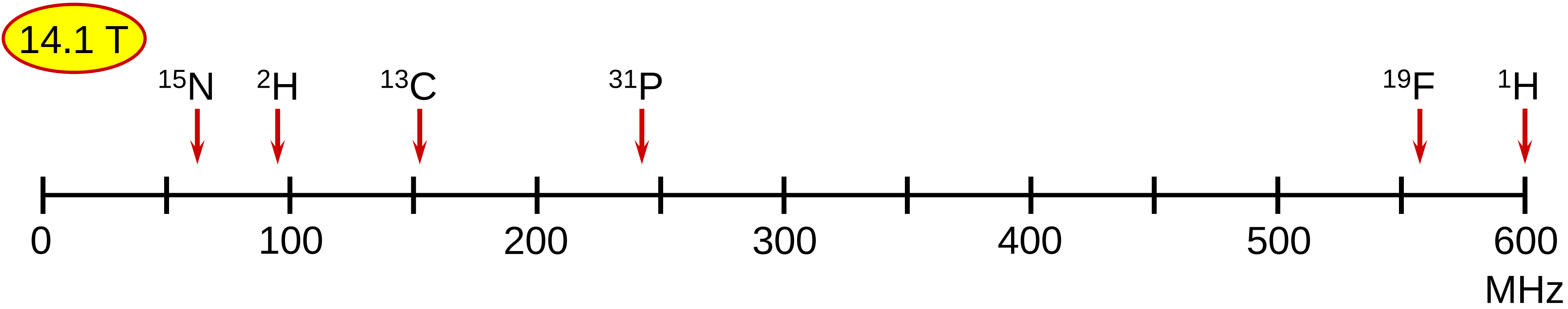
Methods of Double resonance

^{13}C spectra and heteronuclear decoupling, experiments APT and DEPT

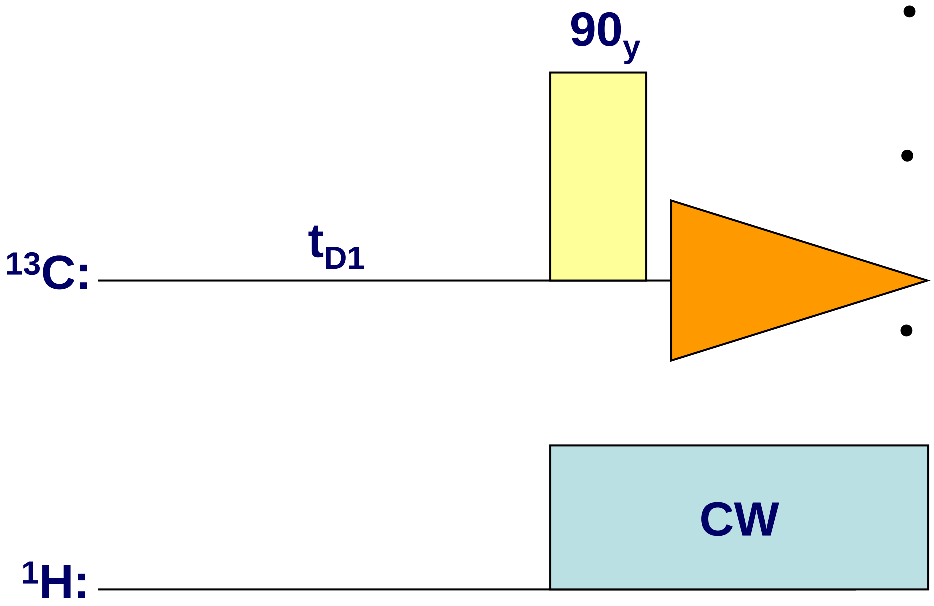
Double resonance



- The Larmor frequencies of the different isotopes are very different
- The radiofrequency field is in resonance with only one isotope
- Multiple radiofrequency irradiations with different frequencies can be used at the same time

Double resonance– two RF fields in resonance with two isotopes

Decoupling and ^{13}C spectrum



- Short RF pulse in resonance with the Larmor frequency of 13C
- Excitation – flipping 13C magnetization into the xy-plane
- Detection of 13C NMR signal

- Continuous RF field (very long pulse) in resonance with the Larmor frequency of 1H

- Fast jumps between levels $m = \pm\frac{1}{2}$

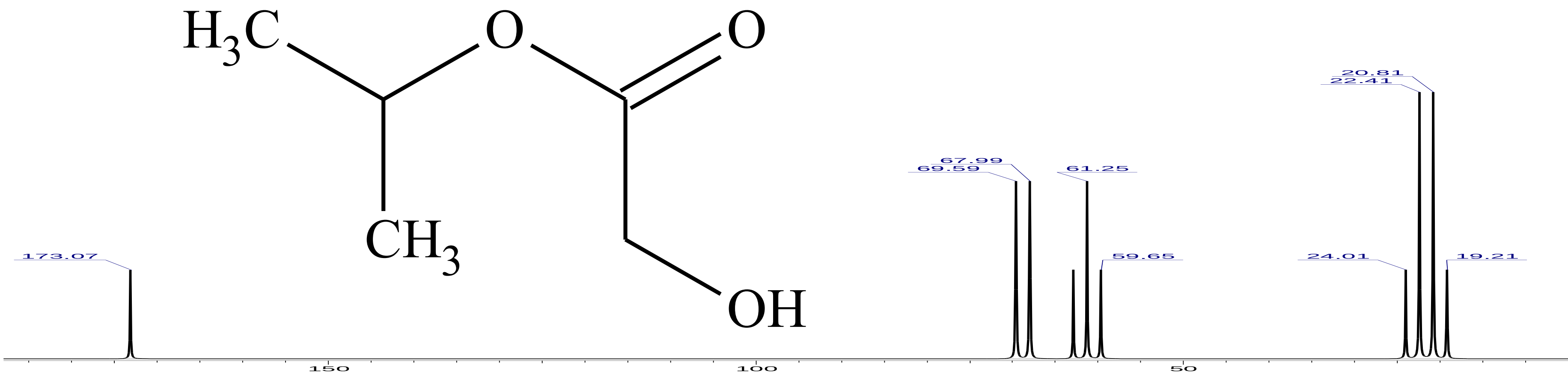
Averaging = effectively spin 0

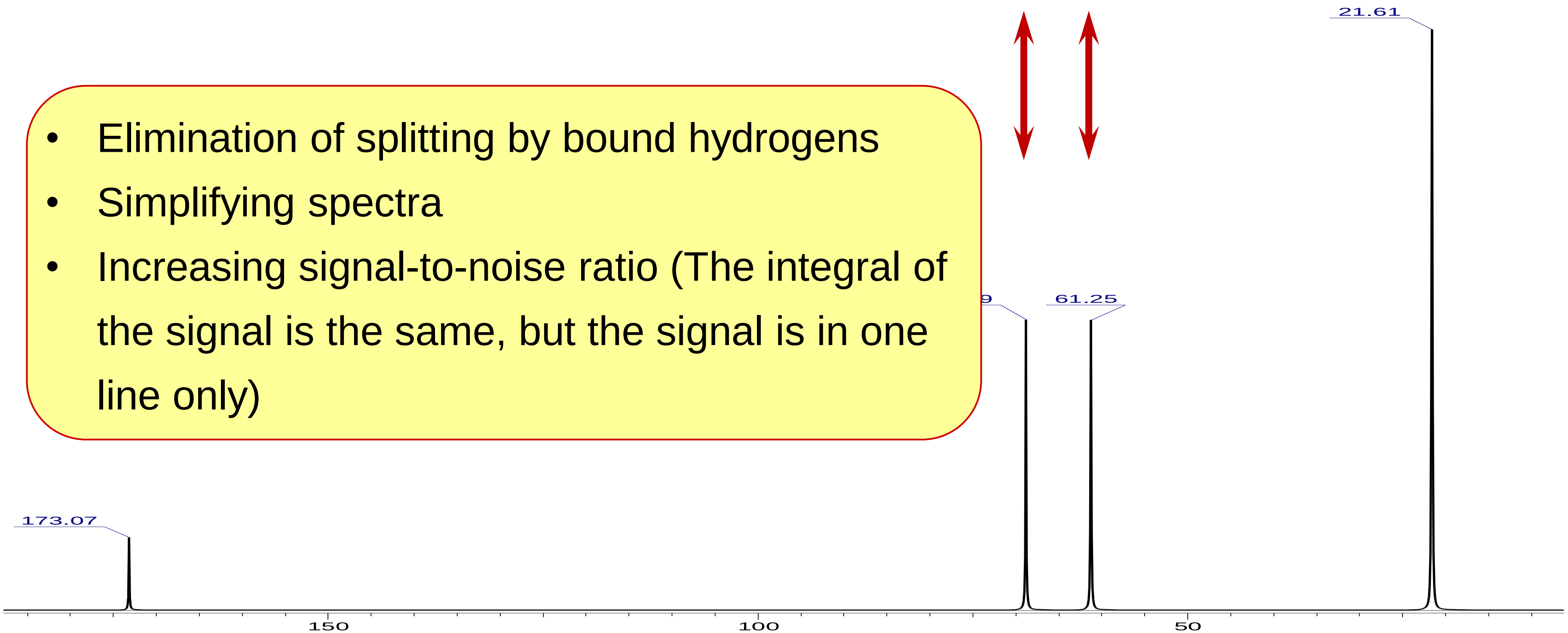
„cancellation“ of J interaction

decoupling

- Different irradiation schemes (sequences of different pulses) for higher efficiency of averaging the spin states – CW, WALTZ, GARP, …

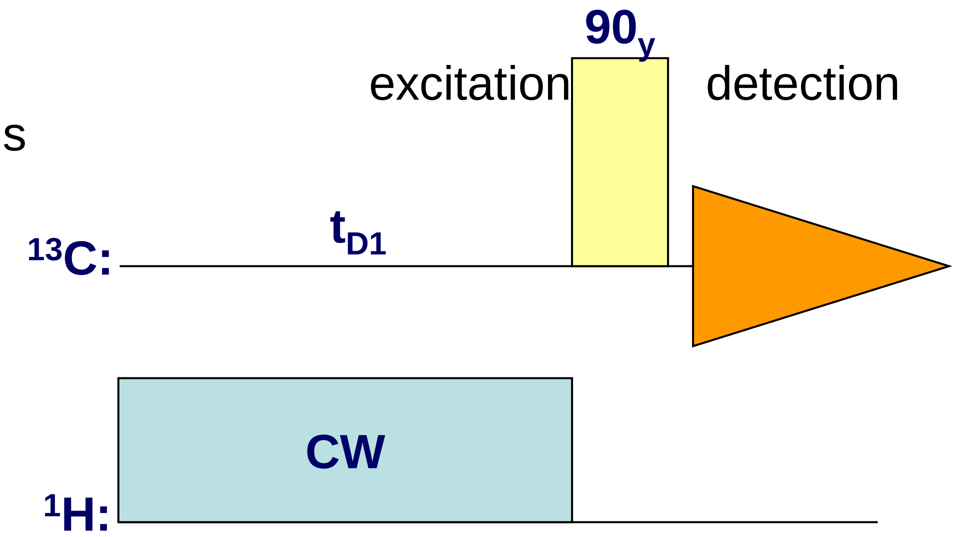
Decoupling and ^{13}C spectrum





- Elimination of splitting by bound hydrogens
- Simplifying spectra
- Increasing signal-to-noise ratio (The integral of the signal is the same, but the signal is in one line only)

Decoupling and heteronuclear NOE



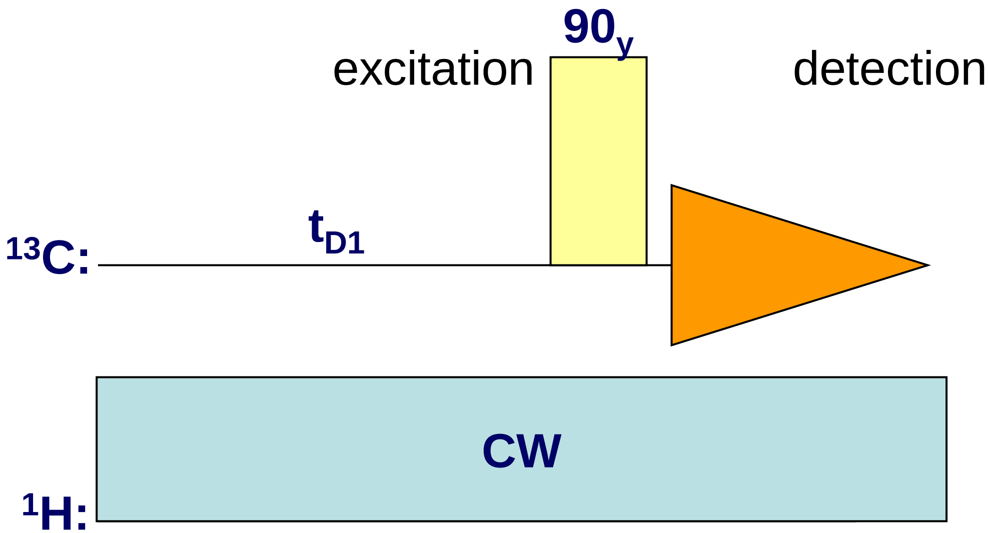
- 13C magnetization is along the z-axis (before the excitation pulse)
- Continuous RF field in resonance with 1H Larmor frequency
- saturation – equalization of level occupancies (of 1H transitions)
- Influencing intensity in 13C transitions = Nuclear Overhauser effect (NOE)

