CHEM / BCMB 4190/6190/8189

Introductory NMR

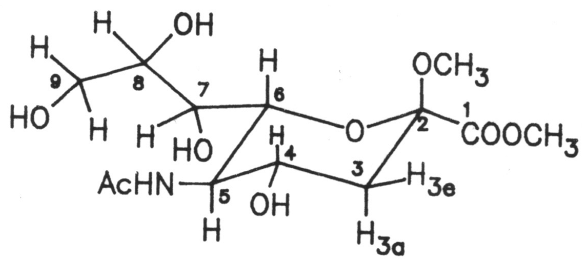
Lecture 10

Introduction to Complex Pulse Sequences

<u>Beyond simple 1D spectra</u>:

Simple 1D ^{1}H and ^{13}C spectra are not always sufficient for assigning even small organic compounds. The main problems are:
1) Assignment of the 1D spectra
2) Low S/N in spectra of insensitive nuclei with low natural abundance (e.g. ^{13}C, ^{15}N)

Example: Neuraminic Acid derivative 1



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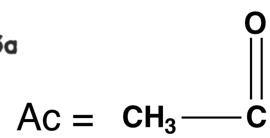
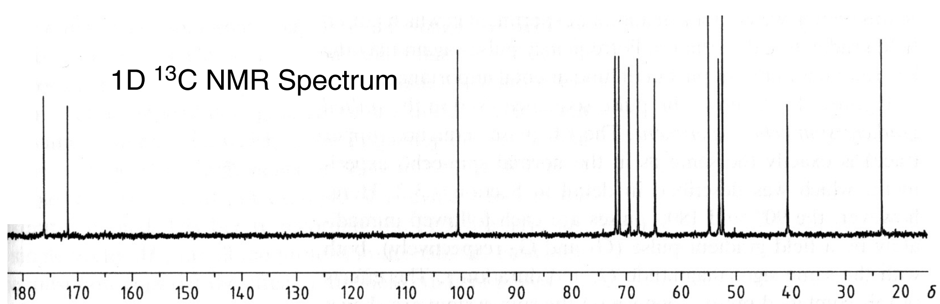
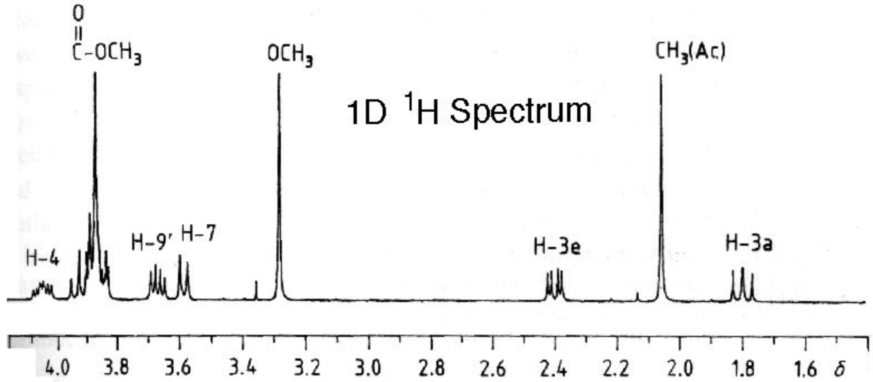






<u>We would also like to use the following information</u>:

1) ^{13}C-^{1}H correlations
2) The number of protons attach to one carbon
3) ^{1}H-^{1}H correlations
4) ^{13}C-^{13}C correlations
etc.

