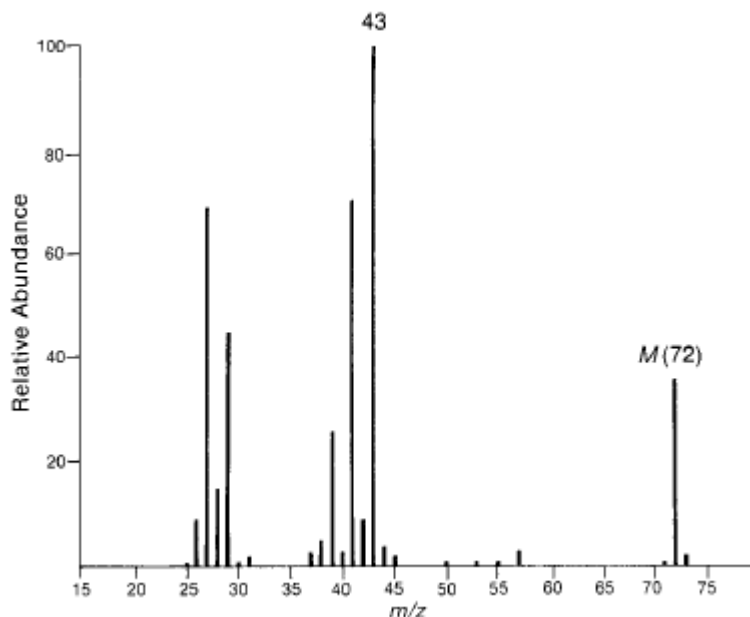


Practical No.4 Interpretation of Mass Spectra

Structure Elucidation using IR and MS data.

In this practical you will use the information provided in the mass spectrum and your knowledge of chemistry and its principles to determine the structure of the molecule. You may use your slide notes, textbook and IR correlation chart to assist you. The most important part of the assessment is that you show how you have used logical reasoning to derive your structure.

Study the example below to help you elucidate the other structures.



Answer

M^+ is present, $m/z = 72$

IR-spectrum shows a strong band at about 1725 cm^{-1} most likely a carbonyl group is present. Therefore, possibly an aldehyde or ketone (Check the Infrared correlation tables).

Apply the 'Rule of 13' go get the base formula; $72 \div 13 = 5$ remainder 7 therefore $C_5H_{5+7} = C_5H_{12}$

Since you know that there is a $C=O$ present that contains an oxygen atom; the base formula is now adjusted to include the O-atom to give the molecular formula; C_4H_8O

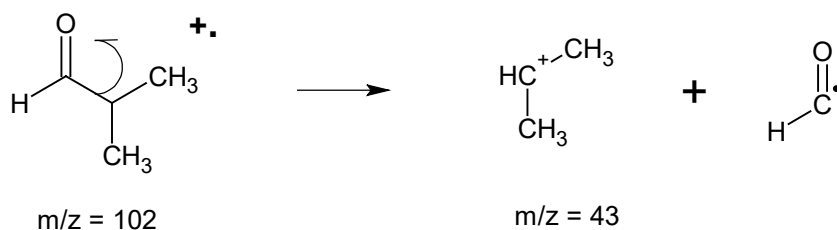
Calculate the IHD = $C_cH_hO_oN_nX_x$

$IHD = 0.5[2(c)+2-h+n-x] = 0.5[2(4)+2-8] = 1$; this value implies that the molecule has a ring or a double bond. However, from the IR-spectrum we confirmed that it is a double bond of the carbonyl group.

The base peak at $m/z = 43$ can be due to $C_3H_7^+$ or $C_2H_3O^+$ cation; there are no other significant fragment ions. The base peak is formed by an $M-29$ fragment. The most likely structure is;

Isobutyraldehyde

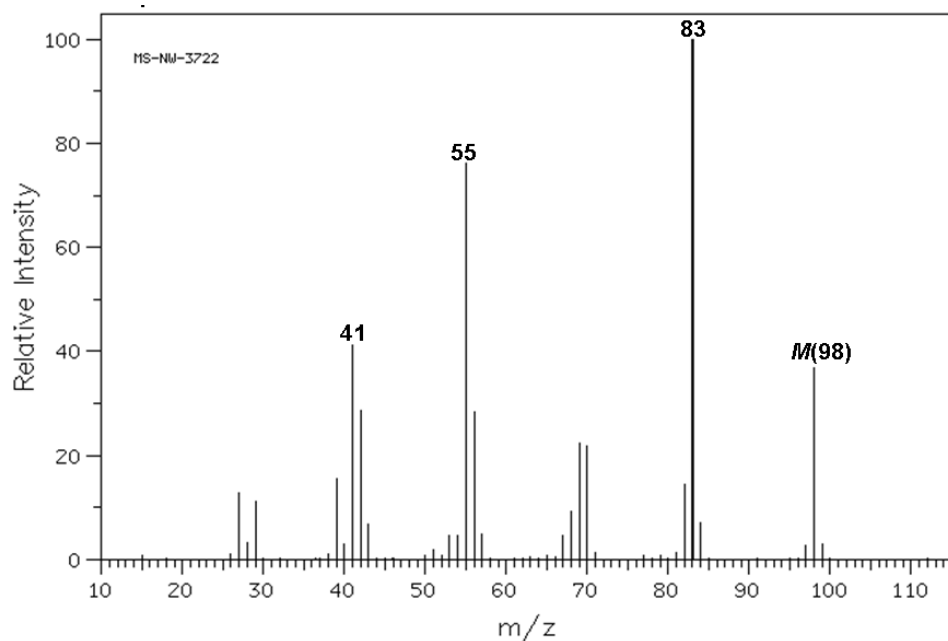
Mechanism leading to $m/z=43$



Note: What is important is that the radical does not appear in a mass spectrum but is the fragment that is lost from the molecular ion i.e. the radical fragment does not have a m/z value.

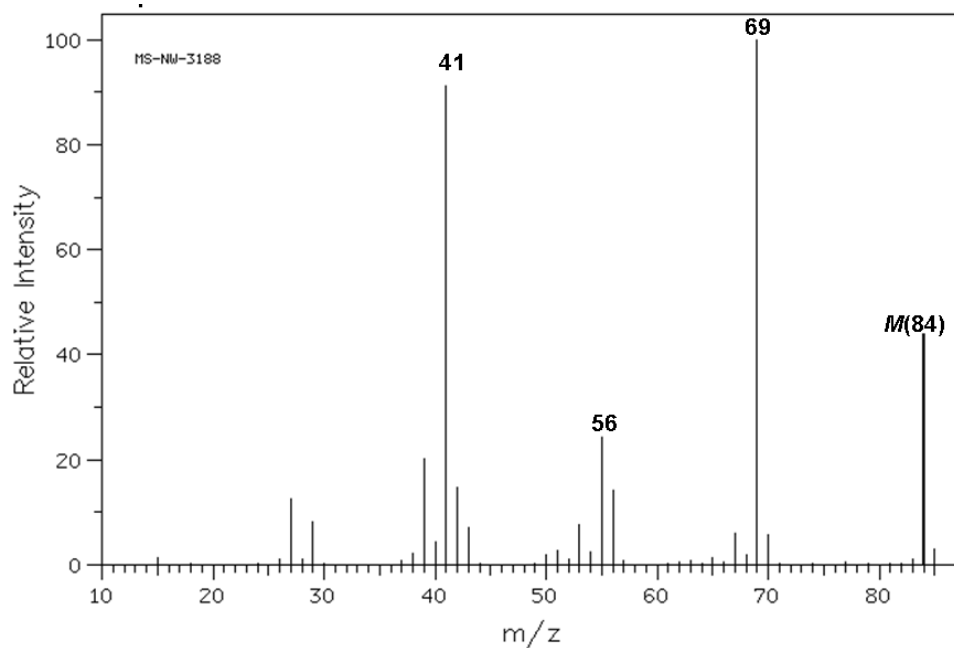
Spectrum No.1

The infrared spectrum has no interesting features except aliphatic C-H stretching and bending. Give the mechanism that lead to the formation of ion fragments at $m/z = 83$ & 55.



Spectrum No.2

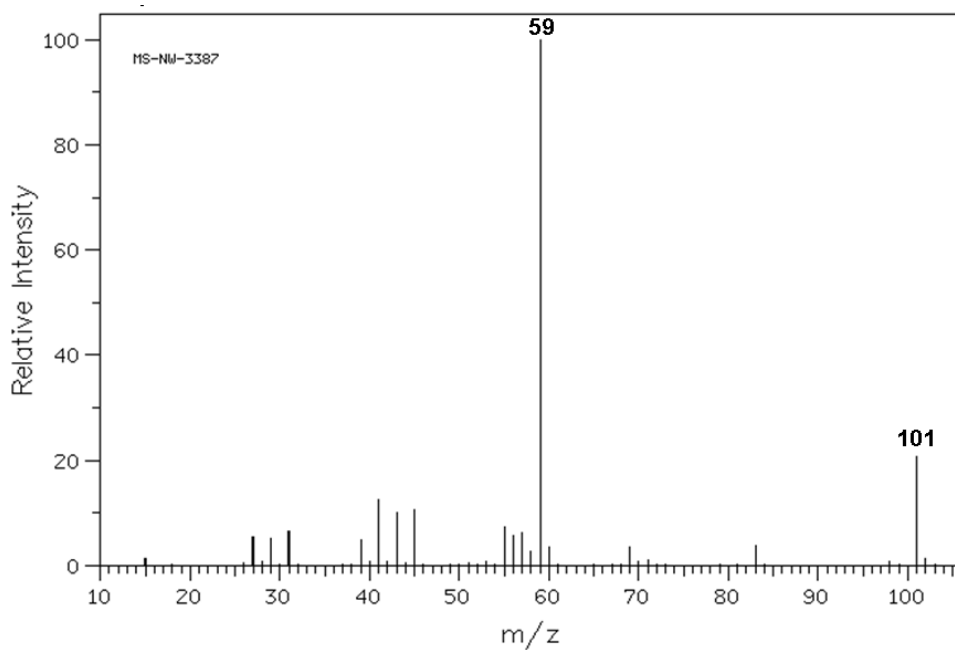
The infrared spectrum has a medium intensity peak at about 1650 cm^{-1} . There is also a C-H out-of-plane bending peak near 800 cm^{-1} . Give the mechanism that lead to the formation of ion fragments at $m/z = 69$.



Spectrum No.3

The infrared spectrum of this compound shows a broad peak at 3370 cm^{-1} . There is also a strong peak at 1159 cm^{-1} , the mass spectrum shows no molecular ion peak. You will have to deduce the molecular weight from the heaviest fragment peak which arises from the loss of a methyl group from the molecular ion.

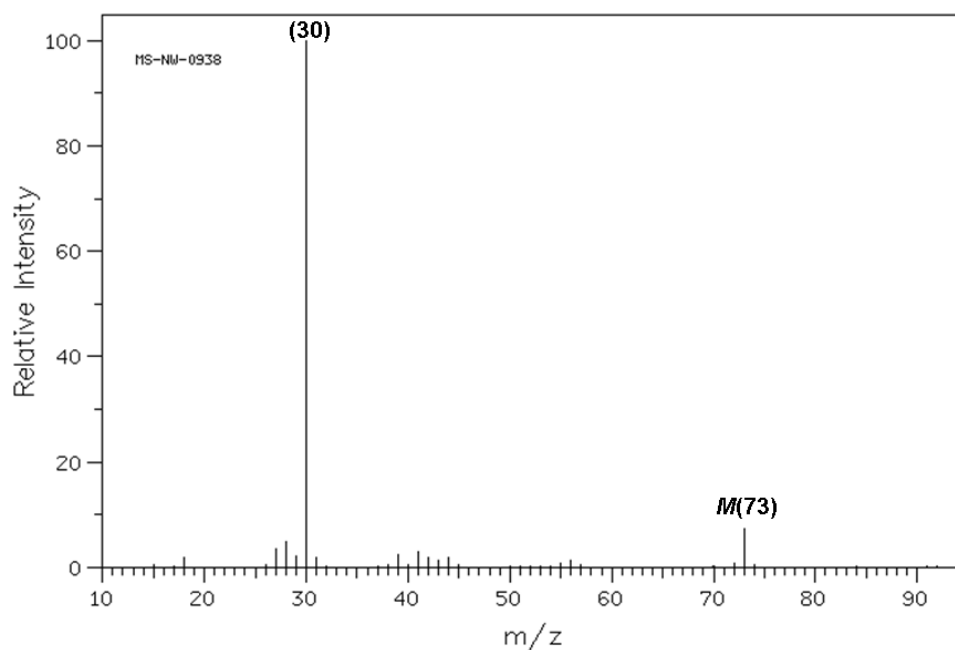
Give the mechanism that lead to the formation of ion fragment at $m/z = 59$



Spectrum No.4

The mass of the molecular ion for this unknown has an odd value and the IR spectrum shows two close bands in the 3450 cm^{-1} region

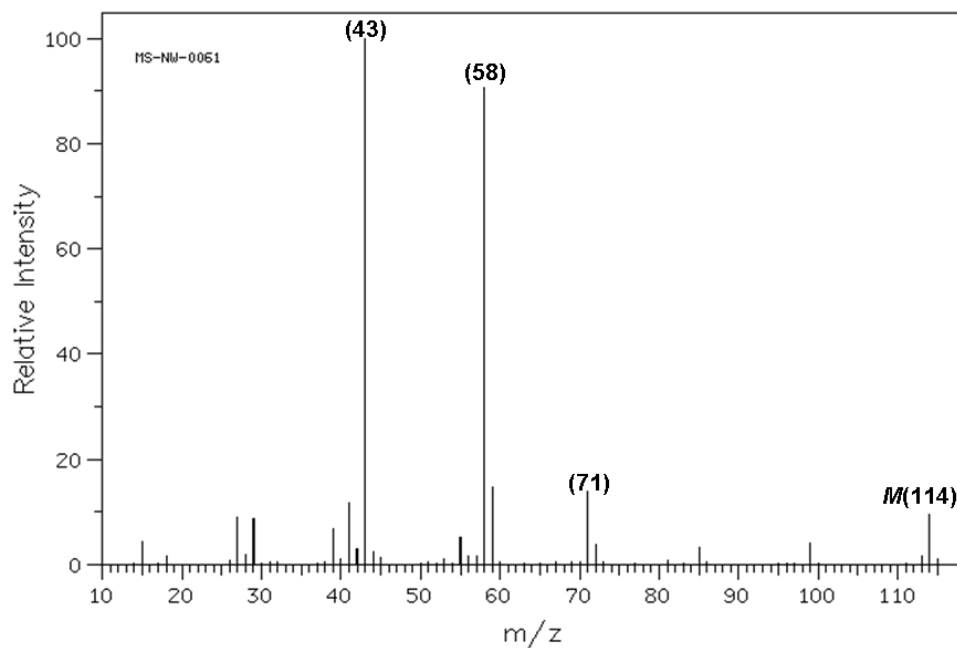
Give the mechanism that lead to the formation of ion fragment at $m/e = 30$



Spectrum No.5

The infrared spectrum of this unknown shows a strong peak near 1715 cm^{-1} .

Give the mechanism that lead to the formation of ion fragments at $m/e = 71$ & 99 .



Spectrum No.6

The infrared spectrum of this unknown shows a very strong, broad peak in the range of $2500\text{--}3000\text{ cm}^{-1}$, as well as a strong, somewhat broadened peak at about 1710 cm^{-1} .

Give the mechanism that lead to the formation of ion fragments at $m/e = 119$ & 91 .

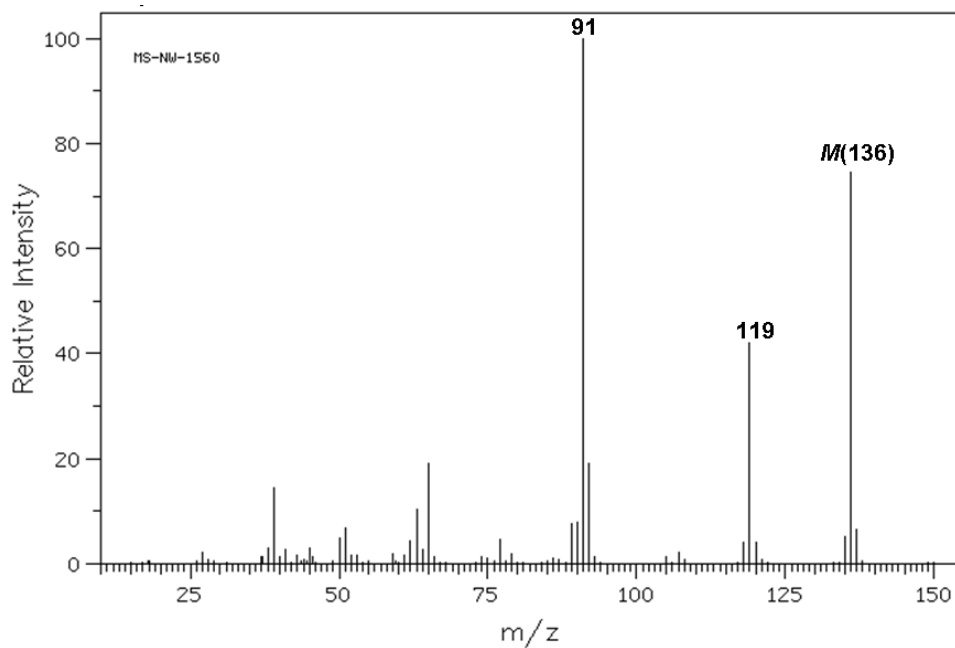


Table of Characteristic IR Absorptions		
<i>frequency, cm⁻¹</i>	<i>bond</i>	<i>functional group</i>
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1830–1800 (s)	C=O stretch band 1	anhydrides
1775–1740 (s)	C=O stretch band 2	
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α,β-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α,β-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH ₂ X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides
m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp		