CH203 Lecture 23

December 7, 2010

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BOSTON UNIVERSITY

Administrative Announcements 12/07/10

- *Exam 3 will be handed out after lecture today (9:15 am)*
- *Final Exam: Thursday December 16th (12:30 – 2:30 pm)*

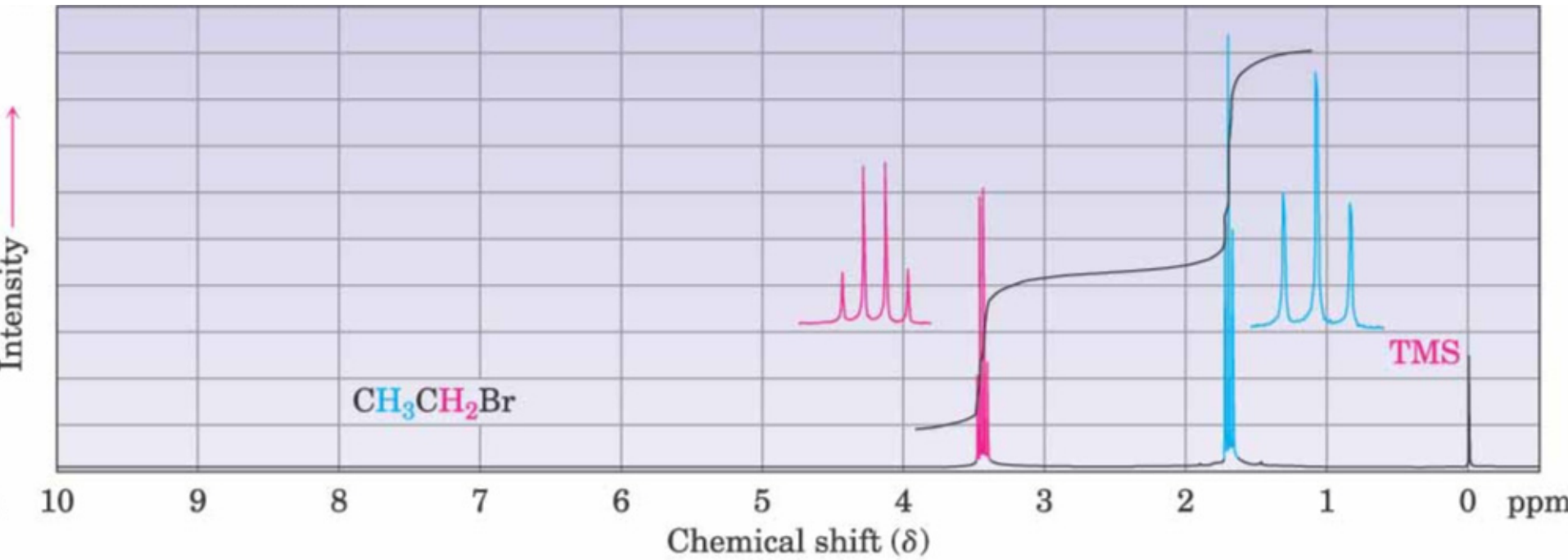
A-S STO B50

T-Z CAS 227

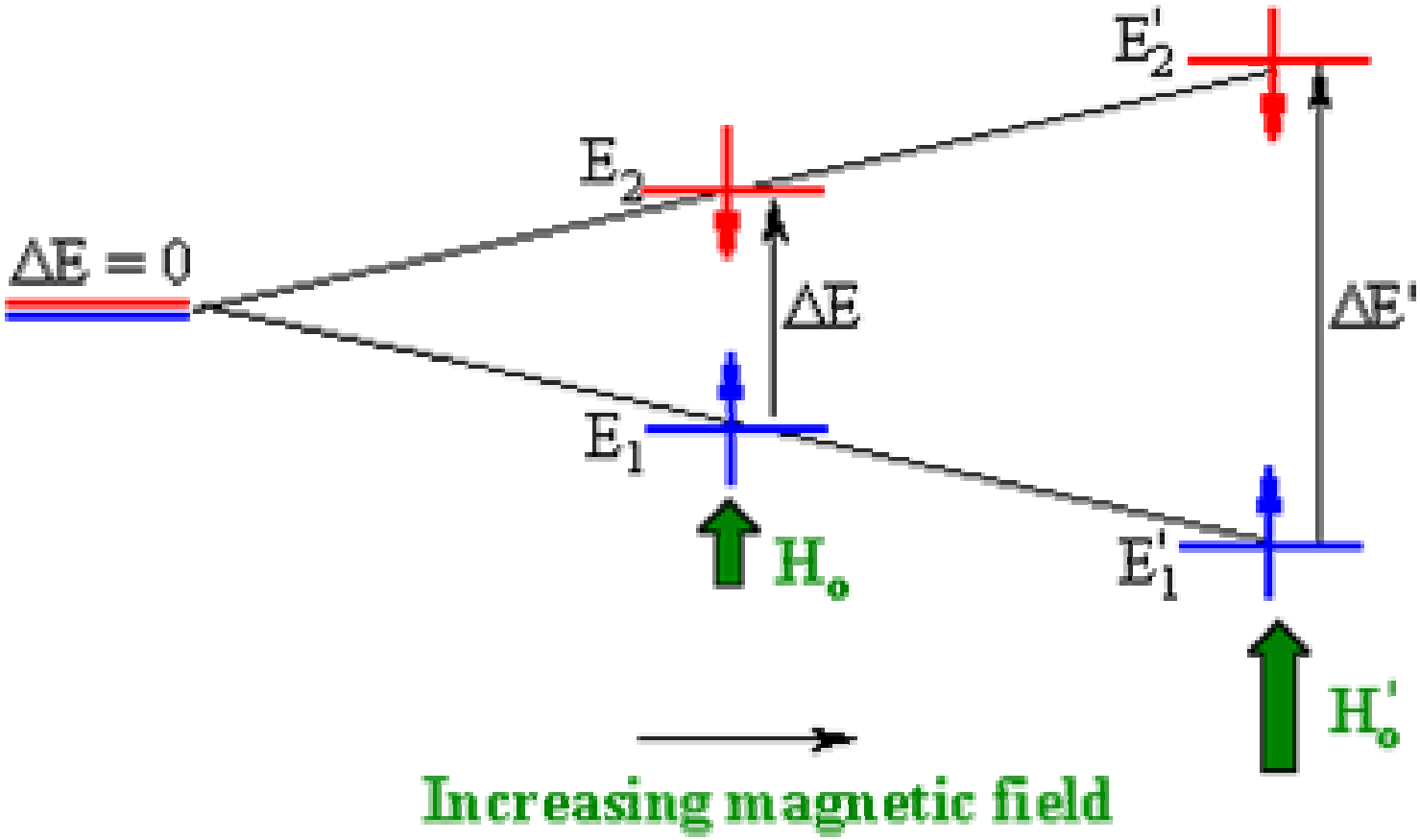
- *NMR problems and NMR shift table (Chapter 13) are now posted on the course website.*

http://people.bu.edu/porcogrp/CH203/Handouts.htm

^1H NMR Spectrum of Bromoethane

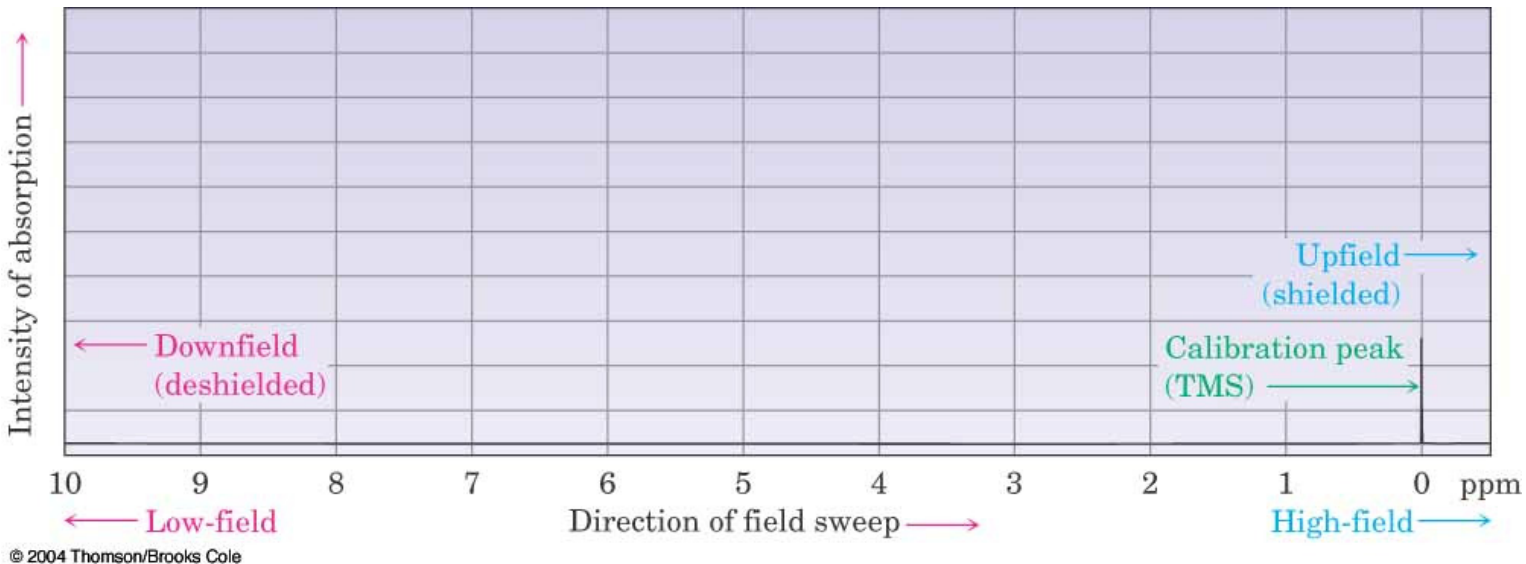


Spin "flips" in Nuclear Magnetic Resonance

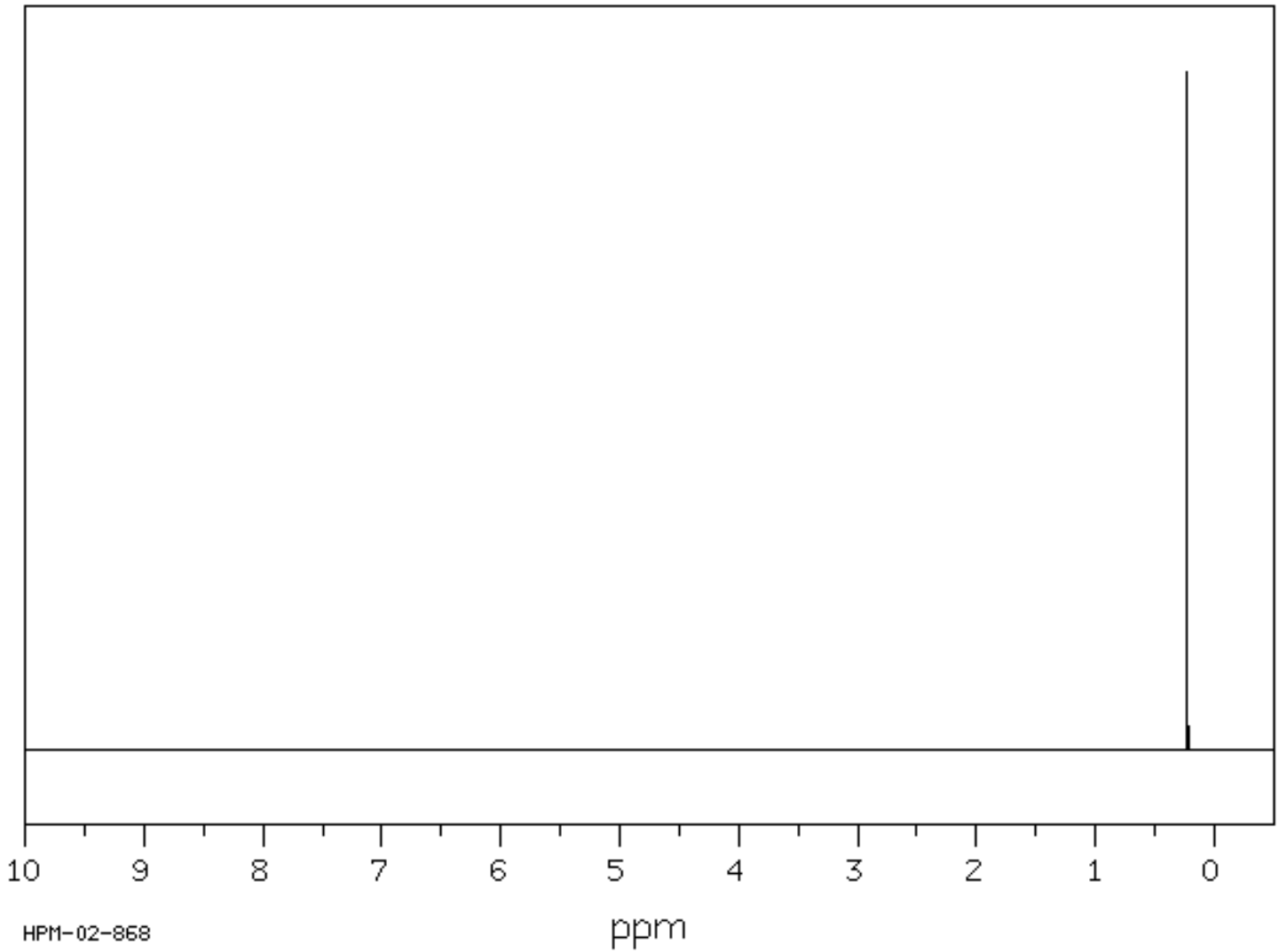


Measuring Chemical Shift

- Numeric value of chemical shift: difference between strength of magnetic field at which the observed nucleus resonates and field strength for resonance of a reference
  - Taken as a ratio to the total field and multiplied by 10^6 so the shift is in parts per million (ppm)
- Absorptions normally occur downfield of TMS, to the left on the chart
- Calibrated on relative scale in **delta (δ) scale**
  - δ is the number of parts per million (ppm) of the magnetic field expressed as the spectrometer's operating frequency (used ahead of value as it is a ratio and not a unit)
  - Independent of instrument's field strength