NOE increases signal strength of 13C nuclei with direclty bonded hydrogens

(up to by 199%)

Depends on relaxation - local mobility
The enhancement is different for different carbons

^{13}C experiment with continuous decoupling



- Natural abundance of 13C is 1%, hence the low signal strength
- The measurement is repeated many times, signal accumulates, noise cancels randomly
- There is a time delay between each measurement when the 13C magnetization recovers (T1 relaxation)

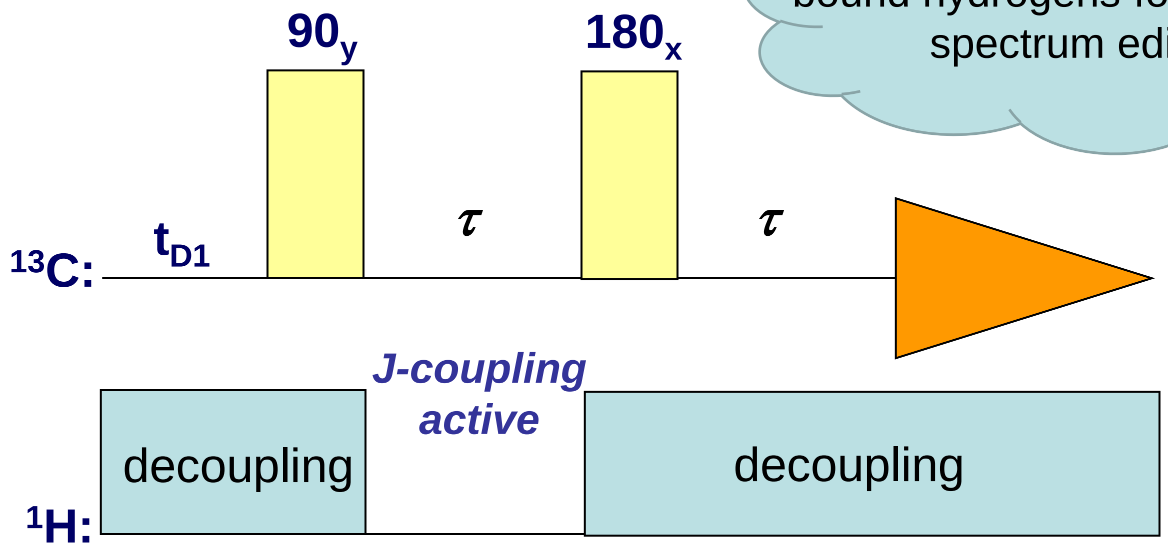
13C spectra **are not quantitative**
- NOE enhancement
- Insufficient relaxation

NOTE: measurement can also be set for quantitative response!!!

