

AQA Chemistry A-level

Topic 3.15 - NMR Spectroscopy

Flashcards



What does NMR stand for?



What does NMR stand for?

Nuclear Magnetic Resonance



What are the basic principles of NMR?



What are the basic principles of NMR?

You can find the structures of complex molecules by placing them in a magnetic field and applying EM waves of radio frequency to them. If radio waves of the right frequency are absorbed, the nuclei flips from parallel to applied magnetic field to anti-parallel. This energy change can be monitored and recorded. Uses the resonance of nuclei with spin.



How would you carry out NMR spectroscopy?



How would you carry out NMR spectroscopy?

Dissolve the liquid sample in suitable solvent, put in a tube along with a small amount of TMS and put the tube into an NMR machine. The sample is spun to even out any imperfections in the magnetic field and the spectrometer is zeroed against the TMS. Radiation with different radio frequencies but a constant magnetic field is applied to the sample and any absorptions (due to resonance) are detected



Give one use of NMR?





Give one use of NMR?

MRI scans



What kind of nuclei does
NMR work with (and
examples)?



What kind of nuclei does NMR work with (and examples)?

Those with an uneven number of nucleons, meaning they will spin e.g. ^1H , ^{13}C



What percentage of carbon atoms are ^{13}C ?



What percentage of carbon atoms are ^{13}C ?

1% - but modern instruments are sensitive enough to detect this



What defines the resonant frequency of a ^{13}C atom?



What defines the resonant frequency of a ^{13}C atom?

The chemical environment that it is in; the amount of electron shielding it has.



What graph is produced by NMR spectroscopy?



What graph is produced by NMR spectroscopy?

Energy absorbed against chemical shift



What is chemical shift?
What is its symbol? What
are its units?



What is chemical shift? What is its symbol? What are its units?

The resonant frequency of the nuclei, compared to that of a ^1H atom in TMS.

Symbol \square

Parts per million (ppm)



What is the range of
chemical shift for ^{13}C NMR?



What is the range of chemical shift for ^{13}C NMR?

0-200ppm



What means ^{13}C atoms
show a different chemical
shift value?



What means ^{13}C atoms show a different chemical shift value?

Having different chemical environments (but equivalent atoms show the same peak)



What kind of environment
leads to a greater chemical
shift?



What kind of environment leads to a greater chemical shift?

A C atom next to more electronegative atom has a greater chemical shift.



Summarise what these mean for ^{13}C NMR:

Number of signals?

Chemical shift?

Area under peak?

Splitting?



Summarise what these mean for ^{13}C NMR:

Number of signals: One signal for each carbon environment (each set of inequivalent ^{13}C atoms)

Chemical shift: Greater δ from atoms closer to electronegative atoms or $\text{C}=\text{C}$

Area under peak: no meaning

Splitting: there is no splitting for ^{13}C NMR



Why is it easier to get a spectrum of ^1H NMR than ^{13}C NMR?



Why is it easier to get a spectrum of ^1H NMR than ^{13}C NMR?

Most H atoms are ^1H - it is much more abundant than ^{13}C . This means almost all H atoms have spin so show up



What is the range of
chemical shift for ^1H NMR?



What is the range of chemical shift for ^1H NMR?

0-10ppm



What leads to a lower
chemical shift value for H
NMR?



What leads to a lower chemical shift value for H
NMR?

^1H with more electrons around them i.e. further
from electronegative groups/atoms



On a low resolution spectrum, what peaks would you expect to see for H NMR?



On a low resolution spectrum, what peaks would you expect to see for H NMR?

One peak for each set of inequivalent H atoms
(each chemical environment shows 1 peak)



What does the area under
the peak represent (for H
NMR)?



What does the area under the peak represent (for H NMR)?

The area under the peak is proportional to the number of ^1H atoms represented by the peak



What is the integration trace?



What is the integration trace?