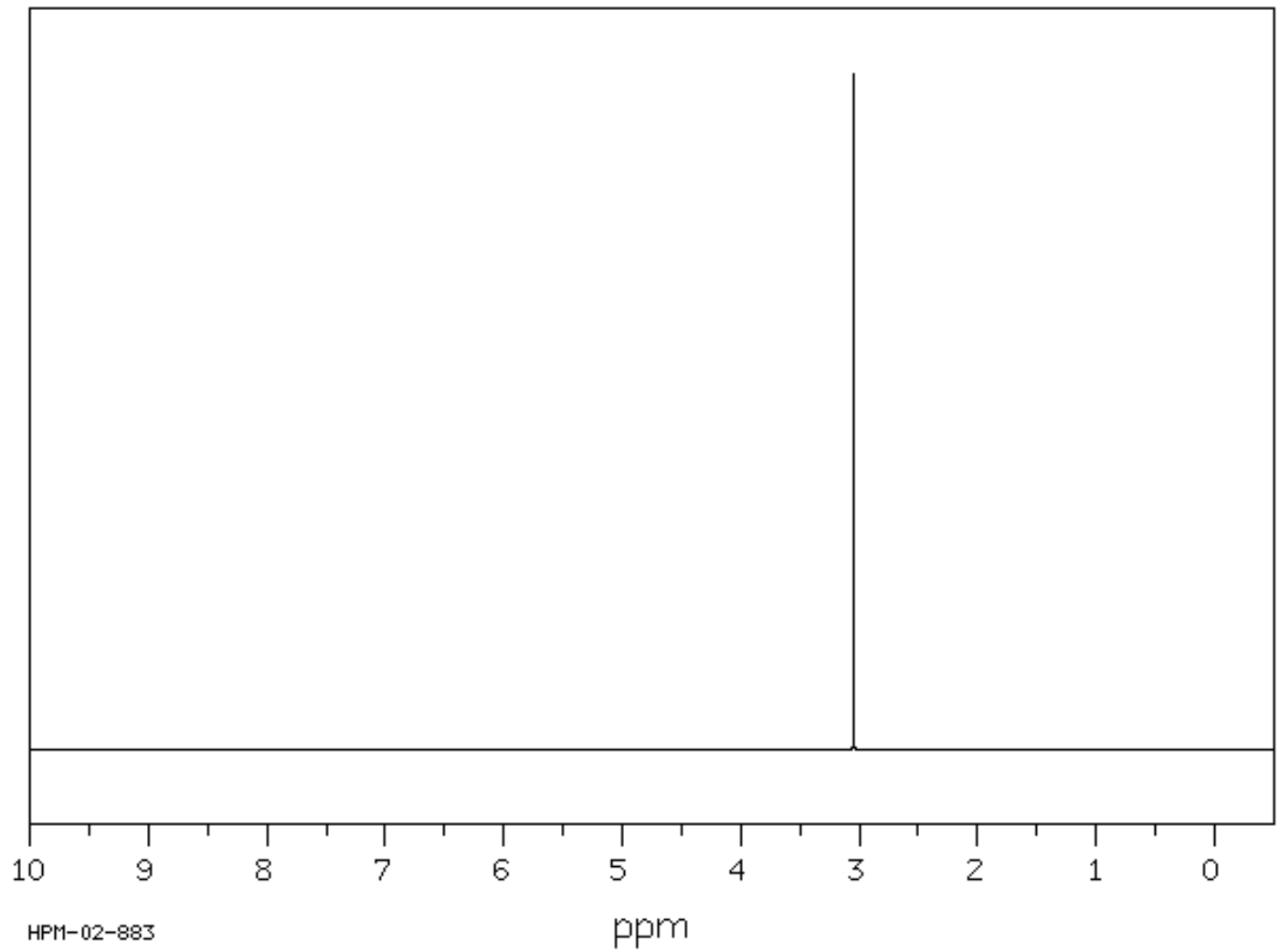
^{1}H NMR Spectrum of Methane



CH_4

δ= 0.3 ppm

^{1}H NMR Spectrum of Chloromethane



CH_3Cl

δ= 3.0 ppm

Chemical Shifts in ^1H NMR Spectroscopy

- Proton signals range from δ 0 to δ 10
- Lower field signals are H's attached to sp^2 C
- Higher field signals are H's attached to sp^3 C
- Electronegative atoms attached to adjacent C cause downfield shift
- See Tables in chapter 13 for a complete list

