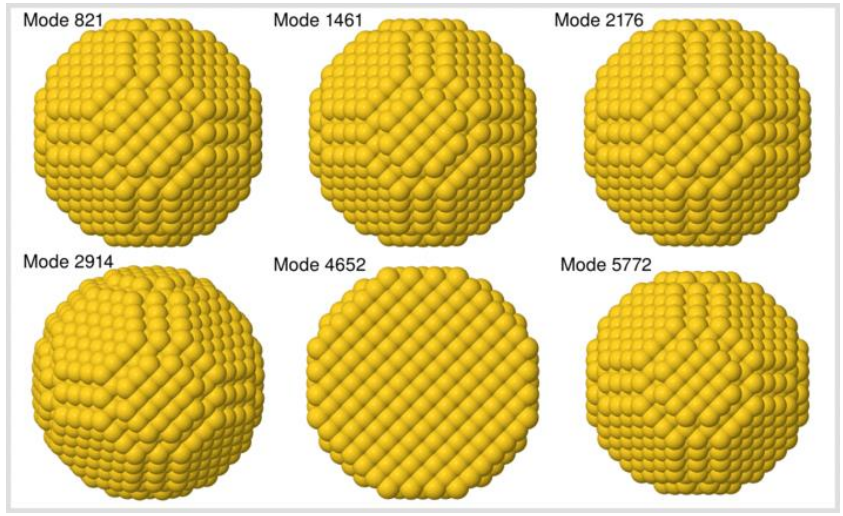


Rez panel with animated gif now.

How many waves are in a cm… Boils down to a measure of frequency

http://webbook.nist.gov/cgi/cbook.cgi?Spec=C7732185&Index=0&Type=IR

Recent computational and experimental results… Can explore vibrations of more complex objects, like gold nanoparticles.

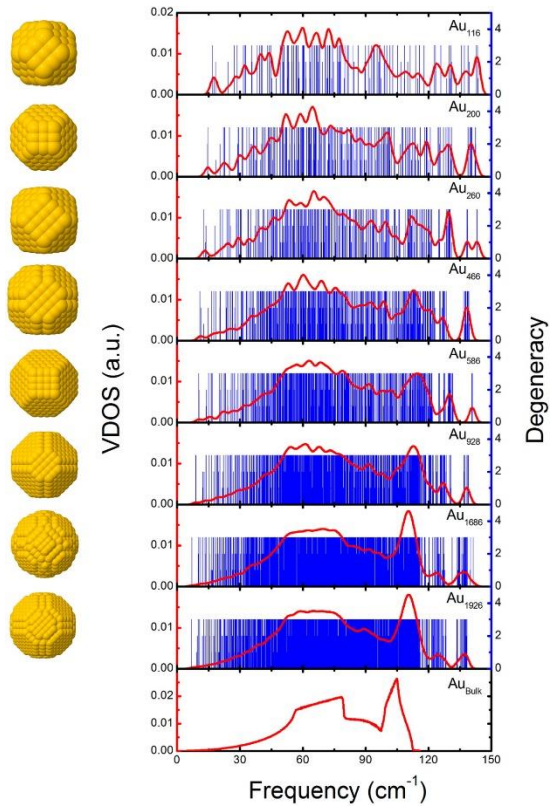


Slide from authors via ACS site next…

Rez panel with animated gif now.

http://pubs.acs.org/doi/media/10.1021/jp408976f/jp408976f_weo_002.gif

H. E. Sauceda *et al*, "Size and Shape Dependence of the Vibrational Spectrum and Low-Temperature Specific Heat of Au Nanoparticles," *J. Phys. Chem. C* **2013,** *117*, 25160-25168. DOI: 10.1021/jp408976f



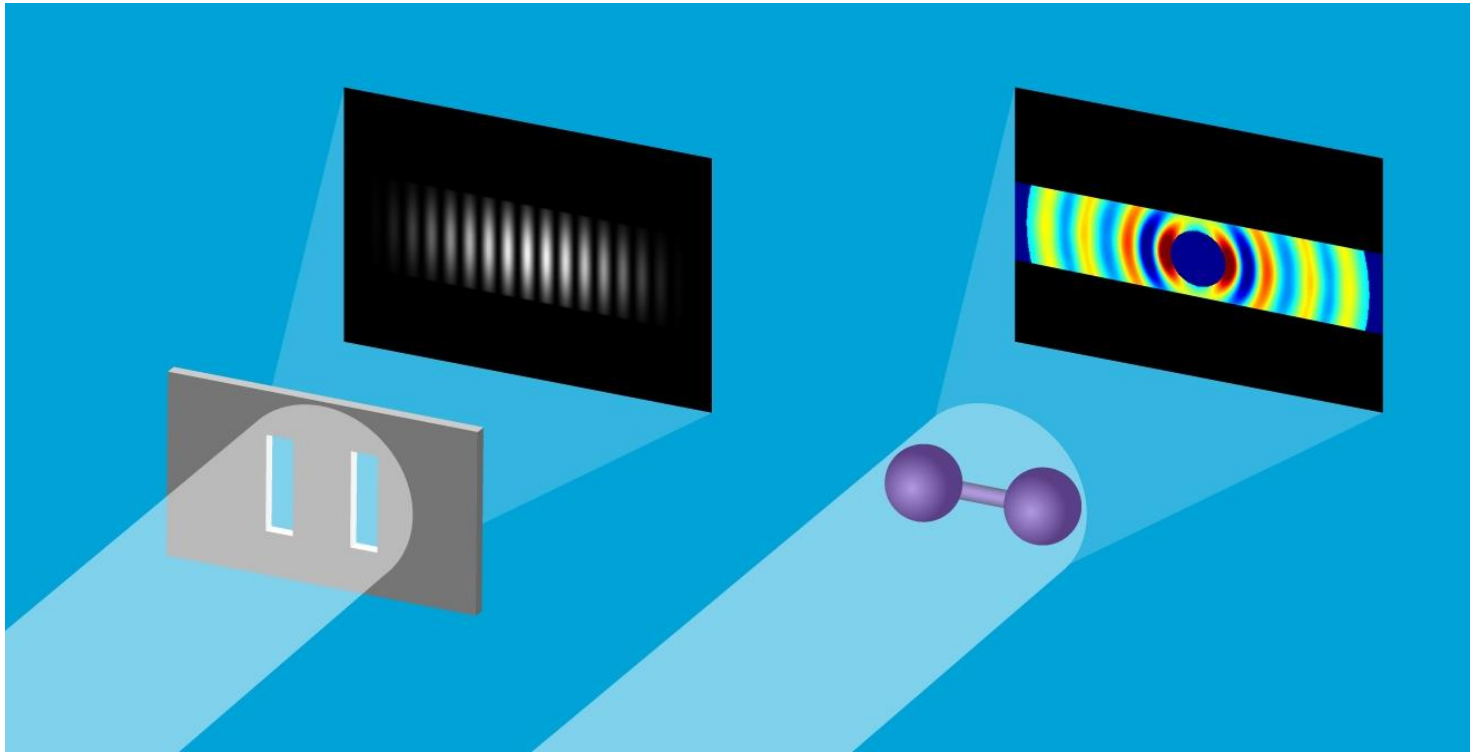
Vibrational frequency spectra (blue bars) and VDOS (red line) of Au nanoparticles with FCC morphologies. The bottom panel displays the Au bulk VDOS calculated for an FCC crystal using the many-body Gupta potential. The VDOSs were scaled to obtain the same value after integration over the whole frequency range. On the left, the corresponding FCC morphologies are displayed.

This slide available from http://pubs.acs.org/doi/full/10.1021/jp408976f

Published in: Huziel E. Sauceda; Fernando Salazar; Luis A. Pérez; Ignacio L. Garzón; *J. Phys. Chem. C* **2013,** 117, 25160-25168.

Cool tools… Ultrafast electron diffraction

1 period = 400 femtoseconds



Rez panel with animated gif now.

https://www6.slac.stanford.edu/files/ued_iodine_gif_final.gif

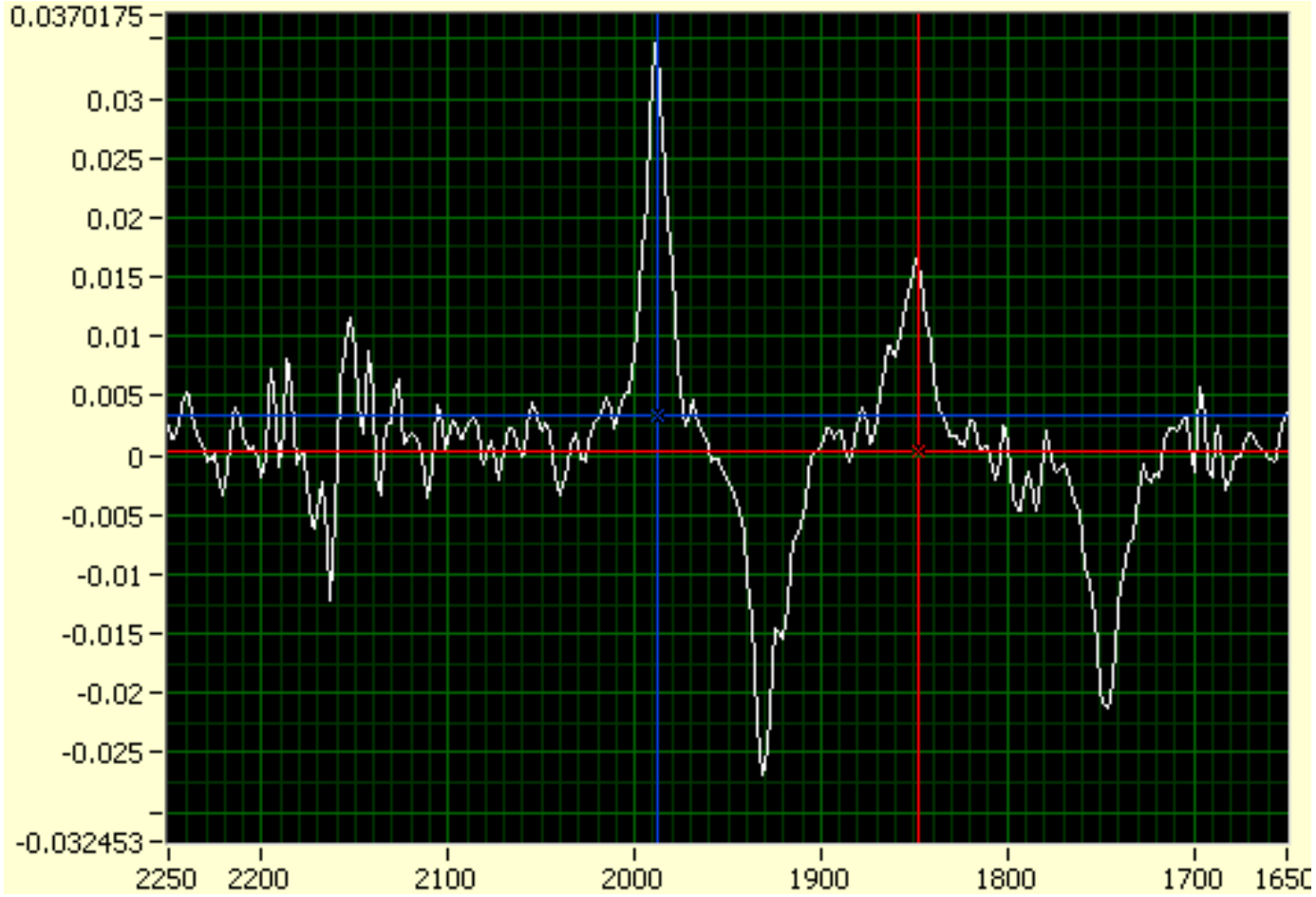
https://www6.slac.stanford.edu/news/2016-08-31-slac-high-speed-electron-camera-films-atomic-nuclei-vibrating-molecules.aspx

J. Yang et al, "Diffractive Imaging of Coherent Nuclear Motion in Isolated Molecules," *Physical Review Letters* **2016**, *117*, 153002. DOI: 10.1103/PhysRevLett.117.153002

An example from my lab

$[Cp^*_2Ru_2(CO)_4]^{0/+}$ redox couple
1.6 to 2.4 s after oxidation, 74 scans

- Time resolved difference spectrum, fiber-optic spectroelectrochemistry.
- M-CO
- More electron rich metal centers, push e^- density into regions on the CO that weakens the C-O bond



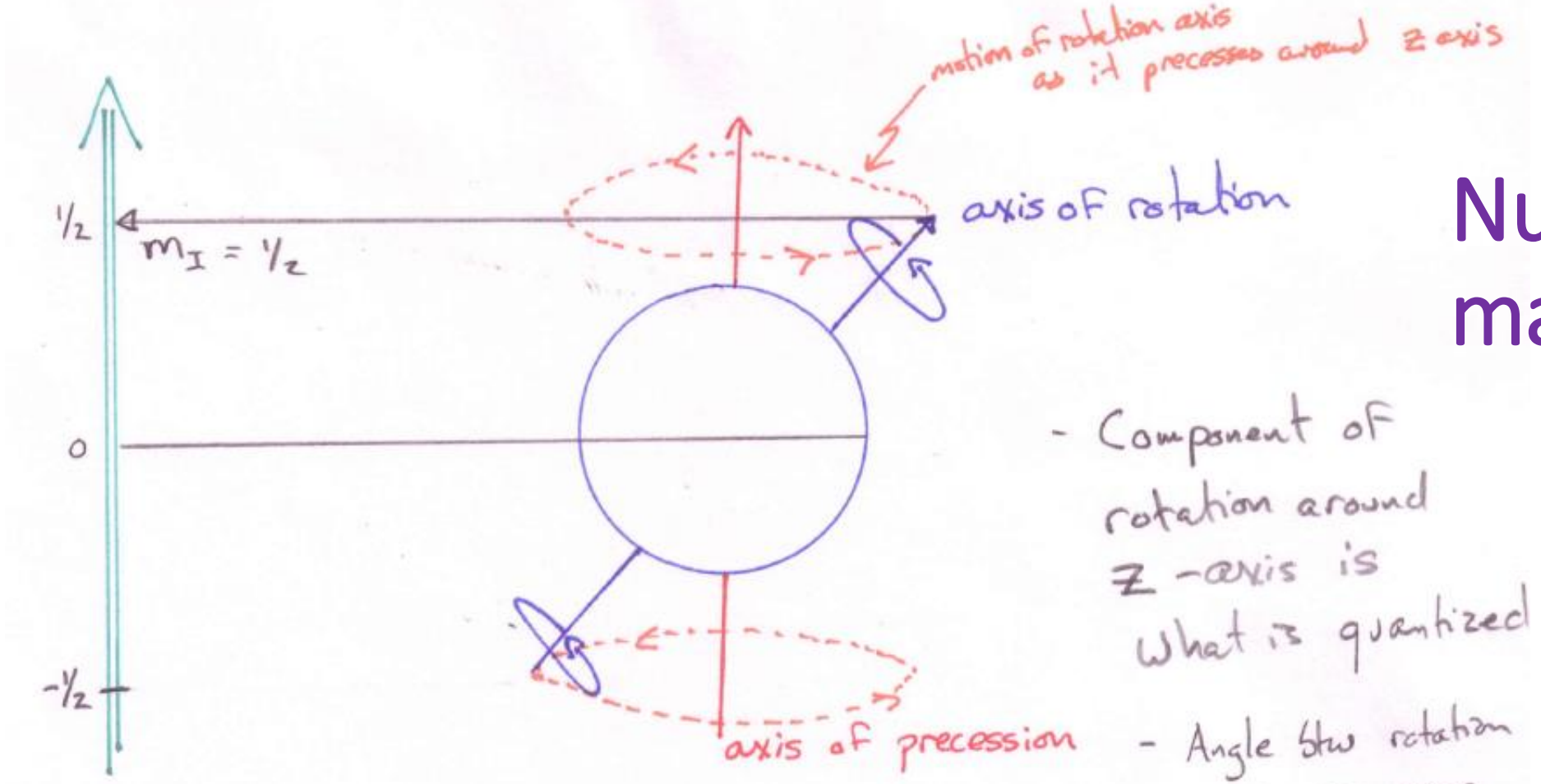
Magnetic Resonance?

- Nuclear Magnetic Resonance!
- No radioactivity!

- Many nuclei have angular momentum = “spin”

- Spinning charge generates magnetic field.
- Can orient a little magnet with or against an external field… takes energy to flip the spin.

Nuclei as magnets



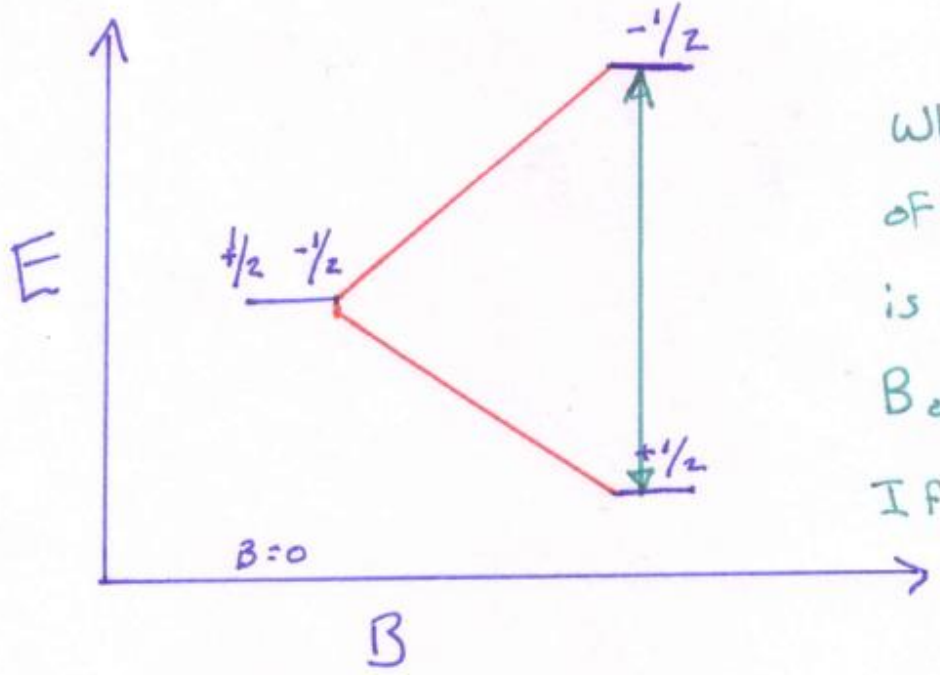
I expect my students to be able to draw this, so I often include hand-drawn images in my classes

Simple Energy Diagram for "Spin-Flip"

Absorption of energy because 2 states are available is the basis for a HUGE number of techniques!

$I = 1/2$ ... Energy Difference btw states proportional to magnetic field B_0 and nucleus' magnetogyric ratio

$E = \gamma \hbar B_0 m_I$



When electromagnetic radiation of the correct wavelength/frequency is applied for a given value of B_0, the states can flip. If more states are flipped from $+1/2$ to $-1/2$, than a net absorption occurs

∴ NMR sensitivity depends on energy difference ....

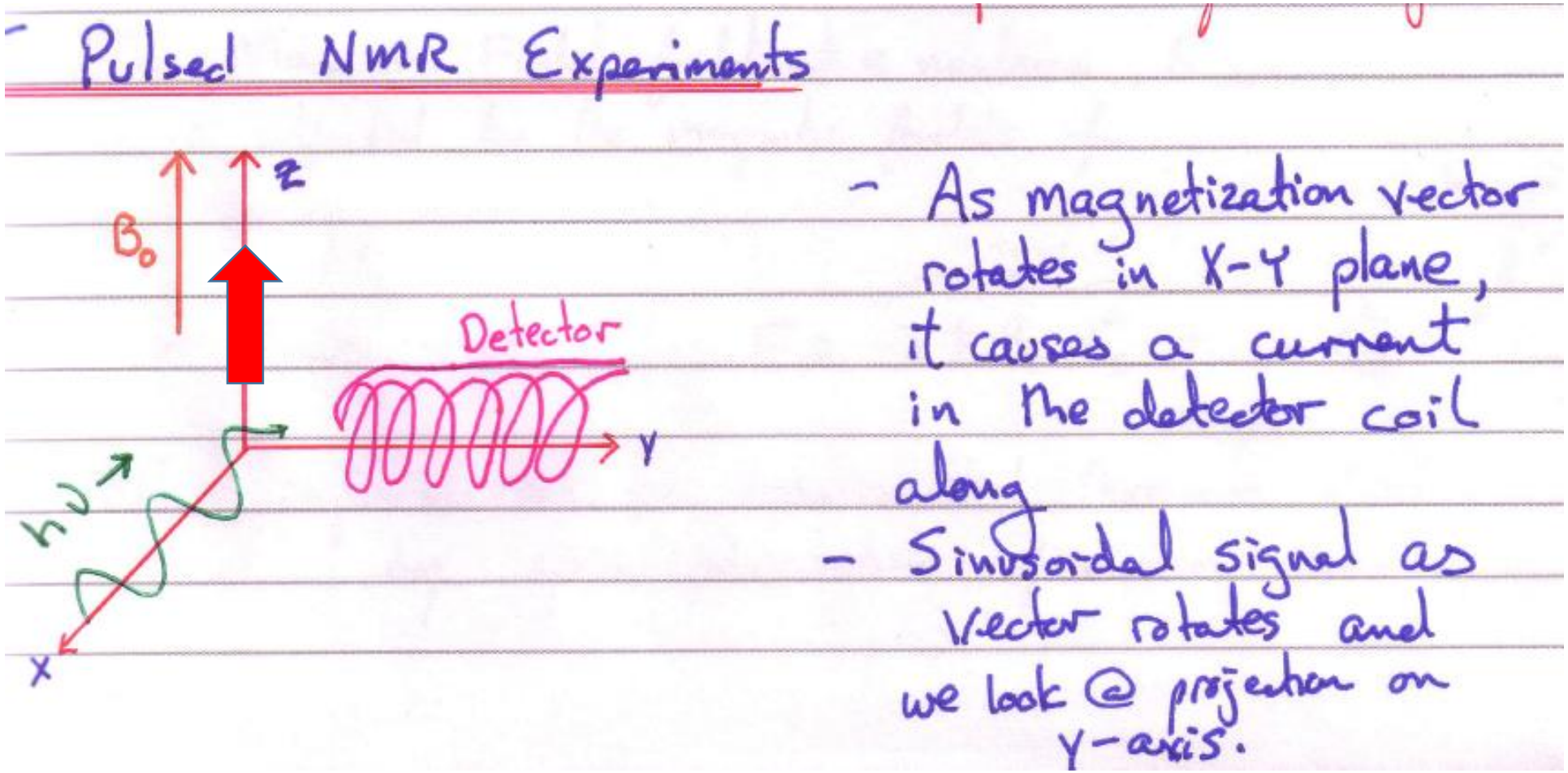
Best for largest $\gamma \rightarrow {}^1H$

For many nuclei….

- Energy difference is very small between 2 states
- At 25°C, often have only 1 in a million excess of lower state
- Still enough to have a “bulk magnetization vector”

Can manipulate direction of this vector by applying bursts of radio waves!

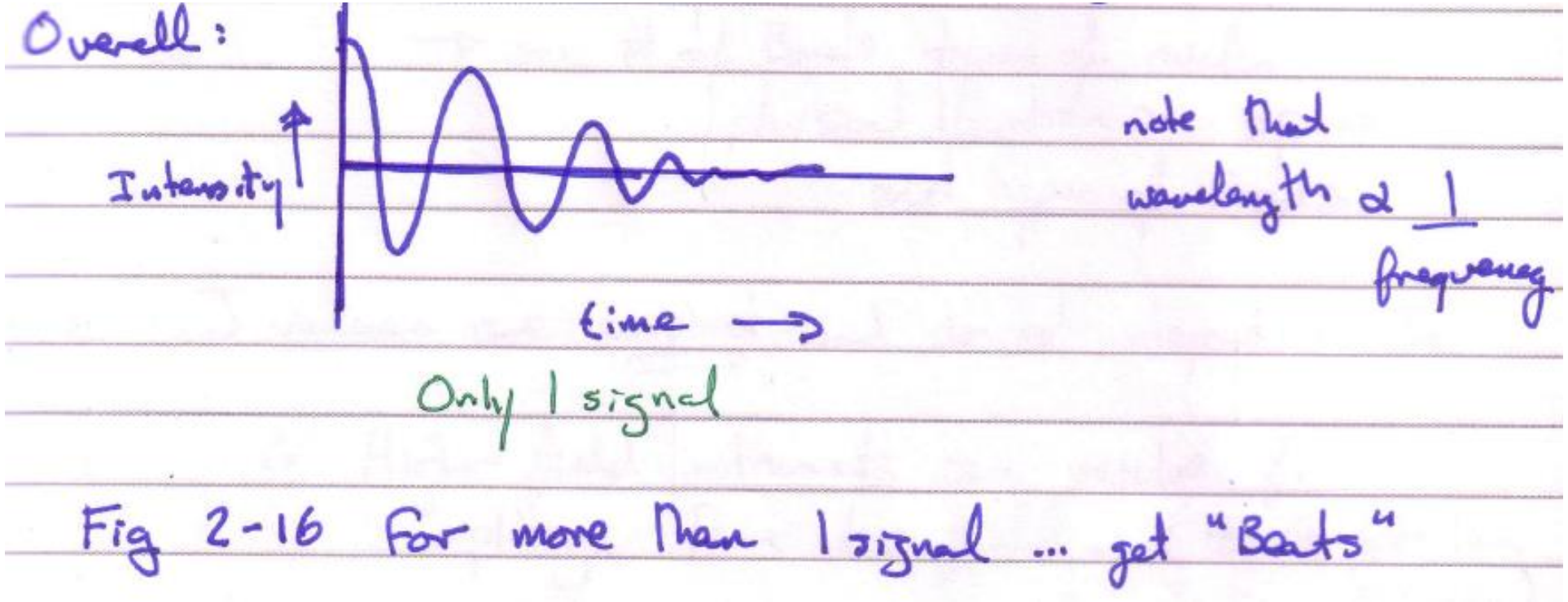
Pulsed NMR experiments



Show https://i.stack.imgur.com/rHsxs.gif

From https://mathematica.stackexchange.com/questions/115675/pulsed-nmr-animation

Overall Signal:



