Solids Techniques - NMR Spectroscopy

Jürgen Schulte

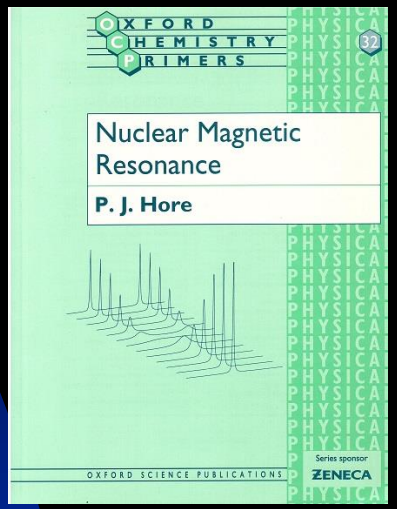
Science 2 S2 – G-14
Smart Energy SN – 1024

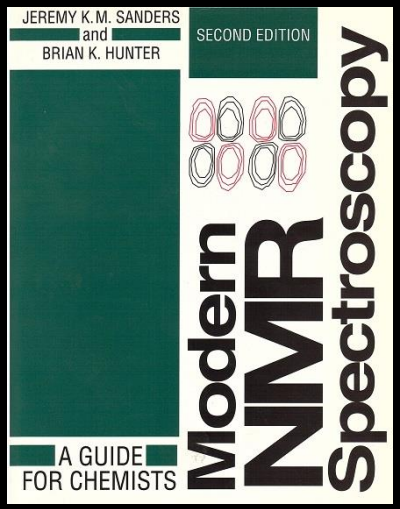
Topics:

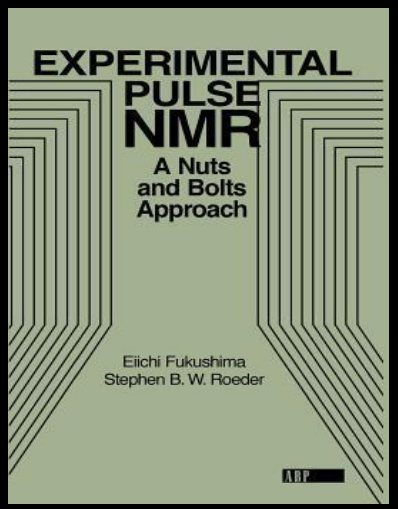
- **Part I – Introduction**
  - **History of NMR**
  - **NMR Hardware**
- Part II – NMR Theory
  - Nuclei – Spin – Magnetic Moments
  - Shielding – Chemical Shifts
  - Coupling – Molecular Structure
  - Relaxation – Linewidth
- Part III NMR Experiments
  - Solution vs. Solids State NMR
  - Techniques for optimizing Solid State NMR

Books for NMR Spectroscopy

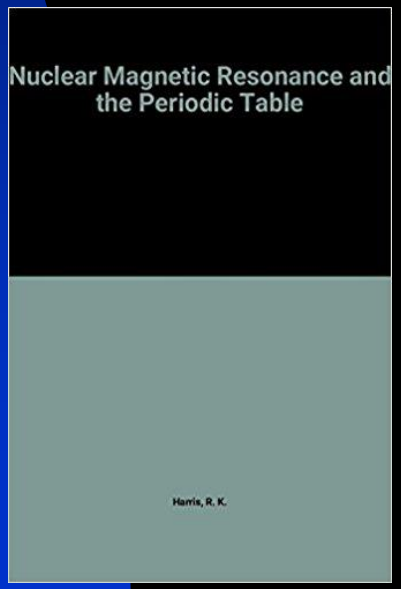
general:

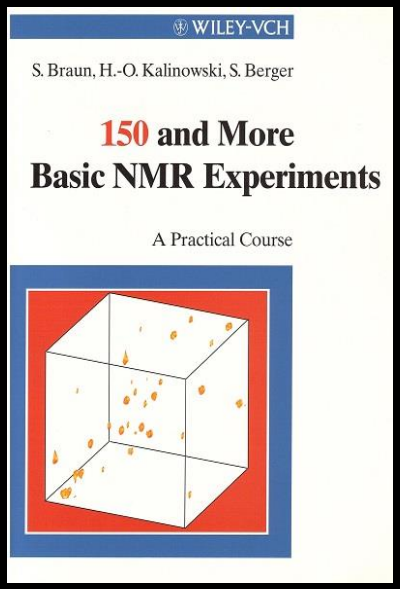


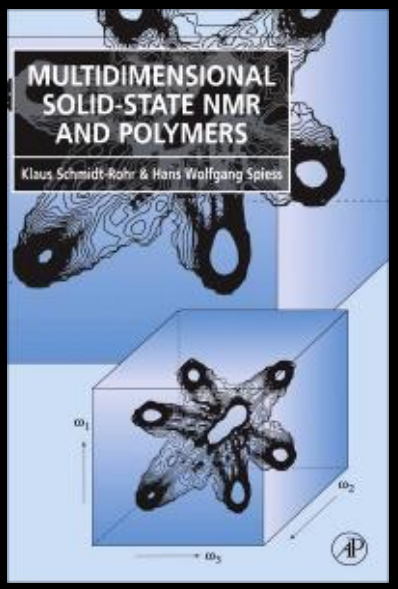




specialized:







Important NMR Milestones

- 1938 - NMR in molecular beams
  Rabi (Columbia University)

- 1946 - NMR of Liquids and Solids
  Purcell, Torrey, Pound (Harvard)
  Bloch, Hansen, Packard (CalTech)

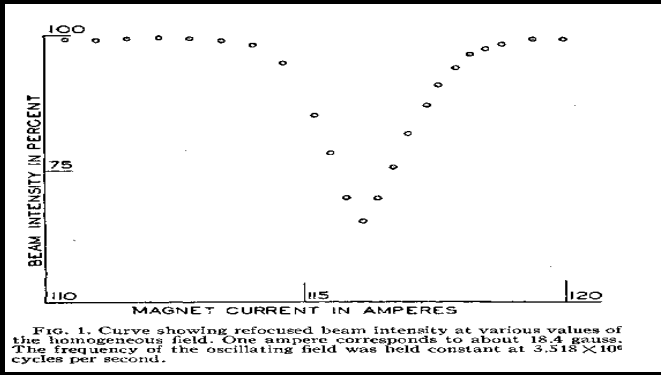


FIG. 1. Curve showing refocused beam intensity at various values of the homogeneous field. One ampere corresponds to about 18.4 gauss. The frequency of the oscillating field was held constant at 3.518×10^6 cycles per second.

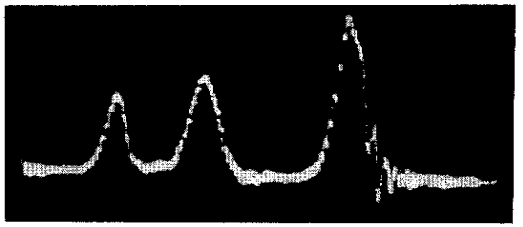


FIG. 1. Oscillograph trace of the nuclear induction signal from ethyl alcohol. The total trace is 75 milligauss wide and was traversed in 2 seconds. The peaks from left to right represent OH, CH_2, CH_3.

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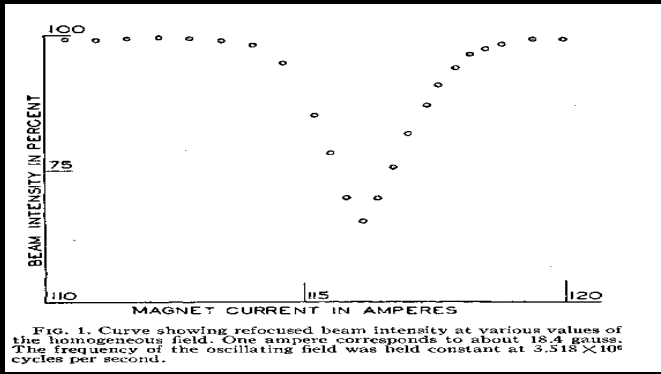

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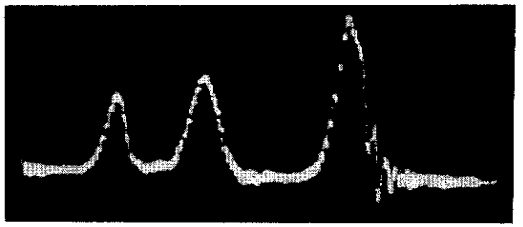
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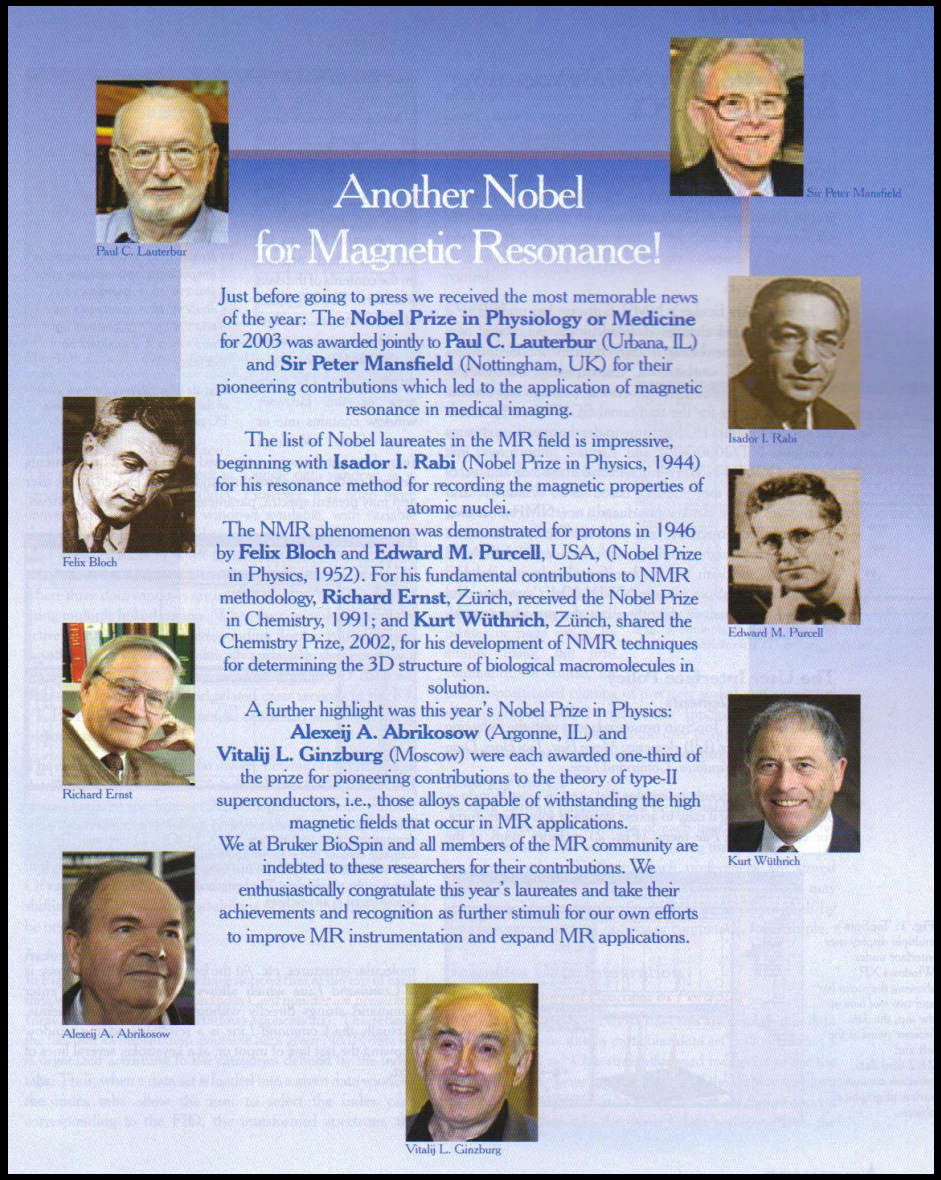
- 1952 - First commercial NMR spectrometer
- 1962 - First Superconducting Magnet for NMR
- 1968 - First Pulse Fourier Transform NMR
- 1969 - First Concept of MRI Scanners
- 1971 - First 2D NMR Experiment
- 1985 - Protein Structures through NMR
- 2009 - Gigahertz NMR Spectrometer

NMR Nobel Prize Winners

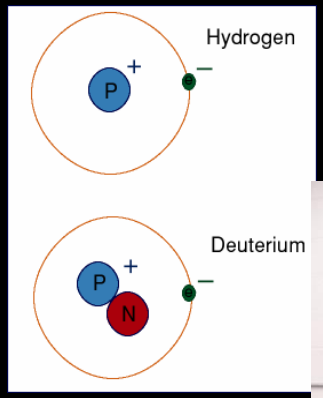
- 1944 (P) Isador Rabi
- 1952 (P) Felix Bloch
  Edward Purcell
- 1991 (C) Richard Ernst
- 2002 (C) Kurt Wüthrich
- 2003 (M) Paul Lauterbur
  Peter Mansfield

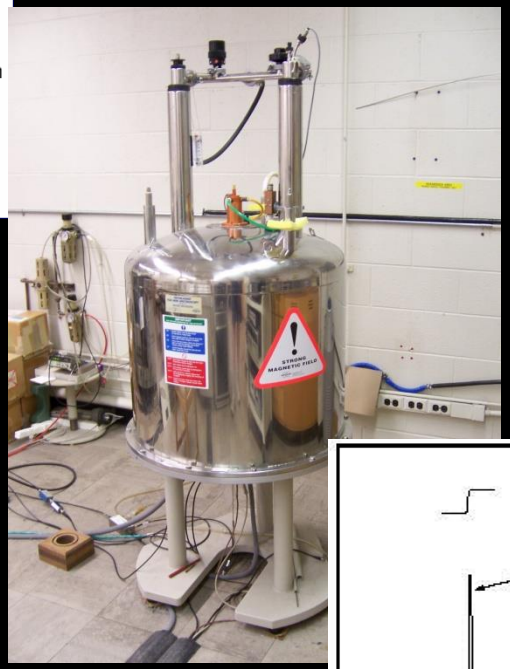


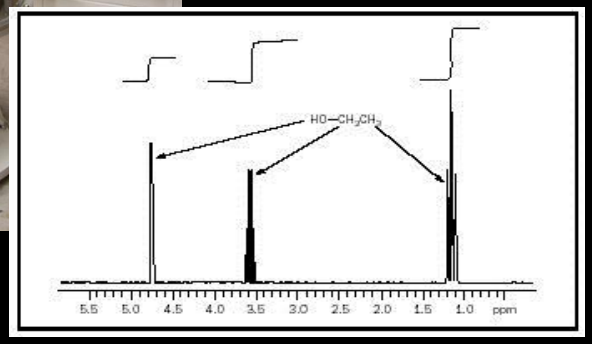
From: Bruker SpinReport, Vol 153

NMR Spectroscopy

- NUCLEAR
- MAGNETIC
- RESONANCE



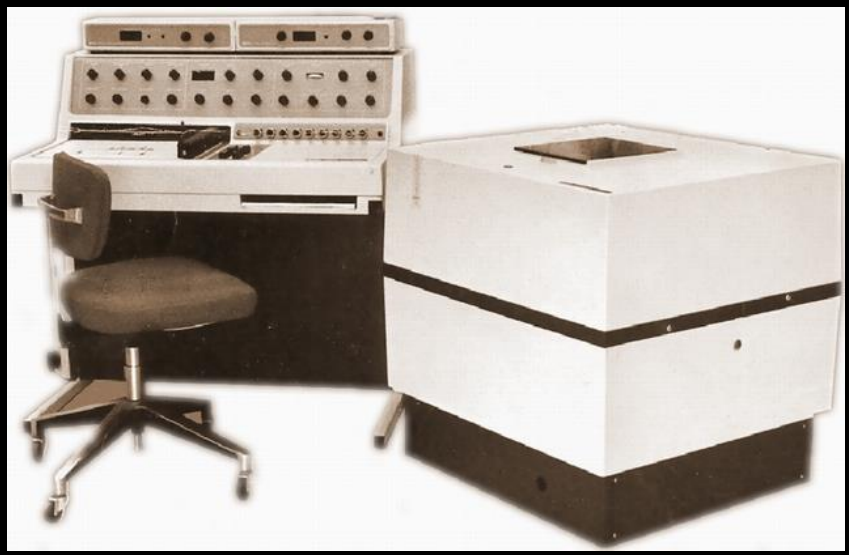




NMR Magnets

Magnet Types:

- Permanent Magnets: low fields (<2 Tesla)
- Electromagnets: high fields
  poor stability and homogeneity



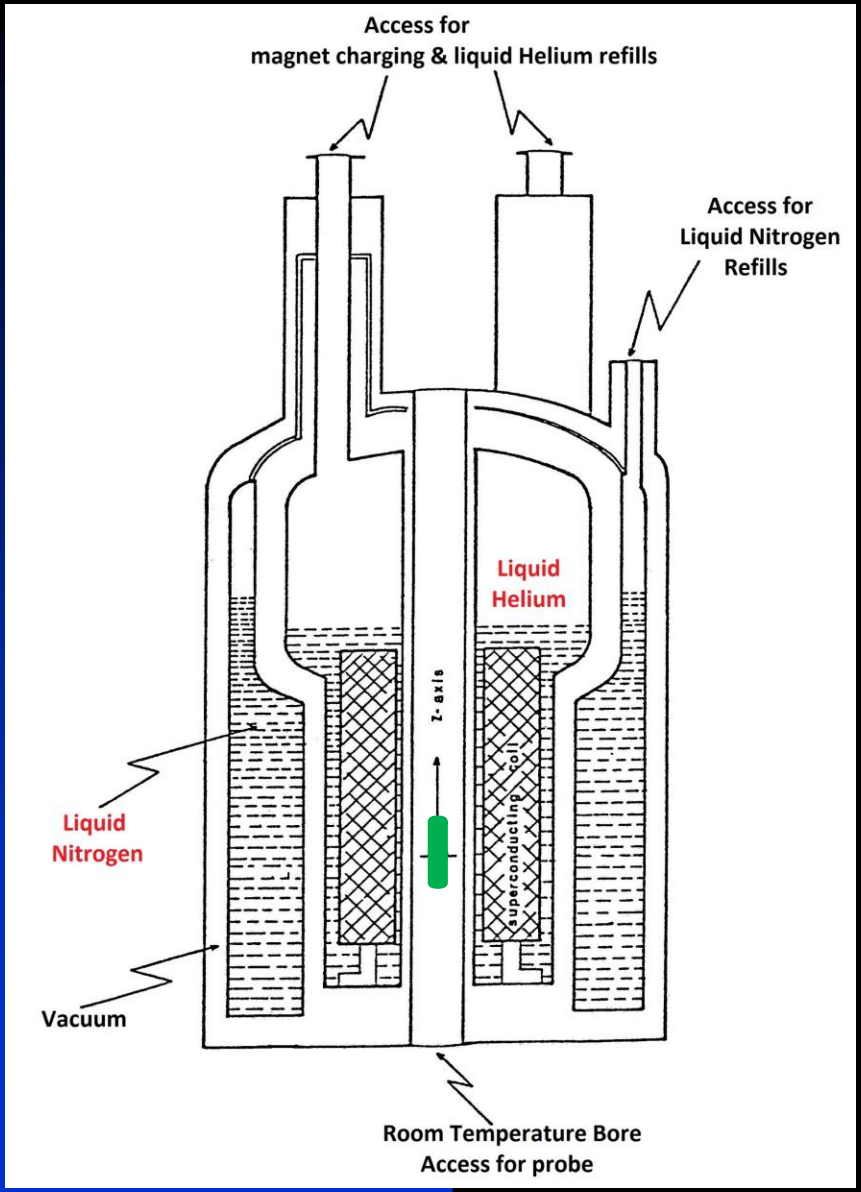
NMR Magnets

Magnet Types:

- Superconducting Magnets (aka. Cryomagnets): high, stable, and homogeneous fields

- Superconducting magnets during Nitrogen refill (left) and Helium refill (right)

NMR Magnets



Cross section of a superconducting magnet:

The superconducting coil is cooled to 4K in a bath of liquid Helium.

The Helium vessel is surrounded by a container of liquid Nitrogen (77K).

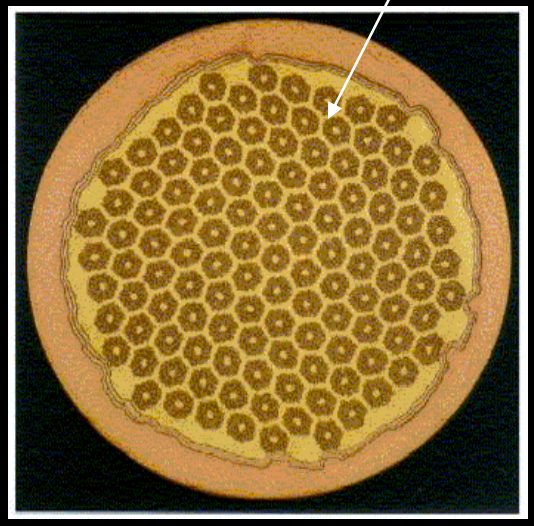
Helium and Nitrogen containers are separated and surrounded by vacuum.

A probe is installed in the bottom of the magnet bore and samples can be inserted from the top of the magnet.

NMR Magnets

Inside a superconducting magnet

Taped wires with
superconducting filaments



NMR Magnets

BU has four NMR Spectrometers:

Field:	B_0 =	2.35 T	7.05 T	9.4 T	14.1 T
Frequency:	$\nu_0\{^1H\}$ =	100 MHz	300 MHz	400 MHz	600 MHz
Location:		Science 2	Science 2	CoE	SN

All four instruments have superconducting magnets.

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Location:		Science 2	Science 2	CoE	SN

All four instruments have superconducting magnets.

Dangers:

- High magnetic fields
  - may cause pacemakers, insulin pumps, and other electronic medical devices to fail,
  - may erase hard disks, credit cards, and your BU ID,
  - will attract ferromagnetic objects and turn them into dangerous projectiles.
- Cryogens (liquid Nitrogen and Helium)
  - will cause burns when contacting eyes or skin,
  - will displace breathable air in case of a quench.
  - https://www.youtube.com/watch?v=59PY2rYS3P8
  - https://www.youtube.com/watch?v=6-sxe79Y5Nc
  - https://www.youtube.com/watch?v=d-G3Kg-7n_M

NMR Magnets

Accidents:

NMR Magnets

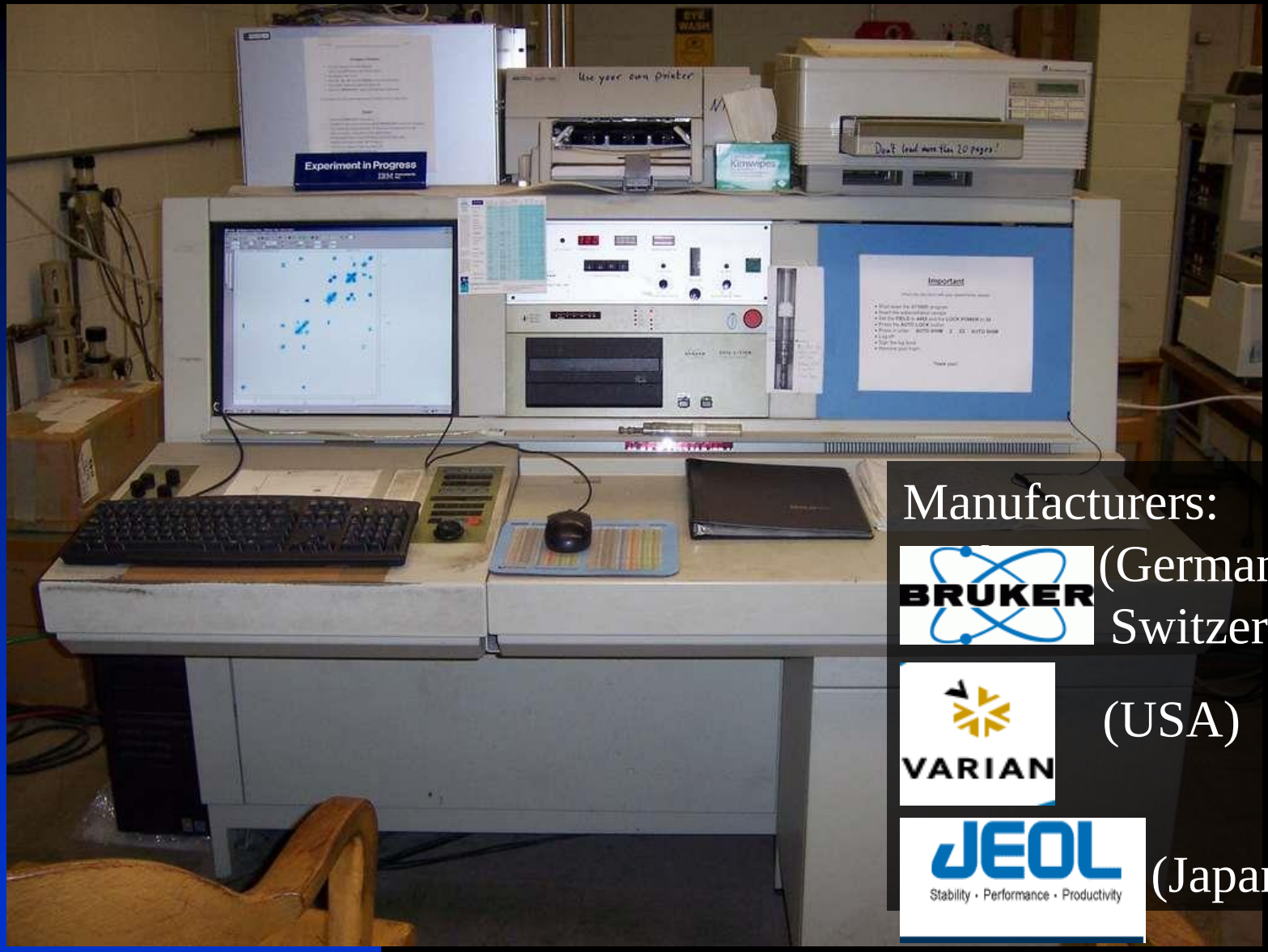
Magnet quench:

An energized magnet can fail when a segment of the superconducting wire becomes resistive due to localized heating.

The entire energy (Mega Joules) stored in the magnet coil is released instantaneously and vaporizes the entire volume of liquid Helium within minutes.

