

ASSIGNMENTS FOR CHAPTERS 13, 14, & 11

CHMY 361
November 16, 2018

November-Dec. 2018

361 Lec 39
Fri 16nov18

Note: Exam 4: Fri., Nov. 30

Homework # 6 Due Tue Nov. 20

Homework # 7 Due Tue Nov. 27

Lectures and Reading Assignments:

<u>Date</u>	<u>Reading</u>	<u>Subjects</u>
Thur 15 Nov	526-530 539-543: NMR I	Vibrational spectroscopy;
Fri 16 Nov	544-548	Magnetic Resonance (NMR)
Mon 19 Nov	562(bottom)-566 Review MRI for HW 7; back to pp 542, 544-546 with Boltzmann and quantum ideas	MRI of simple objects

Tue 20 Nov **Homework #6 Due 9 am.**
555-562(browse) NMR (2D techniques)
565-566 Magnetic Resonance Imaging MRI)

Mon 26 Nov 412-416 Quantum Origins and Concepts; "Understanding"

Tue 27 Nov **Homework #7 Due 9 am.**
417-421 Quantum Calculations: the Schrodinger Eq.
Climate Science I (from Handout and web sites)

Thur 29 Nov Review for Exam 4

Fri 30 Nov EXAM 4 (on material covered through Mon, Nov 27)

Mon 3 Dec Climate Science II, Greenhouse effect (from Handout and web sites)

Tue 4 Dec Learning outcomes obligation: ACS standardized exam.
This is voluntary but important and expected.

Thur, Fri 6-7 Dec Review for Final

Monday	Tuesday	Wednesday	Thursday	Friday
5	6 Election	7	8	9 Ex 3
12	13 Veteran's	14	15	16
19	20 HW#6 due	21 Thank	22 Thank	23 Thank
26	27 HW#7 Due	28	29 Review	30 Exam 4
3	4 ACS PChem Exam Does not affect grade		6 Review for Final	7 Review for Final
			13 FINAL EXAM 4-5:50	

The **FINAL EXAM** is scheduled by the Registrar, and according to the Fall Exams and Finals Schedule is on **Thursday, Dec 13, 4-5:50 PM.**

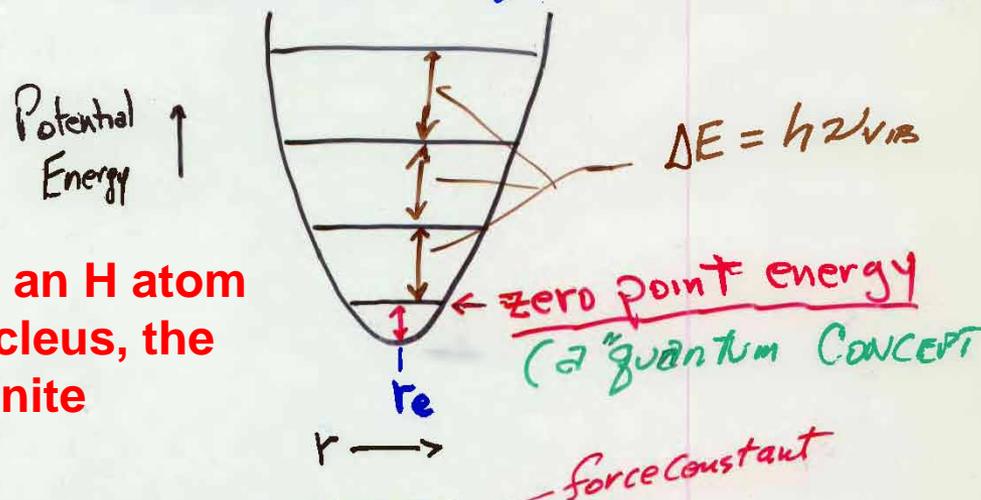
Chemical Bond \cong Hooke's Law Spring

361 Lec 39
Fri 16nov18

$$\text{Potential Energy} = \frac{1}{2} k (r - r_e)^2$$

\uparrow force constant

where r_e = equilibrium bond length



Just as the electron in an H atom does not fall to the nucleus, the bond does sit at a definite distance.

$$\nu_{\text{vib}} = \frac{1}{2\pi} \sqrt{\frac{k}{\text{mass}}}$$

\leftarrow force constant

IF $^{12}\text{C}-\text{H}$ has $\nu_{\text{vib}} = 3000 \text{ cm}^{-1}$
 then $^{13}\text{C}-\text{H}$ " " = $\sqrt{\frac{12}{13}} \times 3000 \text{ cm}^{-1}$
 = 2882 cm^{-1}
 For C-D $\nu_{\text{vib}} = \sqrt{\frac{1}{2}} \times 3000 = 2121 \text{ cm}^{-1}$

