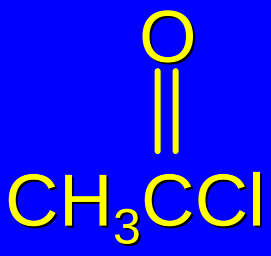
Section 20.21

Spectroscopic Analysis of Carboxylic Acid Derivatives

Infrared Spectroscopy

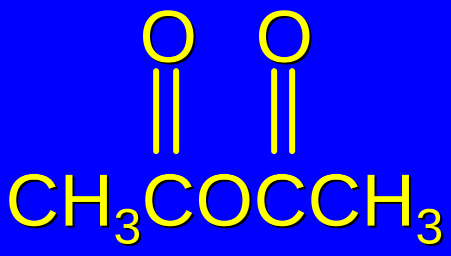
C=O stretching frequency depends on whether the compound is an acyl chloride, anhydride, ester, or amide.

C=O stretching frequency ν



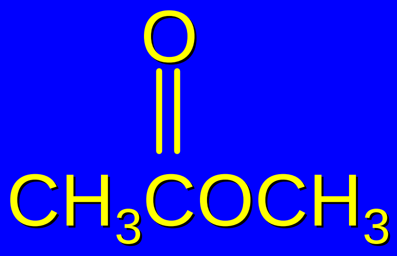
$CH_3\overset{O}{\overset{\|}{C}}Cl$

1822 cm^{-1}



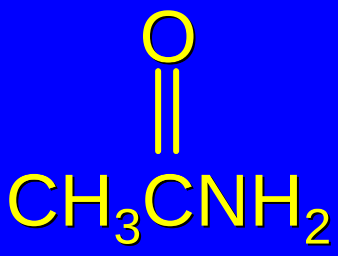
$CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3$

1748
and
1815 cm^{-1}



$CH_3\overset{O}{\overset{\|}{C}}OCH_3$

1736 cm^{-1}



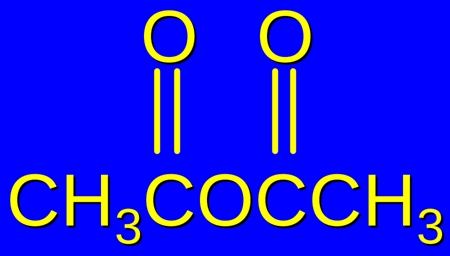
$CH_3\overset{O}{\overset{\|}{C}}NH_2$

1694 cm^{-1}

Infrared Spectroscopy

Anhydrides have two peaks due to C=O stretching. One results from symmetrical stretching of the C=O unit, the other from an antisymmetrical stretch.

C=O stretching frequency ν



$CH_3\overset{O}{\overset{\parallel}{C}}O\overset{O}{\overset{\parallel}{C}}CH_3$

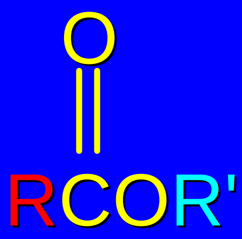
1748
and
1815 cm^{-1}

Infrared Spectroscopy

Nitriles are readily identified by absorption due to carbon-nitrogen triple bond stretching in the 2210-2260 cm^{-1} region.

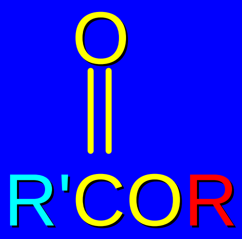
^{1}H NMR

^{1}H NMR readily distinguishes between isomeric esters of the type:

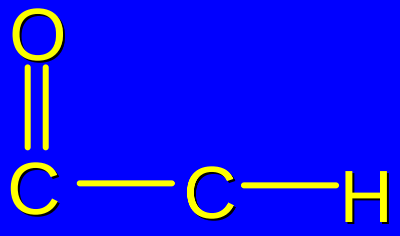


$\text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OR}'$

and



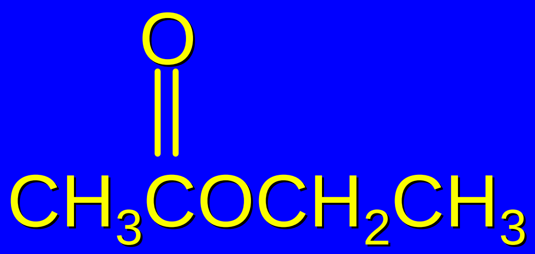
$\text{R}'\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OR}$



$\text{O}-\text{C}-\text{H}$ is less shielded than $\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{C}-\text{H}$

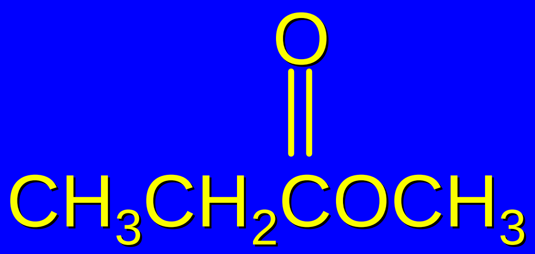
^{1}H NMR

For example:



$CH_3COCH_2CH_3$

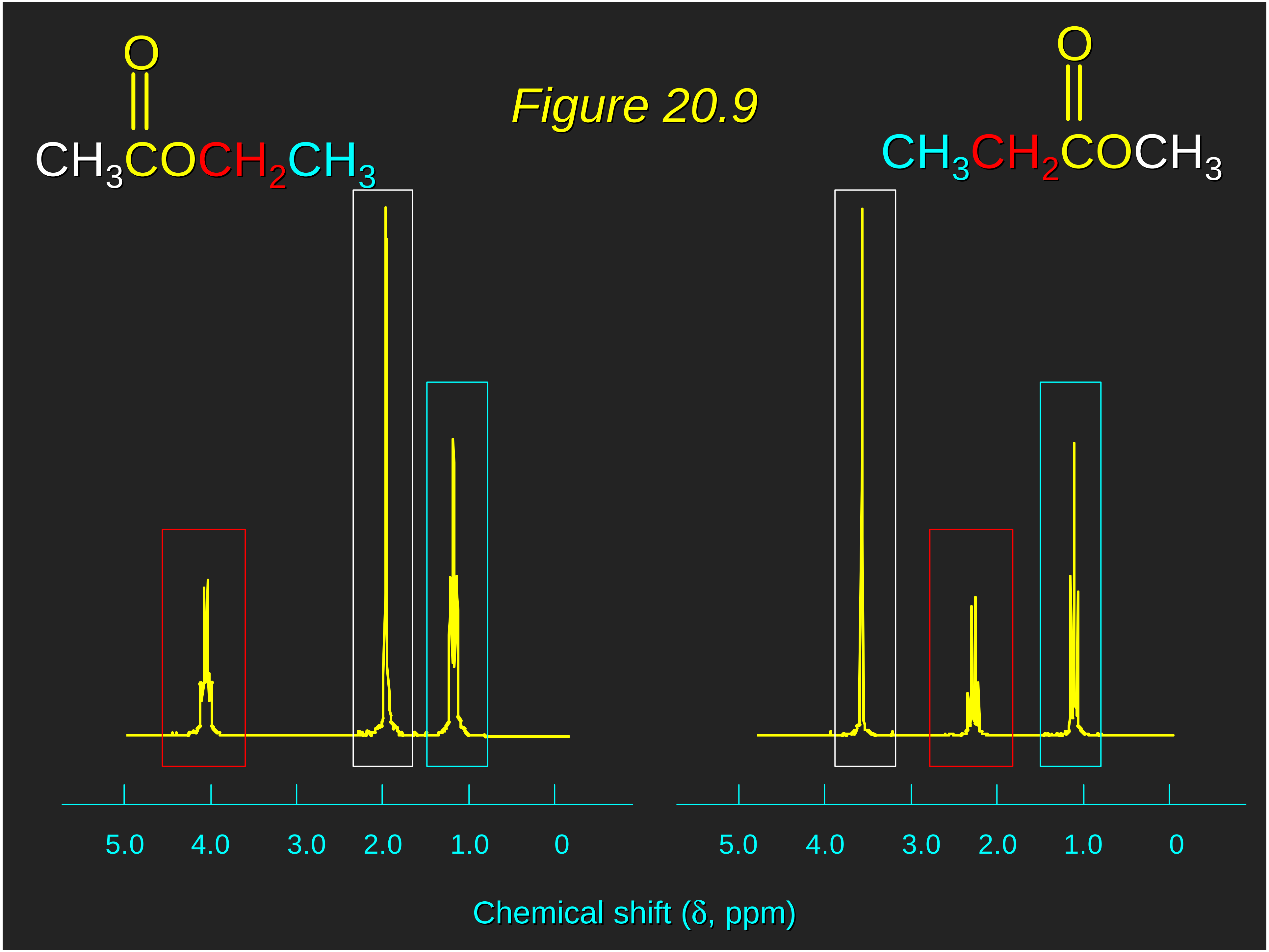
and



$CH_3CH_2COCH_3$

Both have a triplet-quartet pattern for an ethyl group and a methyl singlet. They can be identified, however, on the basis of chemical shifts.

Figure 20.9


$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$

$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3$

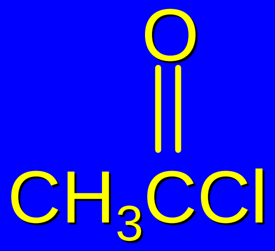
^{13}C NMR

Carbonyl carbon is at low field (δ 160-180 ppm), but not as deshielded as the carbonyl carbon of an aldehyde or ketone (δ 190-215 ppm).

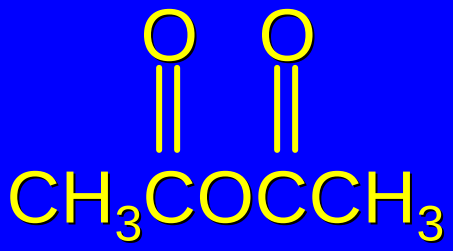
The carbon of a CN group appears near δ 120 ppm.

UV-VIS

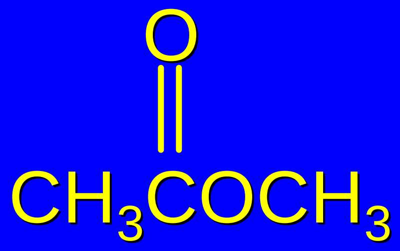
n∅π* absorption: λ_{max}



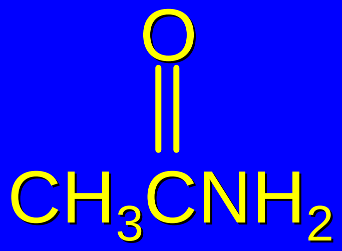
$CH_3\overset{\overset{O}{\|}}{C}Cl$



$CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CH_3$



$CH_3\overset{\overset{O}{\|}}{C}OCH_3$



$CH_3\overset{\overset{O}{\|}}{C}NH_2$

235 nm

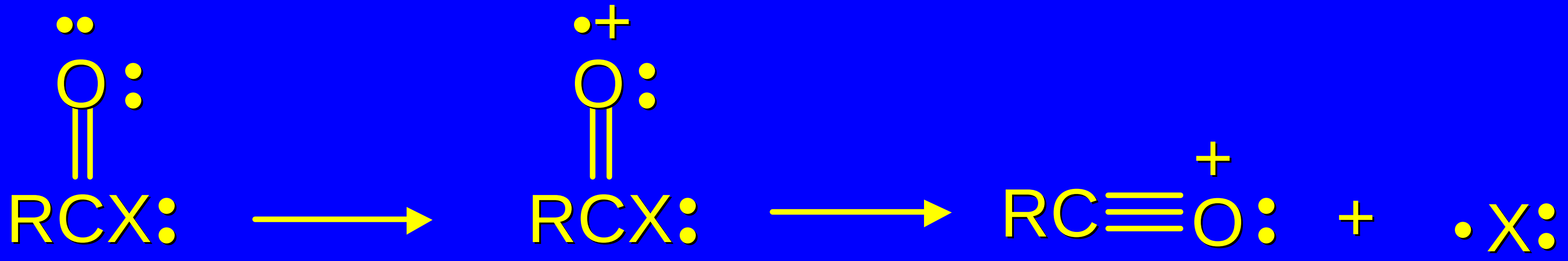
225 nm

207 nm

214 nm

Mass Spectrometry

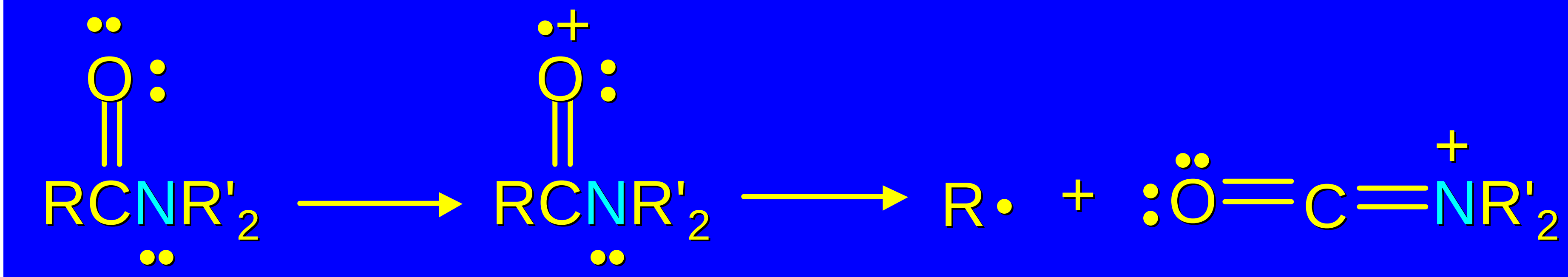
Most carboxylic acid derivatives give a prominent peak for an acylium ion derived by the fragmentation shown.



$$\mathrm{R}\overset{\overset{\ddot{\mathrm{O}}:}{\|}}{\mathrm{C}}\mathrm{X}: \longrightarrow \mathrm{R}\overset{\overset{\overset{\cdot+}{\mathrm{O}}:}{\|}}{\mathrm{C}}\mathrm{X}: \longrightarrow \mathrm{RC}\equiv\overset{+}{\mathrm{O}}: + \cdot\mathrm{X}:$$

Mass Spectrometry

Amides, however, cleave in the direction that gives a nitrogen-stabilized cation.



$$R\overset{\overset{\ddot{O}:}{\|}}{C}\underset{\cdot\cdot}{N}R'_2 \longrightarrow R\overset{\overset{\overset{\cdot+}{O}:}{\|}}{C}\underset{\cdot\cdot}{N}R'_2 \longrightarrow R\cdot \;+\; :\ddot{O}=C=\overset{+}{N}R'_2$$