Massachusetts Institute of Technology
Organic Chemistry 5.13

September 15, 2006
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Notes for Lecture #5

Nuclear Magnetic Resonance (NMR) Spectroscopy

Isotope	Natural Abundance	Spin	Isotope	Natural Abundance	Spin
^{1}H	99.98%	1/2	^{14}N	99.6%	1
^{12}C	98.9%	0	^{16}O	99.8%	0
^{13}C	1.1%	1/2	^{31}P	>99.9%	1/2

^{13}C NMR is useful for:

1. Determining the number of **chemically non-equivalent** (or "different types of") carbon atoms in a molecule, based on the **number of peaks** in the spectrum. (See **substitution test**, below.)
2. Identifying the types of **functional groups** in a molecule based on the **chemical shift** of each peak. In contrast to IR spectroscopy, the *number* of *each* type of functional group (e.g. 2 chemically non-equivalent ketones) often can be determined.

^{1}H NMR is useful for:

1. Determining the number of **chemically non-equivalent** (or "different types of") hydrogen atoms in a molecule, based on the **number of peaks** in the spectrum. Note: "number of peaks" in this case does not include the splitting pattern (see below), e.g. a triplet is considered to be one "peak".
2. Determining the **relative number of chemically non-equivalent** hydrogen atoms by measuring the **relative area** of each peak (by integration of each curve – *not* by measuring the relative peak heights).
3. Identifying neighboring **functional groups** based on the **chemical shift** of each peak, which is a measure of the **chemical environment** of each proton in the molecule.
4. Determining which *carbon* atoms are connected to which based on the **splitting pattern** or **multiplicity** of each peak. *This information is the most useful of all the methods we have discussed in determining the **connectivity** of the molecule, i.e. assembling all of the functional groups and fragments identified into an actual structure.*

The **substitution test** is used to determine whether two atoms or groups are **chemically non-equivalent**:

1. Replace each atom or group in turn with "X".
2. If these two structures are **identical** (can be superimposed) or are **enantiomers**, then the two atoms or groups are **chemically equivalent** (**homotopic** and **enantiotopic**, respectively) and thus are indistinguishable by NMR spectroscopy.
3. If the two structures are **different** (e.g. diastereomers – making the two groups **diastereotopic**, alkene isomers, structural isomers), then the two atoms or groups are **chemically non-equivalent** and *may* be distinguishable by NMR spectroscopy.

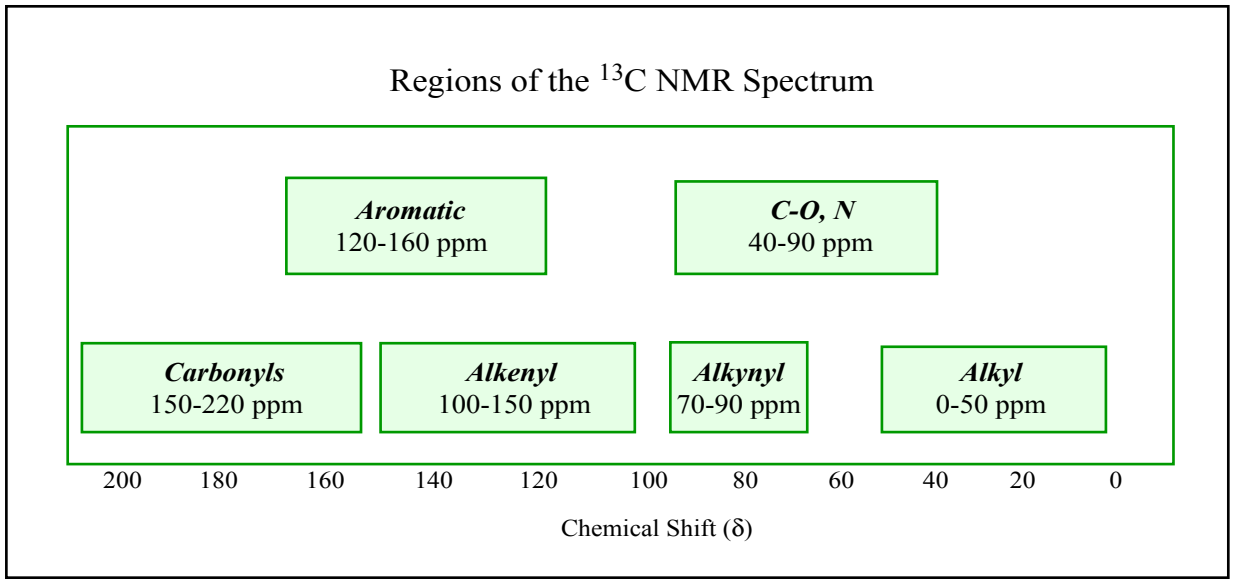


Figure by MIT OCW.

Characteristic Functional Group Chemical Shifts in ^{13}C NMR (ppm)

Alkanes		Organohalogen	
Methyl (RCH_3)	0-30	C–F	70-80
Methylene (RCH_2R')	15-55	C–Cl	25-50
Methine (RCH(R')(R"))	25-55	C–Br	10-40
Quaternary (RC(R')(R")(R'"))	30-40	C–I	–20-10
Alkenes	100-150	Ketones, Aldehydes	185-220
Aromatic	120-160	Carboxyl Derivatives	
Alkynes	70-90	Acids	150-185
Nitriles	110-125	Esters	155-180
Alcohols, Ethers	50-90	Amides	150-180
Amines	40-60	Carbamates	150-160

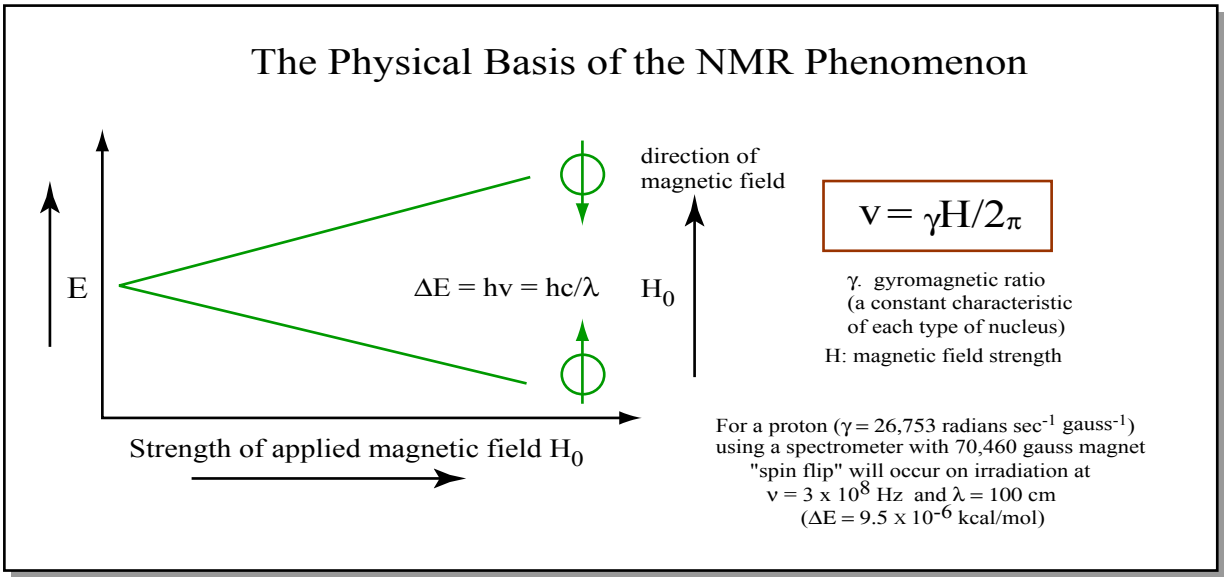
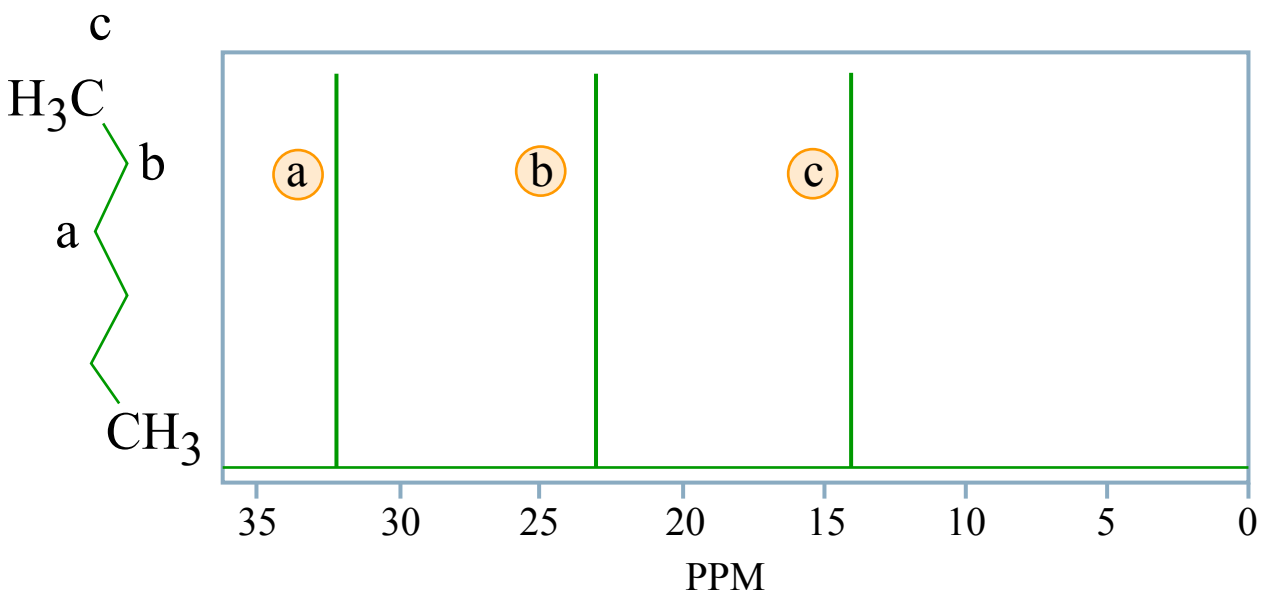
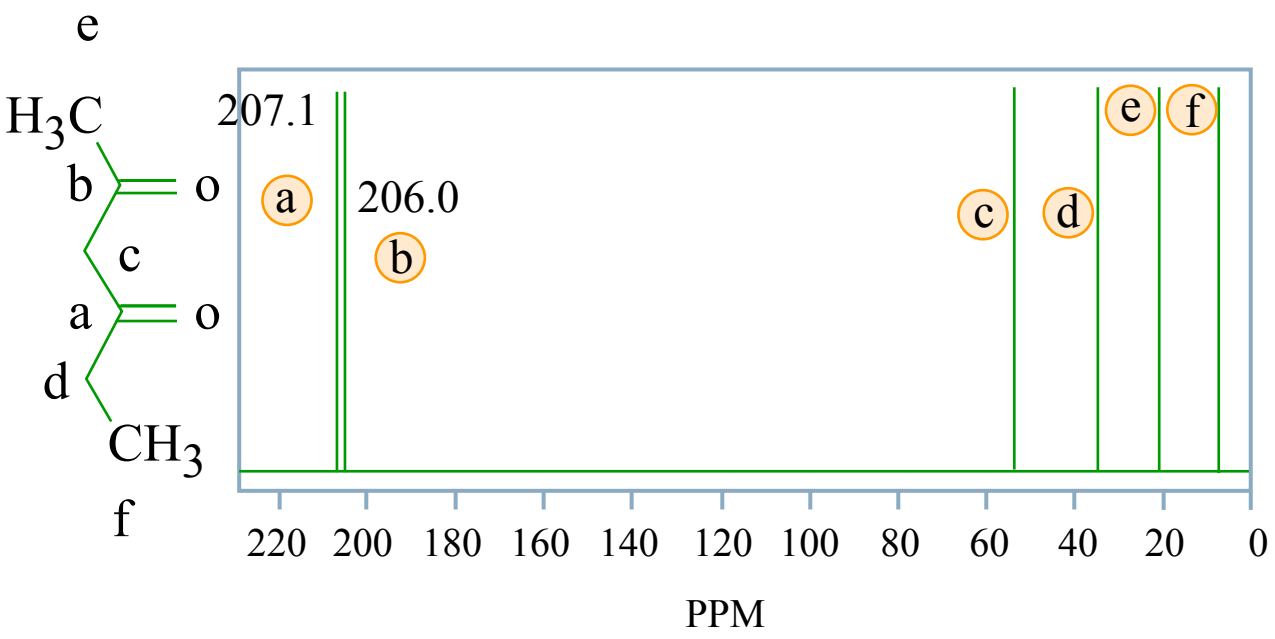


Figure by MIT OCW.

Images of ^{13}C NMR Spectra for 2-pentanone and 3-pentanone removed due to copyright restrictions.
Please see: http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct_frame_top.cgi?lang=eng

Remarkable Sensitivity of ^{13}C NMR to Chemical Structure





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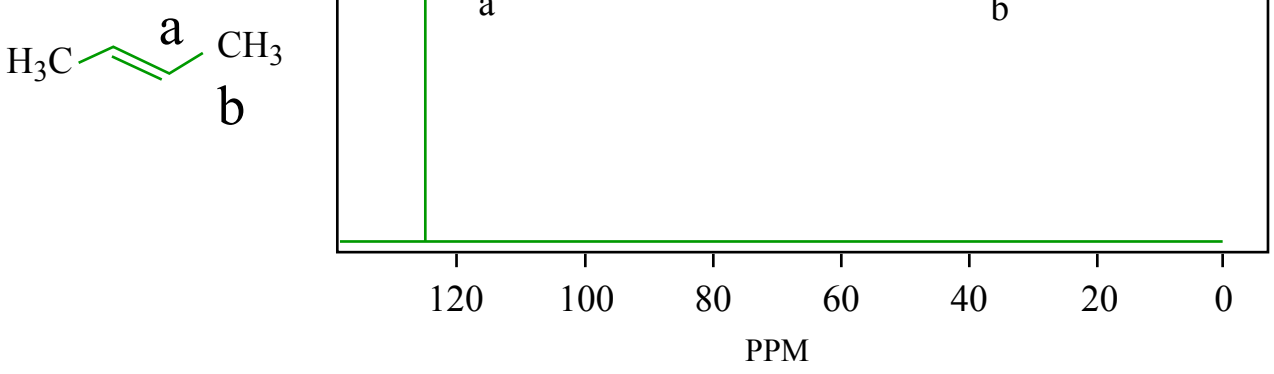
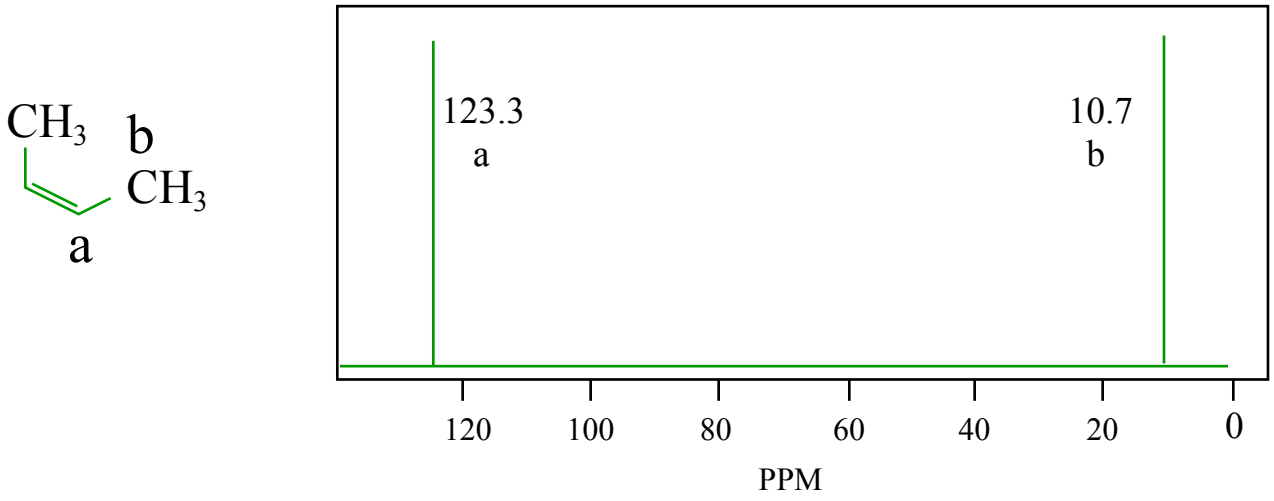
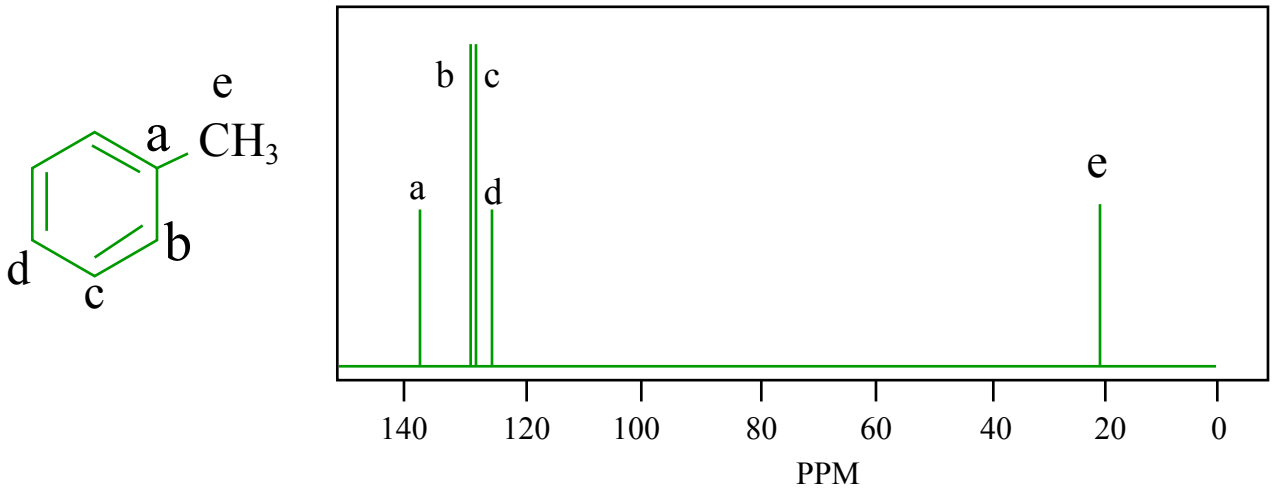
Remarkable Sensitivity of ^{13}C NMR to Chemical Structure (Continued)







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