<u>SOLUTION:</u> **<u>Complex pulse sequences</u>**

Use multiple pulses, delays and decoupling schemes

- **Various pulses:** **hard pulses: 90˚x, 90˚y, 180˚x, 180˚y, etc.**
  selective pulses: 90˚x, 90˚y, 180˚x, 180˚y, etc.
  pulse field gradients

- **Various delays:** **fixed or variable delays**

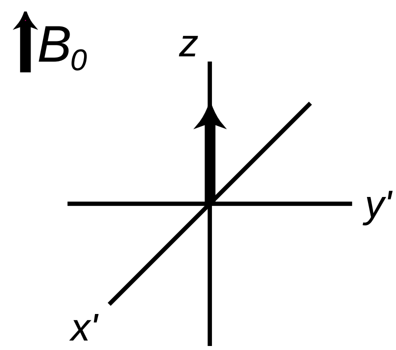
- **Decoupling:** **for selective or broadband decoupling**

<u>To analyze the effect of complex pulse sequences we use</u>:

A) <u>Vector Diagrams</u>:

- **They are EXTREMELY useful, but it is important to know that they have certain limitations i.e. difficult to explain 2nd order spectra, population transfer, zero or multiple quantum coherence, etc.**

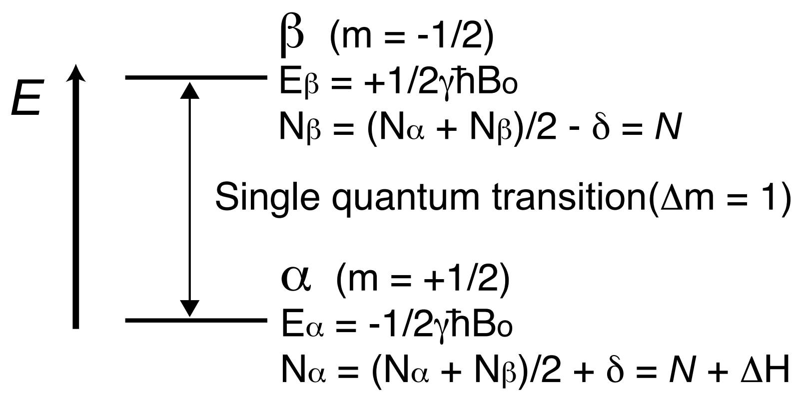
- **For ease of representation, usually in the rotating frame (x', y', and z) instead of the laboratory frame (x, y, and z) . <u>Very important to know what is the</u> <u>frequency (ν) of the rotating frame</u>.**



B) <u>Energy Diagrams:</u>

- **EXTREMELY useful for understanding energy transfer in certain experiments (e.g.: SPT, INEPT, HSQC)**

For ^1H at equilibrium:

