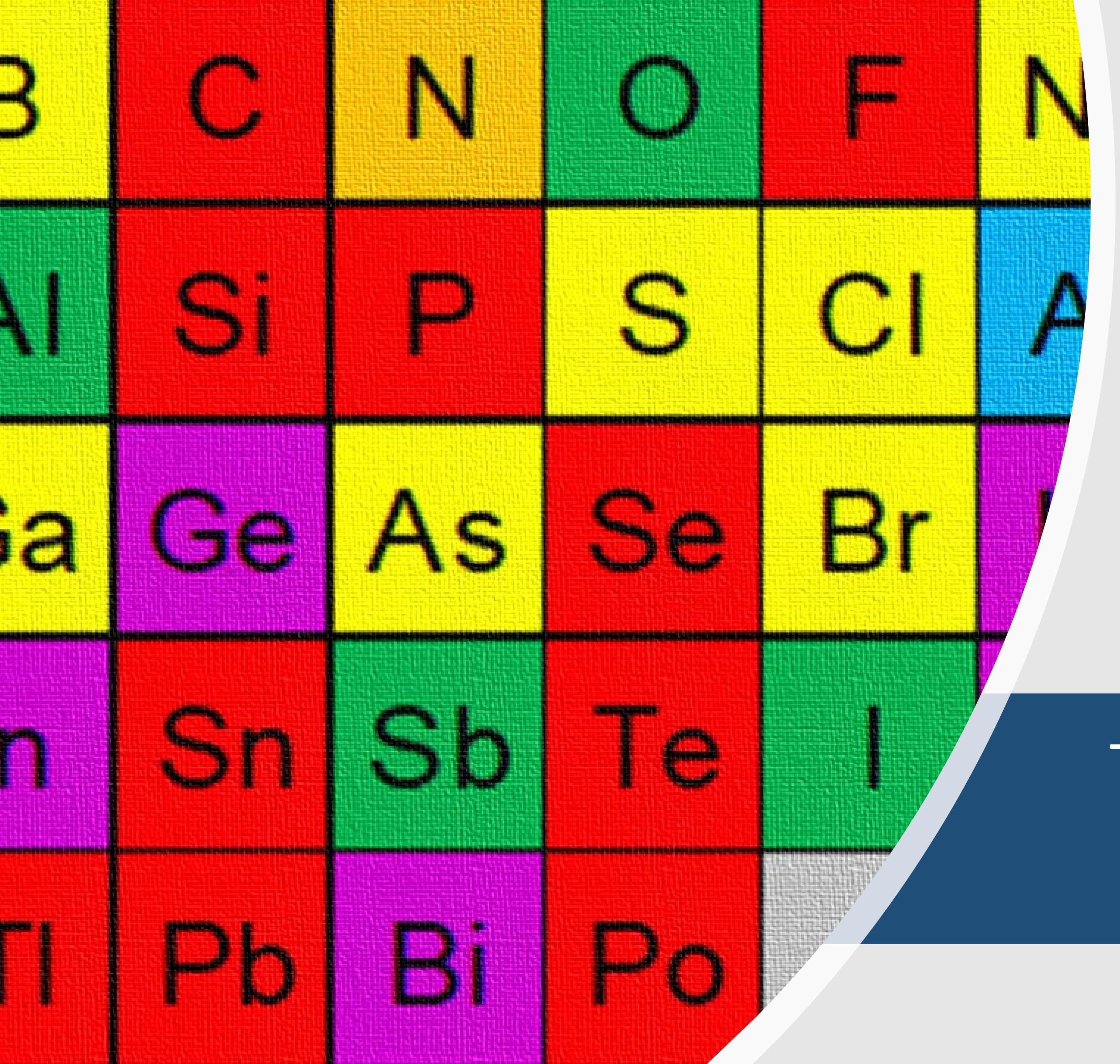

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School of Chemistry

SNUG PG NMR course, Edinburgh

2nd December 2024

There's more to NMR than just protons

Dr Andrew Hall

NMR periodic table

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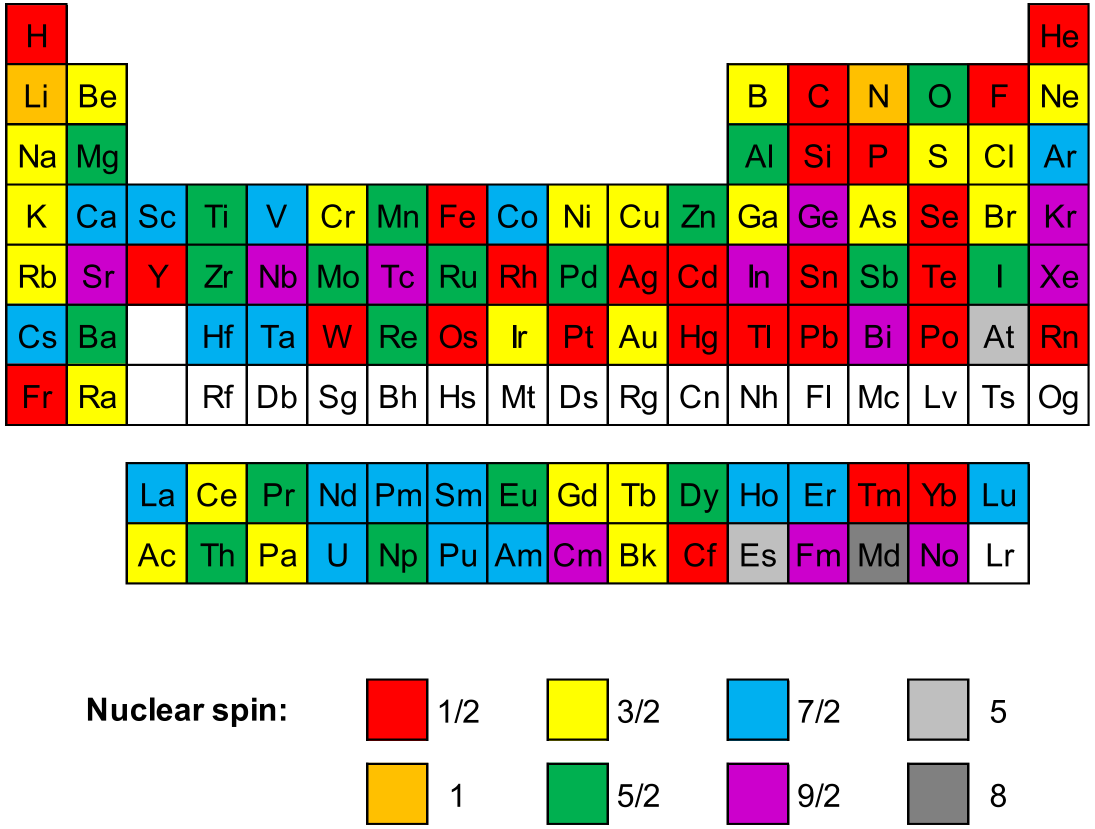

Spin

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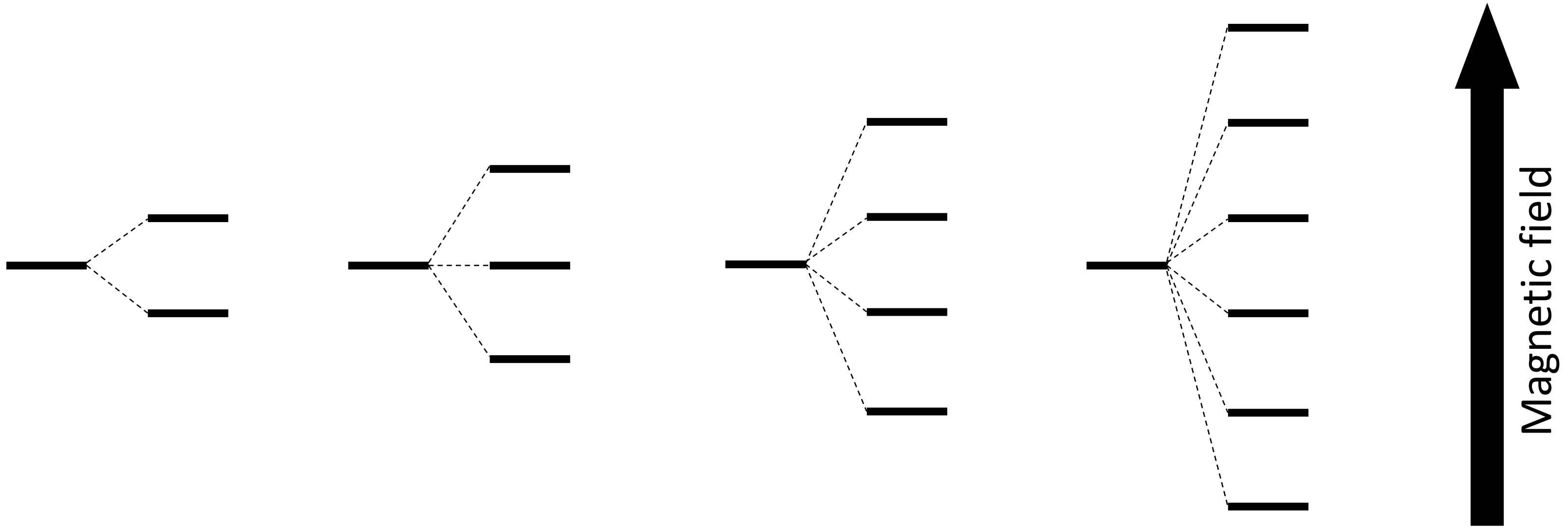
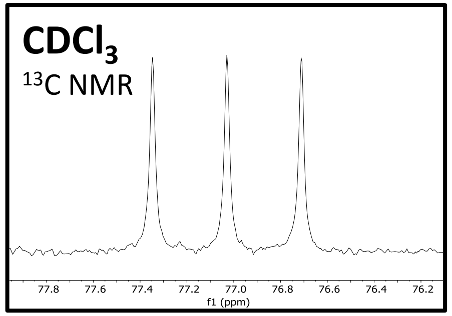
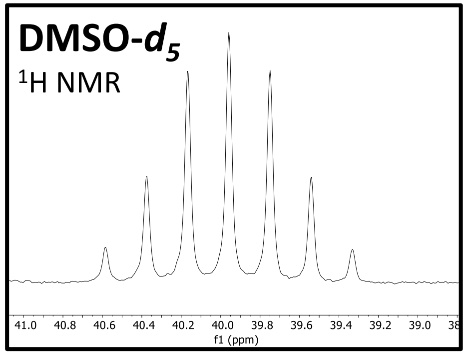
Number of energy levels:

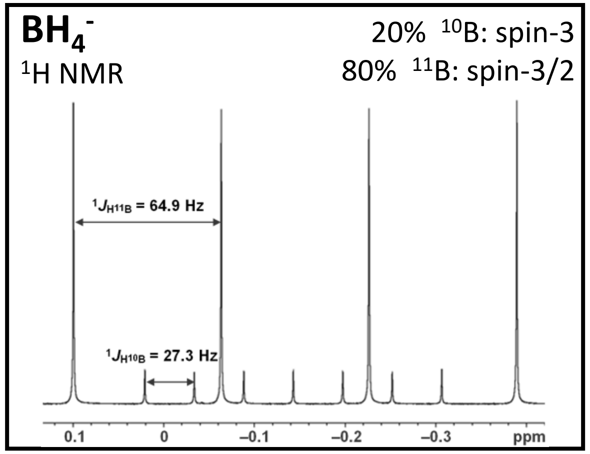
$$2i + 1$$



Spin-1/2	Spin-1	Spin-3/2	Spin-5/2
^{1}H, ^{13}C, ^{19}F, ^{31}P…	^{2}H, ^{6}Li, ^{14}N	^{7}Li, ^{11}B, ^{23}Na ^{35}Cl…	^{17}O, ^{27}Al, ^{23}Na ^{35}Cl…







Quadrupolar nuclei

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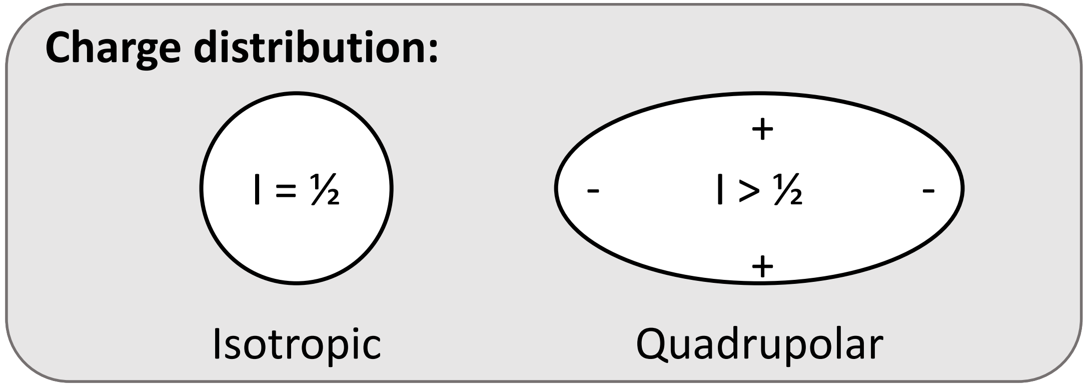
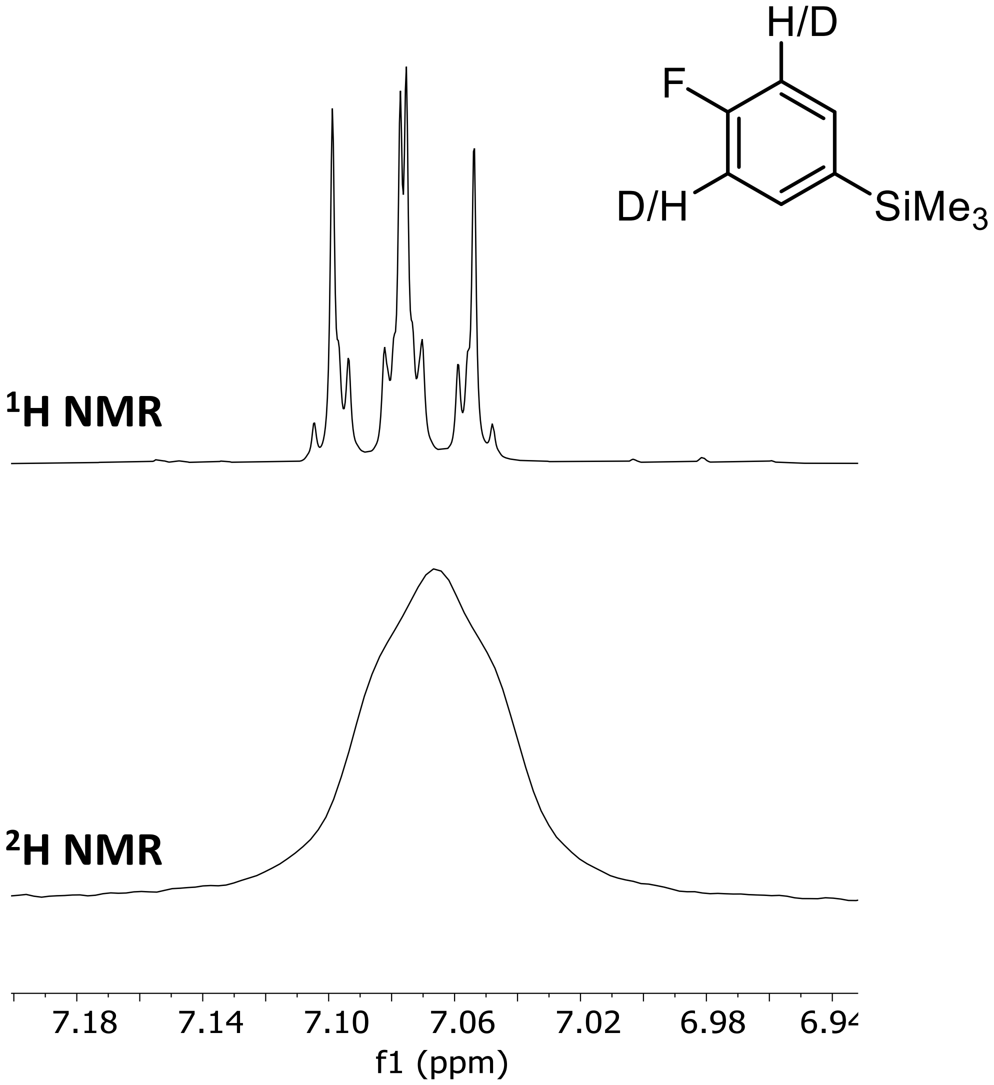
Nuclei with a spin quantum number larger than ½ are **quadrupolar**.

Quadrupolar nuclei have an **asymmetrical** charge distribution.

This causes faster relaxation, resulting in broad peaks.





Data: Pedro Helou De Oliveira & Roisin O'Dea

Probes

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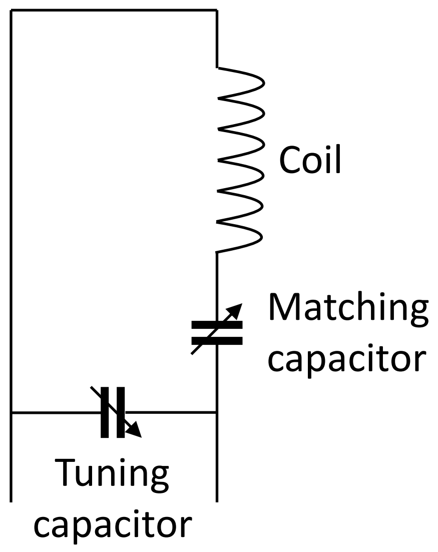
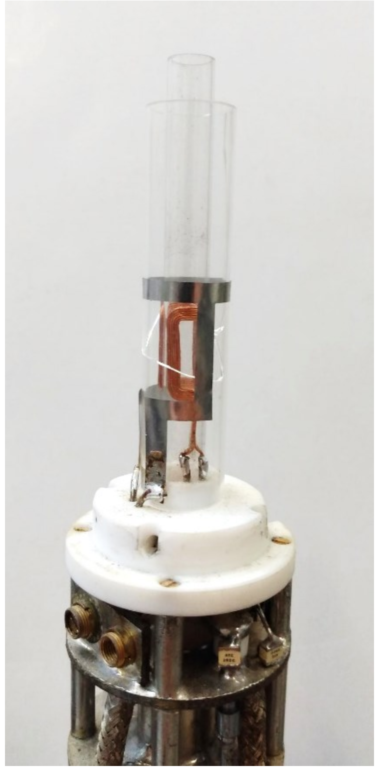
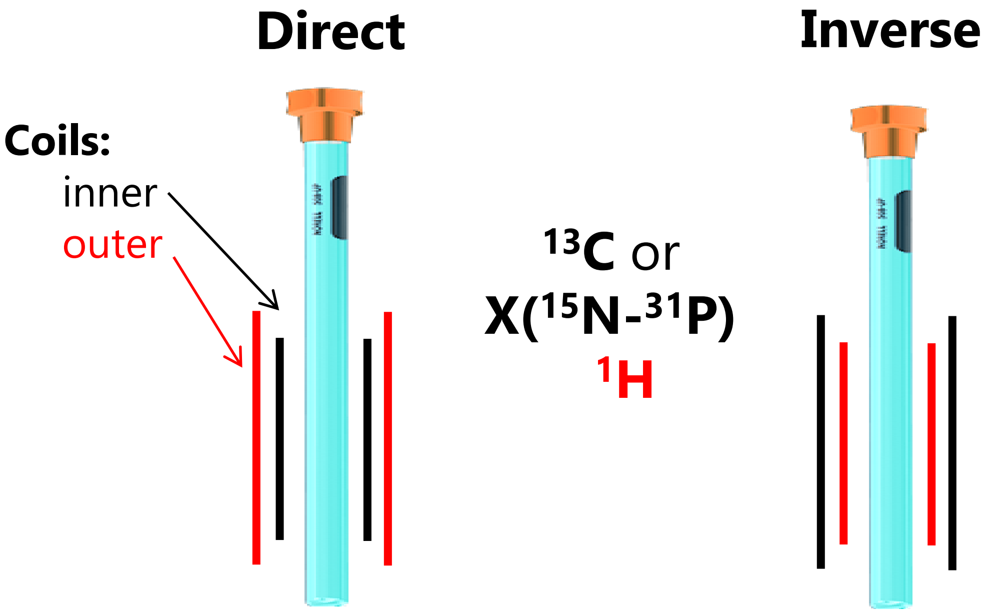
NMR probes usually have two coils, one for ^{1}H (and ^{19}F) and a second that can be tuned to a range of nuclei.
Depending on how the probe is constructed, the coils can be optimized for different nuclei.
Cooling the probe to low temperature (77 or 20 K) can increase the sensitivity.







NMR periodic table

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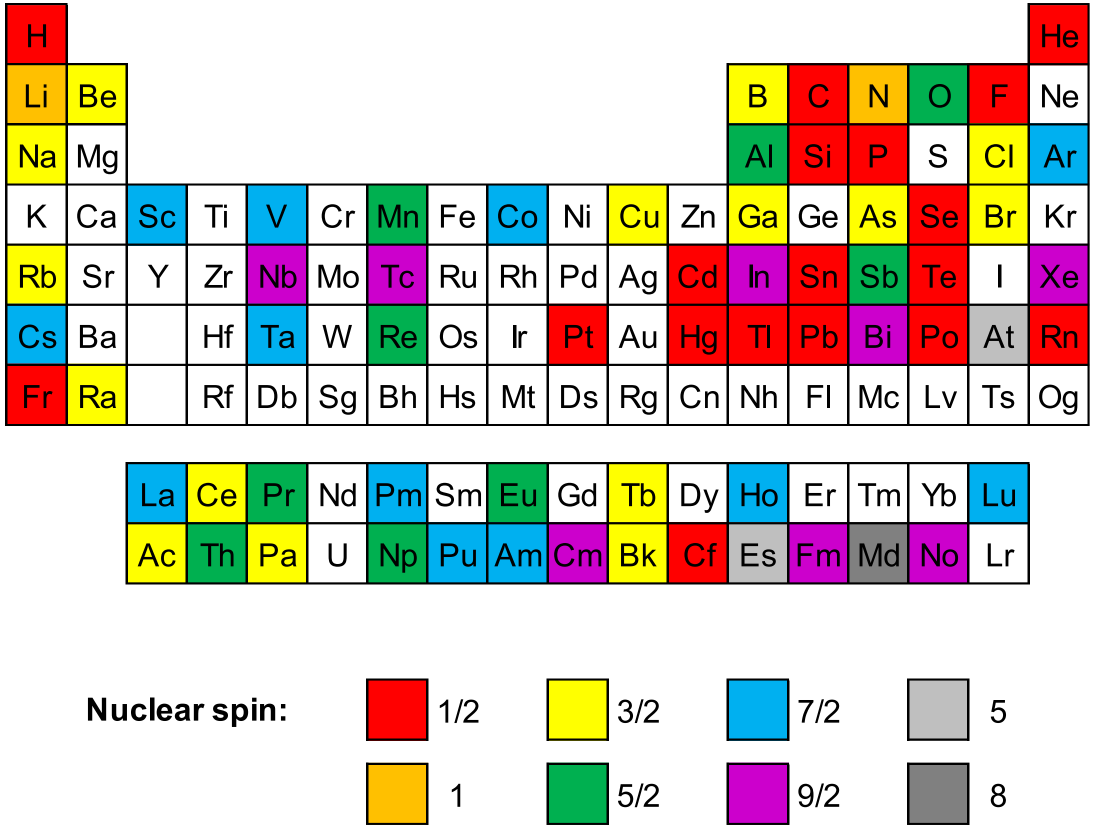
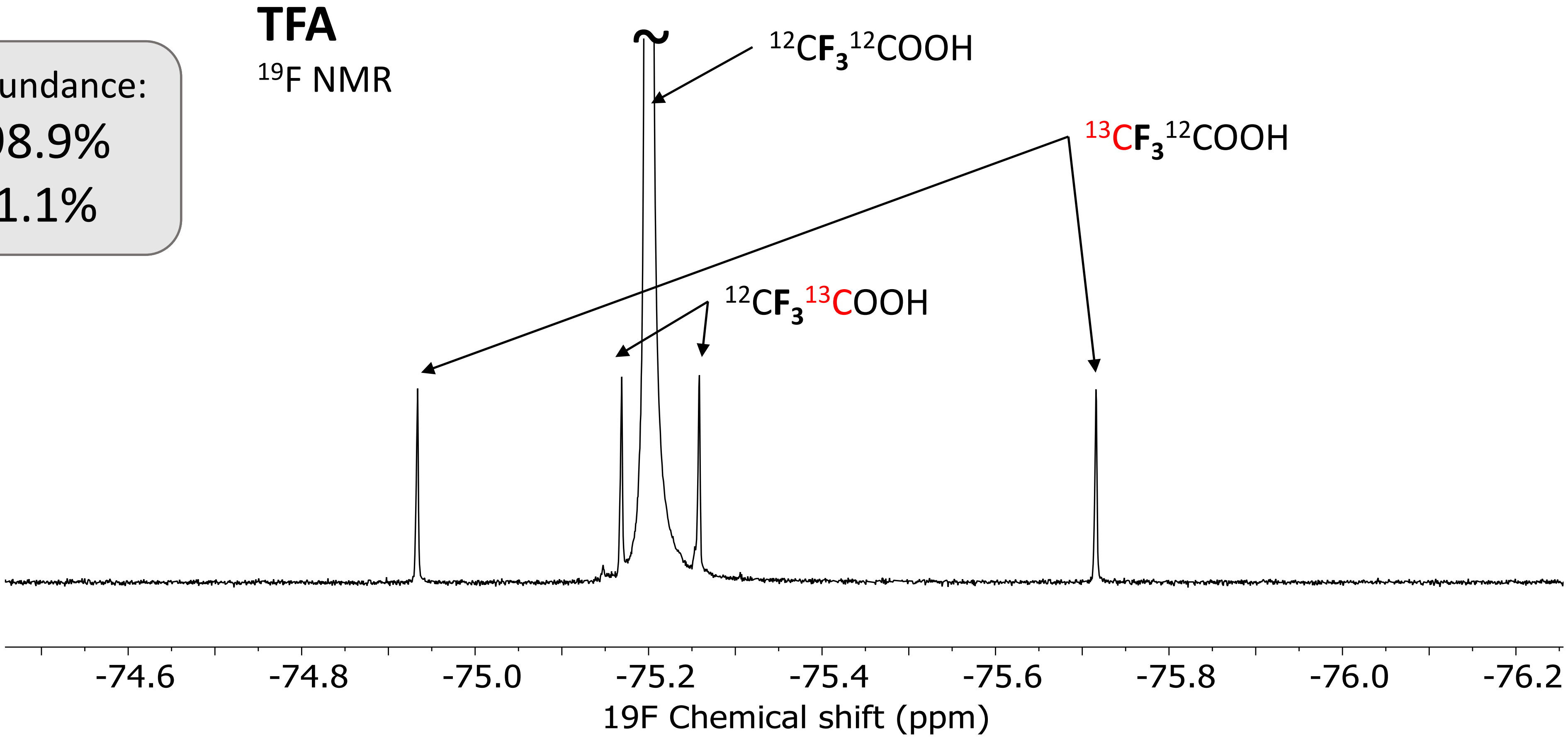
Most probes only detect nuclei with $\gamma > \gamma_N$



Natural abundance

For many heteronuclei, the NMR-active isotope only makes up a small fraction of all nuclei at natural abundance.
Some elements have multiple NMR-active isotopes.

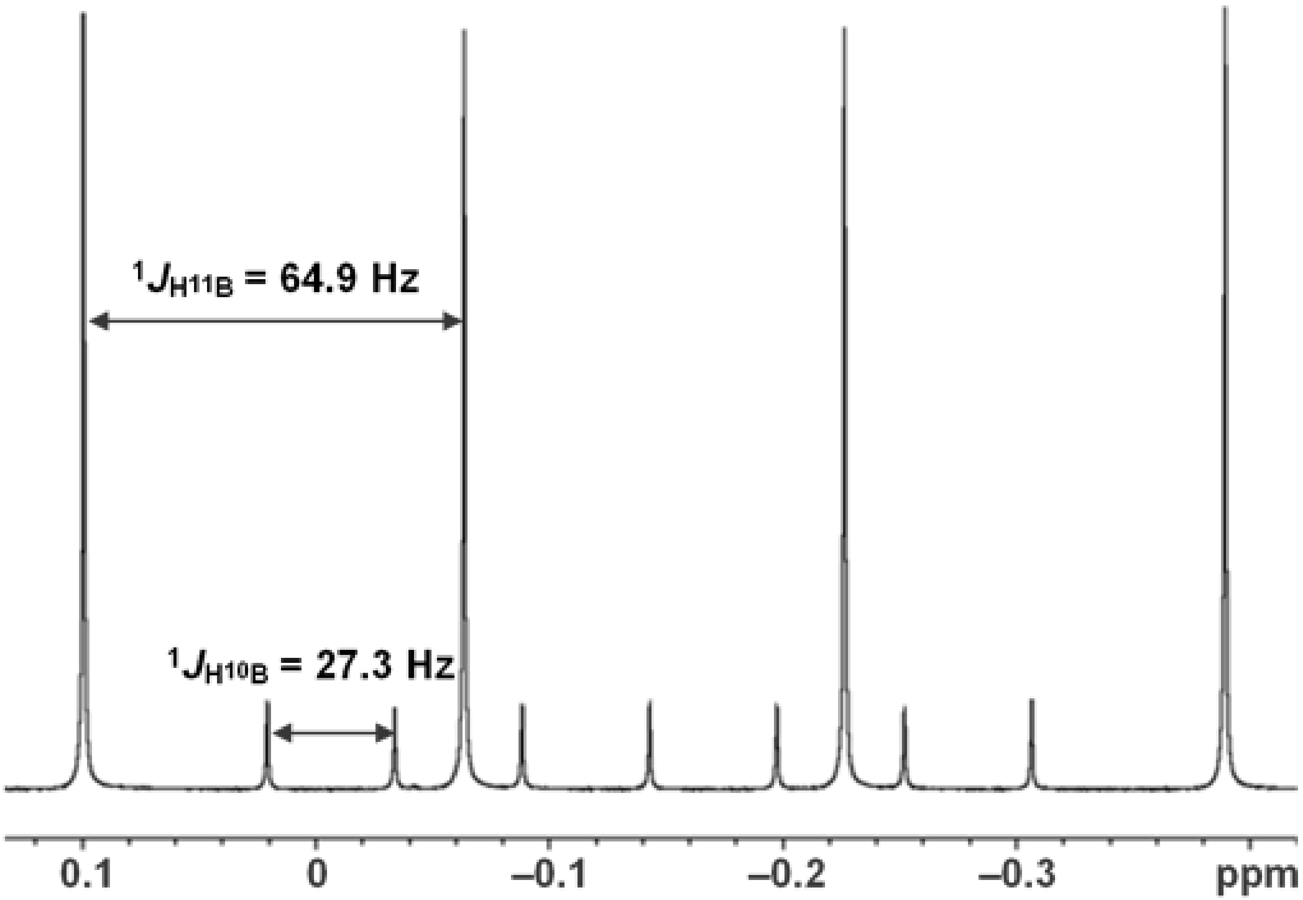
Natural abundance:
^{12}C = 98.9%
^{13}C = 1.1%



Natural abundance

For many heteronuclei, the NMR-active isotope only makes up a small fraction of all nuclei at natural abundance.
Some elements have multiple NMR-active isotopes.

BH_4^-
^{1}H NMR



Natural abundance:
^{10}B = 20%, spin-3
^{11}B = 80%, spin-3/2

https://chem.ch.huji.ac.il/nmr/techniques/1d/row2/b.html

NMR periodic table

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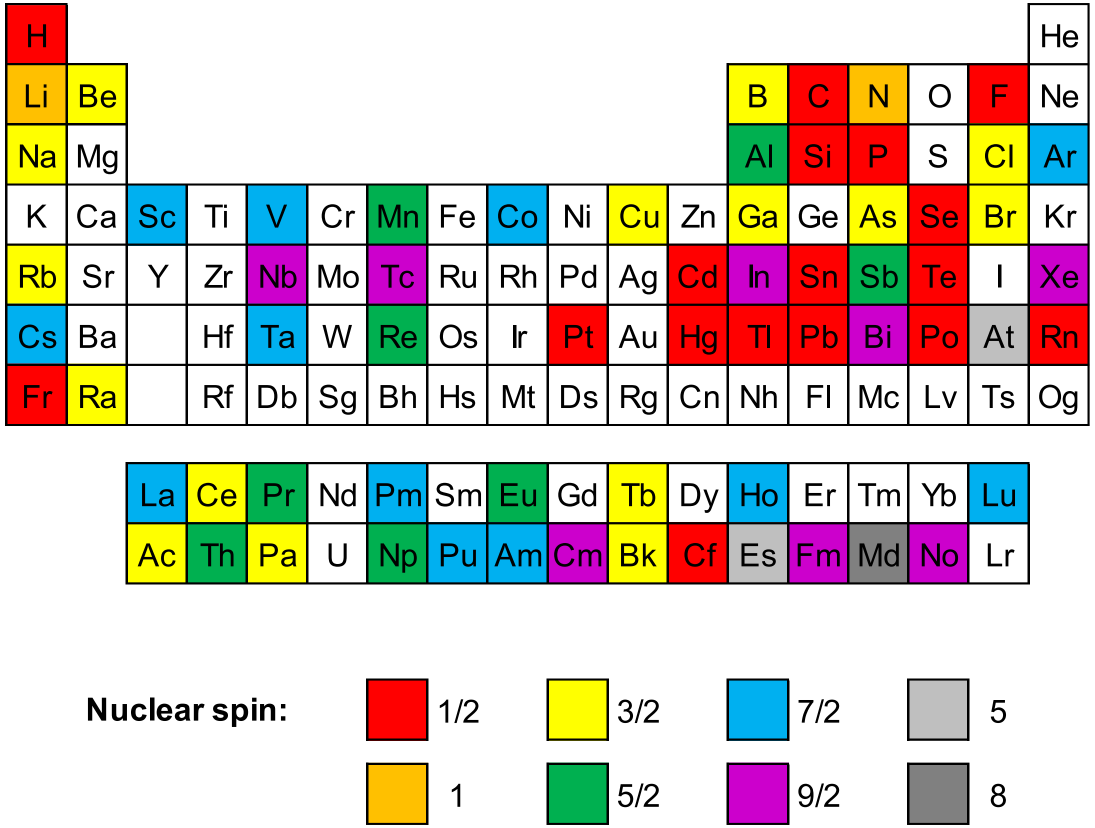
Most probes only detect nuclei with $\gamma > \gamma_N$

Some nuclei have too low natural abundance to detect



NMR periodic table

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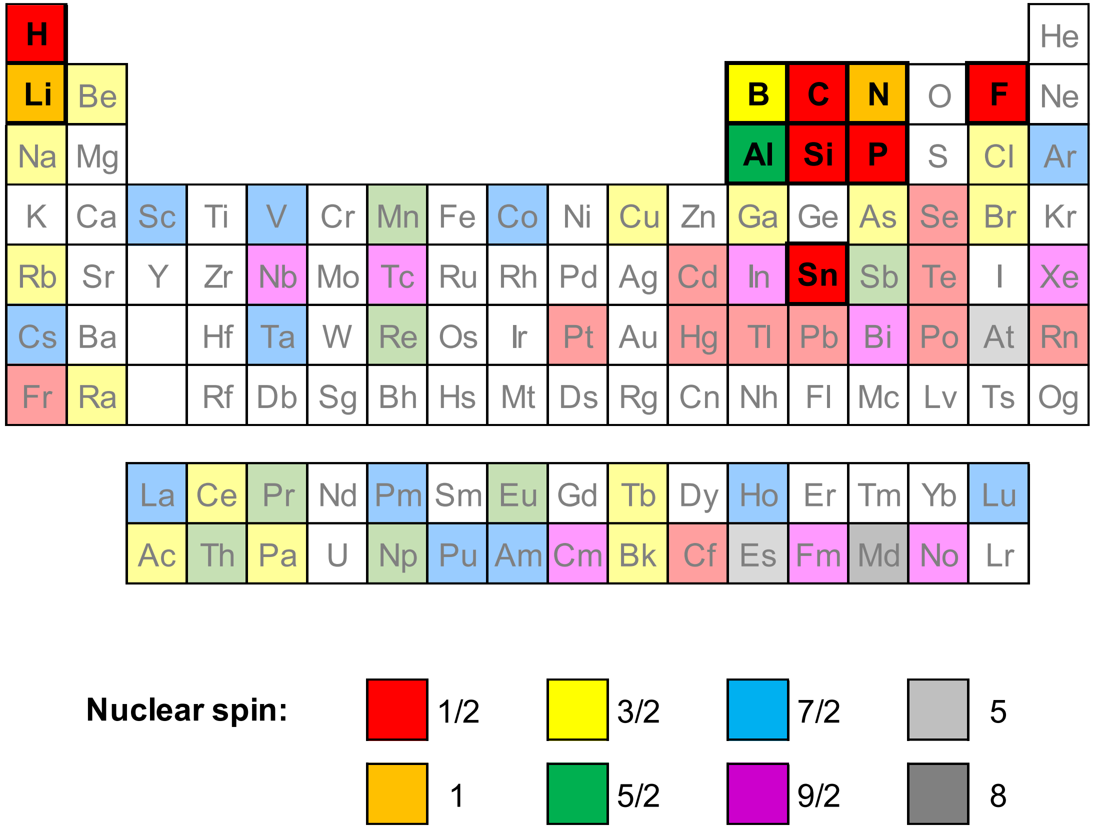
Most probes only detect nuclei with $\gamma > \gamma_N$

Some nuclei have too low natural abundance to detect

Common heteronuclei include ^{7}Li, $^{10/11}$B, ^{13}C, ^{15}N, ^{19}F, ^{27}Al, ^{29}Si, ^{31}P and ^{119}Sn



