

7. This question is about the spectra of haloalkanes

Haloalkanes have been used as aerosol propellants and refrigerants but are now largely banned due to the damage they cause to the ozone layer. Halon 1211 was once commonly used in fire extinguishers (now only found in fighter jets) and 'Halothane' is an inhalational general anaesthetic.



Further examples of haloalkanes are given in the table below.

	Common name	Structural formula
A	CFC-113	$\text{Cl}_2\text{FC}-\text{CClF}_2$
B	CFC-113a	$\text{Cl}_3\text{C}-\text{CF}_3$
C	HFC-134a	$\text{F}_3\text{C}-\text{CH}_2\text{F}$
D	CFC-11 (Freon-11, R-11)	CCl_3F
E	CFC-12 (Freon-12, R-12)	CCl_2F_2
F	CFC-13	CClF_3
G	Halon 1211	CBrClF_2
H	Methylene bromide	CH_2Br_2

Whilst naturally occurring carbon and fluorine exist as essentially the single isotopes ^{12}C and ^{19}F , chlorine consists of 75% ^{35}Cl and 25% ^{37}Cl ; bromine consists of 50% ^{79}Br and 50% ^{81}Br . The presence of chlorine and bromine atoms in molecules therefore leads to characteristic patterns for molecular ions in mass spectrometry. As an example, the mass spectrum of CFC-13 (**F**) includes peaks at $m/z = 104$ ($\text{CF}_3^{35}\text{Cl}^{++}$) and 106 ($\text{CF}_3^{37}\text{Cl}^{++}$) with intensity ratio 3:1.

- (a) Calculate the m/z values and relative intensities for the molecular ion peaks of CFC-12 (**E**).
- (b) Sketch the mass spectrum for the molecular ion peaks of Halon 1211 (**G**). Indicate the relative intensity of each peak and which ion(s) are responsible for them.

A sample of methylene bromide (**H**) was enriched with deuterium (^2H). On analysis it was found that half of the hydrogen content of the sample was deuterium. In the mass spectrum there are molecular ion peaks with m/z values of 172, 173, 174, 175, 176, 177 and 178.

- (c) Calculate the relative intensities of these molecular ion peaks.

NMR spectroscopy is a technique which reveals the number of different environments of certain nuclei in a molecule. NMR active nuclei such as ^1H , ^{13}C and ^{19}F are routinely studied. As an example, the two hydrogen atoms in methylene bromide (**H**) are equivalent and hence would give rise to a single peak in the ^1H NMR spectrum. The same is true for the hydrogens in HFC-134a (**C**).

- (d) In your booklet, complete the table indicating the number of different fluorine environments for the each of the compounds **A-G**.
- (e) The anaesthetic *Halothane* has the formula $\text{C}_2\text{HBrClF}_3$ and shows one signal in its ^{19}F NMR spectrum. Draw the **two** possible three-dimensional structures for Halothane.

The intensity of a signal in a ^1H or ^{19}F NMR spectrum is proportional to the number of nuclei in that particular environment.

- (f) For each compound with more than one signal in its ^{19}F NMR spectrum, indicate in the appropriate column of the table the expected intensity ratio.

NMR spectra are complicated by coupling between nuclei. If an NMR-active nucleus is within three bonds of another similar nucleus *which is in a different chemical environment*, its signal will be split into a number of peaks instead of appearing as a single peak. If a nucleus couples to n NMR-active nuclei, its signal will split into a total of $(n+1)$ peaks.

- (g) The ^{19}F NMR spectrum of one of the haloalkanes from the table is shown below. In your answer booklet draw the structure of the haloalkane and indicate with an arrow which fluorines give rise the signals **X** and **Y**.