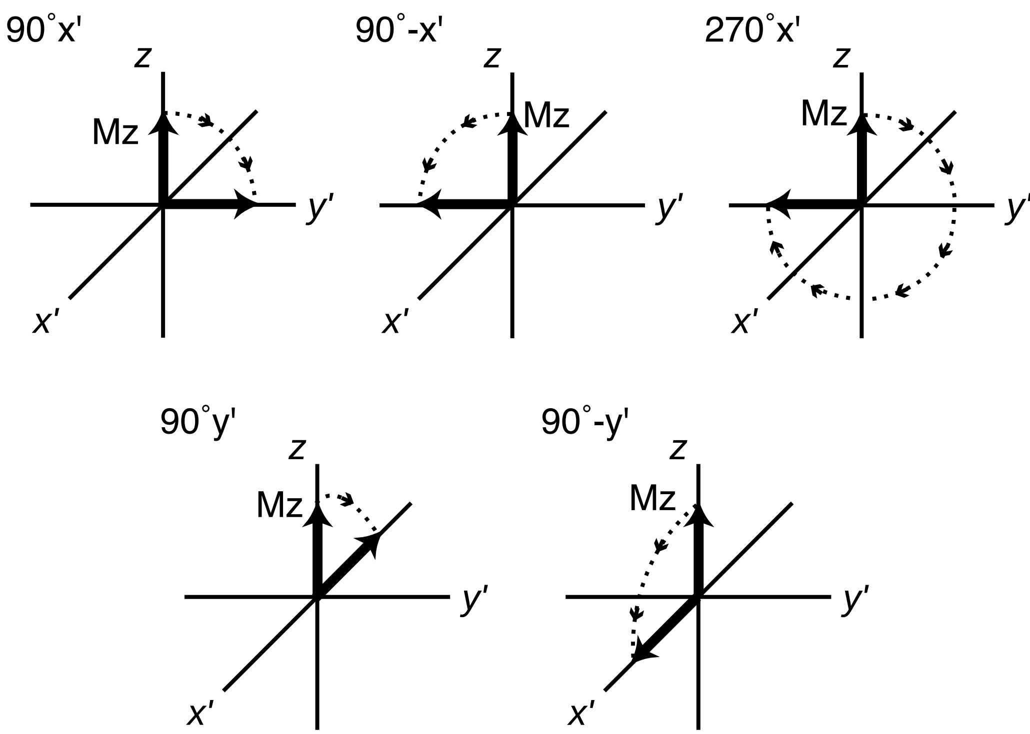


<u>Effect of a pulse on the longitudinal magnetization</u> (Mz):

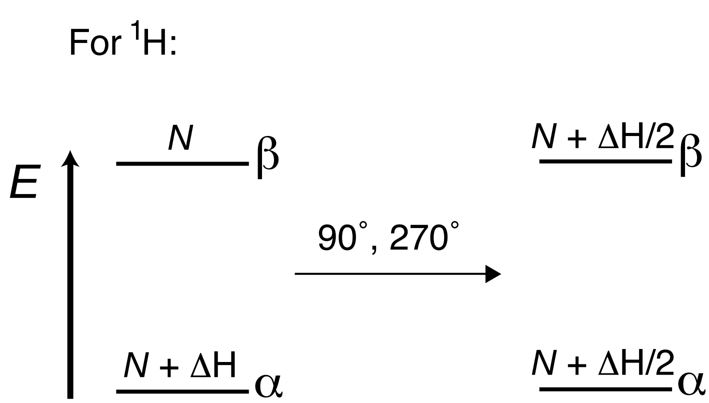
- **At equilibrium (Mz):**
    - ♦ **Bulk magnetization along z caused by Bo**
    - ♦ **Excess population in the α state**

- **After 90˚, 270˚ pulses:**

<u>Vector diagrams</u>: B1 field brings Mz to the x'-y' plane

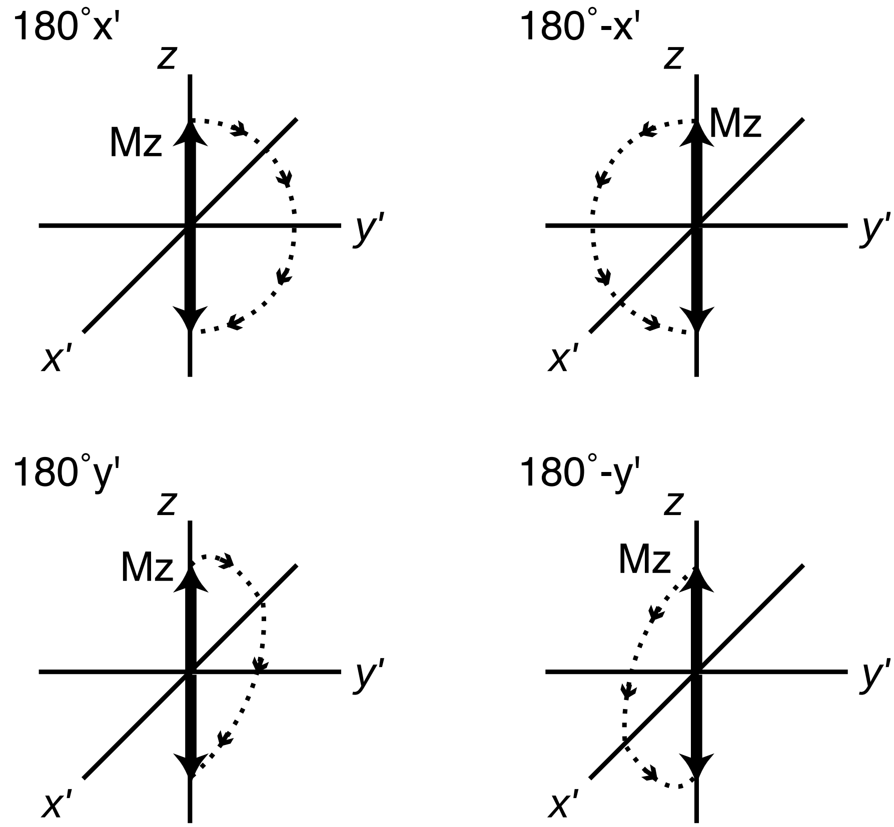


<u>Energy diagram</u>: The populations of α and β are now equal

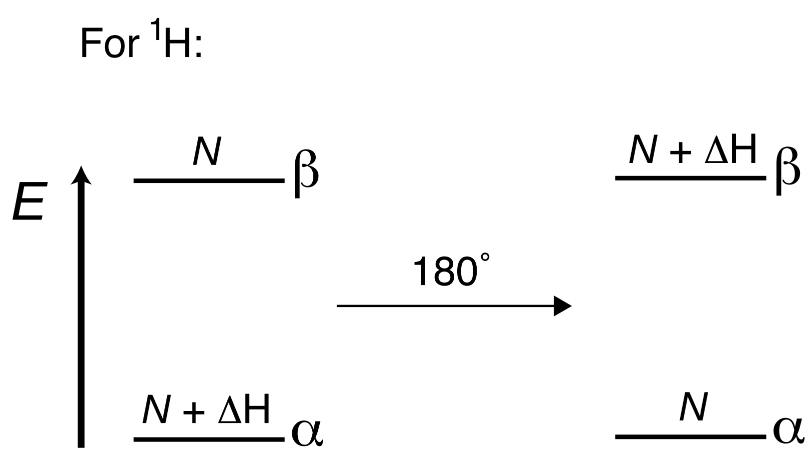


- **After 180° pulses:**

<u>Vector diagrams</u>: B1 field inverts Mz



<u>Energy diagram</u>: The populations of α and β are inverted

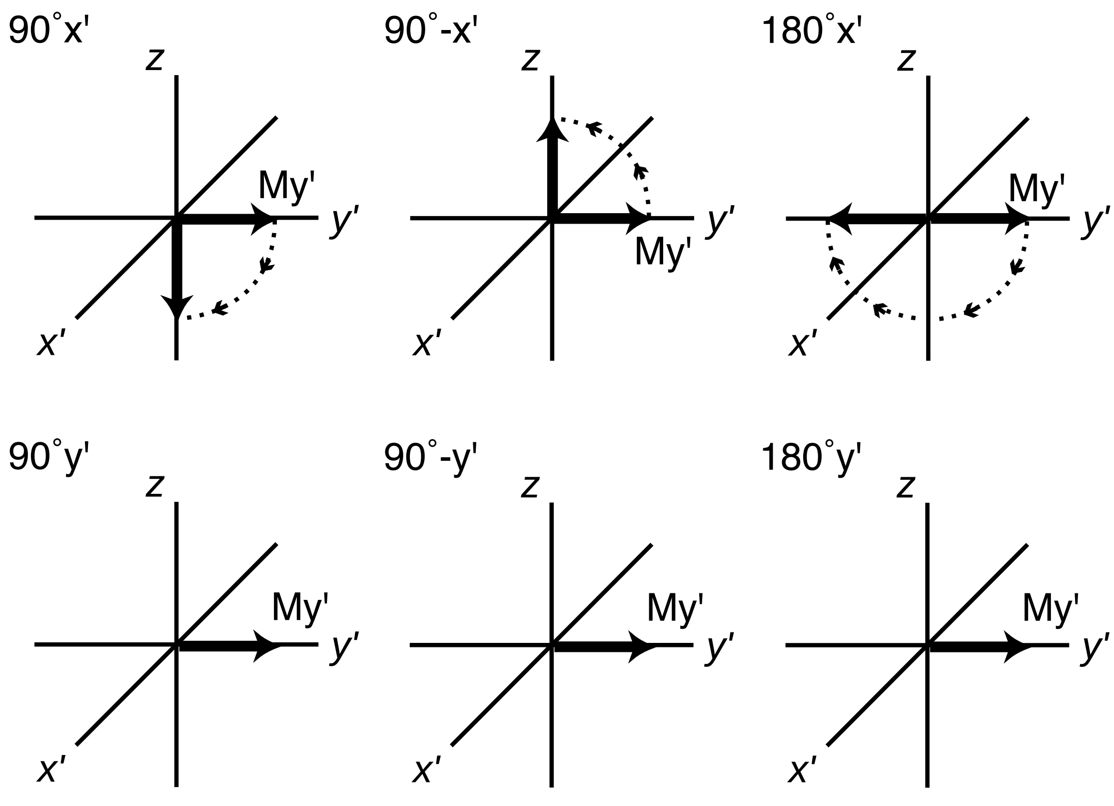


