



Massachusetts Institute of Technology
Organic Chemistry 5.13

September 20, 2006
Prof. Timothy F. Jamison

Notes for Lecture #7

Material Provided on Hour Exam 1 (Friday, September 29, 2006)

The following 4 pages will be provided to you as reference material for the hour exam on Friday, September 29, exactly as they appear here.

(Some of this information has been distributed in previous lecture handouts.)

Infrared Spectra: Tables of Reference

X-H Region

Phenols and Alcohols	ROH	3700-3500 sharp or 3200-3600 broad(H-bonded)
Acids	RCO ₂ H	2800-3600 very broad
Amides and Amines	RCONHR R ₂ NH	3300-3500
C-H bonds	C≡C-H C=C-H C-C-H RCHO	3100-3300 3000-3200 2850-3000 2700-2800

sp Region


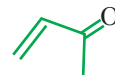
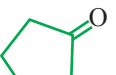

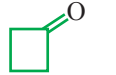
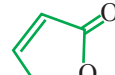
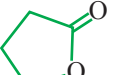
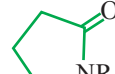
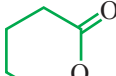
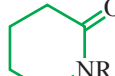
Acetylenes	C≡C	2100
Nitriles	C≡N	2200
Ketenes	C=C=O	2150
Allenes	C=C=C	1950

Double Bond Region

Alkenes	C=C	1600-1670 weak unless conjugated
Imines	C=N	1600-1700
Nitro	-NO ₂	1350-1550(two bands)

Carbonyl Groups

Note: subtract ca. 30 cm⁻¹ for conjugation (e.g. Ketones R₂C=O 1710 (subtract ca. 30 cm⁻¹ for conjugation) with a double bond or aromatic ring)

Anhydrides RC(O)OCOR	1740-1780, 1800-1840 (two bands)		6-membered and larger cyclic ketones 1710		1680
Acid Chlorides RCOCl	1790-1815		1740		1715
Esters RCO ₂ R	1725-1755		1780		1740
Acids RCO ₂ H	1700-1725		1770		1690-1740
Amides RCONR ₂	1630-1700		1730		1650
Urethanes R ₂ NCO ₂ R	1700				
Aldehydes RCHO	1720-1740				

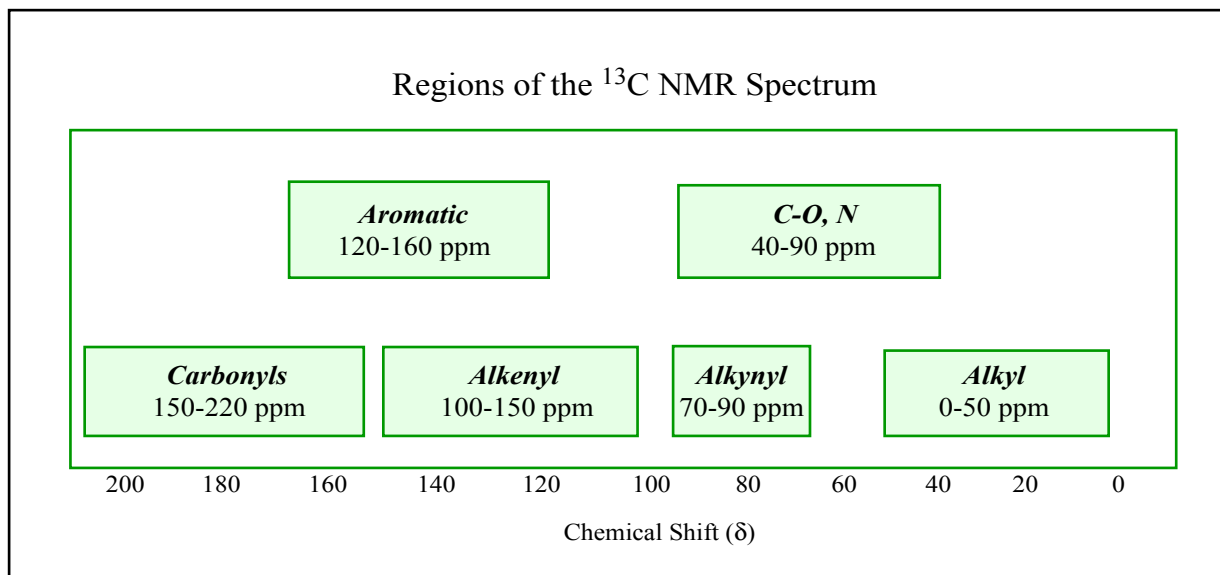


Figure by MIT OCW.

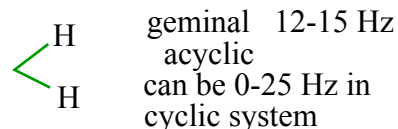
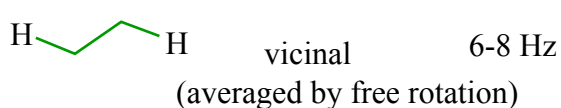
Characteristic Functional Group Chemical Shifts in ^{13}C NMR (ppm)

Alkanes		Organohalogen	
Methyl (RCH_3)	0-30	C-F	70-80
Methylene ($\text{RCH}_2\text{R}'$)	15-55	C-Cl	25-50
Methine ($\text{RCH}(\text{R}')(\text{R}'')$)	25-55	C-Br	10-40
Quaternary ($\text{RC}(\text{R}')(\text{R}'')(\text{R}''')$)	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

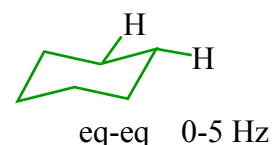
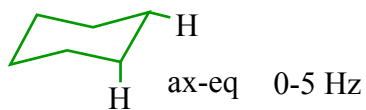
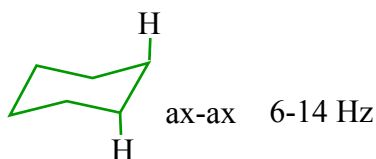
¹H NMR Spectra: Tables of Reference

Average Chemical Shifts (δ) of α -Hydrogens in Substituted Alkanes*				Chemical Shifts of Hydrogens Bonded to Unsaturated Centers		
X	CH ₃ X	RCH ₂ X	R ₂ CHX	Type	Unconjugated	Conjugated*
H	0.233	0.9	1.25	R ₂ C=CH ₂	4.6-5.0	5.4-7.0
CH ₃ or CH ₂	0.9	1.25	1.5	R ₂ C=CHR	5.0-5.7	5.7-7.3
F	4.26	4.4	—	Aromatic	6.5-8.3	—
Cl	3.05	3.4	4.0	Nonbenzenoid aromatic	6.2-9.0	—
Br	2.68	3.3	4.1	Acetylenic	2.3-2.7	2.7-3.2
I	2.16	3.2	4.2	Aldehydic	9.8-9.8	9.5-10.1
OH	3.47	3.6	3.6	R ₂ NCHO	7.9-8.1	—
OR	3.3	3.4	—	ROCHO	8.0-8.2	—
OAr	3.7	3.9	—	* The position depends on the type of functional group in conjugation with the unsaturated group.		
OCOR	3.6	4.1	5.0	Chemical Shifts of Hydrogen Bonded to Oxygen, Nitrogen, and Sulfur		
OCORAr	3.8	4.2	5.1	Functional Group		Chemical Shift, δ
SH	2.44	2.7	—	OH	Akohols	0.5 (Monomeric) 0.5-5 (Associated)
SR	2.1	2.5	—		Phenols	4.5 (Monomeric) 4.5-8 (Associated)
SOR	2.5	—	2.8	NH ₂	Enols	15.5
SO ₂ R	2.8	2.9	3.1		RCO ₂ H	9-12 (Dimeric)
NR ₂	2.2	2.6	2.9		H-bonded to C=O	13-16
NR-Ar	2.9	—	—	NH	Alkylamine	0.6-1.6
NCOR	2.8	—	3.2		Arylamine	2.7-4.0
NO ₂	4.28	4.4	4.7		Amide	7.8
CHO	2.20	2.3	2.4	R ₃ NH ⁺	Alkylamine,	0.3-0.5
COR	2.1	2.4	2.5		Arylamine	2.7-2.8
COAr	2.6	3.0	3.4	Ammonium salts	7.1-7.7 (in CF ₃ COOH)	
COOH	2.07	2.3	2.6	SH	Aliphatic	1.3-1.7
COOR	2.1	2.3	2.6		Aromatic	2.5-4
CONH ₂	2.02	2.2	—	<p>* The tabulated values are average values for compounds that do not contain another functional group within two carbon atoms from the indicated hydrogens.</p> <p>§ Includes polycyclic and many heterocyclic aromatics.</p>		
CR=CR ¹	2.0-1.6	2.3	2.6			
Phenyl	2.3	2.7	2.9			
Aryl δ	3.0-2.5	—	—			
C \equiv CR	2.0	—	—			
C \equiv CN	2.0	2.3	2.7			

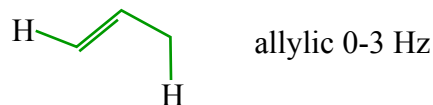
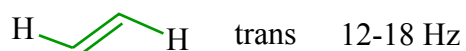
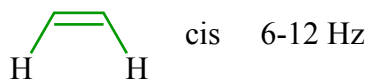
^1H NMR Coupling Constants (Expanded)



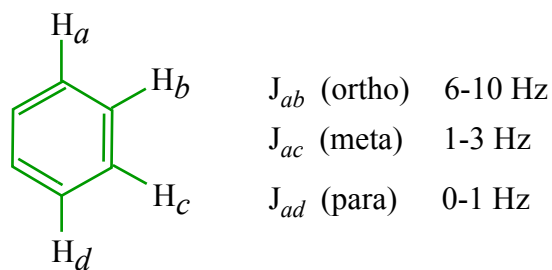
In rigid systems, vicinal coupling can range from 0 to 15 Hz. For example:



Spin-spin coupling in *alkenes*:



Spin- spin coupling in *arenes*:



Note: Structures shown above represent generic coupling situations and not the specific molecules depicted (in which the labeled protons would be chemically equivalent and would not couple).

Figure by MIT OCW.