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Pure shift NMR: How it works

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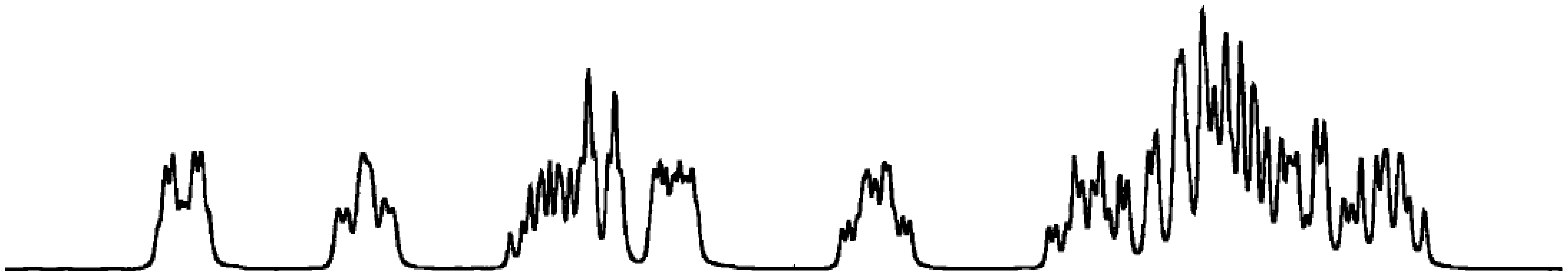
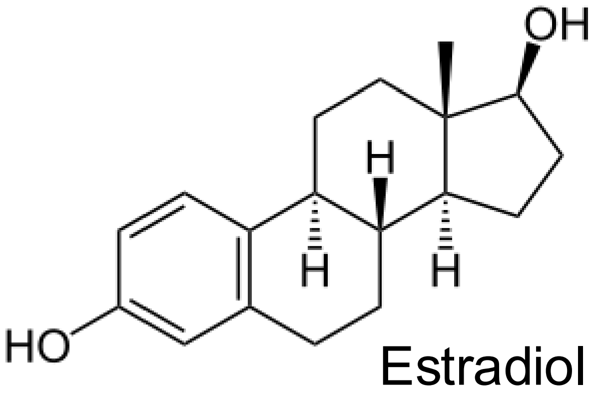
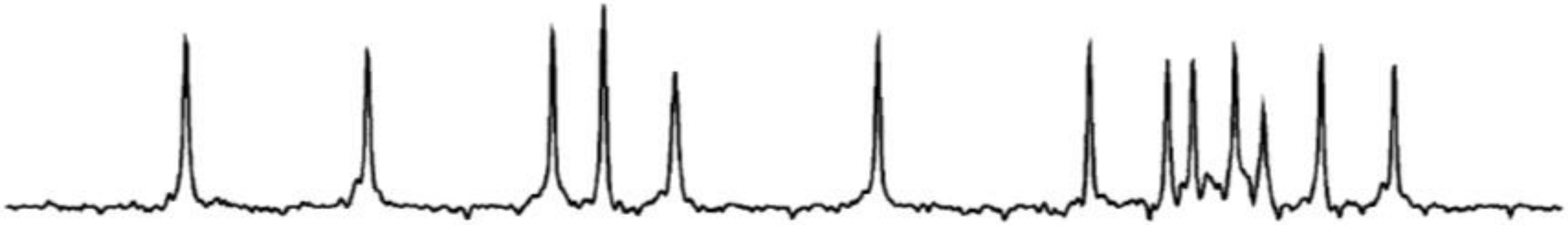
Pure Shift NMR Spectroscopy



Conventional ¹H NMR spectrum

Multiplet with several signals for each chemical site





Homonuclear broadband decoupled *pure shift* NMR spectrum

Single signal for each chemical site

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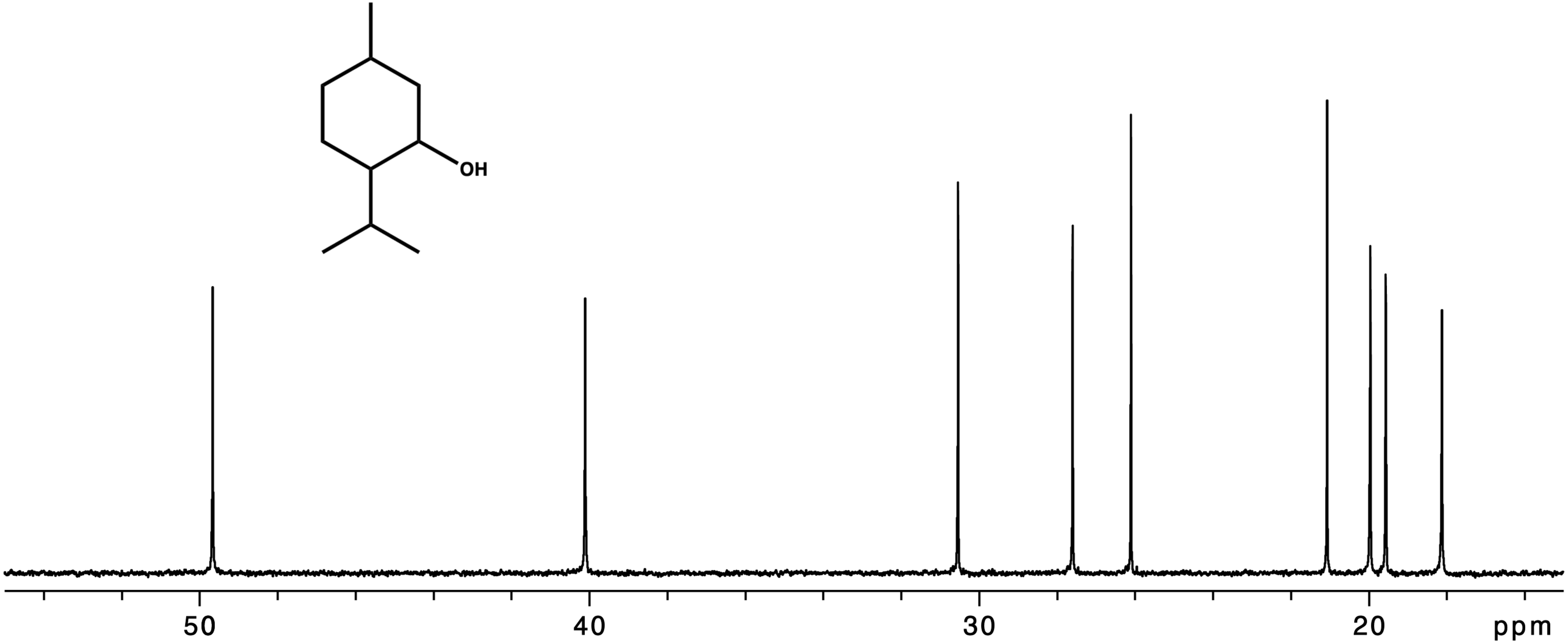
$^{13}C\{^1H\}$ NMR

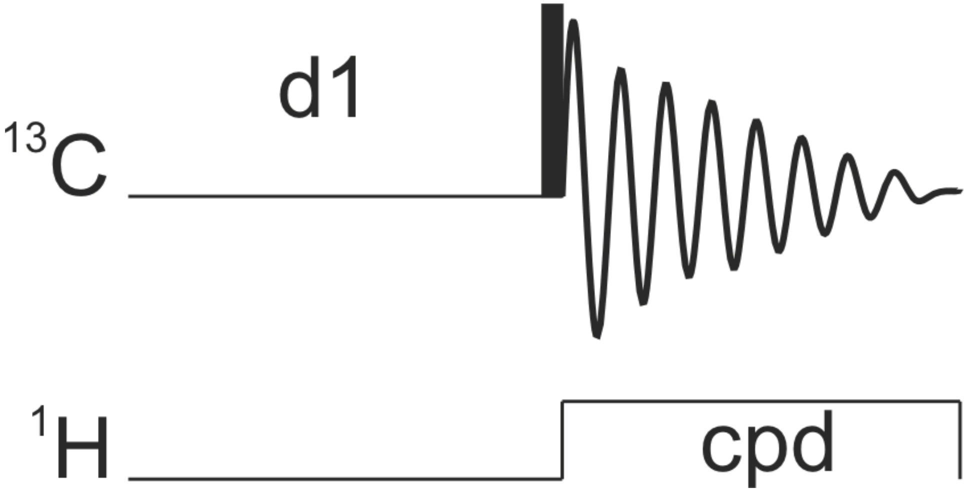
(+)-isomenthol

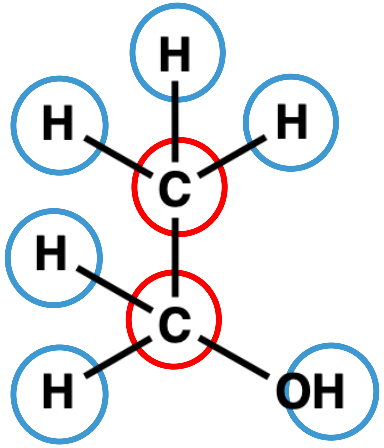


In a $^{13}C\{^1H\}$ spectrum all the couplings between ^{13}C and ^1H are suppressed

Each ^{13}C signal appears as a single spectral line

$^{13}C\{^1H\}$ NMR

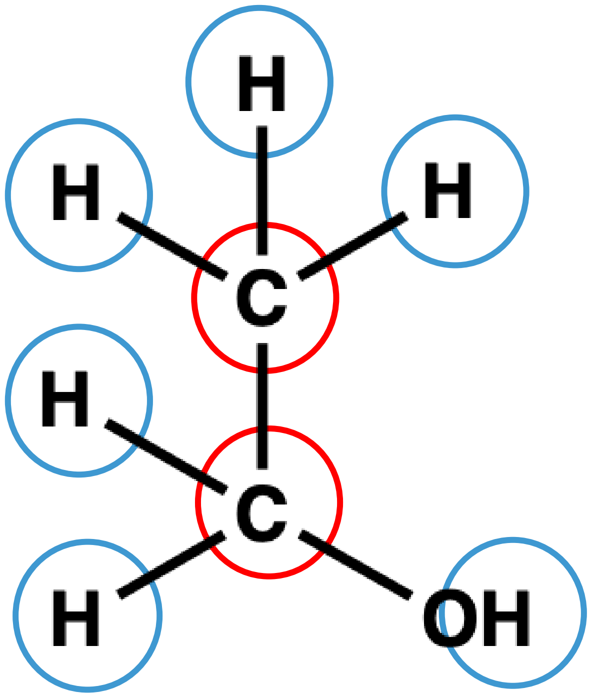




The CPD element rapidly exchanges the ^1H nuclei between up (+1/2) and down (-1/2)

^{13}C nuclei experience an average ^1H spin state of [(+1/2) + (-1/2)]/2 = 0

$^{13}C\{^{1}H\}$ NMR

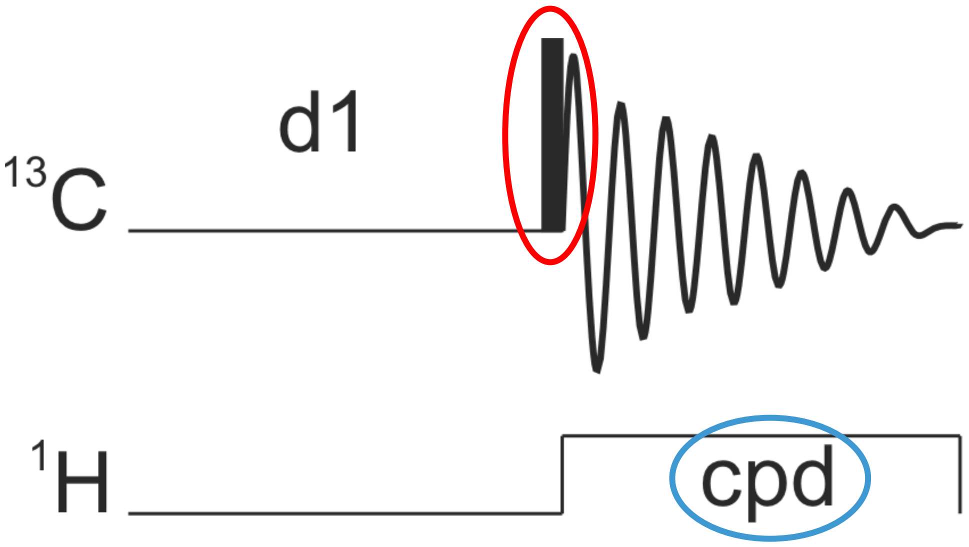


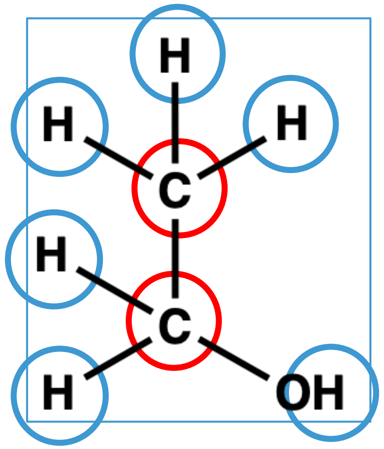
When discussing decoupling, it is useful to define active and passive spins

Active spins are those that we measure (they contribute to the observed signals)

Passive spins are those cause the multiplicity in the observed signals

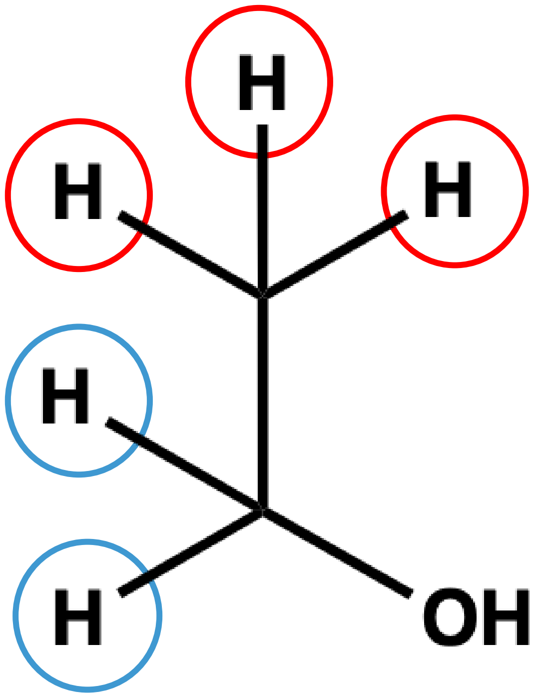
$^{13}C\{^1H\}$ NMR





In the $^{13}C\{^1H\}$ NMR experiment, it is relatively simple to separate the active and passive spins as they have very different frequencies so we can pulse them separately

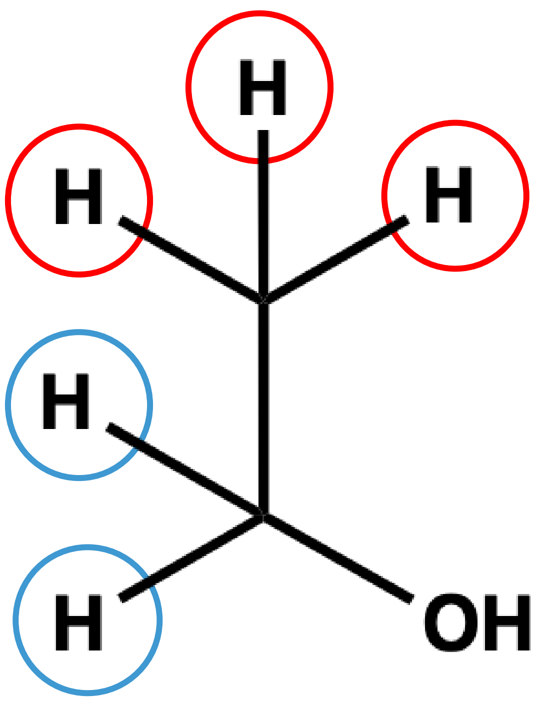
$^1H\{^1H\}$ NMR



To decouple ^1H from other ^1H, we need to separate the spin system into active and passive spins

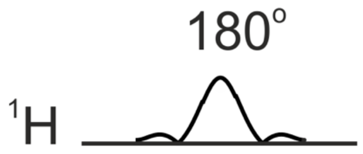
A spin cannot be both active and passive

$^1H\{^1H\}$ NMR

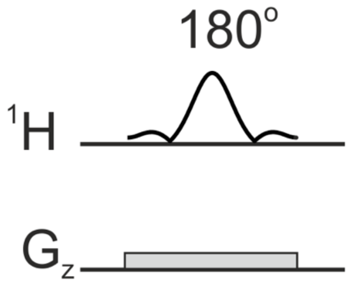


Broadband pure shift NMR methods divide the molecules that we are measuring into pools of spins which contribute separately to the measured spectrum

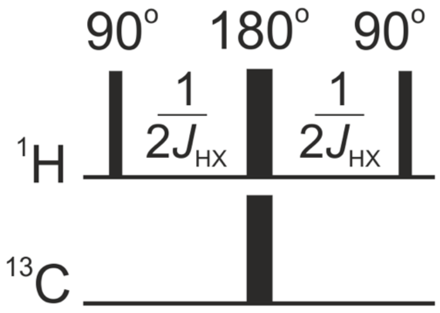
Separating active and passive spins



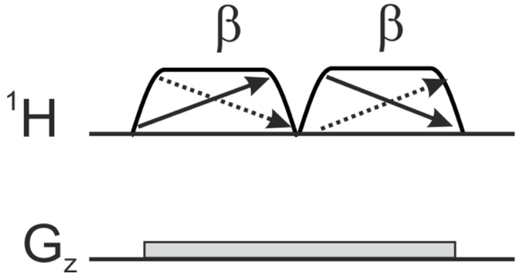
Band Selective



Zangger-Sterk



BIRD



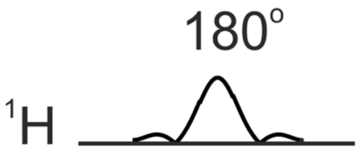
PSYCHE

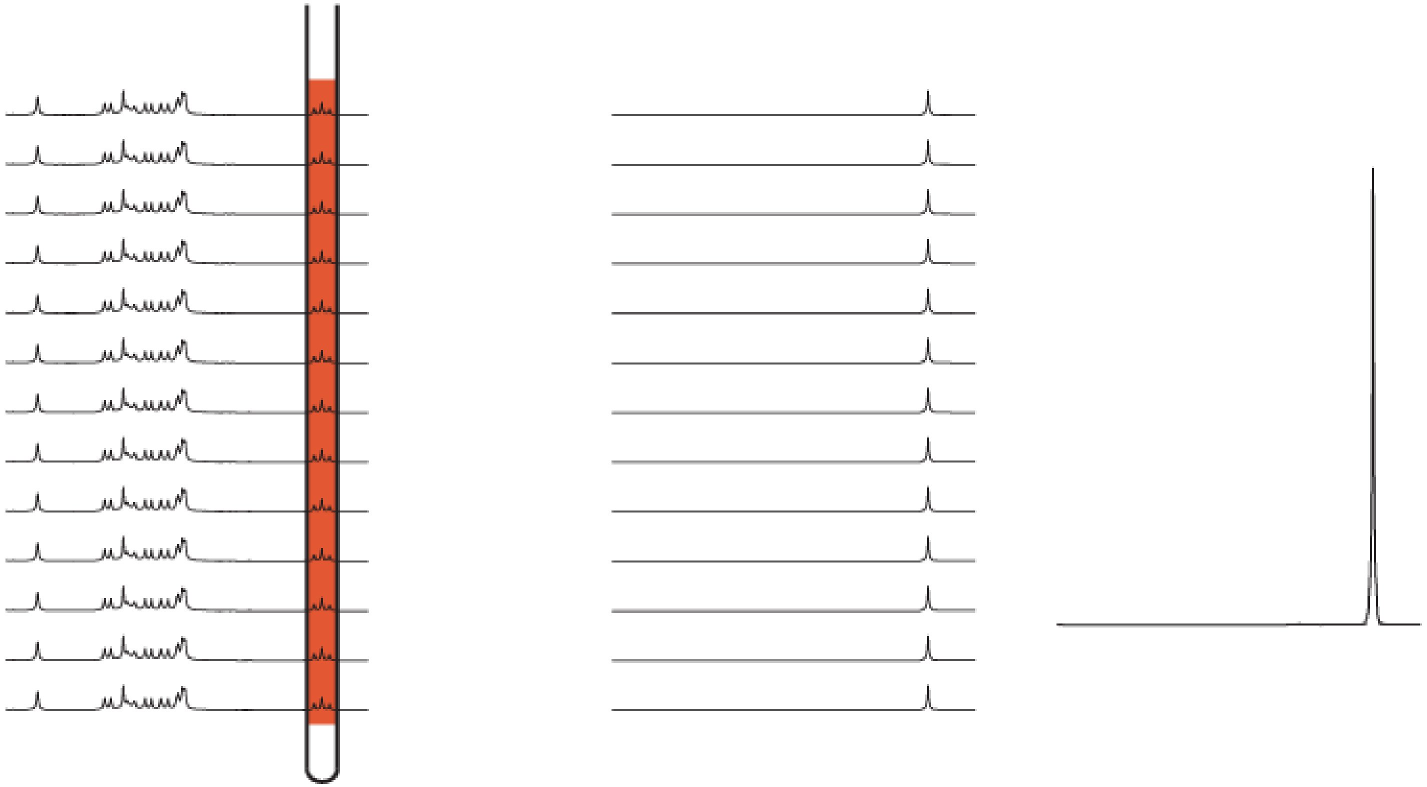
Several methods have been identified that separate spins into active and passive pools

The commonest approach is to use a pulse or pulses that refocus only the active spins

These are known collectively as Active Spin Refocusing (ASR) elements

Band selective active spin refocusing

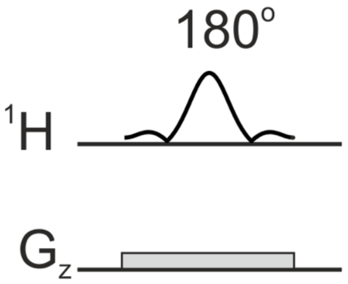


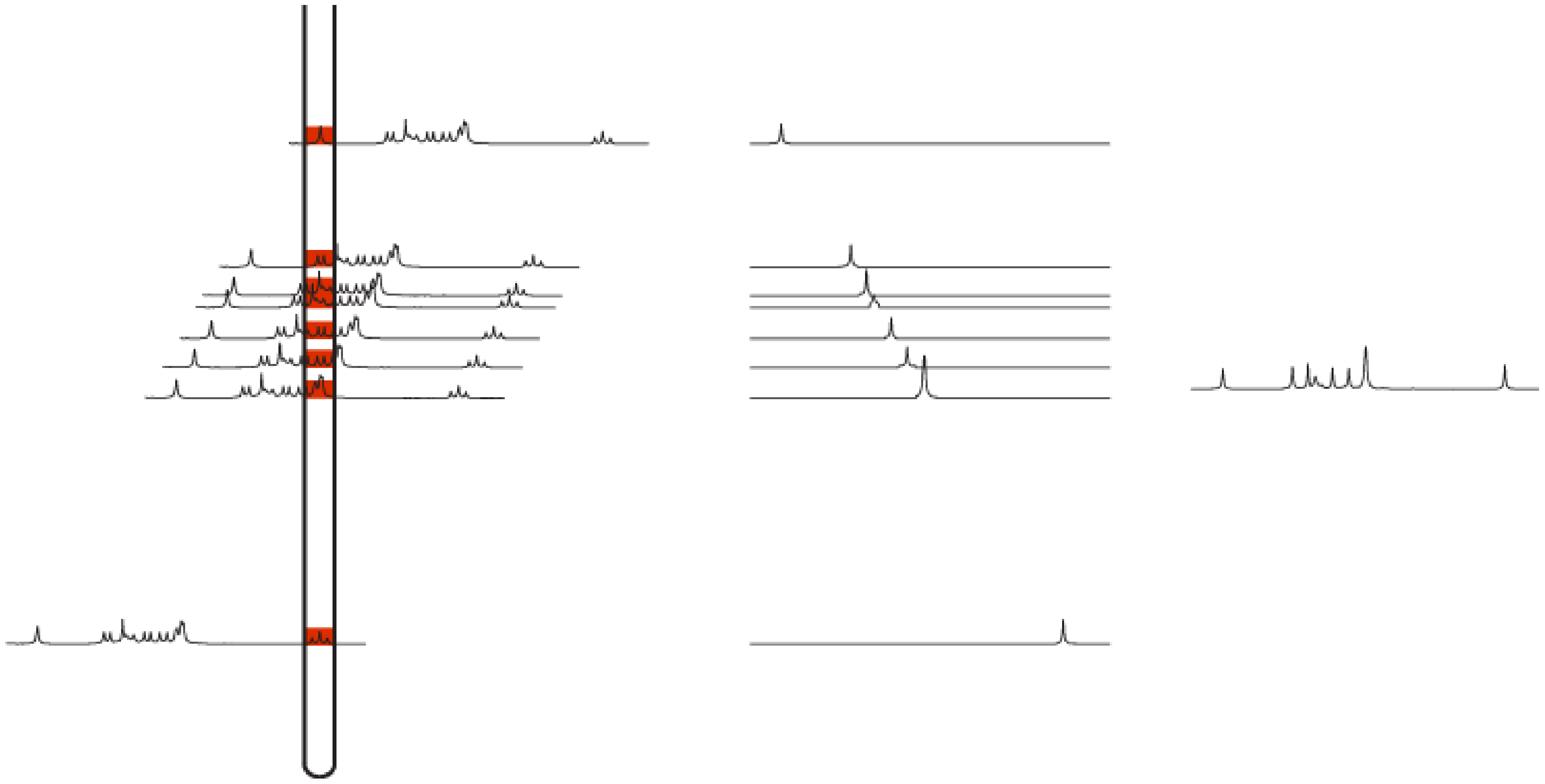


The band selective method uses a frequency-selective pulse to refocus only spins within a specific frequency range

Only spins that experience the pulse are observed in the decoupled spectrum.

Zangger-Sterk (ZS) active spin refocusing

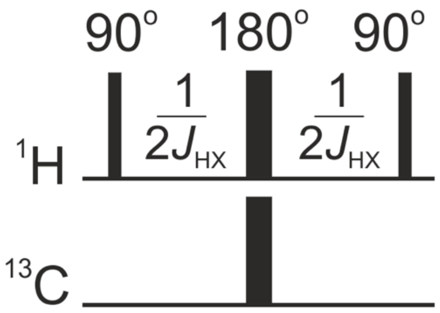


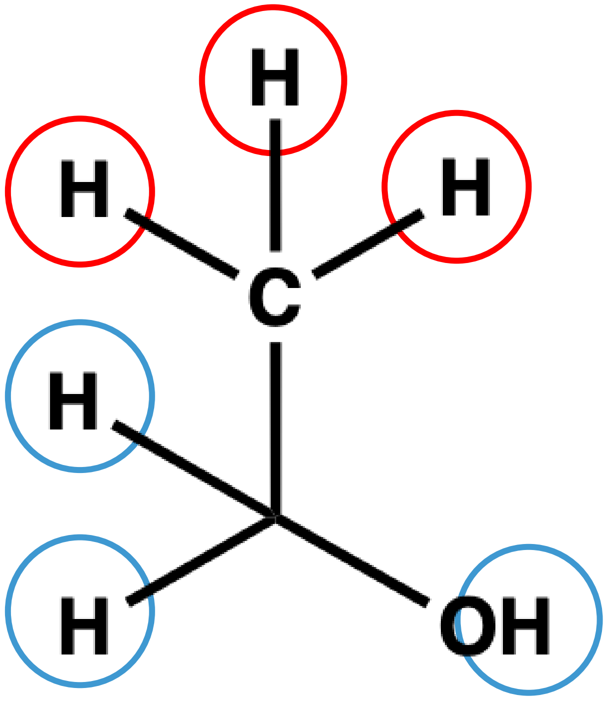


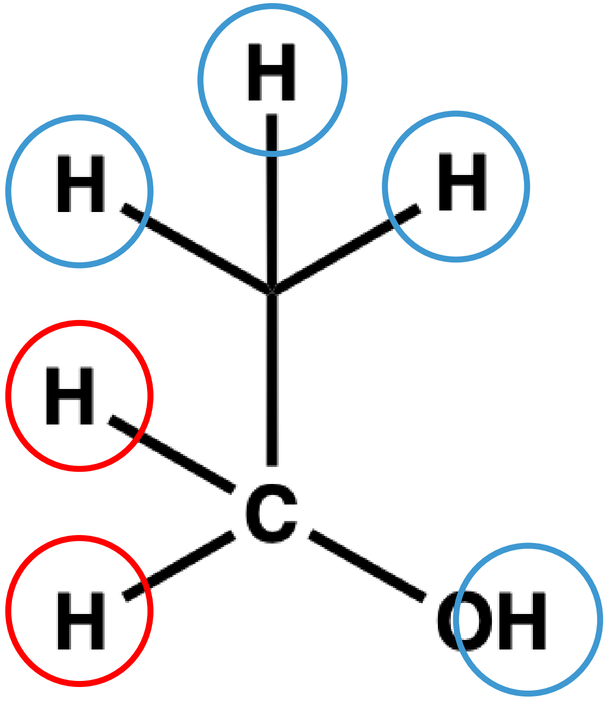
The ZS method uses a simultaneous frequency-selective pulse and field gradient to refocus only spins within a specific position of the NMR tube

The observed spectrum is the sum of the signal produced in each slice of the NMR tube

Bilinear Rotation Decoupling (BIRD) active spin refocusing



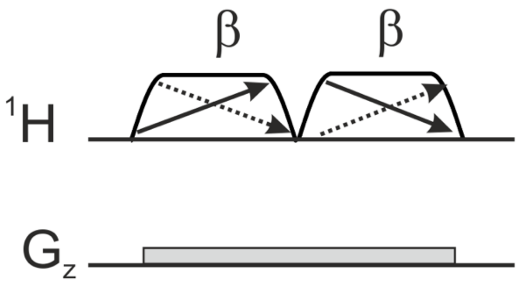


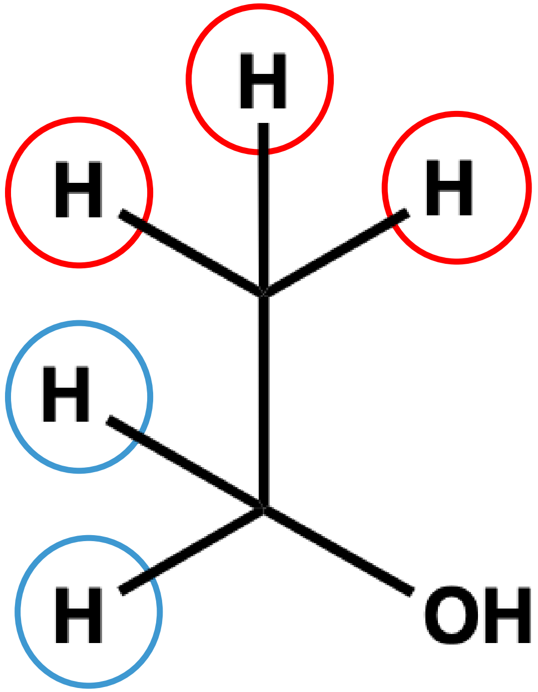


The BIRD method discriminates ^{1}H based on the presence of a 1-bond J coupling to a heteronucleus (e.g. ^{13}C).

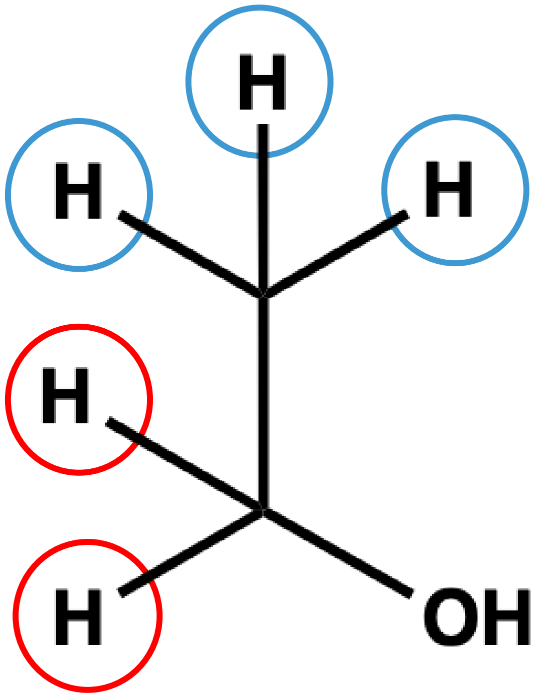
^{1}H with a 1-bond J coupling a ^{13}C experience a 180° pulse and are decoupled from ^{1}H that do not have a coupling to the same ^{13}C

Pure Shift Yielded by Chirp Excitation (PSYCHE) active spin refocusing





$\sin^2\beta$
(c.a.10%)

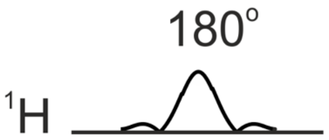


$\sin^2\beta$
(c.a.10%)

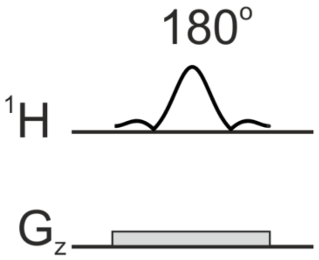
The PSYCHE method is statistical. Depending on the angle β, a random proportion of spins are excited and experience a change in coherence sign (equivalent to a 180° pulse) while the remainder experience no change.

Separating active and passive spins

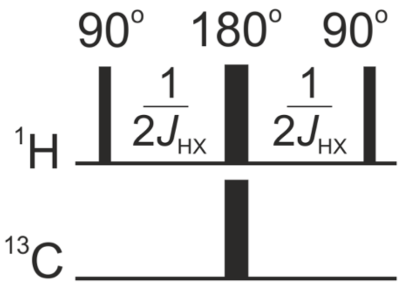
ASR:



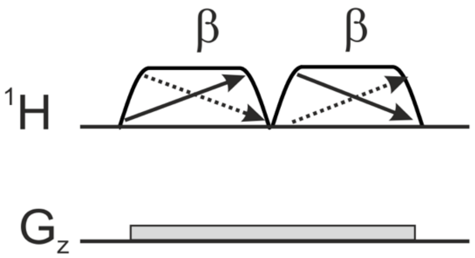
Band Selective



Zangger-Sterk



BIRD



PSYCHE

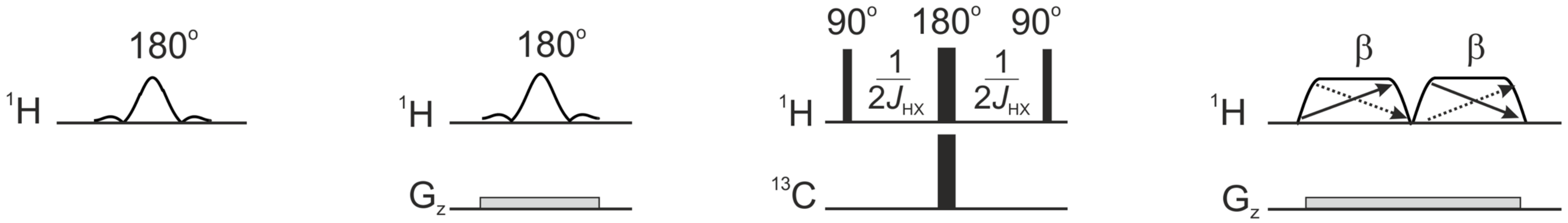
PSYCHE is the most general method

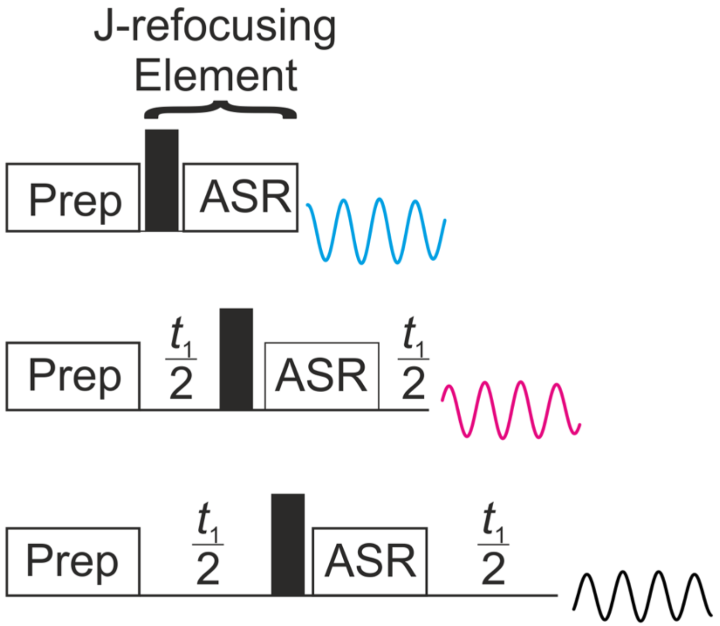
BIRD provides full sensitivity when combined with HSQC

Band Selective provides full sensitivity for targeted signals but is not broadband

Acquisition approaches

ASR:

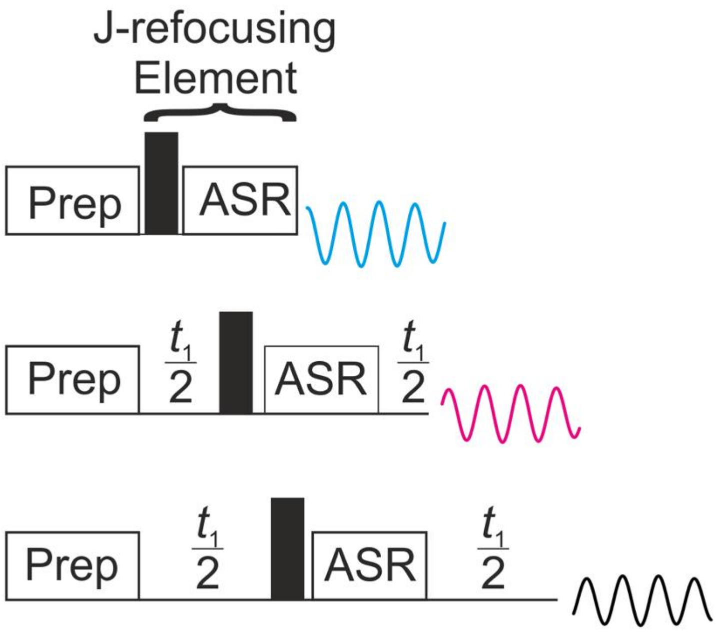




Interferogram Acquisition

Real-time Acquisition

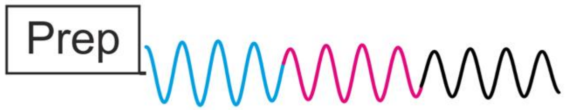
Interferogram acquisition



Collect a pseudo 2D experiment

Typically, t_1 = 20 ms *chunk* of FID in each step

10 – 50 increments gives 200 ms – 1 s FID



Join *chunks* together then Fourier transform to generate the pure shift spectrum

2D acquisition, so experiment duration is extended

Real-time acquisition

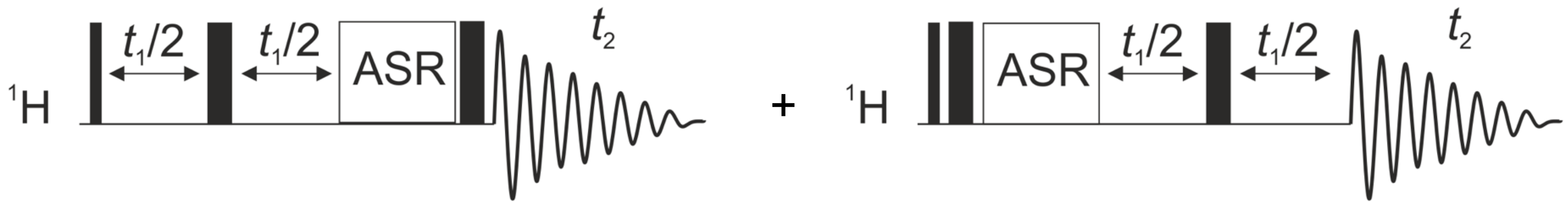
Apply J-refocusing element every 20 ms of *windowed* acquisition

Chunks are joined automatically by the spectrometer.

Fourier transform like a conventional 1D experiment to generate the pure shift spectrum

T_2 relaxation occurs during the refocusing element so there are discontinuities/steps in the FID that lead to sidebands in the spectrum

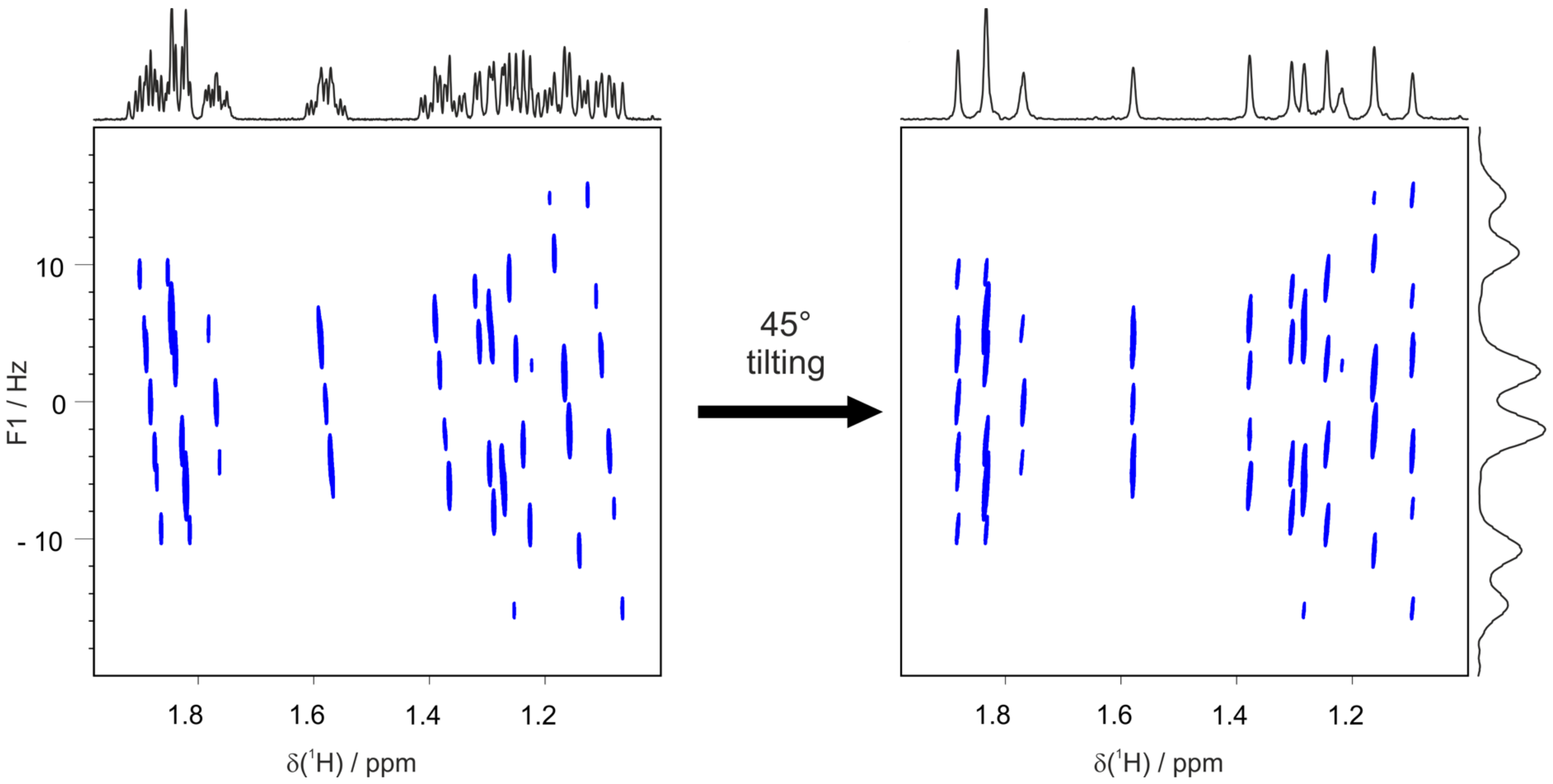
2D J-resolved acquisition



Combing two 2D *J*-resolved spectra with active spin refocusing elements included before and after the spin echo produces absorption mode 2D J spectra that can be processed to produce pure shift spectra but retain multiplets in F_1

Reference., **53**, 6690 (2014)

2D J-resolved acquisition



Combing two 2D *J*-resolved spectra with active spin refocusing elements included before and after the spin echo produces absorption mode 2D J spectra that can be processed to produce pure shift spectra but also retain the J coupling in F_1

Summary

Pure shift NMR requires the division of the spin system into active and passive groups

There are 4 main methods:

- Band selective
- Zangger-Sterk
- Bilinear Rotation Decoupling
- PSYCHE

Pure shift acquisition requires:

- periodic refocusing of J (in a 1D or pseudo-2D manner) *or*
- 2D J spectroscopy acquisition
  - so that the J coupling is suppressed or separated from chemical shift

References

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More Information

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