

# Why is the carbonyl IR stretch in an ester higher than in a ketone?

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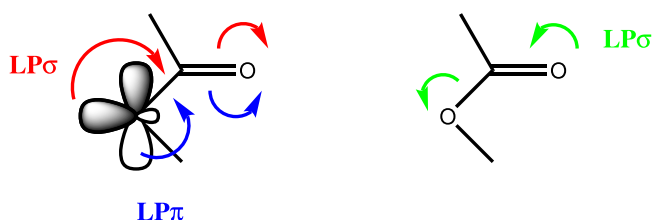
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Infra-red spectroscopy of molecules was introduced 110 years ago by Coblenz[1] as the first *functional group* spectroscopic method (" *The structure of the compound has a great influence on the absorption spectra. In many cases it seems as though certain bonds are due to certain groups.*"). It hangs on in laboratories to this day as a rapid and occasionally valuable diagnostic tool, taking just minutes to measure. Its modern utility rests on detecting common functional groups, mostly based around identifying the nature of double or triple bonds, and to a lesser extent in differentiating between different kinds of C-H stretches[2] (and of course OH and NH). One common use is to identify the environment of carbonyl groups, C=O. These tend to come in the form of aldehydes and ketones, esters, amides, acyl halides, anhydrides and carbonyls which are part of small rings. The analysis is performed by assigning the value of the C=O stretching wavenumber to a particular range characteristic of each type of compound. Thus ketones are said to inhabit the range of  $\sim 1715\text{-}1740\text{ cm}^{-1}$  and simple esters come at  $\sim 1740\text{-}1760\text{ cm}^{-1}$ , some  $20\text{-}30\text{ cm}^{-1}$  higher. Here I try to analyse how this difference arises.

The analysis is based on trying to understand how the components of an ester interact with each other, and in particular how the alkyl oxygen interacts with the carbonyl group. Three electronic interactions in particular can be focused on (below). The first two of these weaken the C=O bond; the last strengthens it. **So which effect wins out?**



1. The donation of an in-plane  $\sigma$  lone pair ( $\text{LP}\sigma$ ) on the alkyl oxygen into the C=O  $\sigma^*$  acceptor (red arrows)
2. The donation of an out-of-plane  $\pi$  lone pair ( $\text{LP}\pi$ ) into the C=O  $\pi^*$  acceptor (blue arrows)
3. The donation of an in-plane  $\sigma$  lone pair ( $\text{LP}\sigma$ ) on the acyl oxygen into the C-O  $\sigma^*$  acceptor (green arrows)

I will start with computational models, which have the advantage that one can dissect how the vibrations arise. The first two rows show a comparison of the experimental gas phase values[3] with a standard "medium level"  $\omega\text{B97XD/6-311G(d,p)}$  calculation. The discrepancy amounts to  $\sim 100\text{-}114\text{ cm}^{-1}$ .

### The carbonyl stretch in esters and ketones

Method:	Ester	Ketone
Expt (gas phase)[3]	1761 <sup>‡</sup>	1737 <sup>‡</sup>
Harmonic $\omega$ B97XD/6-311G(d,p)	1860	1851
Anharmonic $\omega$ B97XD/6-311G(d,p)	1832 <sup>†</sup>	1828 <sup>†</sup>
Harmonic $\omega$ B97XD/aug-cc-pvQZ	1836	1831
Harmonic CCSD(T)/6-311G(d,p)	1826	1792
Corrected CCSD(T)/6-311G(d,p)	~1774~1749	
Expt (gas phase)	1761	1737
Reduced CCSD(T)/6-311G(d,p)	1764	1743

There are several possible causes for such errors:

1. The calculation is for harmonic frequencies; whereas those measured are anharmonic.
2. DFT-level force constants at modestly sized basis set levels are known to be too large compared with a complete basis set calculation (CBS). It used to be the practice in fact to routinely scale the force constants down by ~10% to correct for this effect.
3. The correlation treatment in a DFT approach is incomplete (an error which may in fact be also absorbed into the 10% correction noted above).

So to really get to the root of why an observed ester carbonyl stretch is higher than that of the equivalent ketone, we have to get a handle on these effects above.

1. One can calculate cubic and quartic force constants to get an estimate of the effect of anharmonicity on the (harmonic/quadratic) values, which emerges as 23-28  $\text{cm}^{-1}$
2. Upping the level of the basis set to aug-cc-pVQZ (close to, but not quite a CBS) reveals further corrections of 20-24  $\text{cm}^{-1}$ .
3. Replacing the DFT method with a CCSD(T)-level treatment of the dynamic correlation gives corrections of 34 and 59  $\text{cm}^{-1}$  respectively for ester and ketone. Assuming the corrections can be treated additively, one can apply the first two to the third, producing "corrected" CCSD(T)/6-311G(d,p) values which are only about 12-13  $\text{cm}^{-1}$  higher than the observed value. This remaining discrepancy is probably due to the difference between aug-cc-pvQZ and a complete basis set (CBS) and any remaining errors in the correlation modelled by CCSD(T). We can be assured now that our theory is reproducing experiment very well.

Now that we can assess the accuracy of our computational methods, we need to try to relate the results to the C=O bond itself. Does turning a ketone into an ester really make it stronger? To directly compare the C=O bond of two different molecules, we need to eliminate the effects of mixing the C=O normal stretching mode with similar energy modes arising from other parts of the molecule. A simple way of estimating this is to set the mass of all but two of the atoms to a very small value (0.00001), leaving only the masses of the C and O as normal; this is shown as a reduced frequency in the table above. The harmonic CCSD(T)/6-311G(d,p) C=O "pure" mode reduces to 1764 for methyl ethanoate and 1743  $\text{cm}^{-1}$  for propanone. So after all of this, at least we now know that the force constant for the C=O stretch really is stronger for an ester. The green arrows seem to win out over the blue/red ones.

One calculation too many? The (Wiberg) bond order for the C=O bond can be derived from the wavefunctions. Its value is 1.635 for ester, and 1.681 for ketone (CCSD/6-311G(d,p)) or 1.766/1.848 ( $\omega$ B97XD/aug-cc-pvQZ). This is the opposite to that inferred from the carbonyl stretch, and hence favours the blue/red arrows over the green arrows. I set out in this post to try to bring clarity to how an adjacent oxygen influences how we think of the properties of the C=O functional group, but as happens quite often, the answer you get depends on the measurement you make.

‡ The solution values in e.g. acetonitrile are reduced by ~20  $\text{cm}^{-1}$ , reaching the values often quoted in text books for these functional groups. † The effect on C-H values is greater, e.g. a reduction from 3186 to 2967  $\text{cm}^{-1}$ .

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