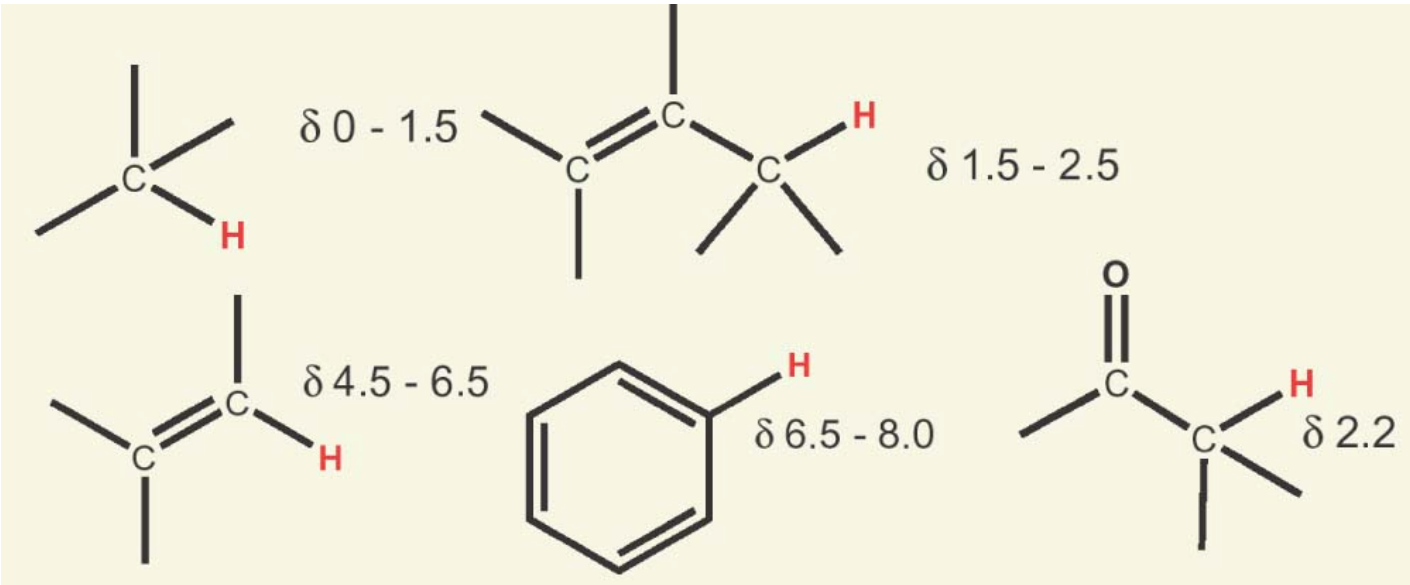
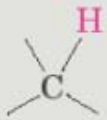
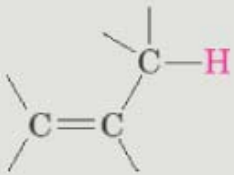
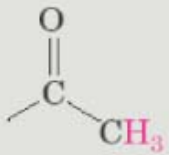
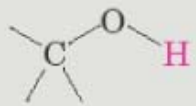
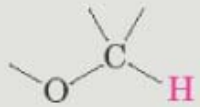
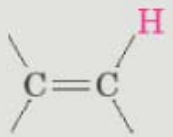
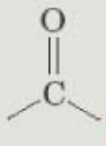
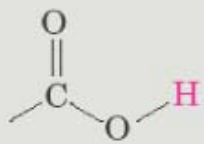
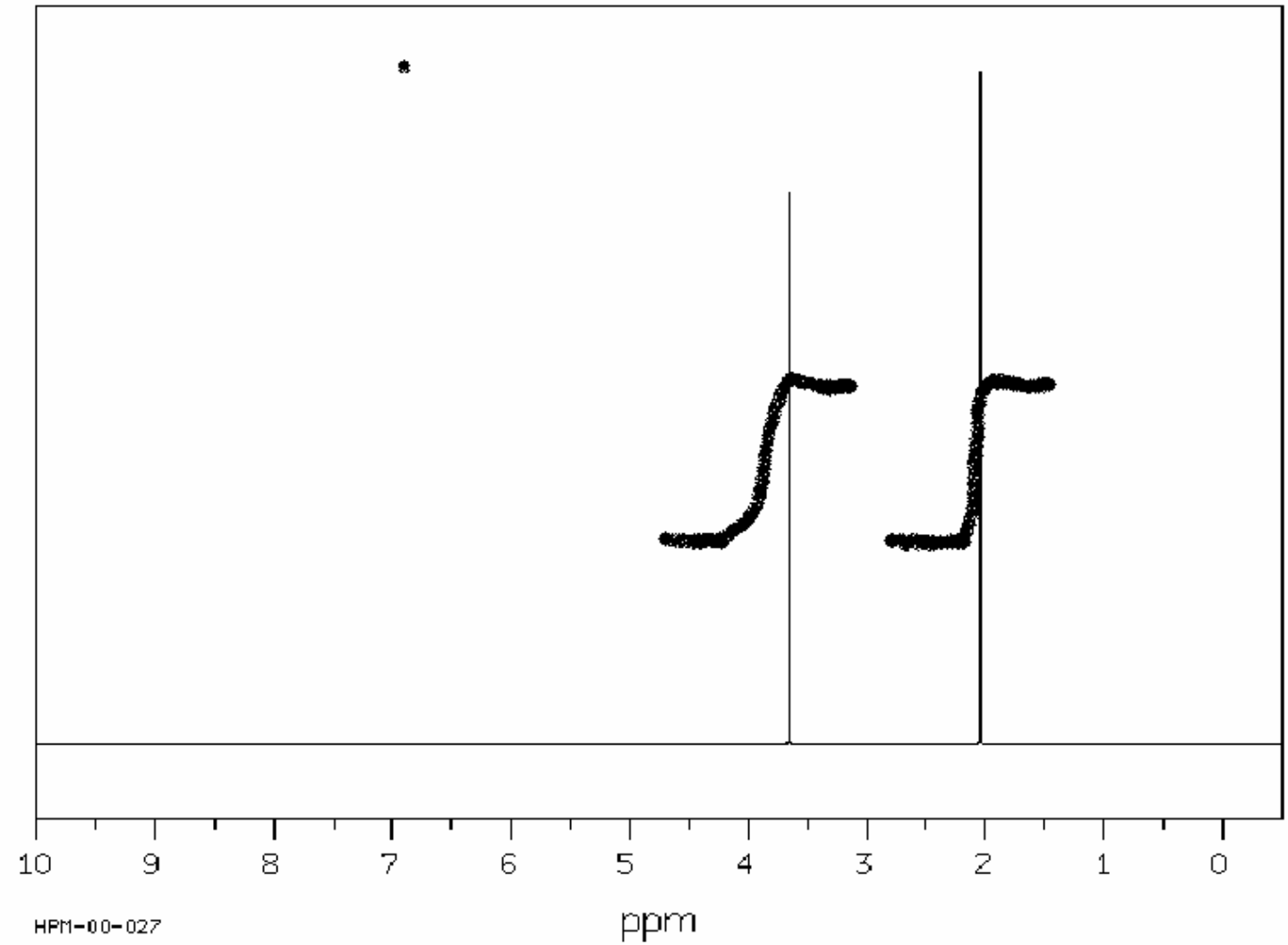


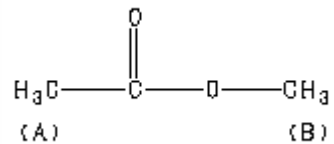
TABLE 13.3 Correlation of ^1H Chemical Shift with Environment

Type of hydrogen		Chemical shift (δ)
Reference	$(CH_3)_4Si$	0
Saturated primary	$-CH_3$	0.7–1.3
Saturated secondary	$-CH_2-$	1.2–1.6
Saturated tertiary		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0

Type of hydrogen		Chemical shift (δ)
Alkyl halide X = Cl, Br, I		2.5–4.0
Alcohol		2.5–5.0 (Variable)
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aromatic	$Ar-H$	6.5–8.0
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0

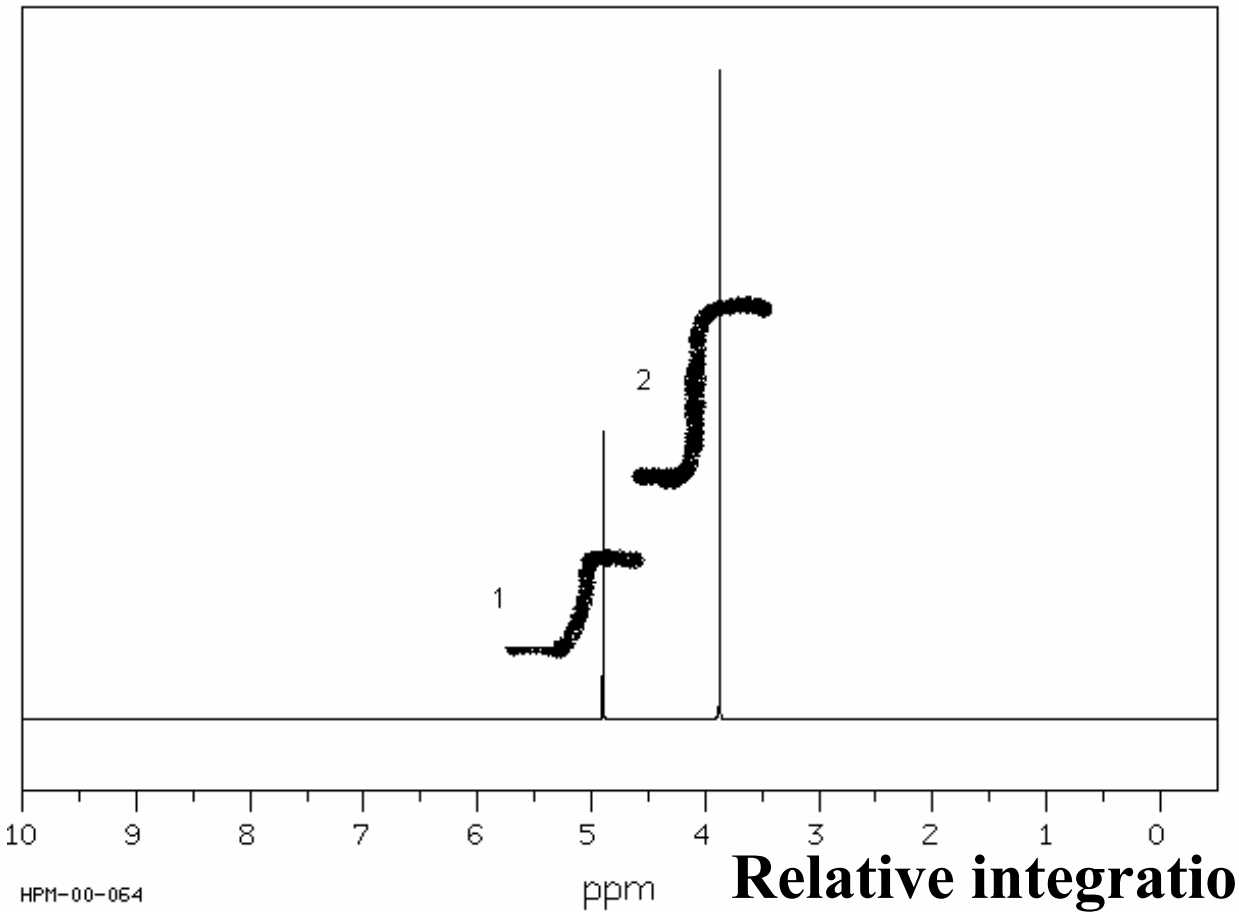
^{1}H NMR Spectrum of methyl acetate





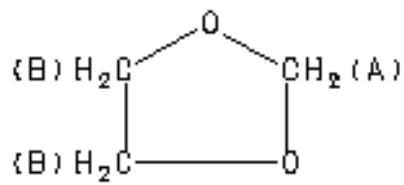
A 2.05 ppm
B 3.66 ppm

^1H NMR Spectrum of 1,3-dioxolane



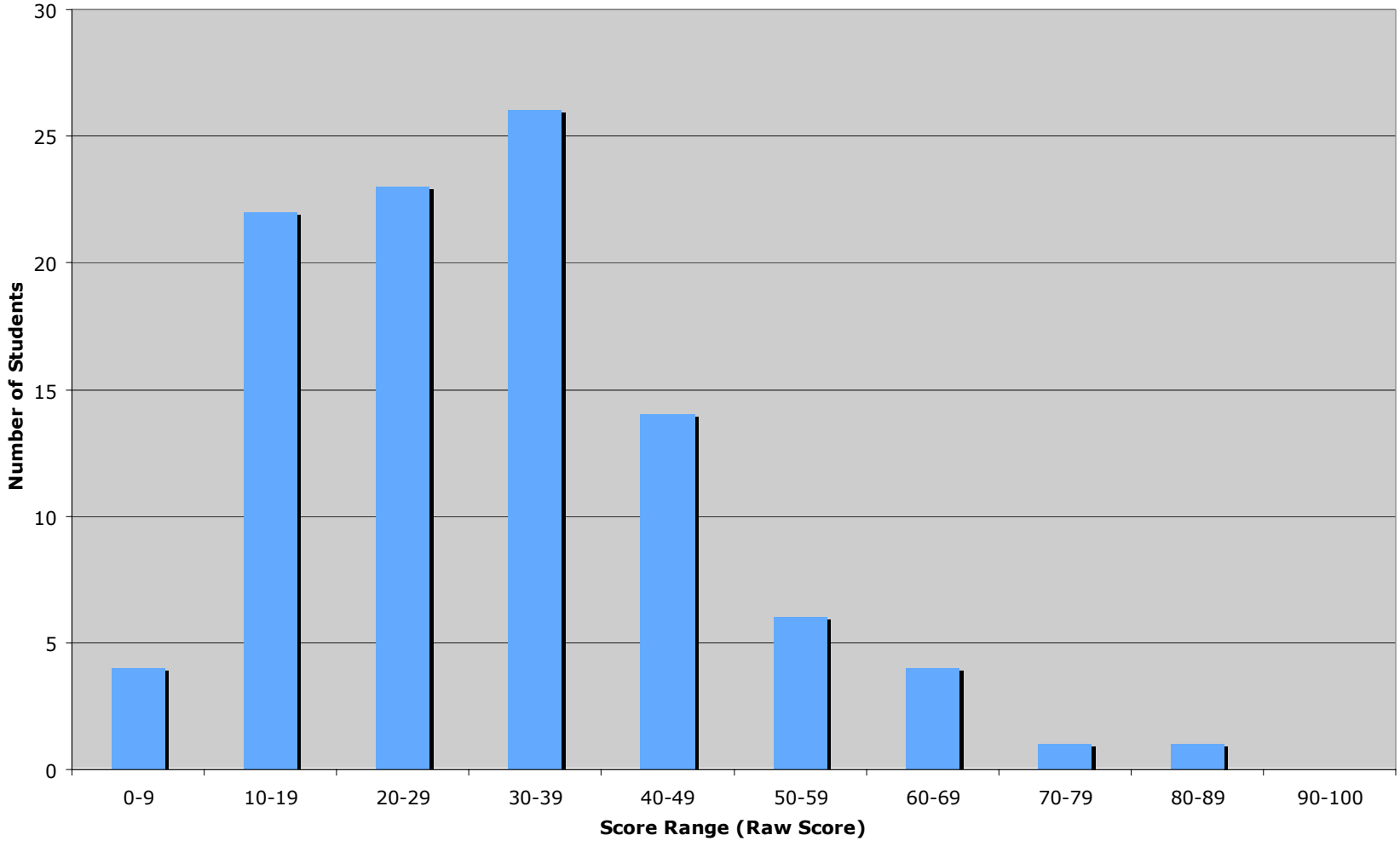
ethylene glycol methylene ether

A 4.9 ppm
B 3.87 ppm



Relative integration of peak at 3.87 ppm is twice that of peak at 4.9 ppm

Exam 3 Score Distribution
Median: 30
High: 85



- **30 points will be added to raw scores (an additional 10 pts. over the "20 points" policy described in the course syllabus).**
- **Please have regrade requests to Neil and John N. by no later than Tuesday December 14th**

NMR Absorptions

- Absorption frequency not all same for all ^1H nuclei

- varies slightly with chemical environ. of H. Nuclei "Shielded" from full effect of circ. e⁻s. moving e⁻s set up tiny local mag. fields. which act in opposition to the applied field

$$B_{effective} = B_{app} - B_{local}$$

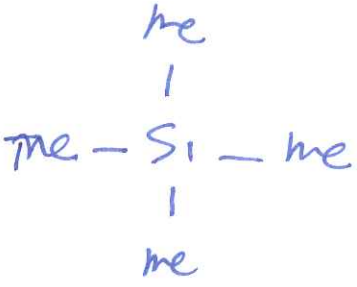
NMR chart (spectrum)

- horizontal axis: effective field strength felt by nuclei
- vertical axis: intensity of absorption of rf energy

each signal referred to as a "resonance"

Each peak corresponds to a chem. distinct ^1H nucleus.

Chemical Shift : Frequency of Signal in NMR



TMS

- Varies slightly with chem envir. of H
- ~~Nuclei are shield~~

- calib or ref peak.
- Si strong e^- donor
- rel to H so CH_3 are shielded

rel to shifts for most org molecules

applied field strength ↑ increased / decreased
left to right

δ scale

$$\delta = \frac{\text{obs. c.s. } CH_2 \text{ from tms)}}{\text{spectr. freq. in MHz.}}$$

Typically δ 0 – 10 ppm.

- Downfield nuclei require lower field strength for resonance
- Upfield, higher field strength for resonance, more shielding

Chemical shift in ^1H NMR

Electronegativity

- e^-'s around a proton create a mag. field that opposes the applied field
- Reduce field at nucleus, shield proton

The chemical shift (δ & ppm) will thus change depending on e^- density around the proton

→ E-neg groups decr. e^- density, less shielding (deshielding) so chem. shift increases

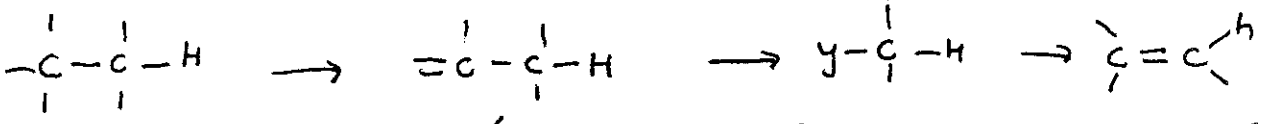
δ 2.0

	CH_3F	CH_3OH	CH_3Cl
Eneg.	4.0	3.5	3.1
δ	4.26	3.4	3.05

δ 2.0, δ 4.0

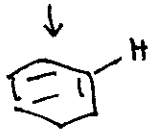
^1H Chemical shifts

cf Table 13.2 p 495



0 – 1.5 | 1.6 – 2.2 "allylic" | 2.5 – 4.0 | 4.5 – 6.5 vinylic protons

- strongly deshielded by neighboring π bond



6.5 – 8.0

} Protons strongly deshielded by π orbitals, more so due to ring current effects

see fig 15.15, p. 580

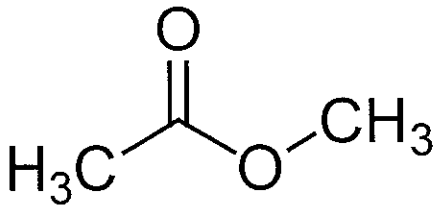
Proton counting or "integration"

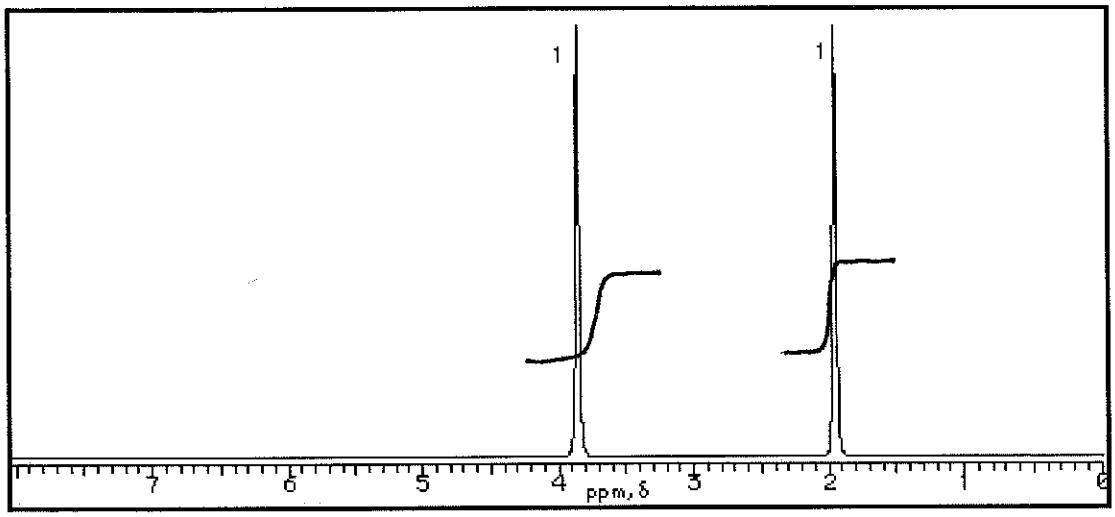
for ^1H NMR, intensity of absorbance of a given nuclei is proportional to the # of protons giving the signal

[^1H NMR of methyl acetate]

- Integral drawn as a "stair step line"
- Area under the peak does not give the absolute # of H's, but the relative # of each H.

^{1}H NMR Spectrum of Methyl Acetate



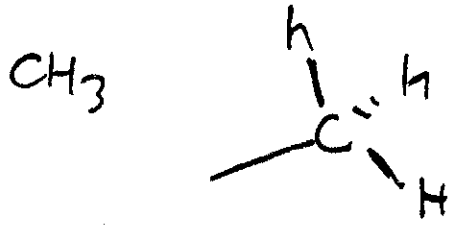


- 3 H's of each CH_3 (methyl group) are chemically ("magnetically")equivalent, and therefore have the same electronic environment

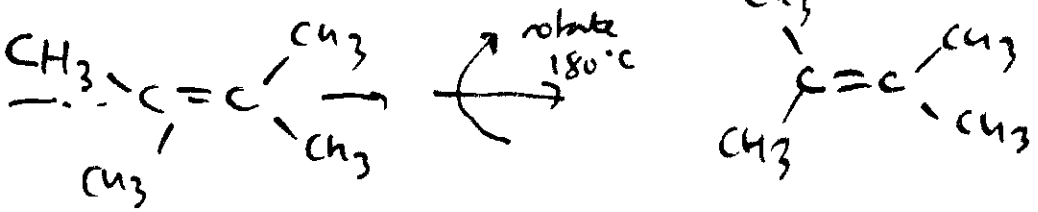
- However, the two CH_3 (methyl groups) are not equivalent and absorb at different positions

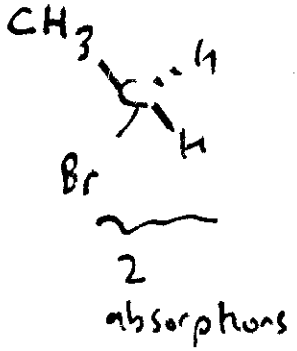
Proton Equivalence

Chemically equivalent protons are "NMR equivalent" e.g.



If two protons can be interchanged via a symmetry operation of the molecule or by rotation around a bond they are considered chemically equivalent





12 chemically equivalent protons