<u>Effect of a pulse on the transverse magnetization</u> (Mx', My'):

- **The transverse magnetization (Mx', My') is not at equilibrium**
  - ♦ **Bulk magnetization in the x'-y' plane**
  - ♦ **Equal populations in the α and β states**

- **Effect of 90˚ and 180˚ x and y pulses on transverse magnetization with My' component only**

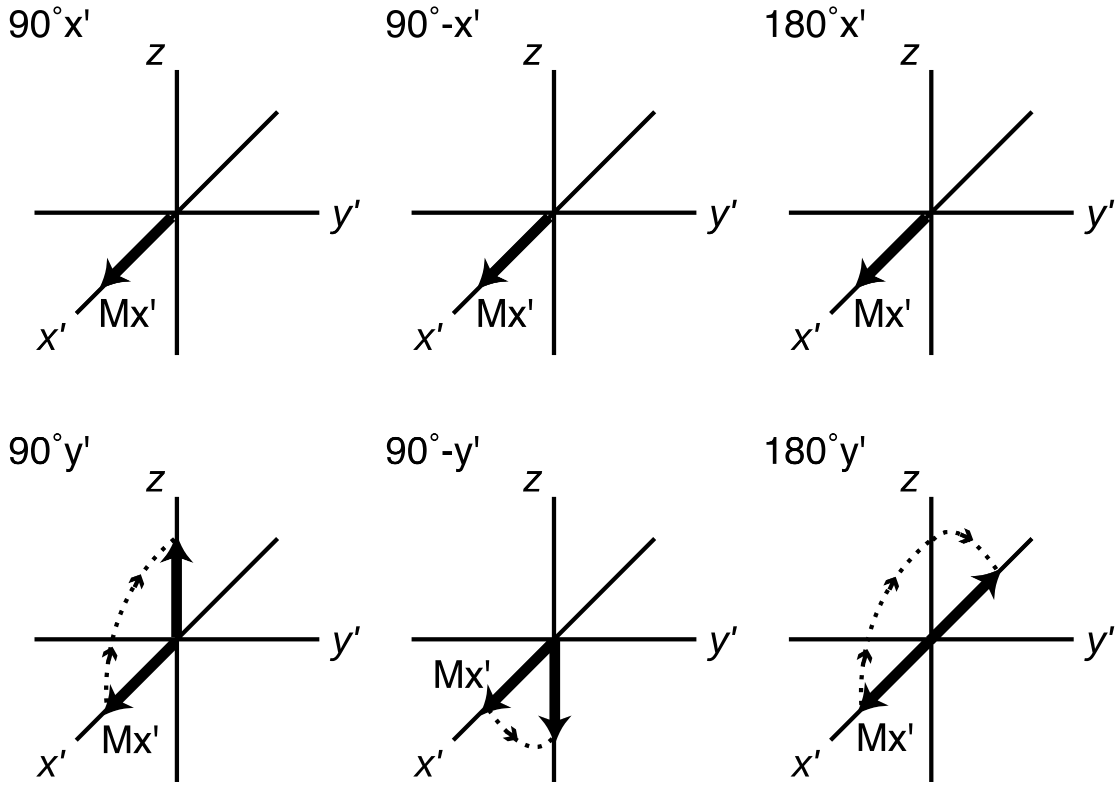
<u>Vector diagrams</u>:



<u>Energy diagrams</u>: It all depends where the final magnetization ends up (See above).

- **Effect of 90˚ and 180˚ x and y pulses on transverse magnetization with Mx' component only**

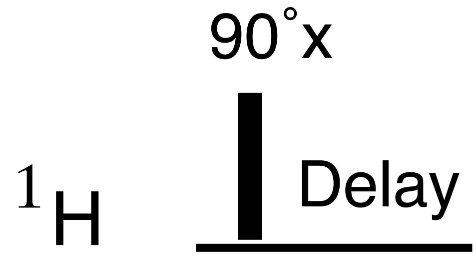
<u>**Vector diagrams**</u>**:**



<u>**Energy diagrams**</u>**: It all depends where the final magnetization ends up (See above).**

- **Transverse magnetization with Mx' and My' components:**

Where does it come from ?
Lets consider a simple pulse sequence:

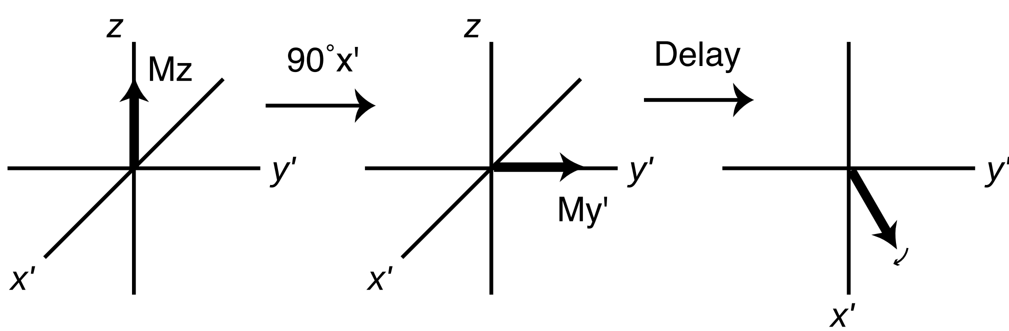


<u>Vector diagrams</u>:

A) Effect of Chemical Shift Evolution:

example:

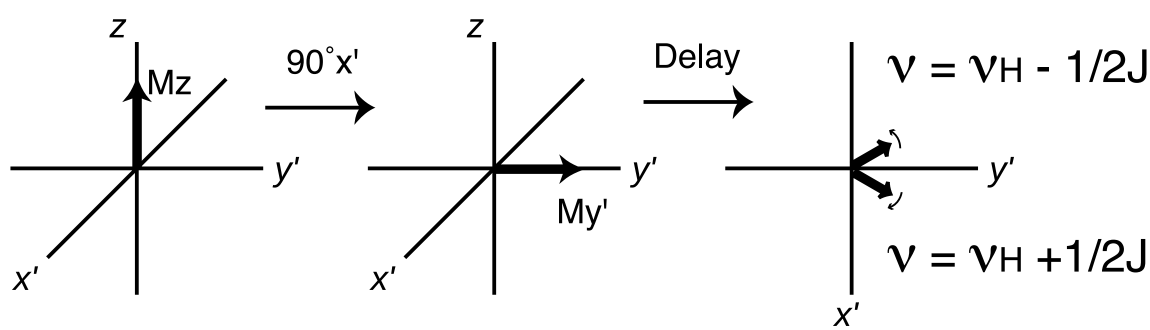
$\nu_H = \nu_{rf} + 200$ Hz



B) Effect of J coupling:

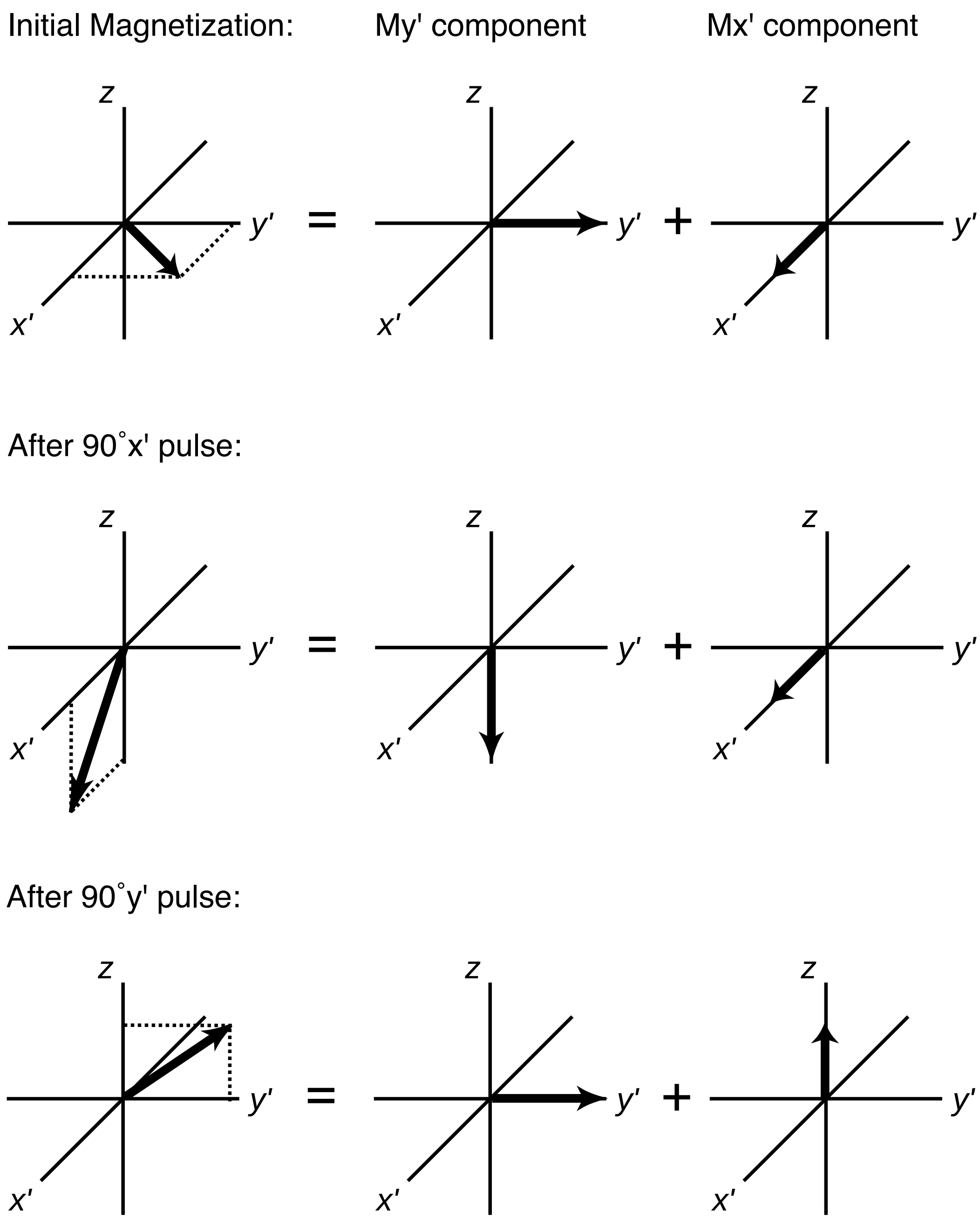
example:

$\nu_H = \nu_{rf}$



- **Effect of 90˚x pulse on transverse magnetization with Mx' and My' components**

<u>Vector diagrams</u>:



- **Effect of 180° x and y pulses on transverse magnetization with Mx' and My' components**

<u>Vector diagrams</u>: