

Proton NMR

1. Principles

1.1. NMR spectroscopy depends on radio frequency absorption by nuclei with nuclear spin

1.2. Proton and carbon are most common nuclei studied

1.3. nuclei can have a magnetic moment and angular momentum

1.3.1. analogous to precessing top in gravitational field

1.3.2. angular momentum depends on I: spin quantum number

1.3.3. for ^1H and ^{13}C , $I = \frac{1}{2}$

1.3.4. ^2H , $I = 1$ and ^{10}B , $I = 3$, see Chapter 6

1.3.5. the number of spin states = $2I + 1$, $+I$ to $-I$ in steps of 1

1.3.5.1. 2 spin states for ^1H ($\frac{1}{2}$ and $-\frac{1}{2}$)

1.3.5.2. for ^{10}B $2(3) + 1 = 7$ (3, 2, 1, 0, -1, -2, -3)

1.3.5.3. sign indicates nuclei field direction relative to external field

1.3.5.4. all are equal energy until they are in an external field

1.4. transition energy between spin states corresponds to frequency of absorption

$$\Delta E = h\nu, \text{ allowed transition, } \Delta I = +1 \text{ or } -1$$

1.4.1. frequency depends on magnetic field, angular momentum, and magnetic moment

$$\nu = \frac{\mu}{2\pi h I} B = \frac{\gamma}{2\pi} B : \mu = \text{magnetic moment, } B = \text{magnetic field, } \gamma = \text{gyromagnetic ratio}$$

1.4.2. B depends on external magnetic field and local magnetic field in molecule at the nucleus, γ depends on the nucleus and isotope

1.4.3. different protons in same molecule absorb at different frequency

1.4.4. likewise for carbon

1.4.5. signal intensity: **sample size, # identical nuclei in compound, B, γ**

1.4.6. individual nuclear dipoles precess in the magnetic field like a top

1.4.7. circumscribe a cone in random directions with no net magnetization in the x,y plane

1.4.8. sum of magnetic moments have net magnetization

1.4.9. at equilibrium, magnetization is aligned with external magnetic field

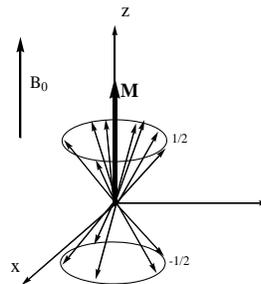
1.4.10. direction of B is set at z axis

1.4.10.1. irradiation stimulates transition from lower to upper and upper to lower state

1.4.10.2. lower to upper absorbs one photon

1.4.10.3. upper to lower **releases** one photon

1.4.10.4. if populations of two states are equal there is no net absorption



1.4.10.5. Boltzmann equation determines population difference for two spin states

$$1.4.10.6. \frac{n_u}{n_l} = e^{-\Delta E/k_B T} = e^{-h\nu/k_B T} = 1 \cdot 10^{-4}$$

1.4.10.7. excess population of lower state is very low: NMR has low sensitivity

1.5. Rotating Frame

1.5.1. Consider static frame of reference, x, y and z axes

1.5.2. a rotating frame can rotate where x' and y' axes rotate about z' axis and z' = z

1.5.3. in frame of reference rotating at Larmour frequency $\nu = \frac{\gamma}{2\pi} B$ (frequency of

nuclear precession) the nuclei do not precess

1.5.4. net magnetization can be treated classically

1.5.5. apply magnetic field B_1 , also rotating at ν , in rotating frame it appear static say along the x' axis.

1.5.6. the net z' magnetization will precess perpendicular around magnetic field (B_1)

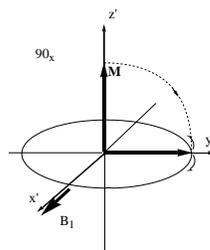
1.5.7. pulse B_1 for short time until magnetization rotates 90° into xy plane along y' axis

