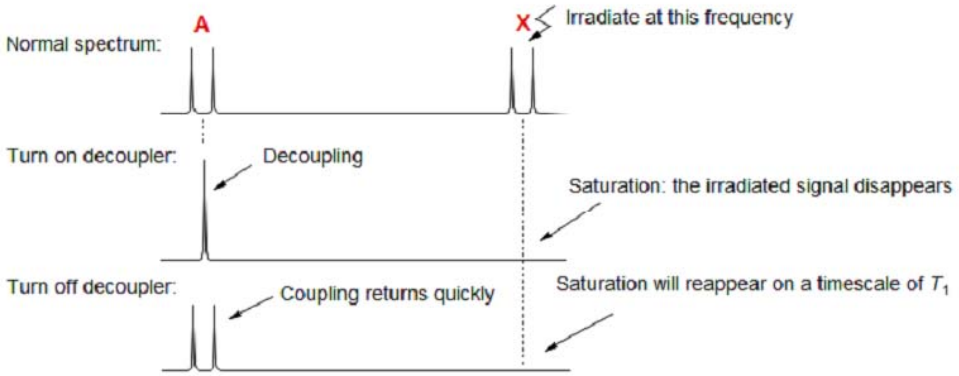
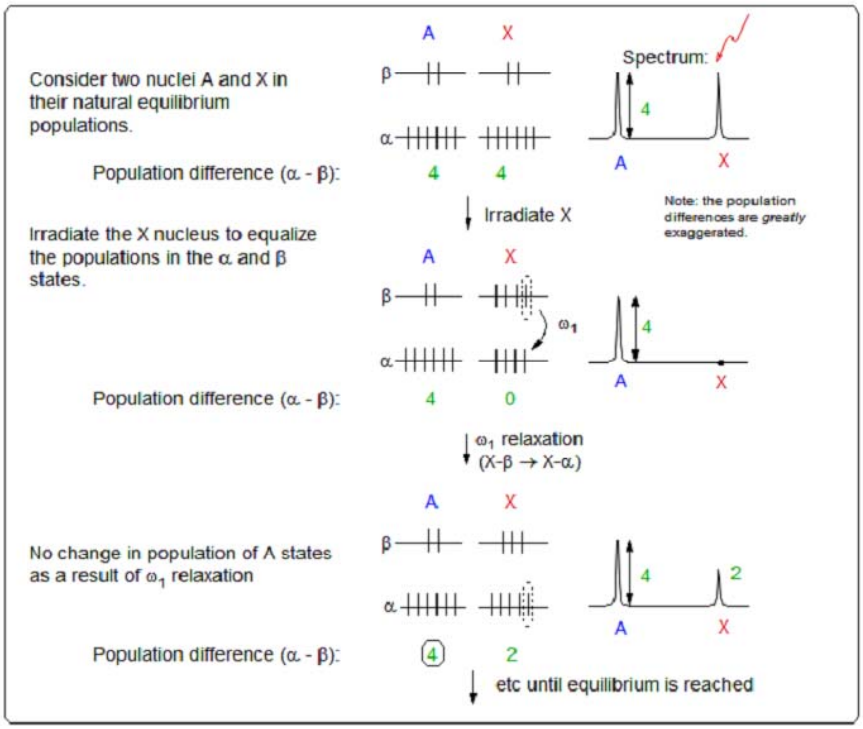
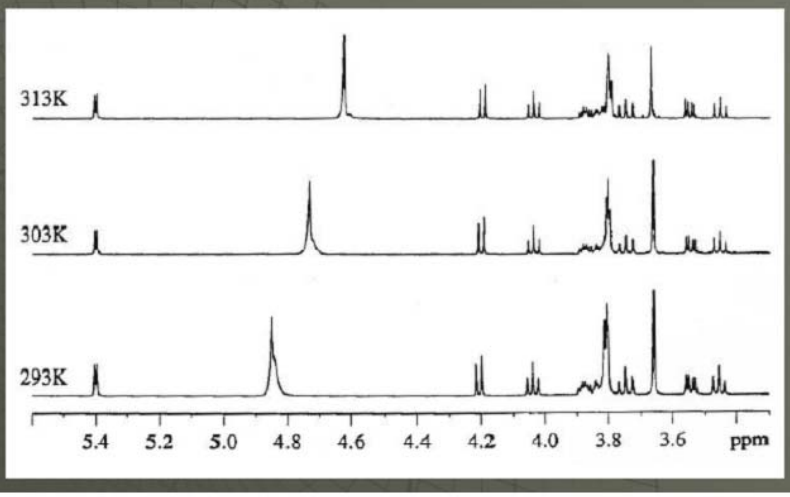
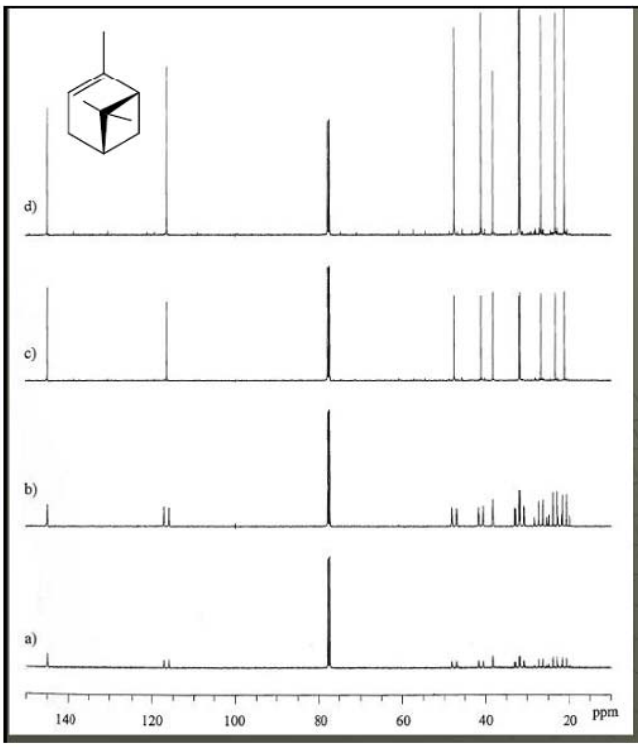

Normal spectrum:
A
X
Irradiate at this frequency
Turn on decoupler:
Decoupling
Saturation: the irradiated signal disappears
Turn off decoupler:
Coupling returns quickly
Saturation will reappear on a timescale of T_1


Consider two nuclei A and X in their natural equilibrium populations.
Population difference (α - β):
4 4
Irradiate X
Spectrum:
Note: the population differences are greatly exaggerated.
Irradiate the X nucleus to equalize the populations in the α and β states.
ω_1
Population difference (α - β):
4 0
ω_1 relaxation
(X-β → X-α)
No change in population of A states as a result of ω_1 relaxation
Population difference (α - β):
4 2
etc until equilibrium is reached

The temperature dependence of HDO signal





^{13}C spectra of α-pinene in $CDCl_3$:

a) with C,H couplings;

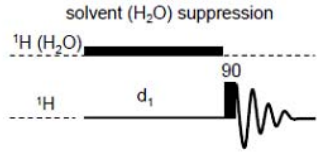
b) with gated decoupling *(coupled spectrum with NOE)*;

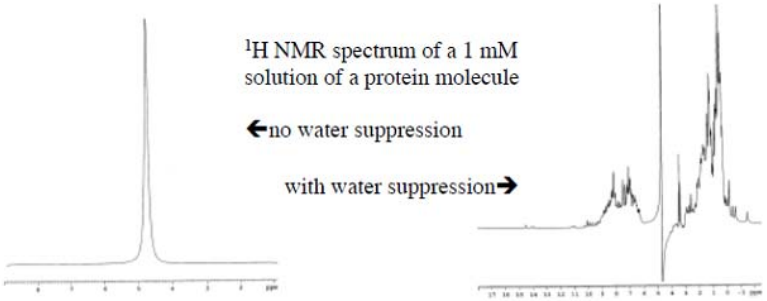
c) with inverse-gated decoupling *(decoupled spectrum without NOE)*;

d) with BB decoupling *(decoupled spectrum with NOE)*.

OTHER DECOUPLING: SOLVENT (H_2O) SUPPRESSION

- ^1H NMR in protonated solvents is problematic
- The concentration of H_2O in H_2O is ~55 M (^1H concentration ~110 M)
- Signals from other molecules are obscured by the large H_2O signal
- One way to attenuate the H_2O signal is by "decoupling", or saturating the resonance (called solvent suppression by "saturation" or "presaturation")
- A long, selective, low power pulse is used to saturate selectively the H_2O frequency, which greatly attenuates the signal in the spectrum

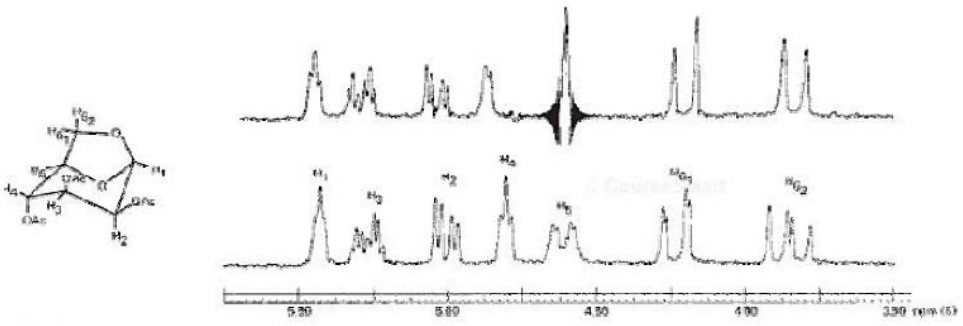




Spin Decoupling.

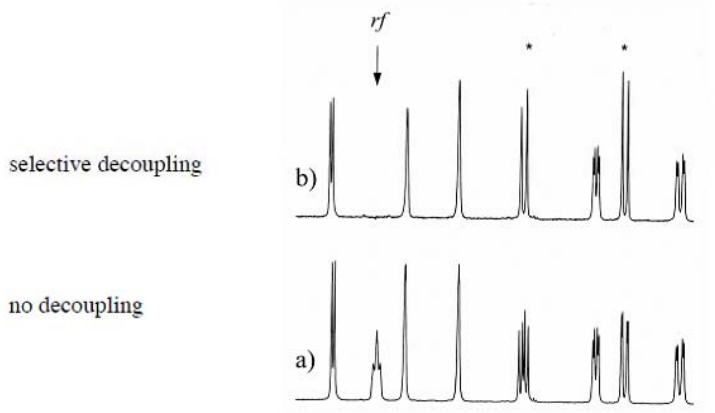
A more complex example is illustrated using the bicyclic sugar mannosan triacetate, which has a nearly first-order spectrum with numerous coupling partners.

Irradiation of H_5 @ δ 4.62 produces simplification of the resonances of its vicinal partners H_4, $H_{6/1}$ $H_{6/2}$ as well as its long- range zigzag partner H_3:



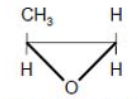
SELECTIVE SPIN DECOUPLING

- selective decoupling can identify signals from coupled nuclei, thus assisting to establish connectivity/structure
- intensities of signals from coupled nuclei are improved (due to multiplet collapse)
  - integrals are unchanged for signals from coupled nuclei

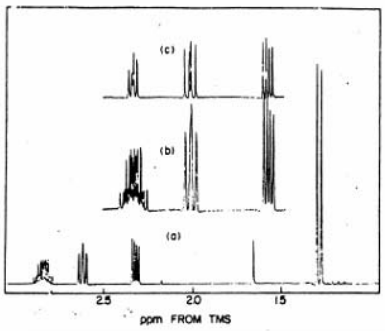


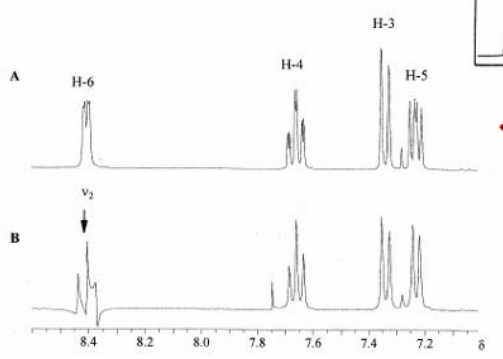
SELECTIVE SPIN DECOUPLING

- (*right*) selective decoupling of the methyl hydrogens (1.3 ppm) of propylene oxide confirms identity of signal from methine H (2.8 ppm)

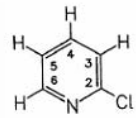


propylene oxide





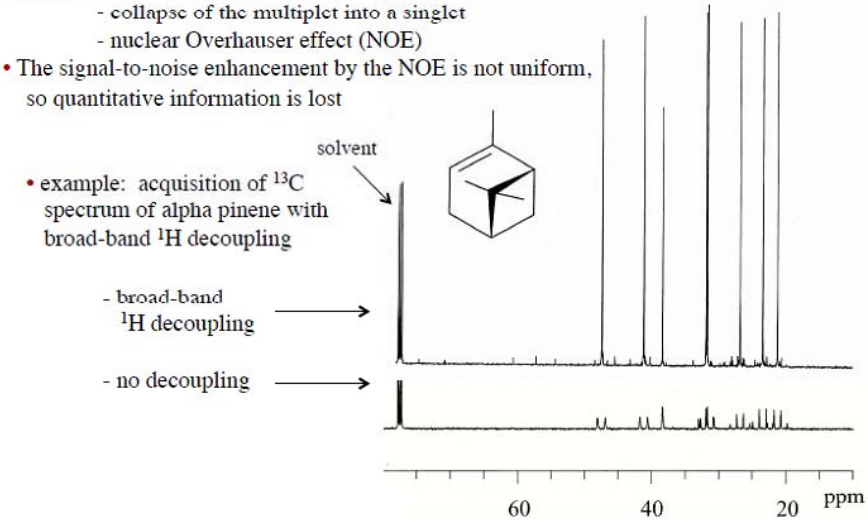
- (*left*) selective decoupling of H-6 of 2-chloropyridine leads to assignment of signals from H-3, H-4 and H-5



2-chloropyridine

BROAD-BAND DECOUPLING

- Substantial spectral simplification (multiplets collapse to singlets)
- Substantial signal-to-noise gains
- Signal-to-noise gains arise from two sources:
  - collapse of the multiplet into a singlet
  - nuclear Overhauser effect (NOE)
- The signal-to-noise enhancement by the NOE is not uniform, so quantitative information is lost
- example: acquisition of ^{13}C spectrum of alpha pinene with broad-band ^{1}H decoupling



سازمان پژوهشهای علمی و صنعتی ایران حسین رحمانی پژوهشکده فناوریهای شیمیایی