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Acquisition

Excitation width

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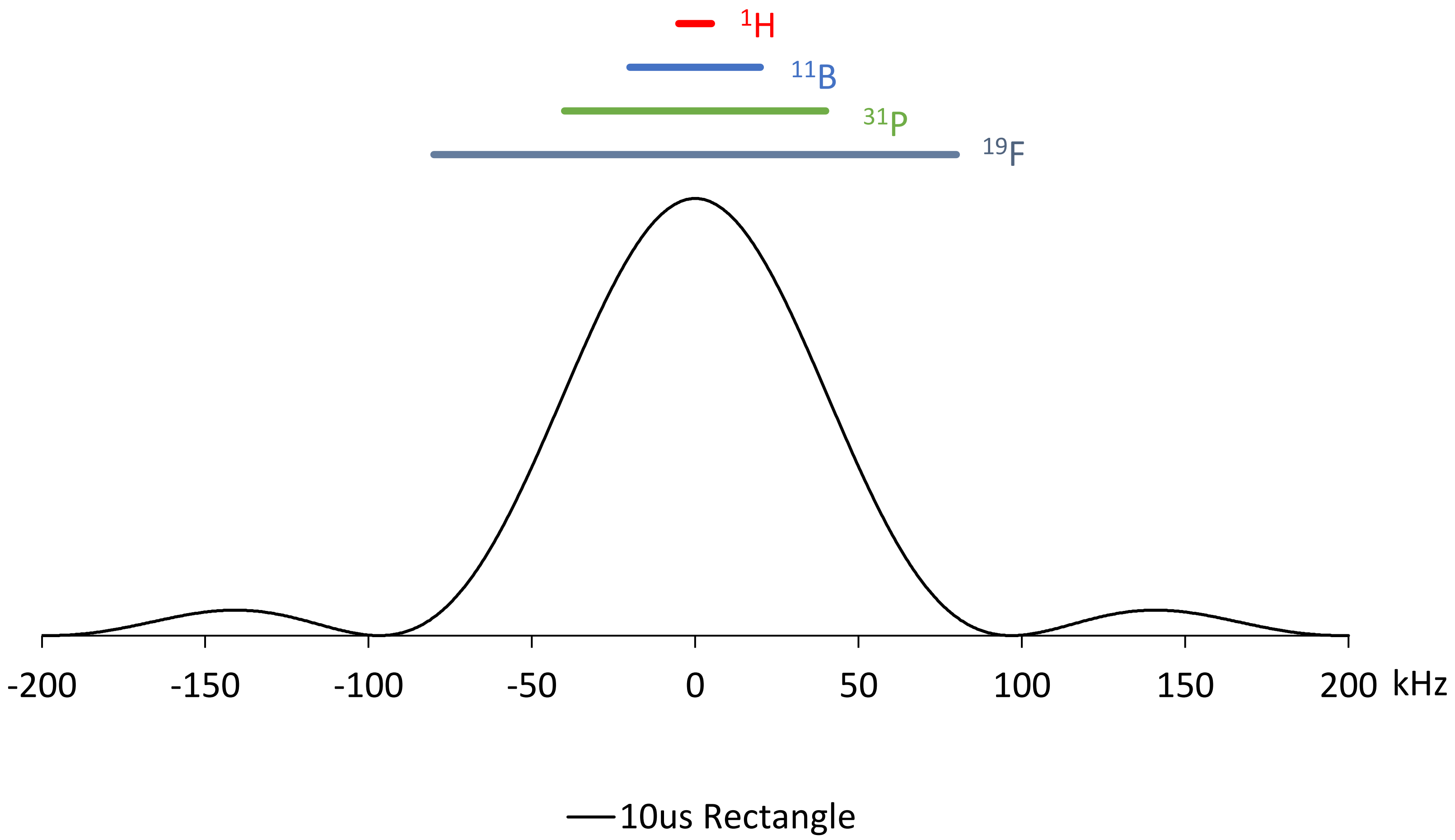
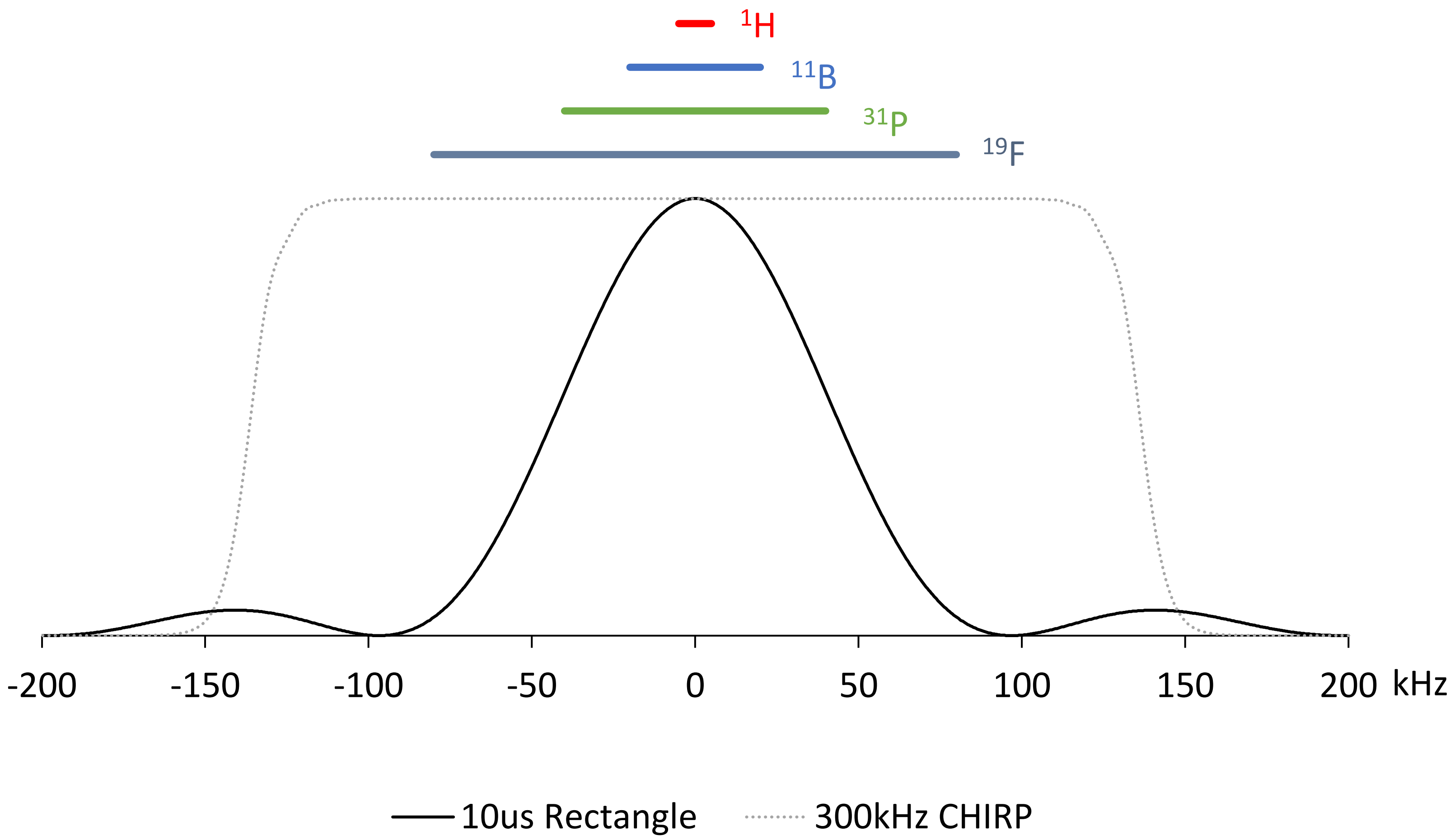
Standard pulses (typically ~10 µs duration) may not excite all peaks equally for nuclei with wide spectral ranges.



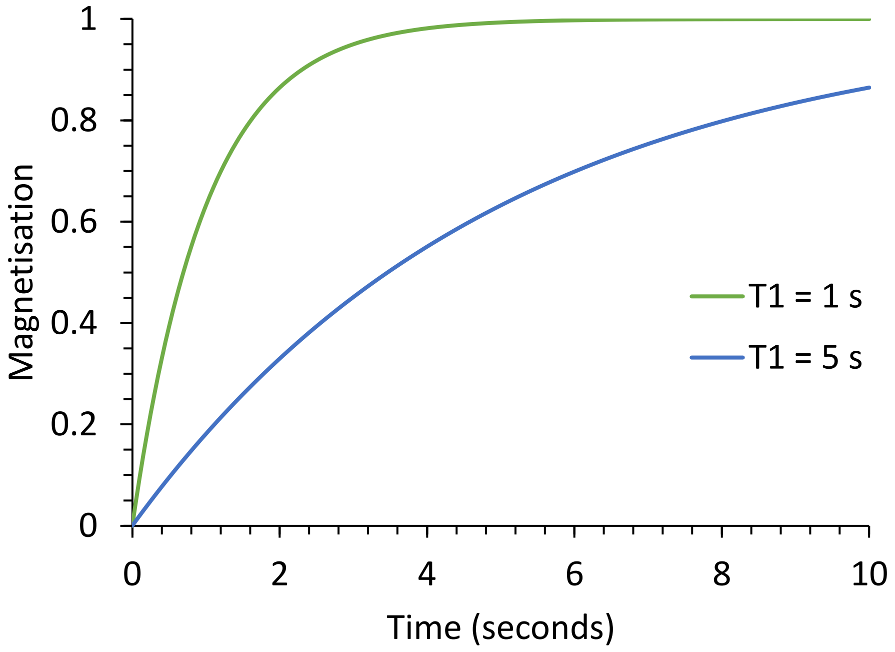
Excitation width

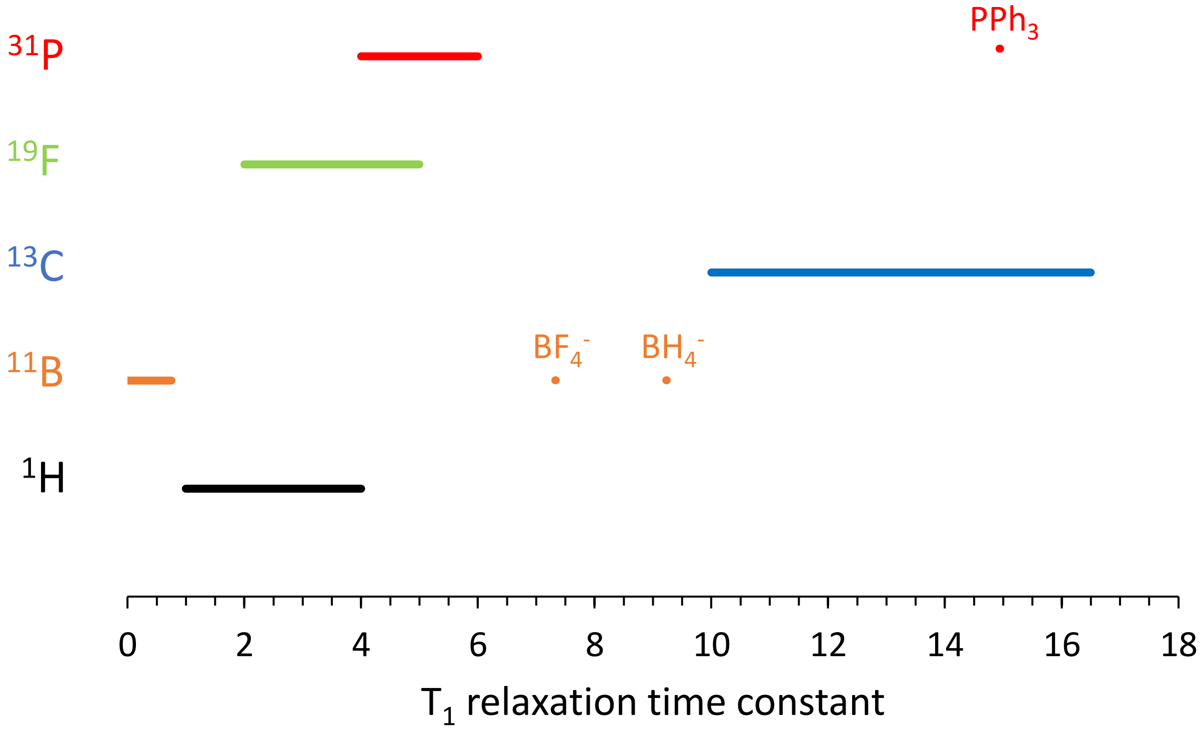
Standard pulses (typically ~10 µs duration) may not excite all peaks equally for nuclei with wide spectral ranges. Other pulses can offer more uniform excitation profiles.



Relaxation time

After the pulse, the NMR signal takes several seconds to recover.
The time taken for the signal to recover is determined by the T_1 relaxation time constant for the nucleus.





Relaxation time

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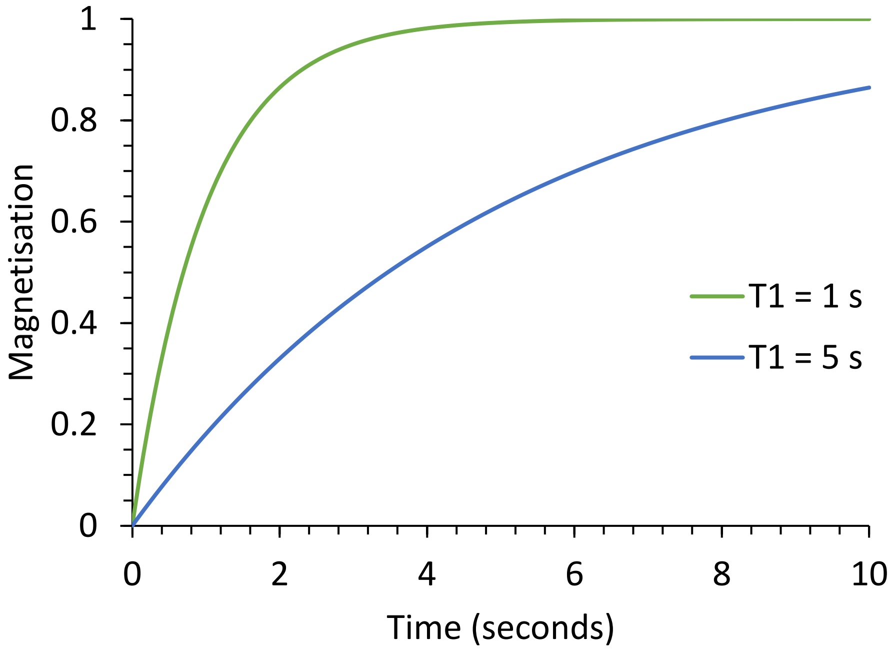
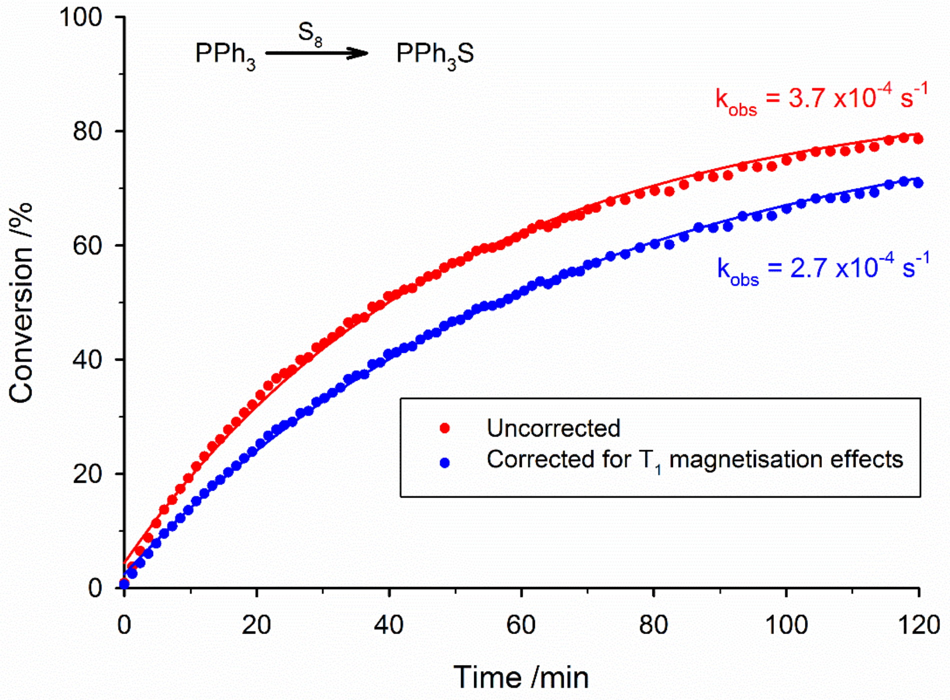
After the pulse, the NMR signal takes several seconds to recover.
The time taken for the signal to recover is determined by the T_1 relaxation time constant for the nucleus.
The spectrum will only be quantitative if the signal is allowed to fully recover, usually >5x T_1.

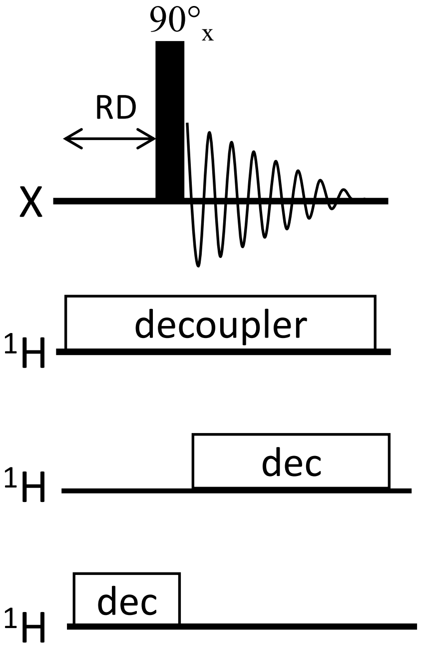




Catal. Sci. Technol., 2016,**6**, 8406-8417

Decoupling

Decoupling uses the second coil to saturate the energy levels of the coupled nucleus, removing peak splitting.
Different decoupling schemes can either enhance signal or enable quantitation.



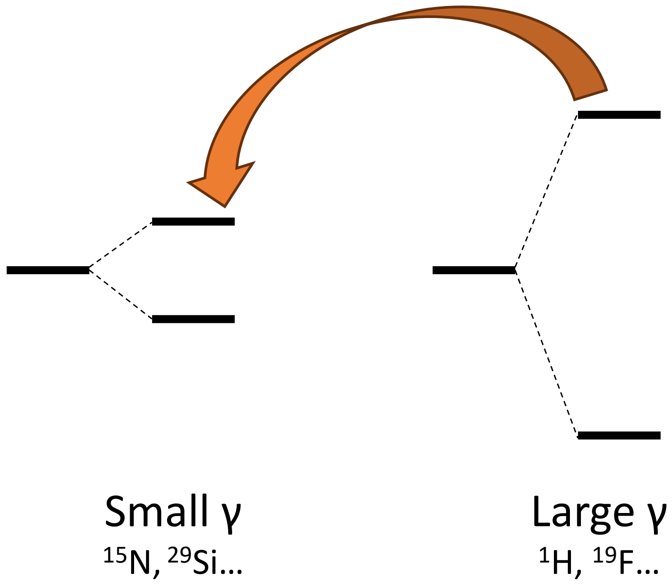
	Multiplicity	NOEs	Quantitation
Continuous ^1H	✗	✓	✗
Inverse-gated ^1H	✗	✗ (RD>= 5-12* T_1)	✓
Gated ^1H	✓	✓	✗

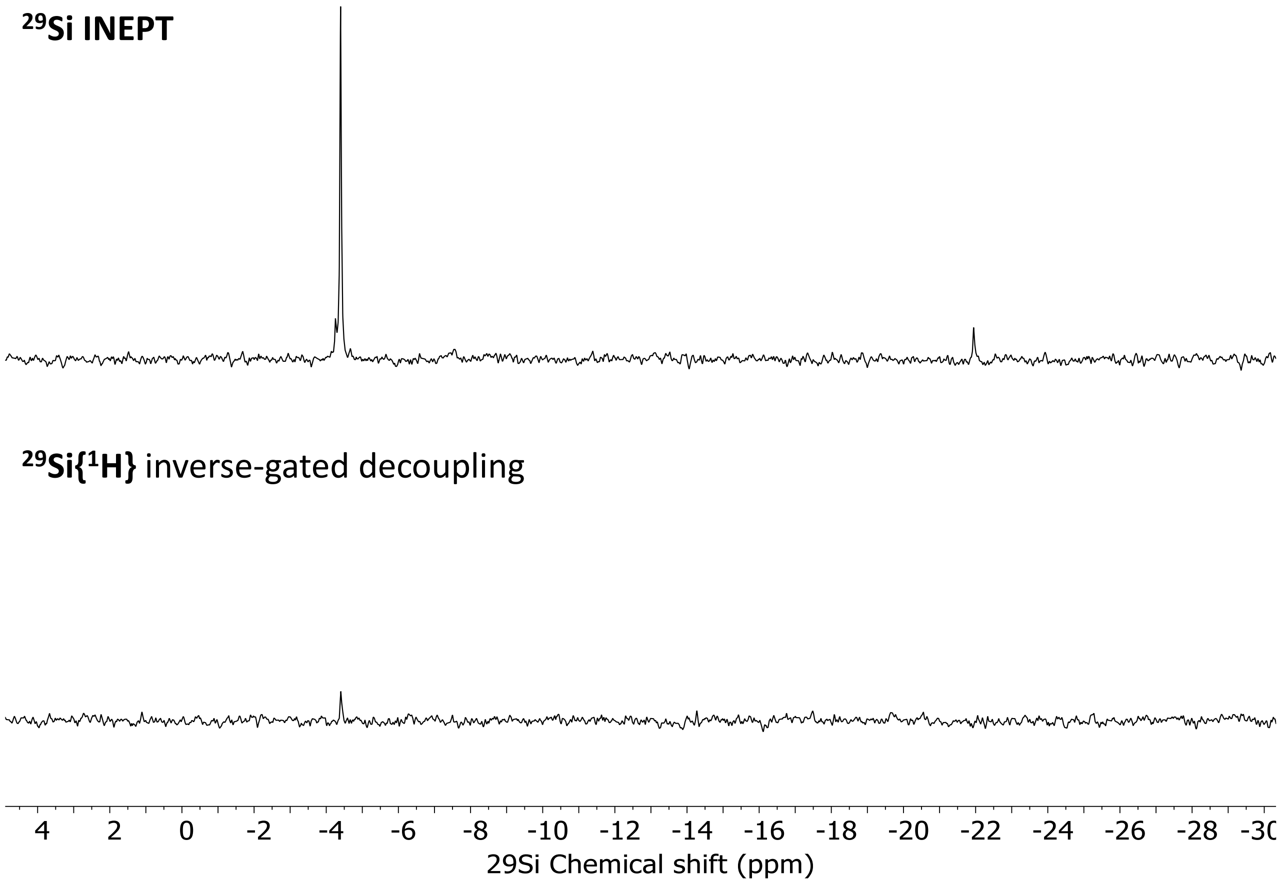
NOEs (Nuclear Overhauser Effects)

INEPT

Nuclei with a low gyromagnetic ratio (e.g. ^{14}N or ^{29}Si) have lower levels of polarization, resulting in weak signals.
Signals can be enhanced by transferring polarization from nearby nuclei with higher gyromagnetic ratio (e.g. ^{1}H or ^{19}F)

INEPT
(**I**nsensitive **N**uclei **E**nhanced by **P**olarization **T**ransfer)





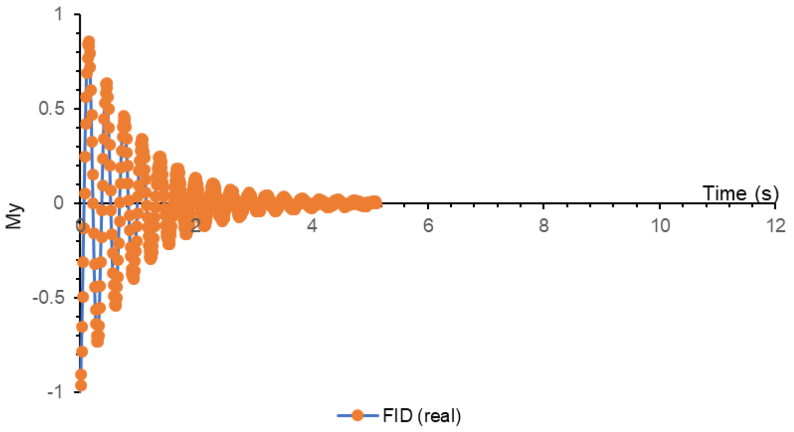
Data: Lorna Murray

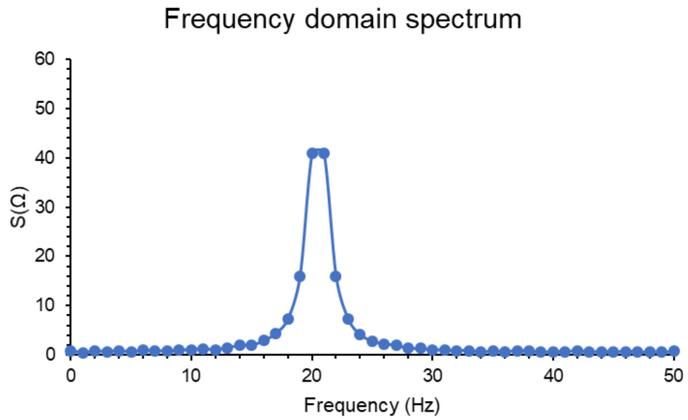
Processing

Zero filling

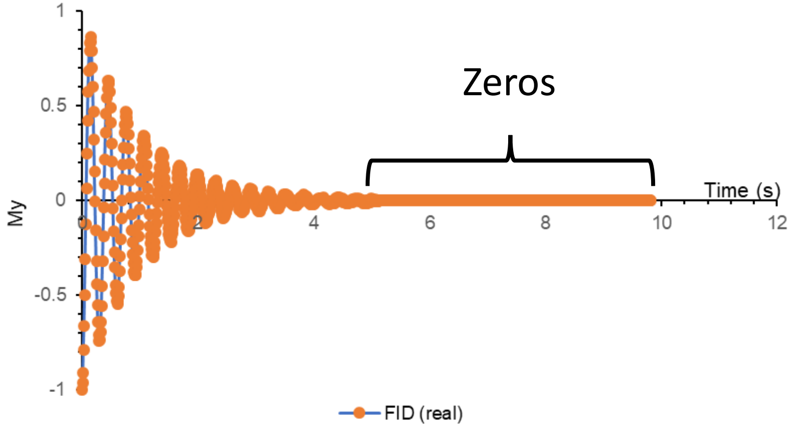
Zero filling gains additional frequency resolution for free, by increasing the number of points available for the Fourier transform. There is no new information added, but the extra points can help with integrating and fitting peaks.

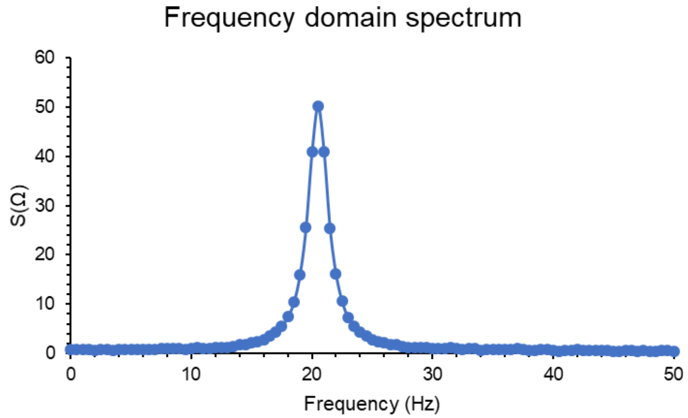
Normal data





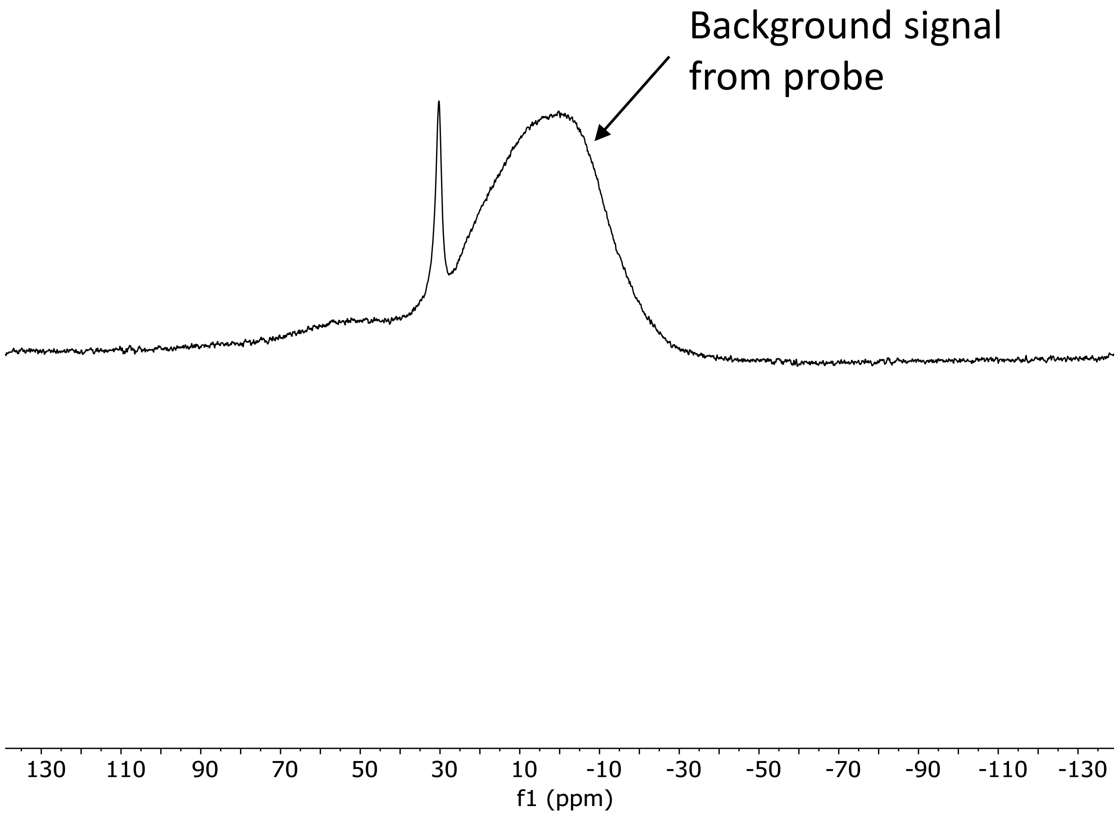
Zero filled

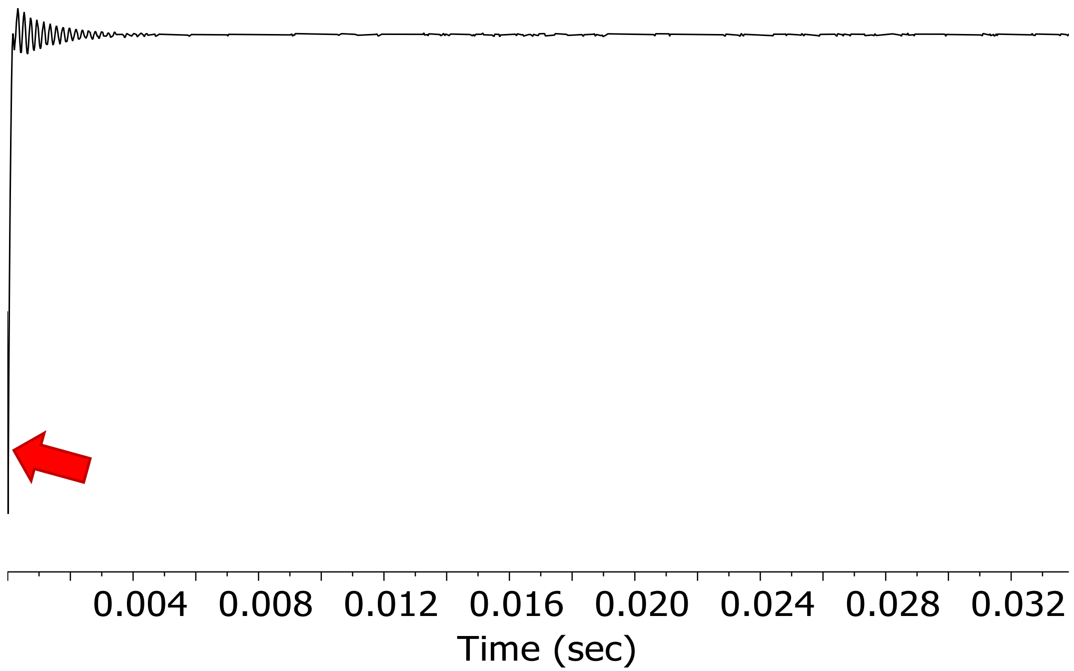




Background signals

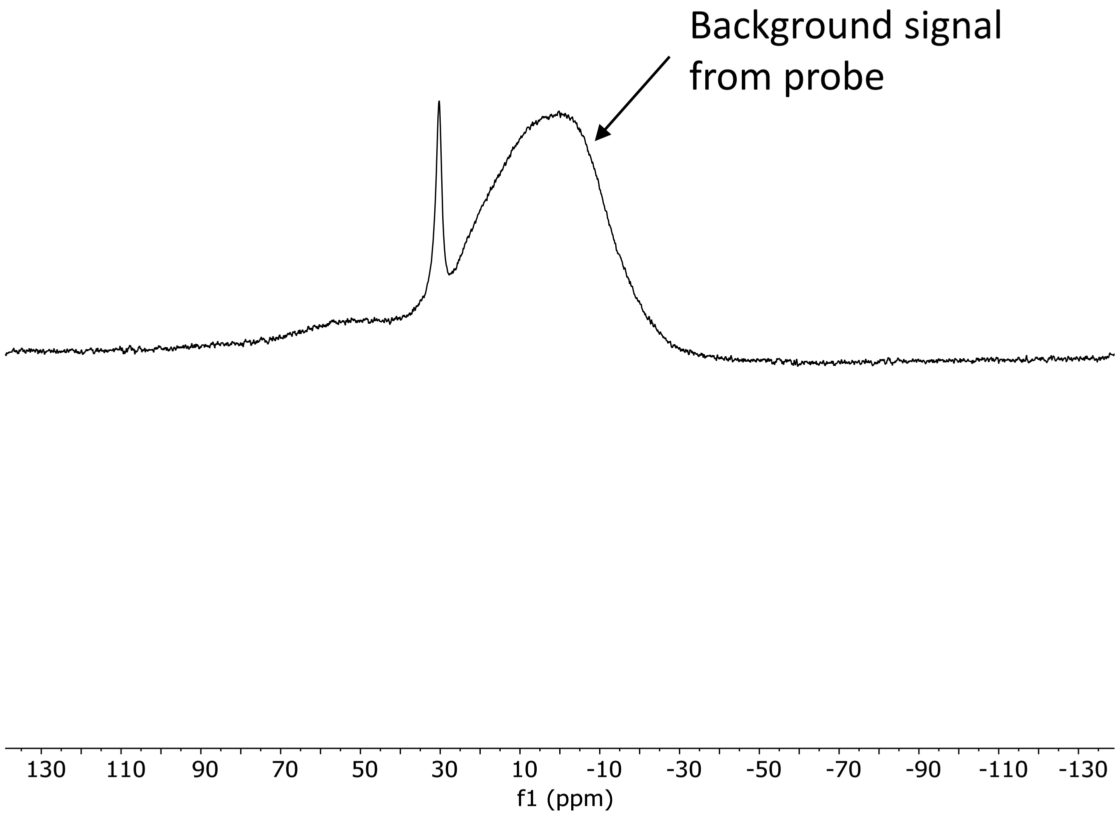
Fast decaying signals from materials in the probe/glass result in broad background signals.





Background signals

Fast decaying signals from materials in the probe/glass result in broad background signals.
Removing the first few points from the FID and then using backward linear prediction can restore a flat baseline.



Further information

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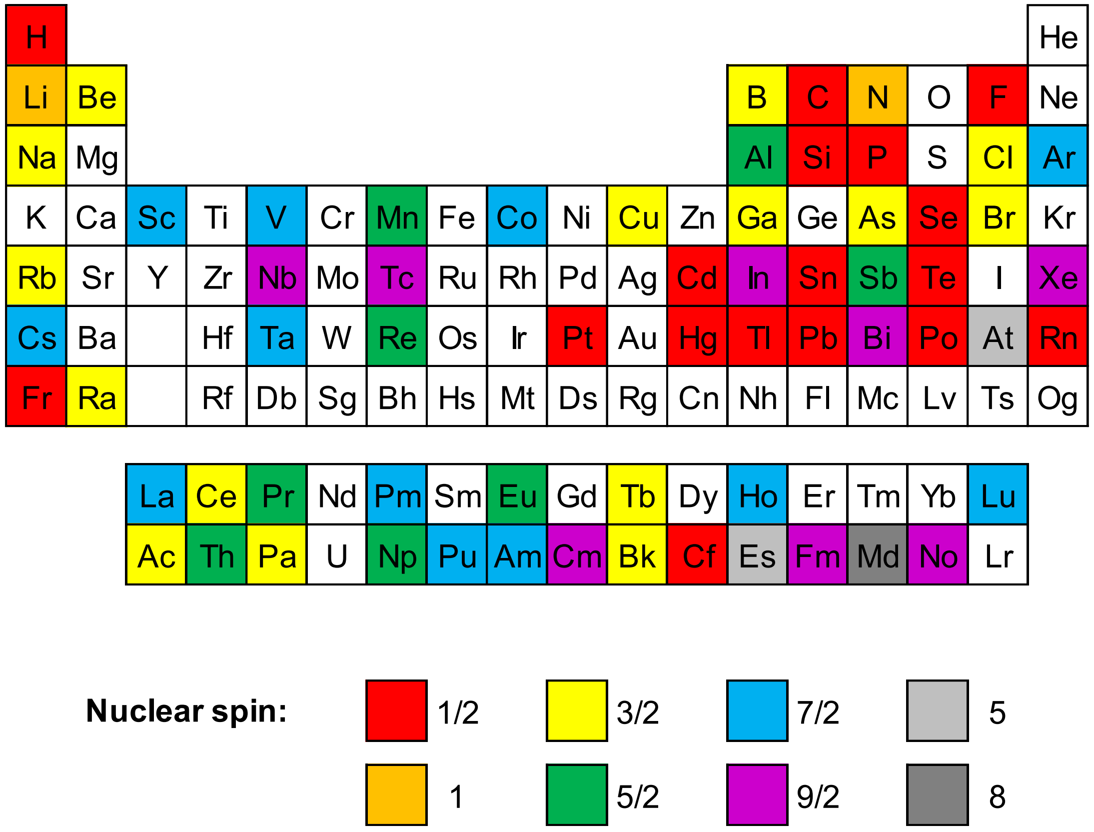
Books & online resources:

- High-Resolution NMR Techniques in Organic Chemistry, Tim Claridge
- http://u-of-o-nmr-facility.blogspot.com
- Mechanistic Analysis by NMR Spectroscopy: a Users Guide, *Prog. Nucl. Magn. Reson. Spectrosc.*, 129, 28–106, 2022

NMR periodic table:

https://imserc.northwestern.edu/guide/eNMR/chem/NMRnuclei.html



Speak to your local NMR staff!