1.5.8. after B_1 is off, observe magnetization rotate in xy plane

of laboratory frame, under influence of B

1.5.8.1. loose magnetization in xy plane, recover along z axis

1.5.8.2. relax back to equilibrium magnetization along z axis

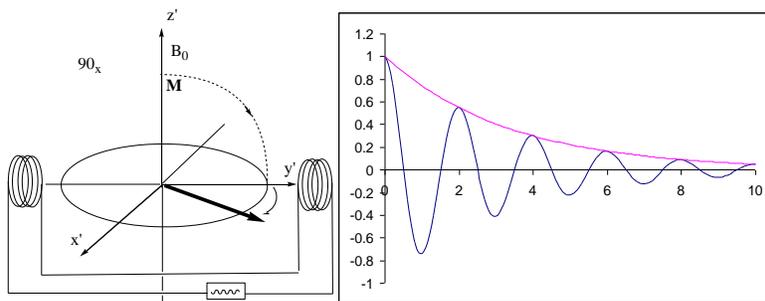


1.6. detection of transverse magnetization: FID

1.6.1. place detector (conducting coil) around sample along x or y axis

1.6.2. magnetization induces alternating current as it passes through coil

1.6.3. FID: free induction decay, induced current in coil oscillates and decay



1.6.4. signal is processed in rotating frame

1.6.4.1. frequency compared to B_1 (transmitter) frequency, $\omega_{\text{obs}} = \omega - \omega_{\text{rf}}$

1.6.4.2. if $\omega = \omega_{\text{rf}}$ then $\omega_{\text{obs}} = 0$, no oscillation is observed, just decay

1.6.4.3. some nuclei precess faster, some slower

1.6.4.4. ω_{obs} is greater or less than zero

1.6.5. frequency of oscillation depends on B for each nuclei and γ (gyromagnetic ratio)

for each nuclei

1.6.6. superposition of sine waves of different frequencies

1.6.7. Fourier Transform (FT) of signal (amplitude versus time) yields frequency

spectrum (amplitude versus frequency): $I(\omega) = \int_0^{\infty} M_y(t) \cos(\omega t) dt$

1.7. Transverse relaxation, lifetime of T_2 seconds

1.7.1. loss of coherence (signal) in xy plane, spins get out of phase

1.7.2. random exchange of spin states

1.7.3. T_2 is lifetime for loss of magnetization in xy plane

1.8. Longitudinal relaxation, lifetime of T_1 seconds

1.8.1. random exchange of energy of spin state

1.8.2. T_1 lifetime for magnetization return along z axis

1.8.3. $T_1 \geq T_2$

2. Chemicals Shifts

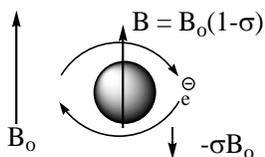
2.1. chemical environment shifts the local magnetic field = chemical shift

2.1.1. source: moving electrons in magnetic field create local field

2.1.2. local field partially "cancels" external: electrons shield nucleus

2.2. extent of shielding is proportional to external field: σ = shielding constant

2.3. effective field is $B = B_0 - \sigma B_0 = B_0(1 - \sigma)$ where B_0 is external field



2.4. neighboring electron-withdrawing groups deshield, and increase frequency since

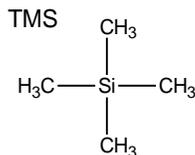
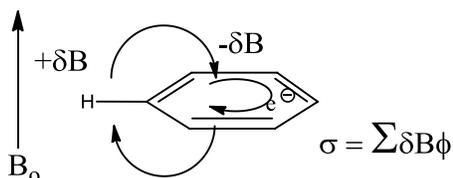
$$\nu = \frac{\gamma}{2\pi} B = \frac{\gamma}{2\pi} B_0(1 - \sigma)$$

2.5. π electron on neighboring groups, especially aromatic rings result in shielding or

deshielding depending on position

2.5.1. sum of all orientations

2.5.2. σ bonds – localized, fewer electrons around H, always in shielding region



2.6. shifts are small compared to total frequency

2.6.1. tetramethylsilane (TMS, reference compound) has a $\nu = 300$ MHz, then

aldehyde proton is at 300.003 MHz or 3000 Hz shift

2.6.2. for double field (B_0), 600 MHz for TMS and 600.006 MHz for aldehyde

2.6.3. shielding is proportional to field (B_0), so is frequency shift ($\Delta\nu$)

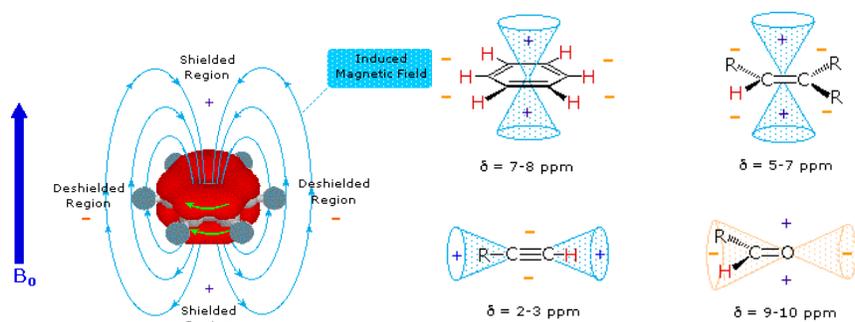
2.6.3.1. double field \rightarrow double frequency \rightarrow double frequency shift

2.6.4. shift relative to frequency ($\Delta\nu/\nu$) is constant, report shift in parts per million

$$2.6.5. \text{chemical shift} = \delta = \frac{\Delta\nu}{\nu_{\text{ref}}} \times 10^6 = \frac{3000\text{Hz}}{300\text{MHz}} \times 10^6 = \frac{6000\text{Hz}}{600\text{MHz}} \times 10^6 = 10 \text{ ppm}$$

2.6.6. $\Delta\nu$ and ν for $\delta=3$ ppm if TMS is 800 Mhz?

2.7. shielding cones: benzene, alkene, alkyne



<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm>

2.8. qualitatively predict chemical shift Figure 3.25 (e160)

2.8.1. R_3CH , 1 ppm

2.8.2. $C=CH$, 5-6 ppm

2.8.3. $C\equiv CH$, 2-3 ppm

2.8.4. $ClCH$, 3-4 ppm

2.8.5. OCH , 3.2-3.8 ppm

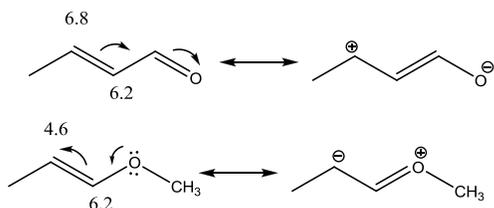
2.8.6. carbonyl β -H, $O=CCH$, 2 ppm

2.8.7. aromatic CH, 7-8 ppm

2.8.8. carbonyl α -H, $O=CH$, aldehyde, 9-10 ppm

2.8.9. NMR of benzyl acetate Figure 3.26 (e160)

2.8.10. delocalization effects



3. spin-spin coupling

3.1. nuclei have their own magnetic fields

3.2. this polarizes the electrons between nuclei

3.3. nucleus such as fluorine ($I = \frac{1}{2}$) produces two different fields at neighboring nuclei,
two frequencies

3.4. single line at $\nu = \frac{\gamma}{2\pi} B$ split into two lines

3.4.1. $\nu^+ = \frac{\gamma}{2\pi} B + 1/2J$, $\nu^- = \frac{\gamma}{2\pi} B - 1/2J$ (difference?)

3.5. equivalent nuclei (or same shift) do not split each other

3.5.1. equivalent sets split **inequivalent** nuclei

3.5.2. first-order splitting occurs when chemical shift

difference is 7 times greater than the coupling

constant Figure 3.27 (e162)

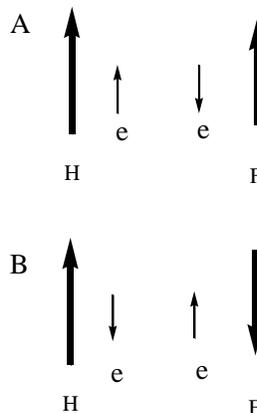
3.5.3. # of lines for first order splitting = $2NI + 1$

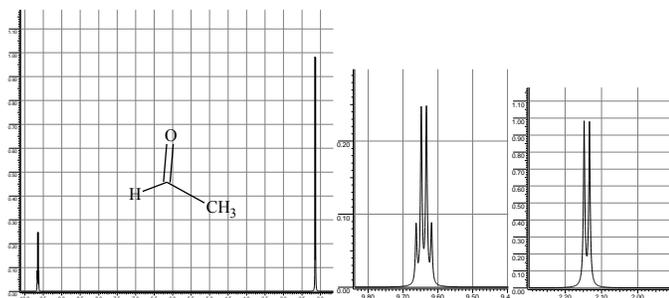
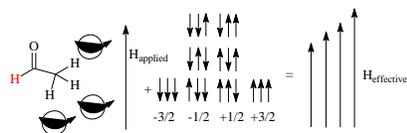
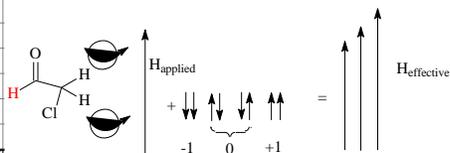
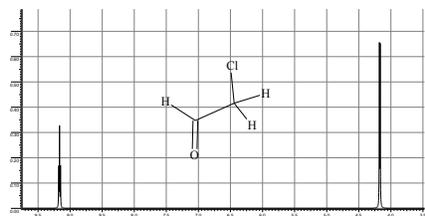
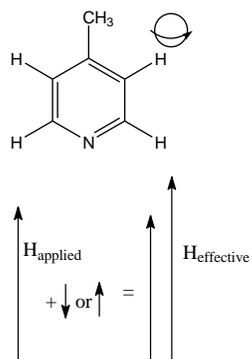
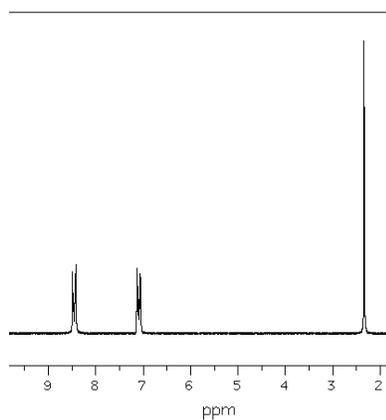
3.5.4. for proton and fluorine, $I = \frac{1}{2}$ so, splitting is well

known $N + 1$ rule

3.5.5. neighbor is 1H: doublet, 2H: triplet, 3H: quartet, 4H: pentuplet

3.5.6. Pascal's triangle predicts relative line intensities (Fig 3.32, 164)





3.5.7. signals for two nuclei that couple to each other have the same splitting

3.5.7.1. if there is a doublet with $J = 12$ Hz, there must be another multiplet with same splitting

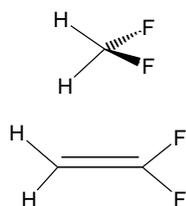
3.5.7.2. complex spectra – multiple coupling pentafluoro xenon cation

3.6. second-order splitting

3.6.1. Chemically equivalent: nuclei have same chemical shift

3.6.2. magnetically equivalent: nuclei have same chemical shift and same coupling to any other single nucleus

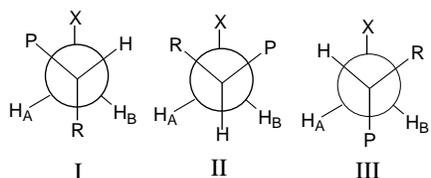
3.6.3. CH_2F_2 , hydrogens are equally coupled to both fluorines magnetically



3.6.4. $\text{H}_2\text{C}=\text{CF}_2$ cis and trans H are not coupled equally to lower fluorine

3.6.5. $J_{\text{cis}} \neq J_{\text{trans}}$

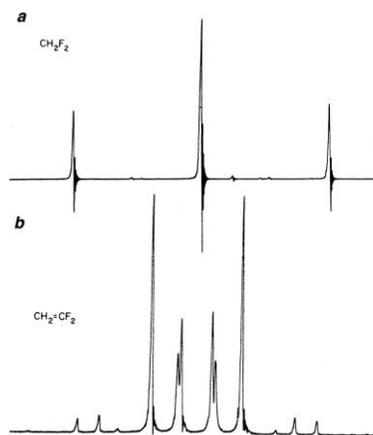
3.7. H_A and H_B are diastereotopic



3.7.1. adjacent to chiral center, chemically

inequivalent, rotation does not make them chemically equivalent

3.7.2. rapid rotations may make average couplings equivalent



3.7.3. 2nd-order splitting occurs when chemical shift difference is less than 7 times greater than the coupling constant, $\Delta\nu/J < 7$, Figure 3.28, leaning multiplets

3.7.4. Figures 3.28, 3.33,

3.8. factors affecting magnitude of J

3.8.1. gyromagnetic ratio

$$3.8.1.1. \quad J_{HX}/J_{DX} = \gamma_{HX}/\gamma_{DX}$$

3.8.2. electron density

$$3.8.2.1. \quad {}^1J_{HC} = 125 \text{ Hz/sp}^3, 160 \text{ Hz/sp}^2, 240 \text{ Hz/sp}$$

3.8.2.2. linear dependence on s character

3.8.2.3. only s has density at nucleus

3.8.2.4. note that electronegativity (and strain) affects hybridization

3.8.3. vicinal sp³-sp³ proton coupling, dihedral angle

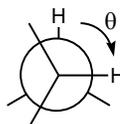
3.8.3.1. Karplus curve: ${}^3J_{HH} = 7 - \cos\theta + 5\cos 2\theta$ (Fig 3.57, e190)

$${}^3J_{HH} = 8.5\cos^2\theta - 0.3 \text{ (0-90}^\circ\text{)}, {}^3J_{HH} = 9.5\cos^2\theta - 0.3 \text{ (90-180}^\circ\text{)}$$

3.8.3.2. large values for $\theta = 0$ and 180° , syn and anti

3.8.3.3. small for $\theta = 60$ and 120° , gauche

3.8.3.4. allylic ${}^4J_{HH}$ is max at 90°



3.8.4. long range W or zigzag coupling

3.8.4.1. only with restricted rotation

3.8.4.2. cyclic compounds – especially bicyclic: norbornane

3.9. Pople notation

3.9.1. letters far from each other (AM and AX) for nuclei with very different shifts

3.9.2. letters near each other (AB) for nuclei with similar chemical shifts

3.9.3. AM and AX = $\nu_1 - \nu_2 > 7J_{12} > \nu_1 - \nu_2 = AB$

3.9.4. chemically equivalent but magnetically inequivalent, same letter with prime

3.9.4.1. CH_2F_2 is A_2X_2

3.9.4.2. $\text{H}_2\text{C}=\text{CF}_2$ is $AA'XX'$

3.9.5. other examples (methylcyclohexane)

4. Exchangeable protons

4.1. OH, NH, SH

4.2. Hydrogen bonding

4.3. pH, concentration, temperature, and solvent dependent

4.4. figures 3.38 (e169) with water and 3.39 (e170) without

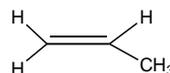
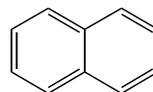
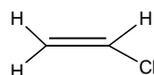
4.5. rotating frame explanation

