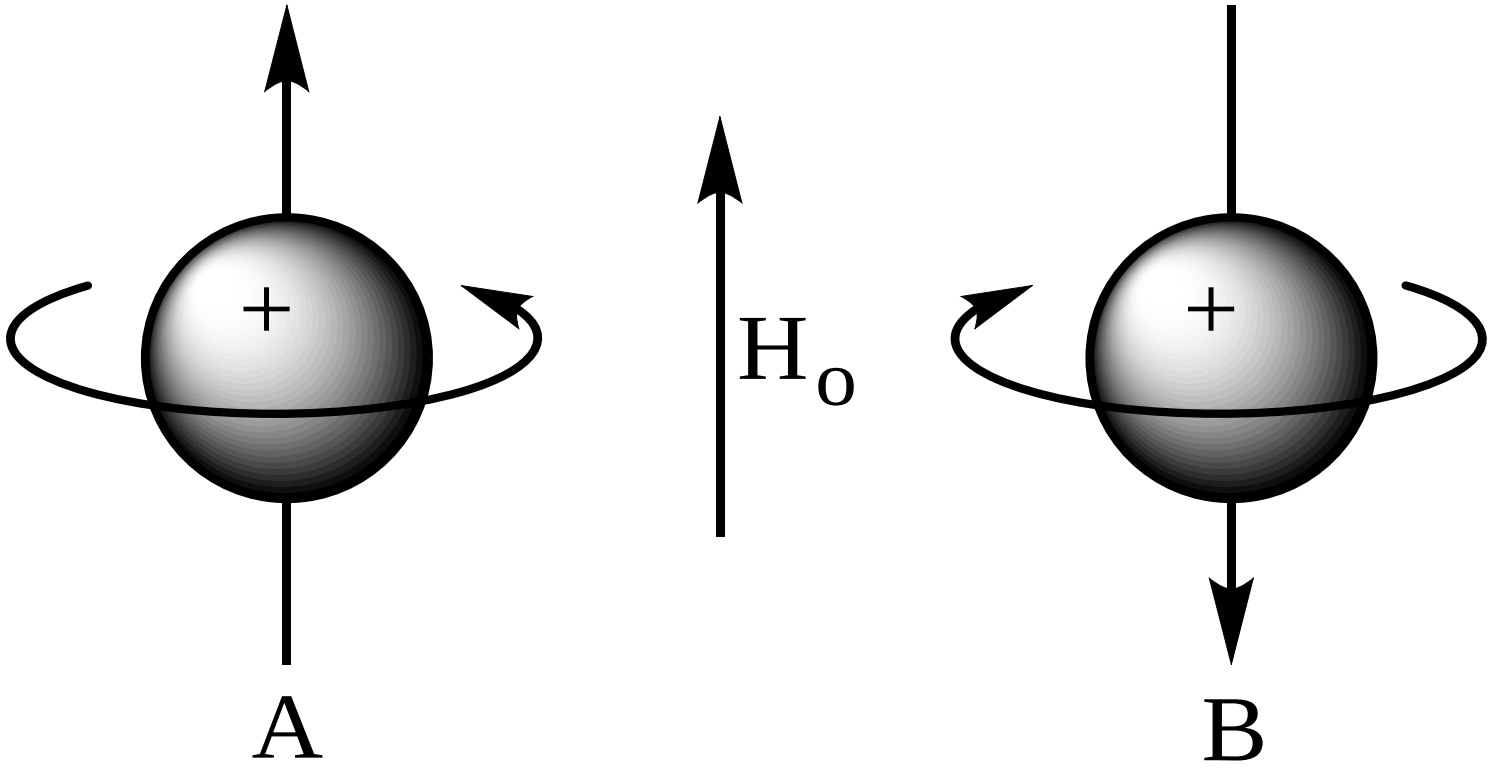