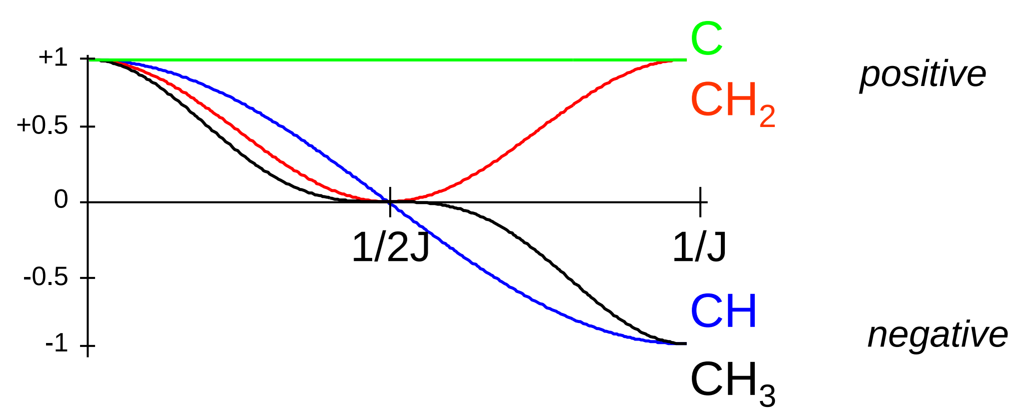
APT Experiment

Uses J-interaction with directly bound hydrogens for controlled spectrum editing

APT – attached proton test



Amplitude of 13C signal is modulated depending on the number bound hydrogens

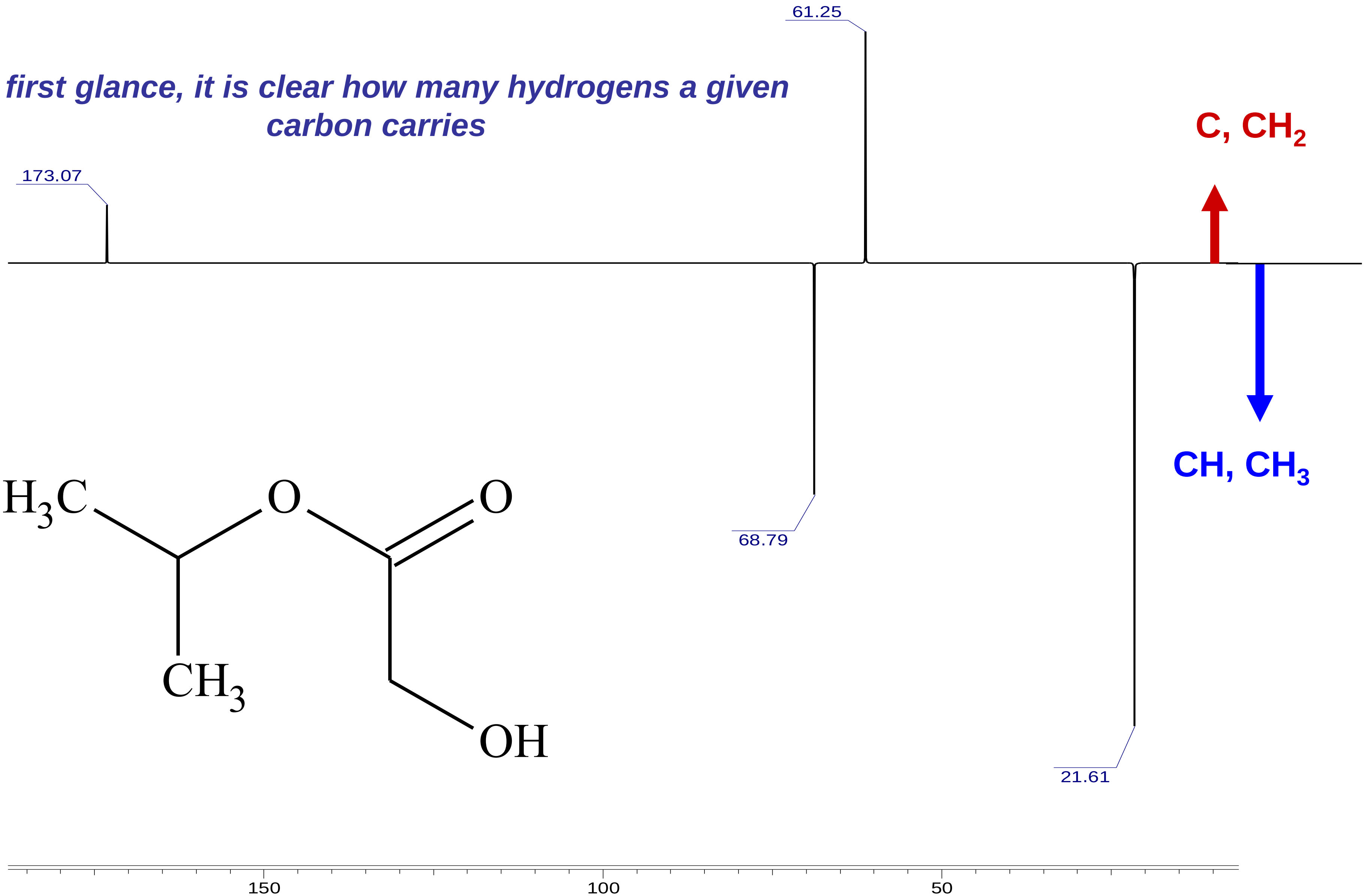


Pulse sequence

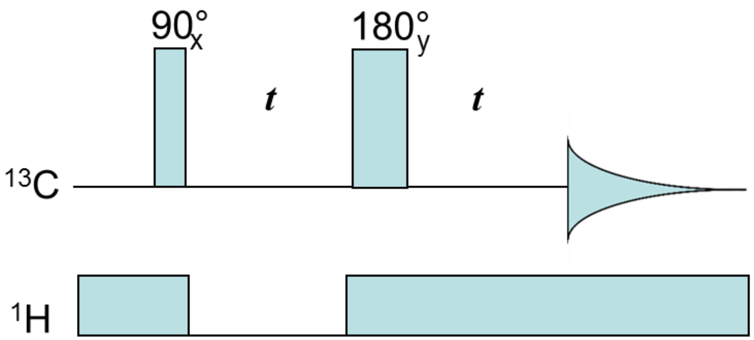
Sophisticated manipulation with spin system (magnetization)

APT experiment

At first glance, it is clear how many hydrogens a given carbon carries



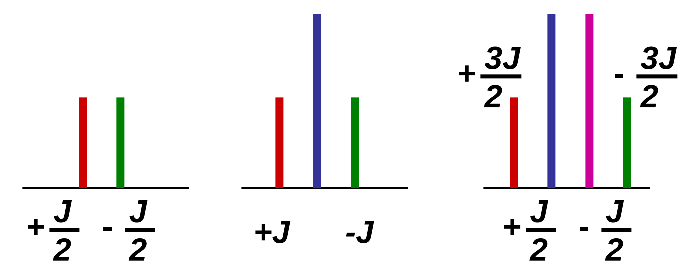
APT experiment – explanation



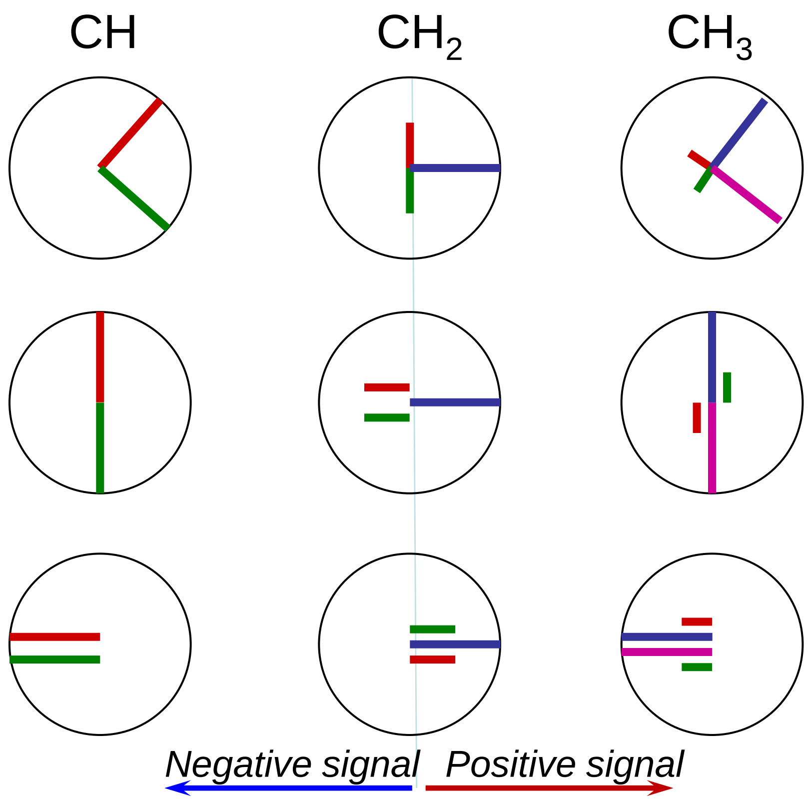
Spin echo refocuses chemical shift evolution

(we'll explain later)

J-coupling is active only in one half of the echo



Components of 13C signal have different rotation frequencies



$t = \frac{1}{4J}$ — *All signals positive*

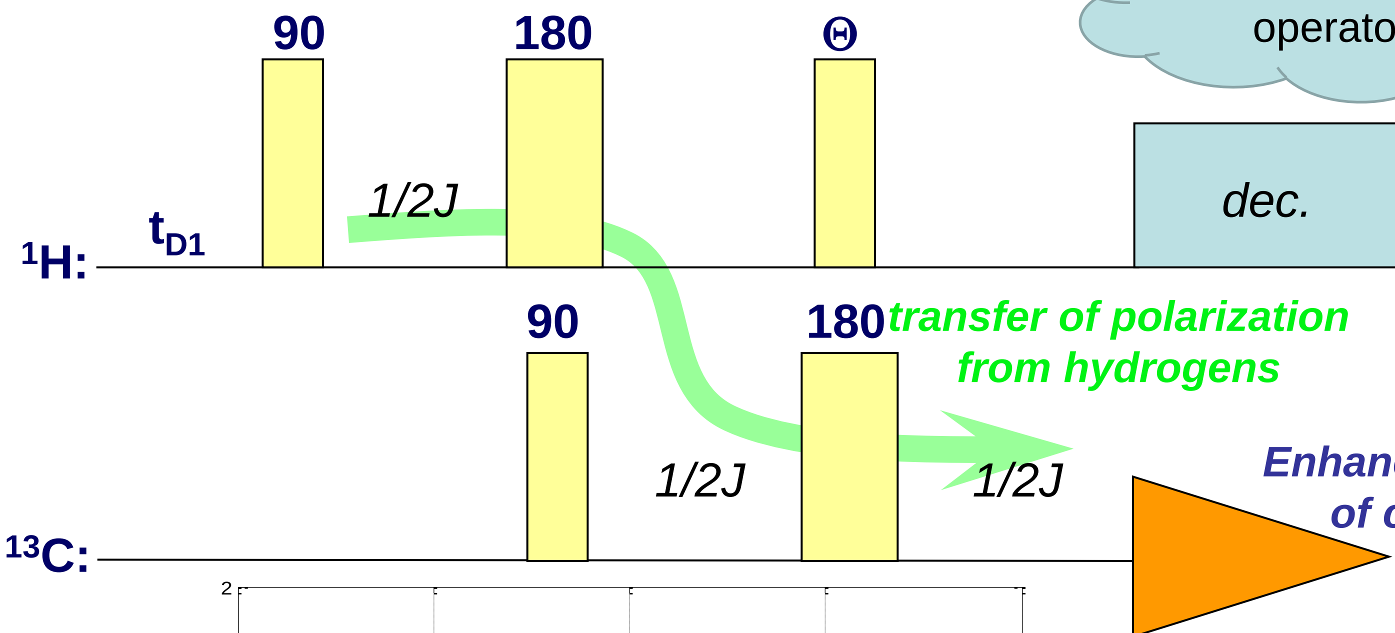
$t = \frac{1}{2J}$ — *Quaternary carbons only*

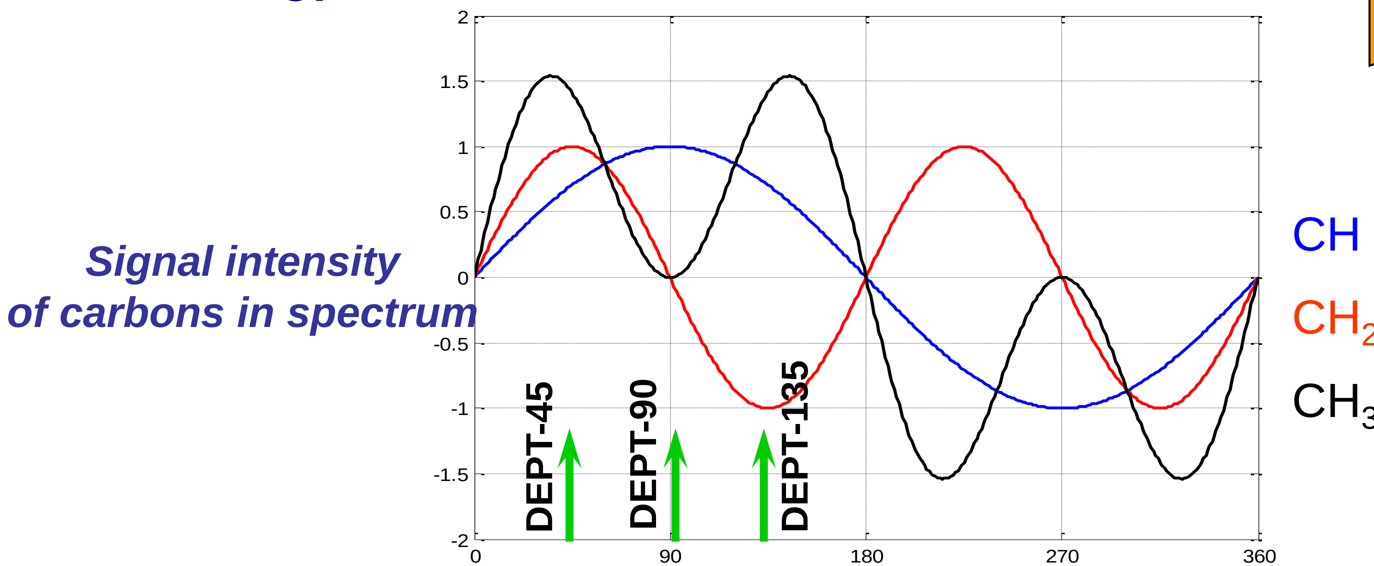
$t = \frac{1}{J}$ — *Negative* *Positive* *Negative*

DEPT experiment

DEPT – distorsionless enhancement by polarization transfer

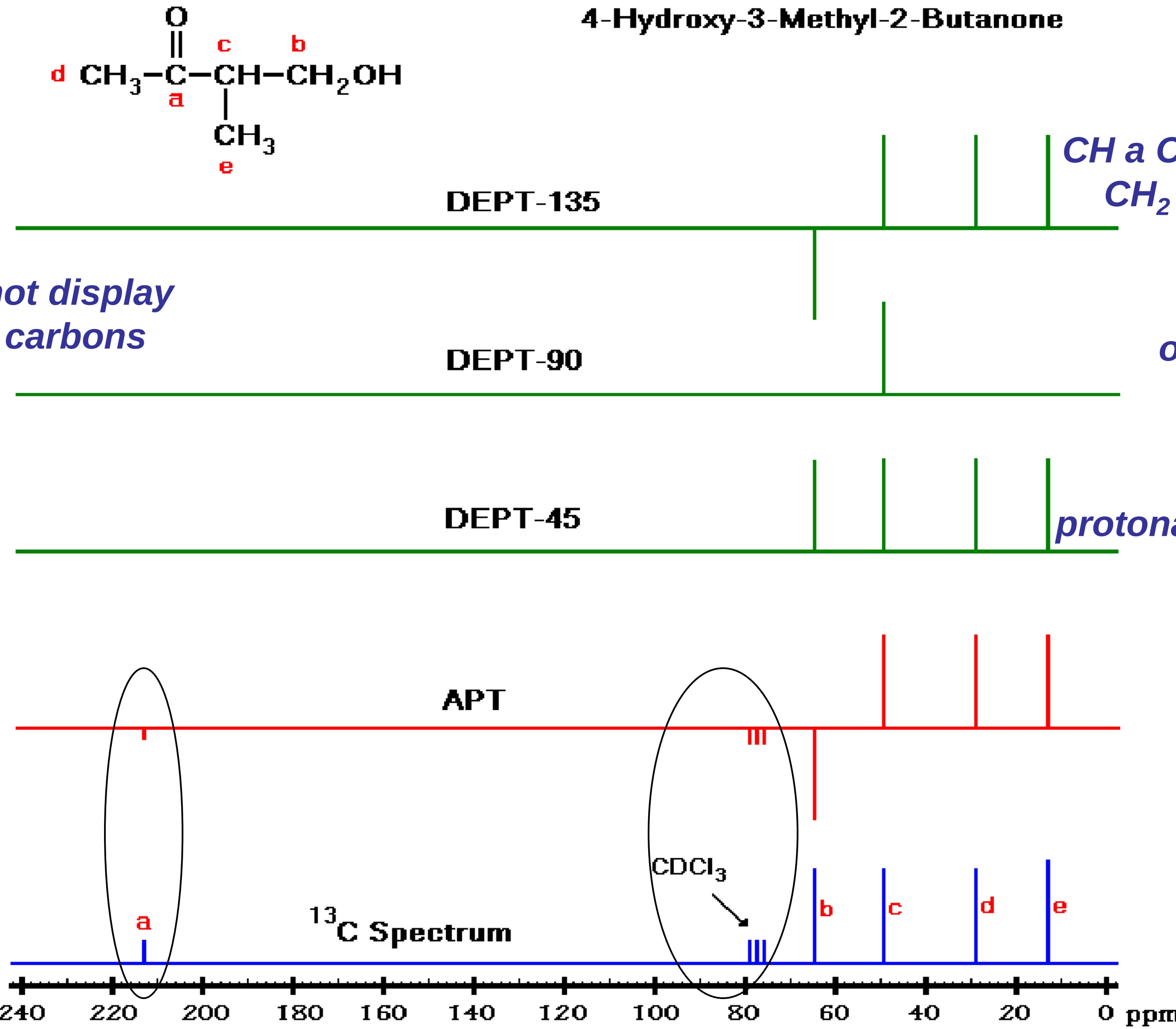
We'll explain later using product operators





editing multiplicity by the last pulse

DEPT experiment



CH a CH_3 positive
CH_2 negative

DEPT does not display quaternary carbons

only CH

all protonated carbons