14.1 Tesla magnet quench
Coil current: 183 Amperes
Energy: 774 kJ

NMR Consoles



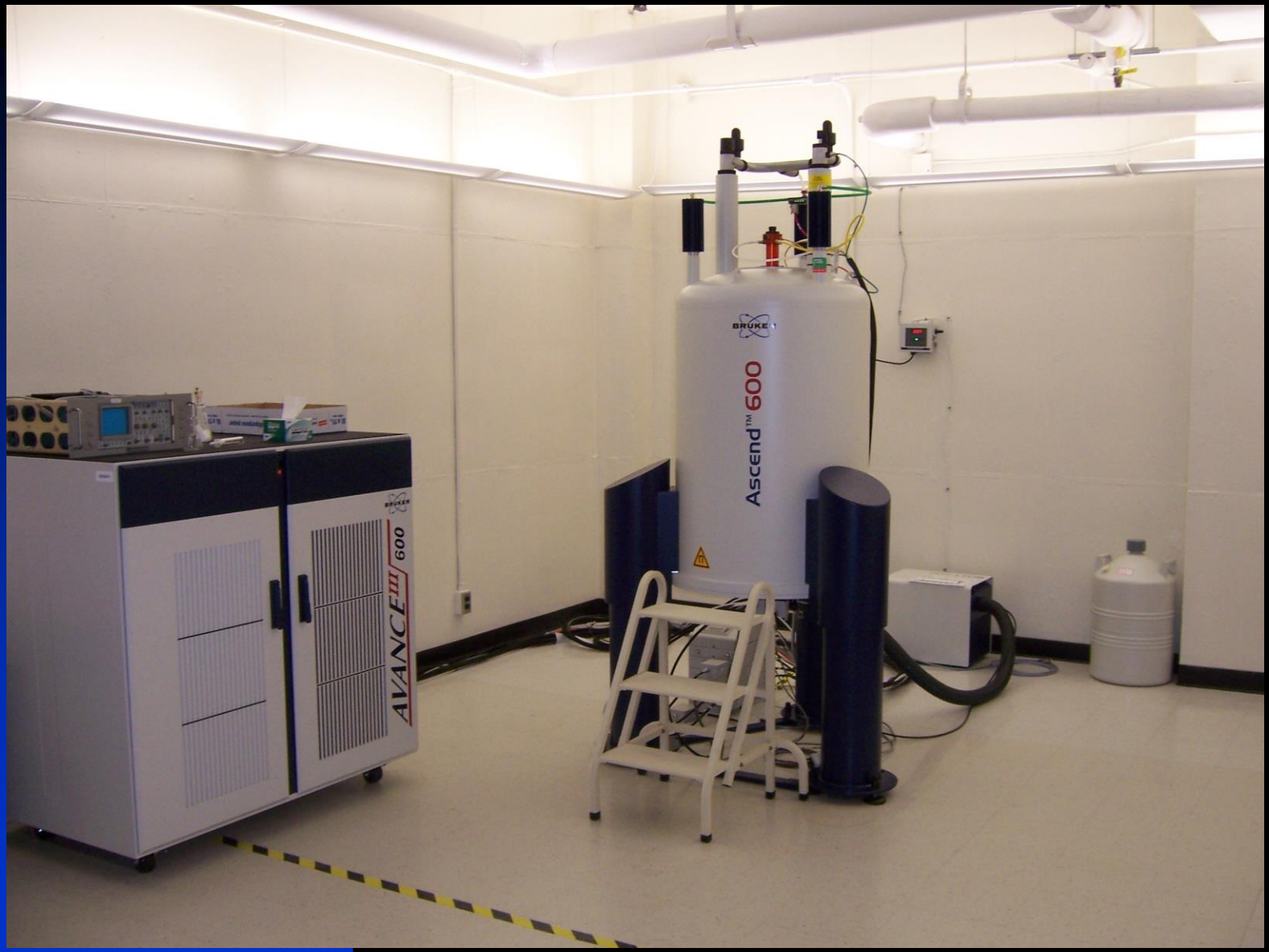
Manufacturers:

BRUKER (Germany, Switzerland)

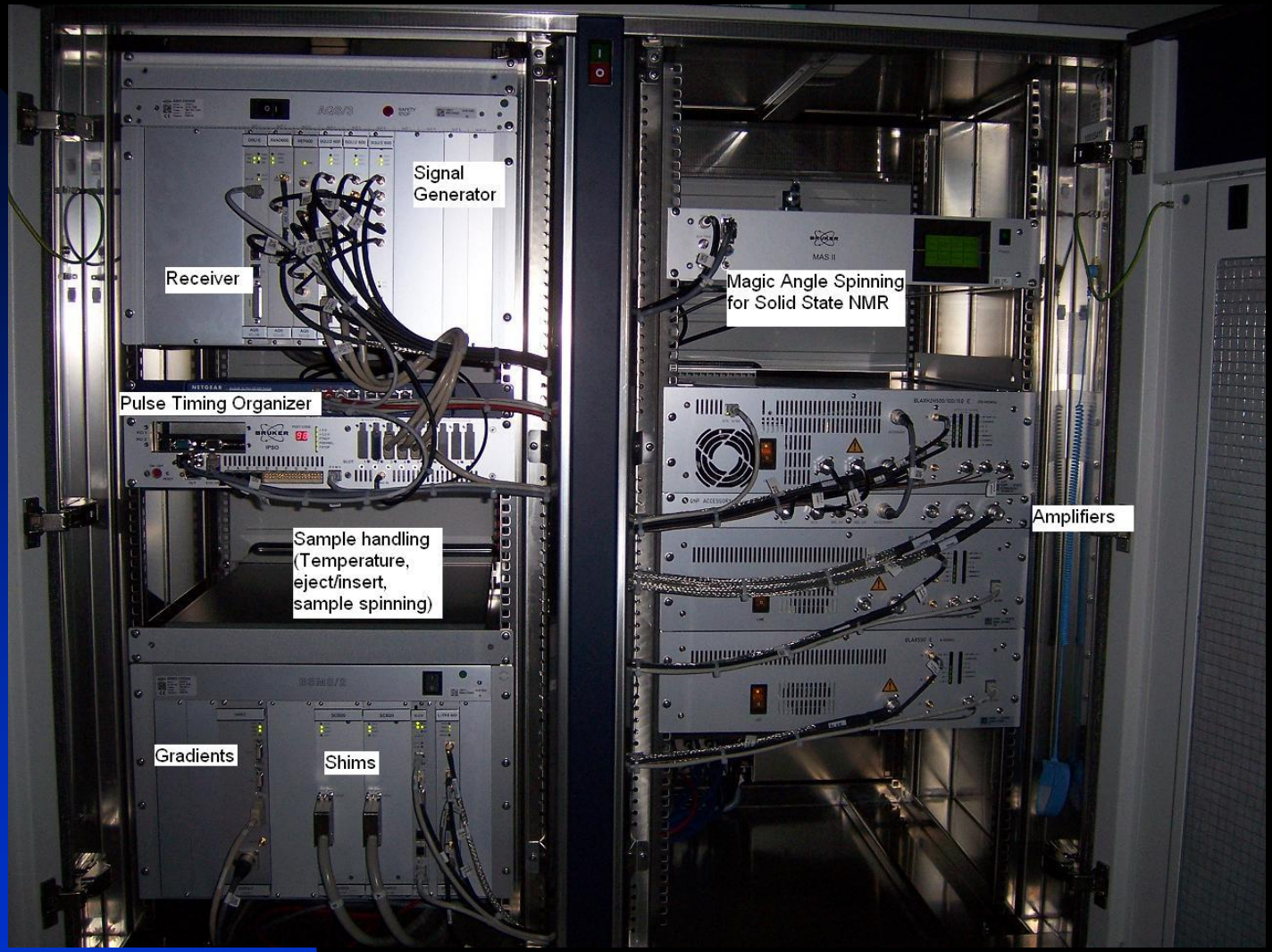
VARIAN (USA)

JEOL Stability • Performance • Productivity (Japan)

Modern NMR Console



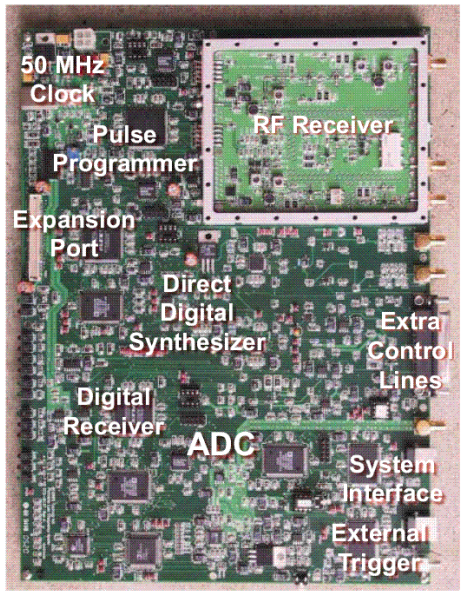
Modern NMR Console



Multiple RF channels, high sensitivity, high resolution

Benchtop NMR Systems

LapNMR with battery, enclosure and AC power adapter for portable usage



^{1}H typically 60 MHz
(1.4 T permanent magnet)
Single RF channel
Low resolution
Low sensitivity

Not good for research.
Good enough for teaching.

NMR Probes…

Liquids

Solids

… and Samples

Topics:

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  - History of NMR
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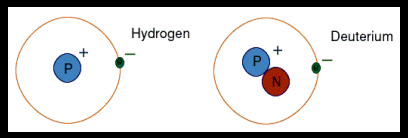
  - Techniques for optimizing Solid State NMR

Nuclear Spin Quantum Number (I)

- Nuclei have to possess a "non-zero spin" to be NMR active. How to calculate?
- Nucleus = Protons + Neutrons



- Even p + even n → I = 0 → no NMR signals (^{12}C, ^{16}O)
- Odd p + odd n → integer I
  - I = 1: ^{2}H, ^{14}N
  - I = 3: ^{10}B
- All other nuclei: half-integer I (1/2, 3/2, 5/2, …)
  - I = 1/2: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P, ^{119}Sn
  - I = 3/2: ^{11}B, ^{23}Na
  - I = 5/2: ^{17}O, ^{27}Al,
  - I = 7/2: ^{51}V

Recap:

(mass) m **X** z (charge)

(atomic #) p n (# of atoms)

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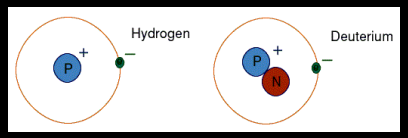

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  - I = 7/2: ^{51}V

Recap:

(mass) m **X** z (charge)

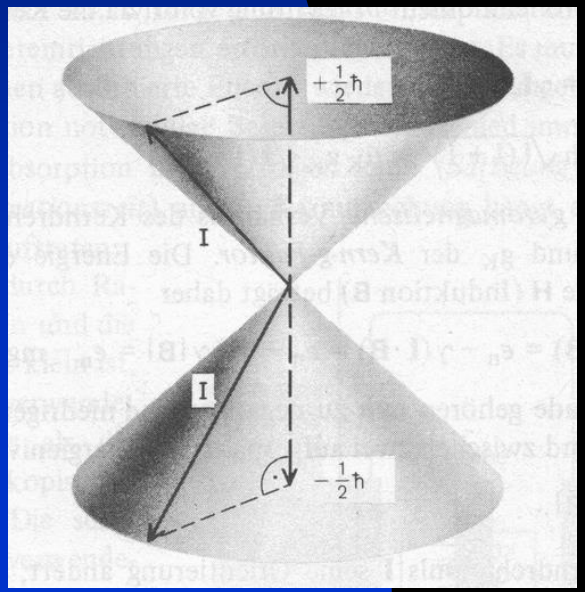
(atomic #) p n (# of atoms)

near 100 % natural abundance

- High natural abundance is great, but…
  In solution NMR "Spin-½" nuclei are preferred because of their sharp signals. (LW: few Hz)
  Nuclei with I > ½ possess an electric quadrupole which can broaden signals. (LW: kHz/MHz)
- Solids NMR spectra of "Spin-½" nuclei *can* produce sharp peaks. (tens/hundreds of Hz)
  Solids NMR spectra of half-integer quadrupolar nuclei have a "sharp" central transition. (kHz)
  Solids NMR spectra of all quadrupolar nuclei have broad satellite transitions. (MHz)
- In Solid State NMR "broad" does not equal "bad"!
  Line width and signal shape can contain a wealth of structural information.

Magnetic Spin Quantum Number (M)

- General condition: **2I + 1** spin states
  $M_I = I, I-1, I-2, \ldots, -I$ i.e.: I=2, M= 2,1,0,-1,-2
- "Spin ½" case ^1H:
  - $M_I = +½$ (α) and $M_I = -½$ (β)
- Magnetic Moment (Z component):
  $\mu_Z = \gamma\hbar M_I = \pm\gamma\hbar I = \pm ½\,\gamma\hbar$

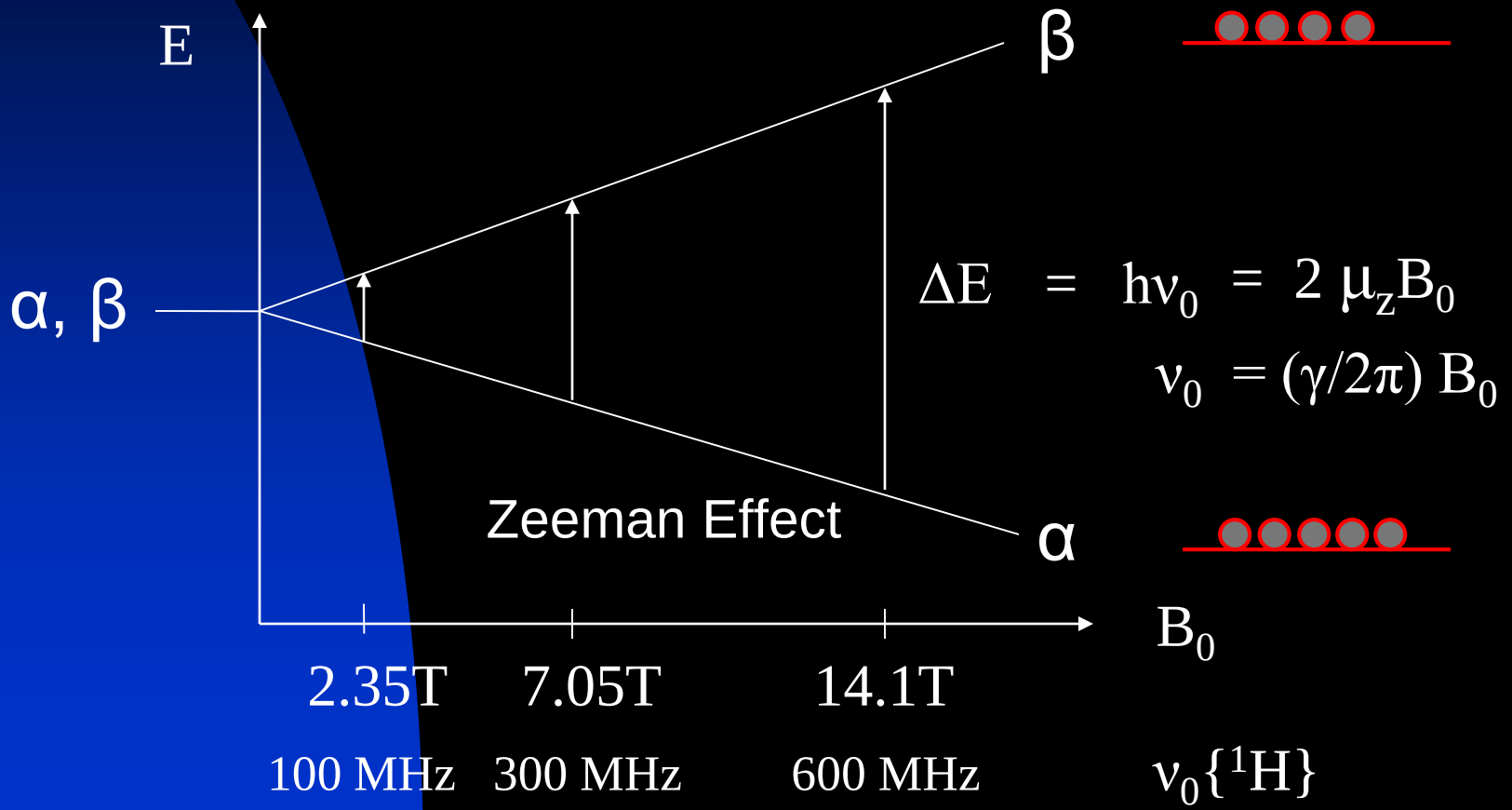


B_0

(Z)

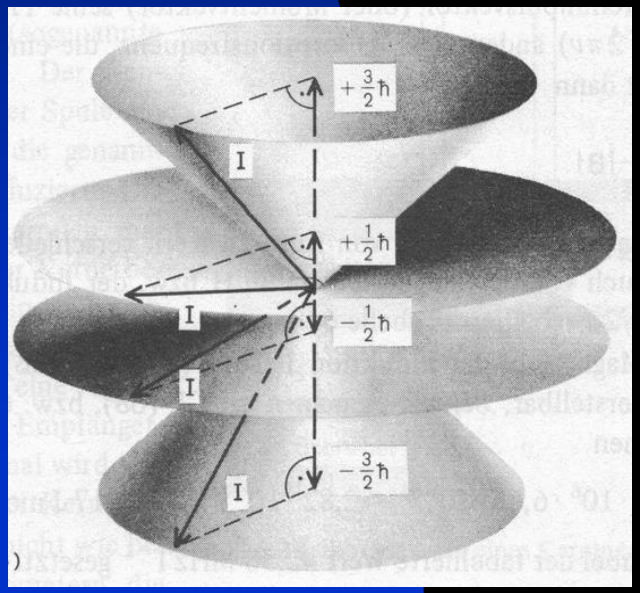
Spins in a Magnetic Field

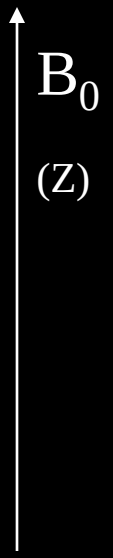
- The α and β states possess the same energies (are degenerate) unless placed into a magnetic field:

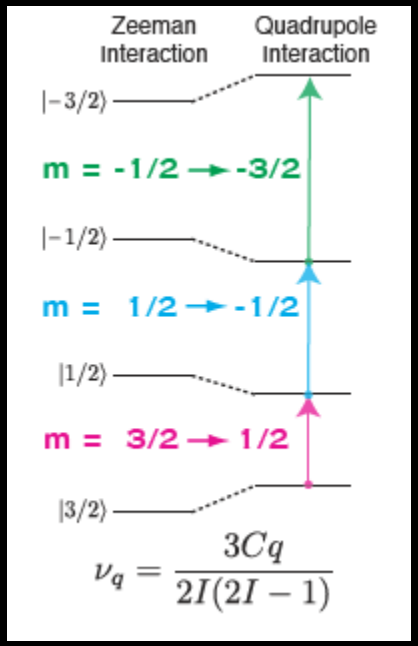


Magnetic Spin Quantum Number (M)

- General condition: **2I + 1** spin states
  $M_I = I, I-1, I-2, \ldots, -I$
- "Spin 3/2" case ^{11}B:
  - $M_I = +3/2,\ +1/2,\ -1/2,\ -3/2.$
- Magnetic Moment (Z component):
  $\mu_Z = \gamma\hbar M_I = \pm\gamma\hbar I = \pm \tfrac{1}{2}\gamma\hbar\ ,\ \pm 3/2\ \gamma\hbar$



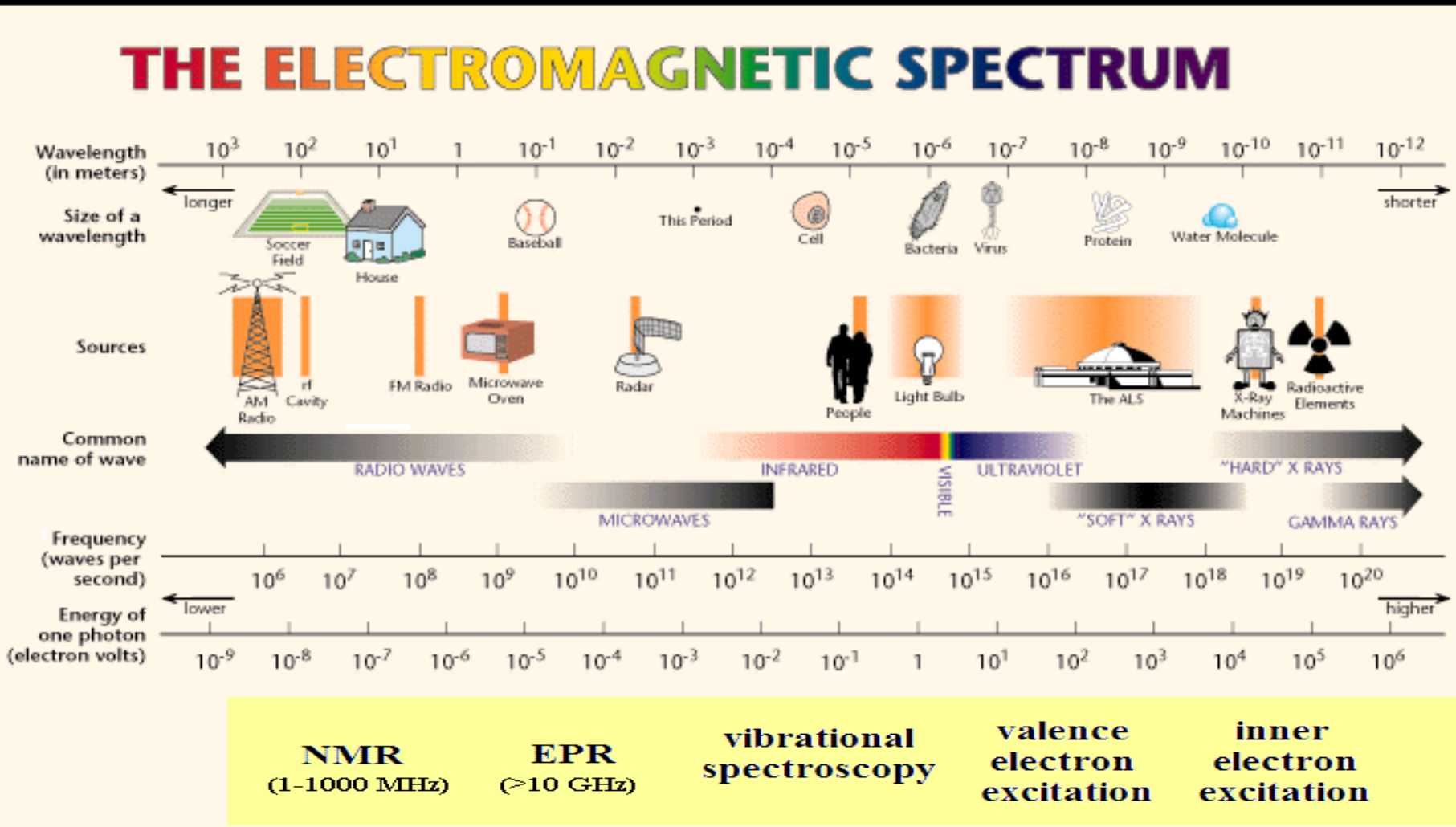




Satellite Transition

Central Transition

Satellite Transition

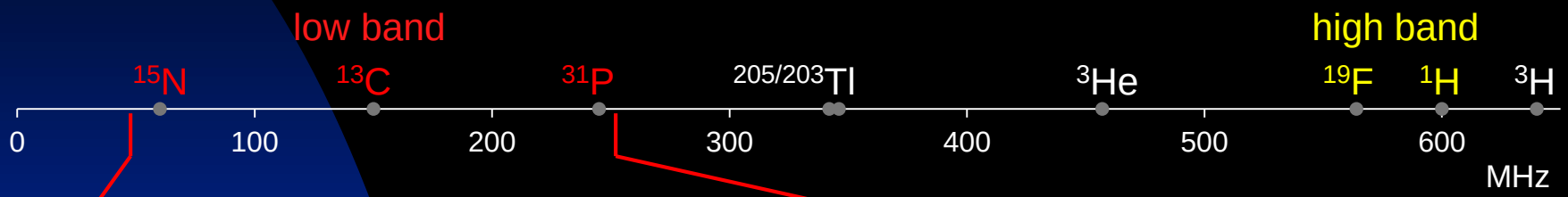


$$\frac{N_\alpha}{N_\beta} = exp\left(\frac{-\Delta E}{kT}\right) = 1.00001$$

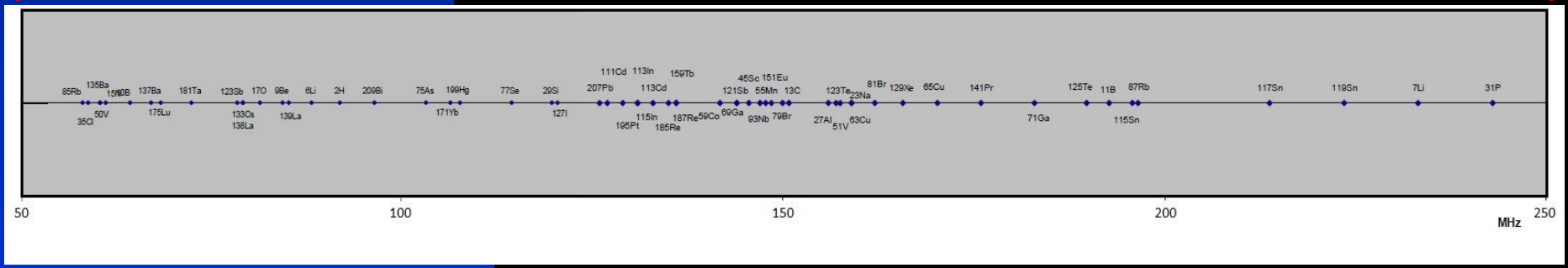
Very low sensitivity compared to other techniques!

EM Spectrum

- NMR Frequency Range
  - Resonance Frequencies of Selected Nuclei at B_0 = 14.1 Tesla



X-Nuclei (BB Nuclei)



EM Spectrum

The Table of NMR Frequencies*

By Mass

Isotope	Spin	2.35 T	4.70 T	7.05 T	9.39 T	11.74 T	14.09 T	16.45 T	17.61 T	18.80 T	21.14 T	Natural Abundance	Relative Receptivity	Absolute Receptivity
1 H	1/2	100.000000	200.057	299.949	399.952	499.843	599.944	700.000	749.948	800.449	900.080	99.985	62.89904	5717.23718
2 H	1	15.350609	30.710	46.044	61.395	76.729	92.095	107.454	115.122	122.874	138.168	0.015	0.22752	0.00310
3 H	1/2	106.663984	213.389	319.938	426.605	533.152	639.924	746.648	799.924	853.791	960.061	0.0	76.33038	0.00000
3 He	-1/2	76.178972	152.401	228.498	304.679	380.775	457.031	533.253	571.303	609.774	685.672	0.000137	27.80669	0.00346
6 Li	1	14.716106	29.441	44.141	58.857	73.557	88.288	103.013	110.363	117.795	132.457	7.5	0.20046	1.36676
7 Li	3/2	38.863790	77.750	116.572	155.437	194.258	233.161	272.047	291.458	311.085	349.805	92.5	3.69215	310.47636
9 Be	-3/2	14.051820	28.112	42.148	56.201	70.237	84.303	98.363	105.381	112.478	126.478	100.0	0.17452	15.86533
10 B	3	10.743658	21.493	32.225	42.969	53.701	64.456	75.206	80.572	85.998	96.702	19.9	0.07800	1.41111
11 B	3/2	32.083974	64.186	96.236	128.320	160.369	192.486	224.588	240.613	256.816	288.781	80.1	2.07734	151.26844
13 C	1/2	25.145020	50.304	75.422	100.568	125.686	150.856	176.015	188.575	201.273	226.325	1.1	1.00000	1.00000
14 N	1	7.226330	14.457	21.675	28.902	36.120	43.354	50.584	54.194	57.843	65.043	99.634	0.02374	2.14987
15 N	-1/2	10.136784	20.279	30.405	40.542	50.668	60.815	70.957	76.021	81.140	91.239	0.366	0.06552	0.02180
17 O	-5/2	13.556430	27.121	40.662	54.219	67.761	81.331	94.895	101.666	108.512	122.019	0.038	0.15670	0.00541
19 F	1/2	94.094008	188.242	282.234	376.331	470.322	564.511	658.658	705.656	753.175	846.921	100.0	52.39984	4763.62168
21 Ne	-3/2	7.894530	15.794	23.680	31.574	39.460	47.363	55.262	59.205	63.192	71.057	0.27	0.03095	0.00760
23 Na	3/2	26.451921	52.919	79.342	105.795	132.218	158.697	185.163	198.376	211.734	238.088	100.0	1.16417	105.83346
25 Mg	-5/2	6.121643	12.247	18.362	24.484	30.599	36.726	42.852	45.909	49.001	55.100	10.0	0.01443	0.13118
27 Al	5/2	26.056890	52.129	78.157	104.215	130.244	156.327	182.398	195.413	208.572	234.533	100.0	1.11279	101.16239
29 Si	-1/2	19.867187	39.746	59.591	79.459	99.305	119.192	139.070	148.994	159.027	178.821	4.67	0.49323	2.09400
31 P	1/2	40.480742	80.985	121.422	161.904	202.340	242.862	283.365	303.585	324.028	364.359	100.0	4.17243	379.31215
33 S	3/2	7.676020	15.356	23.024	30.700	38.368	46.052	53.732	57.566	61.443	69.090	0.75	0.02845	0.01940
35 Cl	3/2	9.797931	19.601	29.389	39.187	48.974	58.782	68.586	73.479	78.427	88.189	75.77	0.05916	4.07523
37 Cl	3/2	8.155764	16.316	24.463	32.619	40.766	48.930	57.090	61.164	65.283	73.408	24.23	0.03412	0.75162
39 K	3/2	4.666423	9.336	13.997	18.663	23.325	27.996	32.665	34.996	37.352	42.002	93.2581	0.00639	0.54186
40 K	-4	5.801987	11.607	17.403	23.205	29.001	34.809	40.614	43.512	46.442	52.223	0.0117	0.01228	0.00013
41 K	3/2	2.561332	5.124	7.683	10.244	12.803	15.367	17.929	19.209	20.502	23.054	6.7302	0.00106	0.00647
43 Ca	-7/2	6.729996	13.464	20.187	26.917	33.639	40.376	47.110	50.471	53.870	60.575	0.135	0.01917	0.00235
45 Sc	7/2	24.291702	48.597	72.863	97.155	121.420	145.737	170.042	182.175	194.443	218.645	100.0	0.90161	81.96439
47 Ti	-5/2	5.637587	11.278	16.910	22.548	28.179	33.822	39.463	42.279	45.126	50.743	7.3	0.01127	0.07479
49 Ti	-7/2	5.639095	11.281	16.914	22.554	28.187	33.831	39.474	42.290	45.138	50.756	5.5	0.01128	0.05640
50 V	6	9.970315	19.946	29.906	39.876	49.836	59.816	69.792	74.772	79.807	89.741	0.25	0.06234	0.01417
51 V	7/2	26.302963	52.621	78.895	105.199	131.474	157.803	184.121	197.259	210.542	236.748	99.75	1.14461	103.79544
53 Cr	-3/2	5.652511	11.308	16.955	22.607	28.254	33.912	39.568	42.391	45.245	50.877	9.501	0.01136	0.09812
55 Mn	5/2	24.789062	49.592	74.355	99.144	123.906	148.720	173.523	185.905	198.424	223.121	100.0	0.95813	87.10270
57 Fe	1/2	3.237778	6.477	9.712	12.950	16.184	19.425	22.664	24.282	25.917	29.143	2.2	0.00213	0.00427
59 Co	7/2	23.727074	47.468	71.169	94.897	118.598	142.349	166.090	177.941	189.923	213.563	100.0	0.84019	76.38075
61 Ni	-3/2	8.936051	17.877	26.804	35.740	44.666	53.611	62.552	67.016	71.529	80.432	1.14	0.04488	0.04652
63 Cu	3/2	26.515473	53.046	79.533	106.049	132.536	159.078	185.608	198.852	212.243	238.660	69.17	1.17258	73.73391
65 Cu	3/2	28.403661	56.824	85.196	113.601	141.974	170.406	198.826	213.013	227.357	255.656	30.83	1.44134	40.39688
67 Zn	5/2	6.256820	12.517	18.767	25.024	31.274	37.537	43.798	46.923	50.083	56.316	4.1	0.01541	0.05742
69 Ga	3/2	24.001255	48.016	71.992	95.993	119.969	143.994	168.009	179.997	192.118	216.030	60.108	0.86965	47.52099
71 Ga	3/2	30.496579	61.011	91.474	121.972	152.435	182.962	213.476	228.708	244.110	274.494	39.892	1.78401	64.69795
73 Ge	-9/2	3.488315	6.979	10.463	13.952	17.436	20.928	24.418	26.161	27.922	31.398	7.73	0.00267	0.01876

EM Spectrum

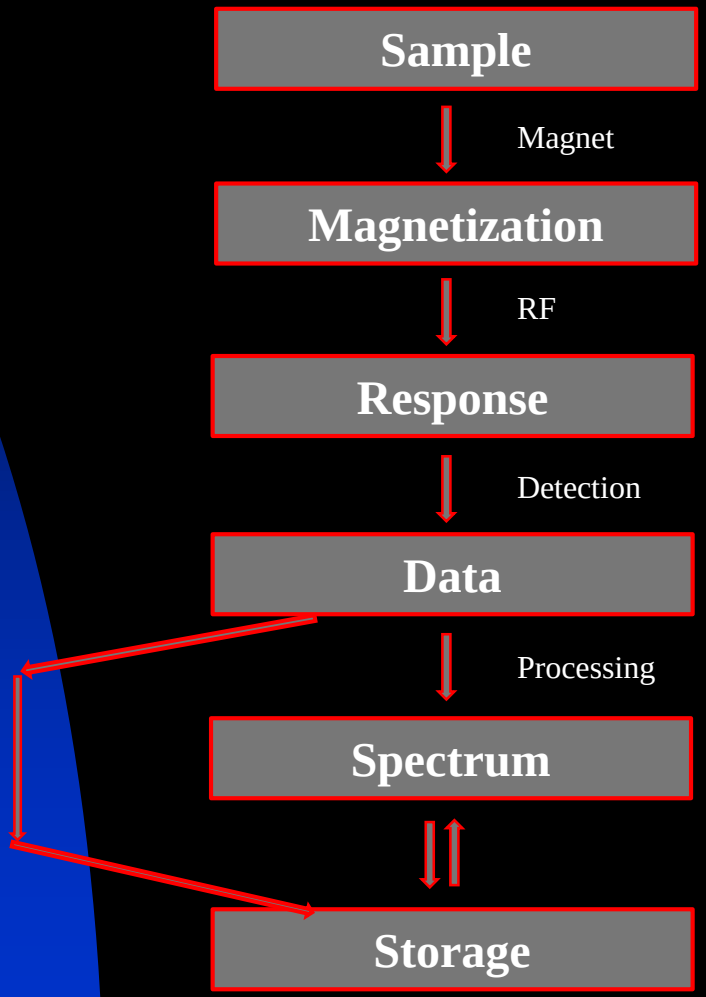
The Table of NMR Frequencies*

By Frequency

Isotope	Spin	2.35 T	4.70 T	7.05 T	9.39 T	11.74 T	14.09 T	16.45 T	17.61 T	18.80 T	21.14 T	Natural Abundance	Relative Receptivity	Absolute Receptivity
3 H	1/2	106.663984	213.389	319.938	426.605	533.152	639.924	746.648	799.924	853.791	960.061	0.0	76.33038	0.00000
1 H	1/2	100.000000	200.057	299.949	399.952	499.843	599.944	700.000	749.948	800.449	900.080	99.985	28.54379	2594.50064
19 F	1/2	94.094008	188.242	282.234	376.331	470.322	564.511	658.658	705.656	753.175	846.921	100.0	23.77922	2161.74685
3 He	-1/2	76.178972	152.401	228.498	304.679	380.775	457.031	533.253	571.303	609.774	685.672	0.000137	12.61877	0.00157
205 Tl	1/2	57.683838	115.401	173.022	230.708	288.329	346.071	403.787	432.599	461.730	519.201	70.476	5.47866	351.01253
203 Tl	1/2	57.123200	114.279	171.340	228.465	285.526	342.707	399.862	428.394	457.242	514.154	29.524	5.32046	142.80115
31 P	1/2	40.480742	80.985	121.422	161.904	202.340	242.862	283.365	303.585	324.028	364.359	100.0	1.89346	172.13307
7 Li	3/2	38.863790	77.750	116.572	155.437	194.258	233.161	272.047	291.458	311.085	349.805	92.5	1.67551	140.89517
119 Sn	-1/2	37.290632	74.603	111.853	149.145	186.395	223.723	261.034	279.660	298.492	335.646	8.59	1.48017	11.55876
117 Sn	-1/2	35.632259	71.285	106.879	142.512	178.105	213.774	249.426	267.223	285.218	320.719	7.68	1.29134	9.01592
87 Rb	3/2	32.721218	65.461	98.147	130.869	163.555	196.309	229.049	245.392	261.917	294.517	27.835	1.00000	25.30455
115 Sn	-1/2	32.718749	65.456	98.140	130.859	163.542	196.294	229.031	245.374	261.897	294.495	0.34	0.99977	0.30902
11 B	3/2	32.083974	64.186	96.236	128.320	160.369	192.486	224.588	240.613	256.816	288.781	80.1	0.94271	68.64611
125 Te	-1/2	31.549789	63.118	94.633	126.184	157.699	189.281	220.849	236.607	252.540	283.973	7.139	0.89640	5.81762
141 Pr	5/2	30.620000	61.257	91.844	122.465	153.052	183.703	214.340	229.634	245.097	275.604	100.0	0.81946	74.49626
71 Ga	3/2	30.496579	61.011	91.474	121.972	152.435	182.962	213.476	228.708	244.110	274.494	39.892	0.80959	29.36014
65 Cu	3/2	28.403661	56.824	85.196	113.601	141.974	170.406	198.826	213.013	227.357	255.656	30.83	0.65409	18.33224
129 Xe	-1/2	27.811008	55.638	83.419	111.231	139.011	166.850	194.677	208.568	222.613	250.321	26.4	0.61399	14.73578
81 Br	3/2	27.007028	54.029	81.007	108.015	134.993	162.027	189.049	202.539	216.177	243.085	49.31	0.56227	25.20486
63 Cu	3/2	26.515473	53.046	79.533	106.049	132.536	159.078	185.608	198.852	212.243	238.660	69.17	0.53212	33.46069
23 Na	3/2	26.451921	52.919	79.342	105.795	132.218	158.697	185.163	198.376	211.734	238.088	100.0	0.52830	48.02757
51 V	7/2	26.302963	52.621	78.895	105.199	131.474	157.803	184.121	197.259	210.542	236.748	99.75	0.51943	47.10271
123 Te	-1/2	26.169767	52.354	78.496	104.667	130.808	157.004	183.188	196.260	209.476	235.549	0.908	0.51158	0.42228
27 Al	5/2	26.056890	52.129	78.157	104.215	130.244	156.327	182.398	195.413	208.572	234.533	100.0	0.50499	45.90782
13 C	1/2	25.145020	50.304	75.422	100.568	125.686	150.856	176.015	188.575	201.273	226.325	1.1	0.45380	0.45380
79 Br	3/2	25.054454	50.123	75.151	100.206	125.233	150.313	175.381	187.895	200.548	225.510	50.69	0.44892	20.68693
151 Eu	5/2	24.860000	49.734	74.567	99.428	124.261	149.146	174.020	186.437	198.992	223.760	47.8	0.43855	19.05681
55 Mn	5/2	24.789062	49.592	74.355	99.144	123.906	148.720	173.523	185.905	198.424	223.121	100.0	0.43480	39.52749
93 Nb	9/2	24.476195	48.966	73.416	97.893	122.343	146.843	171.333	183.559	195.919	220.305	100.0	0.41855	38.04965
45 Sc	7/2	24.291702	48.597	72.863	97.155	121.420	145.737	170.042	182.175	194.443	218.645	100.0	0.40915	37.19570
159 Tb	3/2	24.040000	48.094	72.108	96.148	120.162	144.227	168.280	180.287	192.428	216.379	100.0	0.39657	36.05142
69 Ga	3/2	24.001255	48.016	71.992	95.993	119.969	143.994	168.009	179.997	192.118	216.030	60.108	0.39465	21.56518
121 Sb	5/2	23.930601	47.875	71.780	95.711	119.615	143.570	167.514	179.467	191.552	215.395	57.36	0.39118	20.39806
59 Co	7/2	23.727074	47.468	71.169	94.897	118.598	142.349	166.090	177.941	189.923	213.563	100.0	0.38128	34.66183
187 Re	5/2	22.751602	45.516	68.243	90.995	113.722	136.497	159.261	170.625	182.115	204.783	62.6	0.33616	19.13063
185 Re	5/2	22.524602	45.062	67.562	90.088	112.588	135.135	157.672	168.923	180.298	202.739	37.4	0.32620	11.09078
99 Tc	9/2	22.508316	45.029	67.513	90.022	112.506	135.037	157.558	168.801	180.168	202.593	0.0	0.32549	0.00000
113 Cd	-1/2	22.193175	44.399	66.568	88.762	110.931	133.147	155.352	166.437	177.645	199.756	12.22	0.31201	3.46616
115 In	9/2	21.912527	43.838	65.726	87.640	109.528	131.463	153.388	164.333	175.399	197.230	95.7	0.30032	26.12813
113 In	9/2	21.865656	43.744	65.586	87.452	109.294	131.182	153.060	163.981	175.023	196.808	4.3	0.29840	1.16647
195 Pt	1/2	21.496752	43.006	64.479	85.977	107.450	128.968	150.477	161.214	172.071	193.488	33.8	0.28355	8.71273

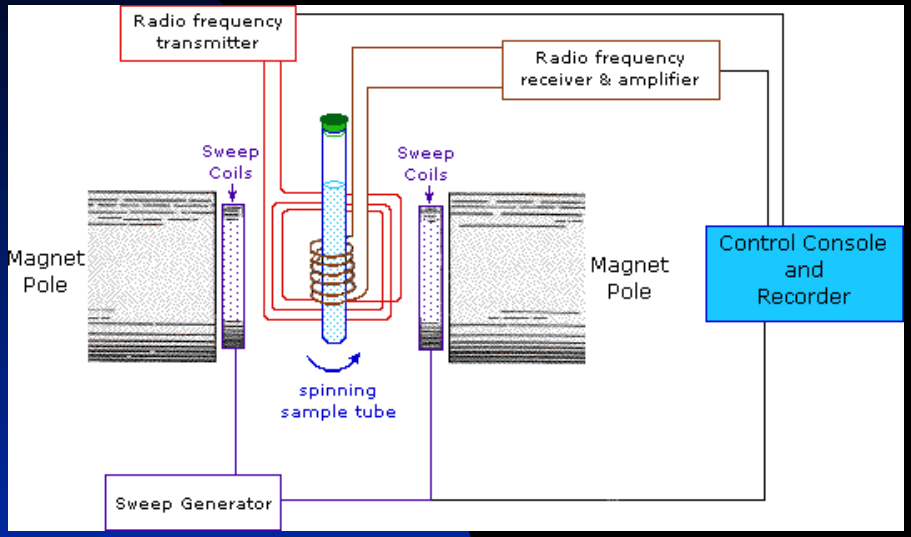
NMR Experiments

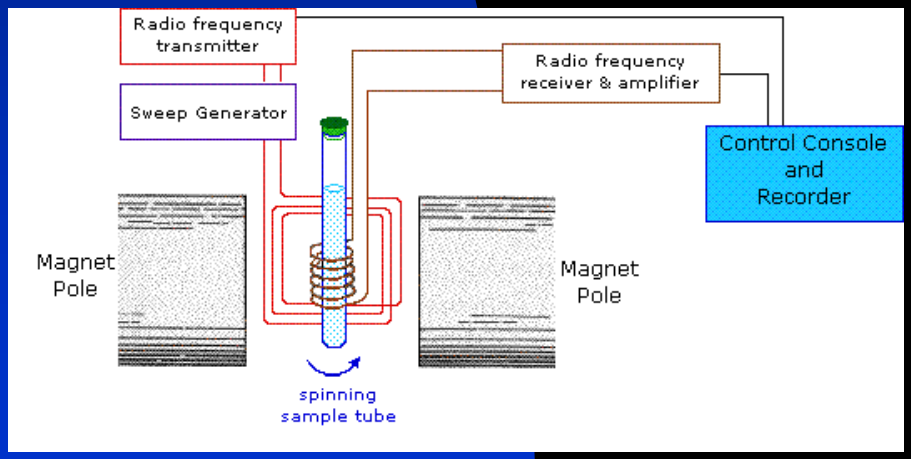
NMR Experiment Flowchart

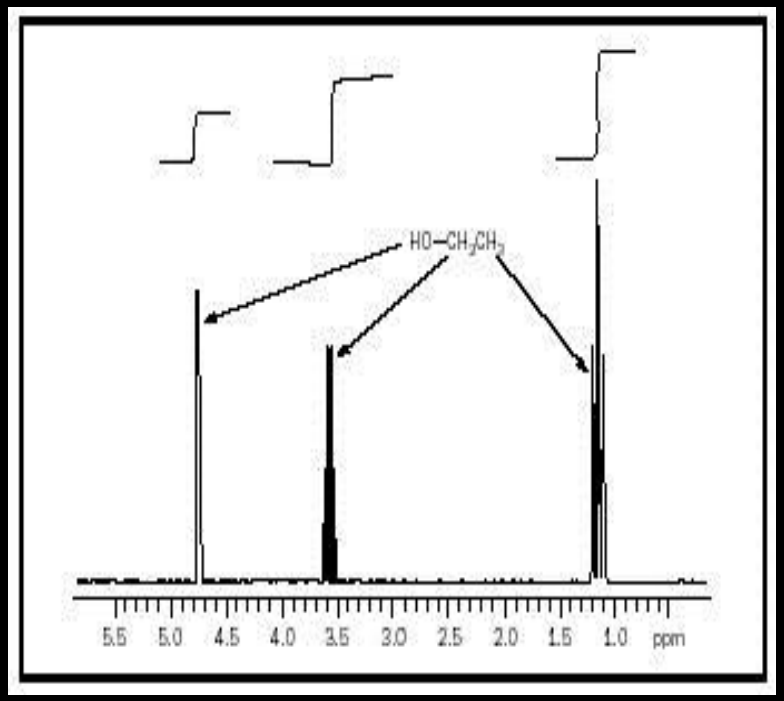


NMR Experiments – Continuous Wave NMR

CW Spectrometer







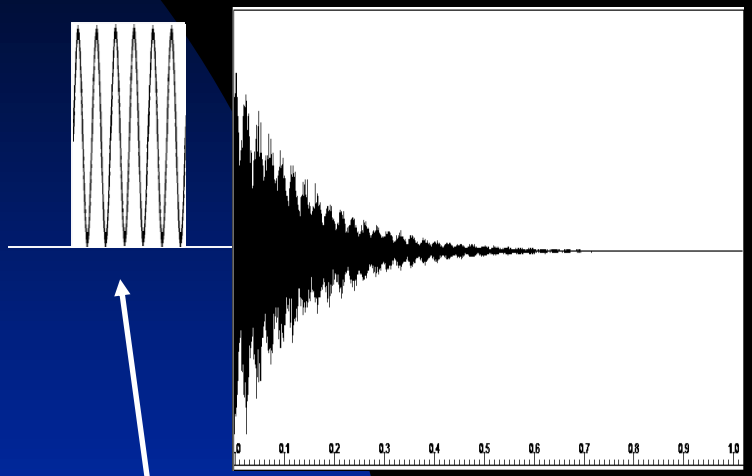
Frequency or field sweeps can be very time consuming.

(several minutes per scan for high resolution)

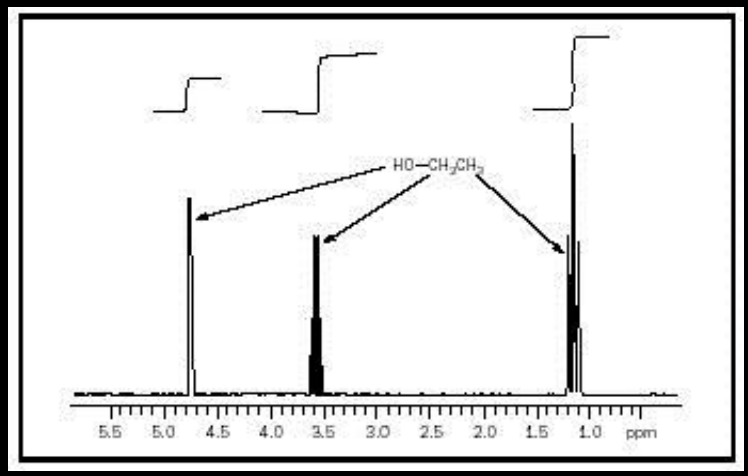
NMR Experiments – Pulse-Fourier Transform

Pulse Fourier Transform Spectrometer

(records time domain data after a radiofrequency pulse)



FT

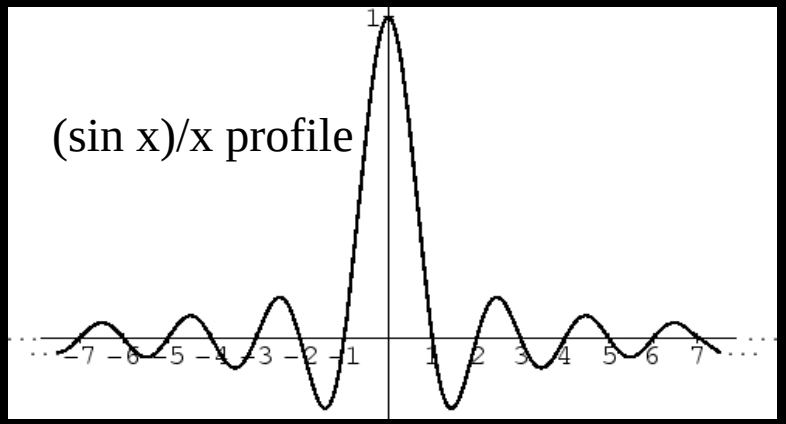


The FID (Free Induction Decay) is Fourier-Transformed into the spectrum

A microsecond RF pulse at ν_0 excites a band of frequencies around ν_0.

RF power is adjusted to excite a 50 kHz band with a 5 μs 90° pulse.

This is also called a "***50 kHz B_1 field***".



Spins – The Vector Model

a) Coherence

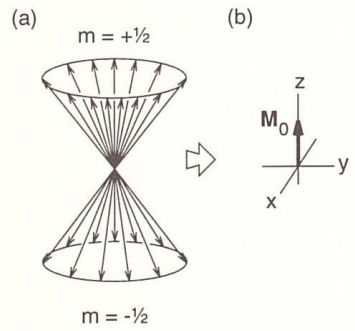


Fig. 6.3 Vector model of a collection of spin-$\frac{1}{2}$ nuclei at thermal equilibrium in a magnetic field along the *z* axis. (a) The magnetic moments of the individual spins: there is a slight excess of nuclei in the $m = +\frac{1}{2}$ state, which is lower in energy than the $m = -\frac{1}{2}$ state (for nuclides with positive gyromagnetic ratio). At equilibrium, the phases of the individual magnetic moments in the *xy* plane are random. (b) The net magnetic moment of a large number of spins.

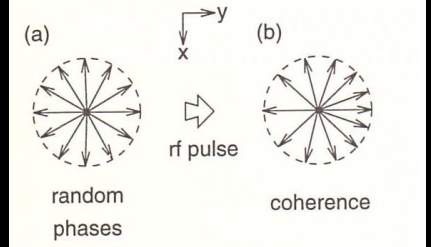


Fig. 6.7 The effect of a radiofrequency pulse on the magnetic moments of the individual spins in an NMR sample (looking down the *z* axis). Starting from the equilibrium state with random phases (a), a pulse along the *x* axis in the rotating frame causes the spins to 'bunch together' to some extent (b), producing a net *y* magnetization in the sample. This phase-correlation amongst the spins is known as *coherence*.

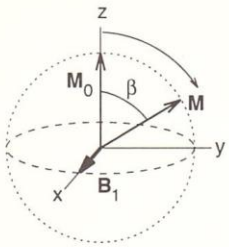
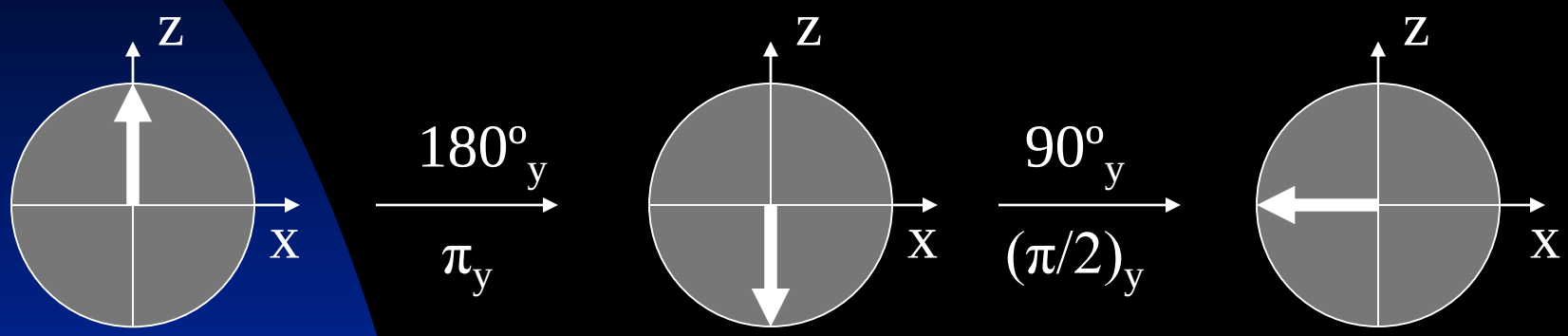


Fig. 6.6 The effect of a radiofrequency pulse on a collection of nuclear spins at equilibrium is to rotate the magnetization away from the *z* axis, around the direction of B_1, through an angle β (eqn 6.5).