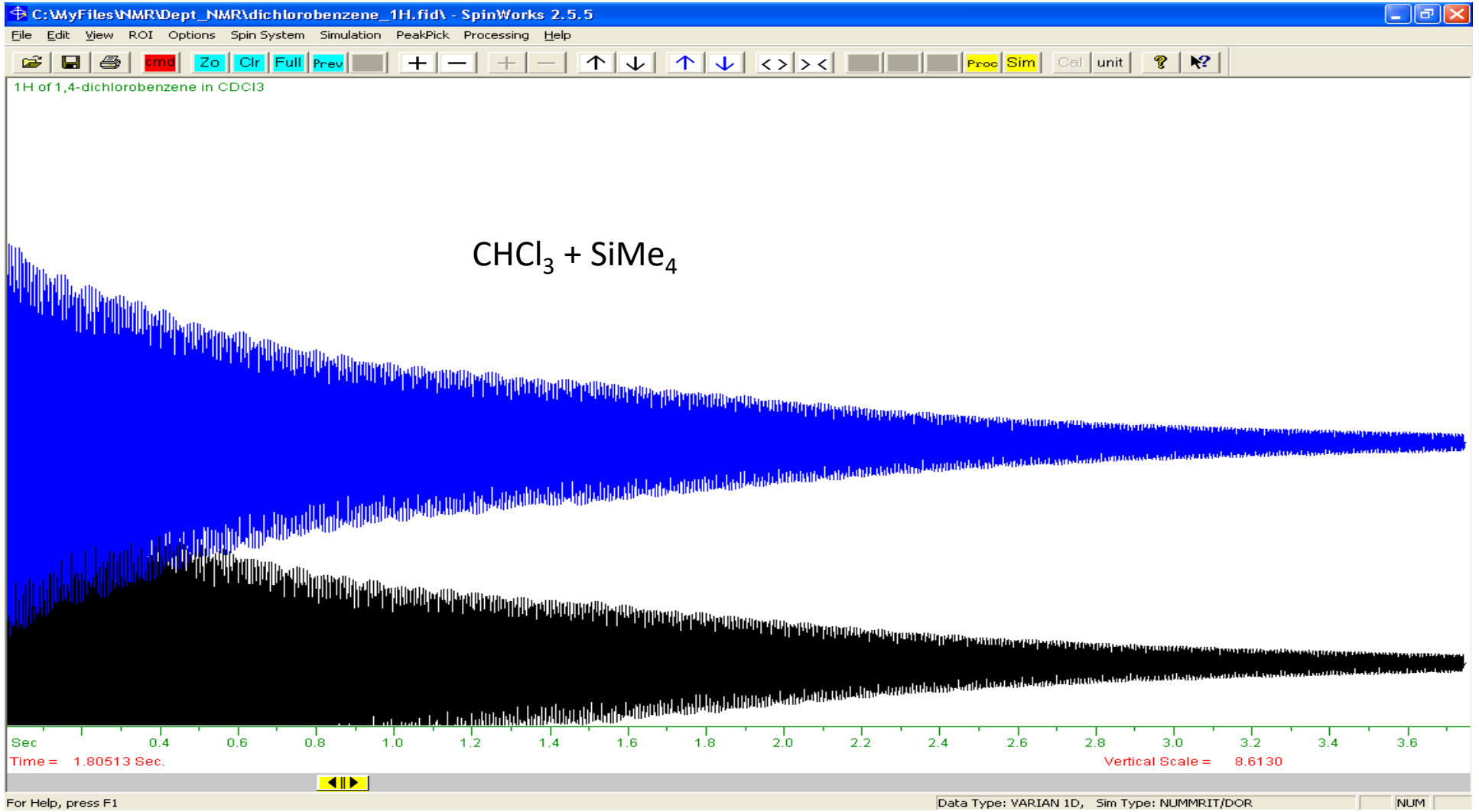
Show https://i.stack.imgur.com/rHsxs.gif

From https://mathematica.stackexchange.com/questions/115675/pulsed-nmr-animation

FID for $CDCl_3$ solvent

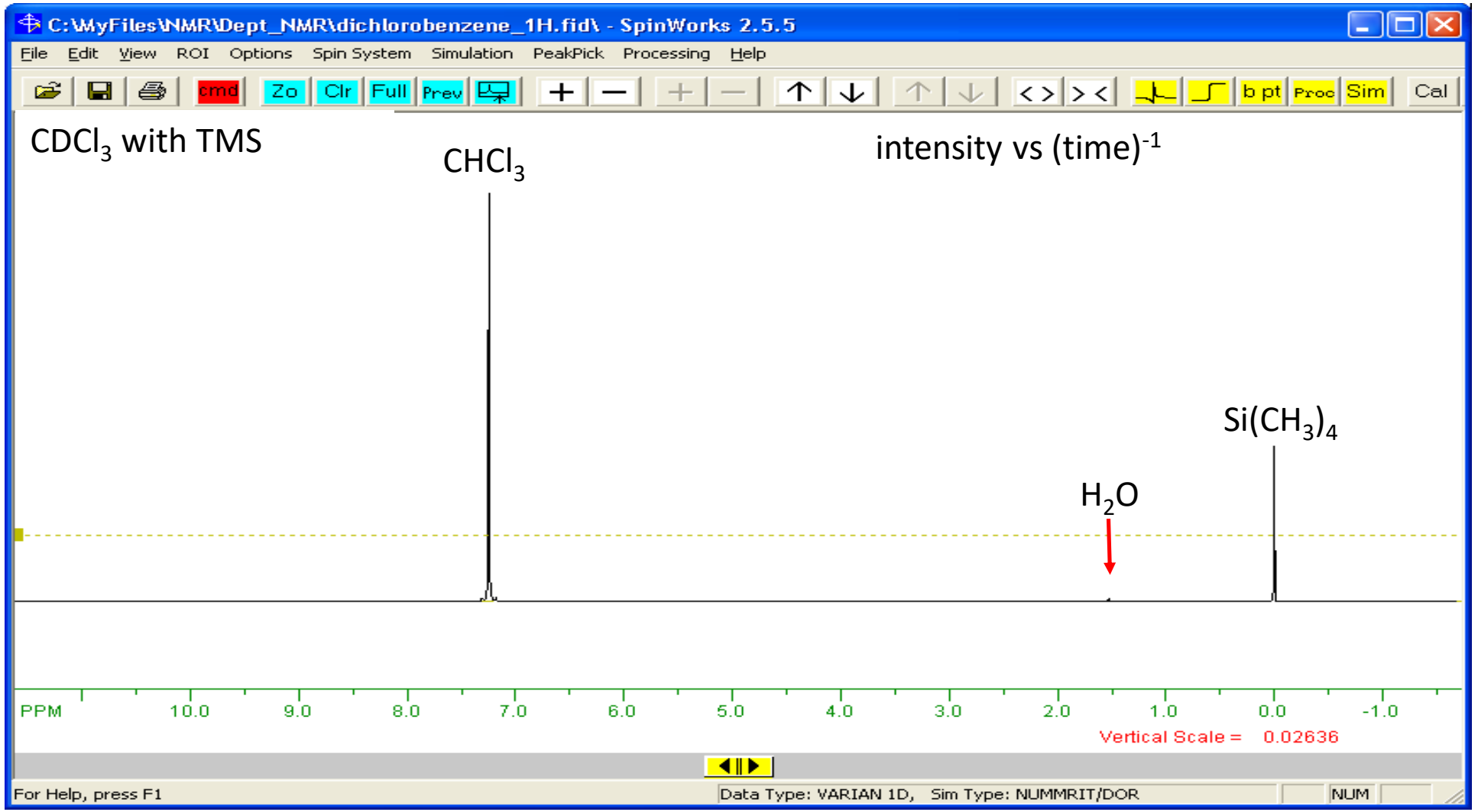
The black plot is a duplicate of blue… ignore.

I collected this data a few years ago on our 300 MHz Varian spectrometer



FT takes “x” axis, and turns it into “1/x” axis

Fourier Transformed ^{1}H Data



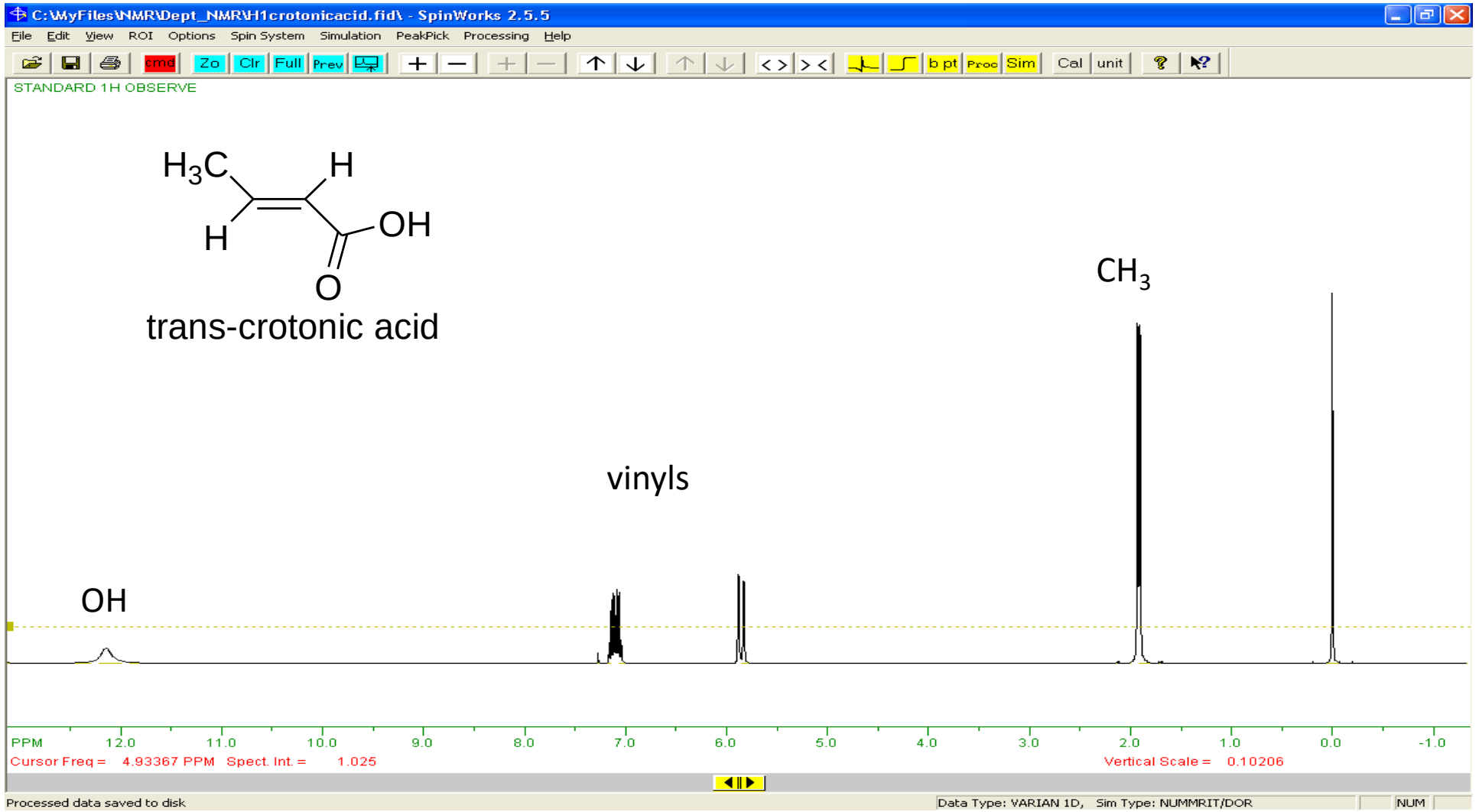
Student had forgotten to dissolve analyte… ended up just seeing what’s in the solvent

Fundamental info

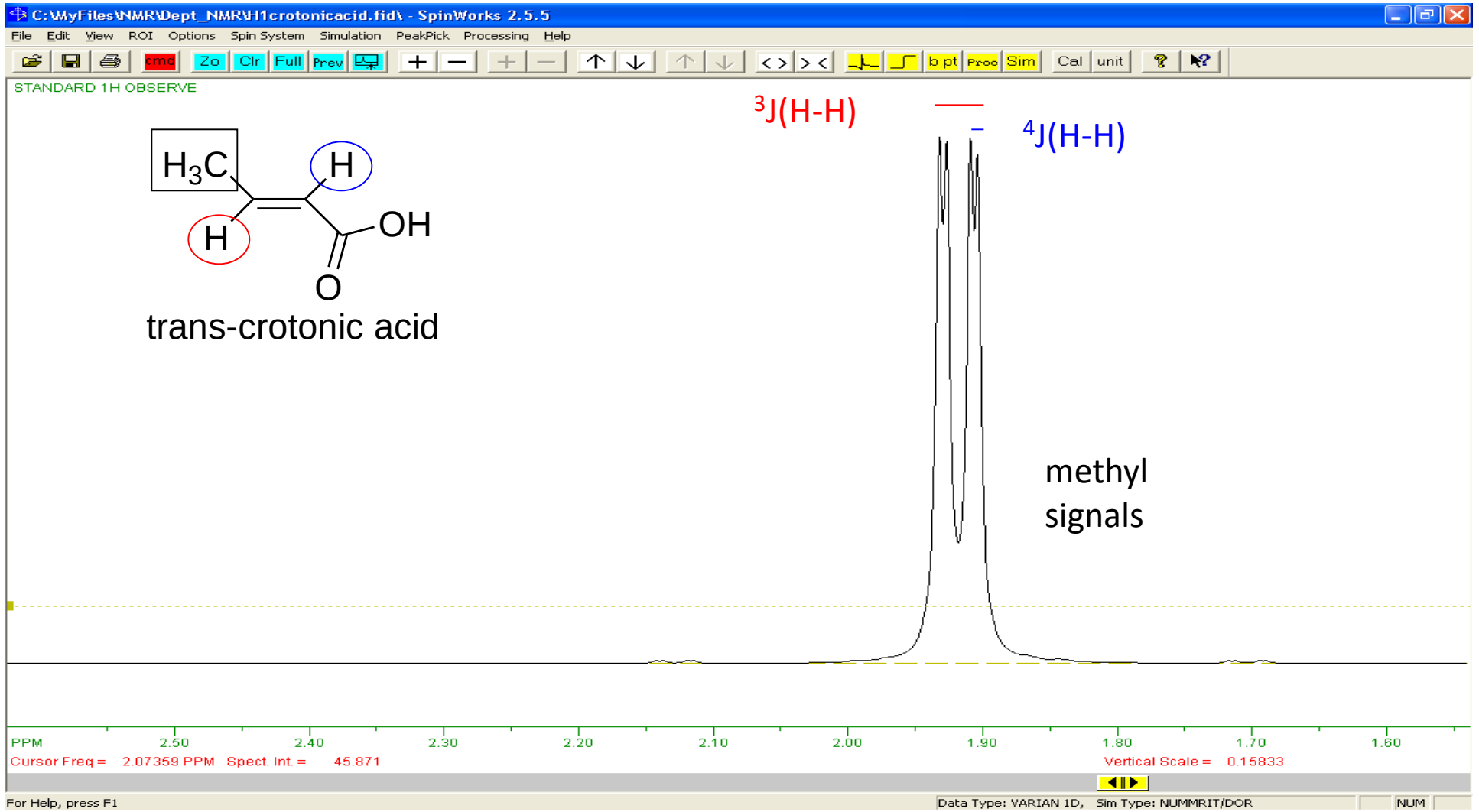
- Areas under peaks
  - Tell you relative numbers of types of nuclei you're looking at
- Position on x-axis
  - Tells you the electronic environment of specific type of nucleus
- "Couplings" or peak splittings
  - Tells you about the closest NMR-active nuclei: what type and how many of the closest

- Can tune to different channels: ^{1}H, ^{2}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P, ^{119}Sn, even ^{195}Pt… dozens more.

More Complicated Couplings: Crotonic Acid



Crotonic Acid Zoom



Basic Theory

Basic theory simplified:

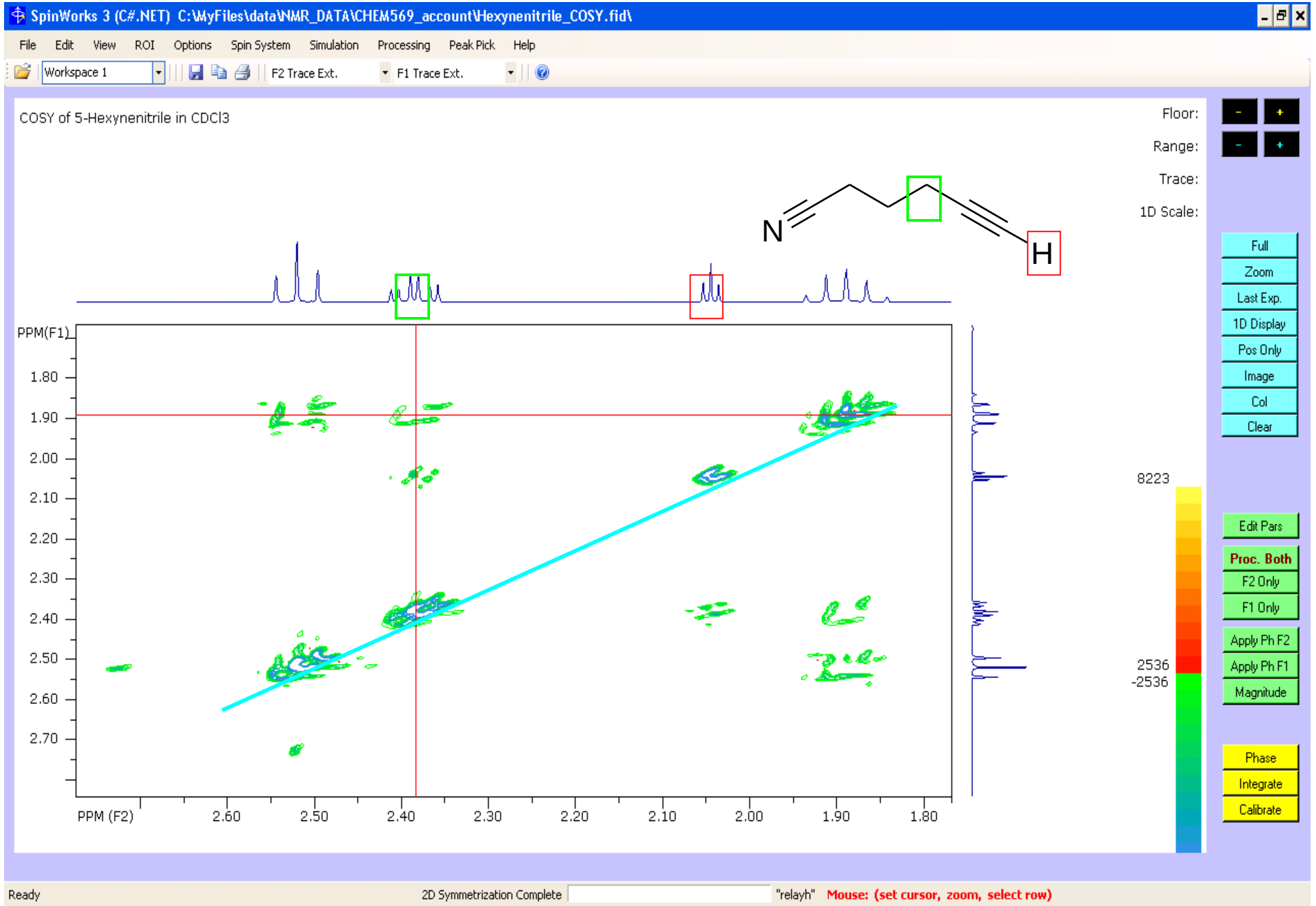
→ a pulse can be expressed as the sum of sine waves

→ therefore, choosing a pulse time + delay is the same as choosing a set of frequencies to direct at sample

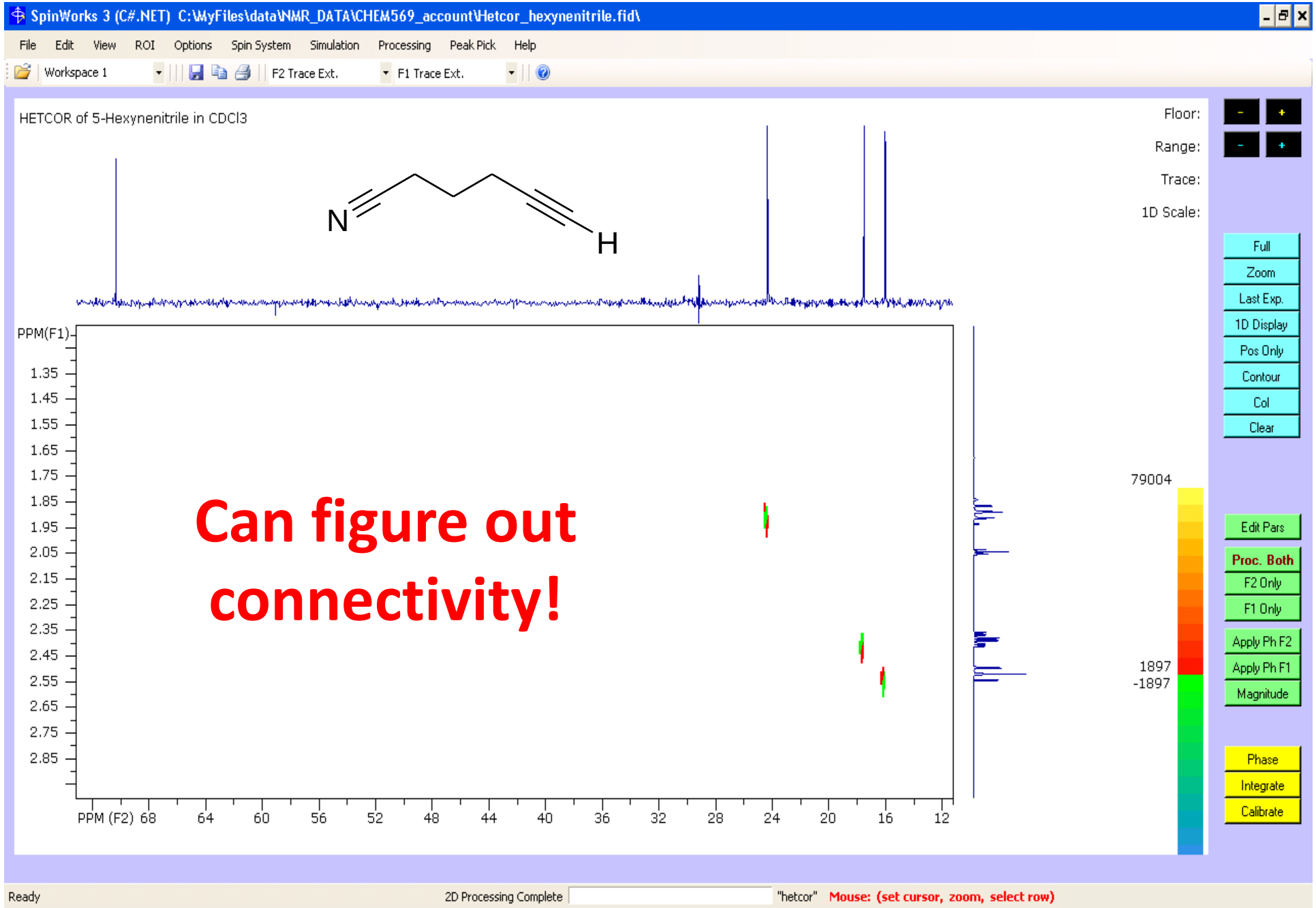
→ can take advantage to selectively irradiate at different frequencies, then determine effect on intensities of rest of signals.

Basis of 2-dimensional NMR!

COSY of 1-hexynenitrile (Alt-PrtSc)



HETCOR of 1-hexynenitrile



NMR is basis of Magnetic Resonance Imaging

- NMR is a huge field…
- Will talk about some types of imaging methods next time.

X-Ray Crystallography… diffraction method

Diffraction:

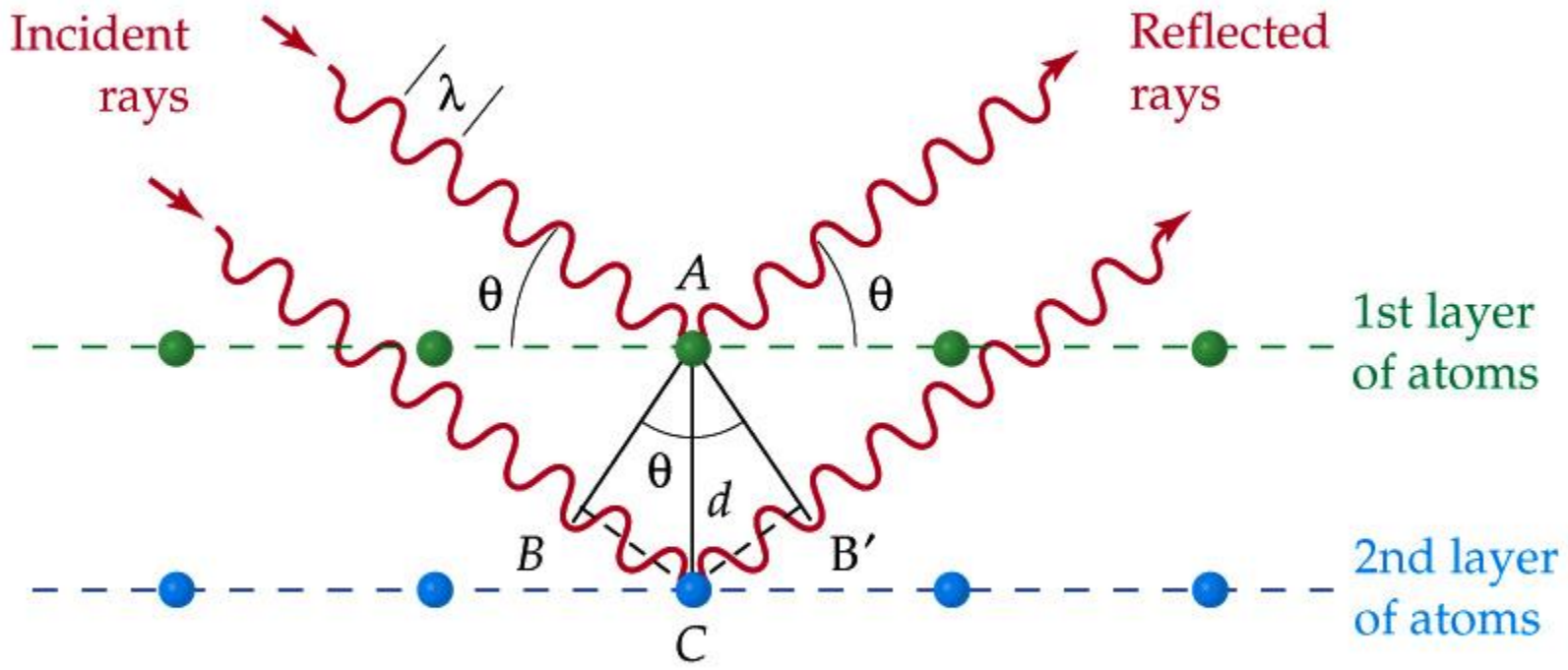
https://upload.wikimedia.org/wikipedia/commons/thumb/0/0f/Doubleslit3Dspectrum-blue.gif/117px-Doubleslit3Dspectrum-blue.gif

Rez panel with animated gif now.

From Wikimedia Commons, image edited by Sbyrnes321, available at https://commons.wikimedia.org/wiki/File:Doubleslit3Dspectrum-blue.gif

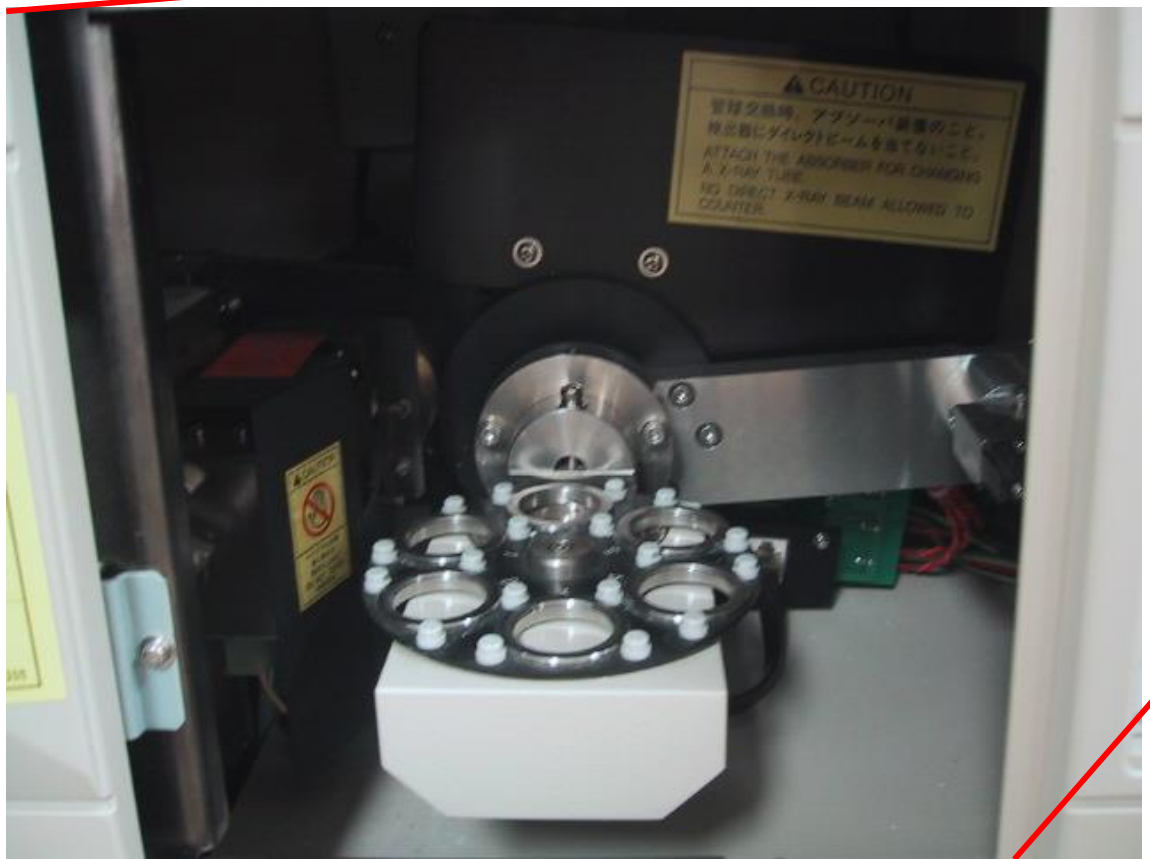
X-Ray

Bragg's Law:
$2d \sin\theta = m\lambda$



3D-lattice of atoms will result in a 3D pattern of bright spots around crystal. Use LOTS of automated math to solve

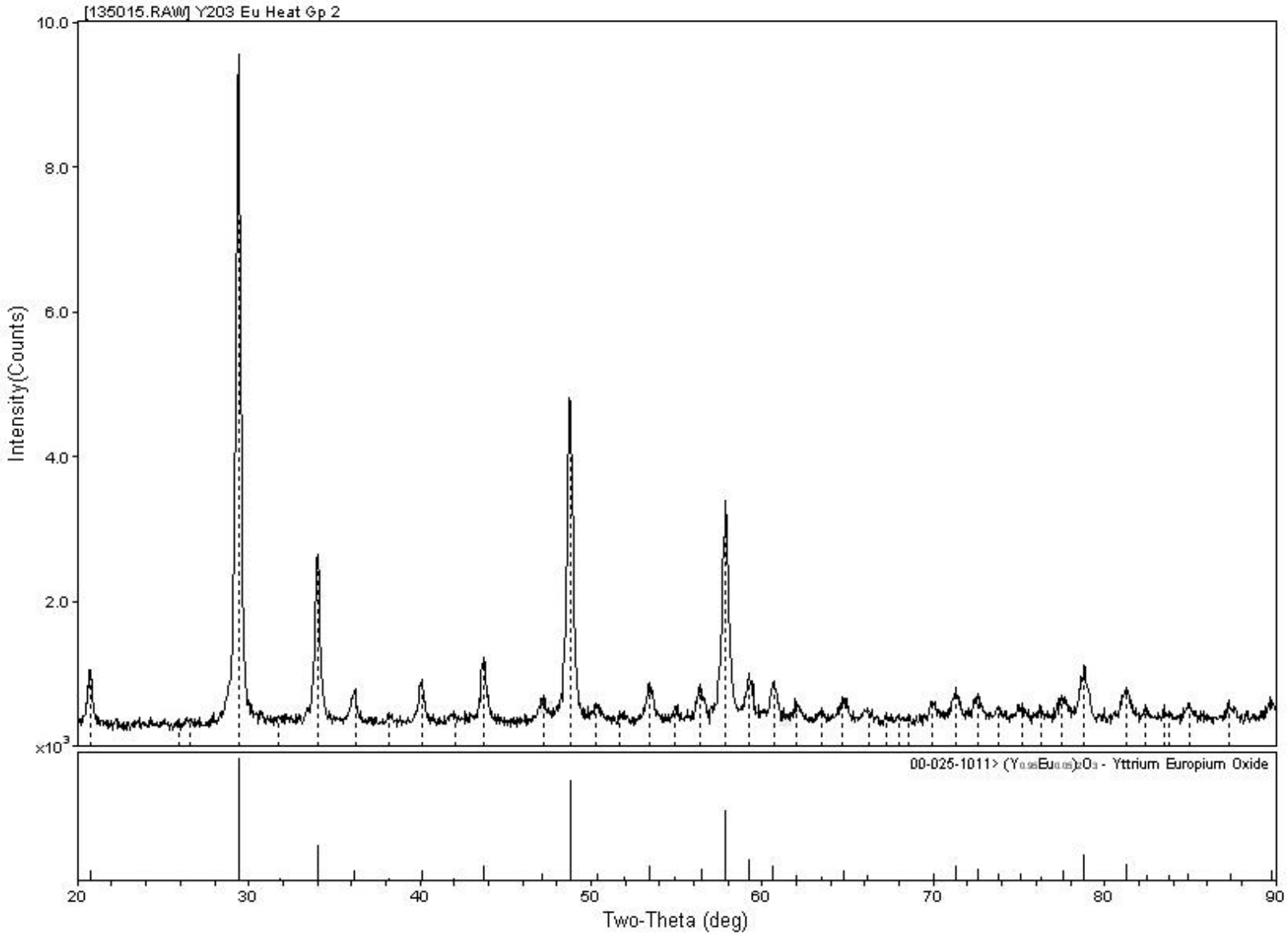
X-Ray Diffractometer



Sample Data for Y_2O_3

Powder data

Gives unit cell, but no detail on what's in the unit cell

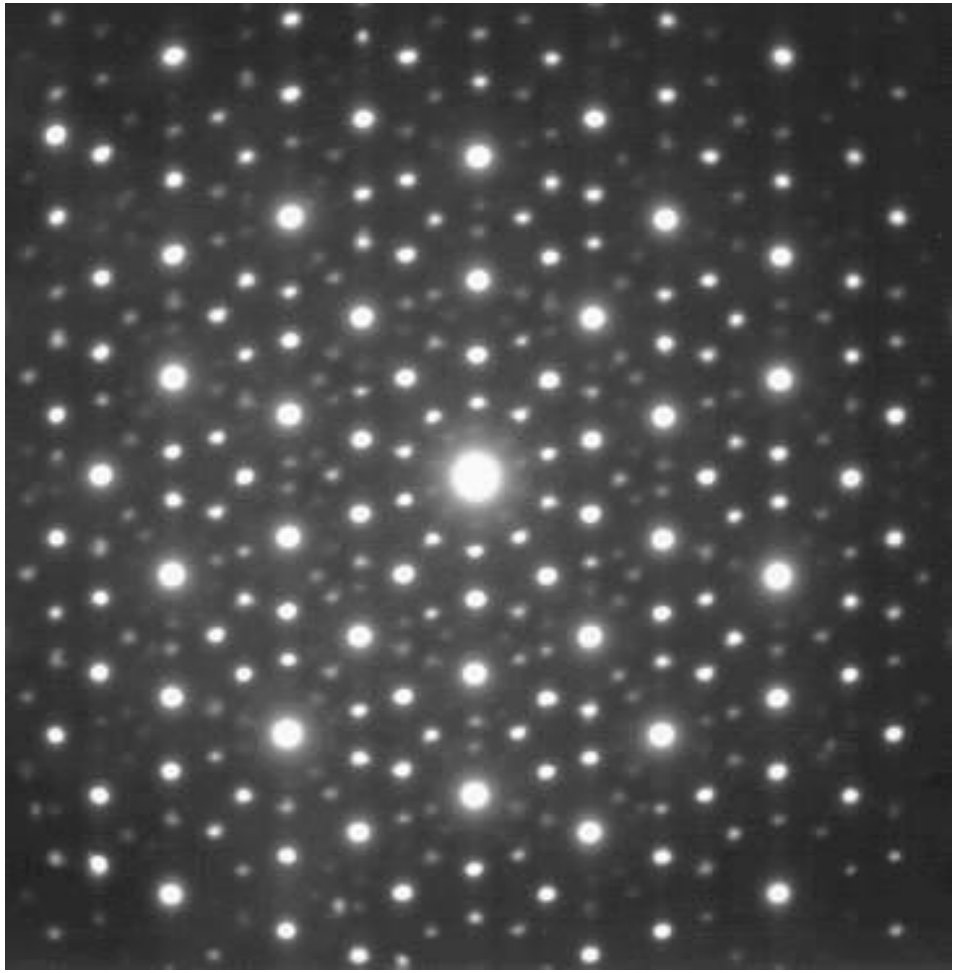


Example diffraction pattern

X-Ray diffraction example:

https://commons.wikimedia.org/wiki/File:Zn-Mg-HoDiffraction.JPG

Pattern implies crystalline structure… an expert could tell you exact structure from the X-Ray pattern



From Wikimedia Commons, the free media repository, uploaded by MaterialScientist, see https://commons.wikimedia.org/wiki/File:Zn-Mg-HoDiffraction.JPG

Single Crystal X-Ray Diffraction

- Gives a “snapshot” of molecular structure
- Very useful when “sporting” methods like IR and NMR aren’t enough.
- Can now use for largish bio-molecules to study drug-receptor interactions

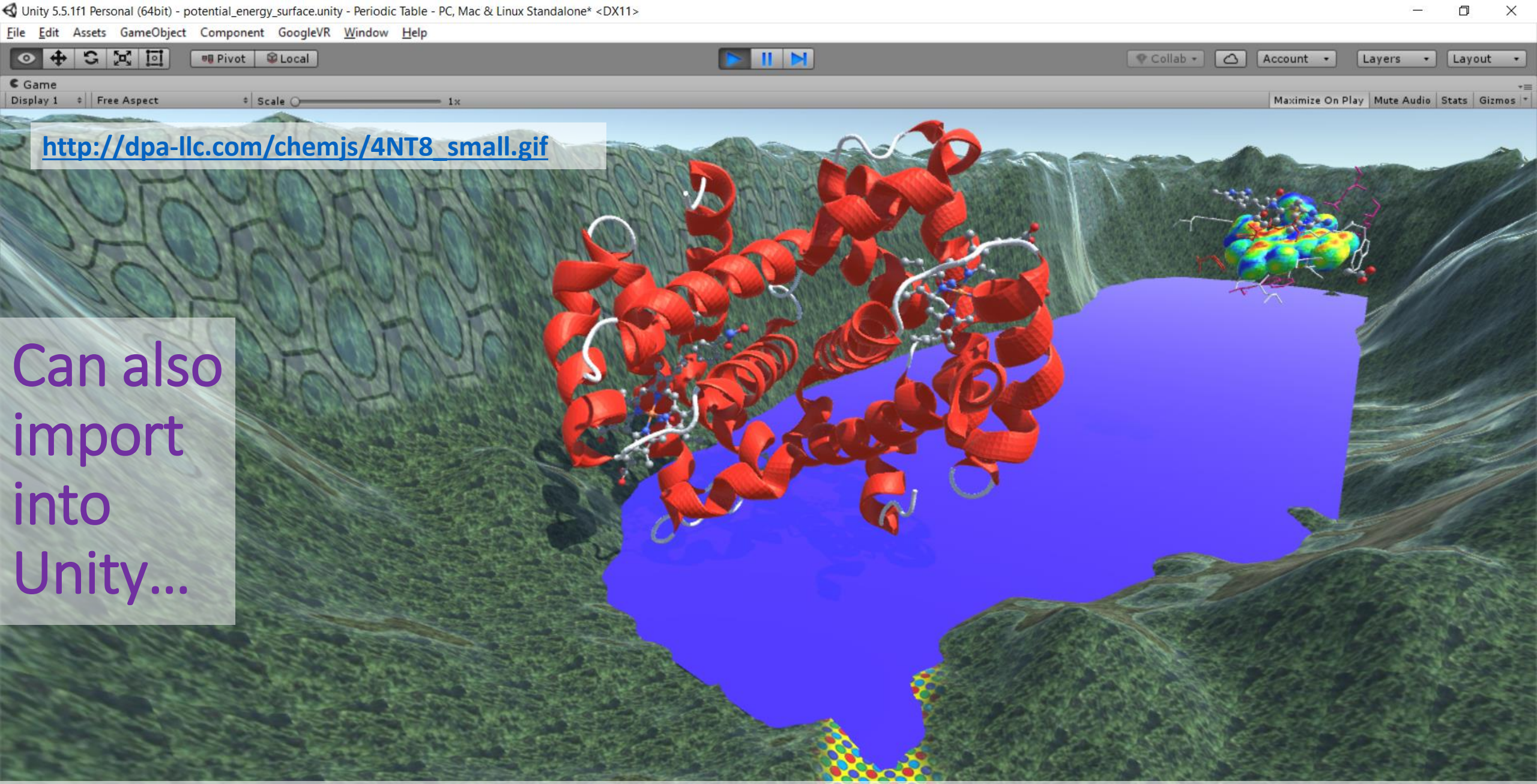
- Open source access via:
- http://www.crystallography.net/cod/index.php
- http://rruff.geo.arizona.edu/AMS/amcsd.php
- http://www.rcsb.org/pdb/home/home.do

Small molecule
American Minerologist site
Protein Crystallography site

Convenient

- Can use JMOL (http://jmol.sourceforge.net/) to view “cif” files, eport as X3D files
- Can use Blender to edit (remove atoms inside of other atoms) and then export as DAE files
- Can import DAE files into Second Life.

- A couple of examples (two iron structures, and a Tc cluster)



3NP5 structure from http://www.rcsb.org/pdb/home/home.do , Human nitric oxide synthase
4NT8 structure from RCSB site, Human hemoglobin-NO complex, Richter-Addo et al.

Thanks!

- Members and Students of the Science Circle!
- Students and Faculty of Dept. of Chem., SIUE.
- Generous support of National Science Foundation for our work on heme-nitrosyl complexes,
  NSF-CHE 1566509
- My cats for their patience…