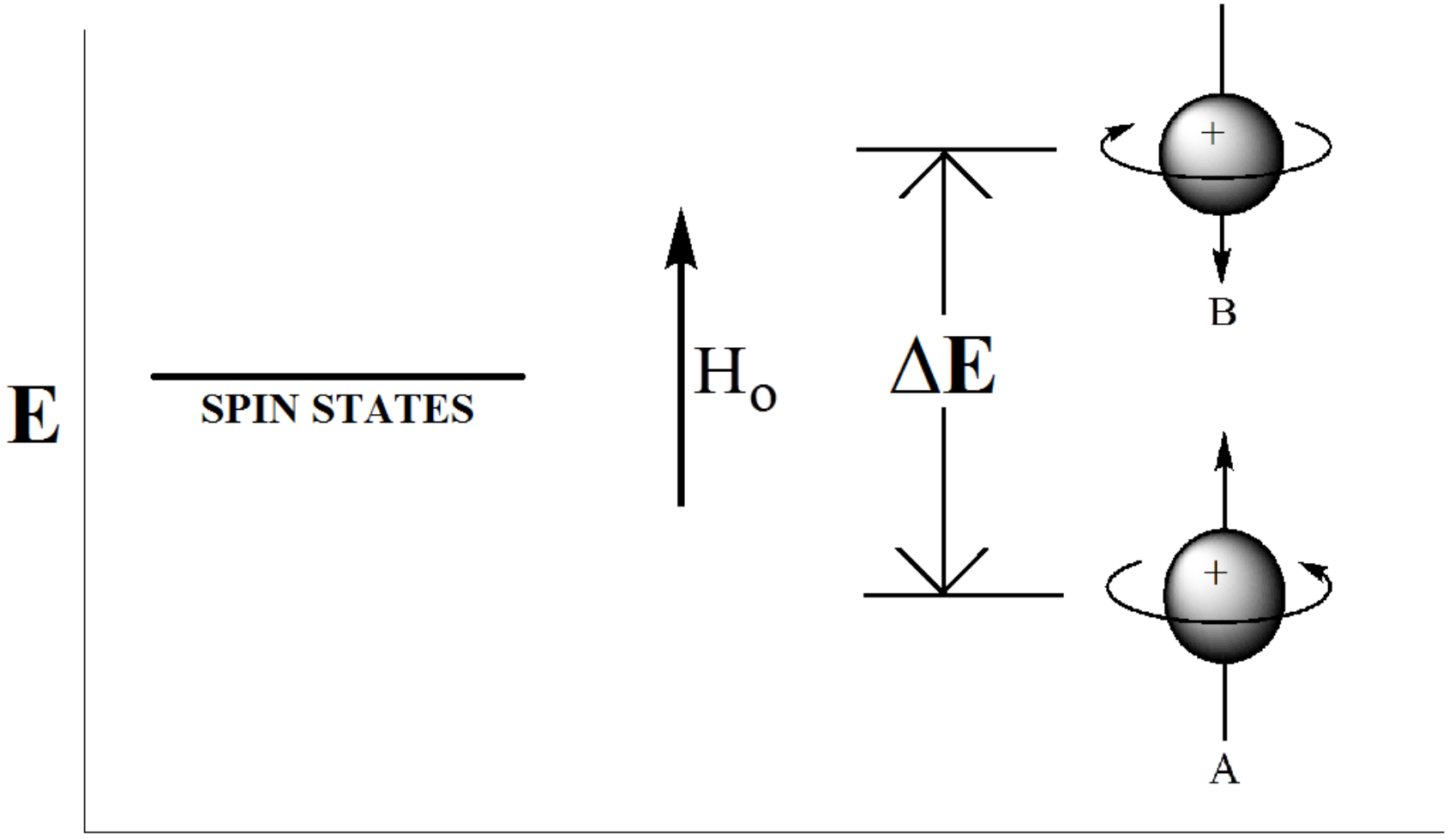
Chemistry 2201 Lab: Keto-Enol