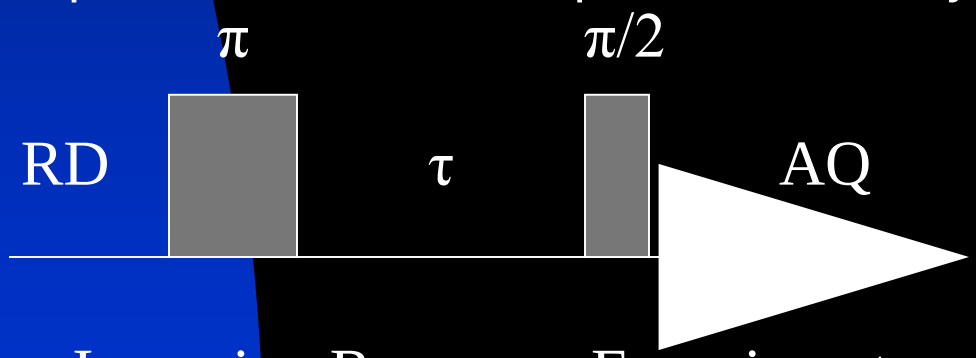
NMR Pulses / Pulse Sequences

Pulses are described by the angle (degree) by which they turn the magnetization:



Only the magnetization in the X,Y plane is observable.

Pulse Sequences are series of pulses and delays:

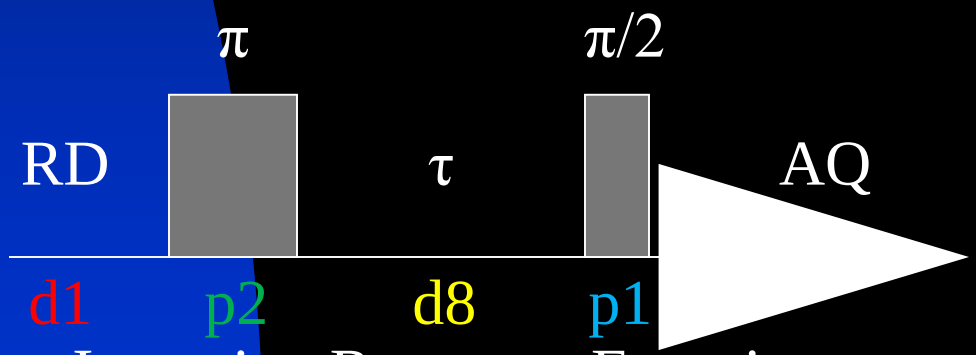


Inversion Recovery Experiment

NMR Pulses / Pulse Sequences

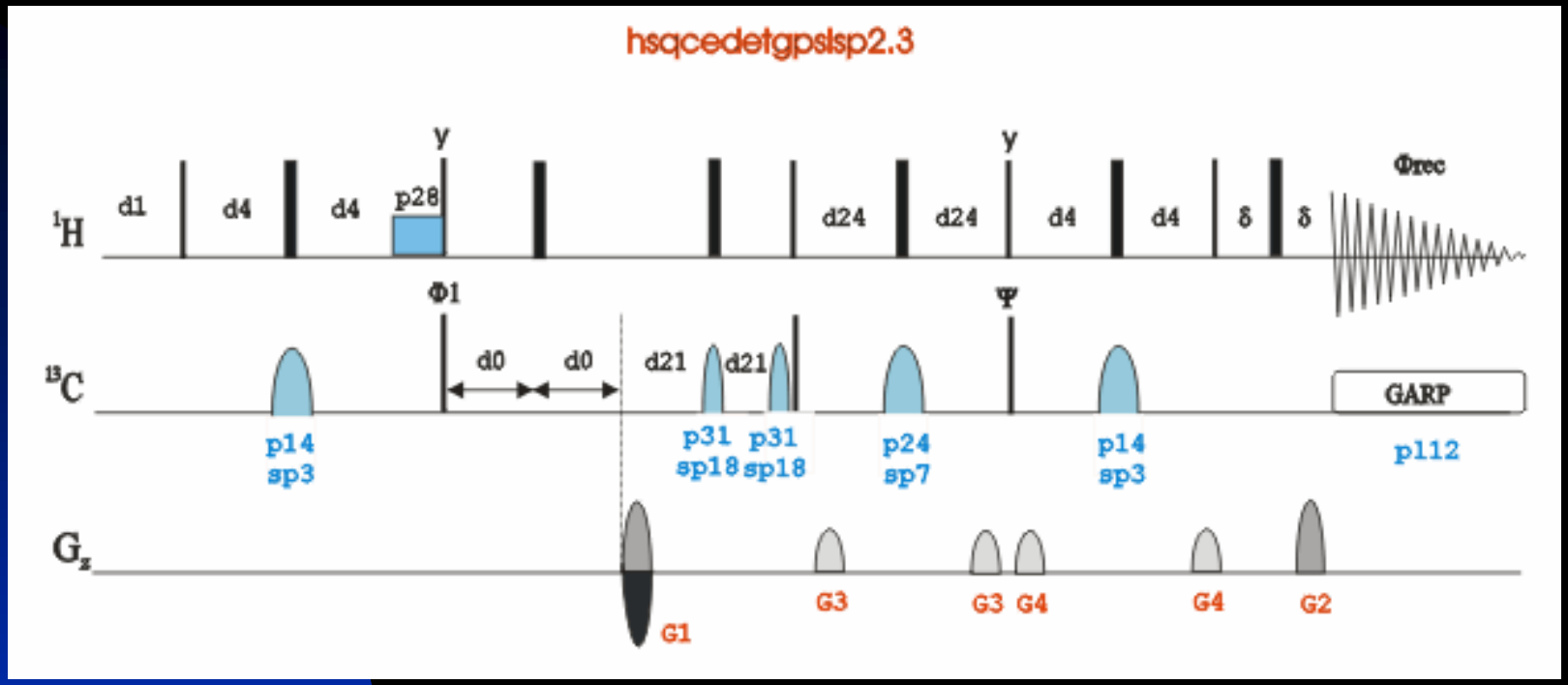
```
"p2=p1*2"
"d11=30m"
"acqt0=-p1*2/3.1416"

1 ze
2 d1
  p2 ph1
  d8
  p1 ph2
3 go=2 ph31
  d11 wr #0 if #0
exit

ph1=0 2
ph2=0 0 2 2 1 1 3 3
ph31=0 0 2 2 1 1 3 3
```

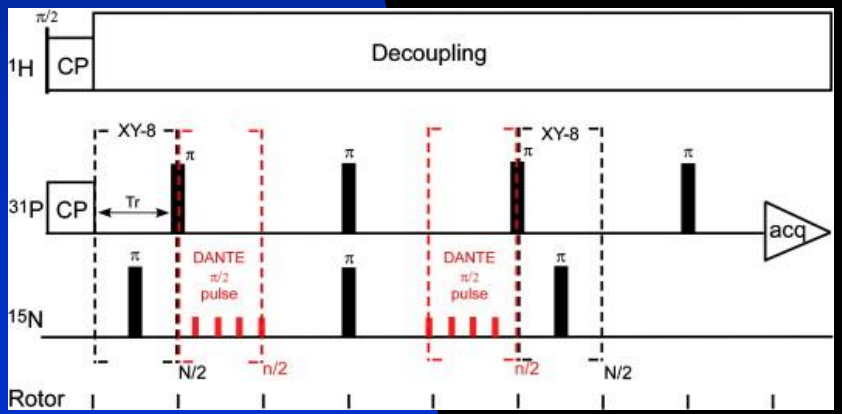
```
;t1ir
;avance-version (07/04/03)
;T1 measurement using inversion recovery

;pl1 : f1 channel - power level for pulse (default)
;p1 : f1 channel -  90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;d1 : relaxation delay; 1-5 * T1
;d11: delay for disk I/O                  [30 msec]
;d8 : recovery delay
;NS: 8 * n
;DS: 4
;td1: number of experiments
```

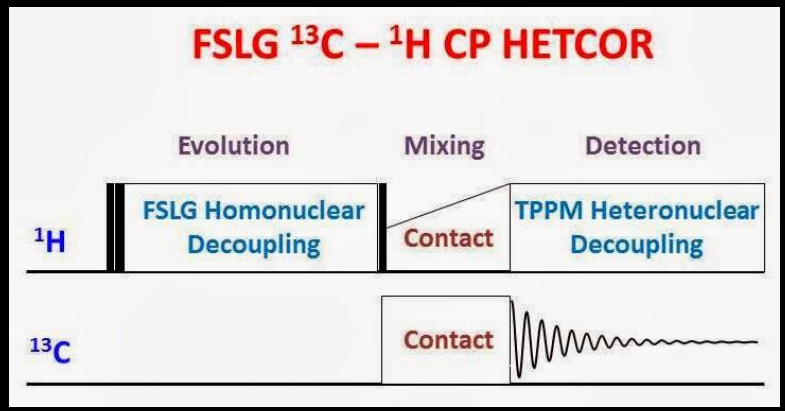


Inversion Recovery Experiment

Pulse Sequences can be very complicated







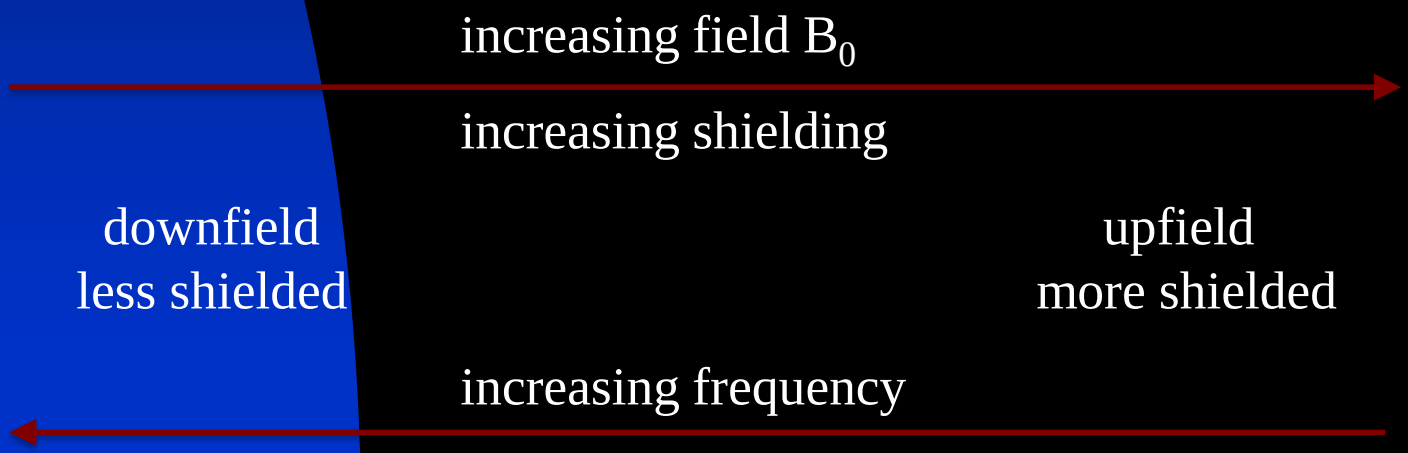
NMR Parameters - Shielding

The general resonance condition: $\nu_0 = (\gamma/2\pi)\, B_0$

Increasing the electron density will shield the nucleus and it will require a higher value of B_0 to achieve resonance: $B_{eff} = B_0 - \sigma\, B_0$

The resonance condition becomes: $\nu = (\gamma/2\pi)\, B_0\, (1 - \sigma)$

The frequency ν is very large (MHz - GHz) and B_0 dependent.
The range $\Delta\nu$ for most nuclei is very small (Hz - kHz).



NMR Parameters - Chemical Shift

The resonance condition: $\nu = (\gamma/2\pi)\, B_0\, (1 - \sigma)$

The problem:
The absolute frequency ν is very large (MHz - GHz) and B_0 dependent.
The range $\Delta\nu$ for most nuclei is very small (Hz - kHz).

i.e. two proton signals at 60,000,000 Hz and 60,000,120 Hz

The solution: Chemical Shift (δ)
Report frequency relative to a reference signal, i.e. tetramethylsilane, and normalize it to the reference frequency:

$$\delta(X) = 10^6 \; [\quad \nu(X) \quad - \quad \nu(TMS) \quad] \; / \quad \nu(TMS)$$

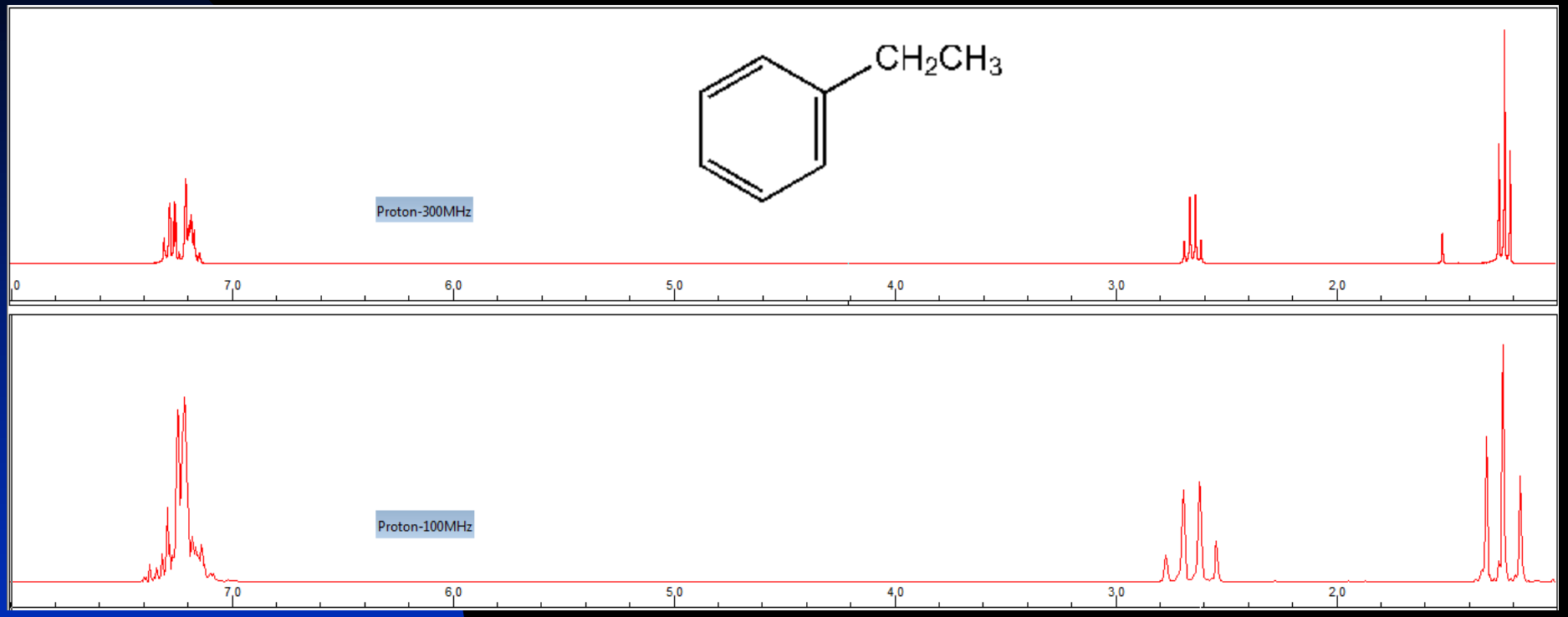
$$\delta(X) = 10^6\, [60{,}000{,}120 - 60{,}000{,}000] \,/\, 60{,}000{,}000 = 2 \text{ (ppm)}$$

Chemical shifts are field independent and are given in ppm with typical ranges of 15 ppm for ^1H and 250 ppm for ^{13}C.

Chemical shifts increase from right to left.

NMR Parameters - Chemical Shift

- Example: ^{1}H spectrum of Ethylbenzene at 7.05 T and 2.35 T

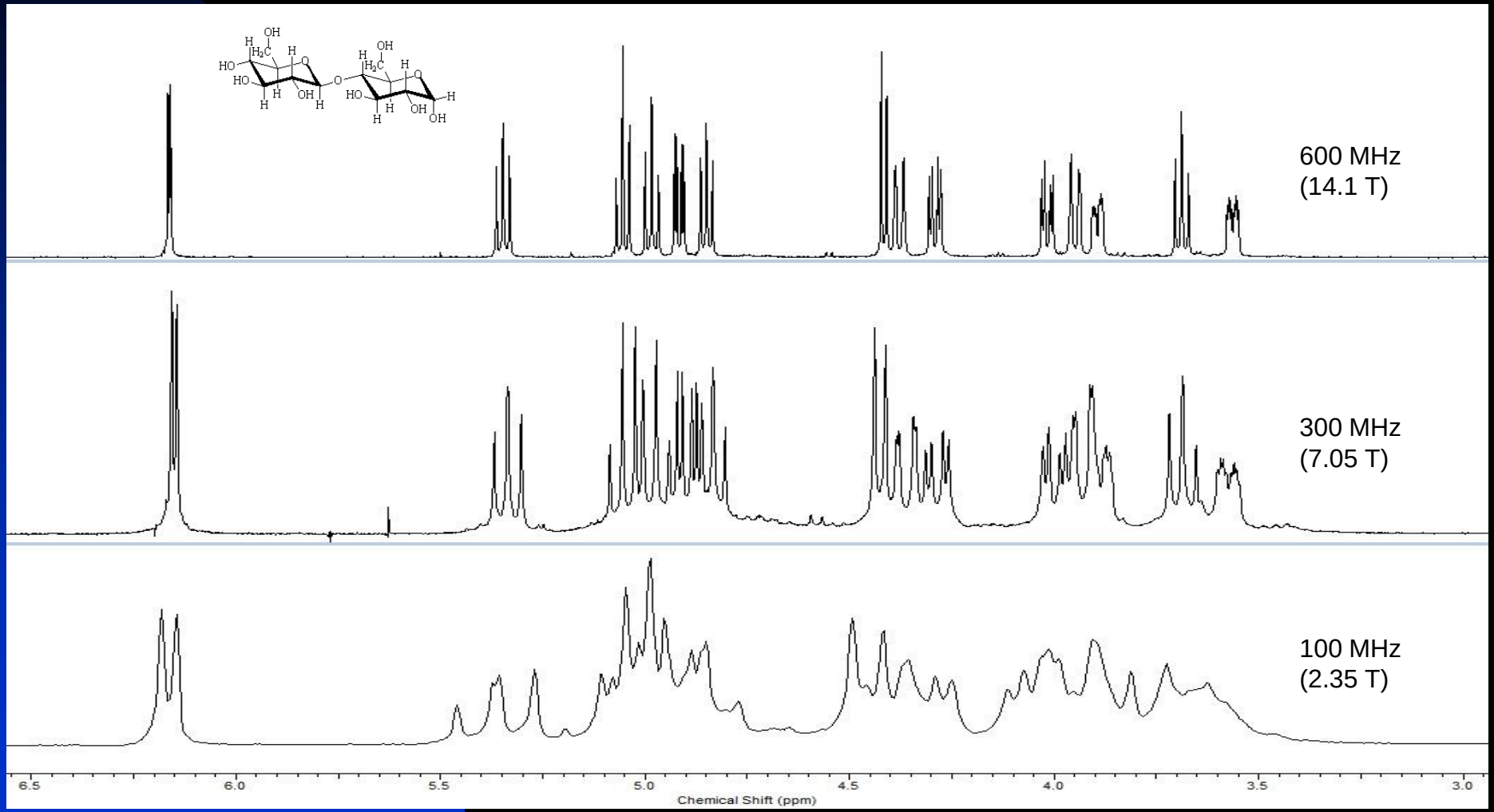


- Chemical shifts (measured in ppm) are identical at different magnetic fields.
- Couplings (Signal splittings, measured in Hertz) are also identical at different fields, but take up less space at higher fields/frequencies.

Better chemical shift dispersion at higher fields.

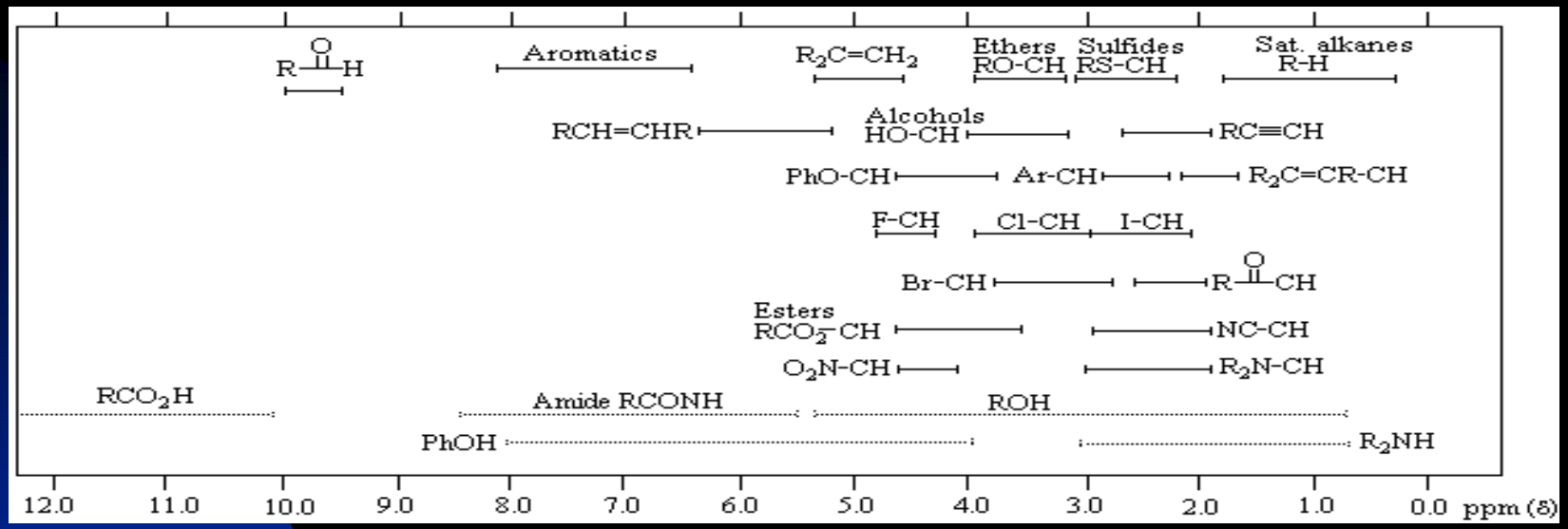
NMR Parameters - Chemical Shift

- Example: ^{1}H spectrum of Cellobiose at 14.1 T, 7.05 T, and 2.35 T

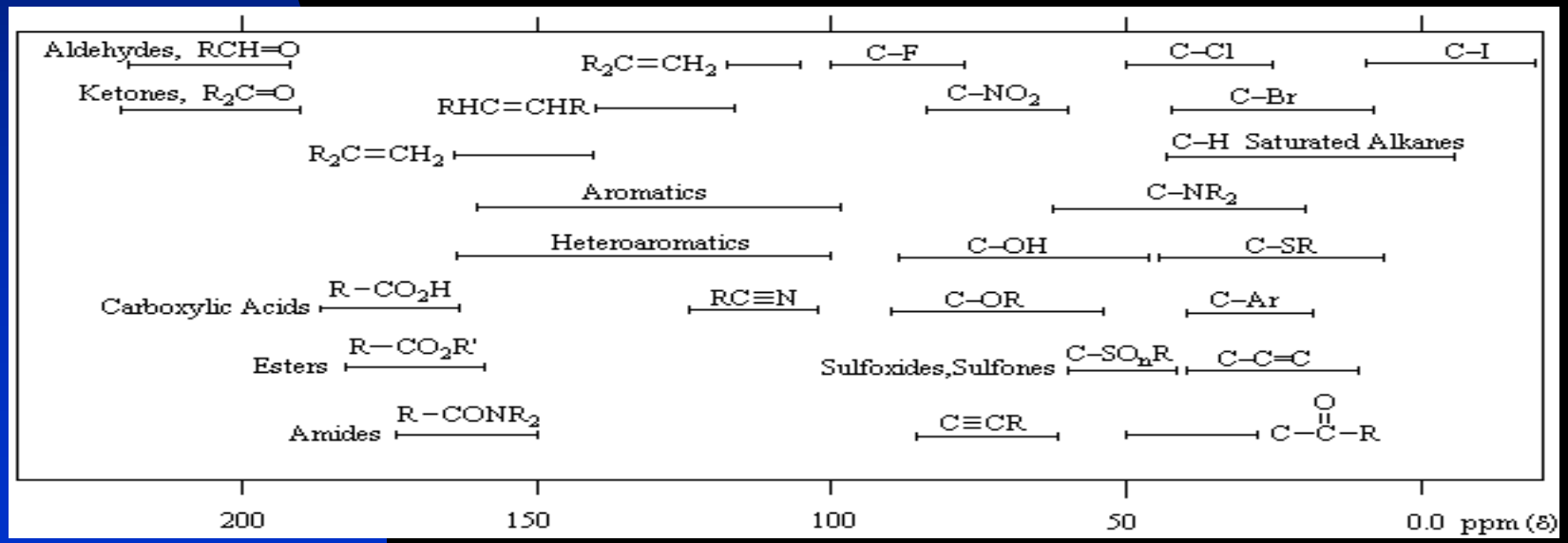


NMR Parameters - Chemical Shift

^{1}H

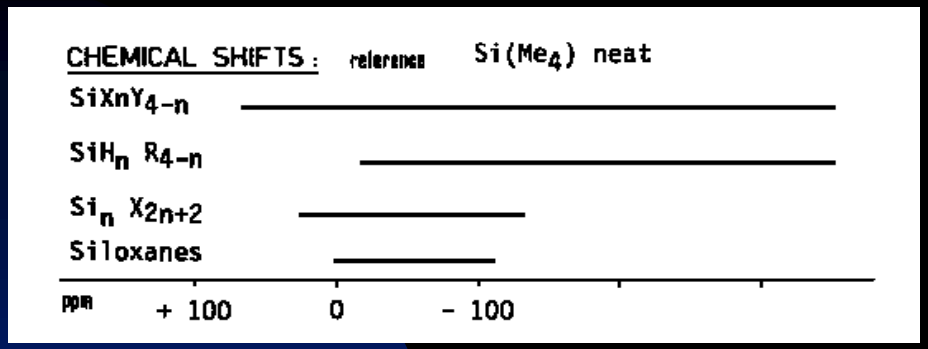


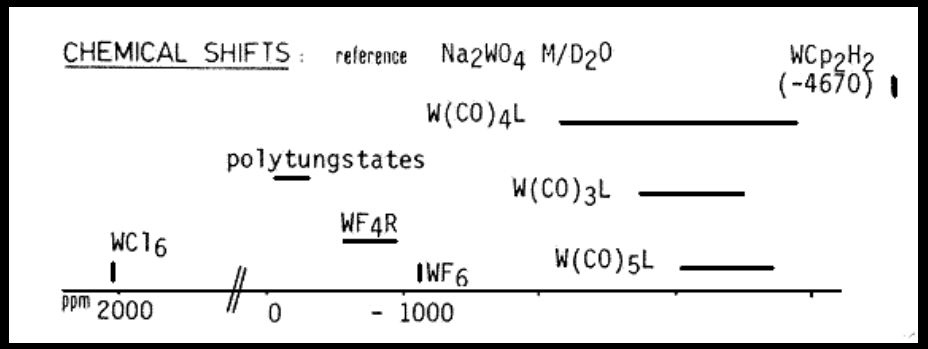
^{13}C

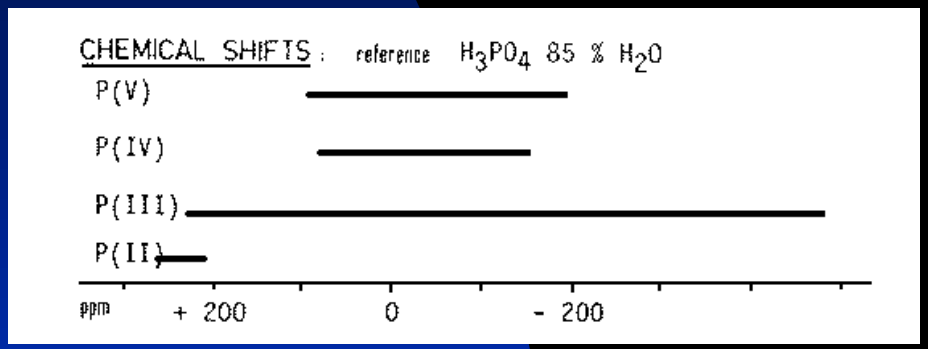


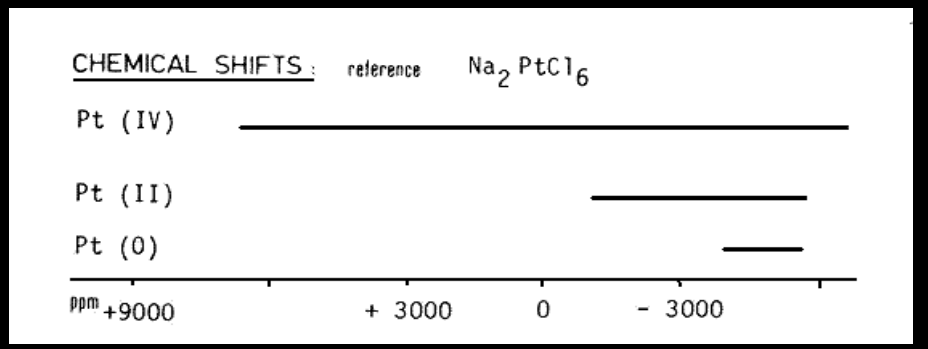
Chemical shifts relative to TMS (0 ppm)

