CHAPTER 2

2.1

$$v = \frac{1}{2\pi c}\sqrt{k\left(\frac{m1m2}{m1+m2}\right)}$$

(k) force constant = $4\pi^2c^2\, v^2\, m_{eff}$

$m_{eff} = \left(\frac{m1m2}{m1+m2}\right)$

$m_{eff} = ({}^1H^{19}F) = \frac{(1.0078 \text{ x } 18.9984)}{(1.0078 + 18.9984)} = 0.9570\ \mu$

$m_{eff} = ({}^1H^{35}Cl) = 0.9796\ \mu$

$m_{eff} = ({}^1H^{81}Br) = 0.9954\ \mu$

$m_{eff} = ({}^1H^{127}I) = 0.9999\ \mu$

(k) $({}^1H^{19}F) = 4 \text{ x } 3.14^2 \text{ x } (2.997 \text{ x } 10^{10} \text{ cm s}^{-1})^2 \text{ x } (4148.2 \text{ cm}^{-1})^2 \text{ x } (0.9570 \text{ x } 1.66 \text{ x } 10^{-27}\text{kg})$
$= 968.3 \text{ kg s}^{-2} = 968.3 \text{ N/m}$

(k) $({}^1H^{35}Cl) = 514.6$ N/m

(k) $({}^1H^{81}Br) = 410.9$ N/m

(k) $({}^1H^{127}I) = 313.6$ N/m

Assume that the force constant for halides are the same when substituting the deuterium -- the calculated bond stretch frequency for halides:

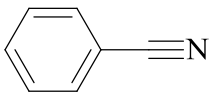
$$v = \frac{1}{2\pi c}\sqrt{k\left(\frac{m1m2}{m1+m2}\right)}$$

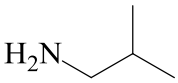
2.2. The gross selection rule for infrared activity is that motion corresponding to a normal mode should be accompanied by a change of dipole moment. So those molecules in which a vibration gives rise to a change in dipole moment are infrared active compounds:
(a) CH_3CH_3, (b) CH_4, (c) CH_3Cl.
It is helpful to write down the structural formulas of the compounds

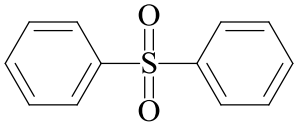
2.3. A nonlinear molecule has 3N-6 normal modes of vibration, where N is the number of atoms in the molecule; a linear molecule has 3N-5.
(a) C_6H_6 has 3(12) – 6 = $\boxed{30}$ normal modes
(b) $C_6H_6CH_3$ has 3(16) – 6 = $\boxed{42}$ normal modes
(c) HC≡C-C≡CH is linear; it has 3(6) – 5 = $\boxed{13}$ normal modes

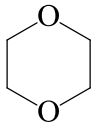
2.4. From top to bottom the: *o*-xylene, *m*-xylene, then *p*-xylene

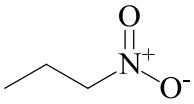
2.5.

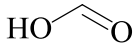

a. benzonitrile

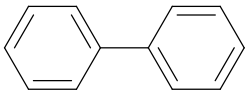

b. isobutylamine

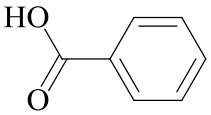

c. diphenyl sulfone

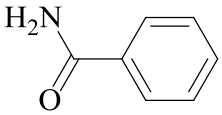

d. dioxane


e. 1-nitropropane


f. formic acid


g. biphenyl


h. benzoic acid

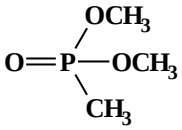
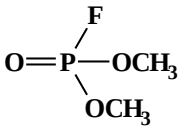
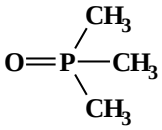
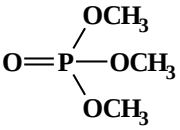

i. benzamide

2.6. For butyric acid and ethyl butyrate, the carbonyl stretching band is a result of a simple fundamental stretching mode. Butyric anhydride, on the other hand, exhibits 2 carbonyl stretching frequencies due to coupling of the carbonyls through the common oxygen atom of the anhydride functional group. The 2 frequencies are respectively the symmetric and asymmetric stretching frequencies.

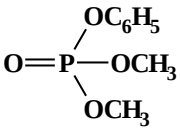
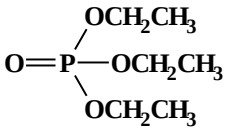
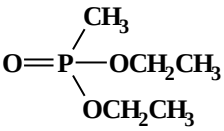
2.7. Combination bands are a result of complex interactions between 2 or more fundamental vibration modes. For instance, if a fundamental vibration does not occur because of the wrong symmetry, it can combine with another fundamental frequency of proper symmetry to produce one or more combination band. A series of useful combination bands is often found between 1700 and 2000 cm^{-1} for aromatic compounds.

For an oscillator, the lowest "natural" frequency is called the fundamental frequency (n=1). Higher order frequencies are called "overtones". The first overtone (n=2) can be found at approximately twice the frequency of the fundamental frequency. Higher overtones are possible but rarely seen. A common overtone band found in IR spectra is the first overtone band of the carbonyl stretch of ketones. The fundamental frequency is typically found at 1715 cm^{-1} while the first overtone is often seen at approximately 3420 cm^{-1}.

2.8. Table 2.10 is used to determine this answer. The more electronegative the functional groups are, the higher the P-O IR stretching frequency.

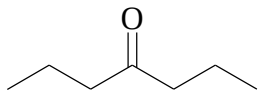





3	7	1	5

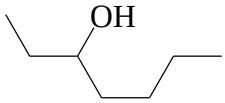
6	4	2

2.9



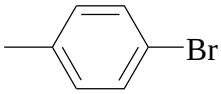
4-Heptanone

A



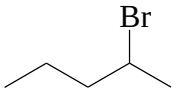
3-Heptanol

B



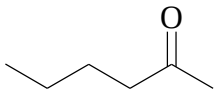
4-Bromotoluene

C



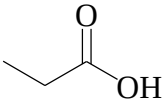
2-Bromopentane

D



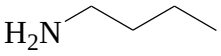
2-Hexanone

E



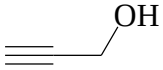
Propionic Acid

F



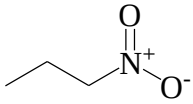
Butylamine

G



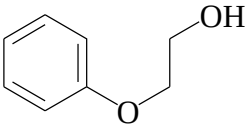
Propargyl alcohol

H



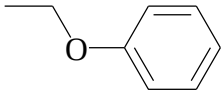
1-Nitropropane

I



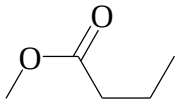
2-Phenoxylethanol

J



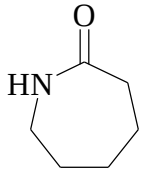
Phenetole

K



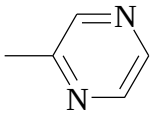
Methyl Butyrate

L



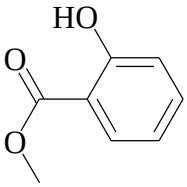
Caprolactam

M



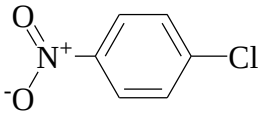
2-methylpyrazine

N



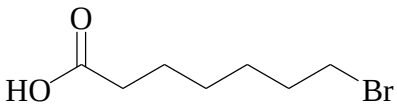
Methyl salicylate

O



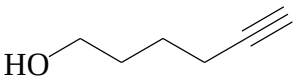
1-Chloro-4-Nitrobenzene

P



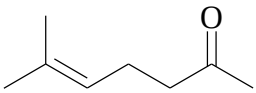
7-Bromo Heptanoic Acid

Q



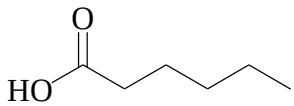
5-Hexyn-1-ol

R



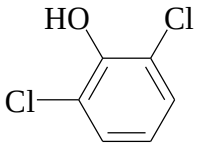
6-Methyl-5-hepten-2-one

S



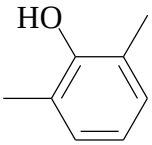
Hexanoic acid

T



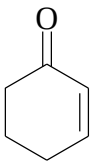
2,6-Dichlorophenol

U



2,6-Dimethylphenol

V



2-Cyclohexen-1-one

W