Fig. 13.26

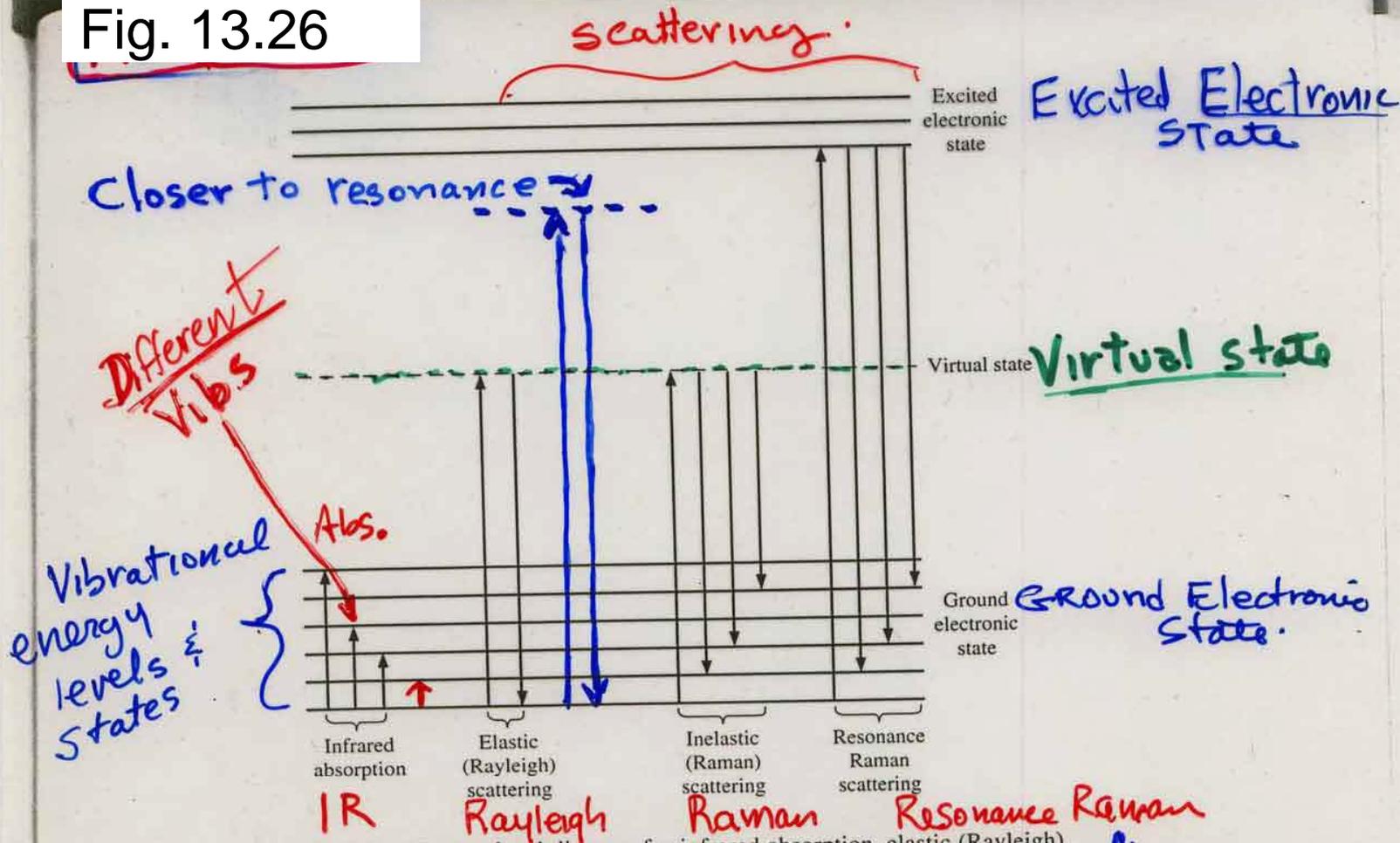


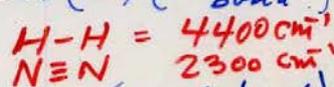
Fig. 10.41 Energy-level diagram for infrared absorption, elastic (Rayleigh) scattering, and inelastic (Raman) scattering. Transitions between vibrational energy levels of the ground electronic state absorb infrared radiation; not all transitions are allowed. For elastic scattering the frequency of the incident light is equal to the frequency of the scattered light. For inelastic scattering the frequency of the scattered light is different from that of the incident light. The virtual state shown can have any energy; the scattering of light occurs in any region of the spectrum.

~ 1000 times enhanced.

Vibrational Signatures

$$\nu_{\text{VIB}} = \frac{1}{2\pi} \sqrt{\frac{k}{\text{mass}}}$$

High Freq. from $\frac{1}{m}$ large force constant (K) (strong bond)
 Small mass



Low Freq. from $\frac{1}{m}$ small force const. (weak bond)
 large mass.



Stretching:
 Bond $\frac{1}{m}$ cm⁻¹

O-H 3600

C-H 3000

C≡C 2100

C=O 1700

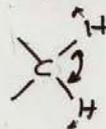
C=C 1600

C-C 900

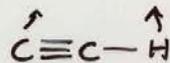
C-I 500

I-I 200

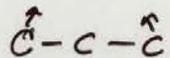
Bending:



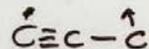
1450 cm⁻¹



700

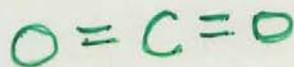


~ 500



300

What if two identical bonds strongly coupled?



Normal Mode Demo.

NORMAL MODES OF BENZENE

C-H stretches

3061 cm^{-1}
1158 cm^{-1}

$3N-6 = 30$ vibrat
mod
N = number of atoms

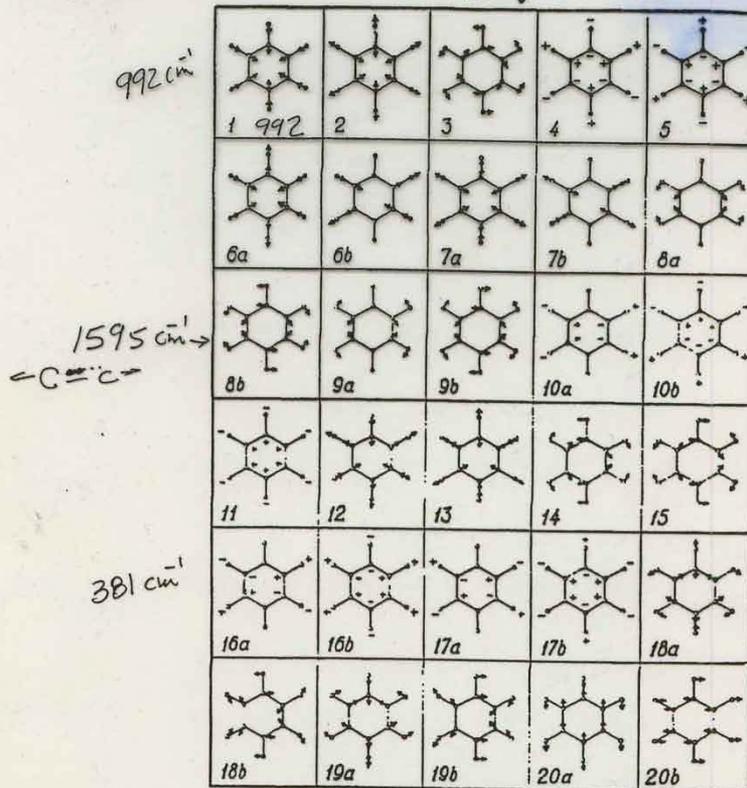
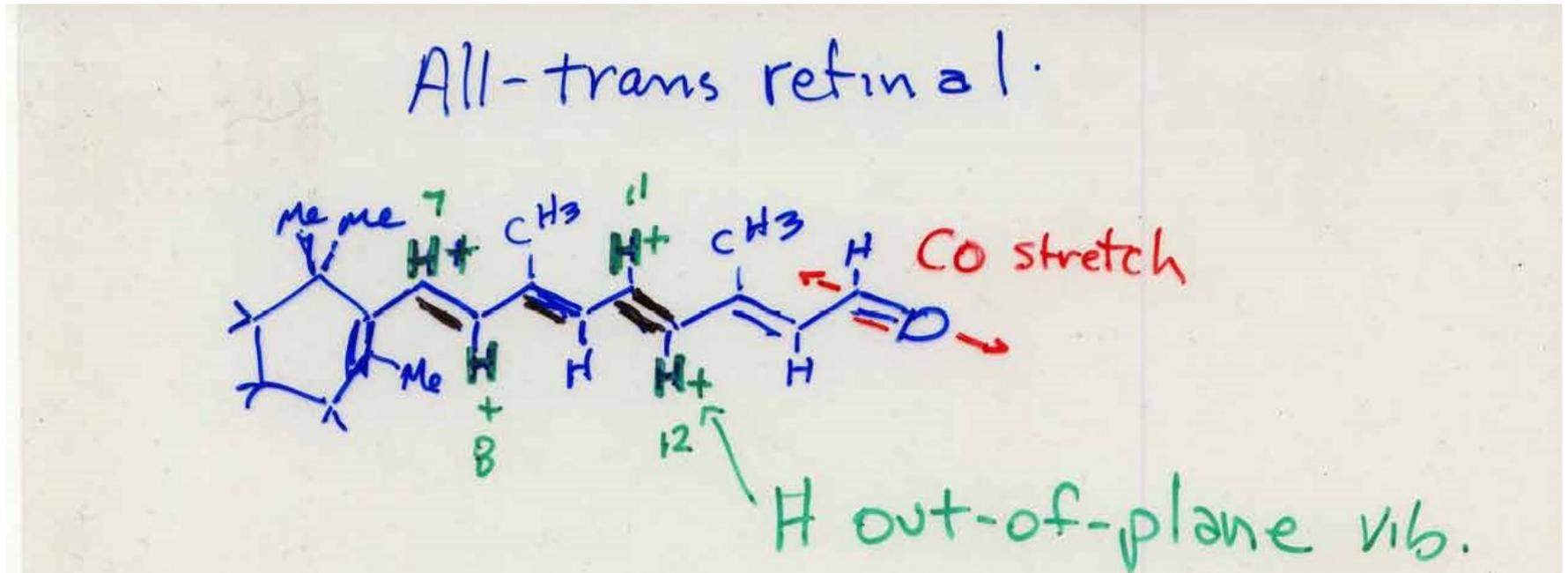


Figure 4

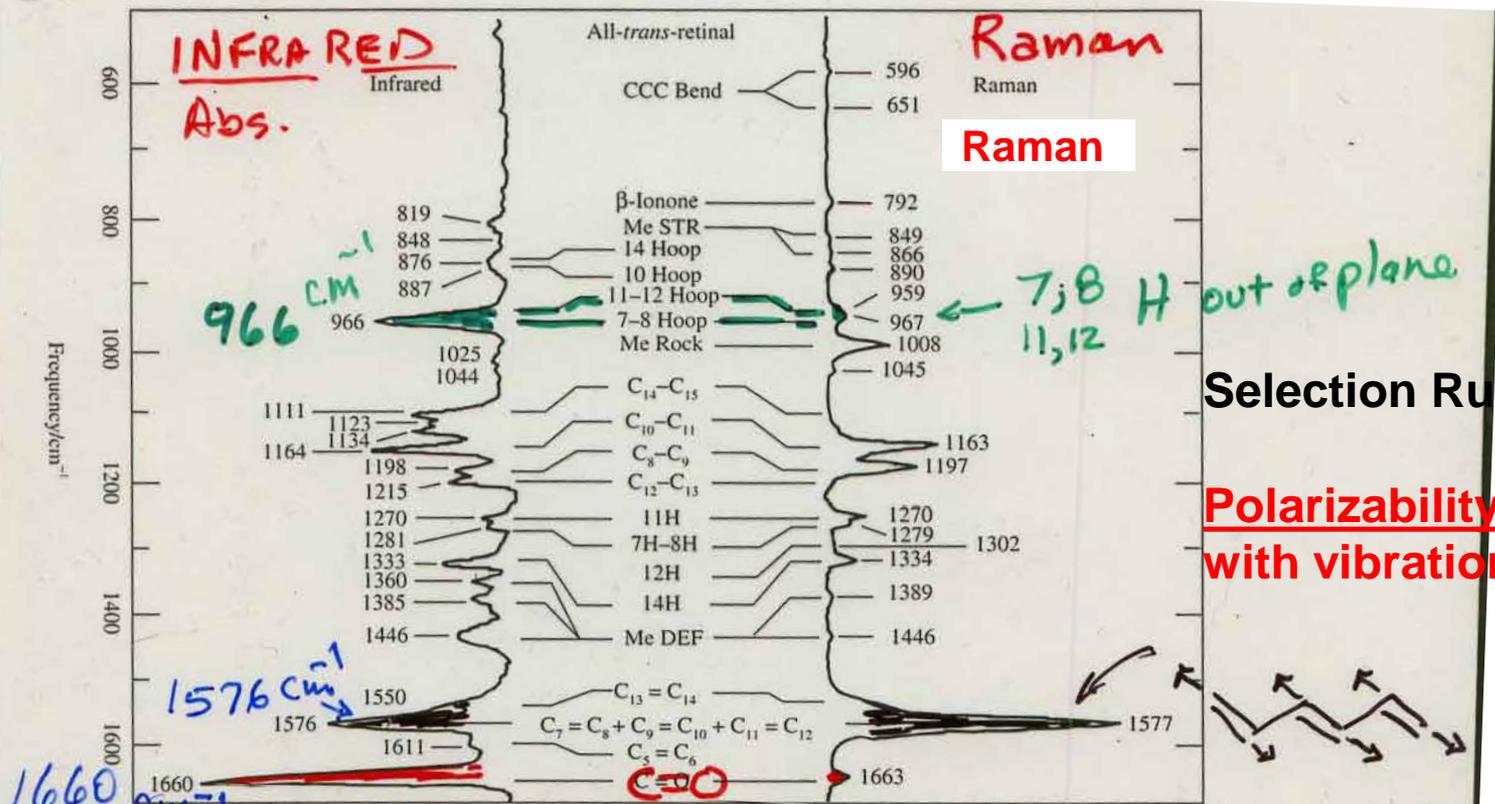
Group Modes

In many instances, functional groups (-OH, -C=O, COOH, NO₂) of organic/ inorganic molecules are not related via symmetry to other parts of the molecule. Under those circumstances, their internal motions are largely isolated from the delocalized normal coordinates of the parent molecule and thus appear in vibrational spectra at energies characteristic of the given functional group. Table 2 lists some of the more common of these group modes. The spread in energies for group modes largely reflects the influence of the rest of the molecule on the local bond strengths of the functional group. In many respects the localized vibrational behavior of functional groups mimics that of isolated small molecules. For instance, the Raman and IR intensities of group modes reflect the

Visional pigment precursor



Selection Rule For IR: Dipole must change with vibrational motion



Selection Rule For Raman:

