Answers to Puzzles of Chapter 11
Spectroscopy: Infrared and Nuclear Magnetic Resonance

11.1 (a) $\lambda = \dfrac{3.0 \times 10^8 \text{ m/s}}{1.0 \times 10^{14}\text{/s}} = 3.0 \times 10^{-6} \text{ m} = 3.0 \text{ μm}$

$E = (3.98 \times 10^{-13} \text{ s·kJ/mol})(1.0 \times 10^{14}\text{/s}) = 40 \text{ kJ/mol}$

(b) $\nu = \dfrac{3.0 \times 10^8 \text{ m/s}}{1.0 \text{ m}} = 3.0 \times 10^8 \text{ Hz}$

$E = (3.98 \times 10^{-13} \text{ s·kJ/mol})(3.0 \times 10^8 \text{ Hz}) = 1.2 \times 10^{-4} \text{ kJ/mol}$

11.2 FM waves have higher ν and so more energetic photons.

11.3 ν in wavenumbers $= \dfrac{1}{8.00 \text{ μm}} \dfrac{10^4 \text{ μm}}{1 \text{ cm}} = 1250 \text{ cm}^{-1}$

11.4 (a) identical melting points (because they are enantiomers)
(b) Identical spectra: enantiomers have identical physical properties unless in a chiral environment.
(c) By dissolving the enantiomers in a chiral solvent.

11.5 An sp^3 C-H bond is a longer, weaker bond than an sp C-H bond.

11.6 ν of C=N stretch < 2270-2230 cm^{-1} (= ν of C≡N stretch)
ν of C-C stretch < 1680-1640 cm^{-1} (= ν of C=C stretch)

11.7 bands at 2950-2850 cm^{-1}: sp^3 C-H

11.8 A benzene ring would also have a band at 1630-1580 cm^{-1} for C═ C, but not one at 1680-1640 cm^{-1} for C=C.

11.9 (a) The less balanced 1-pentyne with a H and an R group on its C≡C would have a stronger band because its dipole changes more during stretching than the more balanced 2-pentyne.
(b) 1-Pentyne alone has sp C-H bands at 3320-3280 and 650-625 cm^{-1}.

11.10 Because a relatively small proportion of bonds in the molecule are sp^3 C-H bonds.

11.11 An alcohol alone would have a strong band at 1320-1000 cm^{-1} from its C-O stretch.

11.12 (a) An sp^3 C-Cl bond is stronger than an sp^3 C-I bond.
(b) So an sp^3 C-Cl bond stretch should absorb IR light at a higher ν.

11.13 **A**: a terminal alkyne (1-hexyne)
3300 cm^{-1} (s): sp C-H; 3000-2850 cm^{-1} (s): sp^3 C-H; 2120 cm^{-1} (m): C≡C;
630 cm^{-1} (s): sp C-H bend

B: an alcohol (2-ethyl-1-butanol)
3330 cm^{-1} (s): O-H; 3000-2850 cm^{-1} (s): sp^3 C-H; 1050 cm^{-1} (s): C-O

C: an alkene & an ether (3-ethoxy-1-propene)
3080 cm^{-1} (m): sp^2 C-H; 3000-2850 cm^{-1} (s): sp^3 C-H; 1650 cm^{-1} (m): C=C;
1110 cm^{-1} (s): C-O; 920 cm^{-1} (s): sp^2 C-H bend

D: an aromatic compound & an alkyl halide (benzyl bromide, i.e. bromophenylmethane)
3100-3000 cm^{-1} (m): sp^2 C-H; 2960 cm^{-1} (m): sp^3 C-H; 1600 cm^{-1} (w): C=C;
760, 690 cm^{-1} (s): sp^2 C-H; 605 cm^{-1} (s): sp^3 C-Br

11.14 nuclear spin: (b), (c), (e)

11.15 (a) ΔE = (3.98 x 10^{-13} s·kJ/mol)(100 x 10^6/s) = 3.98 x 10^{-5} kJ/mol
(b) H = $\dfrac{100\ \text{MHz}}{300\ \text{MHz}}$ x 7.045 tesla = 2.348 tesla

11.16 The less EN Si puts a δ- on each C, which shields the nearby protons.

11.17   δ 4.91: O-CH$_2$-O;   δ 3.91: O-CH$_2$-C

11.18 (a) The signal for the solvent CHCl$_3$, in high concentration, would swamp nearby signals.
(b) This signal is at δ 7.2, brought left by 3 δ+ from χ Cl's.

11.19 (a) 2 signals in 2:3 area ratio   (b) 3 signals in 3:2:3 area ratio
(c) 2 signals in 2:3 area ratio   (d) 4 signals in 1:2:2:3 area ratio   (e) 3 signals in 1:1:6 area ratio
(f) 4 signals in 2:2:2:1 area ratio   (g) 4 signals in 4:1:2:1 area ratio   (h) 2 signals in 1:1 area ratio
(i) 3 signals in 2:1:1 area ratio

11.20 Because they are usually (though not always) equivalent

11.21 (a) CH$_3$O δ 3.2, singlet; CH$_2$ δ 3.4, quartet; CH$_3$C δ 1.2, triplet
(b) CH$_3$ δ 1.7 (d); CH δ 4.1 (heptet)   (c) CH$_2$ δ 3.7 (s)   (d) CH δ 5.8 (t); CH$_2$ δ 4.0 (d)
(e) HC=O δ 9.5 (s); CH$_3$ δ 1.8 (s); CH$_2$ δ 6.2 (d) & 5.9 (d)

11.22 (a) ↓ [alcohol] ↓ amount of intermolecular H "bonding" & ↓ δof protons on O.
(b) The drawing shows a triplet at δ 5.7, a doublet at δ 4.0, and a broad singlet at ~δ 1-3.

11.23   Br$_2$CH triplet: ｜ ｜ ｜
                         → 6 ←
BrCH$_2$ triplet: ｜ ｜ ｜
                    → 8 ←
C-CH$_2$-C doubled triplet: ｜ ｜｜ ｜｜ ｜
                              → 6 ←
                              → 8 ←

11.24

11.25 (a) 1,2-dimethylbenzene: 4 signals; 1,3-dimethylbenzene: 5 signals;
1,4-dimethylbenzene: 3 signals   (b) 1,3-dichlorobenzene, because it alone has 4 signals.

11.26 1:3:3:1 quartet (because of 3 Hs on each C)

11.27 (a) x-rays (higher frequency) (b) blue light (x-rays are invisible)

11.28 C=O because it's more polar and so its polarity changes more during stretching

11.29 (a) $HO-CH_2-CH_2-C\equiv CH$
π bonds & rings $= ((2\cdot4+2) - 6)/2 = 2$
assignments: 3350 cm^{-1}: O-H; 3280 cm^{-1}: sp C-H; 3000-2850 cm^{-1}: sp^3 C-H;
2120 cm^{-1}: C$\equiv$C; 1040 cm^{-1}: O-C; 640 cm^{-1}: sp C-H bend
(b) $HO-CH_2-CH_2-CH=CH_2$
π bonds & rings $= ((2\cdot4+2) - 8)/2 = 1$
assignments: 3320 cm^{-1}: O-H; 3070 cm^{-1}: sp^2 C-H; 3000-2850 cm^{-1}: sp^3 C-H;
1640 cm^{-1}: C=C; 1050 cm^{-1}: O-C; 890 cm^{-1}: sp^2 C-H bend

(c) ⬡=O

π bonds & rings $= ((2\cdot6+2) - 10)/2 = 2$
assignments: 3000-2850 cm^{-1}: sp^3 C-H; 1710 cm^{-1}: C=O

11.30 (a) only 1-pentene shows sp^2 C-H bands at 3100-3000 & 1000-650 cm^{-1} & a C=C band at 1680-1640 cm^{-1}
(b) only 2-butanol shows an O-H band at 3500-3200 cm^{-1}
(c) Only the alcohol shows an O-H band at 3500-3200 cm^{-1} & a C-O band at 1320-1000 cm^{-1}.
Only the ketone shows a C=O band at 1740-1705 cm^{-1}.
(d) Only the alkene shows sp^2 C-H bands at 3100-3000 & 1000-650 cm^{-1} & a C=C band at 1680-1640 cm^{-1}. Only the alkyne shows sp C-H bands at 3320-3280 & 650-625 cm^{-1} & a C$\equiv$C band at 2250-2100 cm^{-1}.
(e) Only the terminal alkyne shows sp C-H bands at 3320-3280 & 650-625 cm^{-1}.
(f) Only the aldehyde shows two sp^2 C-H bands at 2840-2700 cm^{-1}.