A stepped line that makes it easier to measure the area under the curve (height of line = area under that peak)

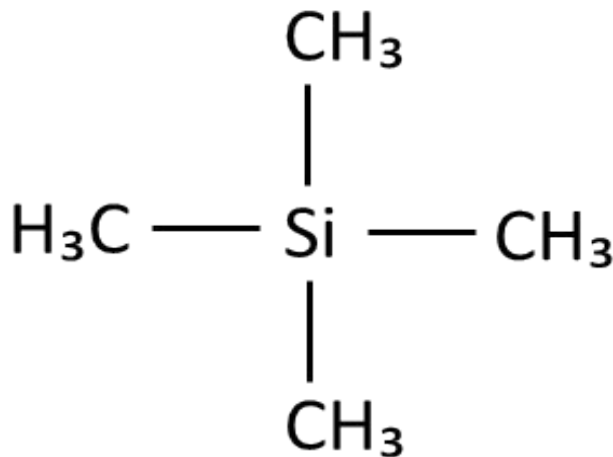


What is TMS (name and structure)?



What is TMS (name and structure)?

Tetramethylsilane



What state is TMS at room temperature?



What state is TMS at room temperature?

liquid



Why is TMS used?



Why is TMS used?

Can be added to sample to calibrate the NMR equipment. It provides a peak at exactly $\delta = 0$ ppm. It is the reference point against which all δ are measured



What are other advantages of using TMS?



What are other advantages of using TMS?

Inert, non-toxic, easy to remove from the sample
(as relatively volatile)



When does splitting/spin-spin coupling occur?



When does splitting/spin-spin coupling occur?

Neighbouring hydrogen atoms (3 or fewer bonds away, or on the adjacent carbon) affect the magnetic field of ^1H atoms and causes their peaks to split



What is the $n+1$ rule?



What is the $n+1$ rule?

If there are n inequivalent ^1H atoms on the neighbouring carbon then the peak will split into $(n+1)$ smaller peaks

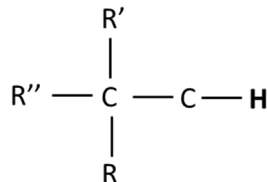


Draw the splitting patterns
for 0, 1, 2 and 3 inequivalent
H atoms 3 bonds or less
away



Draw the splitting patterns for 0, 1, 2 and 3 inequivalent H atoms 3 bonds or less away

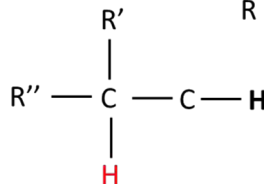
No coupled protons



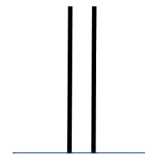
Singlet



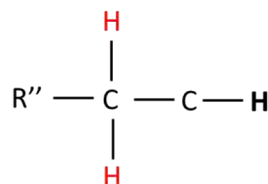
One coupled proton



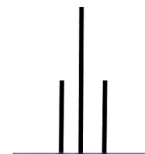
Doublet



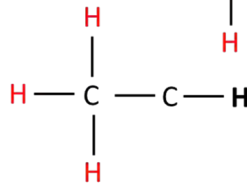
Two coupled protons



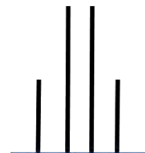
Triplet



Three coupled protons



Quartet



Why must solvents used for ^1H NMR not contain any hydrogen atoms?



Why must solvents used for ^1H NMR not contain any hydrogen atoms?

Signals from the solvent would swamp signals from the sample, as there is much more solvent than sample.



Which solvents are used?



Which solvents are used?

Deuterated solvents: CDCl_3 , D_2O , C_6D_6

CCl_4 - tetrachloromethane



Summarise what these indicate for ^1H NMR:

Number of signals?

Chemical shift?

Splitting?

Area under peak?



Summarise what these indicate for ^1H NMR:

Number of signals: One main signal for each set of inequivalent ^1H atoms (for each hydrogen environment)

Chemical shift: Larger δ for ^1H atoms closer to electronegative atoms or $\text{C}=\text{C}$

Splitting: Number of smaller peaks = 1 + number of inequivalent hydrogen atoms 3 bonds away

Area under peak: Proportional to the number of atoms represented by that peak



Why does the peak from
O-H bonds disappear if D_2O
is used as a solvent?



Why does the peak from O-H bonds disappear if D_2O is used as a solvent?

O-D bond is formed in preference to O-H due to labile protons that move/swap from one molecule to another.