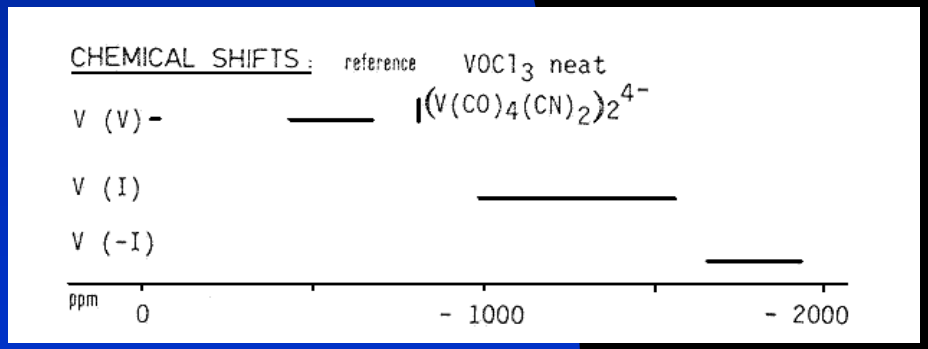
NMR Parameters - Chemical Shift

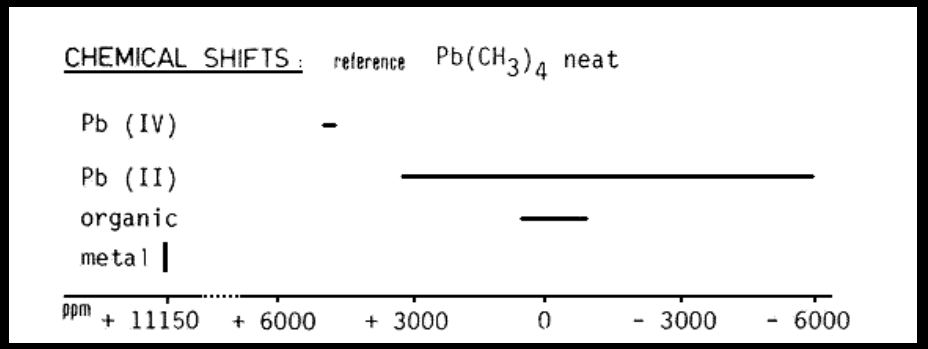










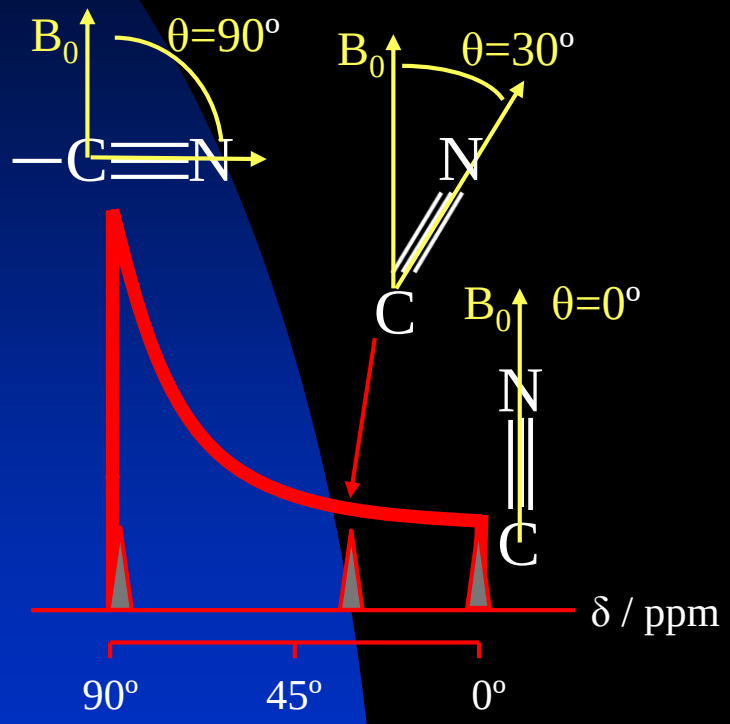


Chemical shift ranges for common inorganic nuclei.

NMR Parameters - CSA

Chemical Shift Anisotropy:

The chemical shift depends on the relative orientation of a molecule or a crystal to the B_0 field.



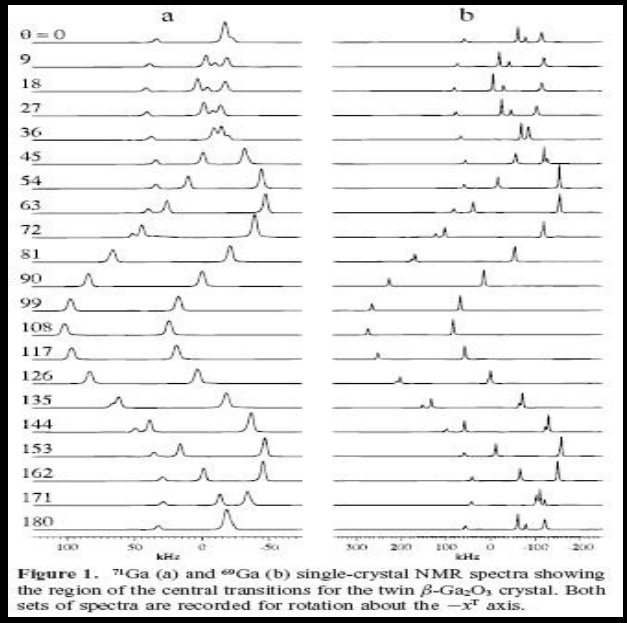


Figure 1. ^{71}Ga (a) and ^{69}Ga (b) single-crystal NMR spectra showing the region of the central transitions for the twin β-Ga_2O_3 crystal. Both sets of spectra are recorded for rotation about the $-x^r$ axis.

A single crystal will have a sharp NMR signal at a chemical shift that depends on the angle θ between B_0 and the principal axis of the crystal:

$$\nu \approx (3 \cos^2 \theta - 1)$$

A powder sample consists of a large number of microscopic crystals at random orientations.

NMR Parameters - CSA

Chemical Shift Anisotropy:

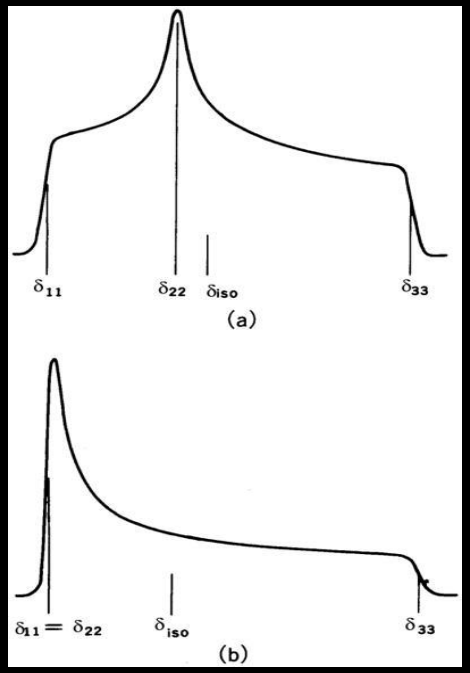
A powder sample consists of a large number of microscopic crystals at random orientations. This leads to a superimposition of the signals of all individual crystals, resulting in a powder pattern spectrum.

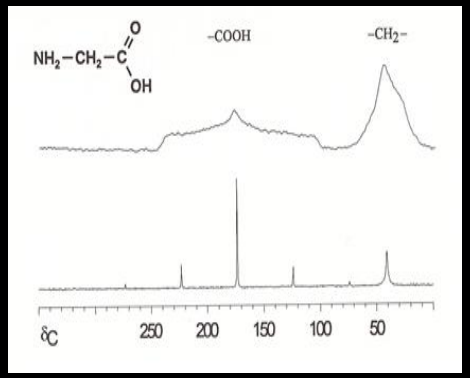
$$\nu \approx (3 \cos^2 \theta - 1)$$

The lineshape is determined by the asymmetry of the electronic and molecular surrounding.

axially asymmetric

axially symmetric



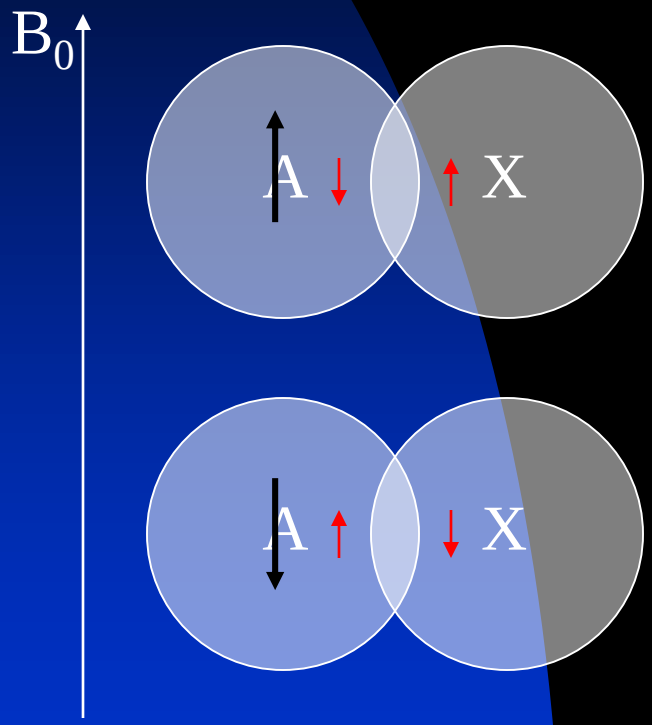


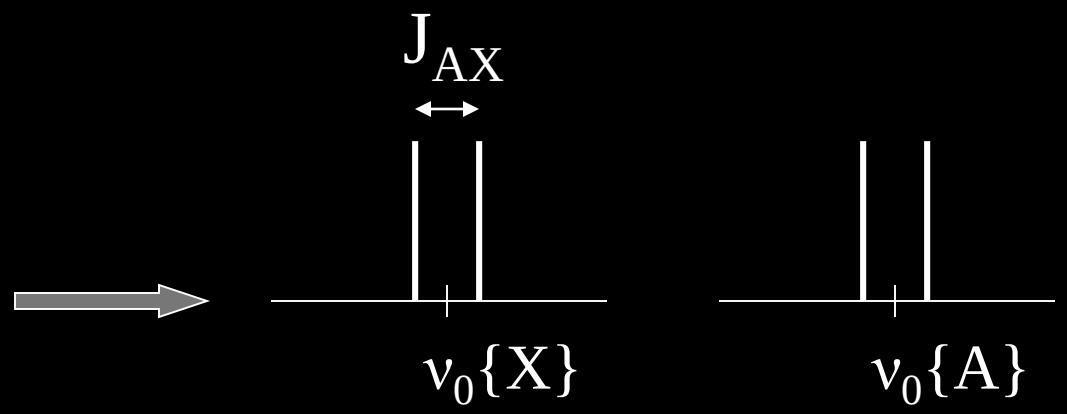
In **solution** the Brownian motion will average all orientations, leading to a single sharp signal. In **solid** samples we need to simulate rapid re-orientation of the molecules:
Spinning a powder sample around the "magic angle" (54.7º) will sharpen the signal around the isotropic chemical shift.

$(3 \cos^2 \theta - 1) = 0$ for $\theta = 54.7^\circ$

NMR Parameters - Couplings

- Spin, Spin Coupling (scalar coupling, J-coupling)
  Interaction between spins through valence electrons





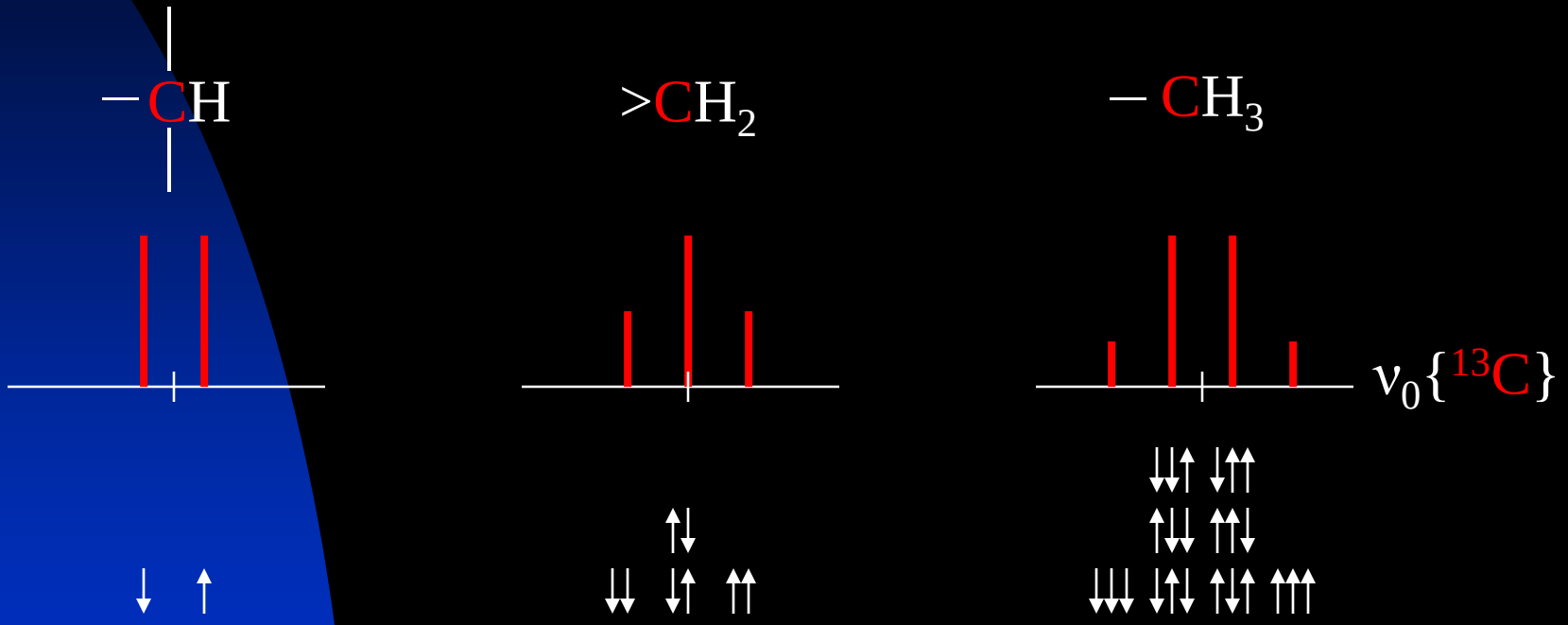
$$\Delta E = J_{AX} \cdot I(A) \cdot I(X)$$

The magnetic field at nucleus X will be enhanced or attenuated depending on the orientation of spin A.

NMR Parameters - Couplings

- Doublets, Triplets, … Multiplets

Couplings to more than one nucleus increase multiplicity.

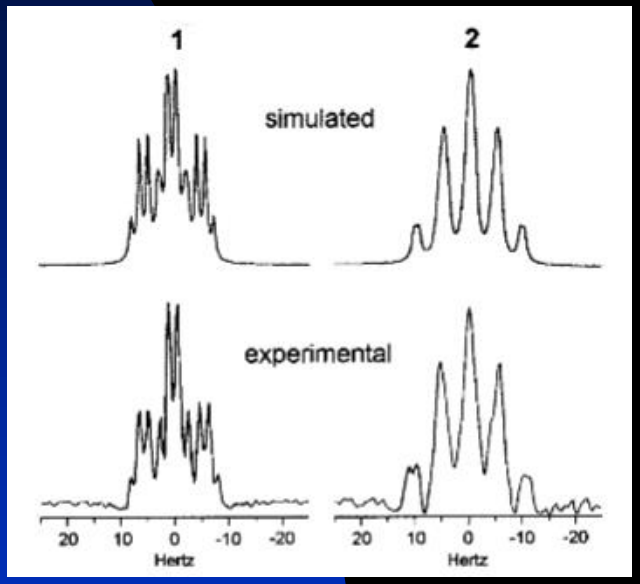


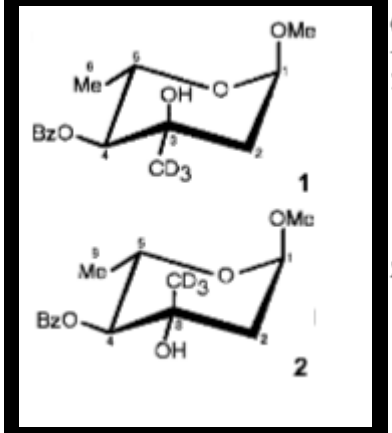
Couplings to chemically and magnetically different spins can lead to complex multiplicity patterns (dd, ddd, dt, ... , m)

NMR Parameters - Couplings

- Doublets, Triplets, … Multiplets

Simulate spectra with measured or calculated couplings to determine multiplicity.





Compound	Proton	*J*(C-3,H)[a] (BFW-COLOC)
1	H-1	5.5
	H-2ax	−1.5
	H-2eq	−5.7
	H-4	2.7
	H-5	2.7
2	H-1	5.9
	H-2ax	−5.2
	H-2eq	−6.0
	H-4	−5.8
	H-5	2.3

•J. Schulte, J. Lauterwein, M. Klessinger, and J. Thiem, *Magnetic Resonance in Chemistry* **41**, 123-130 (2003), "Configurational Assignment in Alkyl-Branched Sugars via the Geminal C,H Coupling Constants."

Couplings to chemically and magnetically different spins can lead to complex multiplicity patterns (dd, ddd, dt, ... , m)

NMR Parameters - Couplings

- single-bond vs. multi-bond coupling constants

C-H	$^{1}J_{CH}$:	100 to 200 Hz
C-C-H	$^{2}J_{CH}$:	-10 to +10 Hz
C-C-C-H	$^{3}J_{CH}$:	0 to +10 Hz
H-C-H	$^{2}J_{CH}$:	-5 to -15 Hz
H-C-C-H	$^{3}J_{CH}$:	0 to +10 Hz

Couplings are always quoted in Hertz units (also: cps)

Couplings are independent of the magnetic field.

Longer range couplings are only visible, if all nuclei in the coupling pathway are in the same plane.
(W configuration – zig-zag arrangement)

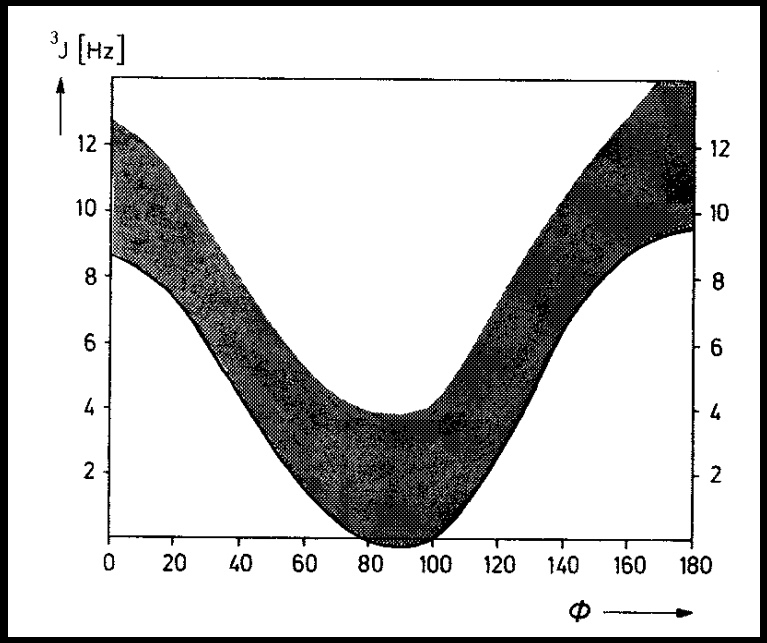
NMR Parameters - Couplings

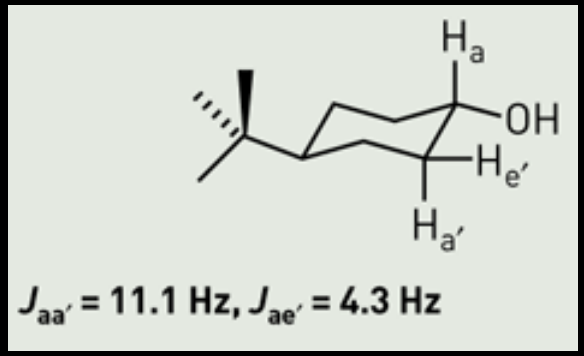
- Structural dependence of vicinal J couplings

Karplus Equation for
H-C-C-H, C-C-C-H and C-O-C-H
dihedral angles:

$^3J(\Phi) = A + B \cos \Phi + C \cos^2 \Phi$

(A, B and C can be tuned to fit
different classes of compounds)

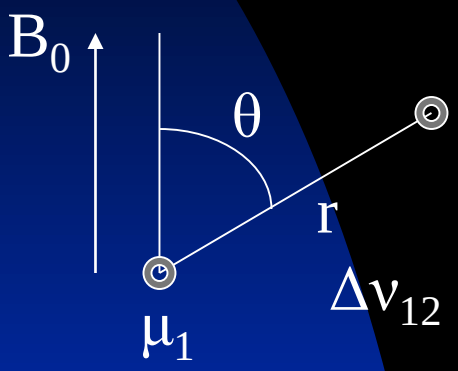




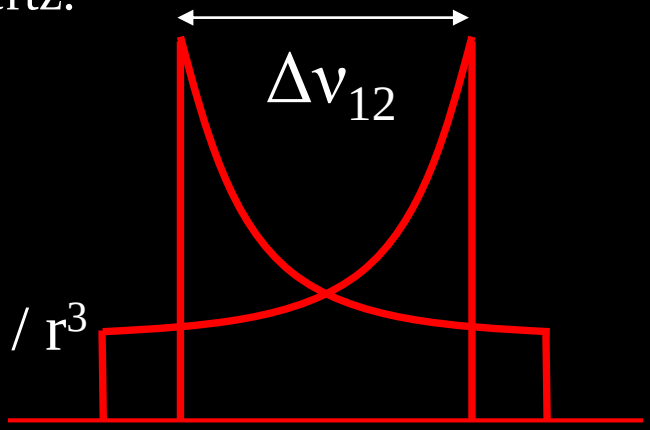
NMR Parameters - Couplings

- Dipolar Coupling (d)

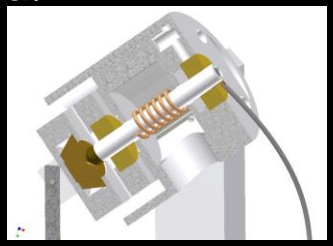
Interaction between spins through space. No bonds are necessary.
Dipolar couplings can span thousands of hertz.



$$\Delta\nu_{12} = 3d_{12}/2\,(3\cos^2\theta - 1) / r^3$$



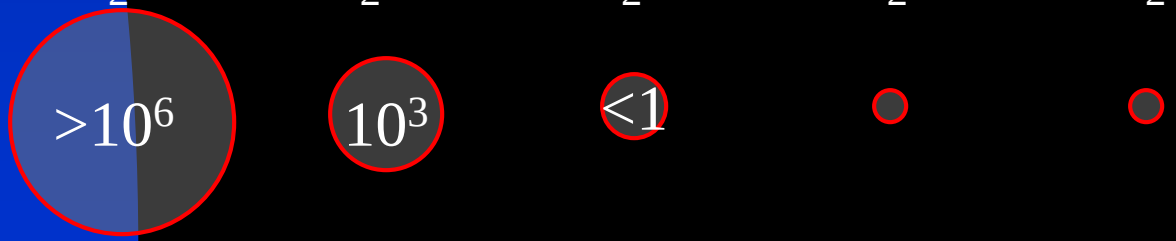
- In liquids the Brownian motion averages all orientations.
  $(3\cos^2\theta - 1) = 0$, no dipolar splitting.
- Solids and molecules dissolved in liquid crystals are aligned.
  $(3\cos^2\theta - 1) \neq 0$, dipolar splitting / broadening.
- Sample spinning around $\theta = 54.7°$ can remove broadening.
  Magic Angle Spinning (MAS)



NMR Parameters - Relaxation

- What is relaxation?
  - Loss of magnetization through interaction of a spin with other spins or with the sample
- Mechanisms for relaxation:
  - Paramagnetic relaxation (paramagnetic metals, organic radicals)
  - Quadrupolar relaxation (nuclei with I > 1/2)
  - Dipolar relaxation ("normal" organic compounds)
  - Chemical shift anisotropy (CSA) relaxation
  - Spin rotation relaxation
- Relaxation rates are additive:

$$R_2 = 1/T_2 = 1/T_2^{para} + 1/T_2^{quad} + 1/T_2^{dipol} + 1/T_2^{CSA} + 1/T_2^{SR} + \ldots$$

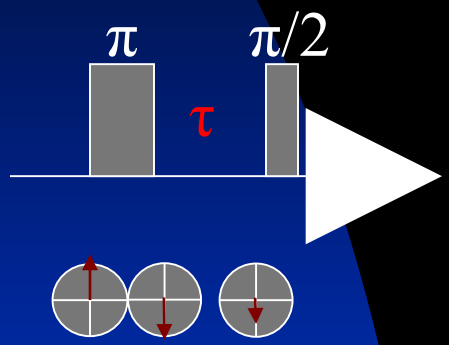


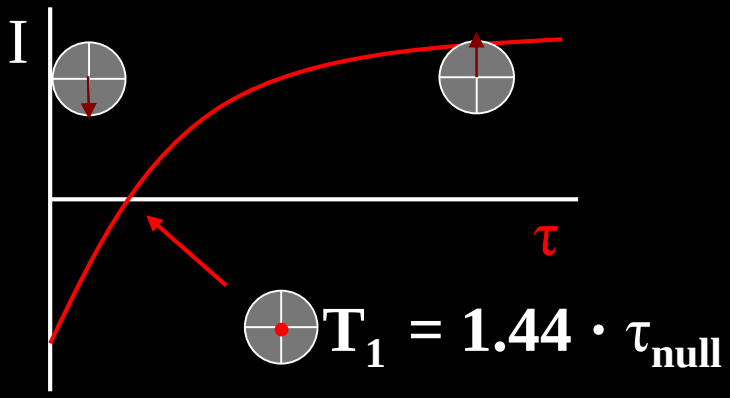
NMR Parameters - Relaxation

- **T_1 relaxation** (spin-lattice relaxation, longitudinal relaxation)

  Heat is released to the lattice (sample) when the spin reverts to the lower energy level.

