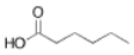
3.8: More Complicated Spectra

Sometimes more complicated heteroatomic functional groups, containing bonds to more than one heteroatom, have slightly different spectra. Carboxylic acids feature a hydroxyl group bonded to a carbonyl. Hexanoic acid, a carboxylic acid in a six-atom chain, is one example.



hexanoic acid

If you look at the IR spectrum of hexanoic acid:

- there are CH_2 bending modes at 1500 cm^{-1}.
- there is a very strong C=O peak around 1700 cm^{-1}.
- there is a medium C-O peak around 1250 cm^{-1}.
- the sp^3 C-H and O-H stretching modes are less clear.

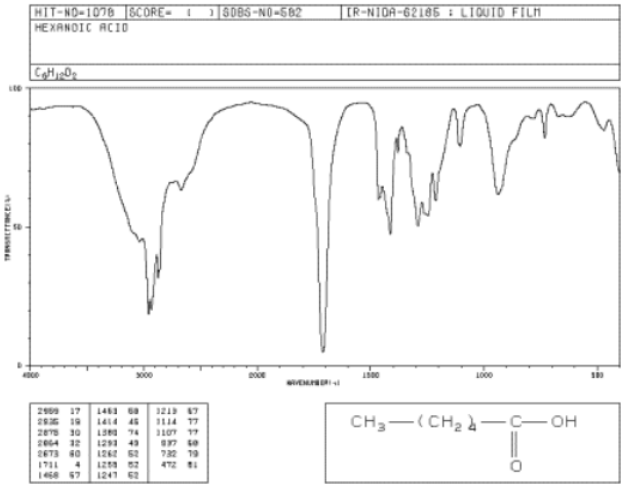
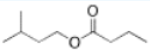


Figure 3.8.1: IR spectrum of hexanoic acid. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

At first, the O-H peak appears to be absent. The C-H stretch appears to be very broad. The wide peak between 3000 and 2600 cm^{-1} is really the usual C-H stretch with a broad O-H stretch superimposed on it. The low frequency vibration of this O-H bond is related to the partial dissociation of protons due to strong hydrogen bonding.

? Exercise 3.8.1

Isopentyl butanoate has a C-O stretch at 1200 cm^{-1}. We saw earlier that an ether had a C-O stretch around 1000 cm^{-1}. Explain the differences in these bond stretches.



isopentyl butanoate aka isopentyl butyrate

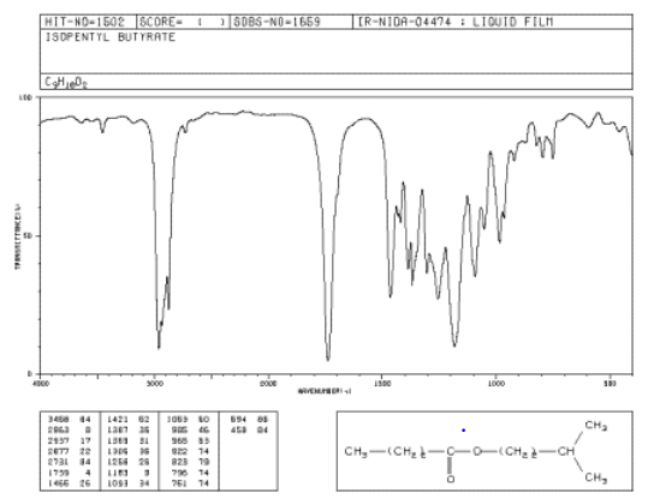
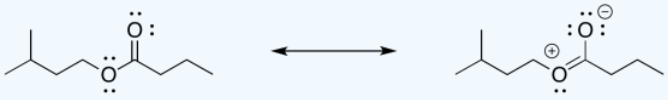


Figure 3.8.2: IR spectrum of isopentyl butanoate. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

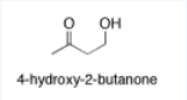
Answer

The $C_{sp}2$-O bond is conjugated, so there is some double bond character, making the bond stronger and moving the IR peak to higher frequency.



Exercise 3.8.2

Locate an O-H, a C-O and a C=O bond stretch in an IR spectrum of 4-hydroxy-2-butanone.



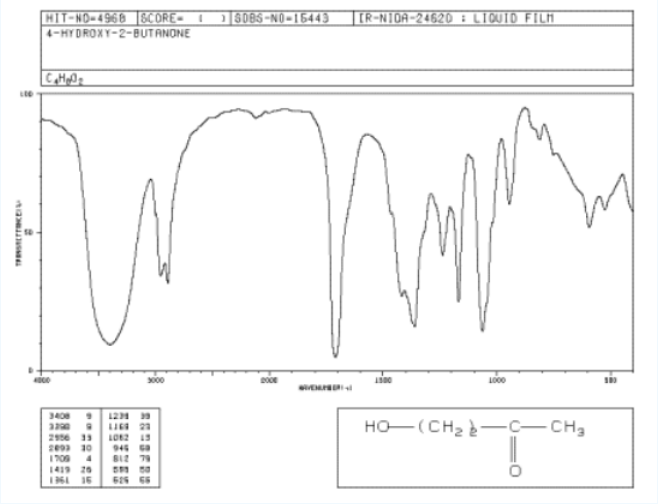


Figure 3.8.3: IR spectrum of 4-hydroxy-2-butanone. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

Answer

OH: 3400 cm^{-1} (strong, broad)

C=O: 1700 cm^{-1} (strong)

C-O: 1050 cm^{-1} (strong)
