Introduction to 1D and 2D NMR Spectroscopy

(4) Vector Model and Relaxations

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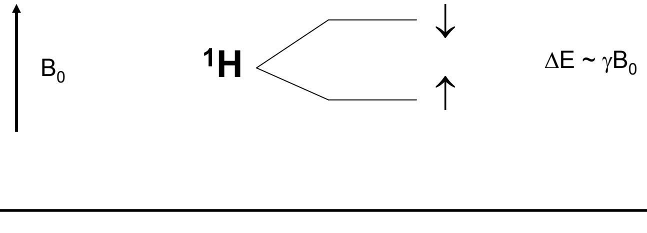
Approximate Description 1: Energy level model

- Magnetic field aligns the nuclei to two directions
  - => energy level splitting
- Population ratio of the two states observes Boltzmann distribution
  - Practically, ratio very close to 1:1 due to the small energy difference
- Radio frequency (RF) pulse pumps nuclei from low energy to high energy level
  - Frequency of the pulse must be equal to the energy splitting – "resonance"
- *Helpful to understand relaxation phenomena*
- *Not accurate for describing many other NMR phenomena*



Approximate Description 2: Vector Model

Spinning Top

- Spinning top creates a “moment”
- When the moment is parallel to gravity, moment keeps constant
- When the moment is not parallel to gravity, it rotates around the gravity direction – “precession”

Nuclear Magnetic Moment

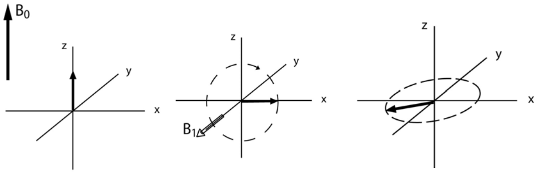
- Nuclear spin has a moment – magnetic moment
- B_0 aligns the moments to up or down direction
  - The net effect is up
- RF pulses create a small magnetic field – B_1
  - The “top” precesses around B_1 to xy plane
- Then the pulse stops and the flipped top precesses around B_0
- Only horizontal component of magnetic moment generates signal

•Vector model is more useful than energy level model; suitable for:

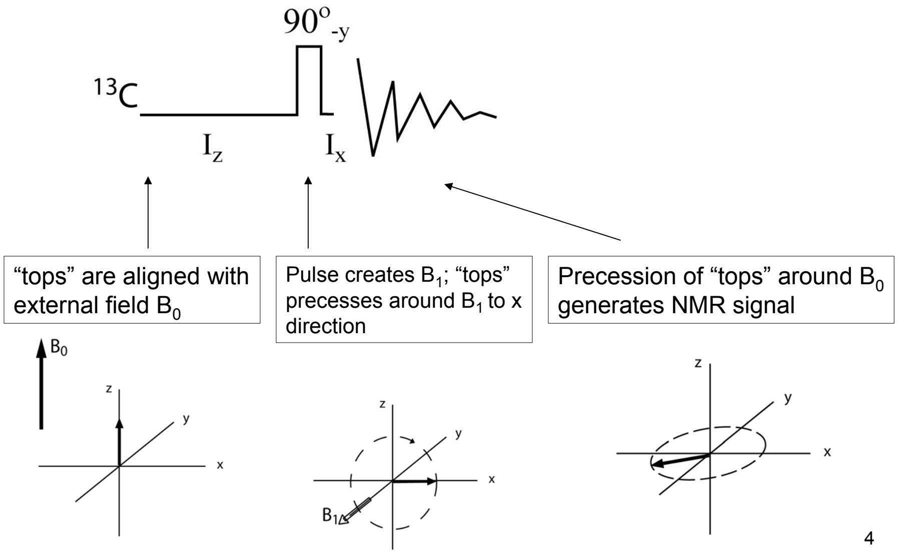
•1D NMR

•Relaxation

• cannot adequately describe coupled spins and 2D NMR



One Dimensional NMR in Vector Model



“tops” are aligned with external field B_0

Pulse creates B_1; “tops” precesses around B_1 to x direction

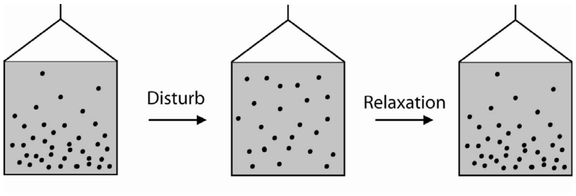
Precession of “tops” around B_0 generates NMR signal

- A “90^o pulse”
- What signal would we observe if we double the pulse length (make it a 180^o pulse)?
- How about tripling the pulse length (a 270^o pulse)?

Accurate Description: Density Operator

- **Uses rigorous quantum mechanics**
- **Magnetic moments are expressed as matrices**
- **Pulses are expressed as operators to matrices**
  - The most complete description
  - But less intuitive

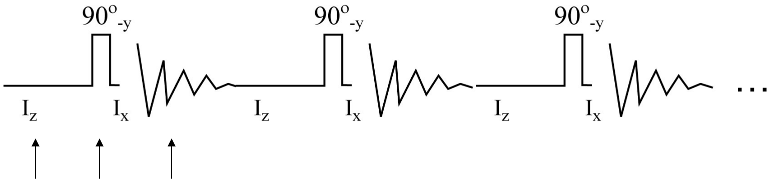
T_1 Relaxation



Equilibrium **Non-Equilibrium** **Equilibrium**

- Relaxation: process from high-energy (excited) state to low-energy (equilibrium) state
- Understanding of relaxation is critical for quantitative and certain 2D NMR

Experimental Considerations



Recycle Delay (*d1*)

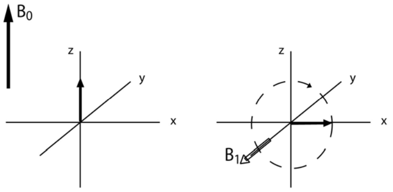
pulsing

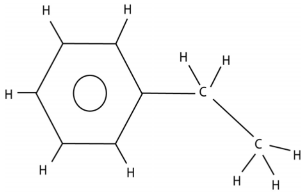
Signal acquisition (*aq*)

- T_1 is the time to recover to original magnitude in *z* direction after each pulsing
  - Low energy state: magnetic moment aligned with B_0
  - High energy state: magnetic moment on horizontal plane
- maximum signal is obtained when T_1 relaxation is complete
  - i.e. when recycle delay (d1) + acquisition (aq) is >= $5*T_1$

T_1 Relaxation: Important Factors

- T_1 relaxation must be facilitated by some energy source
  - Magnetization is very difficult to relax by itself - “fluctuation” is necessary
    - *apples will not fall if you don’t shake the tree!*
    - Reminder: T_1 is the relaxation of a nuclear energy state, driven by molecular motion
  - Fluctuation of dipolar coupling during molecule tumbling is the most important source of T_1 relaxation for common organic molecules
    - Presence of a strong dipolar coupling (interaction between neighboring nuclei)
      - Not J-coupling
      - eg. $CHCl_3$ has a long ^{1}H T_1;
      - Aromatic protons have longer T_1 than aliphatic protons
    - Presence of molecular motion
      - Proton T_1 of typical solution nmr samples ~ 1-5 s; ^{13}C T_1 of diamond > 1000 s



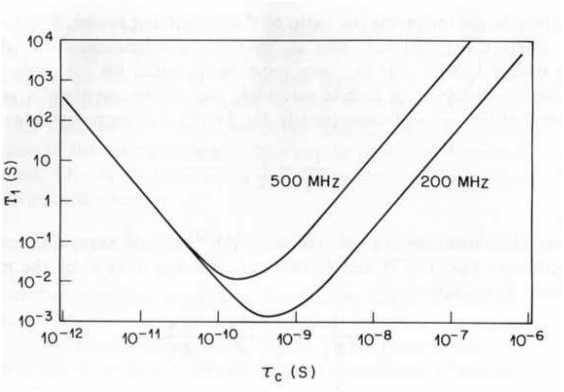


Dipolar Coupling vs. J Coupling

	J-coupling	Dipolar coupling
Participants	Interaction between neighboring nuclei (1H-1H, 1H-13C, etc.)	same
Mechanism	Through Bond (very small at >=5 bonds away)	Through space (very small at >=6Å away)
Important effects	1H multiplets, COSY and HMQC correlation peaks	Relaxations, NOE, NOESY peaks (but not observable on spectra)

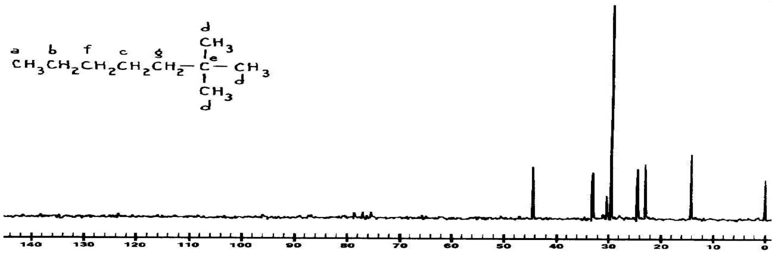
T_1 Relaxation and Motion

- Relaxation is the fastest when motion rate is close to resonance frequency
  - *Swing goes the highest when you pump at the right pace*
- Small molecules in solution are in the “fast motion regime”
- End groups of polymer usually have longer T_1 than the middle units
  - Significance in M_n measurement
- Molecules in crystalline or glassy solid are in the “slow motion regime”



T_1 Relaxation: Examples

- ^1H T_1 ($CHCl_3$) vs. ^1H T_1 (C_6H_6) vs. ^1H T_1 (C_6H_{12})
  - *Why do aromatic protons in ethylbenzene integrate to less than 5?*
- ^{13}C T_1 (non-protonated C) vs. ^{13}C T_1 (protonated C)
- ^{13}C T_1 of toluene
  - Methyl = 16 s
  - C1 = 89 s
  - C2 = 24 s
  - *A fully quantitative 13C spectrum needs very long recycle delay!*



$CH_3CH_2CH_2CH_2CH_2-C(CH_3)_2-CH_3$

NOE (Nuclear Overhauser Enhancement)

- Mechanism: relaxations of dipole-coupled nuclei pairs are related
  - Heteronuclear (eg. H-C) NOE and homonuclear (eg. H-H) NOE
- Effect 1: ^{13}C signal is enhanced when surrounding protons are not fully relaxed
  - By keeping protons from relaxing (using a pulsing technique), we can enhance signal for ^{13}C
  - The enhancement is affected by the distance between ^{13}C and ^{1}H
    - NOE is due to dipolar coupling (through-space)
  - Example: for CH_3COCH_3, NOE($\underline{C}H_3$)>>NOE ($\underline{C}O$)
  - If you want to obtain quantitative ^{13}C spectrum, you need to
    - Either make sure all carbons have the same enhancement coefficient
    - Or turn off NOE
  - ^{13}C spectra with NOE: *rpar* C13CPD
  - ^{13}C spectra without NOE: *rpar* C13IG
- Effect 2: NOE can be used to probe proton-proton distance (NOESY)

How to get quantitative NMR spectra

- All nuclei on the spectrum should be fully relaxed
  - Note: unprotonated carbons and lone protons have long T_1
- NOE should be suppressed
  - Or if you can make sure that the nuclei of interest all have the same NOE enhancement
    - For example, all protonated aliphatic carbons have roughly the same enhencement factor

Summary

- Three theoretical descriptions of NMR
- Vector model – spins “precess” around magnetic field
  - – The most useful model for general NMR users
  - – Principle of a single pulse NMR experiment
- T_1 – important for quantitative NMR
  - – Needs dipolar coupling
    - e.g. quaternary carbon usually has longer T_1
  - – Needs motion
  - – Difference between dipolar coupling and J-coupling
- NOE