T_1 Measurement by "Inversion Recovery" technique:





Typical T_1's:

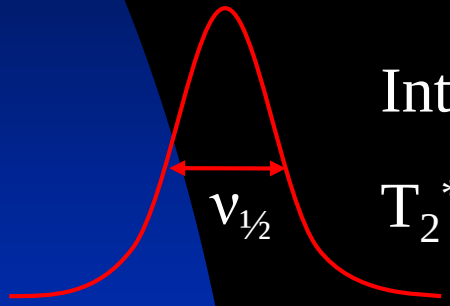
- seconds to minutes for Spin-½ nuclei (^{1}H: 2 sec., ^{13}C: 20 sec., ^{15}N: 200 sec.)
- microseconds for paramagnetic nuclei
- milliseconds for quadrupolar nuclei

NMR Parameters - Relaxation

- **T_2 relaxation** (spin-spin relaxation, transverse relaxation)
  Energy dissipation by interactions between spins.

T_2 is always shorter than T_1 (because of field inhomogeneity).

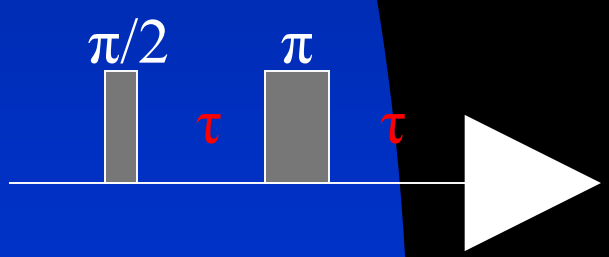
T_2 can be estimated from the width of the signal at half height:

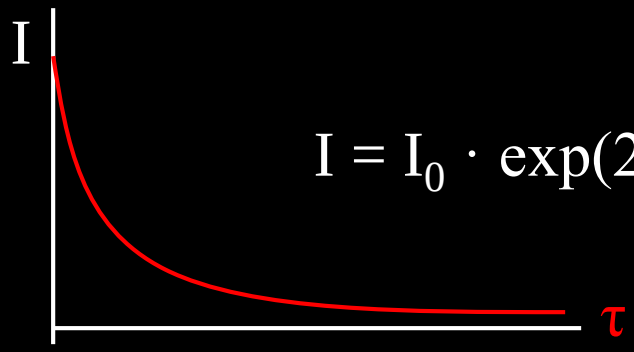


Intrinsic T_2 relaxation:

$T_2^* = 1/\pi \cdot \nu_{½}$ with $1/T_2^* = 1/T_2 + 1/T_2^{inh.}$

T_2 can be measured more accurately by the "Spin-Echo" technique:





$I = I_0 \cdot \exp(2\,\tau / T_2)$

Key Techniques for Solid State NMR:
1. Decoupling

Irradiating one nucleus (typically ^{1}H) will lead to an equal distribution of its α and β populations. ^{1}H will become "invisible" to other nuclei.

Techniques:

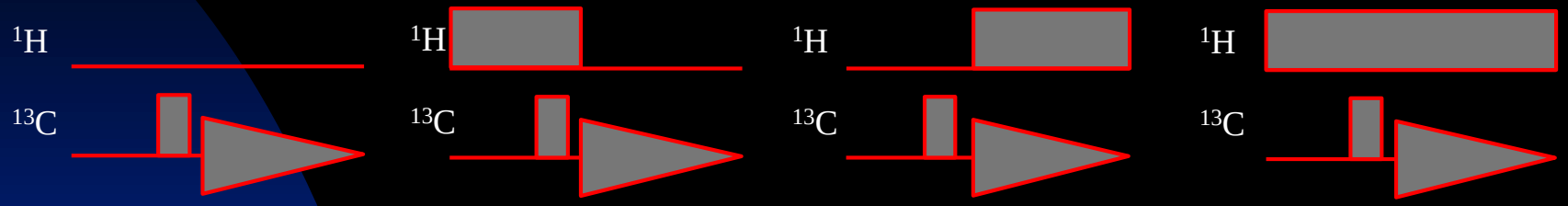
- CW decoupling (single frequency)
- BB decoupling (random 10 ppm frequency modulation)
- CPD decoupling (composite pulses for a more uniform decoupling)

Side effect:

Magnetization is simultaneously being transferred to other nuclei (i.e. ^{13}C), enhancing their signals through the Nuclear Overhauser Effect (NOE).

Key Techniques for Solid State NMR:
1. Decoupling

Decoupling Experiments:

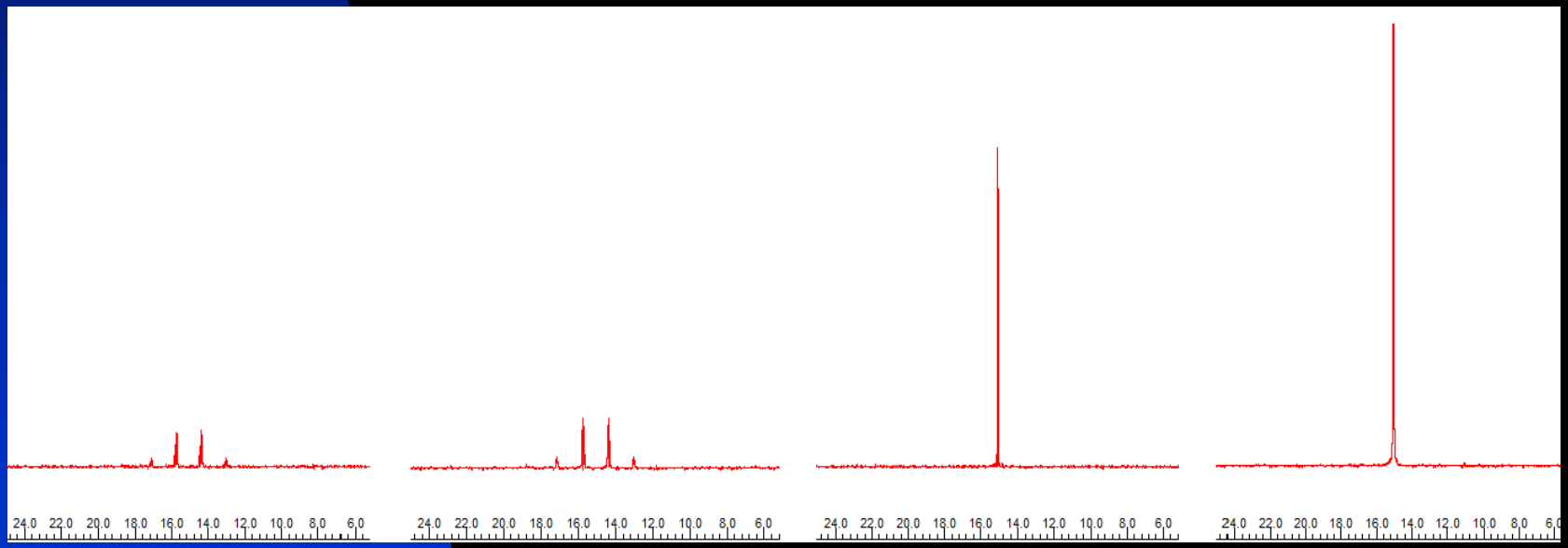


No Decoupling:
(no NOE, no simplification)

Gated Decoupling:
(NOE, no simplification)

Inverse Gated Decoupling
(simplification, no NOE)

Broadband Decoupling
(NOE + simplification)

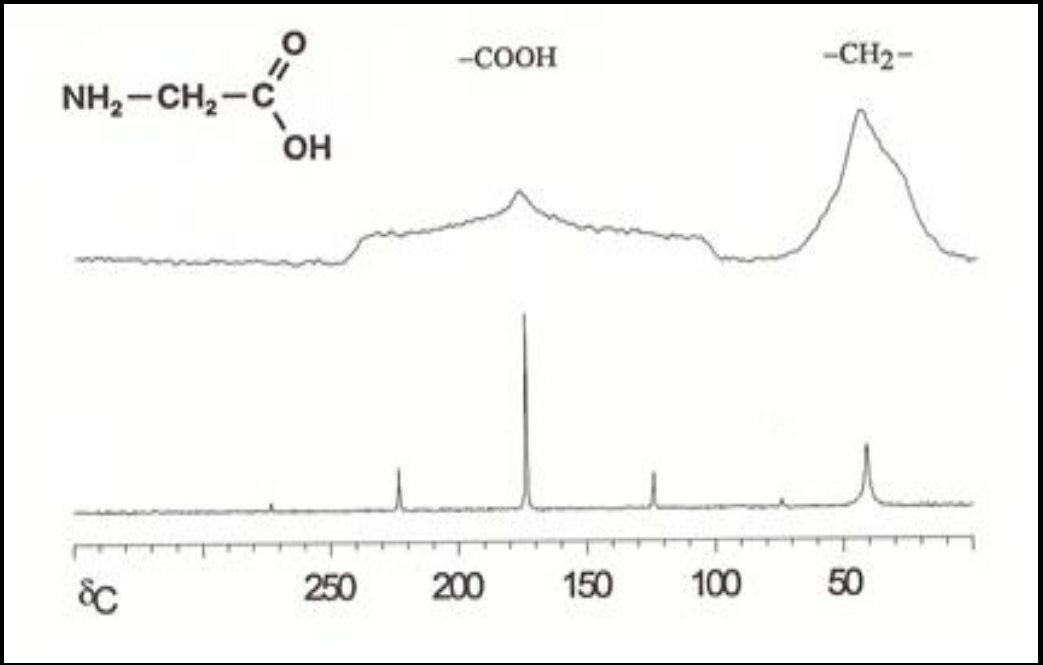


Key Techniques for Solid State NMR:
2. Magic Angle Spinning (MAS)

- MAS will remove dipolar and CSA broadening and collapse the powder pattern into sharp peaks.

- Static sample (Wideline NMR)

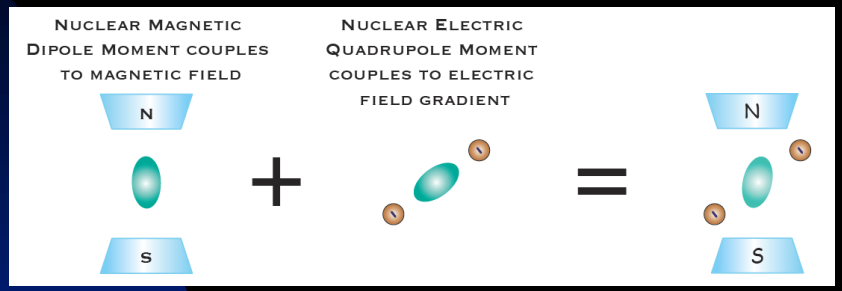
- 5 kHz MAS

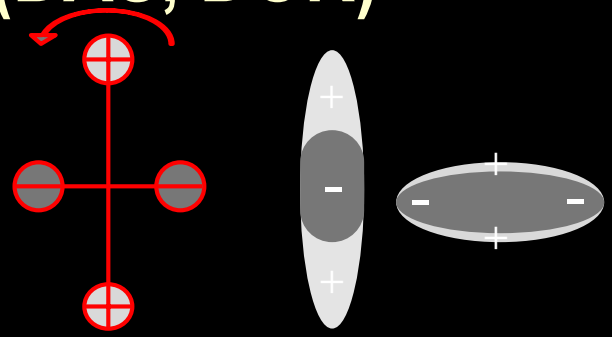


- The isotropic ^{13}C signals for glycine are:
  40 ppm for the methylene carbon and 173 ppm for the carbonyl carbon.
- The other peaks are MAS spinning sidebands.

Key Techniques for Solid State NMR:
3. Double Angle Spinning (DAS, DOR)

Quadrupole nuclei (I > ½)



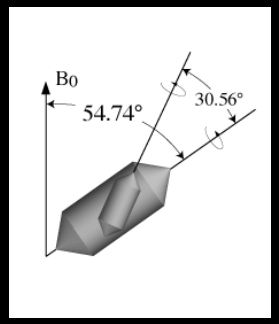


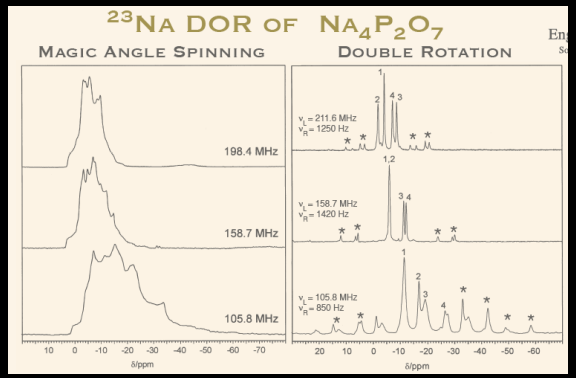
Electrical quadrupole momentum (eQ) couples with and a molecule's electric field (eq):

Quadrupole coupling constant $\chi = (eq_{zz}eQ)/\hbar$ (megahertz)

The quadrupole effect is too large (megahertz) to remove with MAS alone.

- Removing higher order effects requires spinning the sample around a second axis.
  DAS: switches the rotor angle during the experiment
  DOR: spins a rotor within a rotating capsule.

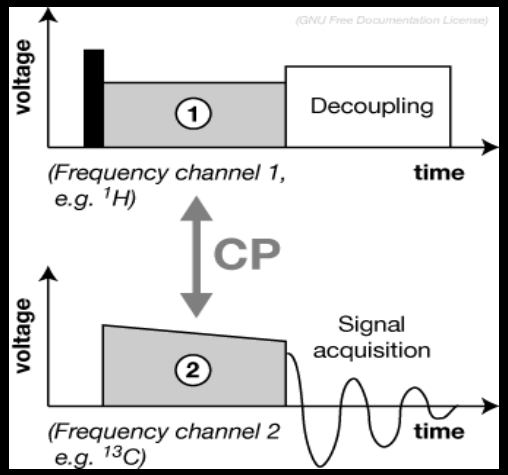




Key Techniques for Solid State NMR:
4. Cross Polarization

- CP is achieved by simultaneously irradiating two nuclei for a duration called contact time. Magnetization is being transferred from the abundant (^1H) to the rare spin (^{13}C).
- Max. signal enhancement: γ_H/γ_X

  H/C = 4 H/P = 3 H/Si = 5

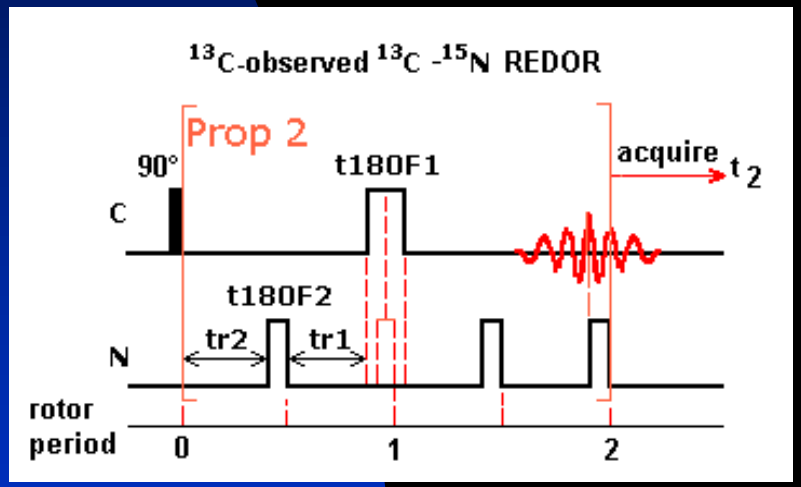


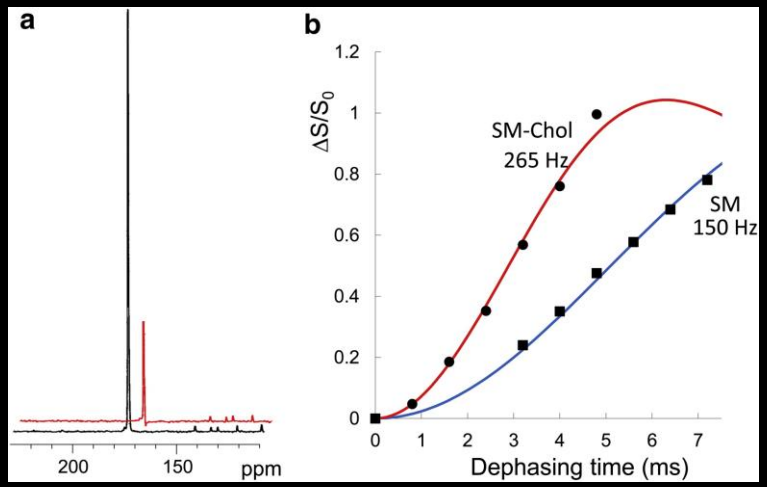
- CP is usually combined with MAS → "CP/MAS"
- CP is most efficient at the "Hartmann-Hahn-match": $\gamma_H B_H = \gamma_C B_C$
  B refers to the B_1 field of the RF pulse, not B_0.

- Surface Analysis:
  Surfaces often carry protons (-OH, -NH, water) and are favorable for CP.
  Nuclei in the interior of a crystal will not benefit from CP.
  Comparison of CP with non-CP spectra can identify location.

Key Techniques for Solid State NMR:
5. Recoupling

- While most couplings are removed by decoupling and MAS, dipolar couplings can be useful, as their size depends on the distance between nuclei.
- Recoupling experiments, i.e. REDOR, selectively re-introduce dipolar couplings between individual nuclei by synchronizing refocusing pulses with the MAS rotor speed.





- The size of the coupling constant determines the speed by which a magnetization of a nucleus is dephased.
  Large coupling → close proximity between nuclei.

Topics:

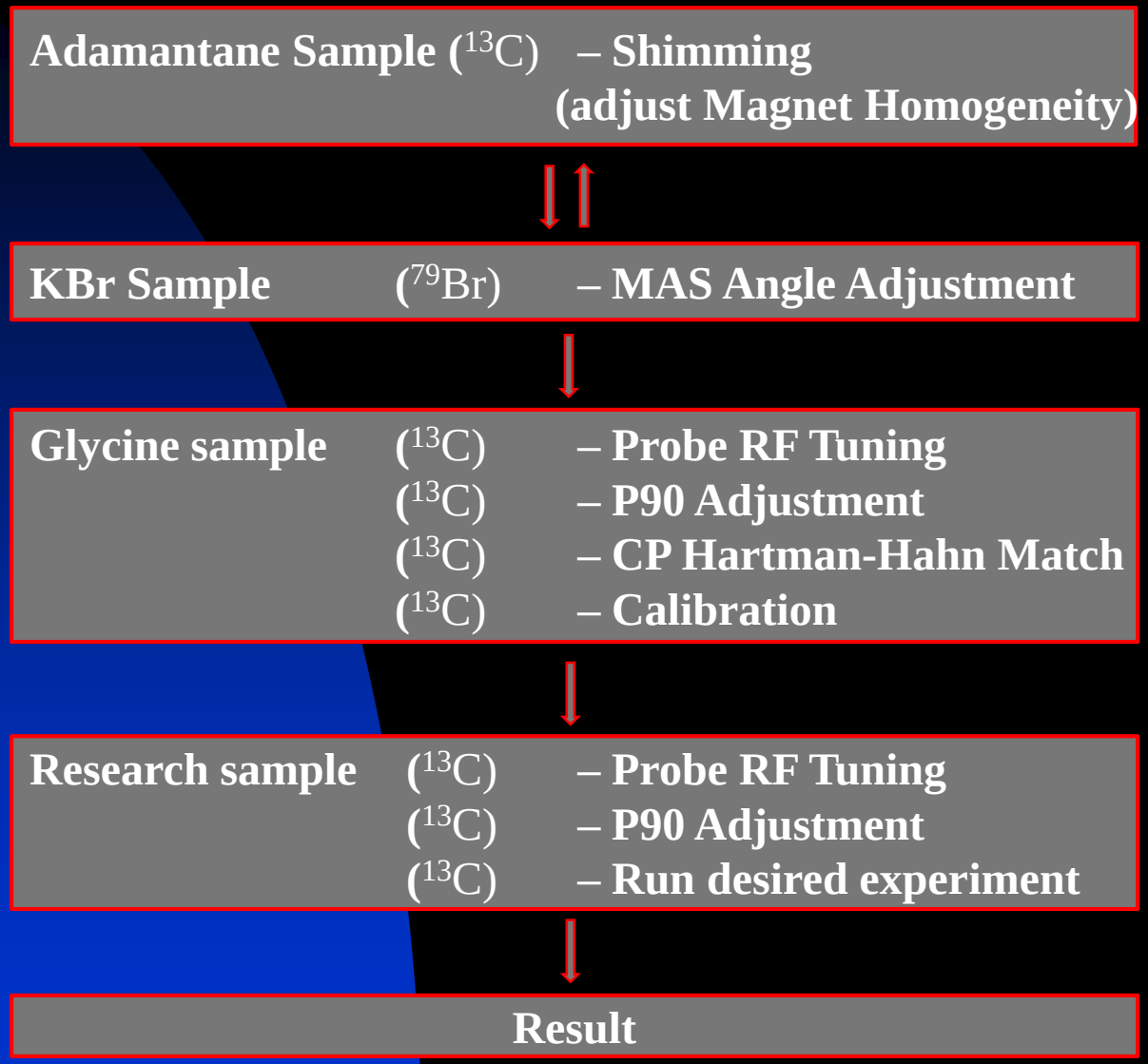
- **Part I – Introduction**
  - **History of NMR**
  - **NMR Hardware**
- Part II – NMR Theory
  - Nuclei – Spin – Magnetic Moments
  - Shielding – Chemical Shifts
  - Coupling – Molecular Structure
  - Relaxation – Linewidth
- Part III – NMR Experiments
  - Solution vs. Solids State NMR
  - Techniques for optimizing Solid State NMR
  - Research Examples

Solid State NMR

Which nuclear properties affect Solid State NMR experiments:

Problem	Symptom	Solution
Low Natural Abundance	Weak Signals	Cross-Polarization
Chemical Shift Anisotropy	Broad Signals	MAS
Dipolar Coupling (homonuclear)	Broad Signals	MAS
Dipolar Coupling (heteronuclear)	Broad Signals	Decoupling (usually ^{1}H)
Quadrupole Nucleus	Broad Signals Satellite Transitions	MAS, DOR MQ-MAS
Paramagnetic Nucleus	Extremely Broad Signals	Record Spectrum in Segments and add together

Solid State NMR Experiments - Flowchart



These steps need only be performed occasionally.

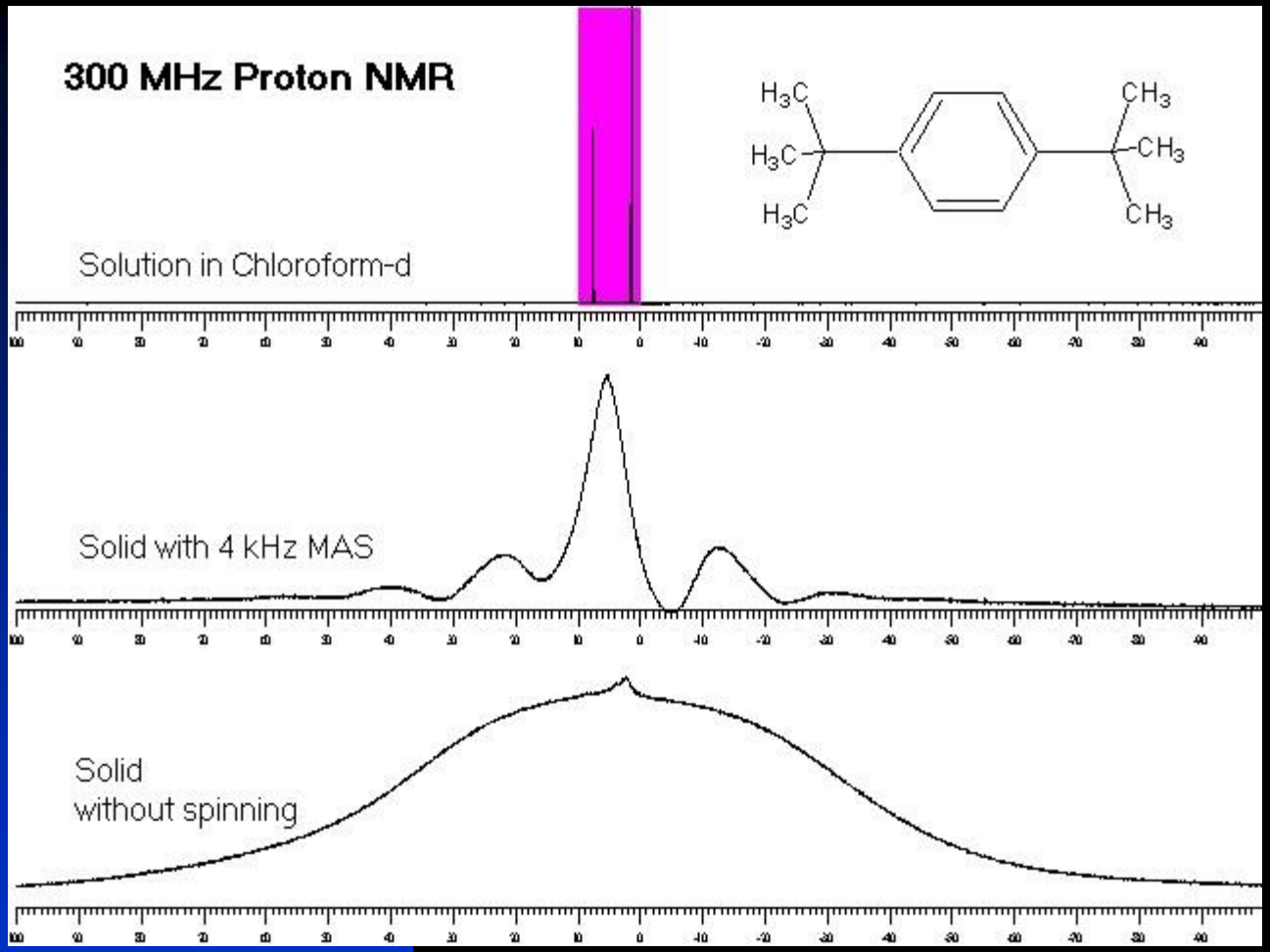
These steps need to be performed for any nucleus to be investigated.

Sample preparation:

- Obviously, no solvents must be used.
- Grind samples into a fine powder.
- Cut films into strips or disks for bundling or stacking.
- Load and compact the rotors tightly and uniformly.

- Watch MAS Sample Preparation Video https://www.youtube.com/watch?v=bNFJj2g0UjI

Solution vs. Solid State NMR

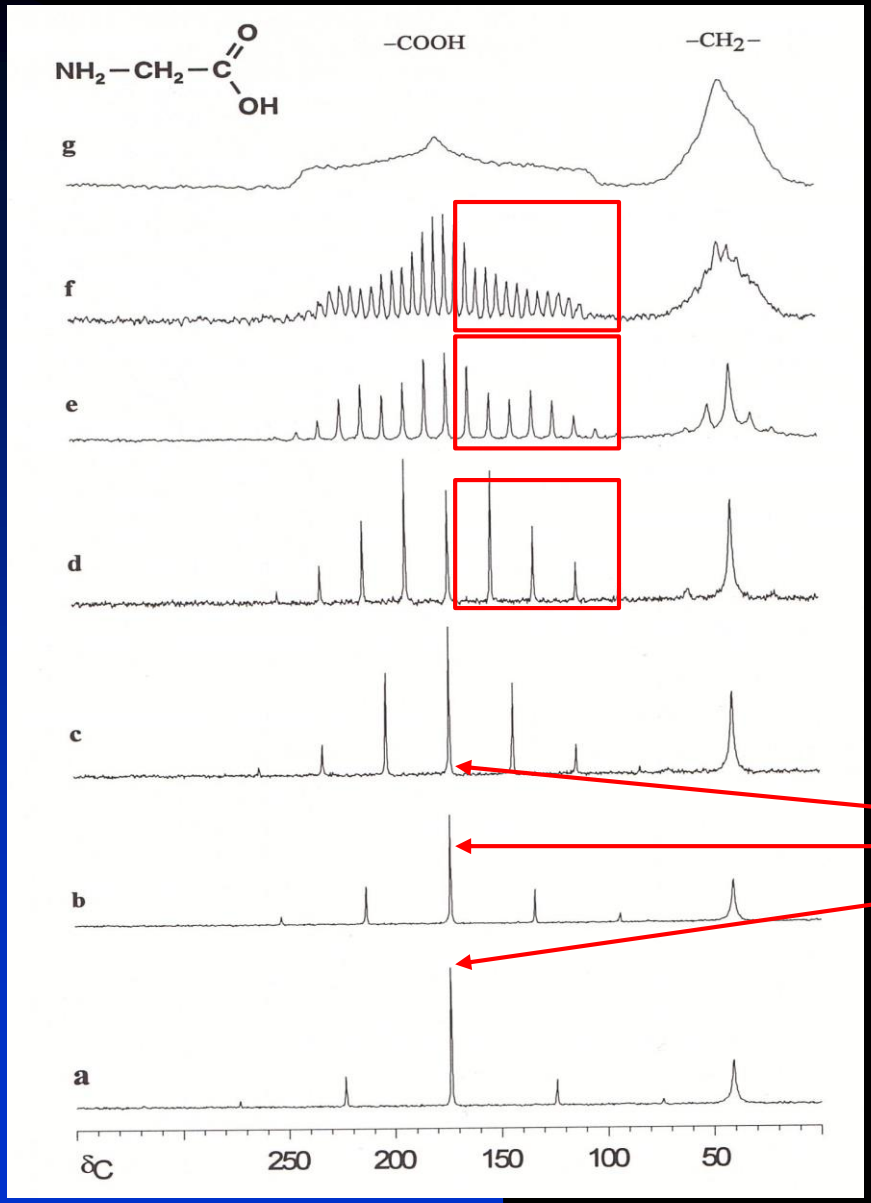


Solution NMR:
Well-resolved spectrum shows individual signals for aromatic and methyl protons.

Solid State NMR:
Severe broadening due to CSA and dipolar couplings can be partially alleviated by "Magic Angle" Spinning.

Slow MAS speeds lead to spinning sidebands occurring at periodic intervals.
Ideally, MAS speeds should be faster than the width of the non-spinning signal. (unrealistic)
Special probes allow MAS speeds of 100 kHz, but 10 kHz is more common.

Optimizing the MAS Speed



Carbon-13 - Glycine

Static powder pattern, no MAS

MAS = 500 Hz

MAS = 1 kHz

MAS = 2 kHz

MAS = 3 kHz

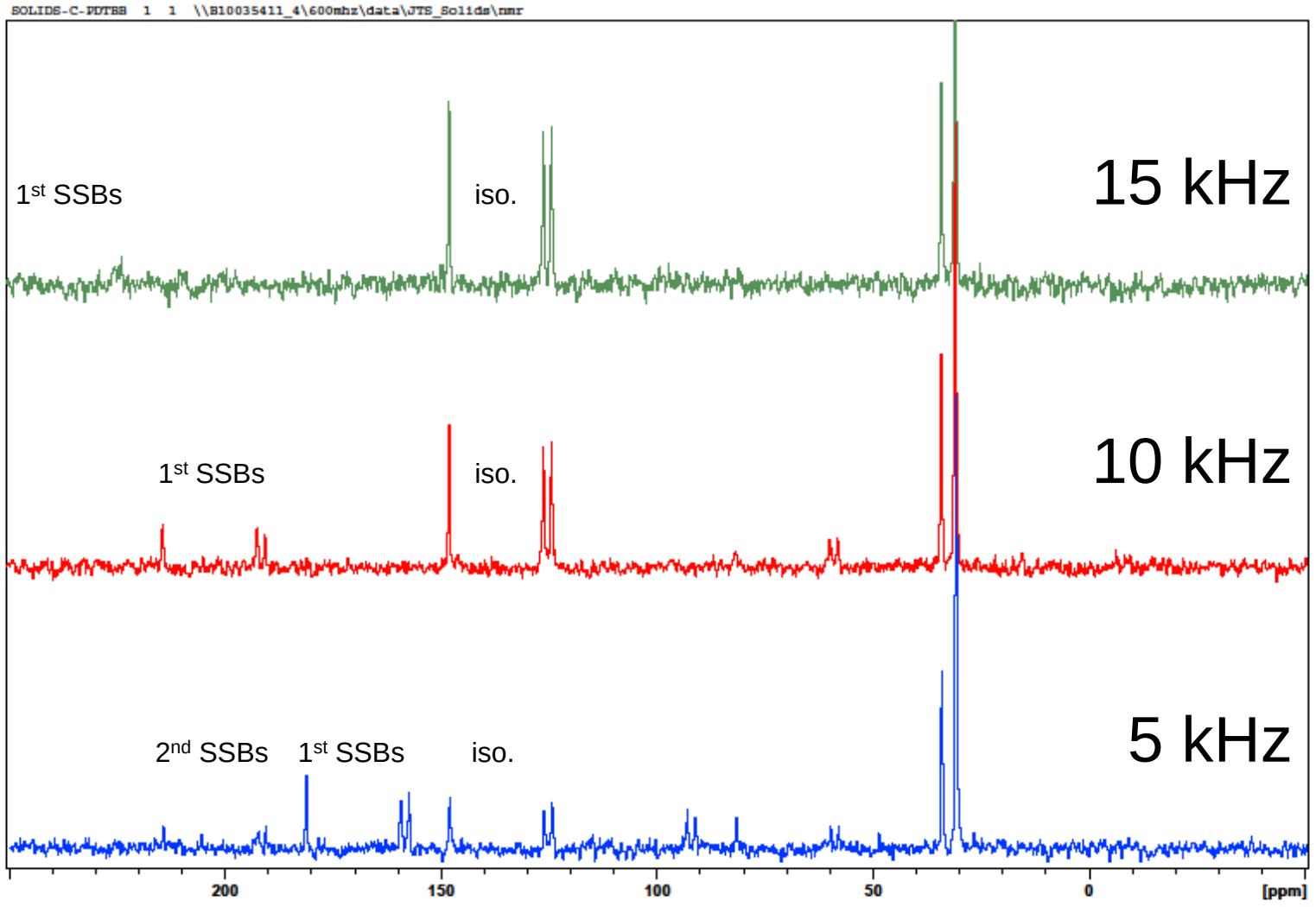
MAS = 4 kHz

MAS = 5 kHz

MAS generates patterns with individual sidebands separated by the MAS speed.

The position of the isotropic peak remains unaffected by the MAS speed. (Isotropic chemical shift)

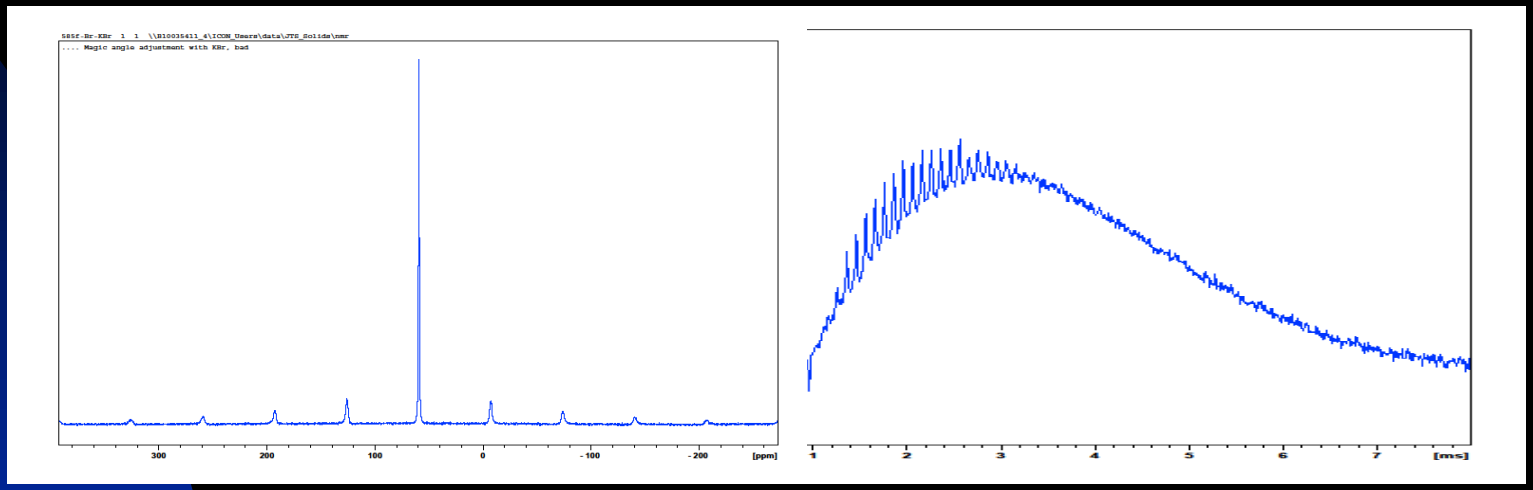
Optimizing the MAS Speed



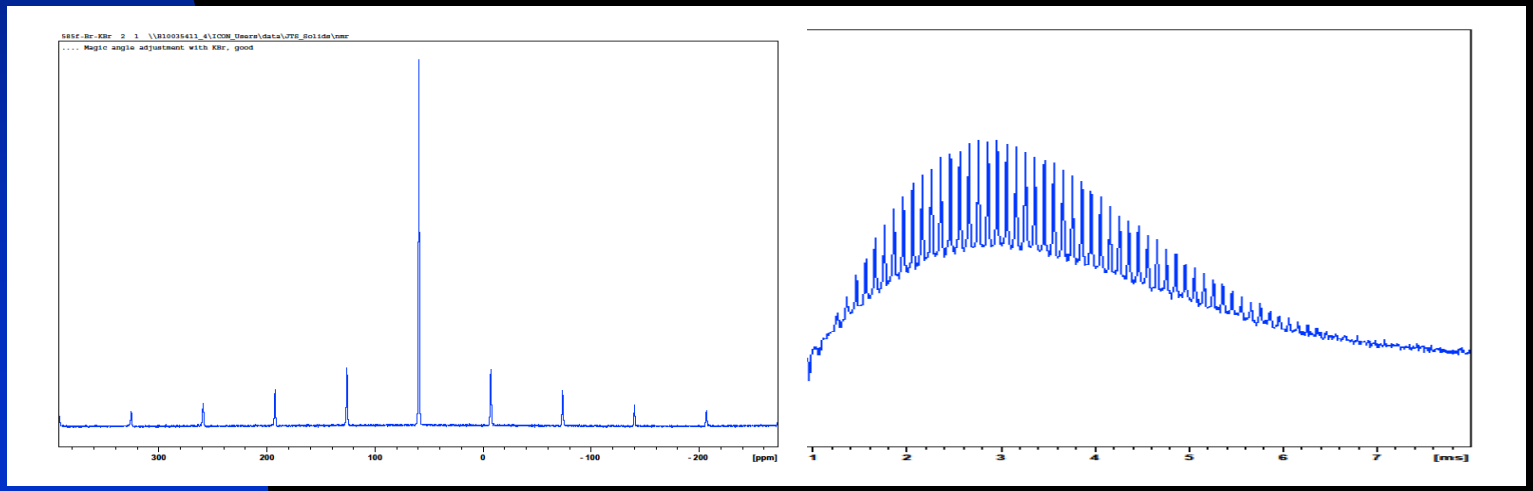
Optimizing the MAS Angle

Br-79 NMR (quadrupole nucleus), Sample: KBr, MAS=10 kHz

54.0°

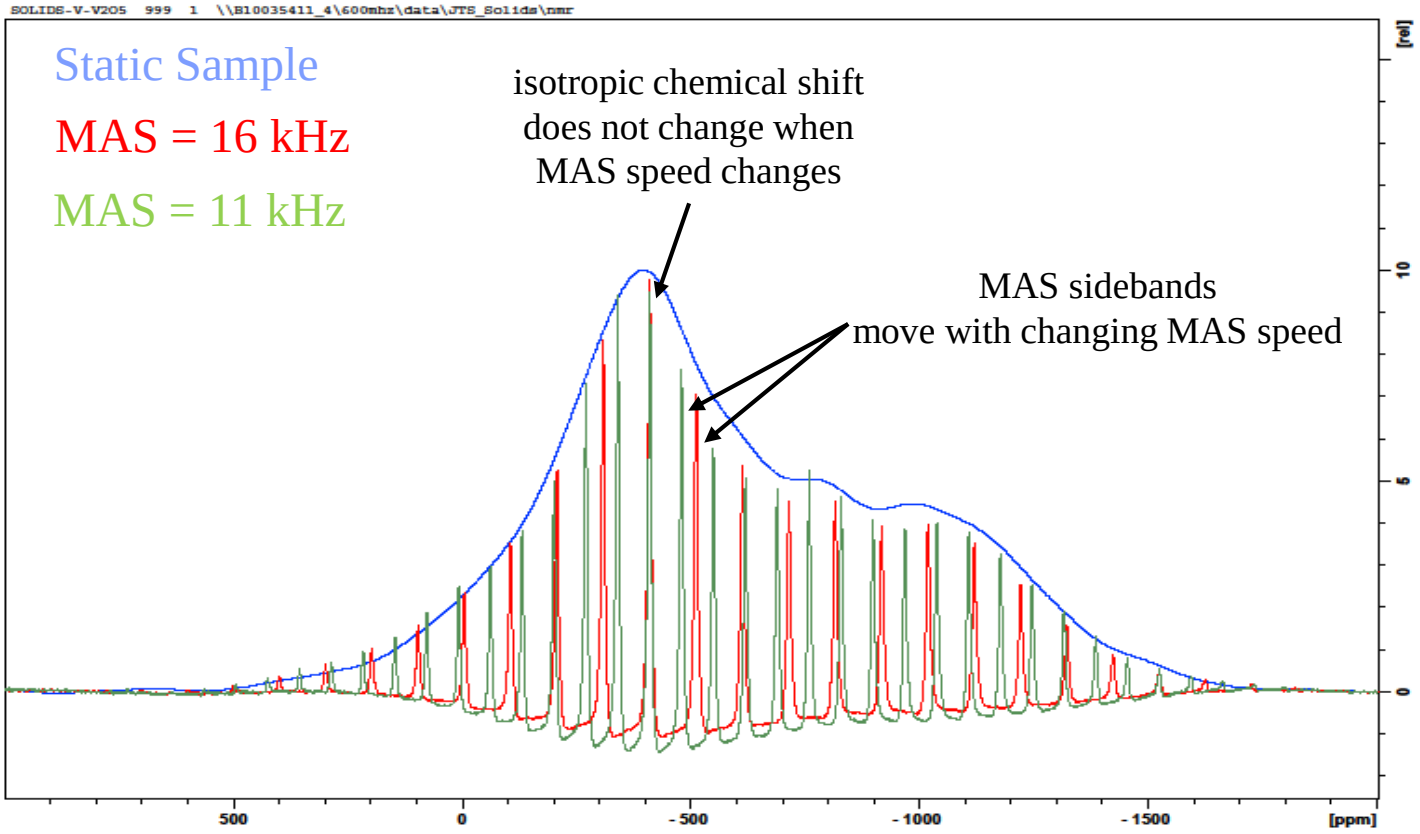


54.7°



Quadrupole Nuclei (I > 1/2)

V-51 (I=7/2), 99.7 % nat. abundance: V_2O_5

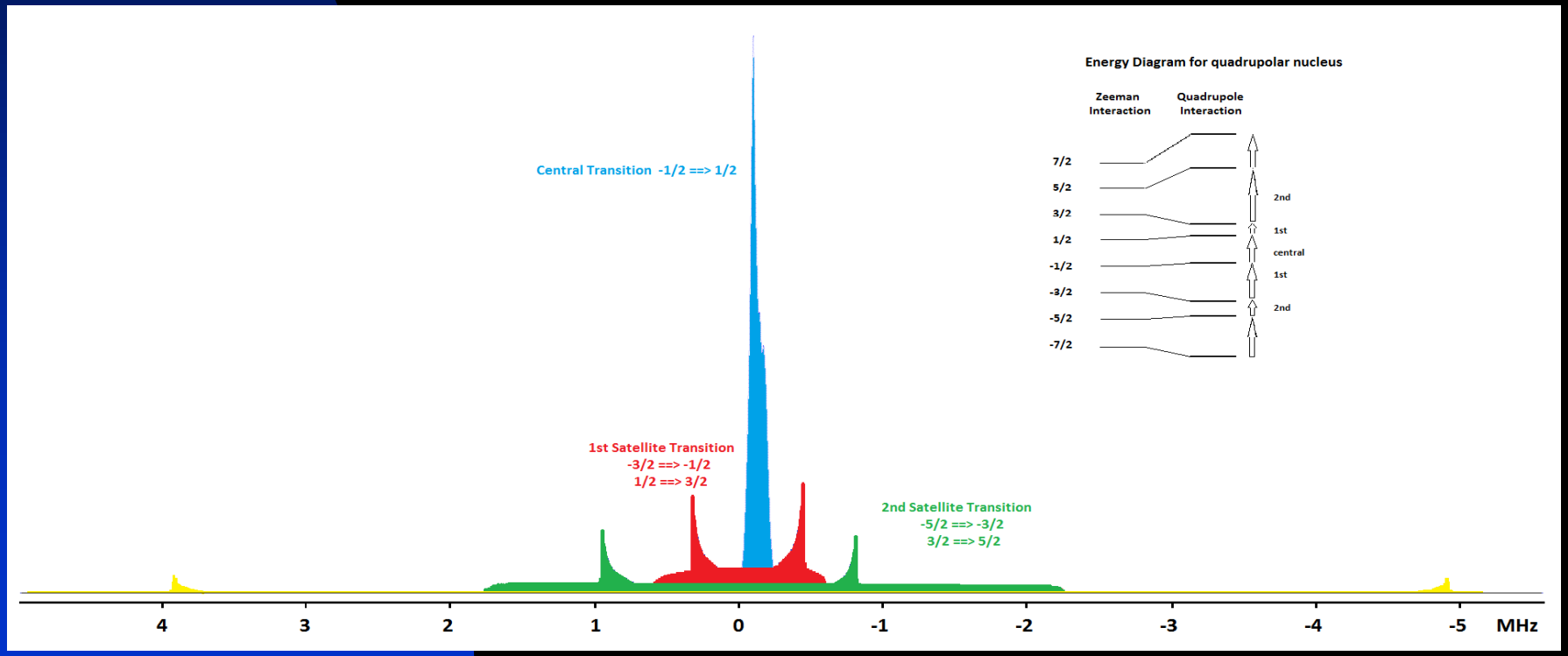


- This is just the central -1/2 ➔ 1/2 transition …

Quadrupole Nuclei (I > 1/2)

V-51 (I=7/2), 99.7 % nat. abundance: V_2O_5

- … transitions between higher spin states can also be detected. They are much weaker in intensity and can span several Megahertz.
- Quadrupolar and dipolar couplings can significantly broaden

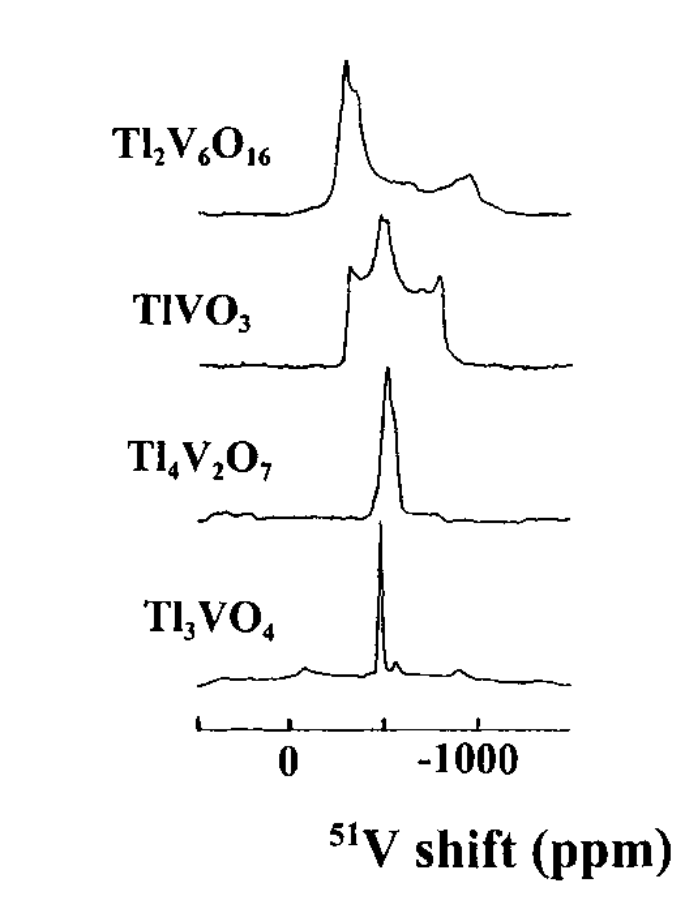


Quadrupole Nuclei (I > 1/2)

V-51 (I=7/2), 99.7 % nat. abundance:

- Shape of the central transition reveals structural details about the geometric surrounding of the vanadium atom:

- distorted octahedral
- octahedral
- distorted tetrahedral
- tetrahedral



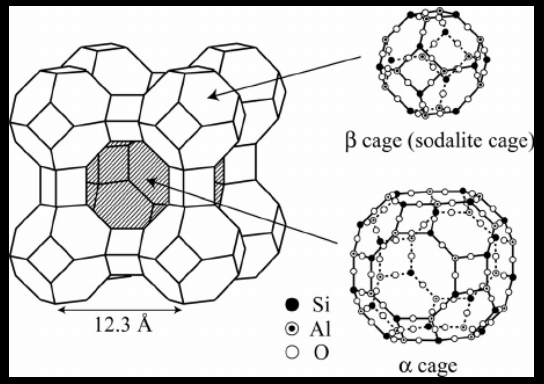
Silicon-29 NMR

Zeolites:

Five Silicon environments – five peaks:

Si4Al … Si3Al ... Si2Al … Si1Al ... Si0Al

Al	Al	Al	Al	Si
O	O	O	O	O
Al O Si O Al	Al O Si O Si	Al O Si O Si	Si O Si O Si	Si O Si O Si
O	O	O	O	O
Al	Al	Si	Si	Si



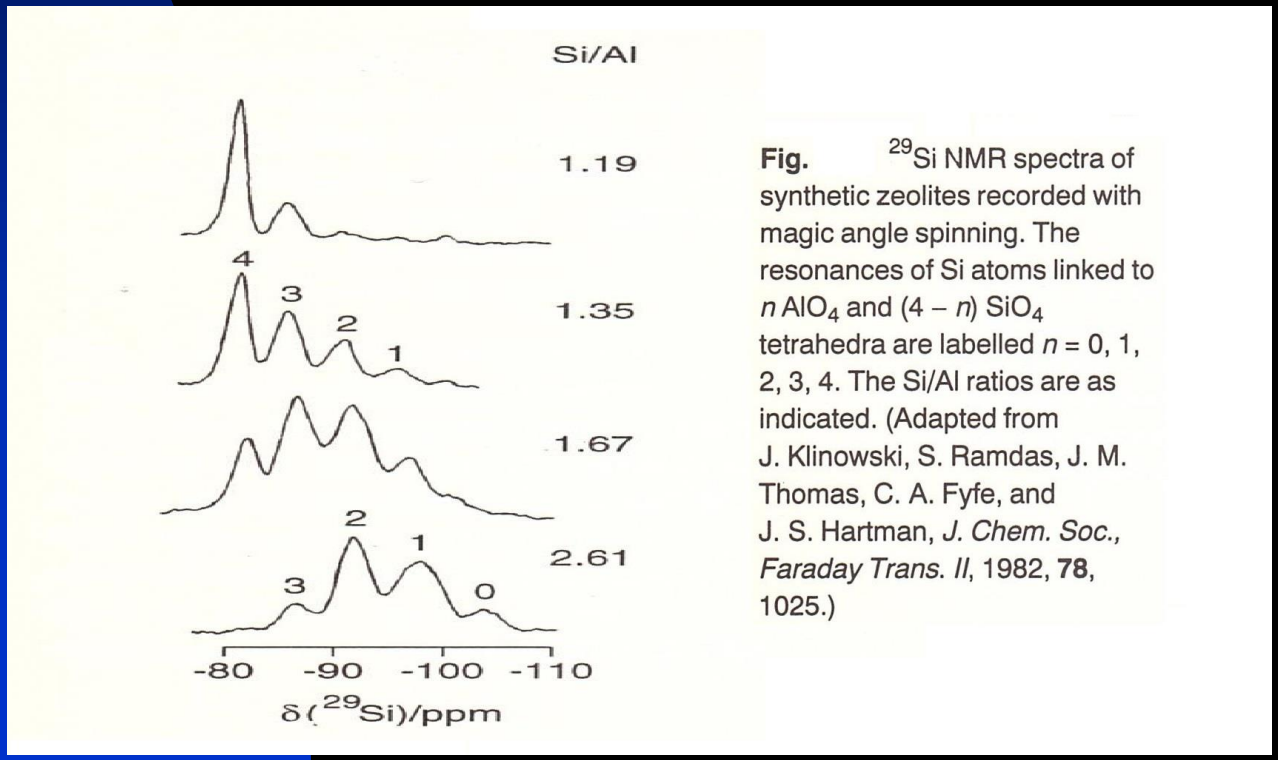


Fig. ^{29}Si NMR spectra of synthetic zeolites recorded with magic angle spinning. The resonances of Si atoms linked to *n* AlO_4 and (4 – *n*) SiO_4 tetrahedra are labelled *n* = 0, 1, 2, 3, 4. The Si/Al ratios are as indicated. (Adapted from J. Klinowski, S. Ramdas, J. M. Thomas, C. A. Fyfe, and J. S. Hartman, *J. Chem. Soc., Faraday Trans. II*, 1982, **78**, 1025.)

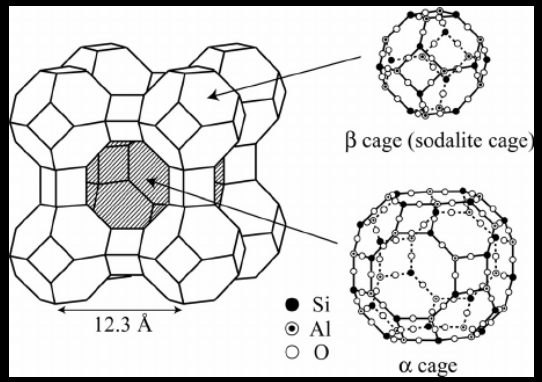
Silicon-29 NMR

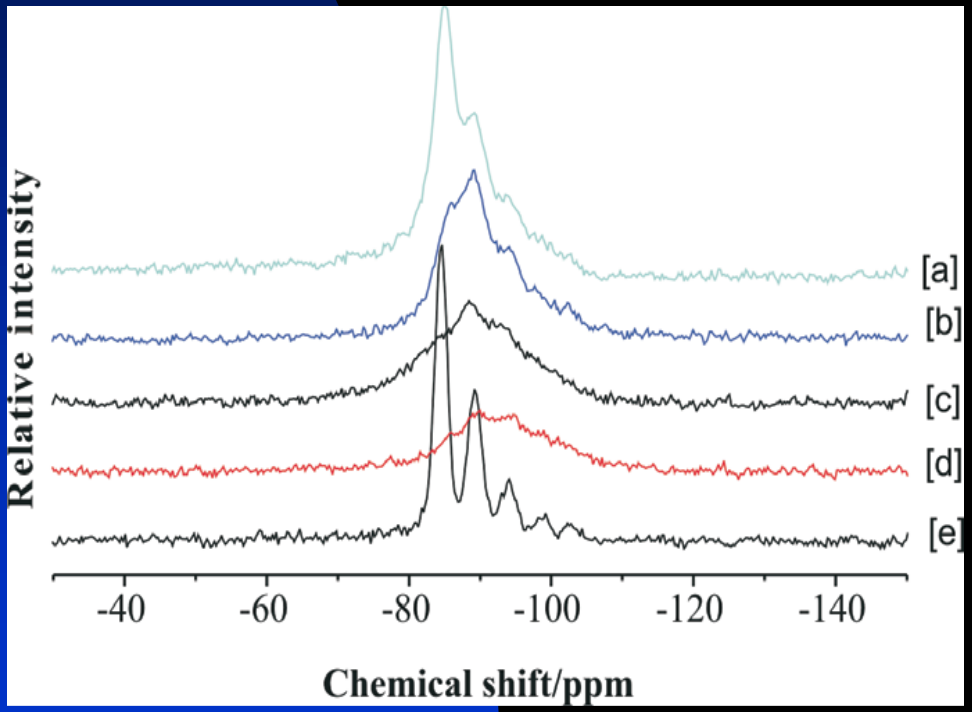
Zeolite: NaX

Addition of paramagnetic Cu^{2+} cations broadens all silicon signals.

Ammonia can remove copper ions through complexation.

Cu^{2+} appears to bind tighter to Al-rich sites.





CuX + max. NH3

CuX + 3 NH3

CuX + 1 NH3

CuX

NaX

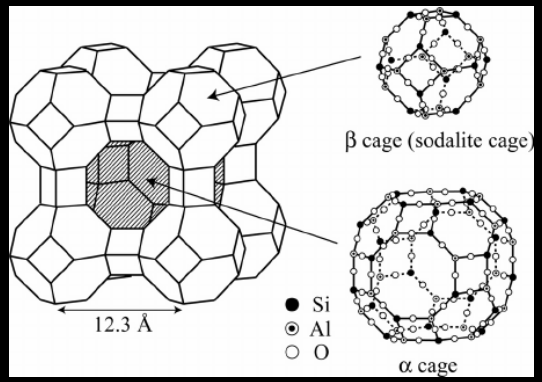
C. C. Kowenje, D. Doetschman, J. Schulte, C. Kanyi, J. DeCoste, S. Yang, B. Jones, *South African Journal of Chemistry* **63**, 6-11 (2010), "Effects of Copper Exchange Levels on Complexation of Ammonia in Cu(II)-exchanged X Zeolite."

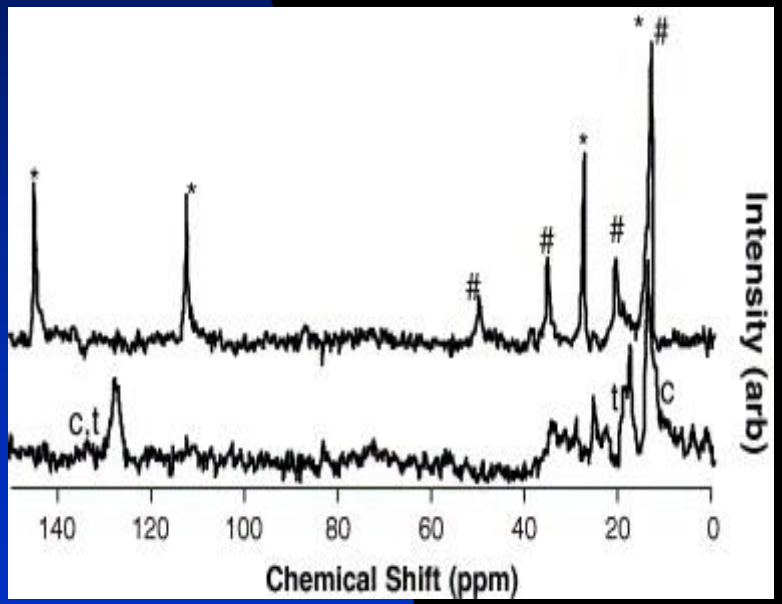
Carbon-13 NMR

Reactions in Zeolites

NaX has high affinity to volatile functionalized organic molecules

(i.e.: used to capture and neutralize chemical warfare agents)





Reaction of 1-chlorobutane:

in NaX → 1-butene

in Na^0/NaX → cis / trans 2-butene

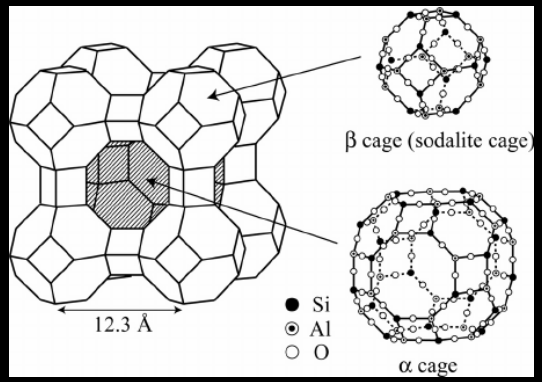
C. Kanyi, D. Doetschman, J. Schulte, K. Yan, R. Wilson, B. Jones, C. Kowenje and S. Yang, *Microporous and Mesoporous Materials* **92**, 292-299 (2006), "Linear, primary monohaloalkane chemistry in NaX and NaY faujasite zeolites with and without Na0-treatment: Zeolites as nucleophilic reagents II."

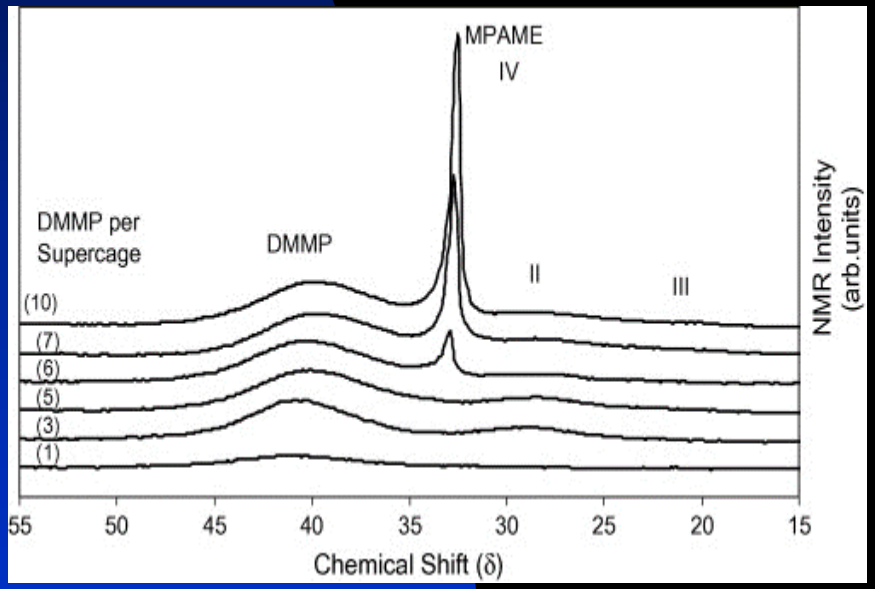
Phosphorus-31 NMR

Reactions in Zeolites:

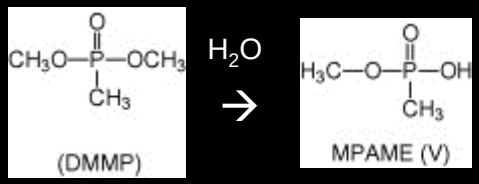
NaX has high affinity to volatile functionalized organic molecules

(i.e.: used to capture and neutralize chemical warfare agents)





Dimethyl Methylphosphate undergoing hydrolysis in NaX.

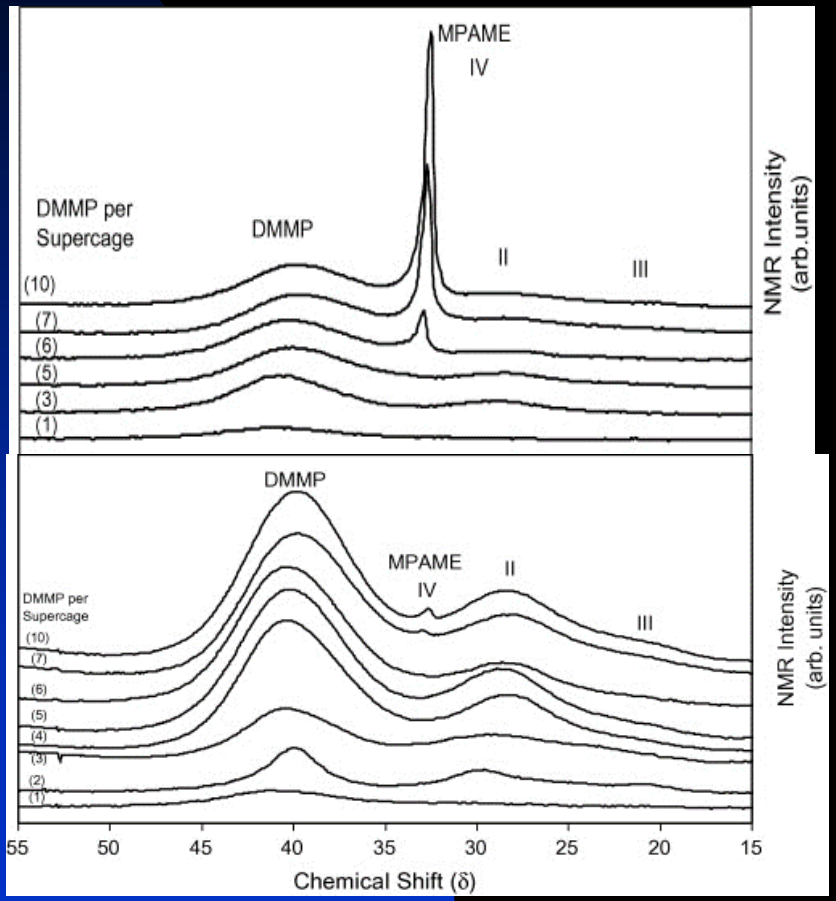


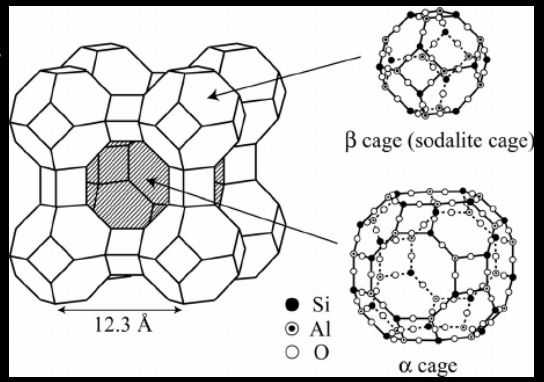
J. Sambur, D. Doetschman, S. Yang, J. Schulte, B. Jones, J. DeCoste, *Microporous and Mesoporous Materials* **112**, 116-124 (2008), "Multiple effects of the presence of water on the nucleophilic substitution reactions of NaX Faujasite zeolite with dimethyl methylphosphonate (DMMP)."

Phosphorus-31 NMR

Surface Analysis: CP vs. non-CP spectra

(Molecules have to be immobilized to benefit from CP.)





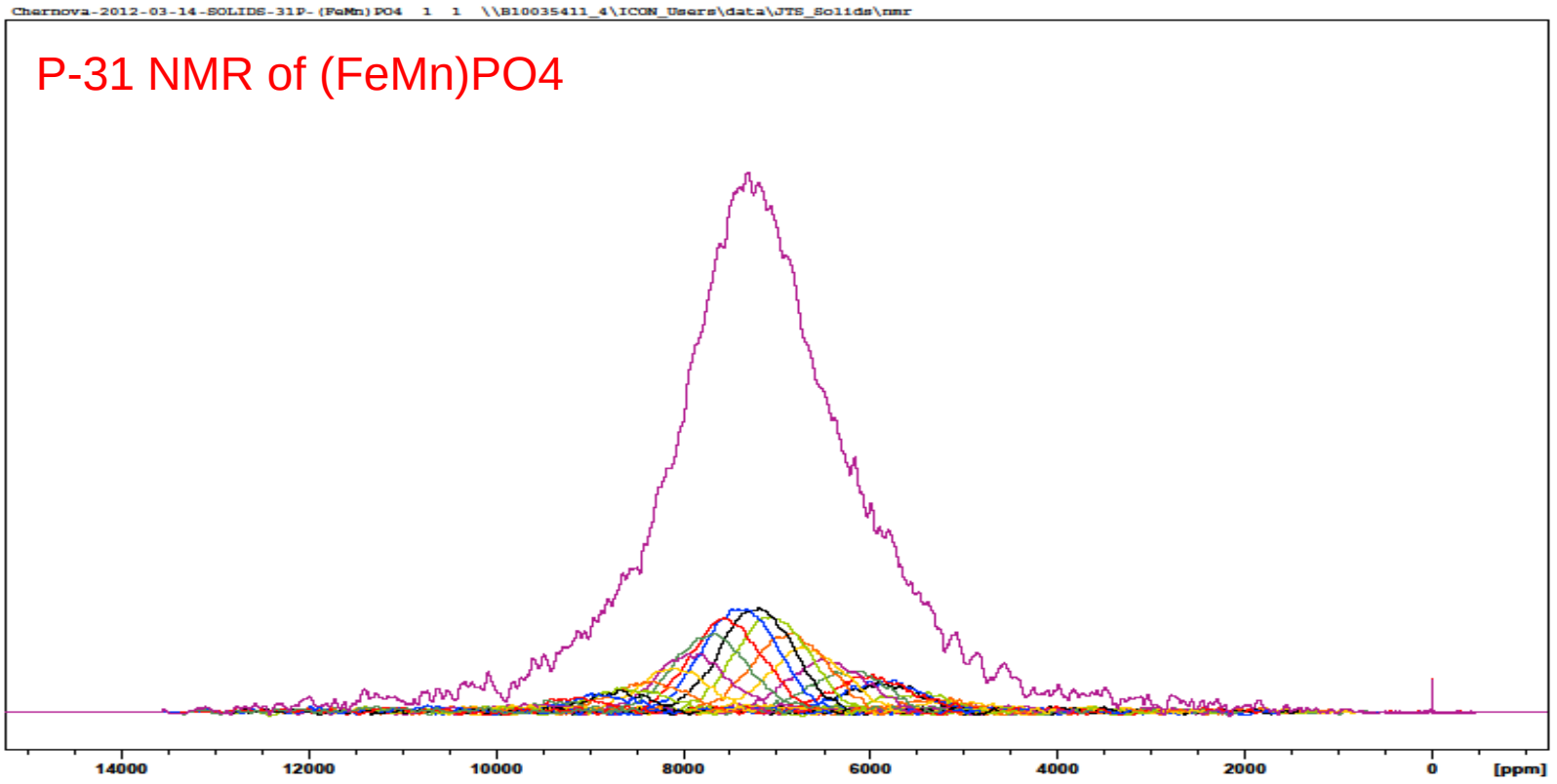
Top: without CP

Bottom: with CP

DMMP is bound to the NaX surface.
MPAME is mobile.

J. Sambur, D. Doetschman, S. Yang, J. Schulte, B. Jones, J. DeCoste, *Microporous and Mesoporous Materials* **112**, 116-124 (2008),
"Multiple effects of the presence of water on the nucleophilic substitution reactions of NaX Faujasite zeolite with dimethyl methylphosphonate (DMMP)."

Paramagnetic compounds



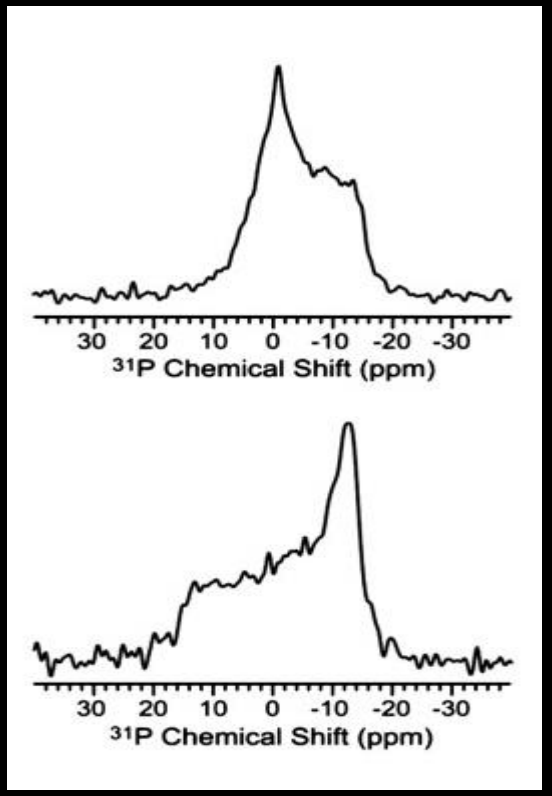
- The “Knight Shift” can shift the signal by several 1000 ppm.
- Signals can be too broad to record in a single experiment.
  ➔ Combine multiple spectra recorded with shifted frequency offsets to cover the entire spectrum.

Biomolecules

Some DNAs, RNAs, peptides, and proteins are insoluble.
Others may be soluble, but we want to study their interactions with insoluble constructs, i.e. cell membranes.

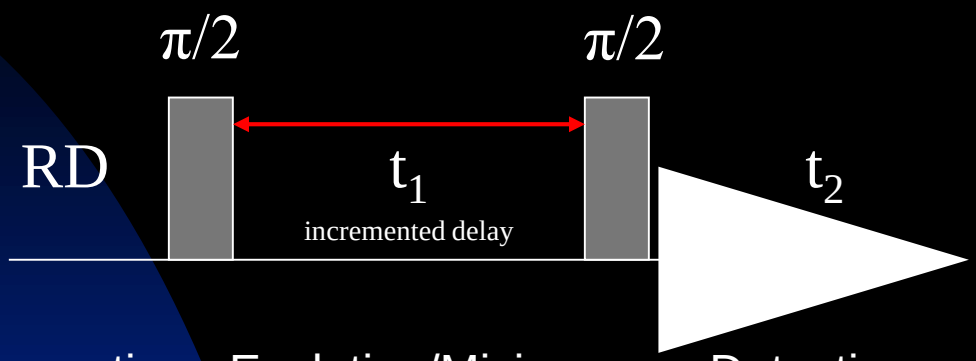
External addition of peptide to lipid bilayer:
Narrow CSA pattern

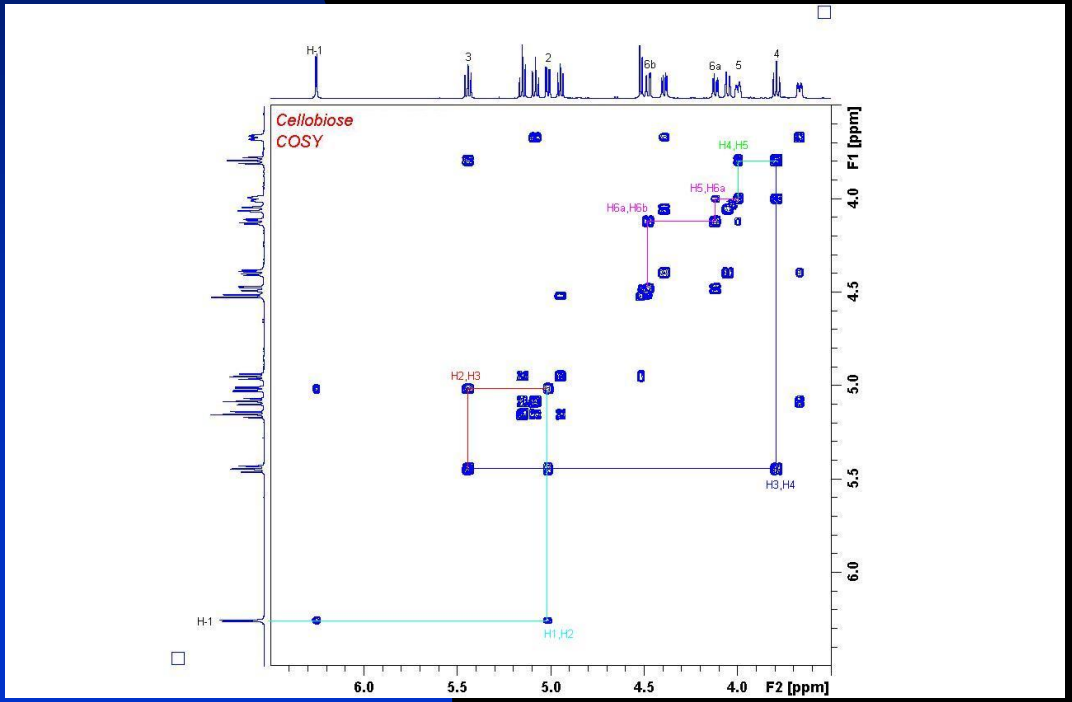
Insertion of peptide in lipid bilayer:
Broad CSA pattern
→ disruption of lipid membranes



W. Qiang, W. Yau, J. Schulte, *Biochemica et Biophysica Acta - Biomembranes* **1848**, 266-276 (2014),
"Fibrillation of beta-amyloid peptides in the presence of phospholipid bilayers and the consequent membrane disruption."

2-Dimensional Experiments





Concept:

A delay in the pulse sequence is systematically incremented to create a second time dependence. Fourier Transform in 2 dimensions creates 2 frequency axes.

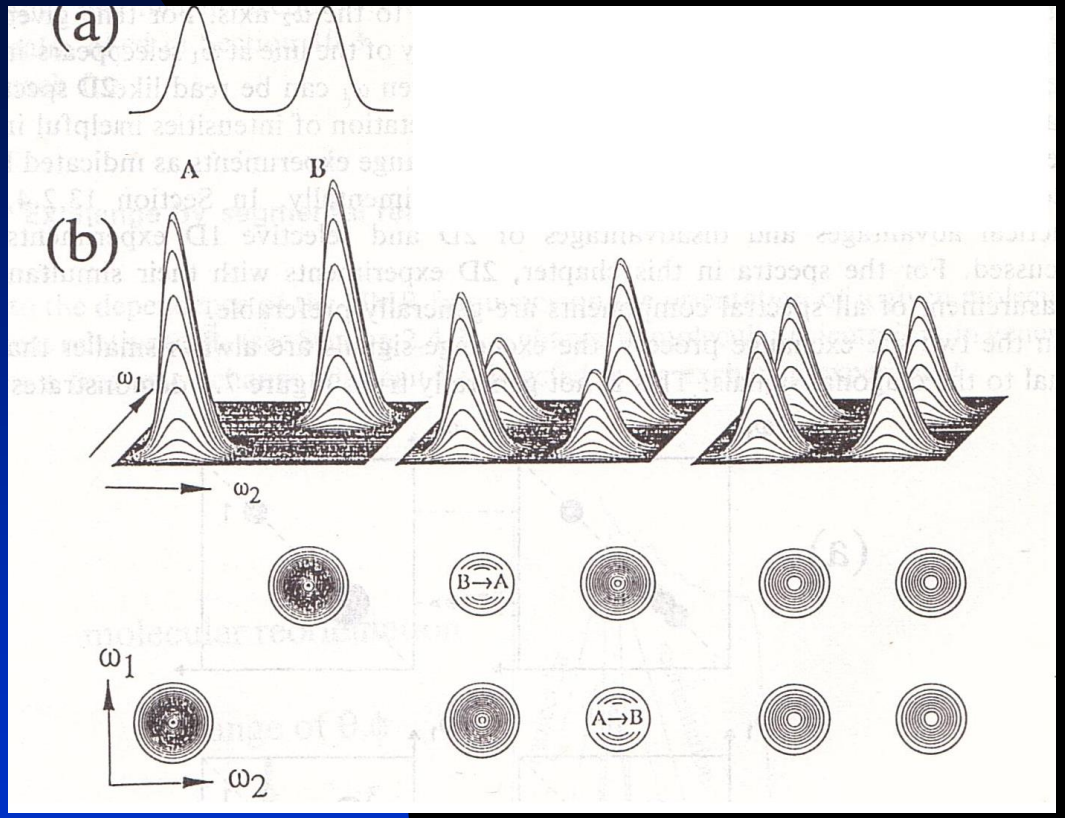
Additional pulses and/delays can be used to probe specific structural properties and interactions.

The resulting 2D spectrum shows correlations between different atoms based on one or more structural parameters, i.e.:

- Couplings
- Proximity
- Exchange
- Diffusion

Polymer Dynamics

Molecule exists in two orientations A and B.
Is there exchange between them?



2D Exchange Spectroscopy allows distinction between:

-motion of the molecule

-internal motion of a fragment

-no motion

no exchange slow exchange fast exchange