Polarizability must change with vibrational motion

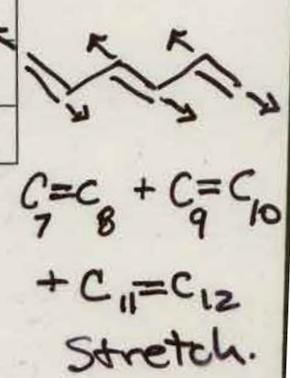


Fig. 13.36

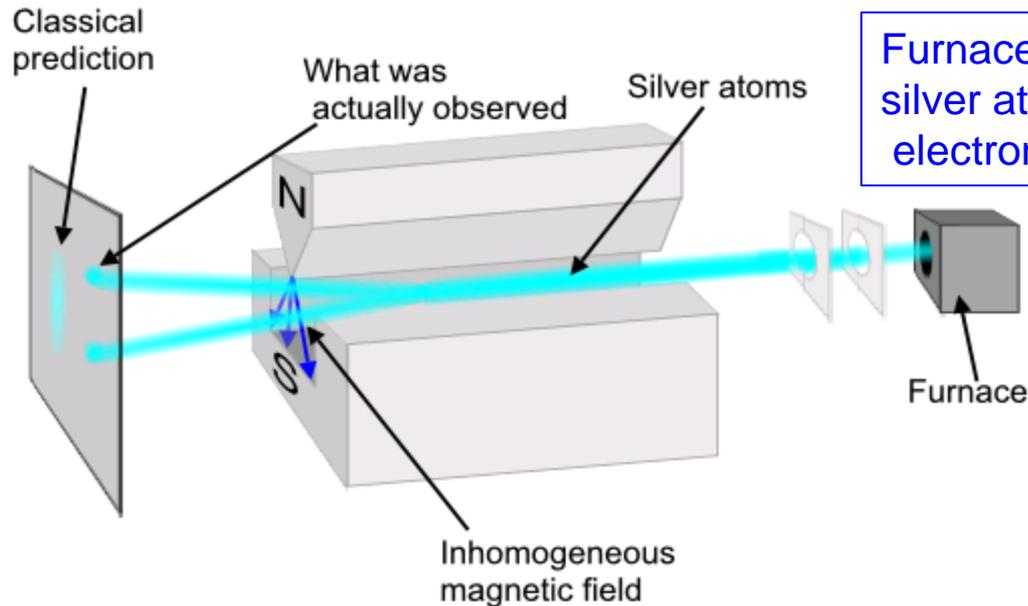
Fig. 13.36 Raman and infrared spectra of all-trans-retinal in the region from 600 cm⁻¹ to 1600 cm⁻¹. The infrared absorbance is inverted to facilitate comparison with the Raman. The Raman spectrum was measured in CCl₄ using 676.4-nm excitation from a krypton ion laser. Solvent peaks were subtracted. The infrared spectrum was measured with a thin film deposited by evaporation from a pentane solution on a KBr window. All peaks have been assigned to particular vibrations of the molecule. Me STR, Me Rock, and Me DEF refer to the stretching, rocking and the deformation of methyl groups; Hoop means out-of-plane motion of H atoms. Note that double bond vibrations occur at higher frequencies than single bond vibrations. (From Curry, Palings, Broek, Pardoen, Mulder, Lugtenburg, and Mathies, *J. Phys. Chem* 88, 688-702 (1984). The figure was kindly supplied by Prof. Richard Mathies, University of California, Berkeley.)

DISCOVERY of SPIN

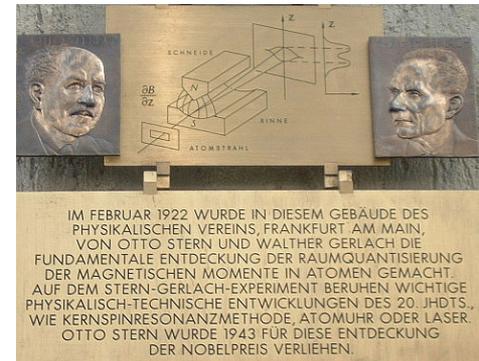
Stern-Gerlach experiment: 1922:

quantization of spin

Before spin quantization was known



Furnace is spewing a beam of **HOT** silver atoms which have unpaired electron i.e., spin of $1/2$



Before entering the magnet, the spins have **same** energy, just as the proton spins in the NMR tube before placed in magnet..

BIG SURPRISE: only observe one of the two energy levels when measured.

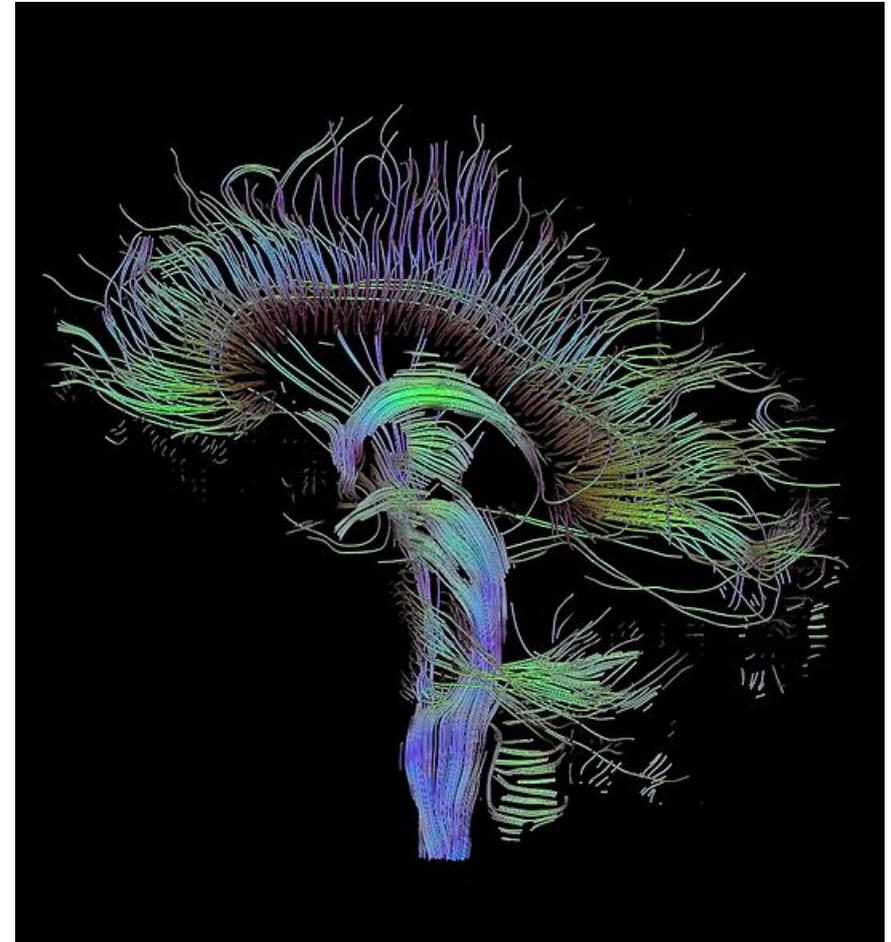
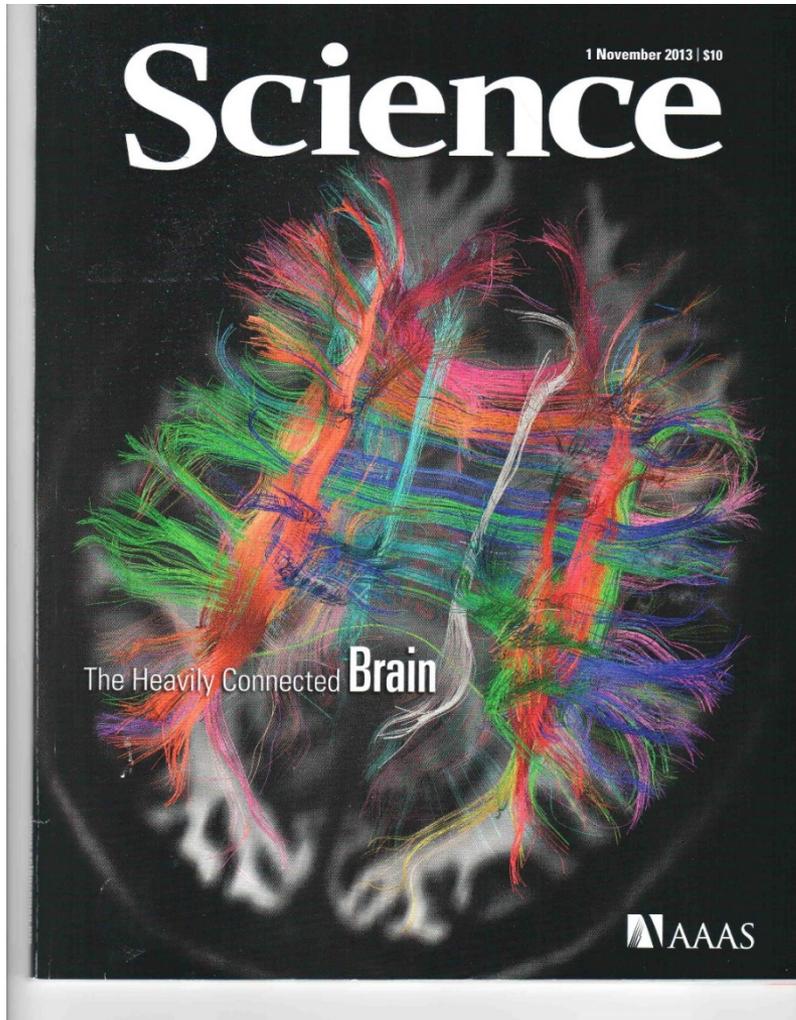
http://en.wikipedia.org/wiki/File:Quantum_spin_and_the_Stern-Gerlach_experiment.ogv

NEW kinds of MRI (magnetic resonance imaging (MRI))

Diffusion Magnetic Resonance Imaging

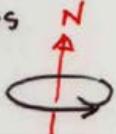
Tractographic reconstruction of neural connections via **Diffusion Tensor Imaging (DTI)**

Water channels



NMR & MRI
 Nuclear Magnetic Resonance & Magnetic Resonance Imaging

1. Angular momentum of charged particles creates a magnetic dipole



2. Angular Momentum is quantized (another quantum concept)

$L^2 = l(l+1)(\frac{h}{2\pi})^2$ or $l = 0, 1, 2, \dots$ **Bosons**
 $= \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ **Fermions**

Orbital motion of electrons } $l = 0, 1, 2, 3$
Rotation of molecules } $\downarrow \downarrow \downarrow \downarrow$
 s p d f

1 s orbital
 3 p orbitals
 5 d orbitals
 7 f orbitals

Photons are **Bosons**
 with spin = 1 (polarization)

Bosons obey Inclusion
LASERS (all in same state)
Fermions obey Exclusion

True for ALL
Angular Momentum

Z component also is quantized:

$L_z = m h/2\pi$
 $m = -l \text{ to } +l$
 $m = -1/2 \text{ and } +1/2$

for electron and proton

Spin Degeneracy = $2l+1$

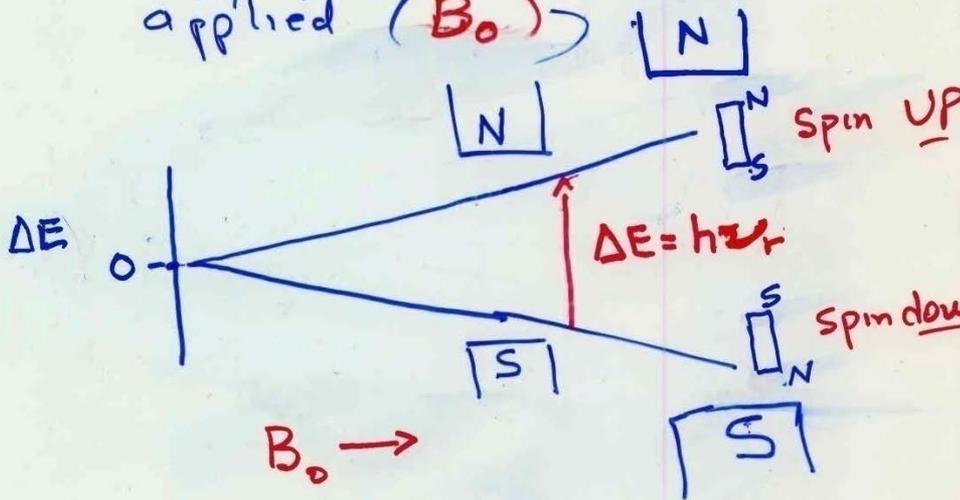
- $l=0$ $2l+1 = 1$ "singlet"
- $l=1/2$ $2l+1 = 2$ "doublet"
- $l=1$ $2l+1 = 3$ "triplet"
- $l=3/2$ $2l+1 = 4$ "quartet"
- $l=2$ $2l+1 = 5$ "quintet"

MAGNETIC RESONANCE RECAP

- Nuclear spins like bar magnets
- Electron & proton $l = 1/2$ spin
- Only 2 quantum states $m = +1/2, -1/2$
i.e., spin up & down



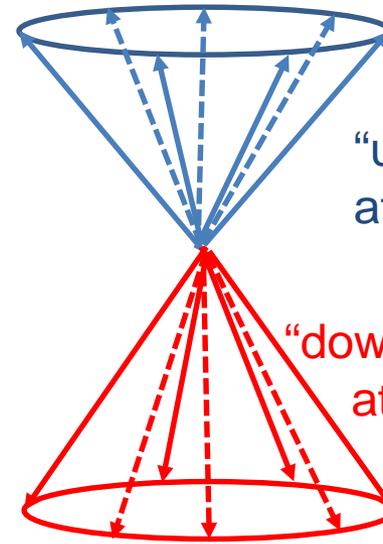
- Energy proportional to MAGNETIC FIELD applied (B_0)



$\nu_r =$ resonant frequency

- When $\nu = \nu_r$, radio frequency is ABSORBED

But what does “spin up”
REALLY mean???



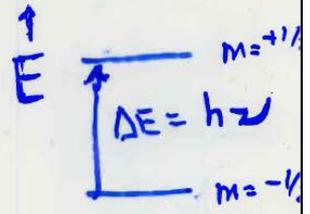
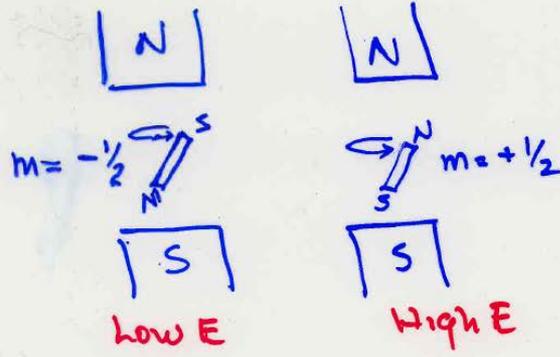
“up” means upward
at a certain angle

“down” means downward
at certain angle

spin up and spin down are two
quantum “energy levels” or
STATIONARY STATES.

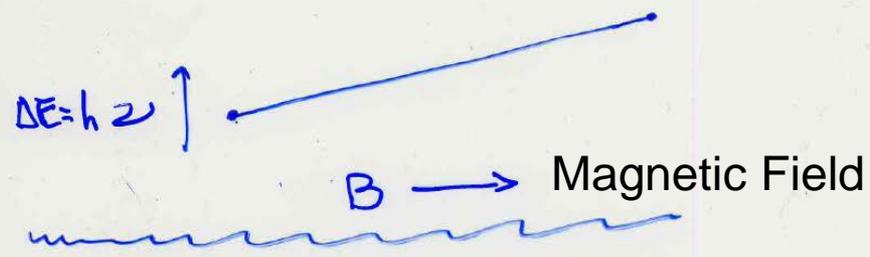
There is Equal Probability to
observe any of the up arrows
in the up state.

No spin ever points up!
But all lie on the cone so $m = +1/2$
The average vector points up

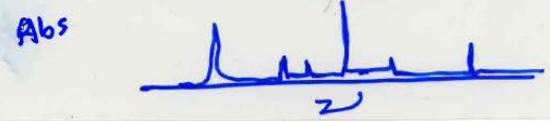


$$\Delta E = -\mu B_0 = h\nu$$
 So RESONANT FREQ ν , proportional to Field.

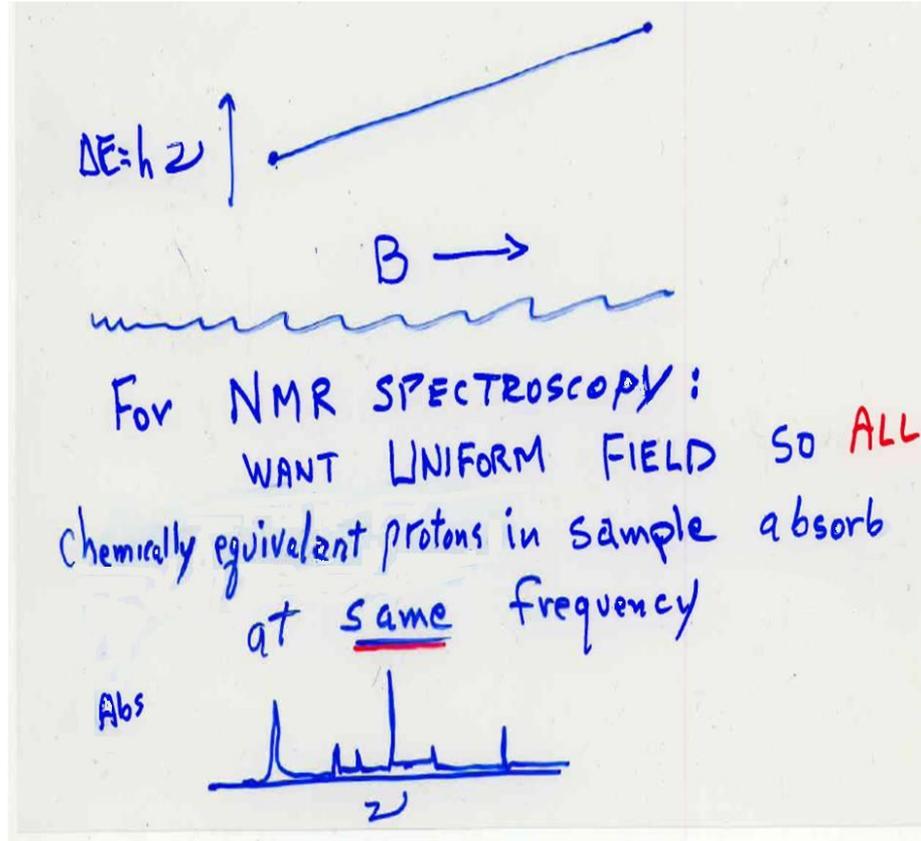
μ magnetic dipole moment
 B_0 Field strength



For NMR SPECTROSCOPY:
 WANT UNIFORM FIELD SO ALL
 Chemically equivalent protons in sample absorb
 at same frequency



NMR Spectroscopy vs. MRI:



The applied magnetic field is same everywhere in sample.

Field at the nucleus is reduced because of electron density
so **each chemically distinct H has a slightly different resonant frequency**
i.e., CHEMICAL SHIFT

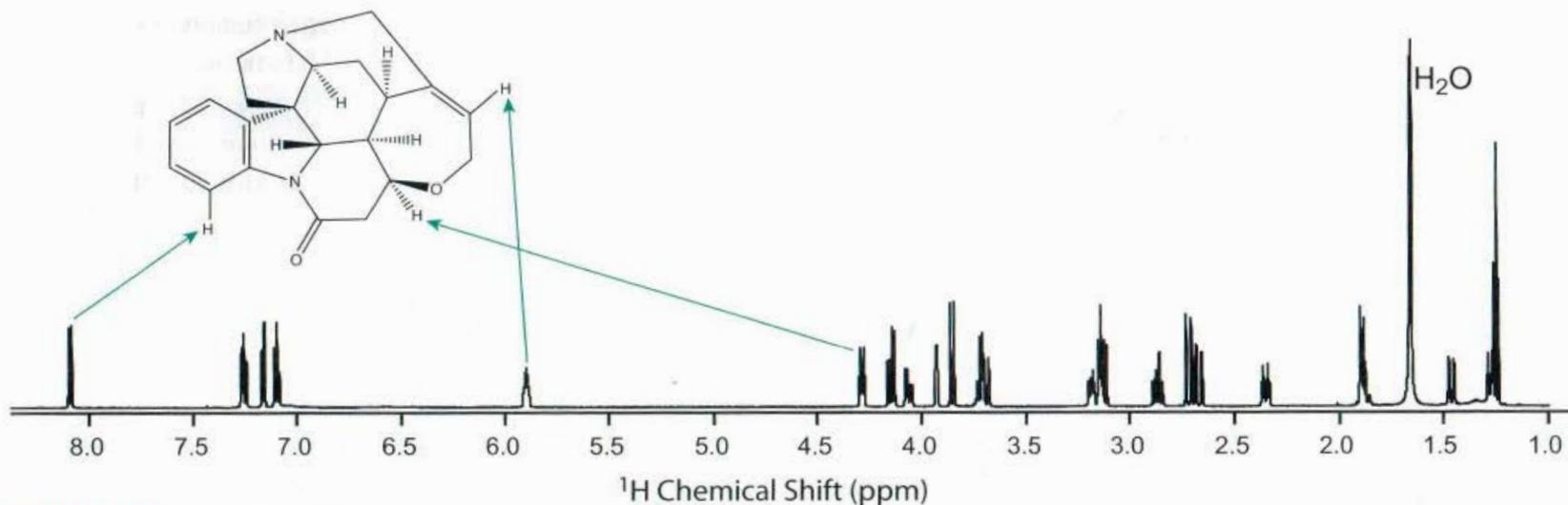


FIGURE 14.1 The ^1H NMR spectrum of strychnine (5 mM, 600 MHz) in deuteriochloroform (CDCl_3) illustrates the ability of NMR to obtain richly detailed information on complex molecules with atomic resolution. Each H atom gives a distinct signal with a characteristic position, splittings and relative intensity that is determined by the structure of the molecule. All signals are assigned, and a few representative assignments are shown on the figure (for clarity, not all H atoms are depicted). Complete assignments are performed with the aid of multidimensional NMR experiments. A residual signal from protonated chloroform (CHCl_3) has been digitally removed, while dissolved H_2O is noted.

For MRI (magnetic resonance imaging):

Applied **field is deliberately made to vary across the sample.**

Frequency set to **ONLY MEASURE WATER**

Then, **protons in different parts of sample will resonate at different frequency**

Only because of POSITION;

NOT because of different chemical shift

MRI Detects primarily two things:

(1) **amount of water at different positions**

(2) and **direction of diffusion** (more difficult)