Nuclear Spin:

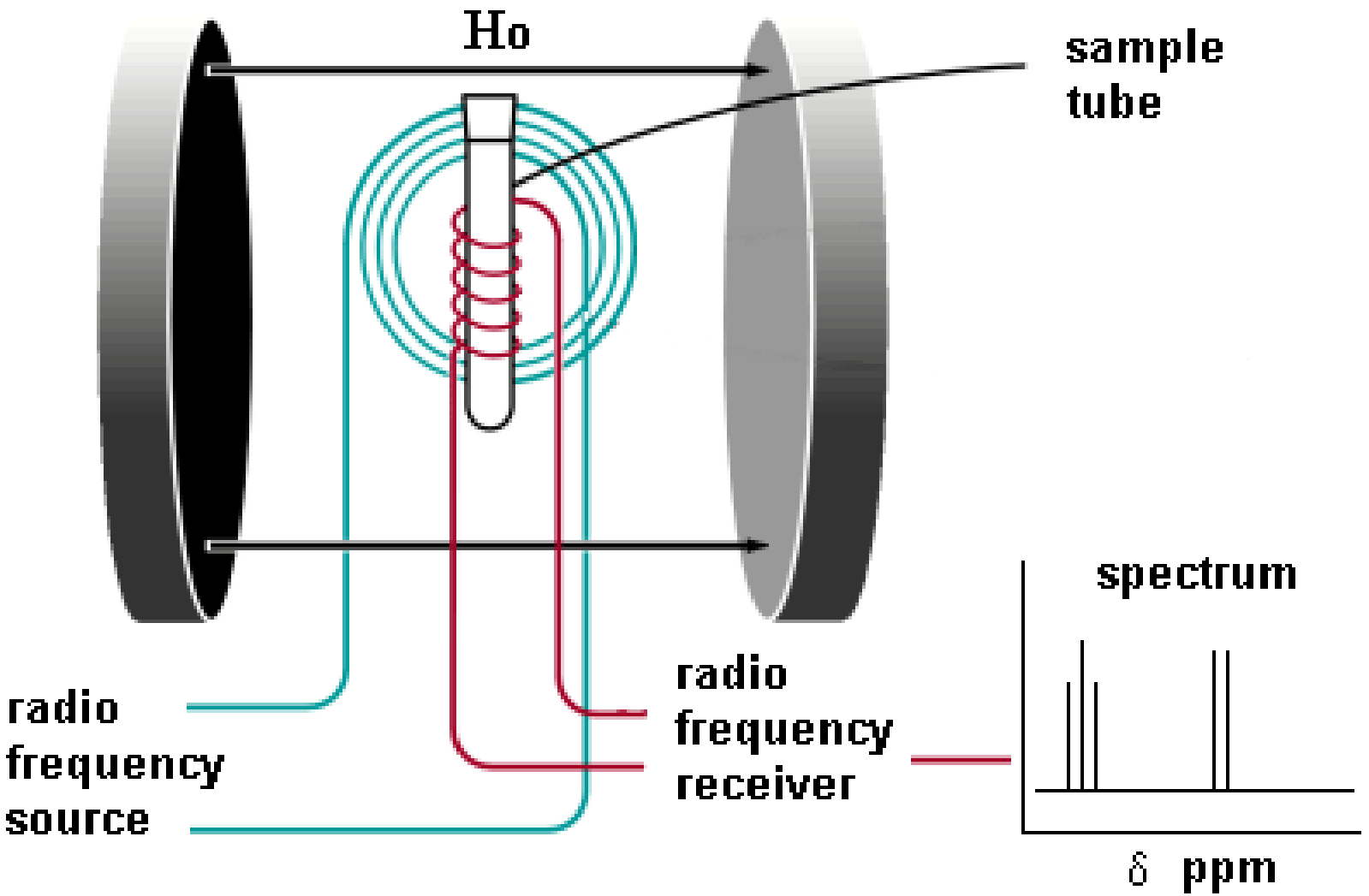
A nucleus is a spinning charged particle. Has a magnetic moment. H_o:External Magnetic Field



Nuclear Spin cont:



NMR Spectrometer:



The Chemical Shift(δ):

The frequency of energy absorbed by a nucleus(resonance) depends on the environment of the nucleus and the strength of the instruments magnetic field.

The chemical shift eliminates the dependence on the type of magnet.

$$\delta = \frac{\text{resonance frequency in Hz} \times 10^6}{\text{spectrometer frequency}}$$

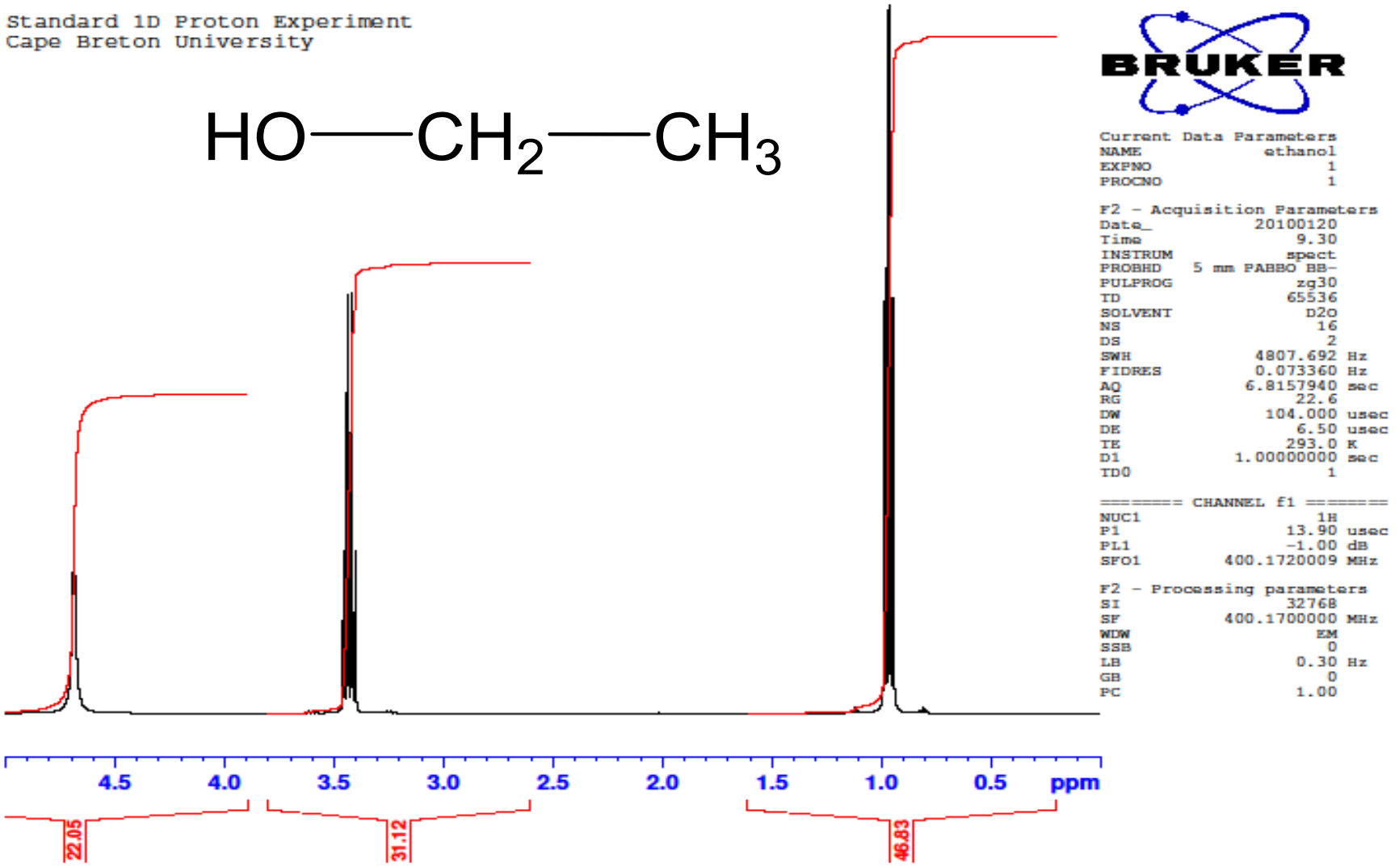
Interpreting NMR Spectra:

Plot of signal strength vs. δ.

The chemical shift(δ) depends on the electron density and the type of atoms bonded to a nuclei.

Nuclei bonded to electronegative atoms are less shielded from the magnetic field(deshielded) and appear at higher **δ.**

Ethanol ^{1}H-NMR



BRUKER

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Current Data Parameters
NAME                  ethanol
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100120
Time                   9.30
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                D2O
NS                        16
DS                         2
SWH                4807.692 Hz
FIDRES             0.073360 Hz
AQ                 6.8157940 sec
RG                      22.6
DW                   104.000 usec
DE                      6.50 usec
TE                     293.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.90 usec
PL1                    -1.00 dB
SFO1           400.1720009 MHz

F2 - Processing parameters
SI                     32768
SF             400.1700000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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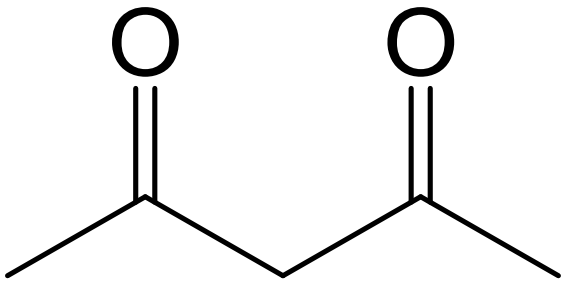
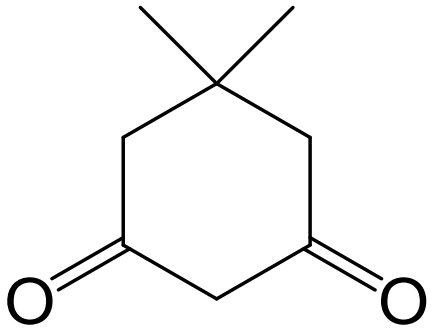
Keto-Enol Equilibrium:

Will be examining the keto-enol equilibrium of the following compounds:

2,4-pentanedione

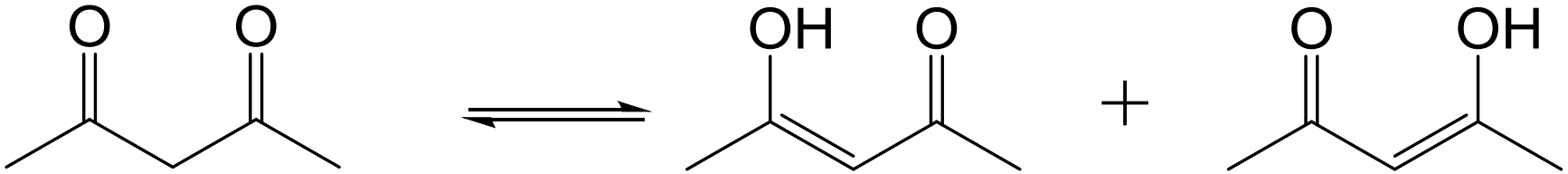


Dimedone



Keto-Enol Equilibrium:

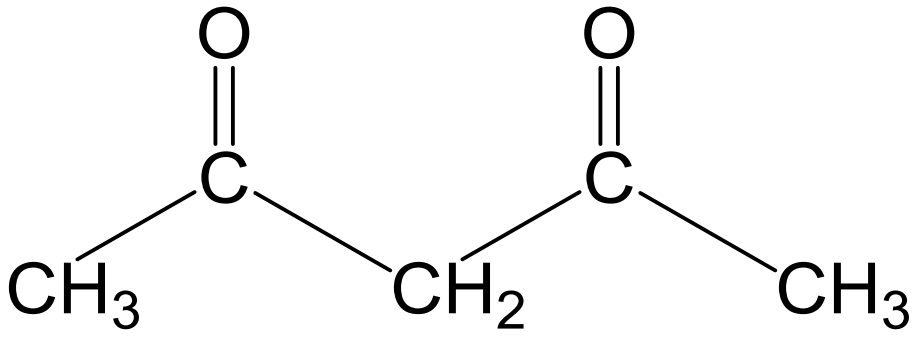
Consider 2,4-pentanedione



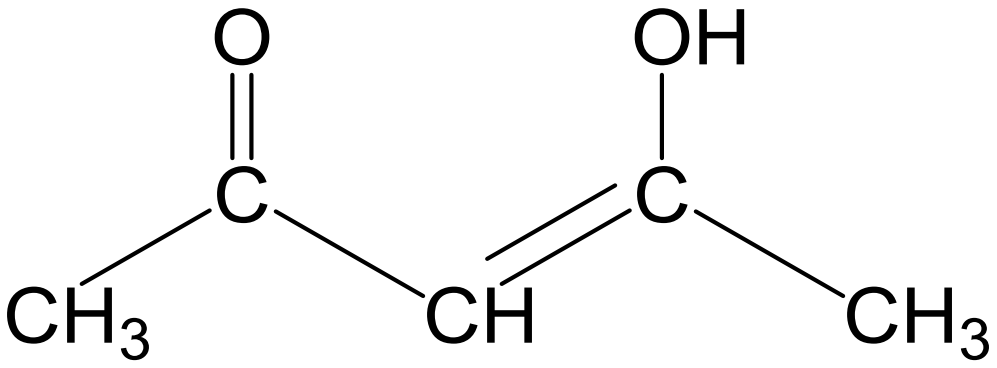
KETO **ENOL**

$$K_c = \frac{\%\ enol}{\%\ keto}$$

Determining Keto-Enol Equilibrium:



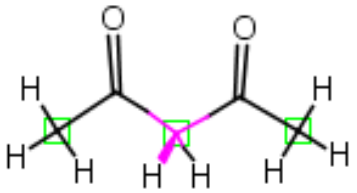
KETO



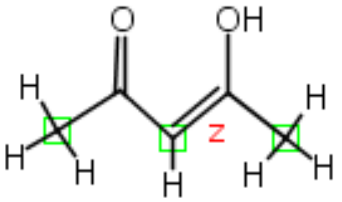
ENOL

Predicted NMR Spectrum:

KETO



ENOL



References

•Banfi, D.; Patiny, L. www.nmrdb.org: Resurrecting and processing NMR spectra on-line *Chimia*, 2008, *62*(4), 280-281.
•Andrés M. Castillo, Luc Patiny and Julien Wist. Fast and Accurate Algorithm for the Simulation of NMR spectra of Large Spin Systems. *Journal of Magnetic Resonance* 2011.
•Aires-de-Sousa, M. Hemmer, J. Gasteiger, "Prediction of 1H NMR Chemical Shifts Using Neural Networks", *Analytical Chemistry*, 2002, *74*(1), 80-90

Determination of K:

From integrated peak areas will determine K.

Will compare K in two different solvents.

Solvent 1: $CDCl_3$: non-polar
Solvent 2: DMSO-d6: aprotic polar solvent

Determination of K as a Function of Temperature:

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

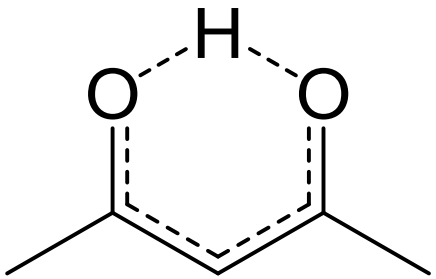
Plot of InK vs. $1/T(K^{-1})$ yields ΔH and ΔS.

Determination of K:

$$K_{eq} = \frac{2 \times Area\ CH\ enol(\delta = 5.7\ ppm)}{Area\ CH_2\ keto(\delta = 3.7\ ppm)}$$

System	Area CH_2 group	Area CH Group	K_{eq}	ΔG (kJ/mole)
acac in $CDCl_3$	883021	3105741	7.03	-4.83
acac in DMSO-d6	10097620	5633233	1.11	-0.27

Enol form more stable in nonpolar solvent.

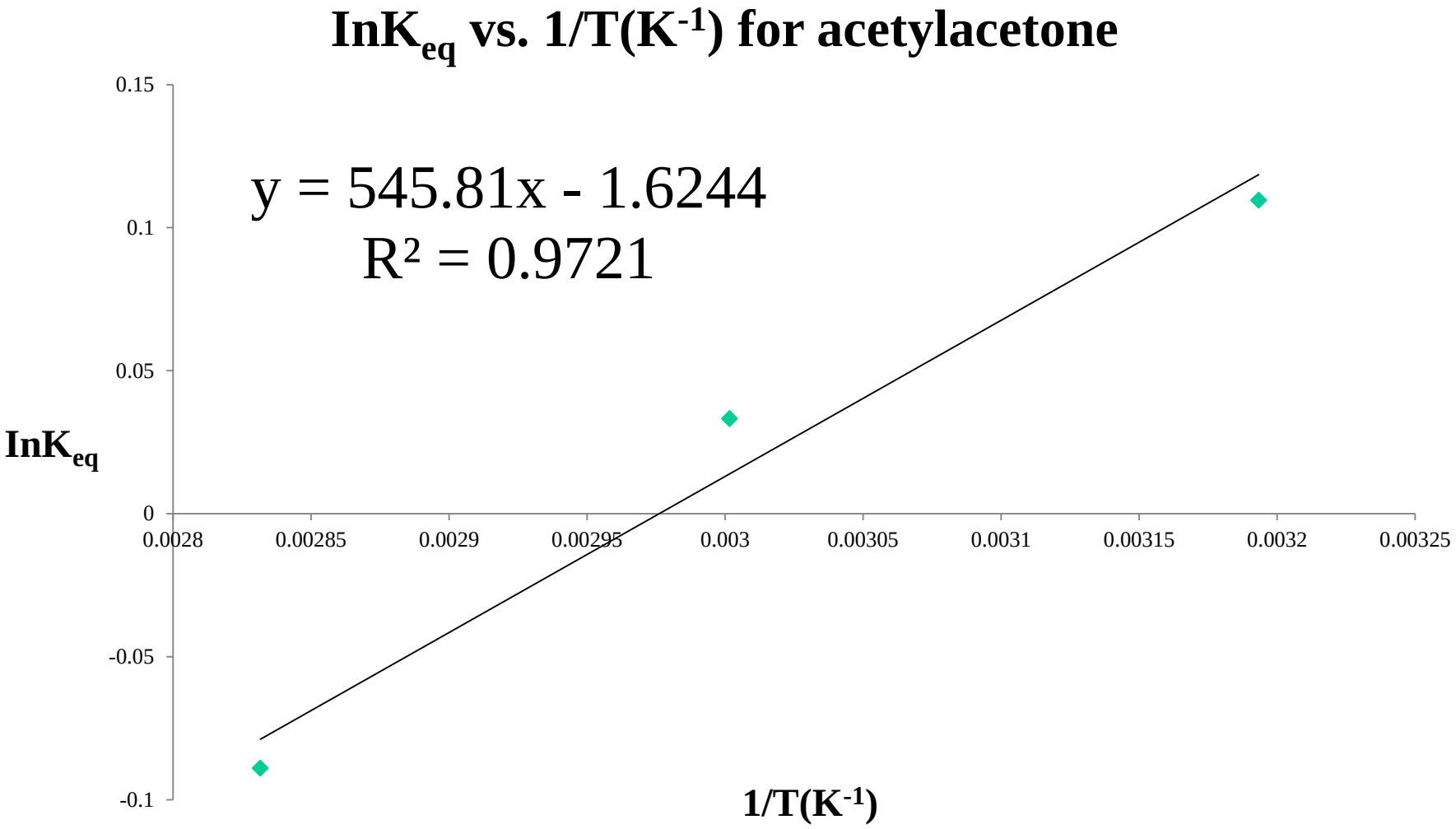


Hydrogen-Bonding in acac

Solvent 1: $CDCl_3$: non-polar
Solvent 2: DMSO-d6: aprotic polar solvent

Enol form of diketone the least polar.
Intramolecular H-Bonding reduces repulsion between carbonyl groups.

Determination of K_{eq} as a Function of Temperature:



$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

y = 545.81x - 1.6244

ΔH= -slope × R **ΔS= y-intercept × R**

	ΔH(kJ/mole)	ΔS(J/K·mole)
acac	-4.54	-13.5

Study of Dimedone by Students: