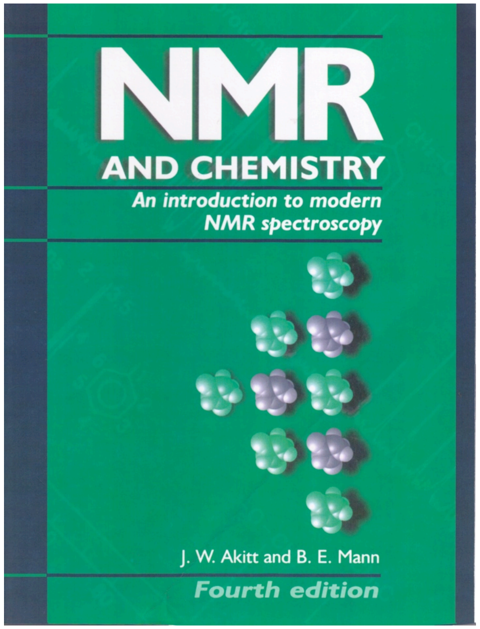
Nuclear Magnetic Resonance

Chem 634
T. Hughbanks

Books, Web sites, etc.

- J. Iggo, "NMR Spectroscopy in Inorganic Chemistry"
- J. K. M. Sanders and B K. Hunter, "Modern NMR Spectroscopy; A Guide for Chemists"
- H. Friebolin, "Basic One- and Two-Dimensional NMR Spectroscopy"
- D. Canet, "Nuclear Magnetic Resonance; Concepts and Methods"
- E. A. V. Ebsworth, D. W. H. Rankin, S. Cradock, "Structural Methods in Inorganic Chemistry", Chapter 2.
- R. S. Drago, "Physical Methods", Chapters 7, 8, and 12.
- For serious NMR students, some excellent on-line resources http://www.spectroscopynow.com/coi/cda/landing.cda?chId=5&type=Education
- Guillermo Moyna's good NMR lectures (from which I've borrowed some) http://208.7.154.206/gmoyna/NMR_lectures/NMR_lectures.html
- A good site for NMR basics: http://www.cis.rit.edu/htbooks/nmr/inside.htm
- A good site for basic organic spectra and some problems: http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm

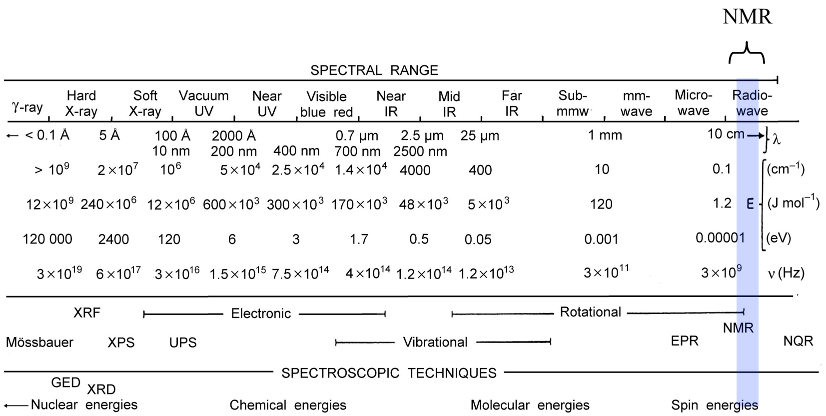

NMR
AND CHEMISTRY
An introduction to modern NMR spectroscopy
J. W. Akitt and B. E. Mann
Fourth edition

More Advanced Inorganic/ Organometallic Reference

NMR is Broadly Applicable

- Nuclear Magnetic Resonance
- Applies to atoms and molecules with nuclear spin quantum numbers greater than zero.
- Applied magnetic field induces Zeeman splittings in spin states, and energy is absorbed from radiation when the frequency meets the resonance condition, $h\nu = \Delta E \propto \mu_N \times H_0$
- $1/\lambda \sim 10^{-3}\ \text{cm}^{-1}$, $\nu = c/\lambda \sim 25\text{–}500$ MHz

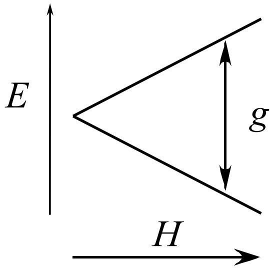
Spectroscopy: The Big Picture



Basic Aspects of the NMR Phenomenon

Zeeman interaction for proton

If a proton is placed in a magnetic field, **H** = $H_z \hat{\mathbf{z}}$, the proton's energy will depend on its m_I value. The Zeeman interaction between the applied field and the magnetic moment of the proton is illustrated as:



$$m_I = -1/2$$

$$g_N \mu_N H_0 = \gamma_N \hbar H_0$$

$$m_I = 1/2$$

For proton:

$$g_N = 5.585$$

$$\gamma_N = 26{,}753$$

(magnetogyric ratio)

$$(\text{radians} \bullet \text{s}^{-1} \bullet \text{G}^{-1})$$

Sensitivity, Populations

Even at 300 MHz (*H* = 7.05 T), the population difference of the two spin states for a proton is ~10^{-5}. Since other nuclei have smaller gyromagnetic ratios, they exhibit even smaller differences at the same field.

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E / k_B T} \simeq 1 - \frac{\Delta E}{k_B T} = 0.99999135$$

$$(H = 7.05\text{T};\ T = 298\text{K})$$

Time Scale

- NMR is generally considered to be a slow technique, with a characteristic time scale, $\tau \sim 10^{-7}$ s. (Recall, $1/\tau = \nu \sim$ 100 MHz.)
- Molecular events occurring in times much faster than 10^{-4} s or less are "time averaged" in NMR (a more careful distinction to come later).

Miscellaneous Familiar Matters

- For solution spectra, the immediate chemical/structural information is conveyed by the *chemical shifts* and the *spin-spin couplings*.
- Nuclei with $I > {}^1/_2$ have quadrupole moments - even solution spectra are broadened when such nuclei experience electric field gradients.
- The ratios of resonance frequencies for a given field are equal to the ratios of the gyromagnetic constants: $\gamma_A/\gamma_B = \nu_A/\nu_B$. For example, on a "300 MHz spectrometer", ^{13}C spectra occur at 75.44 MHz since $\gamma_{^{13}C}/\gamma_{^1H} = {}^{6728}/_{26,753} = {}^{75.44}/_{300}$. (It would be better to call a "300 MHz spectrometer" a 7.046 T spectrometer.)

Chemical Shift Scale

$$\delta = \frac{\nu - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}} \qquad \delta_{\mathrm{ppm}} = 10^6 \times \frac{\nu - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}}$$

- In order to make NMR data independent of the field used, chemical shifts are reported relative to a standard (usually TMS for ^1H and ^{13}C).
- Since the shifts are generally small, they are always given in parts per million (ppm).

Peak differences often in Hz

- It turns out to be more physically useful to think about differences between energies of NMR transitions in terms of differences in frequencies, e.g., $\nu_2 - \nu_1$.

$$\delta_2 - \delta_1 = 10^6 \times \frac{\nu_2 - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}} - 10^6 \times \frac{\nu_1 - \nu_{\mathrm{TMS}}}{\nu_{\mathrm{TMS}}} = 10^6 \times \frac{\nu_2 - \nu_1}{\nu_{\mathrm{TMS}}}$$

$$\Rightarrow \quad \nu_2 - \nu_1 = \frac{\nu_{\mathrm{TMS}}}{10^6}(\delta_2 - \delta_1)$$

Resonance, Larmor Frequency

$$\Delta E = \gamma_N \hbar H_0 = h\nu_L$$

(γ_N is the gyromagnetic ratio for the nucleus in question)

ν_L is the Larmor frequency: $\nu_L = \left|\frac{\gamma_N}{2\pi}\right| H_0$; $\omega_0 = \gamma_N H_0$

including chemical shift: $\nu = \left|\frac{\gamma_N}{2\pi}\right| H_0 \left(1-\sigma\right)$

- NMR transitions are stimulated (absorption *and* emission) by an additional oscillating (electro)magnetic field, H_1, is applied at the Larmor frequency.
- Shielding is proportional to the applied field - hence the units of chemical shift: ppm.

More Familiar Matters

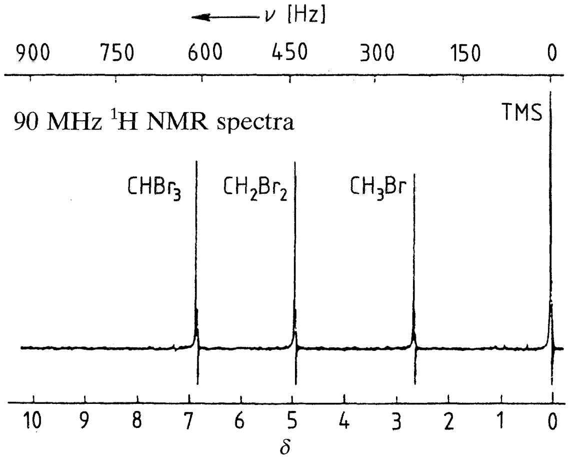
- Resonance frequencies for two interacting nuclei are given by

$$E = -h\sum_A \nu_A m_A + h\sum_{A<B} J_{AB} m_A m_B$$

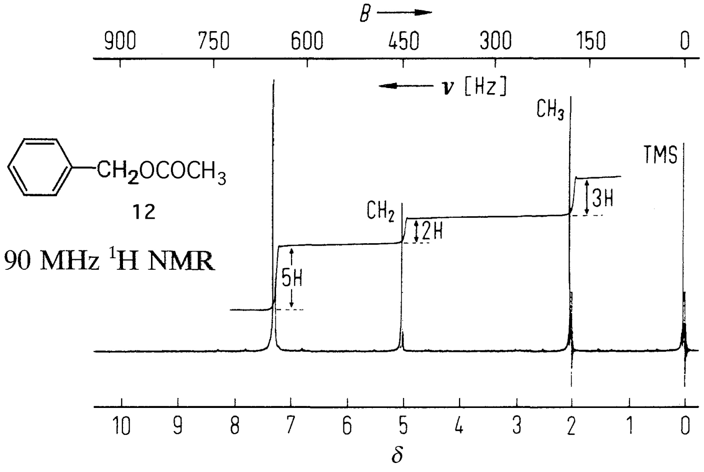
where m_A is the z-component the spin on A, and J_{AB} is the coupling constant for A interacting with B.

- This expression applies when chemical shift differences are much greater than couplings, $|\nu_A - \nu_B| >> J_{AB}$.

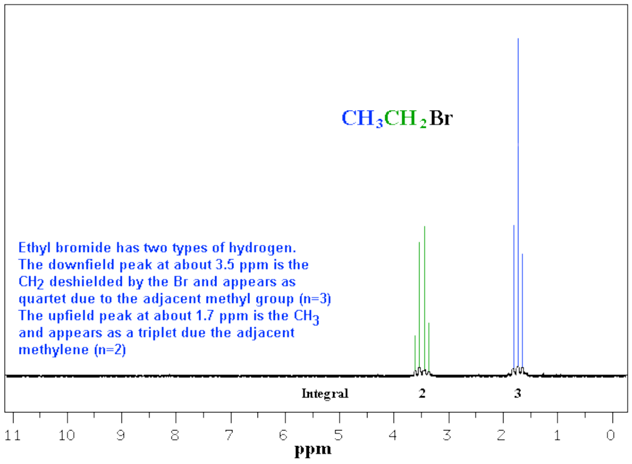
Basic Spectra - ^{1}H



Basic Spectra - ^{1}H

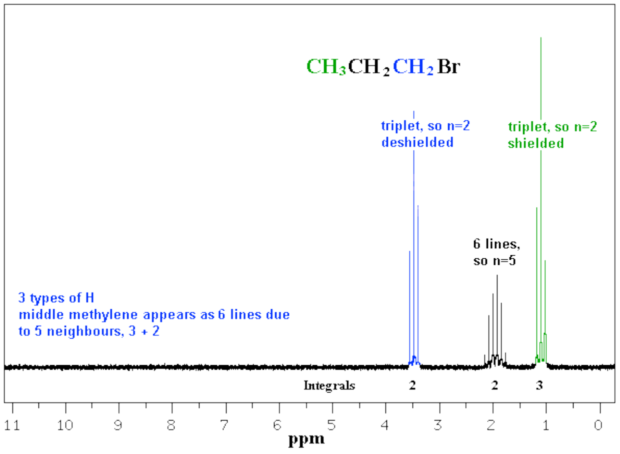


Basic Spectra - ^{1}H

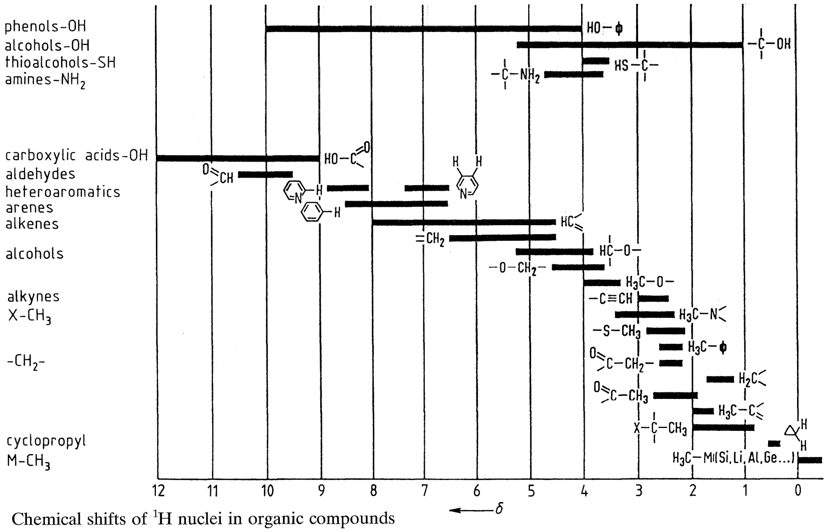


Ethyl bromide has two types of hydrogen.
The downfield peak at about 3.5 ppm is the CH_2 deshielded by the Br and appears as quartet due to the adjacent methyl group (n=3)
The upfield peak at about 1.7 ppm is the CH_3 and appears as a triplet due the adjacent methylene (n=2)

Basic Spectra - ^{1}H



3 types of H
middle methylene appears as 6 lines due to 5 neighbours, 3 + 2



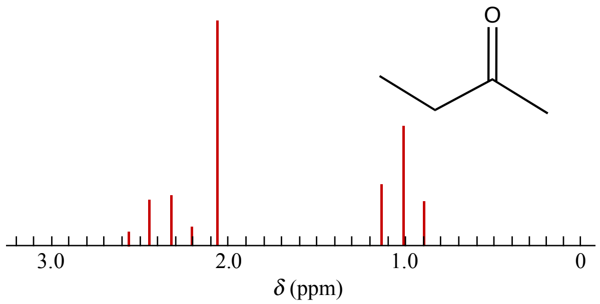
Chemical shifts of ^{1}H nuclei in organic compounds

Notation for labeling nuclei

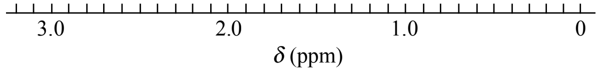
- Chemically and magnetically equivalent nuclei given the <u>same</u> label. (e.g., A)
- Chemically, but not magnetically equivalent nuclei given primes. (e.g, AA′ for two, AA′A″ for three, etc.)
- Nuclei with small chemical shift differences (smaller or comparable to coupling between them) given alphabetically close labels (e.g., A, B, C, D, etc.)
- Inequivalent nuclei with large chemical shift differences given alphabetically distant labels (e.g., AMX, for three)
- One can describe a mix of types of nuclei
  - A_2BMXY is a six-spin system with two equivalent nuclei (A), strongly coupled (compared to $\Delta\nu_{AB}$) to one nucleus B, weakly coupled to one nucleus M (vs $\Delta\nu_{AM}$) and very weakly coupled to X & Y
  - M is weakly coupled to all nuclei
  - B is only strongly coupled to A
  - X & Y are strongly coupled to each other and weakly to all other nuclei

A (disastrous) problem from the 2008 Final

On the next slide is a fairly accurate simulation of the line positions and intensities observed for the ^{1}H NMR spectrum of methylethylketone, $CH_3COCH_2CH_3$, measured on an old continuous-wave 60 MHz (1.4093 T) NMR instrument (the TMS reference is not shown). Assign the spectrum, and in the blank space below the spectrum, draw an analogous stick-like spectrum that shows, *as accurately as possible,* what the spectrum would look like if recorded on a more modern 300 MHz (7.0463 T) instrument. Be careful to accurately place the positions of the peaks and their relative intensities.