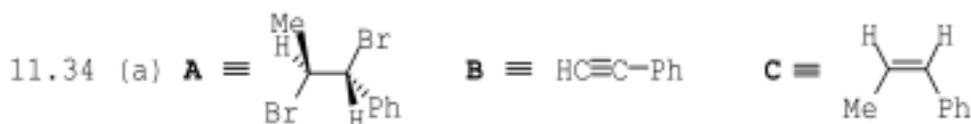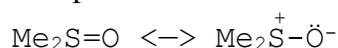11.31 (a) $H_2\overset{+}{C}-CH=C=\overset{-}{N}$
(b) below 2270-2230 cm^{-1}, because resonance makes the bond order of the C-N bond less than 3.

11.32 They are diastereomers with different but similar IR spectra and other physical properties.

11.33 (a)

$Me_2\overset{+}{S}-\overset{-}{O}-CuCl_2$ vs $Me_2\overset{\overset{O}{\|}+}{S}-\overset{-}{PtCl_2}$

In the 1st complex the S-O bond is weaker with a bond order of 1.
(b) Uncomplexed in its 2 resonance forms, the S-O bond is intermediate in bond order:

$Me_2S=O$ <-> $Me_2\overset{+}{S}-\overset{..}{\overset{..}{O}}{}^-$

11.34 (a) **A** ≡ [structure: Me, H on C; Br; Br, H, Ph]   **B** ≡ HC≡C-Ph   **C** ≡ [structure: H, H / Me, Ph alkene]

(b) diastereomers   (c) similar but different spectra because they are diastereomers

11.35 (a) 2 x CH$_3$; 2 x CH$_2$ (b) 3 x CH$_3$; CH   (c) CH$_3$; C-CH$_2$-C; CH$_2$Cl
(d) 2 x CH$_2$Cl; C-CH$_2$-C   (e) 2 x CH$_2$; CH   (f) 5 x CH$_2$
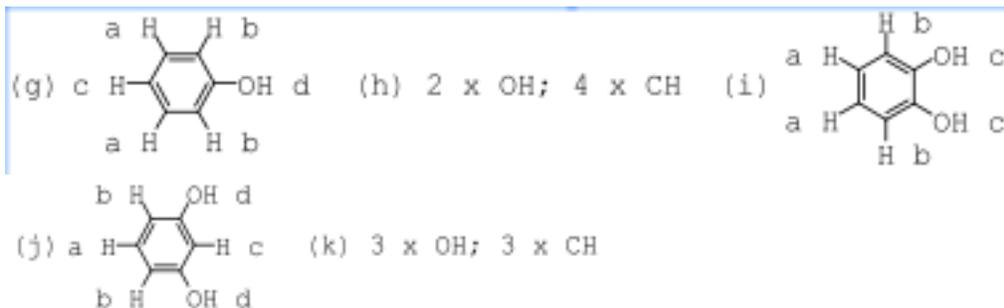
(g), (h) 2 x OH; 4 x CH, (i)

(j), (k) 3 x OH; 3 x CH

11.37 (a) δ 3.5 (q), δ 1.7 (d)   (b) δ 2.7 (q), δ 2 (s), δ 1.1 (t).
(c) δ 3.1 (s), δ 1.1 (d), δ 3.6 (heptet)   (d) δ 1.5 (d), δ 3.6 (q), δ 1.0 (s)

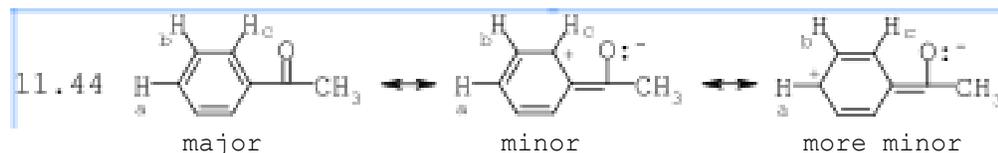11.38 (a) δ 4.0 (heptet), δ 2 (s), δ 1.2 (d)   (b) δ 3.6 (t), δ 2 (s), δ 1.6 (sextet), δ 0.9 (t)

11.39 (a) δ 3.5 (s), δ 2 (s)
(b) OH signal is greatly reduced because most of these Hs are exchanged with Ds from D_2O
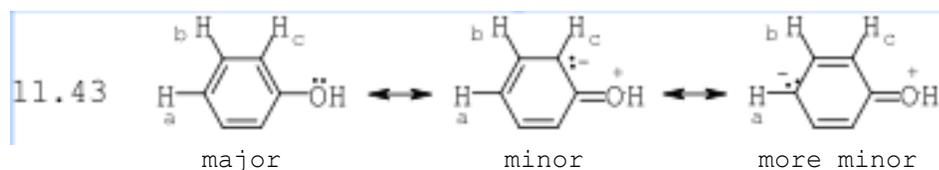
11.43

major   minor   more minor

δ 5.7 (s): OH; δ 6.8 (d): H_c; δ 6.9 (t): H_a; δ 7.2 (t): H_b.
Minor form puts a δ- near H_c. More minor form puts a smaller δ- near H_a. δ- shields the H.

11.44

major   minor   more minor

δ 2.6 (s): CH_3; δ 7.4 (t): H_b; δ 7.5 (t) H_a; δ 7.9 (d) H_c.
Minor form puts a δ+ near H_c. More minor form puts a smaller δ+ near H_a. δ+ deshields the H.

11.45 (a) Cl_2CH-CH_3
π bonds & rings = $((2 \cdot 2+2) - (4+2))/2 = 0$
IR: 3000-2850 cm^{-1} (s): sp^3 C-H; 690 cm^{-1} (s): sp^3 C-Cl
NMR: δ 5.9 (q): Cl_2CH; δ 2.1 (d): CH_3
(b) $ClCH_2-CH_2-CH_2Cl$
π bonds & rings = $((2 \cdot 3+2) - (6+2))/2 = 0$
NMR: δ 3.7 (t): $ClCH_2$; δ 2.2 (quintet): $C-CH_2-C$
(c) $CH_3-CHCl-CH_2-CH_3$
π bonds & rings = $((2 \cdot 4+2) - (9+1))/2 = 0$
NMR: δ 3.9 (sextet): CHCl; δ 1.6 (multiplet): CH_2; δ 1.5 (d): CH_3-CCl; δ 1.0 (t): CCl-C-CH_3
(d) $(CH_3)_2CH-CH_2Cl$
π bonds & rings = $((2 \cdot 4+2) - (9+1))/2 = 0$
NMR: δ 3.4 (d): CH_2Cl; δ 2.0 (multiplet): CH-CCl; δ 1.0 (d): $(CH_3)_2$
(e) $ClCH_2-O-CH_2-CH_3$
π bonds & rings = $((2 \cdot 3+2) - (7+1))/2 = 0$
IR: 3000-2850 cm^{-1} (s): sp^3 C-H; 1140 cm^{-1} (s): C-O; 640 cm^{-1} (s): sp^3 C-Cl
NMR: δ 5.5 (s): $ClCH_2$-O; δ 3.8 (q): O-CH_2-C; δ 1.3 (t): CH_3

(f) H_3C—⬡(O)—$CH=O$
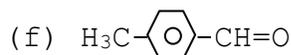
π bonds & rings = $((2\cdot8+2) - (8))/2 = 5$

IR: 3100-3000 cm^{-1} (w): sp^2 C-H; 3000-2850 cm^{-1} (w): sp^3 C-H; 2830, 2720 cm^{-1} (m): OC-H; 1700 cm^{-1} (s): C=O; 1600 cm^{-1} (m): C═C; 850, 800, 760 cm^{-1} (s): sp^2 C-H bend
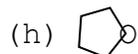
NMR: δ 9.9 (s): CH=O; δ 7.7, δ 7.3 (d): C$_6$H$_4$; δ 2.5 (s): CH$_3$

(g) $(CH_3CH_2)_2C=O$

π bonds & rings = $((2\cdot5+2) - (10))/2 = 1$

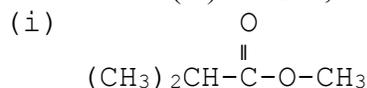IR: 3000-2850 cm^{-1} (s): sp^3 C-H; 1720 cm^{-1} (s): C=O

NMR: δ 2.4 (q): CH$_2$; δ 1.0 (t): CH$_3$

(h) ⬠○

π bonds & rings = $((2\cdot4+2) - (8))/2 = 1$

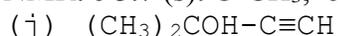IR: 3000-2850 cm^{-1} (s): sp^3 C-H; 1070 cm^{-1} (s): C-O

NMR: δ 3.7 (~t): CH$_2$-O; δ 1.8 (m): CH$_2$-C-O

(i)
$$\begin{array}{c} O \\ \| \\ (CH_3)_2CH-C-O-CH_3 \end{array}$$

π bonds & rings = $((2\cdot5+2) - (10))/2 = 1$

IR: 3000-2850 cm^{-1} (s): sp^3 C-H; 1740 cm^{-1} (s): C=O; 1160 cm^{-1} (s): C-O

NMR: δ 3.7 (s): O-CH$_3$; δ 2.5 (m): CH; δ 1.2 (d): (CH$_3$)$_2$

(j) $(CH_3)_2COH-C\equiv CH$
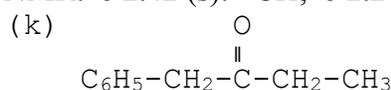
π bonds & rings = $((2\cdot5+2) - (8))/2 = 2$

IR: 3380 cm^{-1} (s, broad): O-H; 3300 cm^{-1} (s): sp C-H; 3000-2850 cm^{-1} (s): sp^3 C-H; 2120 cm^{-1} (w): C$\equiv$C; 1170 cm^{-1} (s): O-H; 650 cm^{-1} (s): sp C-H bend

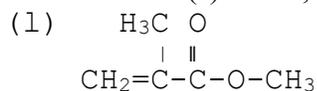NMR: δ 2.42 (s): $\equiv$CH; δ 2.27 (s): OH; δ 1.55 (s): CH$_3$

(k)
$$\begin{array}{c} O \\ \| \\ C_6H_5-CH_2-C-CH_2-CH_3 \end{array}$$

π bonds & rings = $((2\cdot10+2) - (12))/2 = 5$

IR: 3100-3000 cm^{-1} (m): sp^2 C-H; 3000-2850 cm^{-1} (m): sp^3 C-H; 1710 cm^{-1} (s): C=O; 1600 cm^{-1} (w): C═C; 700 cm^{-1} (s): sp^2 C-H bend

NMR: δ 7.20 (s): Ar H; δ 3.60 (s): Ph-CH$_2$; δ 2.35 (q): O=C-CH$_2$-Me; δ 0.95 (t): CH$_3$

(l)
$$\begin{array}{c} H_3C \quad O \\ \;\;\; | \;\;\; \| \\ CH_2=C-C-O-CH_3 \end{array}$$

π bonds & rings = $((2\cdot5+2) - (8))/2 = 2$

IR: 3020 cm^{-1} (w): sp^2 C-H; 3000-2900 cm^{-1} (m): sp^3 C-H; 1720 cm^{-1} (s): conj. C=O; 1640 cm^{-1} (m): conj. C=C; 1160 cm^{-1} (s): C-O; 940 cm^{-1} (m): sp^2 C-H

NMR: δ 6.12, 5.58 (2x s): =CH$_2$; 3.79 (s): OCH$_3$; 1.98 (s): CCH$_3$

11.46 1,2-dichlorobenzene