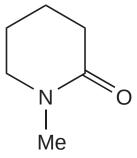
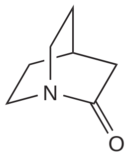
13 Spectroscopy

The following nuclei all have spin $I = \frac{1}{2}$: ^{1}H, ^{13}C, ^{19}F and ^{31}P. Of these nuclei, all but ^{13}C have 100% natural abundance. Unless otherwise stated, you may assume that all ^{13}C spectra have been recorded with broadband proton decoupling.

13.1 The carbonyl stretching frequency for the amide **1** is 1670 cm^{-1}, which is significantly lower than the value for a ketone. For the amide **2** the stretching frequency is 1720 cm^{-1}. Account for these differences.



1



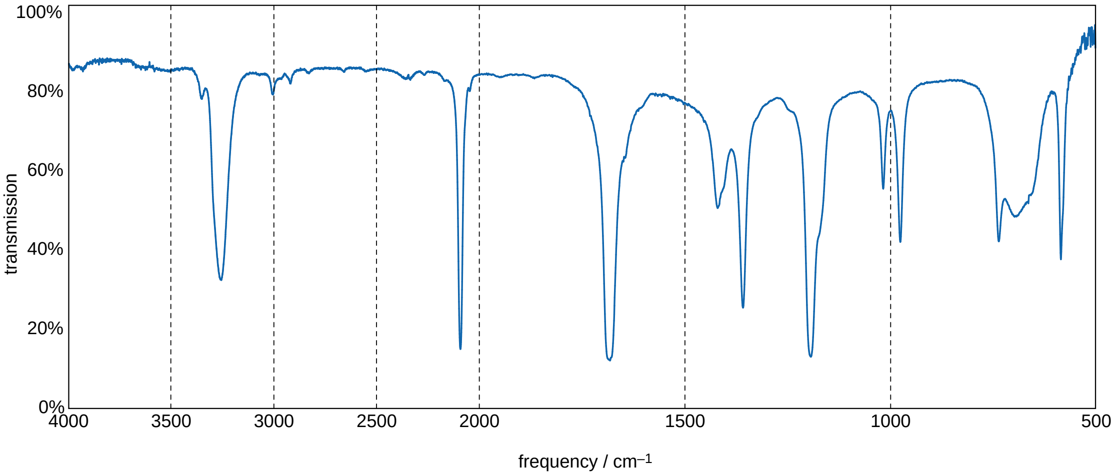
2

13.2 The carboxylate anion, RCO_2^-, shows two absorptions in the C=X region, one at around 1575 cm^{-1} and one at around 1430 cm^{-1}. The C=O vibrational frequency for a typical carboxylic acid, RCOOH, is 1725 cm^{-1}; the vibrational frequency of a C–O single bond is around 1100 cm^{-1}. Discuss these data.

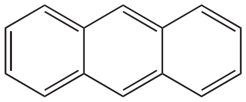
13.3 (a) The relative molecular mass of a compound **X** has been determined by high resolution mass spectrometry to be 68.0261. Using the accurate relative atomic masses below, determine the formula of compound **X**.

$$^{1}H : 1.0078 \qquad ^{12}C : 12.0000 \qquad ^{16}O : 15.9949$$

(b) The IR spectrum of compound **X** is shown below. Use the information from this spectrum, along with your answer to (a), to determine the structure of **X**; give reasons for your answer. [Hint: you will need to measure carefully the carbonyl frequency to distinguish between different possible structures.]



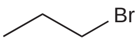
13.4 Predict how many lines you would expect to see in the broadband proton-decoupled ^{13}C NMR spectra of the following molecules, giving brief reasons for your answers in each case (a) benzene, (b) anthracene, (c) 1,4-dinitrobenzene, (d) 1-chloro-4-bromobenzene, (e) 1-chloro-2-nitrobenzene, (f) Et_2O, (g) EtOMe, (h) $CH_3(CH_2)_4COEt$.



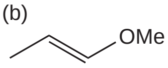
anthracene

13.5 Sketch the ^{13}C NMR spectra that you expect from the following molecules. You should indicate on you spectrum which carbon is responsible for which line in the spectrum. (You cannot give precise values of the shifts, but you can predict the region of the spectrum in which each carbon will give a line, and for similar carbons you can make a reasonable guess as to what order the shifts will come in).

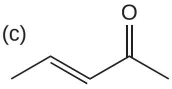
(a)



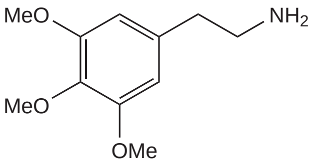
(b)



(c)

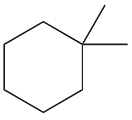


(d)

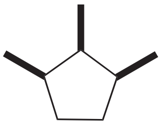


Compound (d) is *mescaline*, an hallucinogenic drug first isolated from certain mushrooms.

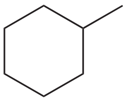
13.6 How can APT NMR spectra be used distinguish between the following hydrocarbons?



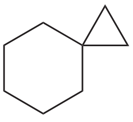
A



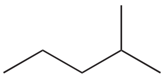
B



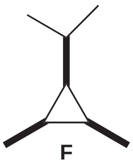
C



D



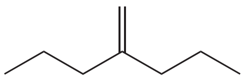
E



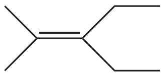
F

13.7 How could the following six isomers be distinguished using ^{13}C NMR?

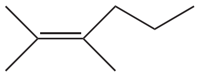
A



B

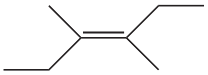


C



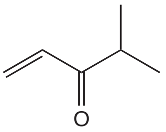
D

E



F

13.8 For organic molecules, 'reduction' involves adding H_2 across double bonds. Reduction of the following molecule gave two products **A** and **B**, both with molecular formula $C_6H_{12}O$.



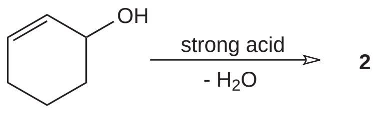
From the following spectroscopic data, identify these two products and explain how the data is consistent with your proposals for the structures of **A** and **B**:

Product **A**: ^{13}C NMR: 137, 115, 85, 36 and 17 ppm; IR: 3400 and 1650 cm^{-1}.

Product **B**: ^{13}C NMR: 213, 38, 31, 17 and 8 ppm; IR: 1710 cm^{-1}.

13.9 (a) Discuss the ^{13}C chemical shifts observed in the following compounds:
methyl lithium: −15 ppm
propene: 134, 116 and 20 ppm
allyl lithium ($LiCH_2CH{=}CH_2$): 143 and 51 ppm.

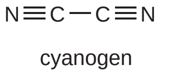
(b) Under acidic conditions **1** gives a very reactive species **2**, whose ^{13}C NMR spectrum can be recorded at low temperatures

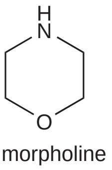


1

The following peaks were observed in the ^{13}C NMR spectra of **1** and **2**:
1: 131, 129, 66, 32, 25 and 19 ppm
2: 224, 142, 37 and 18 ppm.
Suggest a structure for **2** and assign the spectra of both **1** and **2**.

13.10 Cyanogen reacts with morpholine to give a compound **A**, the spectroscopic data for which are given below. Identify **A**, giving your reasons.





^{13}C NMR: peaks at 45.6, 66.2, 110.6 and 142.1 ppm

Significant IR absorptions at 3290, 2234 and 1620 cm^{-1}

13.11 Compound **A** has the formula $C_7H_7NO_3$ and may be reduced to give compound **B** with the formula C_7H_9NO. The ^{13}C NMR and the IR spectra for **A** and **B** are shown in Fig. 13.1 and Fig. 13.2, shown on the next pages. The aromatic region of the ^{1}H NMR spectrum of **A** shows two triplets and two doublets. Deduce the structures of **A** and **B** and, as far as possible, assign the spectra.

13.12 The ^{19}F NMR spectrum of IF_5 consists of a doublet (that is two lines with intensity ratio 1:1) and a quintet (that is five lines with intensity ratios 1:4:6:4:1). Suggest a structure for IF_5 that is consistent with this spectrum, explaining how you arrive at your result. [No splittings are seen due to coupling to the iodine].

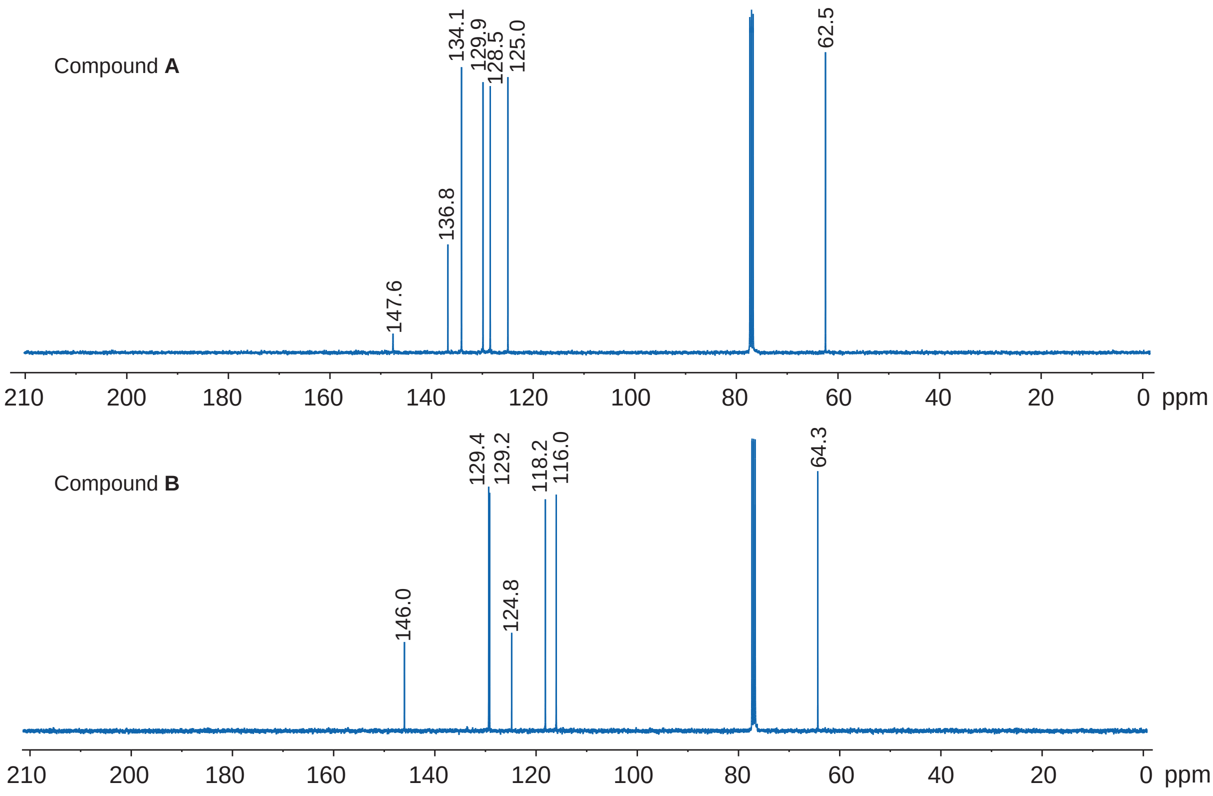


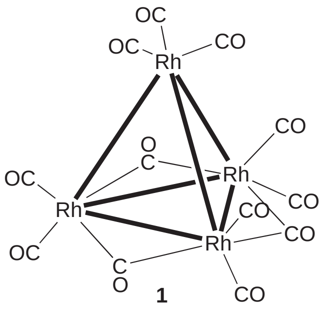
Fig. 13.1 ^{13}C NMR spectra of compounds **A** and **B** from question 13.11.

13.13 Explain why the broadband proton-decoupled ^{13}C spectrum of CH_2Cl_2 consists of a single line, whereas that of CD_2Cl_2 consists of a 1:2:3:2:1 quintet. Predict the form of the ^{13}C spectrum of d_6-DMSO (i.e. CD_3SOCD_3).

13.14 ^{11}B has spin $\frac{3}{2}$ and relaxes sufficiently slowly that couplings to it can be seen. Explain what you would expect to see in the proton NMR spectrum of diborane, B_2H_6, whose structure is shown in Fig. 1.8 on page 18. (You may assume that all the B atoms are ^{11}B, and can ignore any couplings between the protons.)

13.15 Explain why the ^{129}Xe NMR spectrum of XeF^+ is a doublet with J = 7600 Hz, but the ^{19}F spectrum *appears* to be a triplet with J = 3800 Hz. [^{19}F has spin $\frac{1}{2}$ and 100% natural abundance; ^{129}Xe has spin $\frac{1}{2}$ and 26% natural abundance].

13.16 Rhodium and carbon monoxide combine to form a cluster compound with formula $Rh_4(CO)_{12}$ whose structure, **1**, is shown below. Note that in this structure the four rhodium atoms are placed at the corners of a tetrahedron.



1

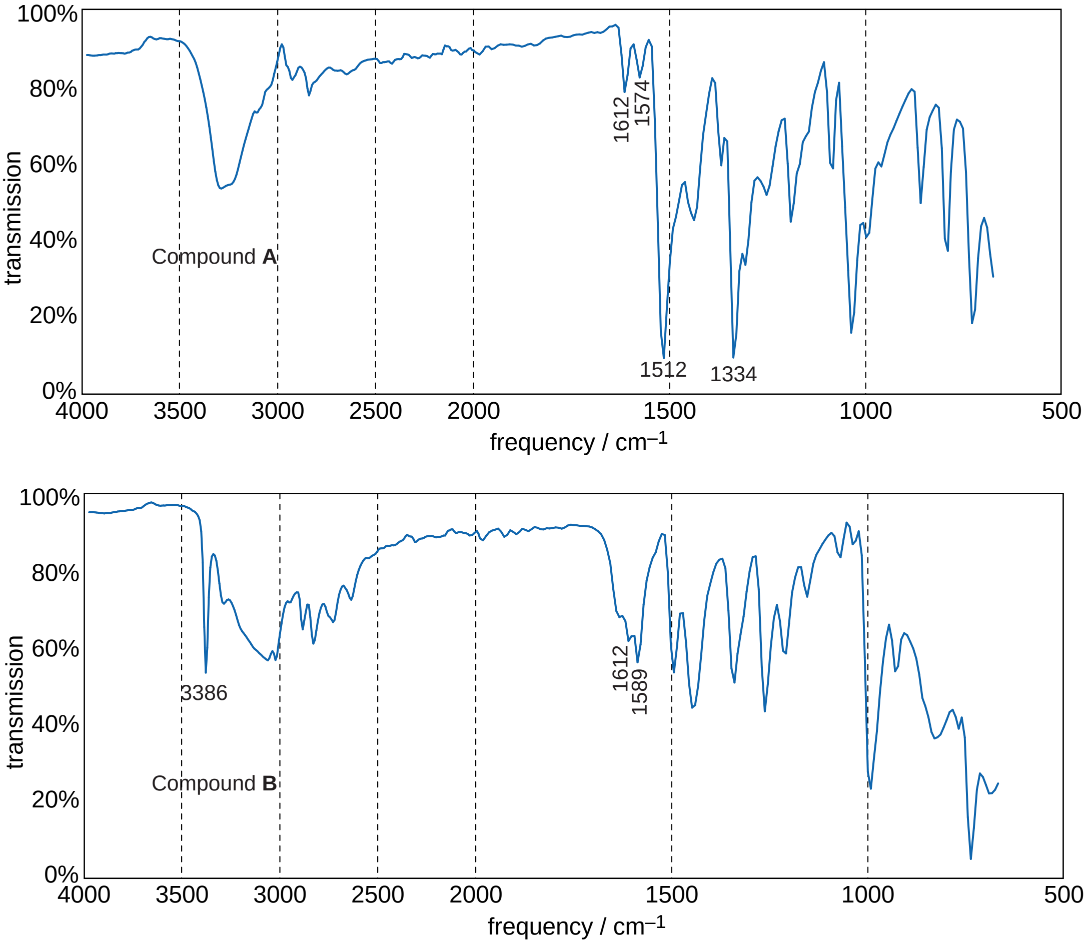


Fig. 13.2 IR spectra of compounds **A** and **B** from question 13.11.

(a) Identify the number of chemically distinct carbon atoms in **1** and hence predict the form of its ^{13}C NMR spectrum. Explain your reasoning carefully. [^{103}Rh is spin-half and has a natural abundance of 100%].

(b) Predict the form of the ^{103}Rh NMR spectrum of **1**. Explain your reasoning carefully.

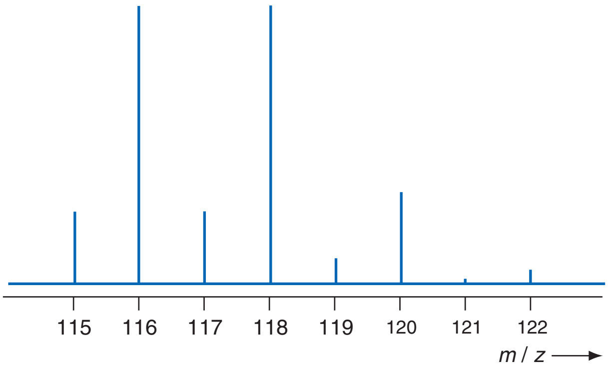
13.17 (a) State the expected structures of BF_3, BCl_3 and BBr_3.

(b) The ^{19}F NMR spectrum of BF_3 shows a 1:1:1:1 quartet. The ^{19}F spectrum of a mixture of BF_3 and BCl_3 shows *three* 1:1:1:1 quartets, likewise the spectrum from a mixture of BF_3 and BBr_3 also shows *three* 1:1:1:1 quartets. The ^{19}F spectrum of a mixture of BF_3, BCl_3 and BBr_3 shows *six* 1:1:1:1 quartets. The chemical shifts at which each of these quartets is centred are given in the table

mixture	shift (ppm)					
BF_3 only	0					
BF_3 and BCl_3	0	51.5	99.0			
BF_3 and BBr_3	0	68.4	130.4			
BF_3, BCl_3 and BBr_3	0	51.5	68.4	99.0	114.8	130.4

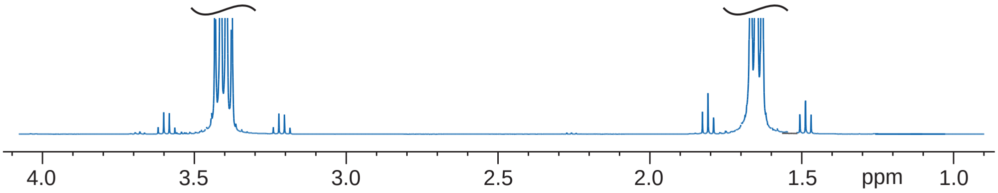
Assuming that only the isotope ^{11}B, which has spin $I = \frac{3}{2}$, is present: (i) identify the species responsible for each quartet and (ii) rationalise the *relative* chemical shifts.

(c) The mass spectrum of BCl_3 is shown below. Explain the spectrum as fully as possible assuming the following isotopic abundances: ^{10}B 20%, ^{11}B 80%,^{35}Cl 75%, ^{37}Cl 25%.

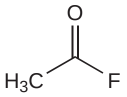


(d) The IR spectrum of BF_3 shows a single absorption in the B–F region of the spectrum at 692 cm^{-1}. The addition of one equivalent of Et_2O causes this peak to shift to 665 cm^{-1} and a second absorption to appear at 770 cm^{-1}. Explain these observations.

13.18 Shown below is a portion of the ^1H NMR spectrum of bromoethane as measured on a 400 MHz spectrometer where 1 ppm ≡ 400 Hz. In order to show the small peaks, the spectrum has been vertically expanded and the strong peaks cropped. Explain the appearance of the spectrum as fully as possible and determine (in Hz) the $^1J_{C\text{–}H}$ coupling constants and the $^3J_{H\text{–}H}$ coupling constant.



13.19 (a) The proton-decoupled ^{13}C NMR spectrum of ethanoyl fluoride (acetyl fluoride) consists of a doublet with a coupling constant of 354.3 Hz and centred at 160.8 ppm, and a doublet with coupling constant 58.3 Hz centred at 18.7 ppm. The IR spectrum includes a strong absorption at 1848 cm^{-1}. Assign the ^{13}C and IR spectra.


ethanoyl fluoride

(b) At low temperatures in an inert solvent, ethanoyl fluoride reacts with Lewis acids such as BF_3, PF_5 or SbF_5 to yield a salt $\mathbf{X}^+\mathbf{Y}^-$ in which the identity of $\mathbf{Y}^-$ depends on the particular Lewis acid used.

The ^{13}C NMR of the salt shows just two singlets at 7.5 ppm and 150.3 ppm. The IR spectrum no longer has an absorption at 1848 cm^{-1}, but now shows a strong absorption at 2297 cm^{-1}.

Suggest a structure for the salt formed between ethanoyl fluoride and BF_3, and explain how your suggestion is consistent with the given spectroscopic data.

(c) Describe the appearance of the ^{31}P NMR spectrum of the salt formed when ethanoyl fluoride reacts with PF_5.

13.20 Given overleaf are details of the ^{1}H and ^{13}C NMR spectra of *five* isomers with the formula C_5H_8O. *Each isomer contains a carbonyl group*.

The second column gives details of the ^{1}H spectrum in an abbreviated form: '2.1, 3H, singlet' means that at a shift of 2.1 ppm there is a *singlet* which the integral indicates is from *three* protons. Similarly '2.32, 2H, doublet of doublets' means that at a shift of 2.32 ppm there is a *doublet of doublets* which the integral indicates is from *two* protons. If a multiplet is too difficult to interpret, it is simply described as a 'complex multiplet'.

The third column gives the number of peaks in the ^{13}C spectrum; apart from one of the peaks corresponding to a carbonyl carbon, the shifts are not particularly useful, and so are not given. The fourth column gives details of the APT spectrum (page 486) which indicates whether there are an odd or even number of protons attached to a particular carbon.

Your task is to identify the structures **A–G**. You may find it useful to adopt the following strategy:

(a) Draw out all the isomers of $C_5H_{10}O$ which contain a carbonyl group. [Hint: there are seven in all].

(b) Identify the number of different environments for all the hydrogen atoms in each structure.

(c) Using the data about the integrals given in the table, work out (in as far as you can) which structure corresponds to which spectrum.

(d) The ^{13}C spectra may also be helpful in sorting out any ambiguities or in confirming your assignment. Identify the number of different carbon atoms in each structure, and check that this matches your proposed structure. Also, check that the APT data are consistent with your answers.

(e) (More difficult) once you are confident of your assignments, try to explain the form of the proton multiplets in terms of the expected couplings.

Struc.	^{1}H spectrum	^{13}C spectrum	APT
A	2.1, 3H, singlet 2.38, 2H, triplet 1.58, 2H, sextet 0.9, 3H, triplet	5	carbonyl down 2 up 2 down
B	9.8, 1H, triplet 2.32, 2H, doublet of doublets 2.23, 1H, complex multiplet 1.0, 6H, doublet	4	carbonyl up 2 up 1 down
C	9.78, 1H, triplet 2.45, 2H, triplet of doublets 1.64, 2H, quintet 1.38, 2H, sextet 0.95, 3H, triplet	5	carbonyl up 1 up 3 down
D	2.43, 4H, quartet 1.05, 6H, triplet	3	carbonyl down 1 up 1 down
E	9.64, 1H, doublet 2.29, 1H, sextet of doublets 1.11, 3H, doublet 1.4-1.8, 2H, complex multiplet 0.97, 3H, triplet	5	carbonyl up 3 up 1 down
F	2.14, 3H, singlet 2.59, 1H, septet 1.1, 6H, doublet	4	carbonyl down 3 up 0 down
G	9.5, 1H, singlet 1.1, 9H, singlet	3	carbonyl up 1 up 1 down

13.21 Phosphine, PH_3, is a colourless, toxic gas. It reacts with aqueous acid HA and methanal (formaldehyde, CH_2O) to give a salt, $\mathbf{X}^+\mathbf{A}^-$. Figure 13.3 on the next page shows various spectra recorded for the species $\mathbf{X}^+$.

The (low resolution) positive-ion electrospray mass spectrum of $\mathbf{X}^+$ shows a main peak at 155, along with three fragments each showing a successive loss of mass 30.

For the ^{1}H and ^{31}P NMR spectra the shifts (in ppm) are some peaks are indicated; note also that the conversion from ppm to Hz is given for each spectrum. The only feature in the *proton decoupled* ^{13}C NMR spectrum (not shown) is a doublet, centred at 48.7 ppm, and with a splitting of 50 Hz.

(a) Explain why it is that the ^{31}P NMR spectrum of phosphine consists of a 1:3:3:1 quartet, whereas the ^{1}H NMR spectrum consists of a 1:1 doublet. [^{31}P, $I = \frac{1}{2}$, abundance 100 %]

(b) By considering the mass spectrum and *all* of the NMR data, suggest a structure for the $\mathbf{X}^+$. Be sure to explain how each spectrum is consistent with your structure and include the actual values for any coupling constants as determined from the spectra. [You may find it helpful to think about the reaction, which starts with a nucleophilic addition to a double bond.]

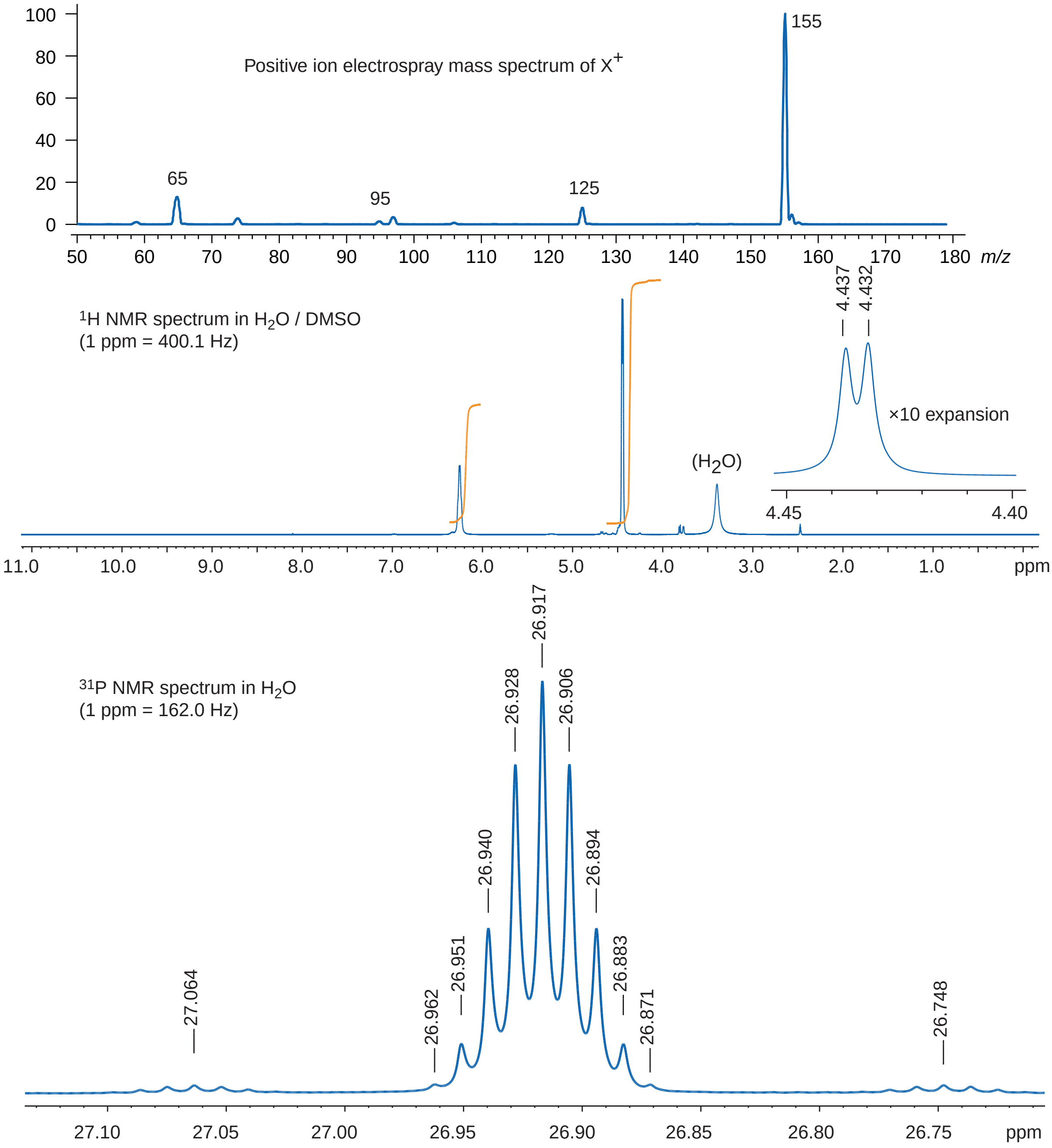


Fig. 13.3 Mass spectrum, ^{1}H and ^{31}P NMR spectra of species $\mathbf{X}^{+}$ from question 13.21.