Handout #3, 5.12 Spring 2003, 2/12/03
Physical Properties: Bond Length, Bond Strength & Acidity

A. Bond Lengths: mostly dependent on atomic size, bond order, and hybridization

Bond Lengths (Å)

sp^3–sp^3	C–C	**1.54**	sp^3–sp^3	C–O	**1.42**
sp^2–sp^2	C=C	**1.34**	sp^2–sp^2	C=O	**1.22**
sp–*sp*	C≡C	**1.20**			

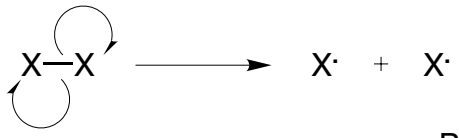
• **Multiple Bonding:** Bond length depends strongly on bond order **(length: single > double > triple)**

Bond Lengths (Å)

sp^3	C–H	**1.09**	sp^3–sp^3	C–C	**1.54**
sp^2	C–H	**1.086**	sp^3–sp^2	C–C	**1.50**
sp	C–H	**1.06**	sp^3–*sp*	C–C	**1.47**

• **Effect of hybridization on length of single bonds:** C–H and C–C bonds shorten slightly with increased *s* character on carbon

B. Bond Strengths/Bond Dissociation Energies (BDEs): Energy for **homolytic** bond cleavage to uncharged radical fragments



Common Bond Strengths (kcal/mol)

C–C	**81**	C–O	**79**
C=C	**145**	C=O	**173**
C≡C	**198**	C–H	**98**

• Bond strengths are bond energies for a certain bond averaged over many different molecules.

• Bond dissociation energies are for a particular molecule and are dependent on the specific molecular structure (Bond Strength ± 20 kcal/mol)

• **Multiple Bonding:** Bond strength depends strongly on bond order **(strength: single < double < triple)**

Data taken from: Advanced Organic Chemistry, 3rd Edition, F. A. Carey and R. J. Sundberg

C. Acidity of Organic Molecules

Functional Group	Acid	Approximate pK_a Values (in water)	Conjugate Base
			increasing basicity ↑
alkane-sp^3	**H–**CH_3	**48**	$^-CH_3$
alkene-sp^2	**H–**$CH{=}CH_2$	**44**	$^-CH{=}CH_2$
amine	**H–**NH_2	**38**	$^-NH_2$
hydrogen	**H–H**	**35**	^-H
alkyne-*sp*	**H–**$C{\equiv}CH$	**25**	$^-C{\equiv}CH$
alcohol	**H–**OCR_3	**17**	$^-OCR_3$
water	**H–OH**	**15.7**	^-OH
thiol	**H–**SR	**10–11**	^-SR
ammonium	**H–**$^+NR_3$	**10–11**	NR_3
nitrile (cyanide)	**H–**$C{\equiv}N$	**9.2**	$^-C{\equiv}N$
phenol	**H–**OAr	**8–11**	^-OAr
carboxylic acid	**H–**$OC(O)R$	**4–5**	$^-OC(O)R$
	H–F	**3.17**	^-F
hydronium	**H–**$^+OH_2$	**–1.74**	OH_2
	H–Cl	**–7**	^-Cl
	H–I	**–10**	^-I
	↓ increasing acidity		

- Acidity increases across a row: H–C < H–N < H–O < H–F (electronegativity)
- Acidity increases down a period: H–F < H–Cl < H–Br < H–I (size)
- Neutral species less acidic than corresponding positively charged species: H–OH < H–$^+OH_2$

pK_a data from: Advanced Organic Chemisry, 4th Ed., J. March