Lecture 2: Identifying Carbonyl Groups using Spectroscopy

Objectives:

By the end of this lecture you will be able to:

- use ^{13}C-NMR spectra to differentiate between the C=O group in a ketone/aldehyde and one in a carboxylic acid derivative;
- use IR spectra to identify different C=O groups in an organic molecule.

Recommended Reading: *Spectroscopic Methods in Organic Chemistry*, D. H. Williams and I. Fleming, McGraw-Hill, Currently in 5th Edition.

Introduction

When carrying out synthetic transformations it is obviously important to be able to identify the products that you make and elucidate their structure. A variety of spectroscopic techniques are available for carrying out this task; NMR spectroscopy is the most important for organic chemistry. It is possible to obtain NMR spectra of all nuclei that are *spin active*. For organic chemists the most important nuclei are ^{1}H, ^{13}C and to a lesser extent ^{19}F and ^{31}P. We will only look at ^{13}C-NMR spectra and see how it can be used to identify the presence of a carbonyl group in a molecule. IR spectroscopy is an older technique and generally less informative than NMR spectroscopy. However it remains a quick and easy method for identifying the types of C=O groups present in a molecule.

^{13}C-NMR Spectroscopy

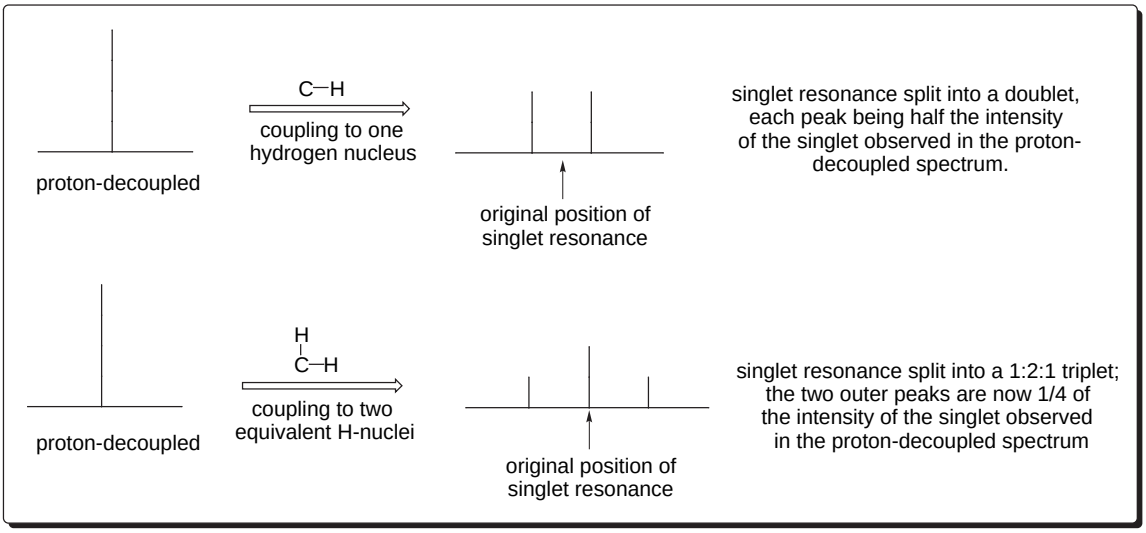
^{13}C-NMR as a Technique for Structure Elucidation

The most common naturally occurring isotope of carbon is ^{12}C. This nucleus is not spin active and therefore cannot be used in NMR spectroscopy. The most abundant spin active (I = 1/2) nucleus of carbon is ^{13}C which has only 1.1% natural abundance. To put this into context, if an organic molecule contains 100 carbon atoms, on average only one of these will be ^{13}C and therefore spin active. This very low natural abundance has important ramifications for using ^{13}C NMR spectroscopy as a tool in structure elucidation:

1. *Amount of sample required:* ^{13}C-NMR is a relatively insensitive spectroscopic technique. Compared with the amount of material (typically 1-10 mg) needed to obtain a ^{1}H-NMR spectrum of a molecule (remember that ^{1}H has ~100% natural abundance), far more

(typically 50-100 mg) is needed to obtain a decent ^{13}C-NMR spectrum of the same molecule.

2. *^{13}C-NMR spectra are normally recorded proton-decoupled:* Coupling of ^{13}C nuclei to proximal ^{1}H nuclei causes the singlet resonances of ^{13}C nuclei to split into more than one peak. This has the effect of *reducing the intensity* of the resonance, which is undesirable bearing in mind the insensitivity of the technique.



As a result, ^{13}C-NMR spectra are normally recorded as *proton-decoupled* spectra. This removes the effects of peak splitting resulting from coupling to proximal protons. To obtain a proton-decoupled spectrum, the sample is irradiated across the range of frequencies at which proton nuclei resonate whilst recording the ^{13}C-NMR spectrum. The net result is to remove the effects of coupling between these protons. ^{13}C resonances therefore appear as singlet resonances. in proton-decoupled spectra.

n.b. The likelihood of a single molecule containing two ^{13}C nuclei bonded closely enough to one another for them to couple to one another, is very low. Splitting of resonances as a result of homonuclear C-C coupling is therefore negligible.

n.b. Coupling to other nuclei *e.g.* ^{19}F and ^{31}P is usually not suppressed.

3. *Integration of ^{13}C-NMR spectra is generally not possible:* Under normal circumstances it is not possible to use the relative intensity of ^{13}C resonances to measure the number of C-atoms resonating at that frequency *i.e.* the number of C-atoms in that specific environment in the molecule. This is in sharp contrast with ^{1}H-NMR spectra where it is possible to obtain quantitative data about the number of H-atoms in a given resonance by integrating the area of the resonances.

Reason: When recording ^{1}H-NMR spectra, all the ^{1}H nuclei have relaxed back from their excited states to their ground states *before* the next radio frequency pulse is made; thus all nuclei receive the same number of pulses and give out the same number of signals. ^{13}C nuclei take quite different times to 'relax' back to their ground states. The rate of relaxation for a ^{13}C nucleus depends on a number of factors although the number of H atoms to which it is bonded is the most important. Significantly quaternary carbons (*i.e.* those which have no H atoms bonded to them) relax very slowly and usually too slowly for all the excited nuclei to have relaxed back to the ground state before it is time for the next radio frequency pulse. The net result is to reduce the number of nuclei which can be excited in this next pulse leading to a decrease in the intensity of the resonance.

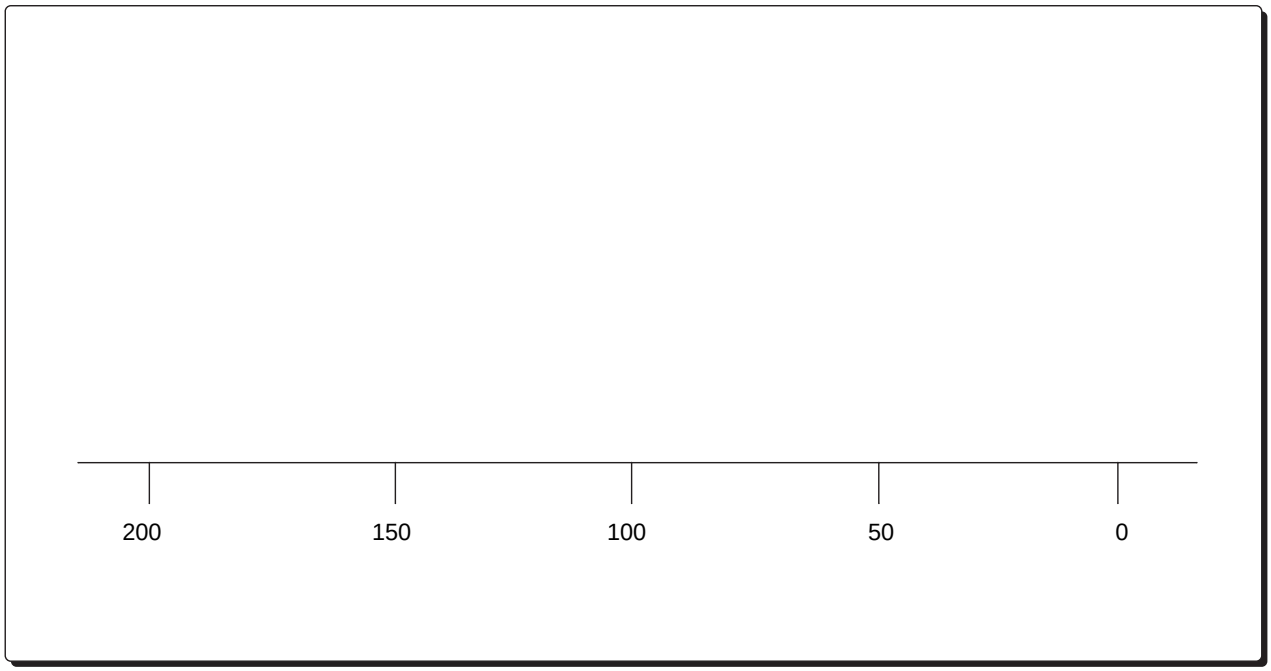
The resonances of quaternary carbons (including those found in C=O groups) are invariably the weakest in the spectrum. This observation can be a good method for identifying quaternary carbons (although it should NOT be relied upon).

^{13}C-NMR Spectra

^{13}C-NMR spectra are normally recorded across the range 0-210 ppm with the carbon resonance in tetramethylsilane (Me_4Si) appearing at 0.0 ppm as a reference. The position of a resonance is strongly dependent on the environment in which the resonating nucleus finds itself.

- Electron-withdrawing groups tend to shift resonances downfield (*i.e.* to higher ppm value).
- Electron-donating groups tend to shift resonances upfield (*i.e.* to lower ppm value).
- Anisotropic effects are important particularly for aromatic carbons and carbons in unsaturated functional groups (*e.g.* C=O groups and double bonds).

We can divide the ^{13}C-NMR spectrum into four regions to obtain a rough guide of the type of carbon nuclei that resonate in each region:



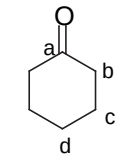
Carbon resonances from carbonyl groups appear in the 160-210 ppm region.

This region can be further divided:

Carbon resonances from ketones and aldehydes generally appear in the 190-210 ppm region, more or less irrespective of the side-chain substituents.

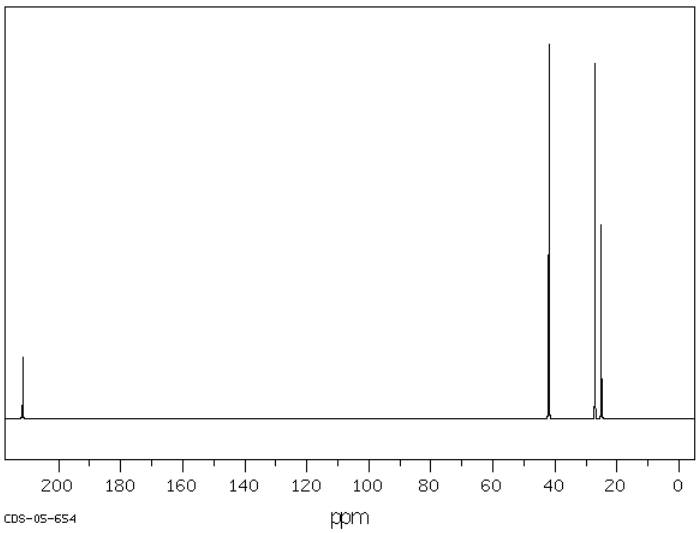
Carbon resonances from carboxylic acid derivatives (amides, esters, carboxylic acids, acid chlorides *etc*) generally appear in the 160-185 ppm region.

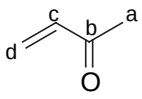
Some examples:



cyclohexanone

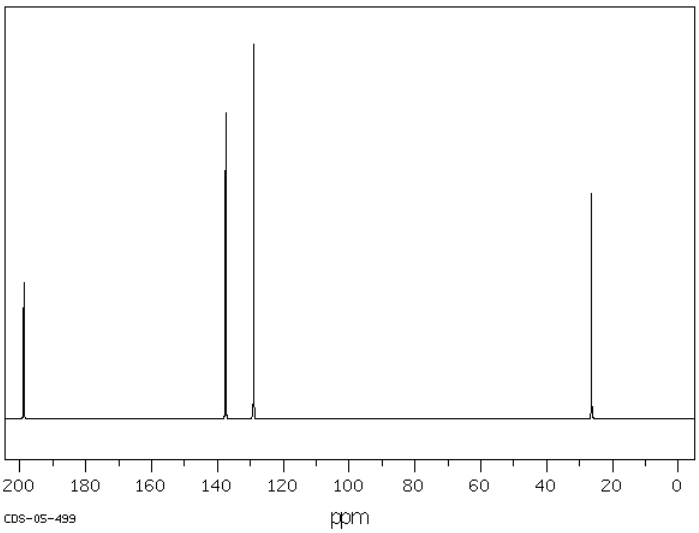
4 different carbon environments, therefore should observe 4 separate resonances in ^{13}C-NMR spectrum

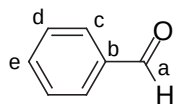




methylvinylketone

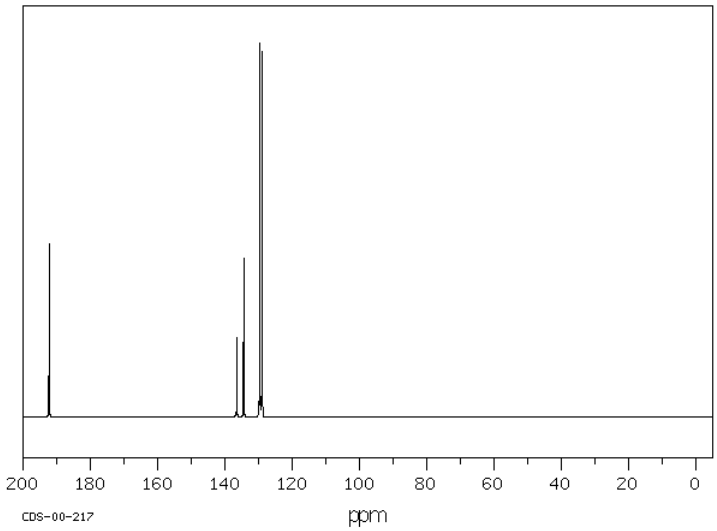
4 different carbon environments, therefore should observe 4 separate resonances in ^{13}C-NMR spectrum

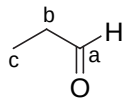




benzaldehyde

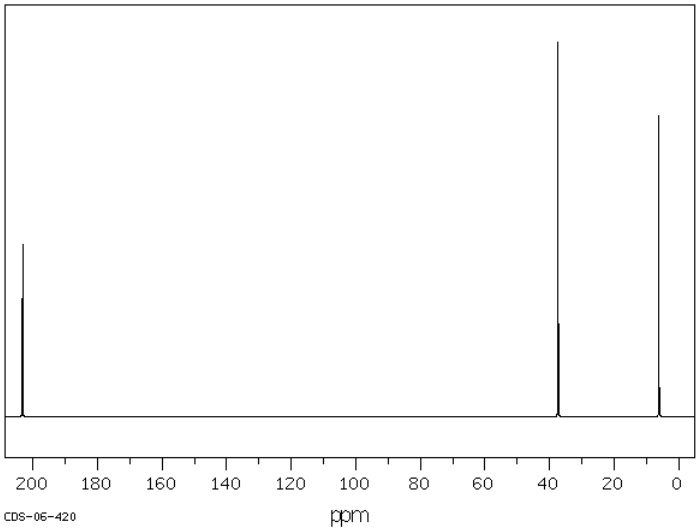
5 different carbon environments, therefore should observe 5 separate resonances in ^{13}C-NMR spectrum

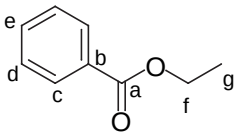




propionaldehyde

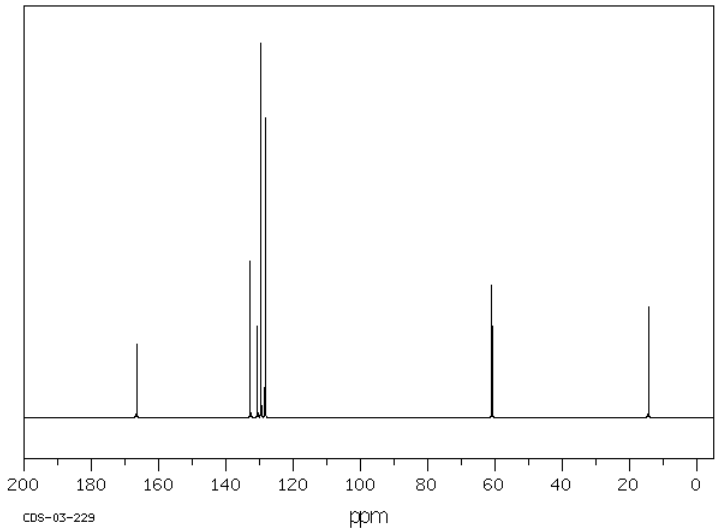
3 different carbon environments, therefore should observe 3 separate resonances in ^{13}C-NMR spectrum

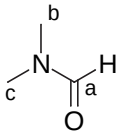




ethyl benzoate

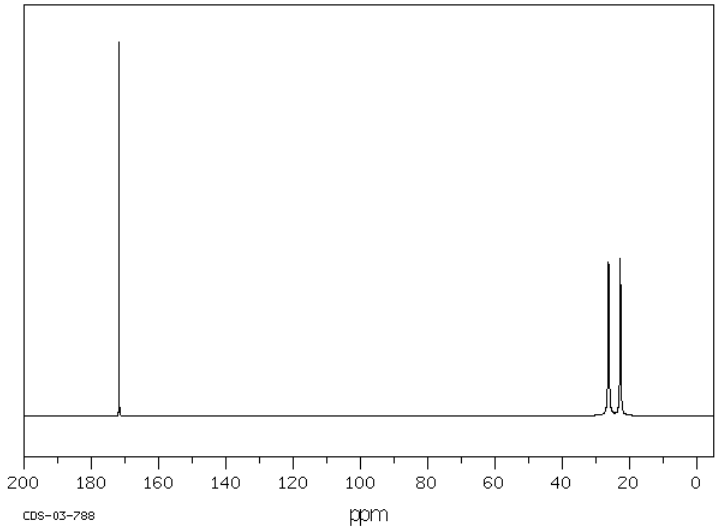
7 different carbon environments, therefore should observe 7 separate resonances in ^{13}C-NMR spectrum

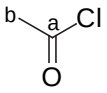




As a result of slow rotation about the amide bond the two Me groups are in different environments; therefore expect 3 resonances in the ^{13}C spectrum

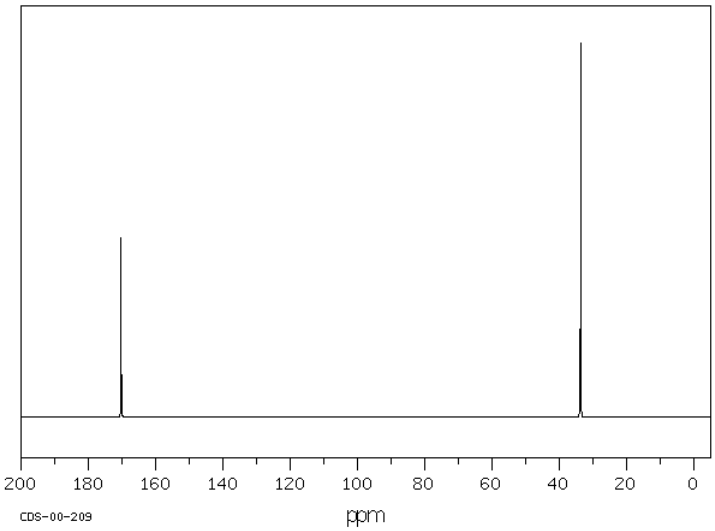
N,N-dimethylformamide

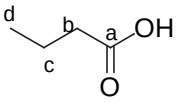




acetyl chloride

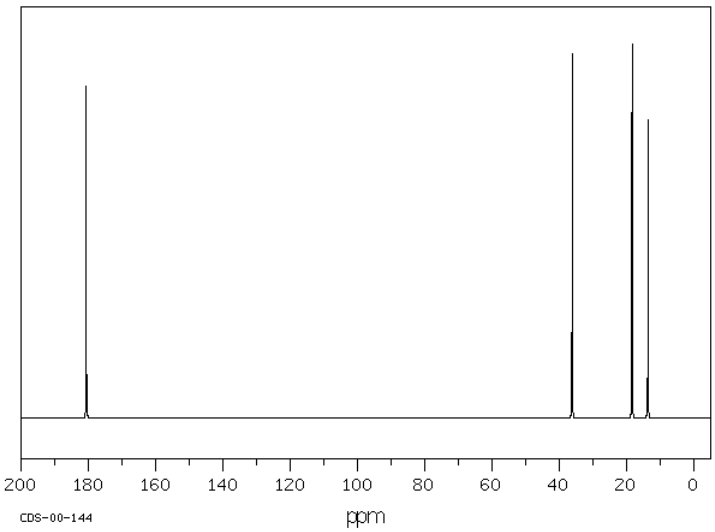
Two different carbon environments; therefore should observe two resonances in the ^{13}C-NMR spectrum





butyric acid

Four different carbon environments; therefore should observe four resonances in the ^{13}C-NMR spectrum



IR Spectroscopy

Molecules are not static entities; quite the opposite in fact, they are always moving: bonds lengthen and shorten, bend, rock and wag. These vibrational modes of movement can be associated with a particular functional group or associated with movement of the whole molecule. The energy required for these molecular vibrations corresponds to that found in the IR-region of the electromagnetic spectrum (*i.e.* relatively low energy).

Functional groups tend to have associated molecular vibrations that appear at characteristic positions in IR spectra. IR-spectra therefore provide a very useful method for identifying what types of functional groups are present in a molecule; they are generally not used to provide much more information than this.

The location of a particular functional group vibration in a spectrum depends on a number of factors.

- *The strength of the bond and its reduced mass.* To a first approximation the stretching vibration of a bond can be assumed to behave like a simple harmonic oscillator; thus the frequency is related to the strength of the bond and the reduced mass:

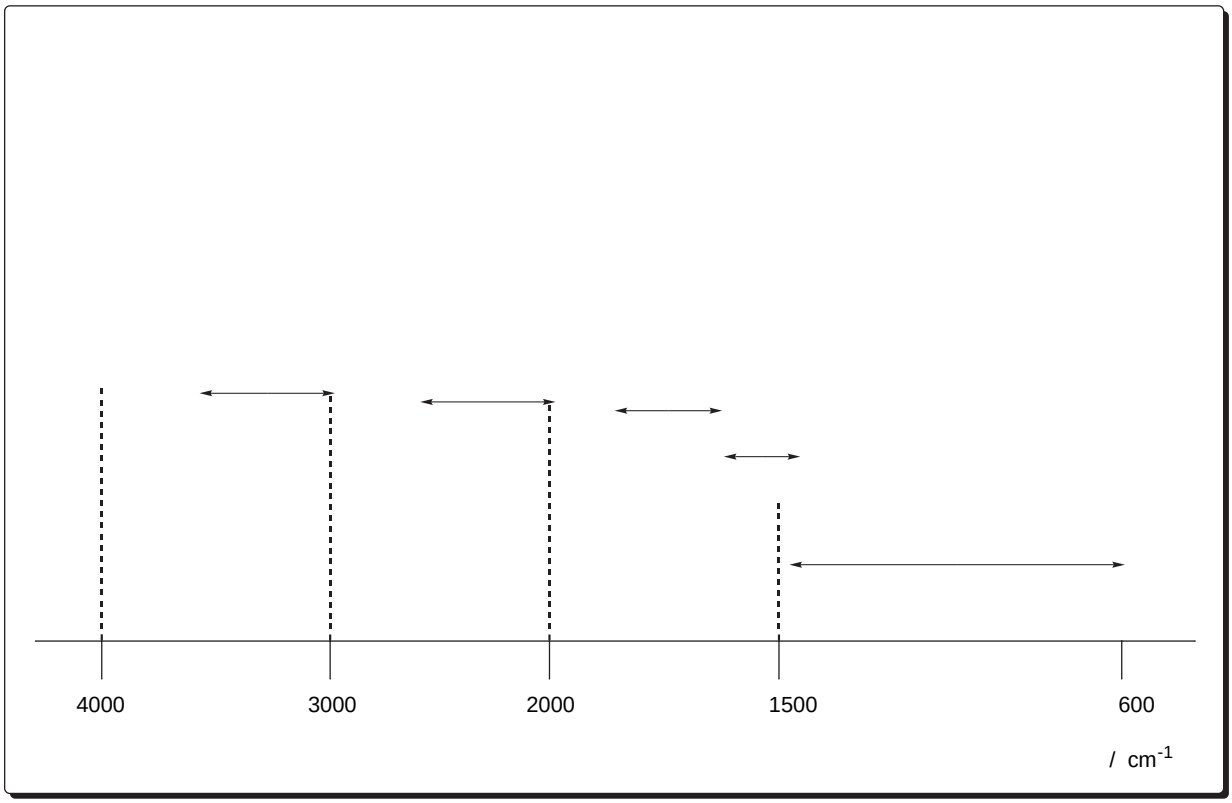
From this relationship, we would predict that the stronger the bond, the higher is the frequency of bond vibration.

***i.e.* triple bonds appear at higher frequencies than double bonds and double bonds appear at higher frequencies than single bonds.**

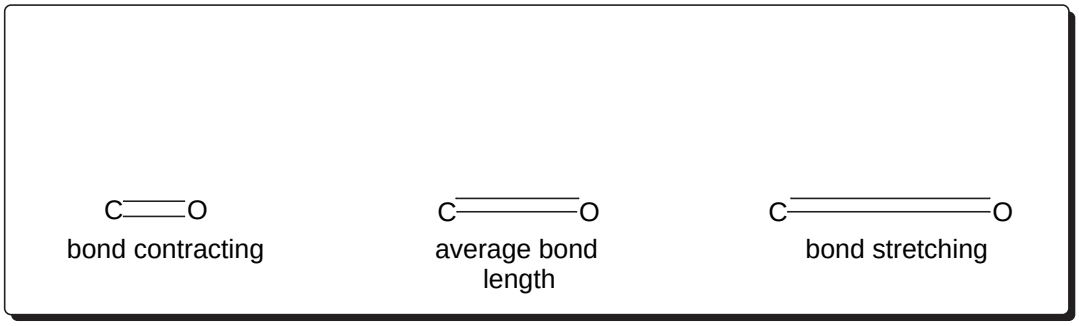
A consequence of the small mass of Hydrogen means that all bonds of the form X–H have stretching vibrations at high frequency. (Reduced mass for C–H bond: 12/13 = 0.92; *c.f.* reduced mass for a C–C bond: 144/24 = 6).

- the *mode* of vibration is important: stretching vibrations tend to appear at higher frequency than bending vibrations.

An IR spectrum can be divided into a number of regions defined by the characteristic stretching vibrations found within each region:



For our purposes we are interested in the C=O stretching region which extends from 1650 cm^{-1} to 1900 cm^{-1}. As we saw in Lecture 1, the difference in electronegativity between oxygen and carbon polarises the electron density in the functional group creating a strong dipole moment across this bond. Since the intensity of a vibrational band is dependent on the *change in dipole moment*, C=O stretching bands are normally some of the most intense bands in an IR spectrum.

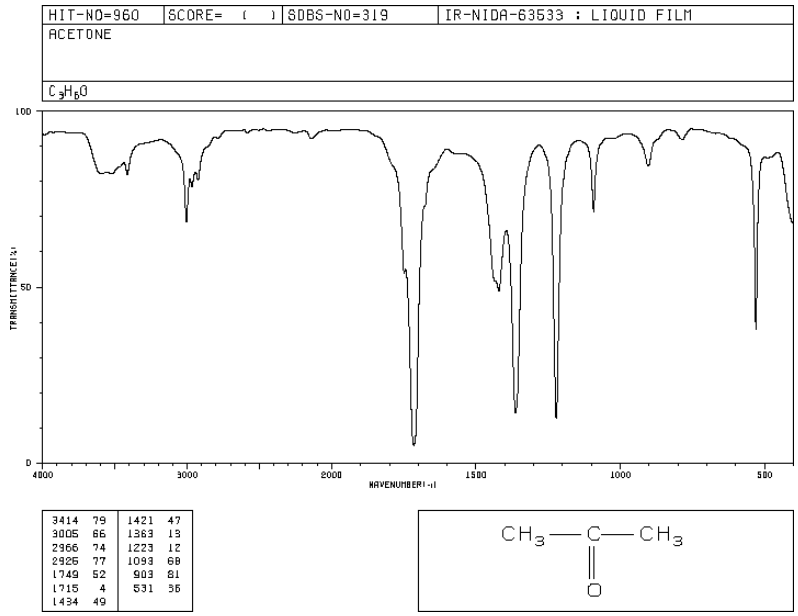


The Carbonyl Stretching Band

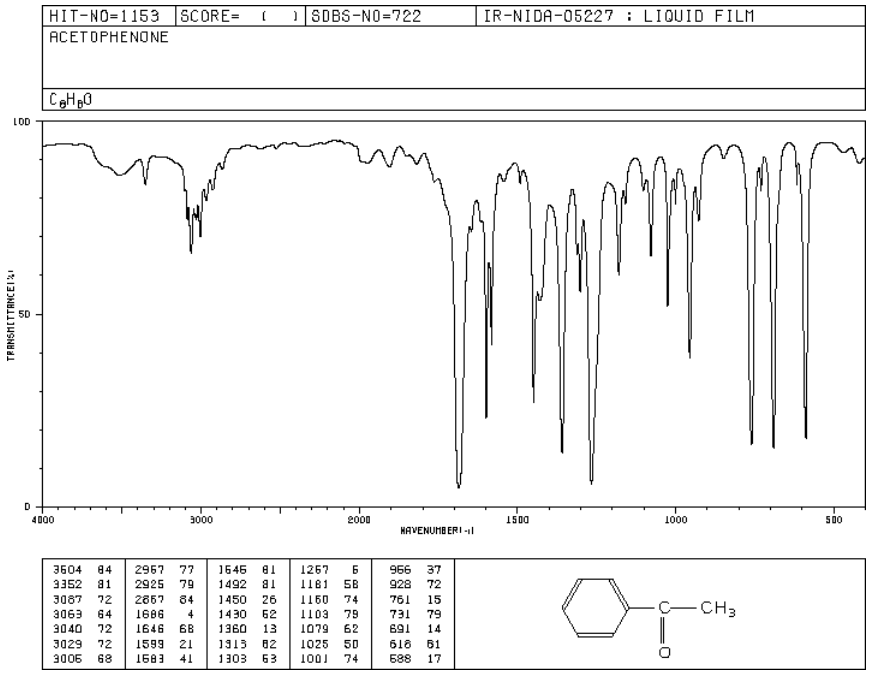
The substituents either side of the carbonyl group affect the exact position of this vibrational band.

We shall take the stretching frequency of a dialkyl ketone (*e.g.* acetone) as a central reference.

C=O peak at 1715 cm^{-1}



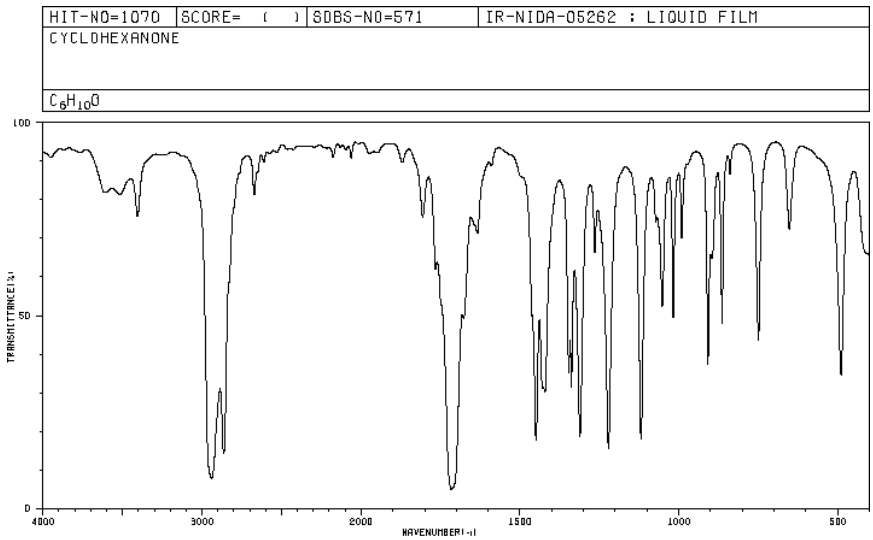
- ***Conjugation* shifts the band to lower frequency.** This may be attributed to the bond having more single bond character (see the resonance forms below):



- ***Ring Strain* (3-5 membered rings) shifts the C=O stretching peak to higher frequency:**

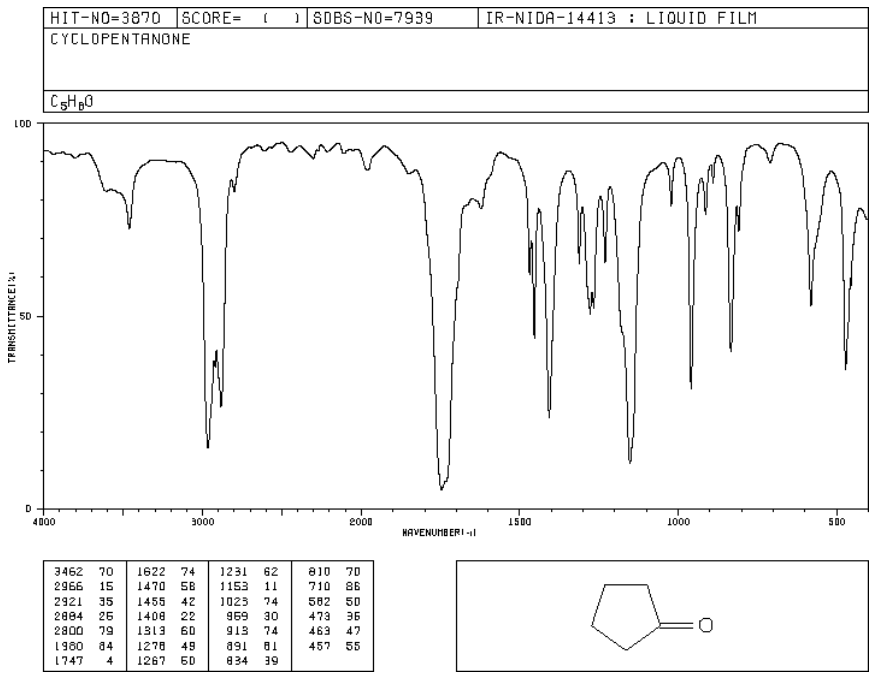
There is relatively little ring strain in a 6-membered ring.

C=O peak at 1716 cm^{-1}



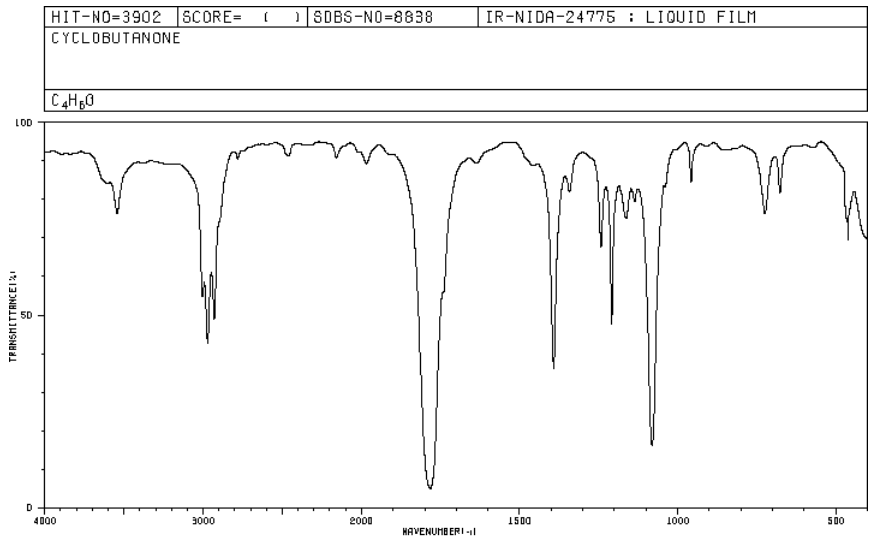
The increase in ring strain in cyclopentanone leads to a shift of around 30 cm^{-1}.

C=O peak at 1747 cm^{-1}.



Removing another CH_2 group produces cyclobutanone and a further increase in ring strain and therefore a shift of around +65 cm^{-1} to higher frequency.

C=O peak at 1785 cm^{-1}.



Cyclopropanone is a highly strained molecule (and not surprisingly very reactive). The high degree of strain causes a shift of around +100 cm^{-1} to high frequency. C=O stretch appears at 1815 cm^{-1}.

- **The more electronegative the substituent in RC(O)X, the greater is the shift to higher frequency. This is an inductive effect operating through the σ-framework.**
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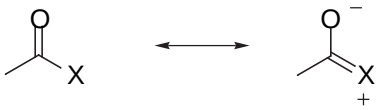
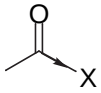
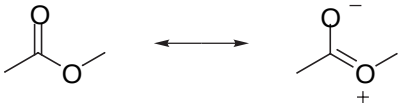
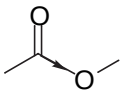
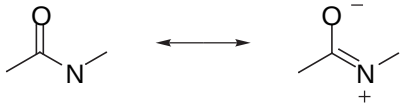
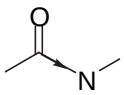
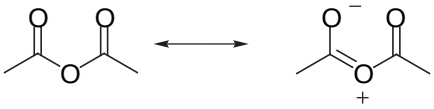
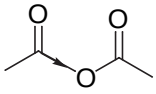
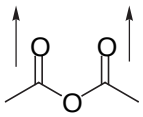
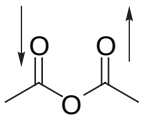
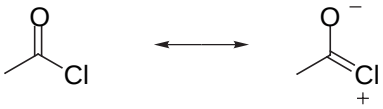
- **This effect is countered by the electron-donating effect of heteroatoms operating through the π-framework, which causes a shift to lower frequency. As to which effect prevails depends on the substituent.**



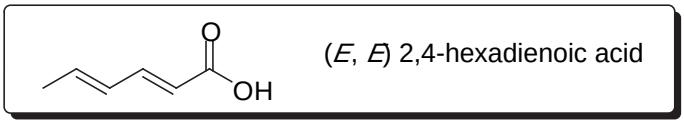
π-electron donation shifts to lower frequency



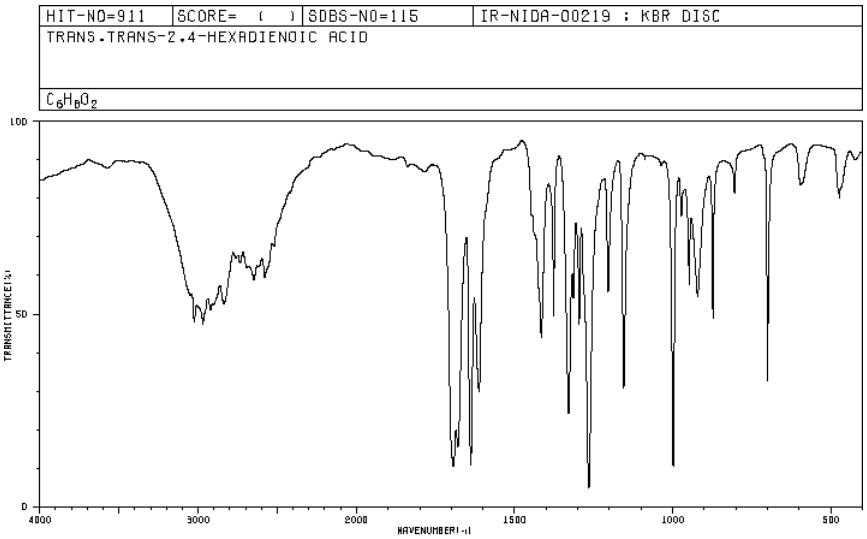
electronegative substituents exert a -/ inductive effect through the σ-framework

Functional Group	shift from reference	observed shift /cm^{-1}	Comment
	reference 1715 cm^{-1}		
	+15 cm^{-1}	1730	H-substituents exert a weaker +/ inductive effect than alkyl groups
 π-electron donation shifts to lower frequency  electronegative O exerts a strong -/ inductive effect through the σ-framework	+ 30	1745	The strong -/ inductive effect prevails
 N is a good electron donor; π-electron donation shifts to lower frequency  electronegative N exerts a weak -/ inductive effect through the σ-framework	-60	1650	The strong conjugative effect prevails producing a large shift to low frequency
 Acetyl group exerts a strong -/ inductive effect and is a very weak π–donor 	+50 and +100	1755 and 1855	Observe *two* stretching bands reflecting two stretching modes:  symmetric stretch  asymmetric stretch
 Cl is a poor π-electron donor but exerts a strong -/ inductive effect	+85	1800	Strong -/ inductive effect dominates producing a large shift to high frequency

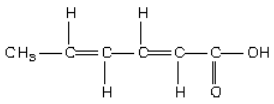
Some more examples:

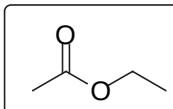


(*E*, *E*) 2,4-hexadienoic acid

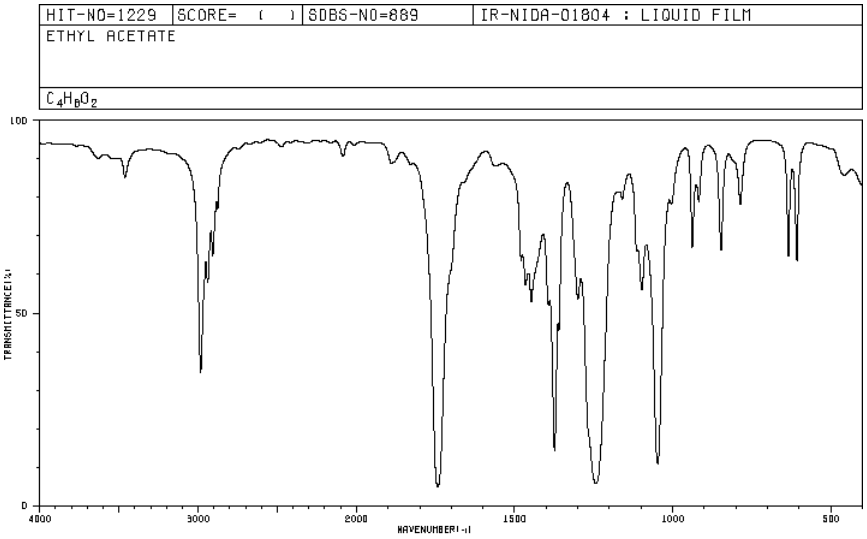


3672	84	2647	57	1613	28	1205	53	873	47
3026	46	2579	57	1416	42	1155	29	805	79
2970	46	1789	84	1377	47	1036	84	701	31
2922	49	1784	84	1330	23	998	10	598	79
2902	50	1694	10	1315	52	973	72	592	81
2837	50	1679	15	1296	46	948	55	580	64
2736	60	1638	10	1266	4	921	52	474	77

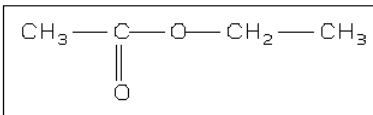


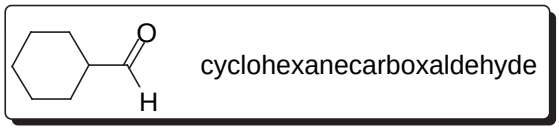


ethyl acetate



3462	81	1480	60	1243	5	847	64
2983	33	1466	55	1160	77	786	74
2940	55	1448	50	1111	84	634	62
2908	62	1393	60	1098	63	608	60
2877	74	1374	13	1048	10	457	81
1869	86	1360	45	939	84		
1743	4	1301	62	917	77		



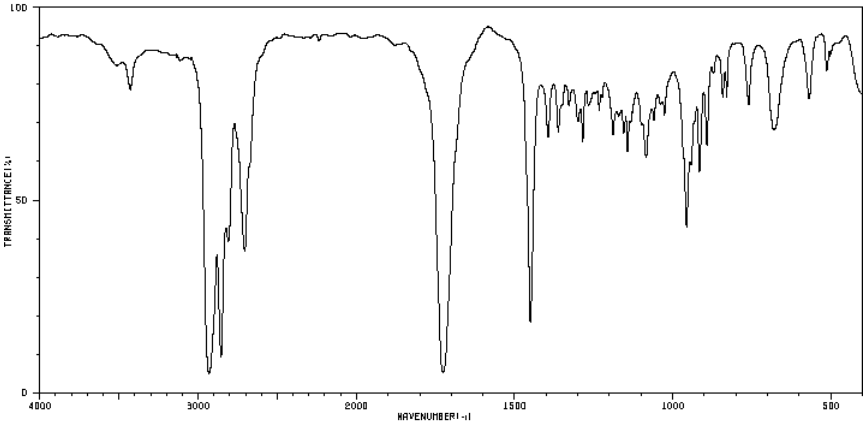


cyclohexanecarboxaldehyde

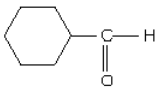
HIT-NO=3097	SCORE= ( )	SDBS-NO=5755	IR-NIDA-58303 : LIQUID FILM

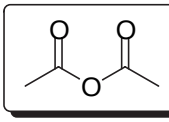
CYCLOHEXANECARBALDEHYDE

$C_7H_{12}O$



2932	4	1395	64	1233	70	1098	66	943	67
2908	13	1362	66	1224	74	1084	58	916	55
2856	8	1351	72	1189	84	1060	68	893	62
2809	37	1329	72	1170	70	1038	72	842	74
2705	35	1300	68	1156	64	1033	72	829	74
1727	5	1285	62	1144	80	1026	70	761	72
1451	17	1267	72	1133	68	967	42	681	66



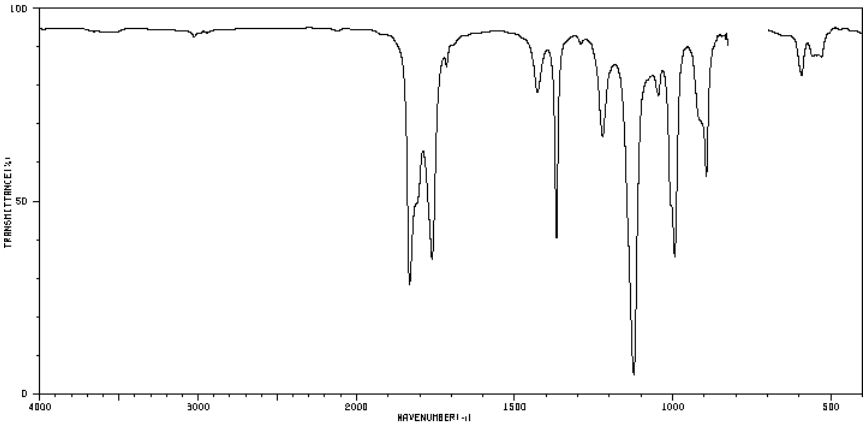


acetic anhydride

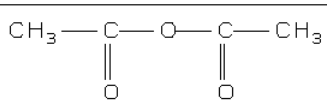
HIT-NO=1061	SCORE= ( )	SDBS-NO=1034	IR-NIDA-08651 : CCL4 SOLUTION

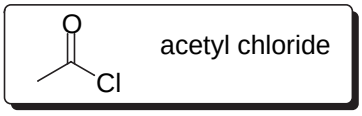
ACETIC ANHYDRIDE

$C_4H_6O_3$



1832	26	1046	74	640	84
1761	33	1005	46		
1715	81	994	34		
1428	74	894	59		
1368	38	603	84		
1222	64	593	79		
1124	4	547	84		



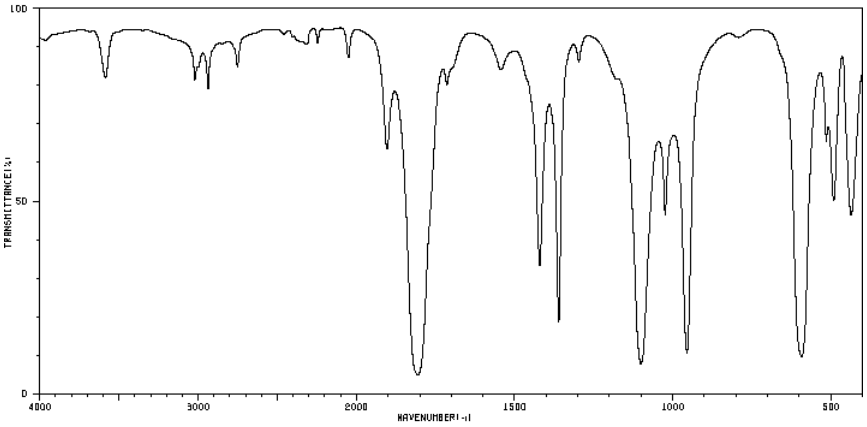


acetyl chloride

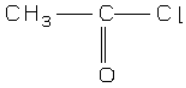
HIT-NO=1359	SCORE= ( )	SDBS-NO=1278	IR-NIDA-04097 : LIQUID FILM

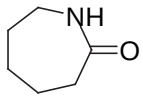
ACETYL CHLORIDE

C_2H_3ClO



3686	79	1806	4	1024	44
3020	79	1714	77	955	10
2997	81	1542	81	595	9
2937	77	1421	32	516	62
2751	81	1361	18	491	47
2051	84	1297	84	461	84
1903	60	1100	7	436	44



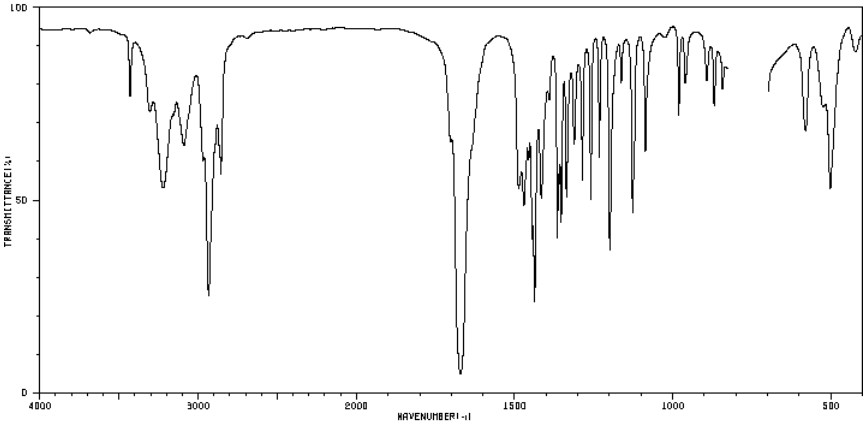


caprolactam

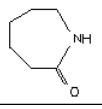
HIT-NO=964	SCORE= ( )	SDBS-NO=577	IR-NIDA-06228 : CCL4 SOLUTION

6-HEXANELACTAM

$C_6H_{11}NO$



3430	74	1487	60	1365	38	1233	68	893	77
3306	70	1471	46	1359	52	1199	35	869	72
3220	50	1458	56	1355	42	1163	77	843	77
3091	62	1446	38	1336	49	1127	44	680	66
2933	23	1438	22	1313	62	1086	60	503	50
2856	55	1418	49	1286	53	981	68	494	50
1671	4	1391	72	1269	49	961	77		



Summary

There are a wide variety of functional groups containing a C=O group. We therefore need to be able to identify and distinguish these when elucidating the structure of a molecule.

Using ^{13}C-NMR spectroscopy we can easily identify whether a molecule contains a C=O group by checking whether there is a resonance (often relatively weak in intensity) above 160 ppm. C=O groups in ketones and aldehydes generally appear above 190 ppm so we can often distinguish this type of C=O group from those found in carboxylic acid derivatives, which appear further upfield (160-185 ppm).

It is also very easy to identify a C=O stretch in an IR spectrum as the stretching peak is normally very intense and comes in a relatively small region between 1650 cm^{-1} and 1900 cm^{-1}. The exact position of the stretch depends on a number of factors (conjugation, ring strain, inductive effects); thus it also often possible to infer what type of C=O group is in the molecule. Caution needs to be exercised here as different effects shift the stretching band in different directions (conjugation shifts to lower frequency; -*I* inductive effects and ring strain shift to higher frequency).