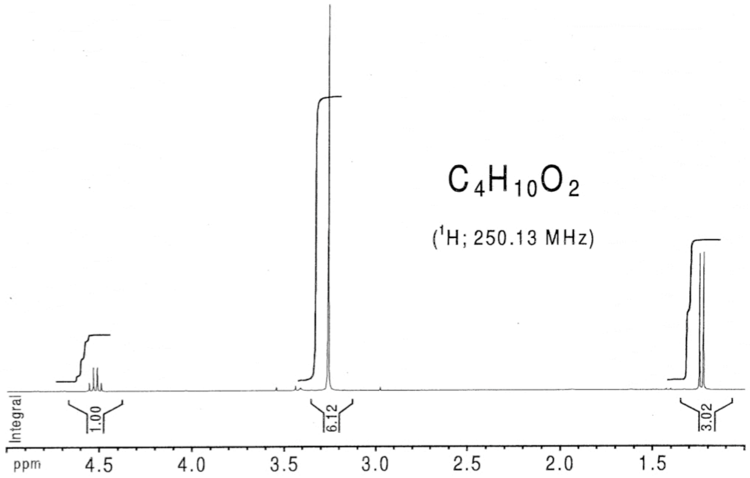


^{1}H NMR, 60 MHz



^{1}H NMR, 300 MHz

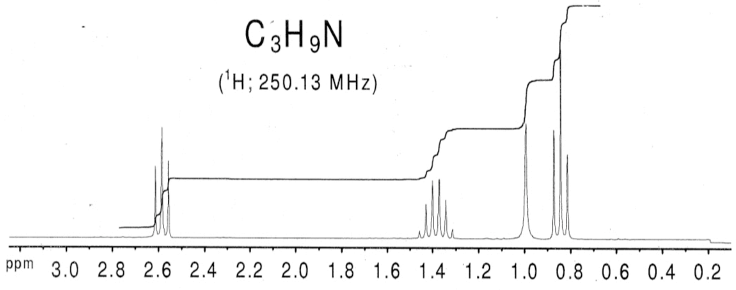
An “unknown” example - ^{1}H



$C_4H_{10}O_2$

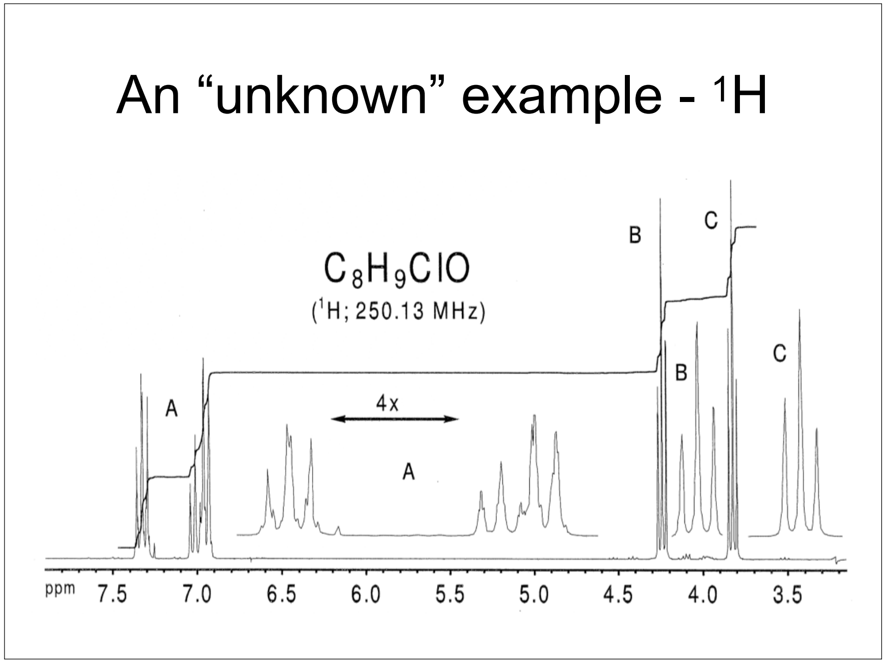
(^{1}H; 250.13 MHz)

An “unknown” example - ^{1}H

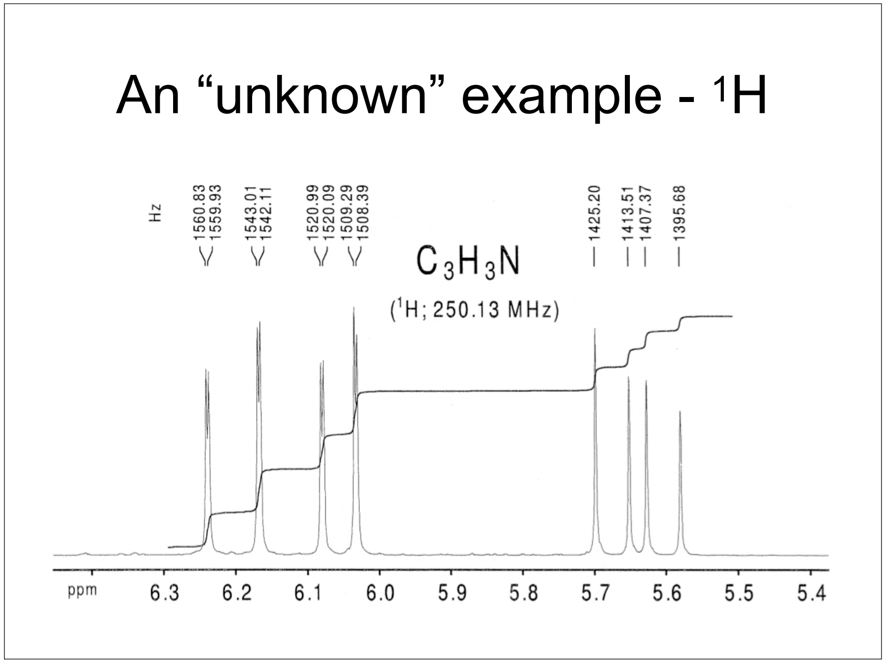


C_3H_9N

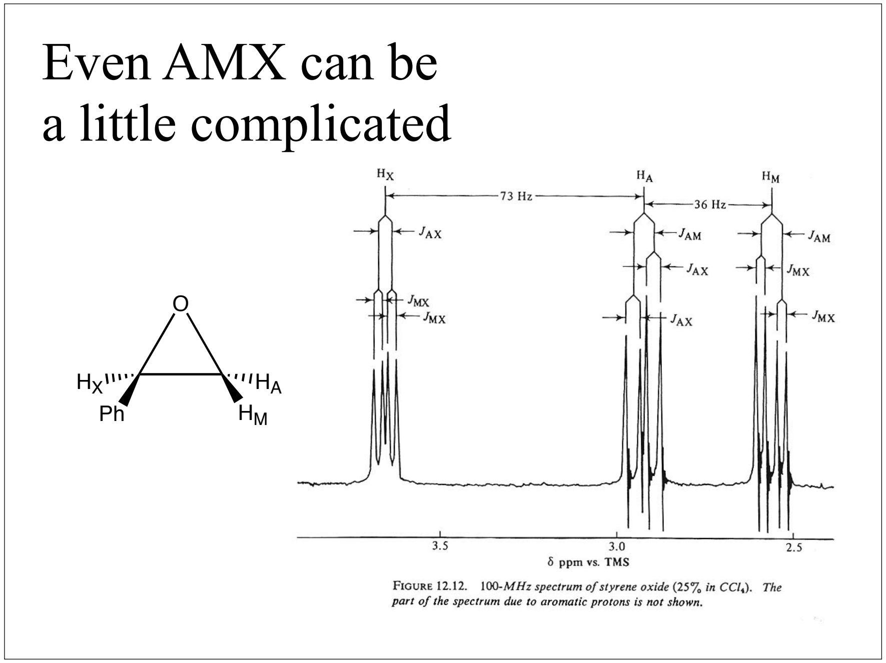
(^{1}H; 250.13 MHz)



An “unknown” example - ^{1}H

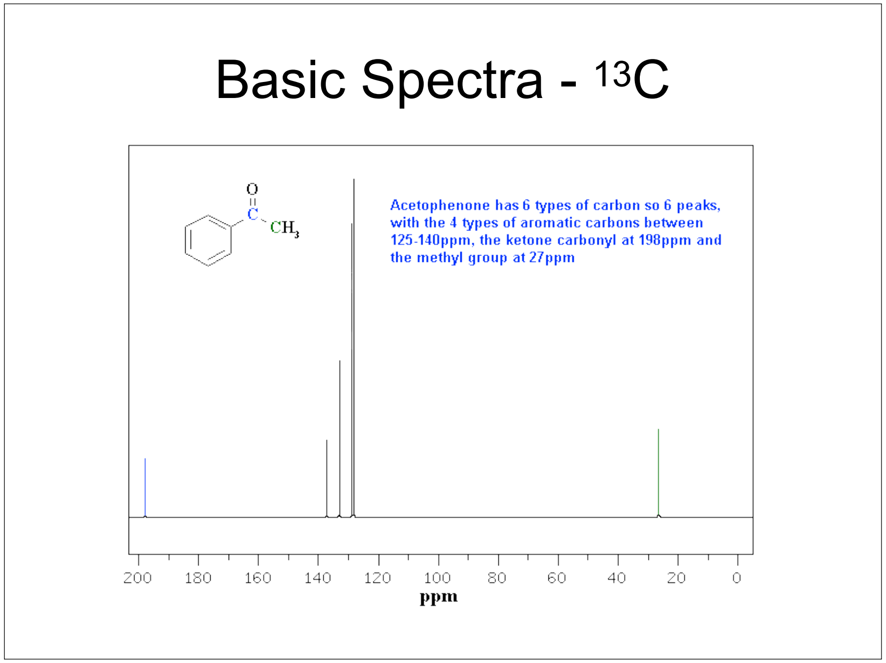


An “unknown” example - ^{1}H



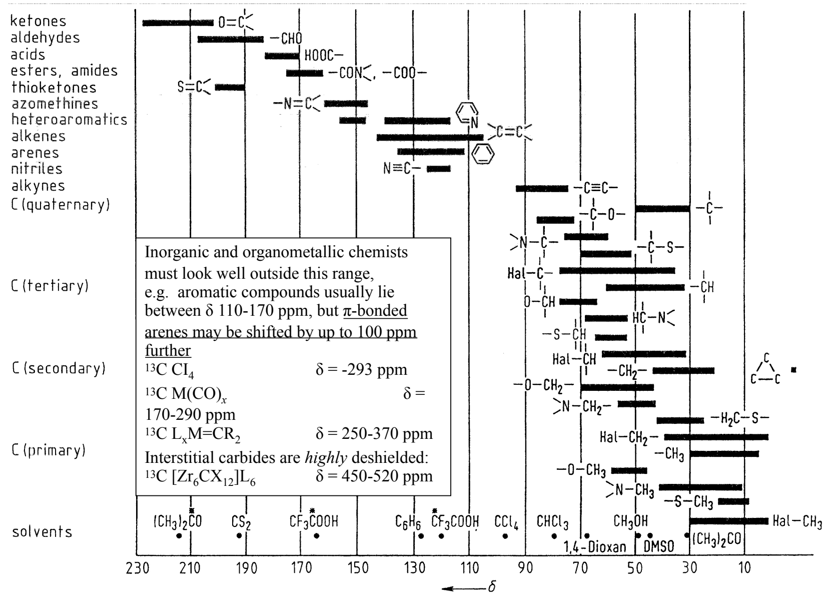
Even AMX can be a little complicated

FIGURE 12.12. *100-MHz spectrum of styrene oxide (25% in CCl_4). The part of the spectrum due to aromatic protons is not shown.*



Basic Spectra - ^{13}C

Acetophenone has 6 types of carbon so 6 peaks, with the 4 types of aromatic carbons between 125-140ppm, the ketone carbonyl at 198ppm and the methyl group at 27ppm



Inorganic and organometallic chemists must look well outside this range, e.g. aromatic compounds usually lie between δ 110-170 ppm, but π-bonded arenes may be shifted by up to 100 ppm further

^{13}C CI_4 δ = -293 ppm

^{13}C $M(CO)_x$ δ = 170-290 ppm

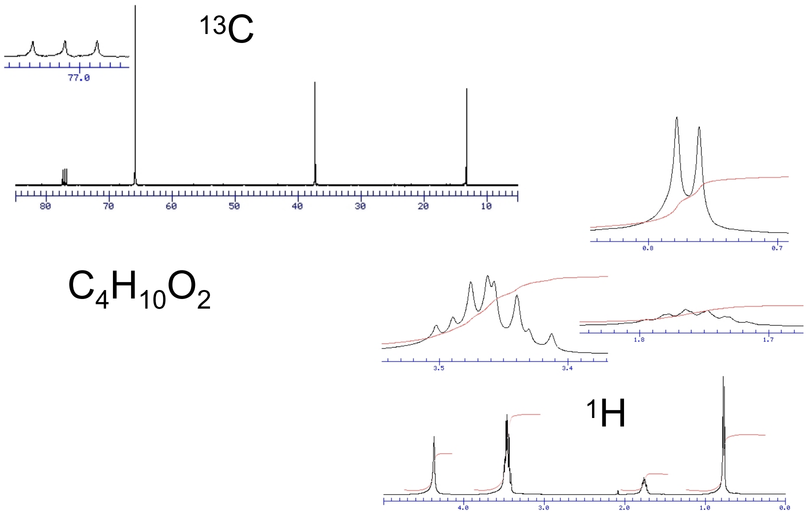
^{13}C $L_xM{=}CR_2$ δ = 250-370 ppm

Interstitial carbides are *highly* deshielded:

^{13}C $[Zr_6CX_{12}]L_6$ δ = 450-520 ppm

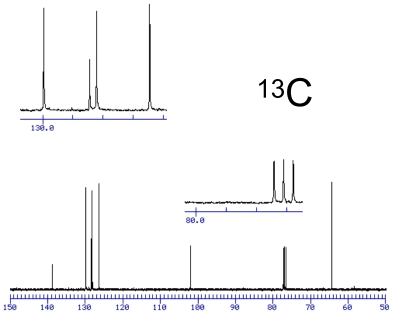
Chemical shifts of ^{13}C nuclei in organic compounds.

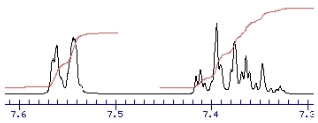
An “unknown” example - ^{1}H & ^{13}C

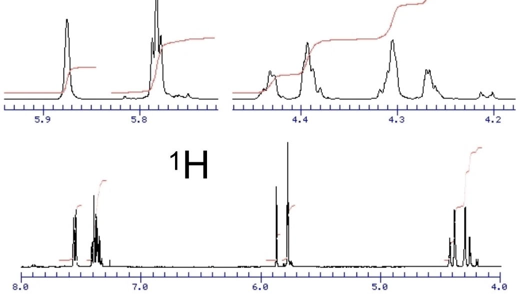


$C_4H_{10}O_2$

An “unknown” example - ^{1}H & ^{13}C







$C_{11}H_{12}O_2$

Origins of Chemical Shifts (Shielding)

$$H = H_0(1-\sigma) \quad ; \quad \sigma = \sigma_d + \sigma_p$$

$$\sigma_d(zz) = \frac{e^2}{2mc^2}\langle 0|\frac{x^2+y^2}{r^2}|0\rangle$$

$$\sigma_p(zz) = -\left(\frac{e\hbar}{2mc}\right)^2 \sum_n \left\{ \frac{\langle 0|L_z|n\rangle\langle n|\frac{2L_z}{r^3}|0\rangle}{E_n - E_0} + \frac{\langle 0|\frac{2L_z}{r^3}|n\rangle\langle n|L_z|0\rangle}{E_n - E_0} \right\}$$

- Shielding consists of a diamagnetic (σ_d) and paramagnetic (σ_p) response of the electrons to the applied field.
- σ_d arises from a first-order effect, reflecting the electron density distribution in the ground state. (Often dominant in proton spectra.)
- σ_p arises from a second-order mixing of paramagnetic excited states into the ground state by the applied field (much like TIP). Often dominant for other nuclei.

$\gamma_N = \frac{g_N \mu_N}{\hbar}$

TABLE 1.1. Nuclear Moments and Spins

	Nucleus	I	g_N	γ_N (radians sec^{-1}·gauss^{-1})	Nucleus	I	g_N	γ_N (radians sec^{-1}·gauss^{-1})	Q (10^{-24} cm^2)
	H^1	1/2	5.585	26,753	D^2	1	0.857	4,107	0.00274
	C^{13}	1/2	1.405	6,728	Li^7	3/2	2.171	10,398	0.02
	N^{15}	1/2	−0.567	−2,712	B^{11}	3/2	1.791	8,853	0.00355
	F^{19}	1/2	5.257	25,179	N^{14}	1	0.403	1,934	0.02
4.7%	Si^{29}	1/2	−1.111	−5,319	O^{17}	5/2	−0.757	−3,628	−0.0265
100%	P^{31}	1/2	2.263	10,840	Na^{23}	3/2	1.478	7,081	+1.00 or −0.836[a]
33.7%	Pt^{195}	1/2	1.120	5,747					
					S^{33}	3/2	0.429	2,054	−0.064
					Cl^{35}	3/2	0.548	2,624	−0.079
					Cl^{37}	3/2	0.456	2,184	−0.062
					K^{39}	3/2	0.261	1,250	0.113

Nuclei with no spin: C^{12} O^{16} O^{18} Si^{28} S^{32} Ca^{40}

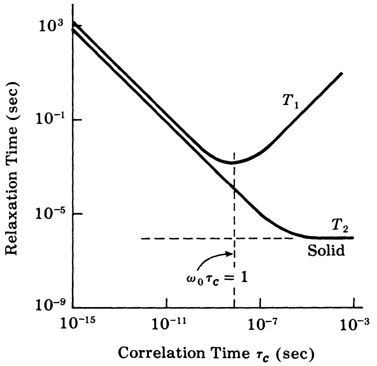
[a] The quadrupole moment of Na^{23} is uncertain.

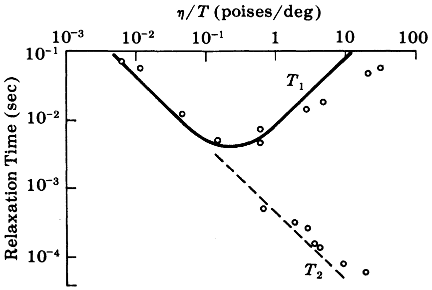
Relaxation

Iggo, Sec .1-10

- Refers to processes by which spins nonradiatively lose energy
- The phenomenon of relaxation is crucial to NMR. In the (obsolete) continuous wave method, signals would rapidly saturate because spin populations can become equal. In FT-NMR, relaxation is necessary to bring system to equilibrium between pulses.
- T_1: spin-lattice relaxation, dissipation of energy to surroundings (non-spin degrees of freedom)
- T_2: spin-spin relaxation, transfer of energy to other spins. $T_1 \geq T_2$
- Quadrupole moments, Q, cause T_2 to shorten greatly, leading to line-broadening

Correlation times and Relaxation





Proton relaxation times in glycerine between 60°C and 35°C. Measured at 29 Mc/s.

Relaxation effects depend on the frequency spectrum of the local fields experienced by a nuclear spin. The correlation time, τ_c, is a characteristic time scale of fluctuations (due to molecular tumbling ~ rotational Brownian motion) in solution. Relaxation is most efficient when $1/\tau_c \sim \nu$.

Table 2.2 NMR properties of some quadrupolar nuclei[a]

Isotope	Spin	Natural abundance/ %	Magnetogyric ratio[b]/ 10^7 rad T^{-1}s^{-1}	Relative NMR frequency/ MHz	Relative receptivity	Quadrupole moment[b]/ 10^{-28}m^2
^{2}H[c]	1	0.015	4.1066	15.4	1.5×10^{-6}	2.8×10^{-3}
^{6}Li	1	7.4	3.9371	14.7	6.3×10^{-4}	-8×10^{-4}
^{7}Li	3/2	92.6	10.3975	38.9	2.7×10^{-1}	-4×10^{-2}
^{9}Be	3/2	100.0	−3.7596	14.1	1.4×10^{-2}	5×10^{-2}
^{10}B	3	19.6	2.8746	10.7	3.9×10^{-3}	8.5×10^{-2}
^{11}B	3/2	80.4	8.5843	32.1	1.3×10^{-1}	4.1×10^{-2}
^{14}N[c]	1	99.6	1.9338	7.2	1.0×10^{-3}	1×10^{-2}
^{17}O	5/2	0.037	−3.6279	13.6	1.1×10^{-5}	-2.6×10^{-2}
^{23}Na	3/2	100.0	7.0801	26.5	9.3×10^{-2}	1×10^{-1}
^{25}Mg	5/2	10.1	−1.639	6.1	2.7×10^{-4}	2.2×10^{-1}
^{27}Al	5/2	100.0	6.9760	26.1	2.1×10^{-1}	1.5×10^{-1}
^{33}S	3/2	0.76	2.055	7.7	1.7×10^{-5}	-5.5×10^{-2}
^{35}Cl	3/2	75.5	2.6240	9.8	3.6×10^{-3}	-1×10^{-1}
^{37}Cl	3/2	24.5	2.1842	8.2	6.7×10^{-4}	-7.9×10^{-2}
^{39}K[d]	3/2	93.1	1.2498	4.7	4.8×10^{-4}	4.9×10^{-2}
^{43}Ca	7/2	0.15	−1.8025	6.7	8.7×10^{-6}	2×10^{-1}[e]
^{45}Sc	7/2	100.0	6.5081	24.3	3.0×10^{-1}	-2.2×10^{-1}
^{47}Ti	5/2	7.3	−1.5105	5.6	1.5×10^{-4}	2.9×10^{-1}
^{49}Ti	7/2	5.5	−1.5109	5.6	2.1×10^{-4}	2.4×10^{-1}
^{51}V[d]	7/2	99.8	7.0453	26.3	3.8×10^{-1}	-5×10^{-2}
^{53}Cr	3/2	9.6	−1.512	5.7	8.6×10^{-5}	3×10^{-2}
^{55}Mn	5/2	100.0	6.608	24.7	1.8×10^{-1}	4×10^{-1}
^{59}Co	7/2	100.0	6.317	23.6	2.8×10^{-1}	3.8×10^{-1}
^{61}Ni	3/2	1.2	−2.394	8.9	4.1×10^{-5}	1.6×10^{-1}
^{63}Cu	3/2	69.1	7.0974	26.5	6.5×10^{-2}	-2.1×10^{-1}
^{65}Cu	3/2	30.9	7.6031	28.4	3.6×10^{-2}	-2.0×10^{-1}
^{67}Zn	5/2	4.1	1.6768	6.3	1.2×10^{-4}	1.6×10^{-1}
^{69}Ga	3/2	60.4	6.4323	24.0	4.2×10^{-2}	1.9×10^{-1}
^{71}Ga	3/2	39.6	8.1731	30.6	5.7×10^{-2}	1.2×10^{-1}
^{73}Ge	9/2	7.8	−0.9357	3.5	1.1×10^{-4}	-1.8×10^{-1}
^{75}As	3/2	100.0	4.595	17.2	2.5×10^{-2}	2.9×10^{-1}
^{79}Br	3/2	50.5	6.7228	25.1	4.0×10^{-2}	3.7×10^{-1}
^{81}Br	3/2	49.5	7.2468	27.1	4.9×10^{-2}	3.1×10^{-1}

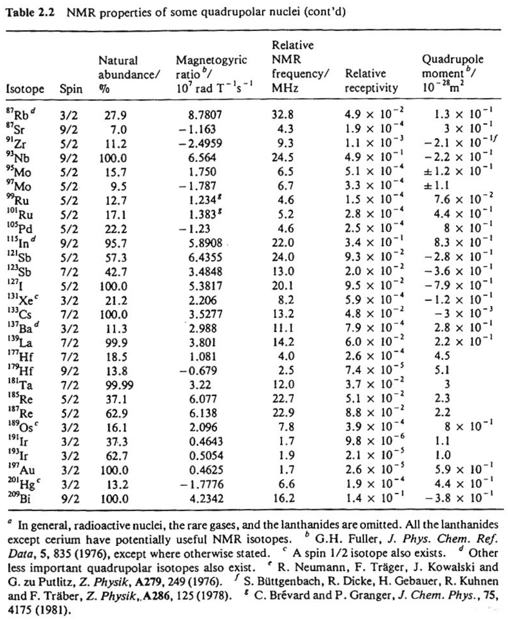


Table 2.2 NMR properties of some quadrupolar nuclei (cont'd)

Isotope	Spin	Natural abundance/ %	Magnetogyric ratio[b]/ 10^7 rad $T^{-1}s^{-1}$	Relative NMR frequency/ MHz	Relative receptivity	Quadrupole moment[b]/ $10^{-28}m^2$
^{87}Rb[d]	3/2	27.9	8.7807	32.8	4.9×10^{-2}	1.3×10^{-1}
^{87}Sr	9/2	7.0	−1.163	4.3	1.9×10^{-4}	3×10^{-1}
^{91}Zr	5/2	11.2	−2.4959	9.3	1.1×10^{-3}	-2.1×10^{-1}[f]
^{93}Nb	9/2	100.0	6.564	24.5	4.9×10^{-1}	-2.2×10^{-1}
^{95}Mo	5/2	15.7	1.750	6.5	5.1×10^{-4}	$\pm 1.2 \times 10^{-1}$
^{97}Mo	5/2	9.5	−1.787	6.7	3.3×10^{-4}	±1.1
^{99}Ru	5/2	12.7	1.234[g]	4.6	1.5×10^{-4}	7.6×10^{-2}
^{101}Ru	5/2	17.1	1.383[g]	5.2	2.8×10^{-4}	4.4×10^{-1}
^{105}Pd	5/2	22.2	−1.23	4.6	2.5×10^{-4}	8×10^{-1}
^{115}In[d]	9/2	95.7	5.8908	22.0	3.4×10^{-1}	8.3×10^{-1}
^{121}Sb	5/2	57.3	6.4355	24.0	9.3×10^{-2}	-2.8×10^{-1}
^{123}Sb	7/2	42.7	3.4848	13.0	2.0×10^{-2}	-3.6×10^{-1}
^{127}I	5/2	100.0	5.3817	20.1	9.5×10^{-2}	-7.9×10^{-1}
^{131}Xe[c]	3/2	21.2	2.206	8.2	5.9×10^{-4}	-1.2×10^{-1}
^{133}Cs	7/2	100.0	3.5277	13.2	4.8×10^{-2}	-3×10^{-3}
^{137}Ba[d]	3/2	11.3	2.988	11.1	7.9×10^{-4}	2.8×10^{-1}
^{139}La	7/2	99.9	3.801	14.2	6.0×10^{-2}	2.2×10^{-1}
^{177}Hf	7/2	18.5	1.081	4.0	2.6×10^{-4}	4.5
^{179}Hf	9/2	13.8	−0.679	2.5	7.4×10^{-5}	5.1
^{181}Ta	7/2	99.99	3.22	12.0	3.7×10^{-2}	3
^{185}Re	5/2	37.1	6.077	22.7	5.1×10^{-2}	2.3
^{187}Re	5/2	62.9	6.138	22.9	8.8×10^{-2}	2.2
^{189}Os[c]	3/2	16.1	2.096	7.8	3.9×10^{-4}	8×10^{-1}
^{191}Ir	3/2	37.3	0.4643	1.7	9.8×10^{-6}	1.1
^{193}Ir	3/2	62.7	0.5054	1.9	2.1×10^{-5}	1.0
^{197}Au	3/2	100.0	0.4625	1.7	2.6×10^{-5}	5.9×10^{-1}
^{201}Hg[c]	3/2	13.2	−1.7776	6.6	1.9×10^{-4}	4.4×10^{-1}
^{209}Bi	9/2	100.0	4.2342	16.2	1.4×10^{-1}	-3.8×10^{-1}

[a] In general, radioactive nuclei, the rare gases, and the lanthanides are omitted. All the lanthanides except cerium have potentially useful NMR isotopes. [b] G.H. Fuller, *J. Phys. Chem. Ref. Data*, 5, 835 (1976), except where otherwise stated. [c] A spin 1/2 isotope also exists. [d] Other less important quadrupolar isotopes also exist. [e] R. Neumann, F. Träger, J. Kowalski and G. zu Putlitz, *Z. Physik*, **A279**, 249 (1976). [f] S. Büttgenbach, R. Dicke, H. Gebauer, R. Kuhnen and F. Träber, *Z. Physik*, **A286**, 125 (1978). [g] C. Brévard and P. Granger, *J. Chem. Phys.*, 75, 4175 (1981).

The NMR Experiment

http://www-keeler.ch.cam.ac.uk/lectures/

Chapter 3: The Vector Model

Chapter 4: Fourier Transformation and Data Processing

Chapter 5: How the Spectrometer Works

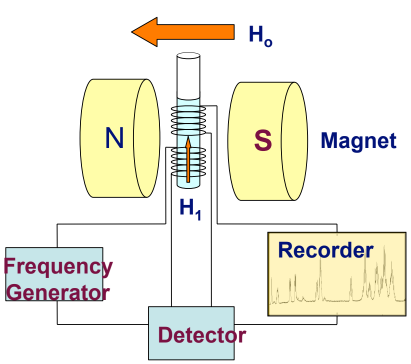
NMR Spectrometers

- Typical now are 5-10T magnets - must be very stable and highly homogeneous
- RF transmitter and pick-up coils
- Decoupler
- Recording device, computer for Fast Fourier Transforms, FID storage

More Experimental Aspects

- Must lock on a resonance frequency of a nucleus that is not the one being measured to maintain stability. ^{1}H NMR uses ^{2}H (i.e., D).
- Probe is at the center of the field and consists of a sample holder with coils. The radiofrequency of the nucleus under investigation is applied to the sample via the transmitter coil, and, at resonance, a voltage is induced in the receiver coil which detects sample magnetization.
- The sample is spinning during the experiment to ensure optimum field homogeneity. The sample holder acts as a turbine driven by compressed air.
- Most instruments have another coil used as decoupler and a variable temperature device.

NMR Instrumentation



Magnet - Normally superconducting. Some electromagnets and permanent magnets (EM-360, EM-390) still around.

Frequency generator - Creates the alternating current (at ω_r) that induces $\mathbf{H_1}$. Continuous wave or pulsed.

Detector - Subtracts a constant base frequency very close to ω_0 that is essentially the frequency of the "rotating frame", ω_r. The output frequencies, $\omega_0 - \omega_r$, are much lower and much easier to deal with. (In this respect, an NMR machine is much like a an expensive FM radio.)

Recorder - XY plotter, oscilloscope, computer, etc.

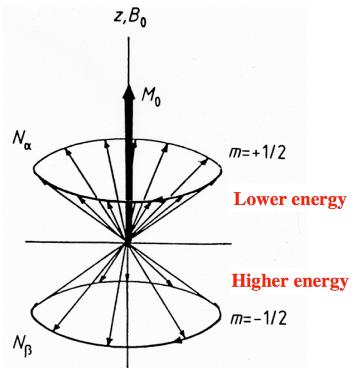
Macroscopic Magnetization

The molar bulk nuclear magnetization (H_0 = applied field),

$$M = g_N^2 \frac{\mu_N^2 N_A}{3k_BT} I(I+1)H_0 = \gamma_N^2 \hbar^2 \frac{N_A}{3k_BT}\left[I(I+1)\right]H_0$$

- This applies to a mole of nuclei with spin I and is derived in exactly the same way as for Curie's law for electronic magnetic moments.
- It is *very* small, since $\mu_N = (\mu_B/1836)$.

Resultant Magnetization

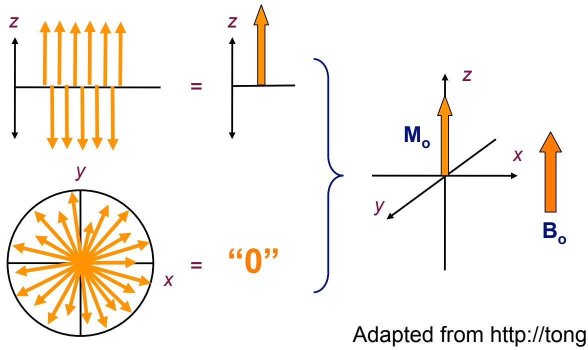


- At equilibrium, there is no transverse component to the magnetization.
- In many instances, the behavior of $\boldsymbol{M}_0$ is envisioned as it "evolves" in NMR experiments.

Iggo, Sec .1-12

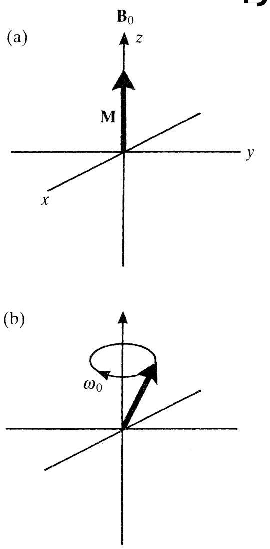
Resultant Magnetization

- At equilibrium, there is a slight excess of "spins-up", but no net transverse component to the magnetization.



Adapted from http://tonga.usip.edu/gmoyna/NMR_lectures/NMR_lectures.html, lecture 1

Basic Pulse Experiment - Assume one type of nucleus

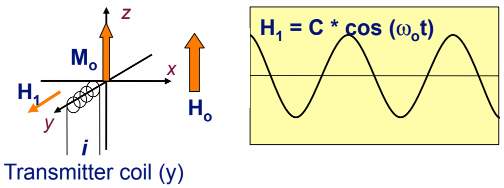


a) Begin at equilibrium magnetization for the applied field.

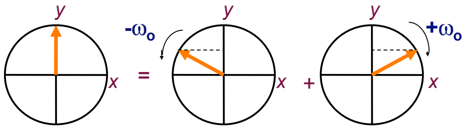
b) Perturb the system with a transverse RF pulse and **M** will precess about the *z*-axis at the Larmor frequency, $\omega_0 = \gamma H_0$.

Basic Pulse Experiment - Assume one type of nucleus

a) Apply a perturbing field, H_1, oscillating at angular frequency ω_0 along the *x*-axis. The energy source is an oscillating electromagnetic radiation generated by an alternating current:



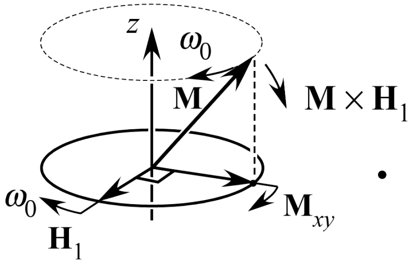
b) The linear oscillating field H_1 can be described as a superposition of two fields rotating away from the *x*-axis:



c) We can restrict attention to the circular component moving in the same direction as the precession of **M**.

Basic Pulse Experiment

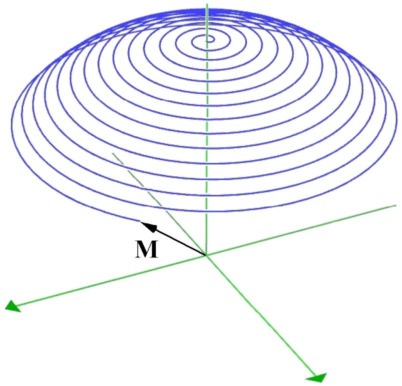
$$\omega_0 = \gamma_N H_0$$



The relative orientations of the magnetization, **M**, its *xy* component, $\mathbf{M}_{xy}$, and the rotating RF field, $\mathbf{H}_1$.

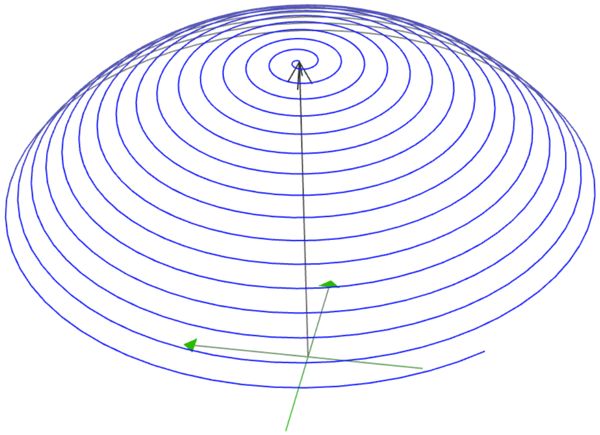
- $\mathbf{H}_1$, oscillating at angular frequency ω_0 in the laboratory frame, follows **M**'s motion around the *z*-axis and applies a torque to **M** that drives **M** into the *xy*-plane.

Motion of **M** in the Lab Frame



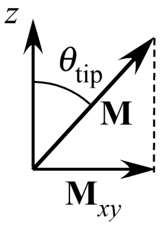
The magnetization vector, **M**, traces a complex path (referred to as *nutation*) in the laboratory frame when rf field $\mathbf{H}_1$ is applied.

Most vector diagrams of **M** therefore refer the rotating frame - rotating at the Larmor frequency.



Motion of M in the Lab Frame

View in the rotating frame



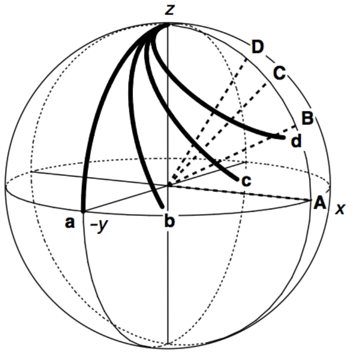
$$\theta_{\text{tip}} = \gamma H_1 t_{\text{pulse}}$$

$$H_1 = H_1(\omega_r) \;\; ; \;\; \omega_r \simeq \omega_0 = \gamma H_0$$

It is understood that 'tip angle diagrams' refer to the *rotating frame*.

- If we adopt a frame of reference that rotates at an angular frequency at (or very near to) ω_0, $\mathbf{H}_1$ and $\mathbf{M}$ are fixed (or nearly fixed) in time.
In general, $\gamma H_1 \gg |\gamma H_0 - \omega_r|$
- If $\mathbf{H}_1$ is applied as a pulse for time t_p (~ 10 μs), the 'tip angle', θ, through which $\mathbf{M}$ is tilted is $\theta = \gamma H_1 t_p$.
- Usually, the time of the pulse is referred to by the tip angle (i.e., as a π/2

More than one kind of nucleus



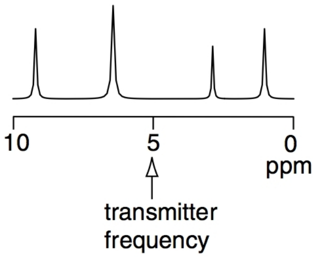
Effect of a $\pi/2$ pulse on $\mathbf{M}$ paths:
path **a**: on resonance ($\omega_{\mathbf{a}} = \omega_r$)
path **b**: $\gamma H_1 = 2|\omega_{\mathbf{b}} - \omega_r|$
path **c**: $\gamma H_1 = |\omega_{\mathbf{c}} - \omega_r|$
path **d**: $1.5\gamma H_1 = |\omega_{\mathbf{d}} - \omega_r|$
A,**B**,**C**,**D**: respective effective field directions.

- Inequivalent nuclei have different Larmor frequencies.
- It is therefore impossible for $\mathbf{H}_1(\omega_r)$ to be exactly "on resonance" with all the lines in the spectrum.
- The greater a peak is offset from ω_r, the greater those nuclei's magnetizations will be from those which are on resonance.
- For nuclei **b**, **c**, and **d**, this pulse is "soft" and not really a $\pi/2$ pulse. To make the pulse "hard", we want to increase H_1 and shorten t_p.

<u>Hard</u> Pulse - Example

- Consider a proton spectrum spanning 10 ppm to be measured on a 500 MHz spectrometer
- Put the transmitter (source of $\mathbf{H}_1(\omega)$) near 5 ppm
- Maximum offset ≈ 5 × 500 Hz = 2500 Hz
- On a typical spectrometer, a 90° pulse might last about 12 μs.

Is the RF power "strong" over all the spectrum?



Range of offsets one might see in a typical proton spectrum. If the transmitter frequency is chosen as shown, the maximum offset of a resonance will be 5 ppm.

Hard Pulse - Example

- Consider a proton spectrum spanning 10 ppm to be measured on a 500 MHz spectrometer
- Put the transmitter (source of $\mathbf{H}_1(\omega)$) near 5 ppm
- Maximum offset ≈ 5 × 500 Hz = 2500 Hz
- On a typical spectrometer, a 90˚ pulse might last about 12 μs. Calculating,

The tip angle is given by $\theta_{\text{tip}} = \gamma H_1 t_{\text{pulse}}$

$$\text{Therefore, } \omega_1 = \gamma H_1 = \frac{\theta_{\text{tip}}}{t_{\text{pulse}}} = \frac{\pi/2}{12\times10^{-6}\,\text{s}} = 1.3\times10^{5}\ \text{s}^{-1} = 130000 \text{ radians s}^{-1}$$

Maximum offset is $2\pi\times 2500$ Hz $= 15700$ radians s^{-1}

- RF field frequency is about 8 times the offset.✓

Data Acquisition

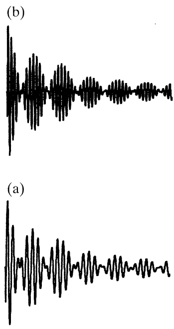
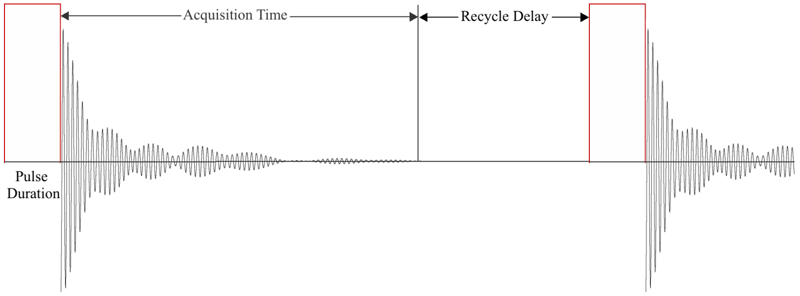


Fig. 1.9. One second of the FID, and the spectrum, of a system containing two frequencies: (a) reference is 30 Hz from the central frequency; (b) reference is 50 Hz from the central frequency; (c) Fourier transformed spectrum from (b).

- After the pulse is applied, data is collected as “Free Induction decays” (FIDs) until the signal begins to descend into the noise.
- FIDs are Fourier transformed to pull our their characteristic frequencies (or their differences with respect to a reference frequency).

Basic 1-Pulse FT NMR Experiment



- Summary: After the pulse, the time-domain FID data is collected over the “acquisition time”. Then there is a delay time to allow the spin system to return to equilibrium…then another pulse…

http://www.scs.uiuc.edu/~mainzv/Basics/basics.htm

Peak intensities and Relaxation times

The intensity observed for a given resonance (I_A) is proportional to the extent to which the pulse induced magnetization decays to its equilibrium value:

$$I_A \propto \left(M_0 - M_z(0)\right)\left(1 - e^{-\tau/T_{1A}}\right)$$

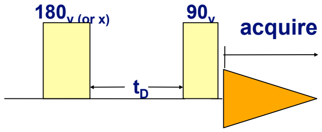
$$\frac{[A]}{[B]} = \frac{I_A}{I_B} \times \frac{1 - e^{-\tau/T_{1B}}}{1 - e^{-\tau/T_{1A}}}$$

M_0 is the equilibrium longitudinal magnetization, $M_z(0)$ is the longitudinal magnetization after the perturbing pulse, τ is the acquisition time, and T_{1A} is the spin-lattice relaxation time for nucleus A.

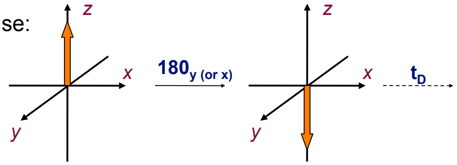
See Canet, Chapter 4.

Measuring T_1: Inversion Recovery

- Measurement of $\mathbf{T_1}$ is important, as the relaxation rate of different nuclei in a molecule can tell us about their local mobility. We cannot measure it directly on the signal or the FID because $\mathbf{T_1}$ affects magnetization we don't detect. We use the following pulse sequence:

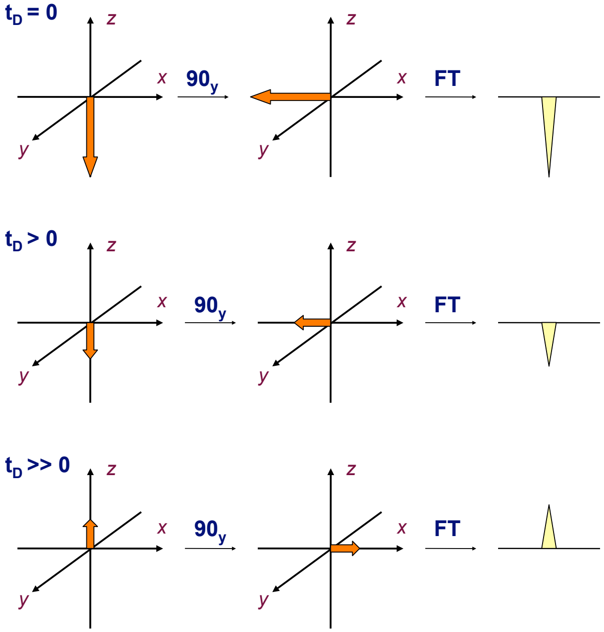


- analyze after the π pulse:



- we are letting the signal decay by different amounts exclusively under the effect of longitudinal relaxation ($\mathbf{T_1}$), we'll see how different $\mathbf{t_D}$'s affect the intensity of the FID and the signal after FT.

Inversion Recovery, cont.



Depending on the $\mathbf{t_D}$ delay we use we get signals with varying intensity, which depends on the $\mathbf{T_1}$ relaxation time of the nucleus (peak) we are looking at.

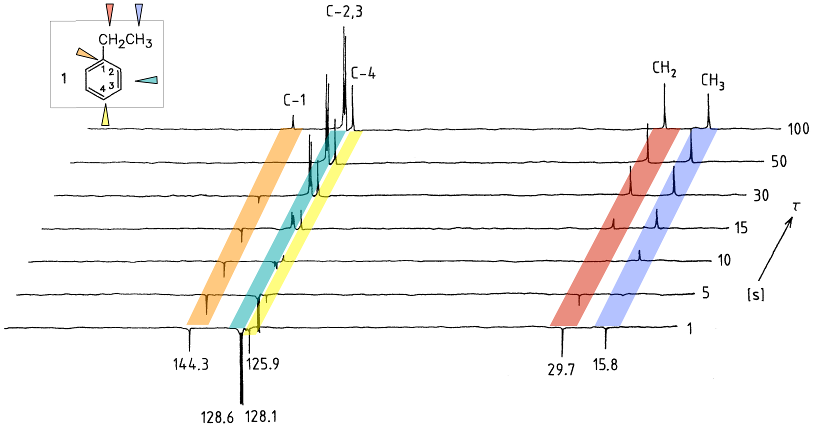
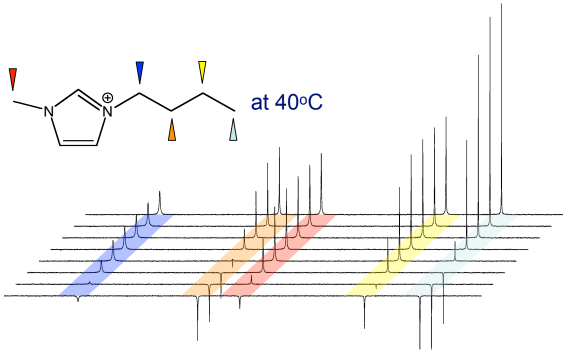
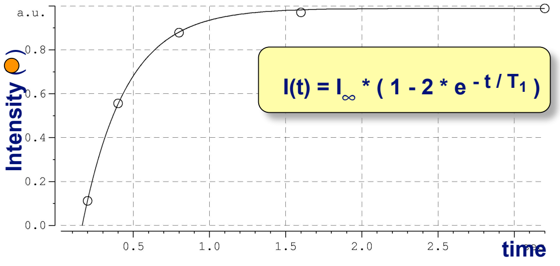


Figure 7-3.
22.63 MHz ^{13}C NMR spectra of ethylbenzene (**1**), recorded by the inversion recovery method (Fig. 7-2) with τ = 1, 5, 10, 15, 30, 50 and 100 s [1].

Inversion Recovery, cont.



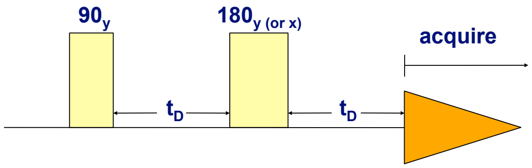
If we plot intensity versus time ($\mathbf{t_d}$), we get the following:



$$I(t) = I_\infty * (1 - 2 * e^{-t/T_1})$$

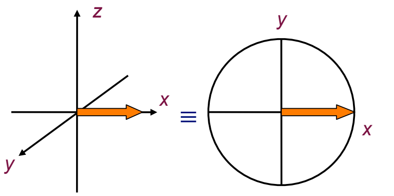
Spin Echo - T_2 measurement

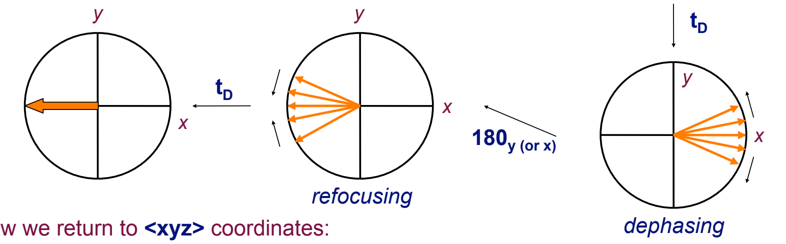
- Measurement of T_2 can in principle be performed by calculating the decay in the FID envelope (which determines the line widths) because the signal on $\mathbf{M}_{xy}$, in theory, decays only due to transverse relaxation. In practice, however, contributions due to field inhomogeneity can dominate.
- The *spin-echo pulse sequence* allows us to avoid contributions inhomogeneous broadening:



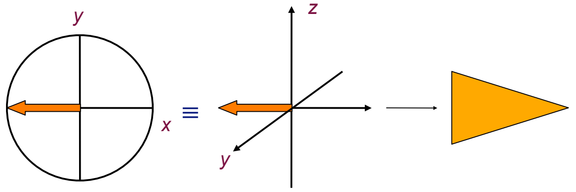
Spin echoes (continued)

- We do the analysis after the 90_y pulse:

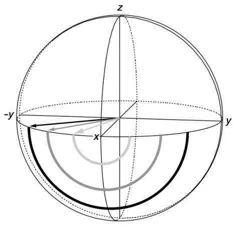




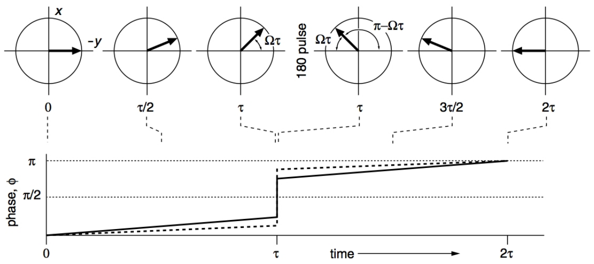
•Now we return to **<xyz>** coordinates:



The 180˚ pulse: refocusing



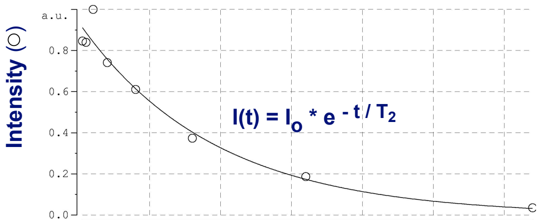
Vectors that lag in the delay are jumped ahead in the 180˚ pulse. The second delay refocuses them.



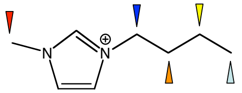
- Different nuclei in the sample move away from the y-axis (to which $\mathbf{M}$ is tipped in the $\pi/2$ pulse) at different rates because of chemical shift differences and field inhomogeneity. The Hahn spin-echo sequence allows them to refocus at the $-y$ axis. But transverse relaxation still attenuates the magnitude of $\mathbf{M}$.

Spin echoes (continued)

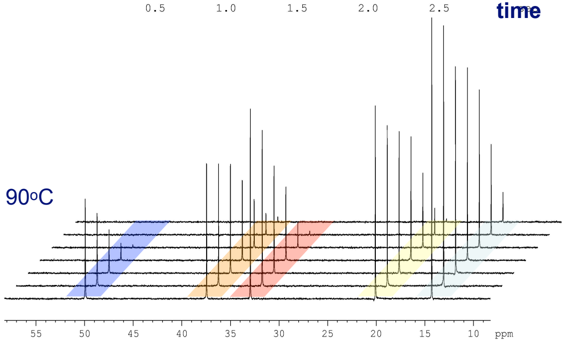
- If we acquire an FID right after the echo, the intensity of the signal after FT will affected only by $\mathbf{T_2}$ relaxation and not by dephasing due to an inhomoge-neous $\mathbf{B_o}$. We repeat this for different $\mathbf{t_D}$'s and plot the intensity against $\mathbf{2 \cdot t_D}$. In this case it's a simple exponential decay, and fitting



$$I(t) = I_o * e^{-t/T_2}$$



at 90°C



A Little Theory of 1-D NMR

Origins of Chemical Shifts (Shielding)

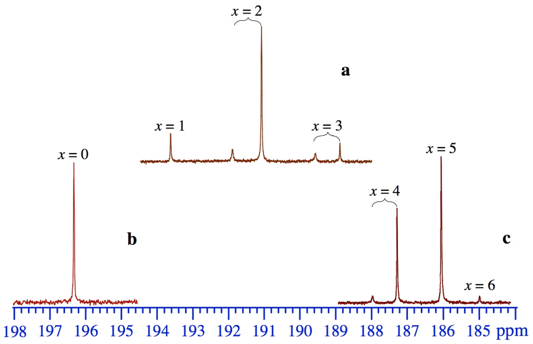
$$H = H_0\left(1-\sigma\right) \quad ; \quad \sigma = \sigma_d + \sigma_p$$

$$\sigma_d\left(zz\right) = \frac{e^2}{2mc^2}\left\langle 0\right|\frac{x^2+y^2}{r^2}\left|0\right\rangle$$

$$\sigma_p\left(zz\right) = -\left(\frac{e\hbar}{2mc}\right)^2 \sum_n \left\{ \frac{\left\langle 0\right|L_z\left|n\right\rangle\left\langle n\right|\frac{2L_z}{r^3}\left|0\right\rangle}{E_n - E_0} + \frac{\left\langle 0\right|\frac{2L_z}{r^3}\left|n\right\rangle\left\langle n\right|L_z\left|0\right\rangle}{E_n - E_0} \right\}$$

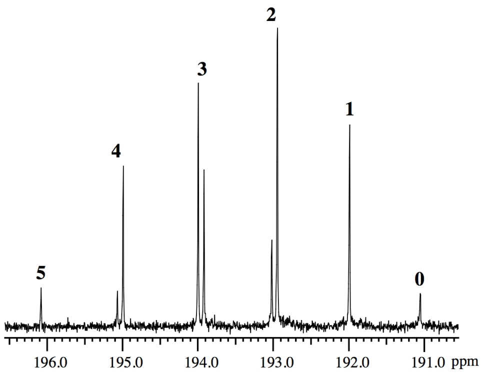
- Shielding consists of a diamagnetic (σ_d) and paramagnetic (σ_p) response of the electrons to the applied field.
  - σ_d arises from a first-order effect, reflecting the electron density distribution in the ground state. (Often dominant in proton spectra.)
  - σ_p arises from a second-order mixing of paramagnetic excited states into the ground state by the applied field (much like TIP). Often dominant for other nuclei.

Chemical Shift Example: $[Zr_6\mathbf{B}Cl_{12}(MeCN)_{(6-x)}Cl_x]^{1-x}$



^{11}B NMR spectra for $Rb_5Zr_6Cl_{18}B$ in acetonitrile with (a) no added ligand, (b) 6 eq. added $TlPF_6$, and (c) 10 eq. added PPNCl. Labeling on the peaks (x = 0 – 6) indicates the number of terminal chlorides in $[(Zr_6BCl_{12})(NCCH_3)_{6-x}Cl_x]^{1-x}$.

Chemical Shift Example: $[Zr_6\mathbf{B}Cl_{12}(MeOH)_{(6-x)}py_x]^+$



^{11}B spectrum of $[Zr_6BCl_{12}(MeOH)_6]^+$ in methanol solvent, to which pyridine was added until the pyridine mole fraction was 5%.

More on Spin-spin Coupling

- The nuclear spin Hamiltonian for two interaction nuclei, A and X, is

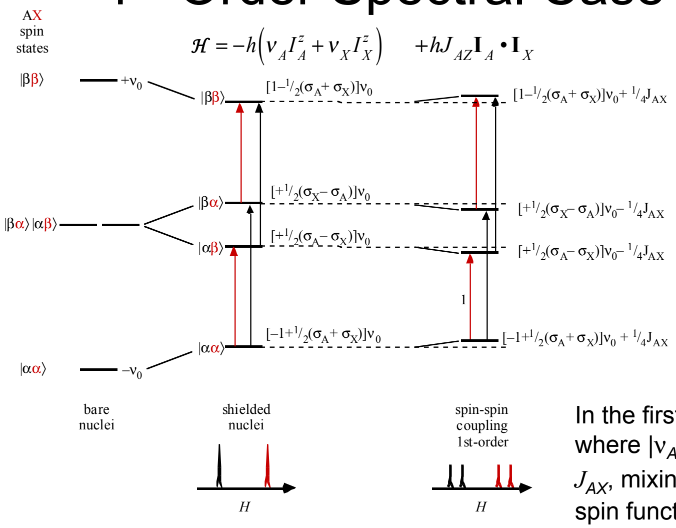
$$\mathcal{H} = -h\left(\nu_A I_A^z + \nu_X I_X^z\right) + hJ_{AZ}\mathbf{I}_A \bullet \mathbf{I}_X$$

where I_A^z and I_X^z are operators for the z-component the spin on A and X, and J_{AX} is the coupling constant for A interacting with X.

- This Hamiltonian will yield the energy expression given earlier (when chemical shift differences are much greater than couplings, $|\nu_A - \nu_B| >> J_{AB}$.

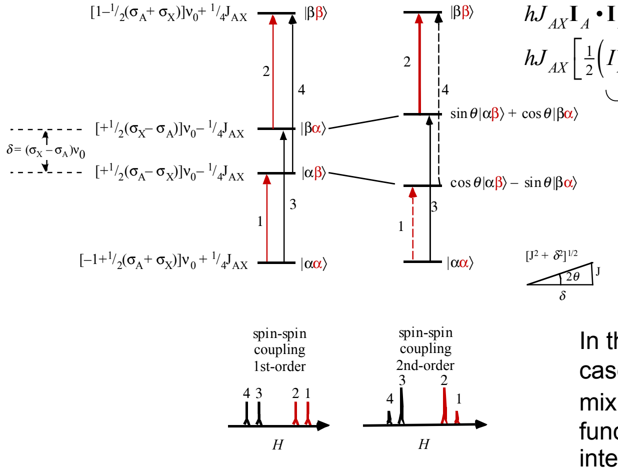
1st-Order Spectral Case

$$\mathcal{H} = -h\left(\nu_A I_A^z + \nu_X I_X^z\right) \quad + hJ_{AZ}\mathbf{I}_A \bullet \mathbf{I}_X$$



In the first-order case where $|\nu_A - \nu_X| >> J_{AX}$, mixing of the spin functions is neglected.

2nd-Order Spectral Case



$$hJ_{AX}\mathbf{I}_A \bullet \mathbf{I}_X =$$

$$hJ_{AX}\left[\underbrace{\tfrac{1}{2}\left(I_A^+ I_X^- + I_A^- I_X^+\right)}_{\text{mixes } |\alpha\beta\rangle \text{ and } |\beta\alpha\rangle} + I_A^z I_X^z\right]$$

See Drago, Chapter 7.

$I_{1,4} \sim 1 - \sin 2\theta$

$I_{2,3} \sim 1 + \sin 2\theta$

In the 2nd-order case, $|\nu_A - \nu_X| \sim J_{AX}$, mixing of the spin functions leads to intensity changes (the rooftop effect) and line shifting.

Range of cases

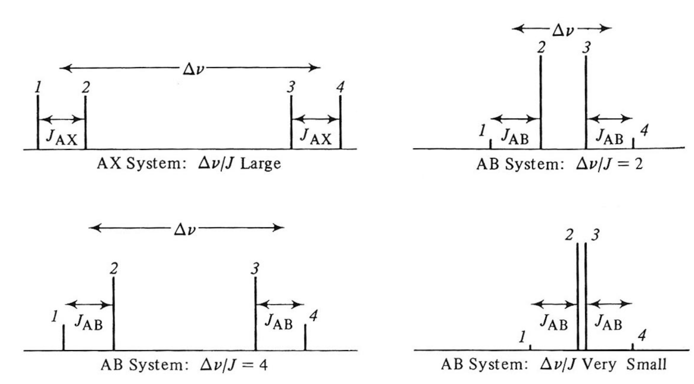
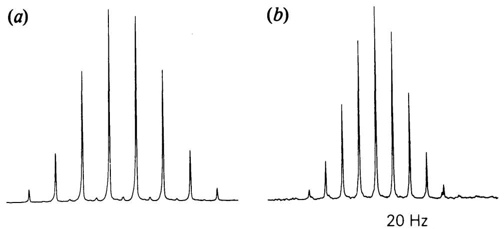


FIGURE 12.11. *Calculated spectra of two-spin systems.*

Miscellaneous Examples

Coupling Examples



(*a*) ^{31}P spectrum of P(OMe)$_3$ and (*b*) ^{29}Si spectrum of SiMe$_4$. In the second case the outermost lines are too weak to be seen. Weak lines between the strong ones arise from small amounts of ^{13}C

Coupling of spin-1/2 nuclei works in pretty much the same way in all cases.

Coupling to non-spin-1/2 Nuclei

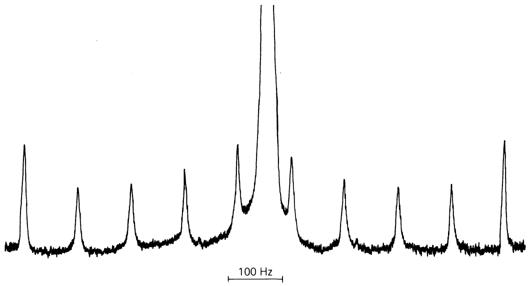
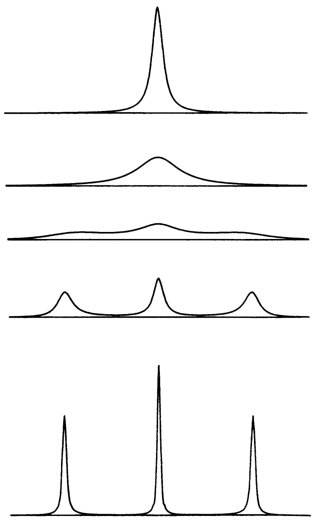


Fig 2.14 ^{1}H NMR spectrum of GeH$_4$. The ten evenly spaced lines are due to the 8% of the molecules which contain ^{73}Ge (I = 9/2). The intense central line arises from all other isotopic species.

^{73}Ge (I = 9/2, 8% abundance) couples to equivalent protons in ^{73}GeH$_4$.

(^{1}H spectrum)

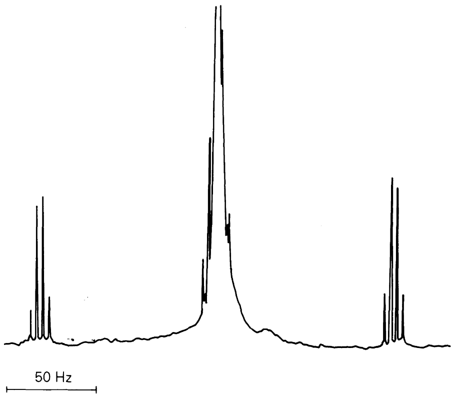
Coupling to Quadrupole Nuclei



Calculated band shapes for a spin 1/2 nucleus (^{1}H) coupled to a spin 1 nucleus (^{14}N). The shape depends on the ratio of ^{14}N relaxation rate to the NH coupling. For very fast relaxation just a single line is observed, while for slow relaxation there are three lines of equal intensity.

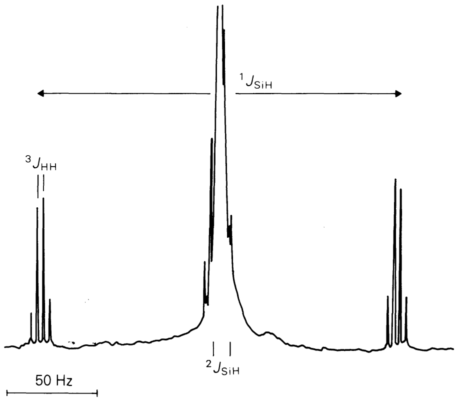
- Because spin-spin coupling induces spin wavefunction mixing, the relaxation of a quadrupole nucleus is partially “transferred” to spin-1/2 nuclei to which it is coupled.

Si_2H_6 (^1H spectrum)



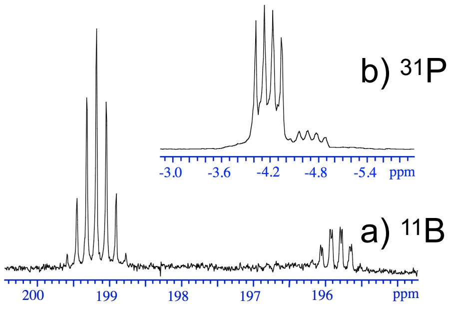
^{29}Si (I = 1/2, 4.7% abundance)

Si_2H_6 (^1H spectrum)



^{29}Si (I = 1/2, 4.7% abundance)

$[Zr_6BCl_{12}(PEt_3)_6]^+$ + ?



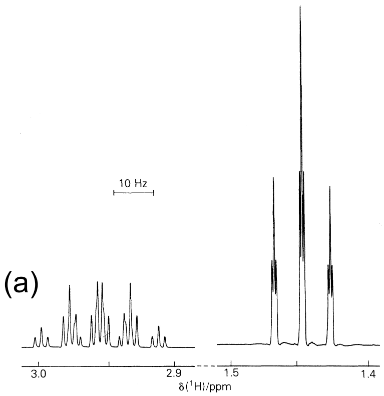
a) ^{11}B spectrum of $[Zr_6BCl_{12}(PEt_3)_6]^+$ plus an impurity.

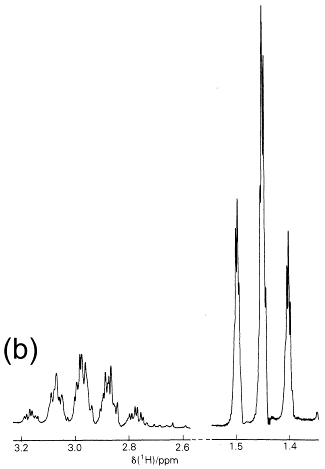
b) ^{31}P spectrum of $[Zr_6BCl_{12}(PEt_3)_6]^+$ plus an impurity.

What is the impurity?

^{11}B (I = 3/2, 81.2% abundance), ^{10}B (I = 3, 18.8% abundance)

1st and 2nd-order spectra





a) 360 MHz ^1H spectrum for $CH_3CH_2SPF_2$. (1st order)

b) 80 MHz ^1H spectrum for $CH_3CH_2SPF_2$. (2nd order)

Coupling: Structural Correlations

Correlations like the well-known Karplus relation shown here ultimately derive from the manner in which *s*-electron density is involved in wavefunctions that spread over two coupled nuclei.

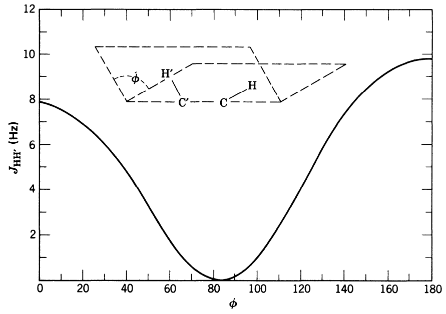
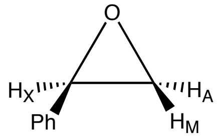


Fig. 46.
The vicinal Karplus correlation. Relationship between dihedral angle and coupling constant for vicinal protons.

For 3-bond coupling constants the empirical relation here is useful:

$$^3J_{XY} = A\cos 2\phi + B\cos\phi + C$$

$$J_{\mathrm{AM}} > \underbrace{J_{\mathrm{AX}} > J_{\mathrm{MX}}}_{\text{vicinal protons}}$$



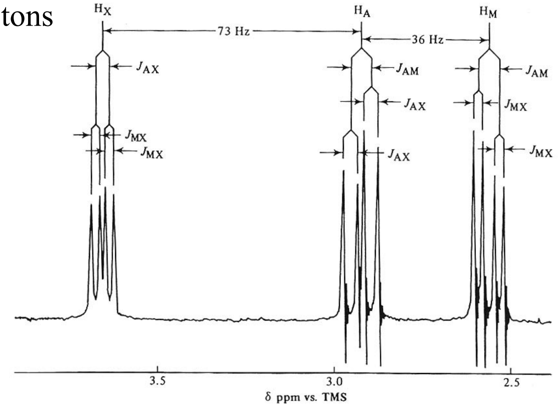
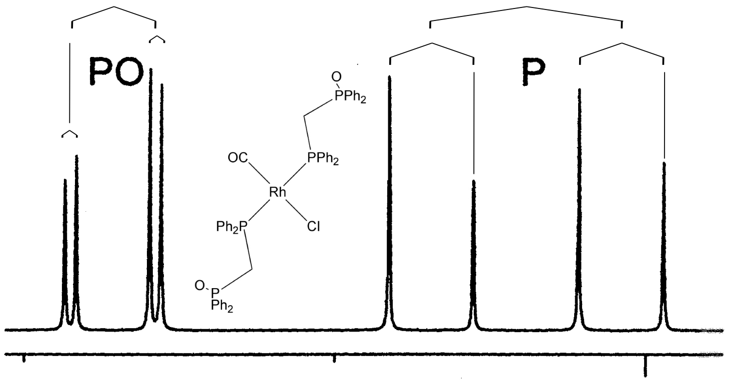


FIGURE 12.12. 100-*MHz spectrum of styrene oxide (25% in CCl₄). The part of the spectrum due to aromatic protons is not shown.*

---

trans-Rh(CO)Cl{$Ph_2PCH_2P(O)Ph_2$}$_2$: ^{31}P{^{1}H}: First- and Second-order Coupling



^{103}Rh I = $^1/_2$ abundance = 100%

Coupling: Structural Correlations

Correlations ultimately derive from the manner in which *s*-electron density is involved in wavefunctions that spread over two coupled nuclei.

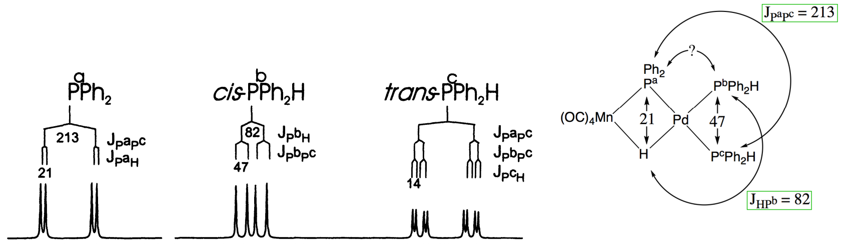


Fig. 2.19 The size of the coupling constant is a good indication of the interbond angle, being smaller between similar groups in a *cis* orientation than when the coupling nuclei are mutually *trans*. Here the ^{31}P NMR spectrum of a palladium hydride complex is shown. The larger couplings are between *trans* groups. From data in Braunstein *et al. Inorg. Chem.*, 1992, **31**, 411.

A Typical (Simple) Structural problem

2.4 The ^{13}C NMR spectrum of the carbonyl groups in one isomer of $[W(CO)_4P(OMe)_3(SPh)]^-$ is shown in Fig. 2.46. Identify the isomer and account for the form of the spectrum. What would you expect to see in the ^{13}C spectrum of the other isomer? [The figure is adapted, with permission, from D.J. Darensbourg, K.M. Sanchez and J. Reibenspies, *Inorg. Chem.*, **27**, 3636 (1988). Copyright (1988) American Chemical Society.

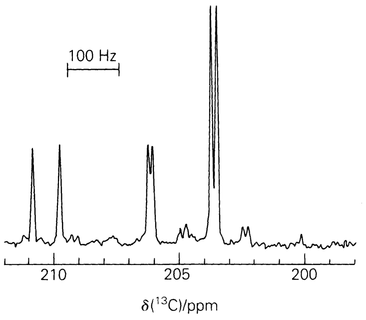
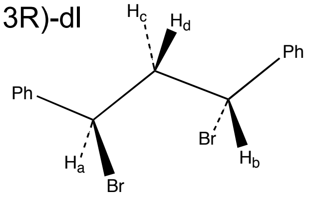


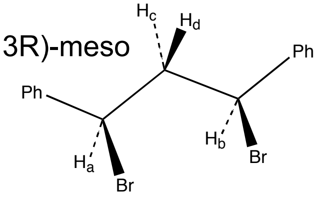
Fig. 2.46

Chemical Shift Equivalence (isochronous nuclei)

(1R,3R)-dl



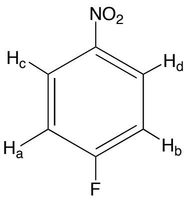
(1S,3R)-meso



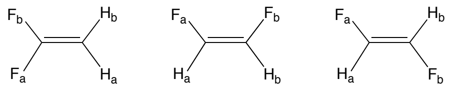
- Two isomers of 1,3-dibromo-1,3-diphenylpropane
- How many chemical-shift equivalent sets of aliphatic protons in each isomer?

Magnetic (In)equivalence

p-fluoronitrobenzene



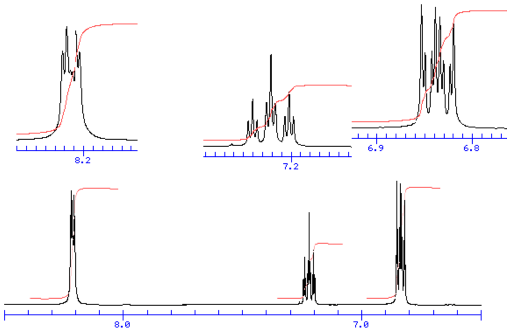
difluoroethylenes



- Magnetically equivalent nuclei are coupled equally to every third nucleus in the spin system.
- In each molecule the protons are *chemical shift equivalent*?
- Which sets are *magnetically equivalent*?

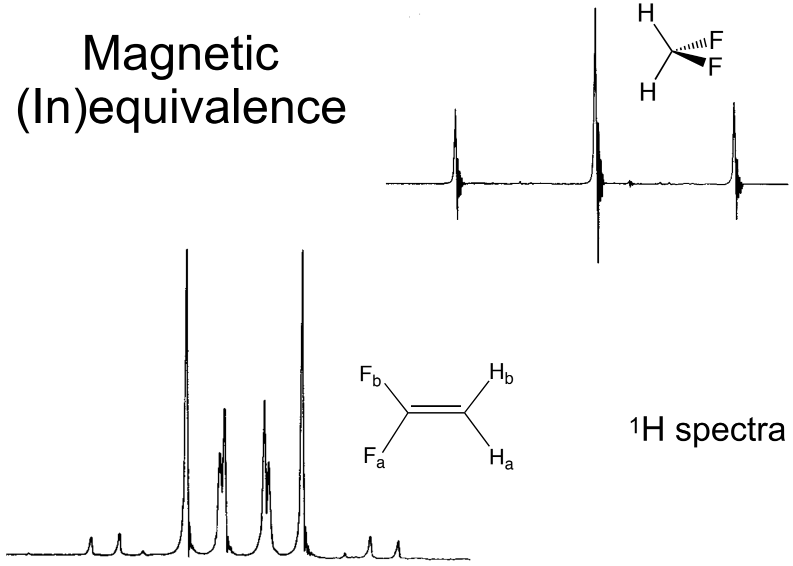
Magnetic (In)equivalence

C_5H_5N (simulated)



- Magnetically equivalent nuclei are coupled equally to every third nucleus in the spin system.
- The “unknown” here is an easy one, but the spectrum is more complicated than you might have expected.

Magnetic (In)equivalence



^{1}H spectra

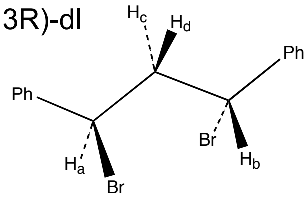
Notation for labeling nuclei

- Chemically and magnetically equivalent nuclei given the <u>same</u> label. (e.g., A)
- Chemically, but not magnetically equivalent nuclei given primes. (e.g, AA′ for two, AA′A″ for three, etc.)
- Nuclei with small chemical shift differences (smaller or comparable to coupling between them) given alphabetically close labels (e.g., A, B, C, D, etc.)
- Inequivalent nuclei with large chemical shift differences given alphabetically distant labels (e.g., AMX, for three)
- One can describe a mix of types of nuclei
  - A_2BMXY is a six-spin system with two equivalent nuclei (A), strongly coupled (compared to $\Delta\nu_{AB}$) to one nucleus B, weakly coupled to one nucleus M (vs $\Delta\nu_{AM}$) and very weakly coupled to X & Y
  - M is weakly coupled to all nuclei
  - B is only strongly coupled to A
  - X & Y are strongly coupled to each other and weakly to all other nuclei

---

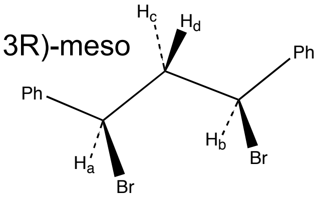
Examples (ignoring phenyl groups)

(1R,3R)-dl



- AA′MM′

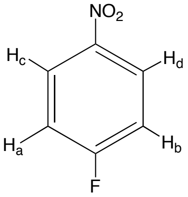
(1S,3R)-meso



- ABM_2

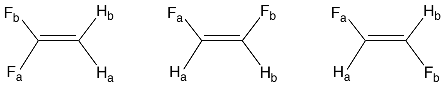
More Examples

P-fluoronitrobenzene



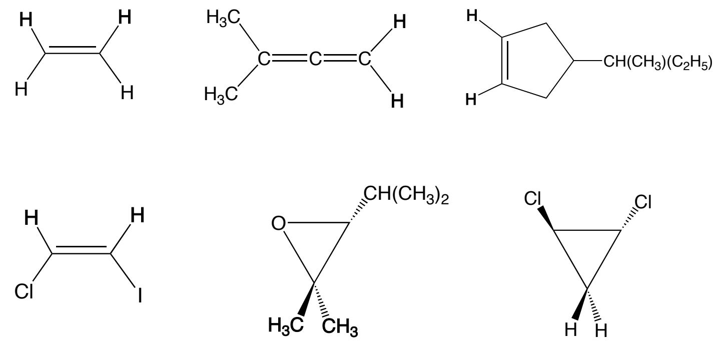
- AA′BB′ (in a sufficiently high field, AA′MM′)

difluoroethylenes

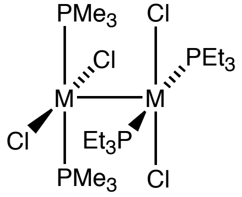


all AA′XX′ (AA′MM′ equally good)

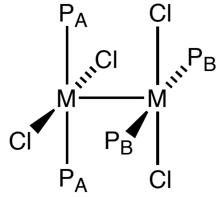
Characterize indicated protons as to chemical-shift and/or magnetic equivalence



More Examples (^{31}P)

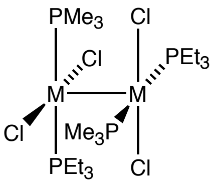


A_2B_2



- Both $^{31}PMe_3$ couple to each of the $^{31}PEt_3$ in an equivalent fashion (and vice versa).

More Examples



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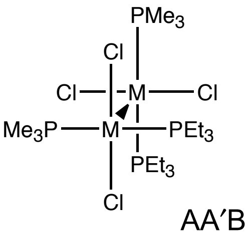
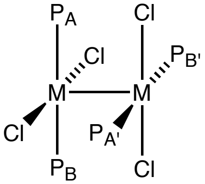
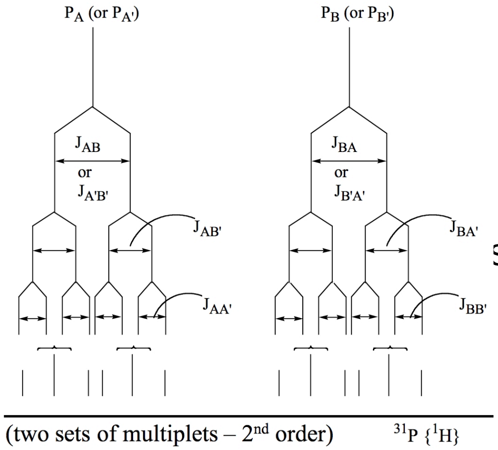


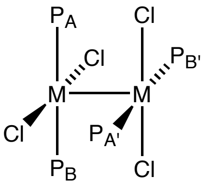


$AA'BB'$

- The $^{31}PMe_3$ couple to <u>each</u> of the $^{31}PEt_3$ *differently* (and vice versa), ∴ magnetically inequivalent.
- Sample data:
  - $J_{AB} = J_{A'B'} = 104$ Hz
  - $J_{AA'} = J_{A'A} = 20$ Hz
  - $J_{BB'} = J_{B'B} = 19.2$ Hz
  - $J_{A'B} = J_{AB'} = J_{BA'} = J_{B'A} = 23$ Hz

Expected ^{31}P {^1H} Spectrum





$AA'BB'$

Sample data:

- $J_{AB} = J_{A'B'} = 104$ Hz
- $J_{AA'} = J_{A'A} = 20$ Hz
- $J_{BB'} = J_{B'B} = 19.2$ Hz
- $J_{A'B} = J_{AB'} = J_{BA'} = J_{B'A} = 23$ Hz

Dynamic NMR

See Chapter 7,
NMR and Chemistry, 4th Edition, J.W. Akitt and B. E. Mann.

Time Scale

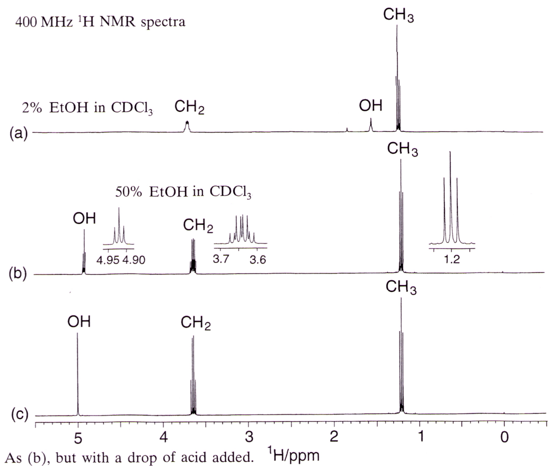
$$\Delta E = \gamma_N \hbar H_0 = h\nu_L$$

$$\nu_L = \left|\frac{\gamma_N}{2\pi}\right| H_0 \; ; \; \omega_0 = \gamma_N H_0$$

$$\text{including chemical shift: } \nu = \left|\frac{\gamma_N}{2\pi}\right| H_0 \left(1-\sigma\right)$$

- NMR is generally considered to be a slow technique, with a characteristic time scale, $\tau \sim 10^{-7}$ s. (Recall, $1/\tau = \nu \sim 100$ MHz.)
- This is actually much faster than rates usually measured with NMR. Reactions with half-lives of 10^{-2} s to 10^{-3} s are more typical, I.e., the *difference* between resonance frequencies.

A Familiar Example - Proton Exchange



Thermodynamic and Kinetic Exchange Parameters

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

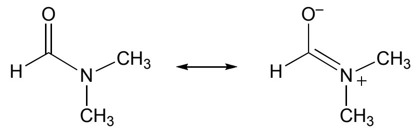
Well **below** the coalesence point), the individual line widths are given by:

$$\Delta\nu_A = \frac{k_A}{\pi} = \frac{1}{\pi\tau_A} \quad ; \quad \Delta\nu_B = \frac{k_B}{\pi} = \frac{1}{\pi\tau_B}$$

In the limit of fast exchange (**above** the coalesence point), the line width is given by:

$$\Delta\nu = \frac{4\pi p_A p_B (\delta\nu_{AB})^2}{k_A + k_B}$$

p_A and p_B are the fractional populations of sites A and B.



Hindered Rotation

A 2-site example illustrating different line-shape regimes in a dynamic process amenable to NMR study.

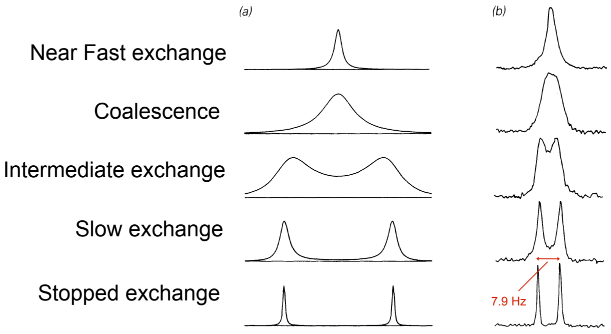
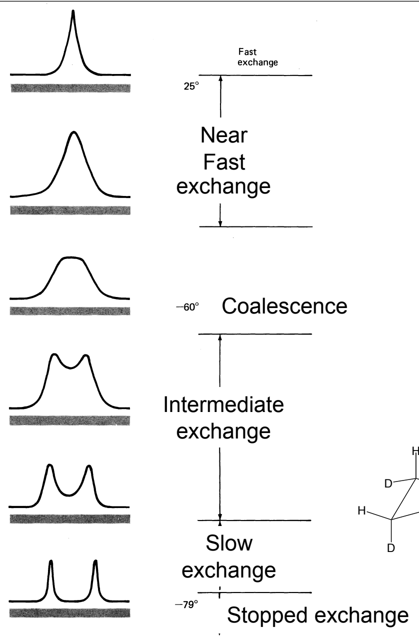
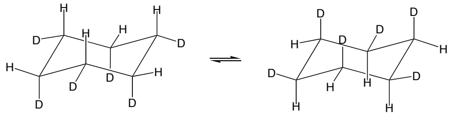


Fig. 2.40 (*a*) Calculated band shapes for various values of exchange rate relative to frequency difference for two equally populated sites. (*b*) Gas-phase ^{13}C NMR spectra of *N*,*N*-dimethyl-$^{13}C_2$-formamide, 2.XXXI. The spectra, recorded at 427, 415, 410, 397 and 373 K, show two distinct resonances at low temperatures, when rotation about the central C—N bond is rapid. Spectra in (*b*) are taken, with permission, from B.D. Ross and N.S. True, *J. Am. Chem. Soc.*, **106**, 2451 (1984). Copyright (1984) American Chemical Society.



Cyclohexane Interconversion

Another 2-site example illustrating different line-shape regimes in a dynamic process amenable to NMR study.



T_C and k_C

If (a) the exchange process is first-order,

(b) there is no coupling between exchanging nuclei, and

(c) the two singlets have equal intensities:

For the coalescence temperature, T_C, the rate constant, k_C, is

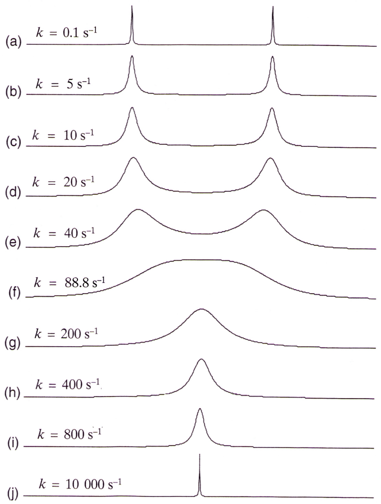
$$k_C = \frac{\pi \Delta \nu}{\sqrt{2}} \cong 2.22\, \Delta \nu$$

$\Delta \nu$ is the chemical shift difference (in Hz) in the absence of exchange (determined at low temperature but extrapolated to high T).

- Even when (a), (b), and (c) are not exactly fulfilled, this is usually a decent estimate for k_C.

T_C and k_C

- Coalescence is defined as the point at which the minimum between the high temperature peaks becomes a flat plateau.



Calculated spectra for exchange between two equally populated sites separated by 40 Hz. T_2 values of both sites are 1 s.

$$k_C = \frac{\pi \Delta \nu}{\sqrt{2}} = \frac{40\pi}{\sqrt{2}} = 88.8\ s^{-1}$$

The Slow Exchange Regime

$$W_{1/2} = \frac{1}{\pi T_2}$$

when spin-spin relaxation is the mechanism controlling a spin's lifetime

$$W_{1/2} = \frac{1}{\pi T_2} + \frac{1}{\pi \tau_{\mathrm{ex}}} = \frac{1}{\pi T_2} + \frac{k}{\pi}$$

where k is the rate constant for exchange

Linewidth determined by time a spin spends at one location (nucleus)

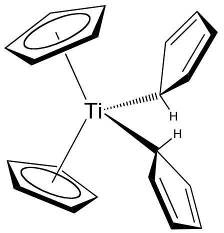
When exchange is occurring there are two mechanisms that shorten the lifetime of the spin state

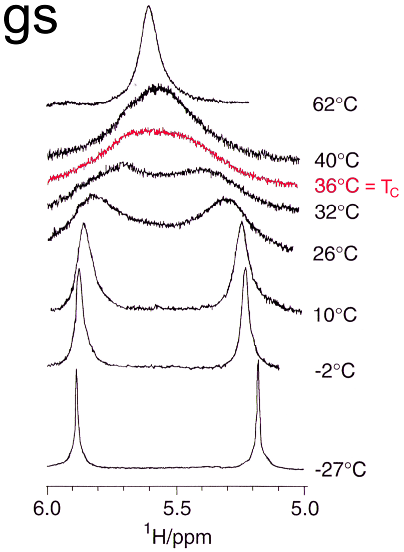
$$\therefore \quad k = \pi\left[\left(W_{1/2}\right)_{\mathrm{ex}} - \frac{1}{\pi T_2}\right] = \pi\left[\left(W_{1/2}\right)_{\mathrm{ex}} - \left(W_{1/2}\right)_0\right]$$

fairly accurate when $\left(W_{1/2}\right)_{\mathrm{ex}}$ is substantially larger than $\left(W_{1/2}\right)_0$

Fluxional Cp Rings

- The η1- and η5-Cp proton resonances coalesce at 36 ˚C. (What process must be quite rapid even at -27 ˚C?)





T_C and k_C - more

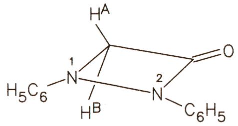
- When expressed in ppm, chemical shifts are field independent. But Δν is in Hz, which means that Δν ∝ H. Therefore, T_C and k_C increase with the field used in the NMR experiment (and the highest available field may not be the most appropriate).
- Coupling between exchanging nuclei can be handled: If nuclei A and B are exchanging and are coupled (with constant J_{AB}) k_C is

$$k_C = \frac{\pi \Delta\nu}{\sqrt{2}} \cong 2.22\sqrt{\left(\Delta\nu\right)^2 + 6J_{AB}^2}$$

An example with Coupling

- H^A and H^B are clearly inequivalent at -55 ˚C, but are equivalent in the fast exchange regime at 35 ˚C.
- How would this study have changed if carried out on a 300 MHz instrument?

1,2-diphenyldiazetidinone



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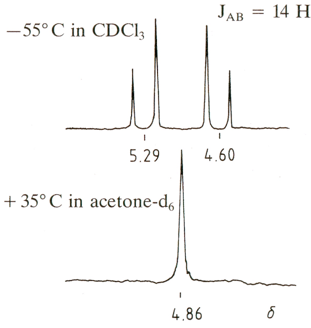
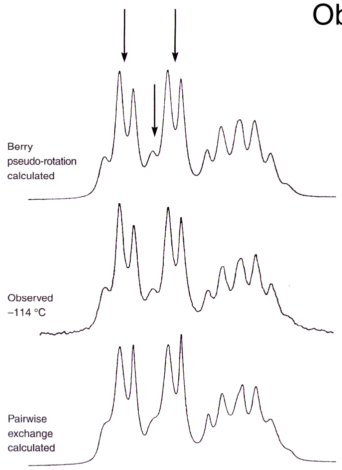


60 MHz ^{1}H NMR signals of the ring protons H^A and H^B

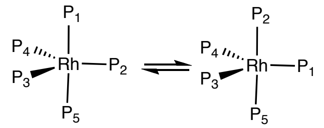
Complete Line Shape Analysis

- Record spectra at different temperatures, e.g.,
  - 3 slow-exchange spectra (incl. 1 stopped-exchange)
  - 5-10 spectra in coalescence regime
  - 3 spectra in near-fast and fast regime
- Analyze spectrum in stopped exchange regime
  - Get ν's, J's, line-widths ($\Delta\nu_{1/2}$'s)
- Calculate spectra in the coalescence regime, varying k(s) until observed and calculated spectra match. Repeat at other temperatures.
- If necessary, calculate spectra in fast-exchange limit.

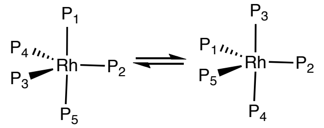
Evidence for Berry Pseudorotation



Observed and calculated 36.43 MHz $^{31}P\{^{1}H\}$ spectra of $[Rh\{P(OMe)_3\}_5]^+$ in $CHClF_2/CH_2Cl_2$ (9:1) at –114 ˚C.



pairwise exchange (turnstile) mechanism



Berry pseudorotation (P_4 pivot)

Activation Parameters

- Use of the Arrhenius plots (ln$k$ vs. $1/T$) are a lot of work since they require data for a range of temperatures (many measurements *and* full line-shape analyses)
- Estimate for ΔG‡ using the Eyring equation is easy with T_C in hand:

$$k = \aleph\frac{k_B T}{h}e^{-\Delta G^{\ddagger}/RT} = \aleph\frac{k_B T}{h}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT} \quad \text{or} \quad \Delta G^{\ddagger} = RT\left\{23.759 + \ln\left(\frac{k}{T}\right)\right\}$$

$$\left(\text{at } T = 298.15\text{ K}, \frac{k_B T}{h} = 6.21\times10^{12}\text{ s}^{-1}, \aleph \text{ is usually taken to be} \sim 1\right)$$

An Eyring plot, ln(k/T) vs. $1/T$, would should yield ΔH‡ and ΔS‡, but again, much more work. WARNING: This approach is still fraught with the potential for large errors, because the range temperatures on can measure is small, chemical shift dependence on T, linewidth misestimates, poor T calibration, and broadening due to unresolved coupling (see Akitt & Mann).

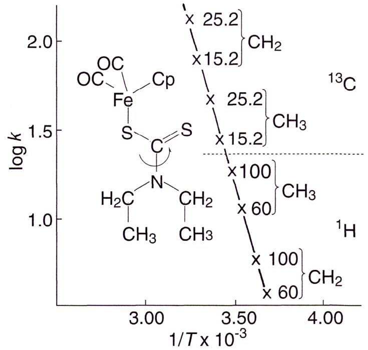
More Accurate Activation Parameters

Better activation parameters can be obtained from NMR kinetic studies:

(1) Use different spectrometers, with different frequencies. The *frequency difference* between resonances varies with field strength when the peak differences are due to chemical shifts (only the ppm values remain the same). For this reason, a rate study might be better carried out on a lower field instrument. (Coalescence occurs at a lower temperature in lower field.)

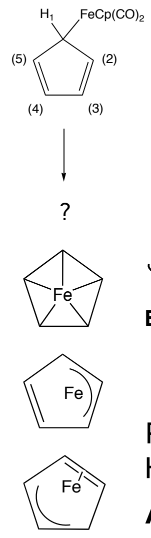
(2) Different nuclei might be used (see example).

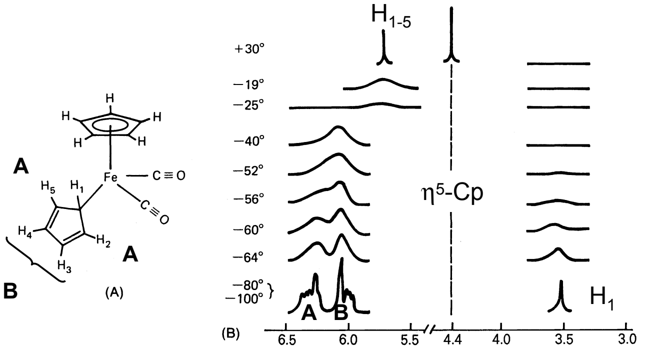
(3) Different methods are useful in different regimes; e.g., lineshape analysis when rates are within an order of magnitudes of the coalescence rate and magnetization transfer for lower temperatures with slower rates.



$$\ln\left(\frac{k}{T}\right) = \frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right) - \left(\frac{\Delta S^{\ddagger}}{R} + 23.759\right)$$

How does the ring whiz?



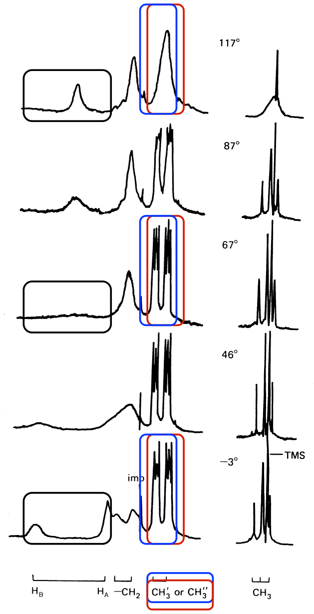


Peaks at δ ≈ 6.0 (**B**) & 6.3 (**A**) are assigned to $H_{3,4}$ & $H_{2,5}$, respectively.

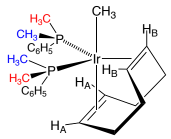
A resonances collapse faster than **B** resonances.

Mechanism? See problem set!

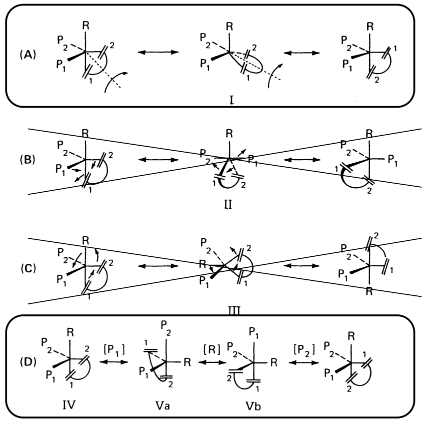
Competing Mechanisms?



- At -3˚C, the COD ethylenic protons and the diastereotopic $(CH_3)P$ are not exchanging.
- At 67˚C, the COD ethylenic protons are exchanging, but the diastereotopic $(CH_3)P$ groups are not.
- At 117˚C, the COD ethylenic protons and the diastereotopic $(CH_3)P$ are both exchanging.



Competing Mechanisms?



- At -3˚C, the COD ethylenic protons and the diastereotopic $(CH_3)P$ are not exchanging.
- At 67˚C, the COD ethylenic protons are exchanging, but the diastereotopic $(CH_3)P$ groups are not.
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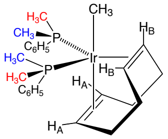

Short Questions

- Explain each of the following observations.
  - **(a)** The ^{1}H spectrum of GeH_4 shows ^{73}Ge satellites but the spectra of $GeFH_3$ and $GeClH_3$ do not.
  - **(b)** The ^{13}C-$\{^{1}H\}$ NMR spectrum of (bis)allylnickel at 200 K shows three resonances, of equal intensity; at 250 K, only two resonances are observed, in a 2:1 intensity ratio.
  - **(c)** The ^{1}H NMR spectrum of rigorously dried ^{14}N-ammonia is a broad 1:1:1 triplet that becomes broader as the temperature is lowered; the ^{1}H NMR spectrum of ^{15}N-ammonia containing a trace of $Na^{15}NH_2$ is a broadened 1:1 doublet that becomes sharper as the temperature is lowered.

Problem

Reaction of IF_7 and SbF_5 gives a 1:1 product. The ^{19}F NMR spectrum contains two sets of resonances: one with 6 lines of equal intensity; the other with overlapping patterns of 6 lines of equal intensity and 8 lines of equal intensity, the former being somewhat stronger. Explain.

^{121}Sb $^5/_2$, 57.3 %, ^{121}Sb $^7/_2$, 42.7 %, ^{127}I $^5/_2$, 100 %

Problem

What coupling pattern would you expect to observe for a single proton coupled to (a) one and (b) two equivalent ^{11}B nuclei? (c) Same as (b) but with a “real sample?

^{11}B $^3/_2$, 80.4 %, ^{10}B 3, 19.6 %

Problem

The ^1H NMR spectrum of $GeFH_3$ consists of two lines separated by 42 Hz. What are the relative positions and intensities of all the lines in the ^{19}F spectrum of

(a) $GeDFH_2$

(b) GeD_2FH

(c) GeD_3F

Problem

$W(CO)_6$ reacts with $NaBH_4$ to give an anionic product. Its tetraethylammonium salt has the empirical composition $C_{18}H_{21}NO_{10}W_2$. Its ^1H NMR spectrum includes a triplet, intensity ratio 1:6:1, at δ -22.5 ppm, with a separation between the outer peaks of 42 Hz. What can you deduce about the structure of the anion?

^{183}W, S = $^1/_2$, 14.4 %