4.6. nuclear quadrupole figure 3.40 (e172), methylisonitrile

5. Dynamic NMR???

5.1. thioacetal at 25 C, assign peaks

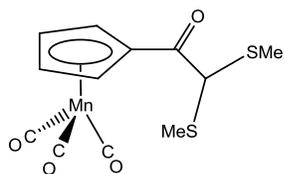
CH_3OH

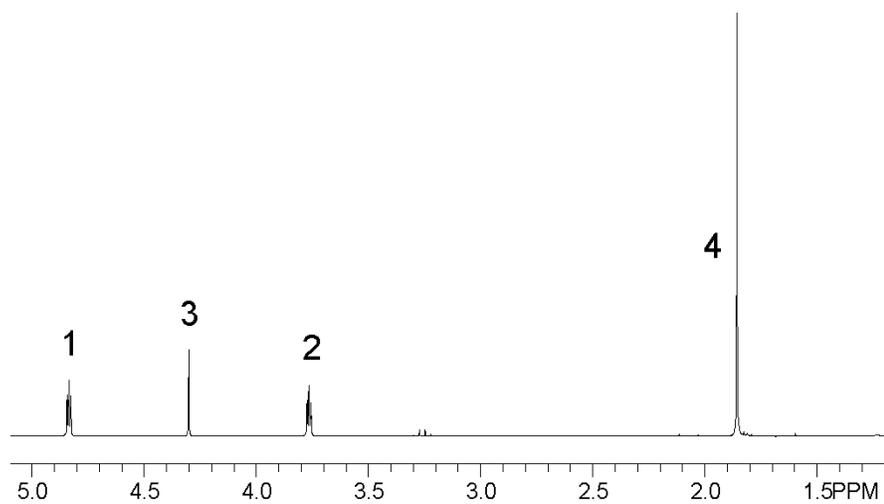


$^{13}\text{CH}_2\text{F}_2$

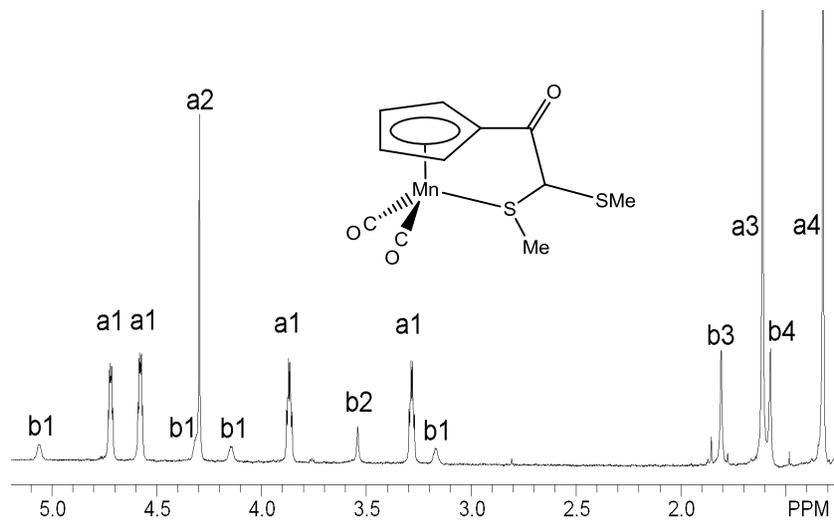
$\text{CH}_3\text{CH}_2\text{NO}_2$

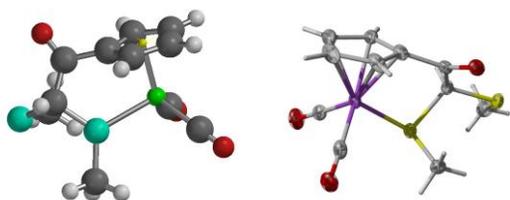
$\text{CH}_2\text{ClCH}_2\text{NO}_2$



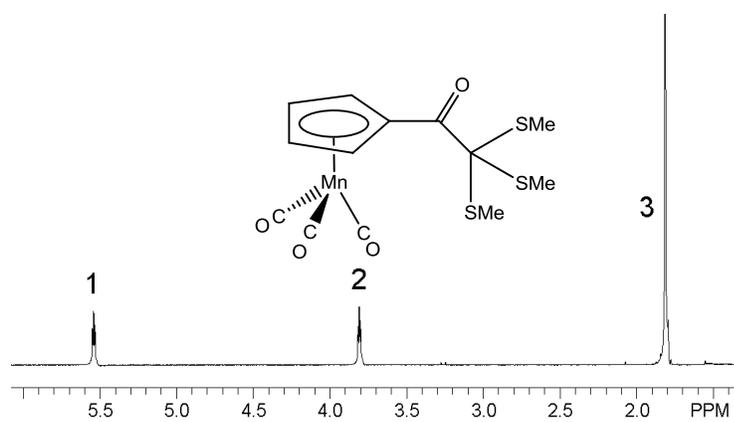


5.2. Chelate of thioacetal, compare spectra, make assignments

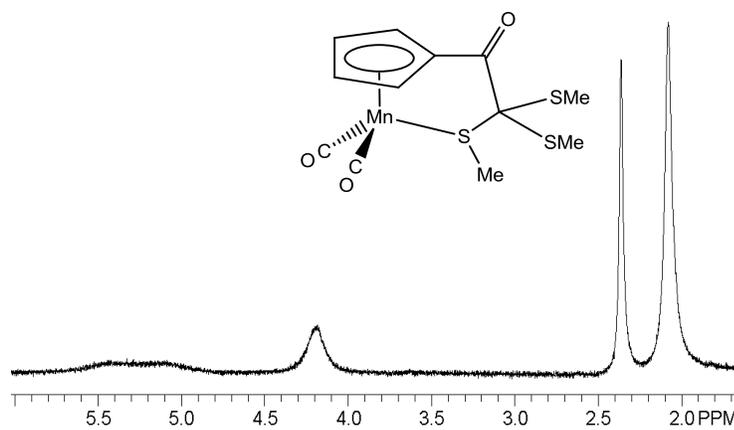




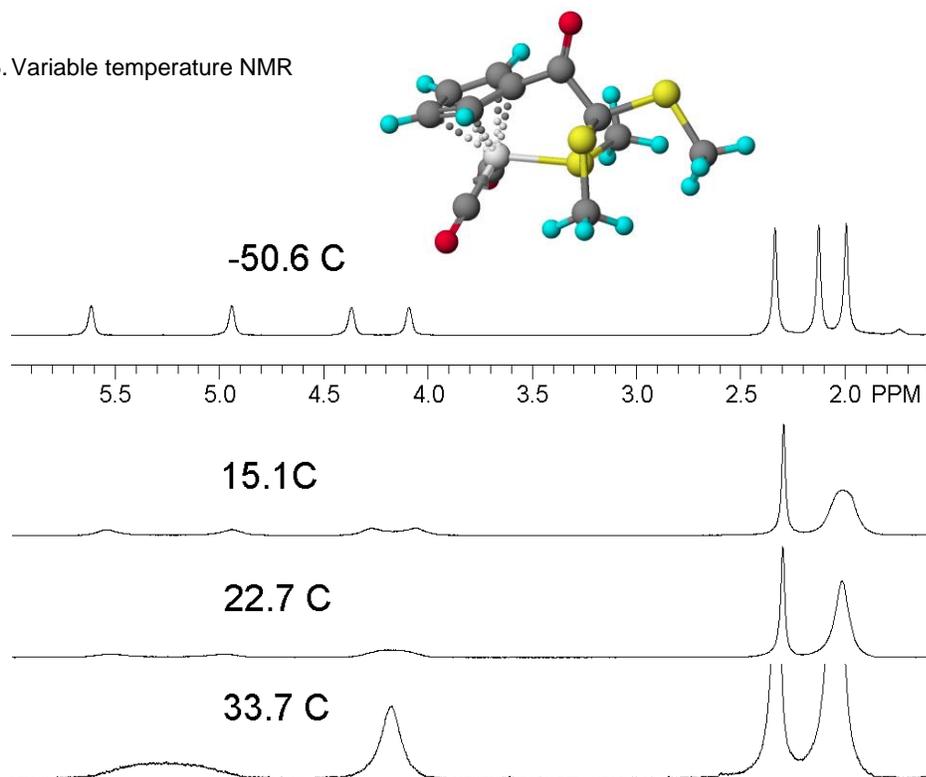
5.3. Orthothioester, assign peaks



5.4. Chelate of orthothioester, assign peaks



5.5. Variable temperature NMR



5.6.

6. Spin decoupling use rotating frame (e192)

6.1. continuously irradiate at low power at a single frequency

6.2. causes magnetization for nuclei at that frequency to flip rapidly between upper and lower spin states

6.3. coupled nuclei observe average spin of zero, no coupling

6.4. simplifies spectrum, shows which nuclei are coupled, neighbors

https://umdrive.memphis.edu/tburkey/public/NMR_exercises.pdfhttps://umdrive.memphis.edu/xythoswfs/webui/xy-13208309_docstore1-t_SvHIEH6h

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