Carbonyl Compounds

Carbonyl group is present in:

- aldehydes,
  - ethanal

- ketones,
  - propanone

- acids,
  - ethanoic acid
esters,

amides,

acid chlorides, and

anhydrides.
• This group absorbs strongly in the range from 1850 to 1650 cm\(^{-1}\) because of its large change in dipole moment.

• Since the C=O stretching frequency is sensitive to attached atoms, the common functional groups already mentioned absorb at characteristic values.
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The C=O frequency of a ketone, which is approximately in the middle of the range, is usually considered the reference point for comparisons of these values.

acid chlorides > anhydrides > ester > aldehydes > ketones > carboxylic acid > amides
The range of values shown in Table 1 above may be explained through the use of

- electron-withdrawing effects (inductive effects),
- resonance effects, and
- hydrogen bonding.

The first two effects operate in opposite ways to influence the C=O stretching frequency.
• First, an electronegative element may tend to draw in the electrons between the carbon and oxygen atoms through its electron-withdrawing effect,
• so that the C=O bond becomes somewhat stronger.
• A higher-frequency (higher-energy) absorption results.
• Since oxygen is more electronegative than carbon,
• this effect dominates in an ester to raise the C=O frequency above that of a ketone.
• Second, a resonance effect may be observed when the unpaired electrons on a nitrogen atom conjugate with the carbonyl group, resulting in increased single-bond character and a lowering of the C=O absorption frequency.
• This second effect is observed in an amide.
• Since nitrogen is less electronegative than an oxygen atom, it can more easily accommodate a positive charge.
The resonance structure shown here introduces single-bond character into the C=O group and thereby lowers the absorption frequency below that of a ketone.

Ester

\[
\begin{array}{c}
\text{Electron-withdrawing effect raises } \\
\text{C=O frequency}
\end{array}
\]

Amide

\[
\text{Resonance effect lowers C=O frequency}
\]
In acid chlorides,

- the highly electronegative halogen atom strengthens the C=O bond through an enhanced inductive effect and shifts the frequency to values even higher than that found in esters.

- Anhydrides are likewise shifted to frequencies higher than that found in esters because of a concentration of electronegative oxygen atoms.

- In addition, anhydrides give two absorption bands that are due to symmetric and asymmetric stretching vibrations.
• Carboxylic acid exists in **monomeric** form in very dilute solution, absorbs at about 1760 cm\(^{-1}\) because of the **electron-withdrawing** effect.

• Acids in **concentrated** solution, in form of neat liquid, or in the solid state (KBr pellet and Nujol) dimerizes via hydrogen bonding.

• Dimerization **weakens** the C=O bond, **lowers** the stretching force constant \(K\), resulting in a **lowering** of the carbonyl frequency of saturated acids to about 1710 cm\(^{-1}\).
• Ketones absorb at a lower frequency than aldehydes because of their additional alkyl group, which is electron donating (compared to H) and supplies electrons to the C=O bond.
• This electron-releasing effect weakens the C=O bond in the ketone and lowers the force constant and the absorption frequency.
Factors Affecting the C=O Stretching Vibration

Conjugation Effects.

• Introduction of a C=C bond adjacent to a carbonyl group results in delocalization of the $\pi$ electrons in the C=O and C=C bonds.

• This conjugation increases the single-bond character of the C=O and C=C bonds in the resonance hybrid and hence lowers their force constants,

• resulting in a lowering of the frequencies of carbonyl and double-bond absorption. Conjugation with triple bonds also shows this effect.
Generally, the introduction of an $\alpha$, $\beta$ double bond in a carbonyl compound results in a $25$- to $45$-$\text{cm}^{-1}$ lowering of the C=O frequency from the base value given in Table 1.
• Similar lowering occurs when an adjacent aryl group is introduced.

• Further addition of unsaturation (γ, δ) results in a further shift to lower frequency, but only by about 15 cm⁻¹ more.

• In addition, the C=C absorption shifts from its "normal" value, about 1650 cm⁻¹, to a lower-frequency value of about 1640 cm⁻¹, and the C=C absorption is greatly intensified.
• Usually two closely spaced C=O absorption peaks are observed for these conjugated systems, resulting from two possible conformations, the $s$-cis and $s$-trans.

• The $s$-cis conformation absorbs at a frequency higher than the $s$-trans conformation.

• In some cases, the C=O absorption is broadened rather than split into the doublet.
The following examples show the effects of conjugation on the C=O frequency.

**α,β-Unsaturated ketone**

1715 → 1690 cm⁻¹

**Aryl-substituted aldehyde**

1725 → 1700 cm⁻¹

**Aryl-substituted acid**

1710 → 1680 cm⁻¹
Conjugation does not reduce the C=O frequency in amides. Introduction of α, β unsaturation causes an *increase in frequency* from the base value given in Table 1.

Introduction of sp2-hybridized carbon atoms removes electron density from the carbonyl group and *strengthens* the bond instead of interacting by resonance as in other carbonyl examples.

Since the parent amide group is already highly stabilized, the introduction of the C=C unsaturation does not *overcome* this resonance.
Ring-Size Effects.

• Six-membered rings with carbonyl groups are unstrained and absorb at about the values given in Table 1.

• Decreasing the ring size increases the frequency of the C=O absorption.

• The functional groups listed in Table 1, which can form rings, give increased frequencies of absorption with increased angle strain.

• For ketones and esters, there is often a 30-cm\(^{-1}\) increase in frequency for each carbon removed from the unstrained six-membered ring values.
Some examples are:

In ketones, larger rings have frequencies that range from nearly the same value as in cyclohexanone (1715 cm\(^{-1}\)) to values slightly less than 1715 cm\(^{-1}\). For example, cycloheptanone absorbs at about 1705 cm\(^{-1}\).
a-Substitution Effects.

• When the carbon next to the carbonyl is substituted with a chlorine (or other halogen) atom, the carbonyl band shifts to a higher frequency.

• The electron-withdrawing effect removes electrons from the carbon of the C=O bond.

• This removal is compensated for by a tightening of the π bond (shortening), which increases the force constant and leads to an increase in the absorption frequency.

• This effect holds for all carbonyl compounds.
In ketones, two bands result from the substitution of an adjacent chlorine atom.

One arises from the conformation in which the chlorine is rotated next to the carbonyl, and

the other is due to the conformation in which the chlorine is away from the group.
• When the chlorine is next to the carbonyl, nonbonded electrons on the oxygen atom are repelled, resulting in a **stronger** bond and a **higher** absorption frequency.

• Information of this kind can be used to establish a structure in rigid ring systems, such as in the following examples.
Hydrogen-Bonding Effects.

- Hydrogen bonding to a carbonyl group lengthens the C=O bond and lowers the stretching force constant $K$, resulting in a lowering of the absorption frequency.

- Examples of this effect are the decrease in the C=O frequency of the carboxylic acid dimer and the lowering of the ester C=O frequency in methyl salicylate caused by intramolecular hydrogen bonding:

![Methyl salicylate structure](image)