

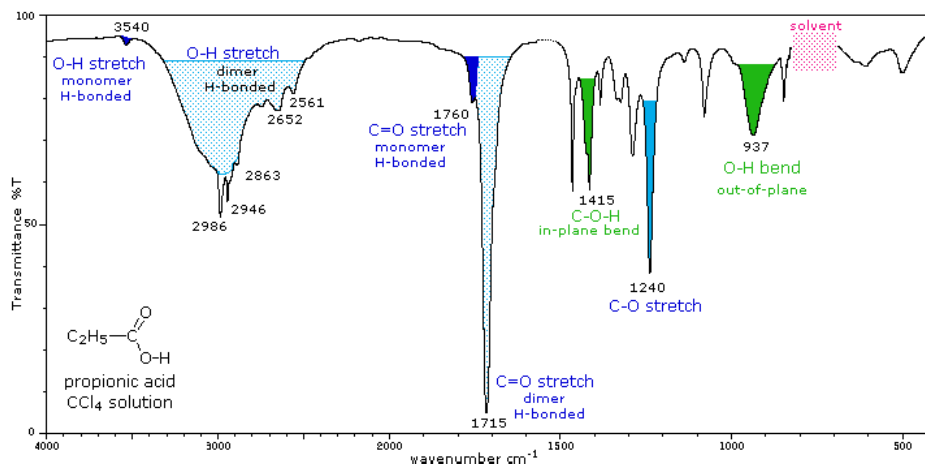
## 21.3: SPECTROSCOPY OF CARBOXYLIC ACIDS

### IR

The carboxyl group is associated with two characteristic infrared stretching absorptions which change markedly with hydrogen bonding. The spectrum of a  $\text{CCl}_4$  solution of propionic acid (propanoic acid), shown below, is illustrative. Carboxylic acids exist predominantly as hydrogen bonded dimers in condensed phases. The O-H stretching absorption for such dimers is very strong and broad, extending from 2500 to 3300  $\text{cm}^{-1}$ .

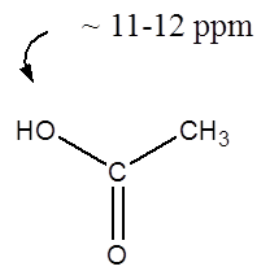


This absorption overlaps the sharper C-H stretching peaks, which may be seen extending beyond the O-H envelope at 2990, 2950 and 2870  $\text{cm}^{-1}$ . The smaller peaks protruding near 2655 and 2560 are characteristic of the dimer. In ether solvents a sharper hydrogen bonded monomer absorption near 3500  $\text{cm}^{-1}$  is observed, due to competition of the ether oxygen as a hydrogen bond acceptor. The carbonyl stretching frequency of the dimer is found near 1710  $\text{cm}^{-1}$ , but is increased by 25  $\text{cm}^{-1}$  or more in the monomeric state. Other characteristic stretching and bending absorptions are marked in the spectrum.

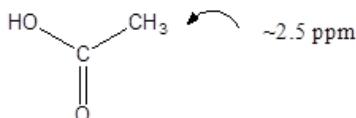


### NMR

The combination of anisotropy and electronegativity causes the O-H hydrogen in a carboxylic acid to be very deshielded.



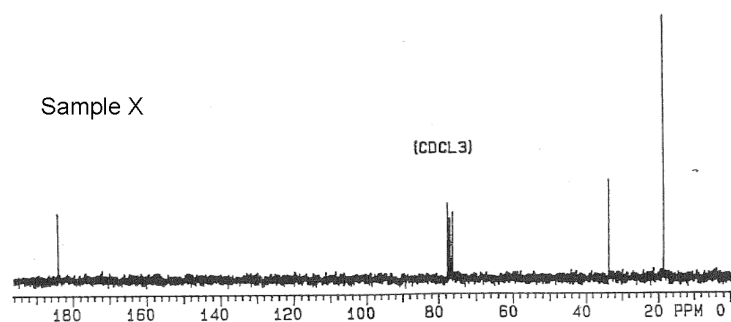
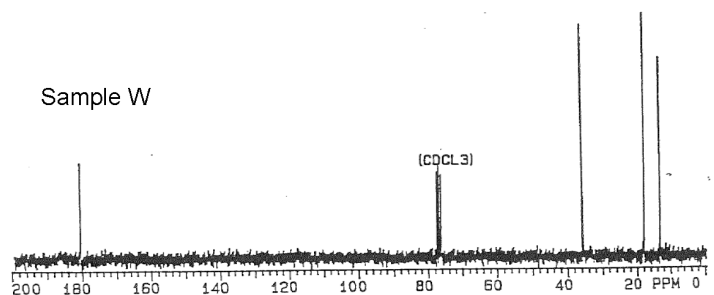
Hydrogen environments adjacent to a carboxylic acid are shifted to the region of 2.5-3.0 ppm. Deshielding occurs due to the fact that the  $\text{sp}^2$  hybridized carbon in the carboxylic acid is more electronegative than a  $\text{sp}^3$  hybridized carbon.



### Exercise

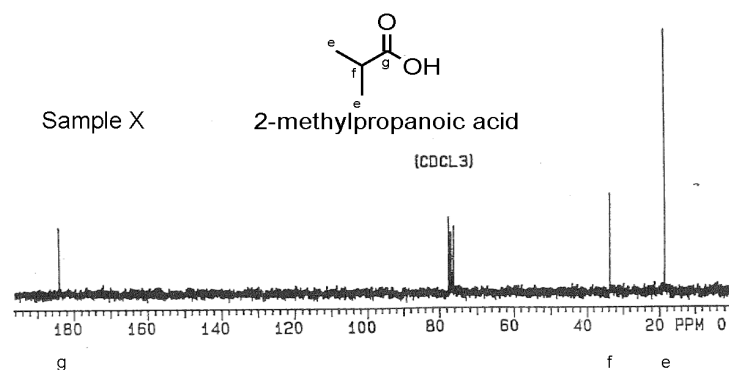
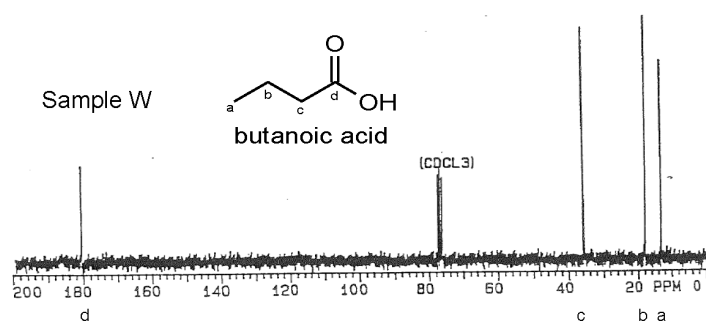
2. Sample W is a reactant for a wide range of biochemical processes. Sample X was isolated from vanilla beans. Elemental analysis indicated the compounds are structural isomers with the composition: 54.52% C, 9.16% H and 36.32% O. The IR spectrum for each compound showed a broad absorption from 3500 - 2500  $\text{cm}^{-1}$  and a strong band near 1710  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR is being serviced, so only the  $^{13}\text{C}$  NMR spectra shown below were available.

Name and draw the bond-line structures for Samples W and X and correlate the  $^{13}\text{C}$  NMR spectral signals to their respective compounds.



### Answer

2.



## CONTRIBUTORS AND ATTRIBUTIONS

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- Prof. Steven Farmer ([Sonoma State University](#))

21.3: Spectroscopy of Carboxylic Acids is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.