

## SHIELDING & H-NMR SPLITTING

Carbon or hydrogen nuclei in non-polar environments are '*shielded*' since there is high electron density around them. The opposite is true for nuclei in polar environments.

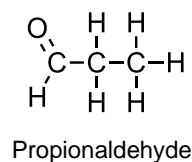
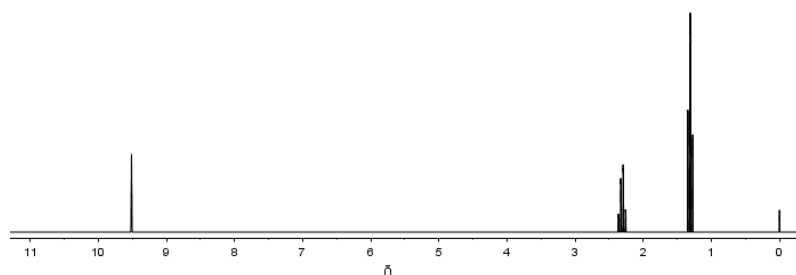
Therefore:

- Nuclei in shielded (non-polar) environments need *more* magnetic energy to resonate and have *low* chemical shift.
- Nuclei in de-shielded (polar) environments need *less* magnetic energy to resonate and have *high* chemical shift.

Understanding shielding, and its effects on chemical shift, can be useful when interpreting NMR spectra as it reduces your reliance on the data booklet.

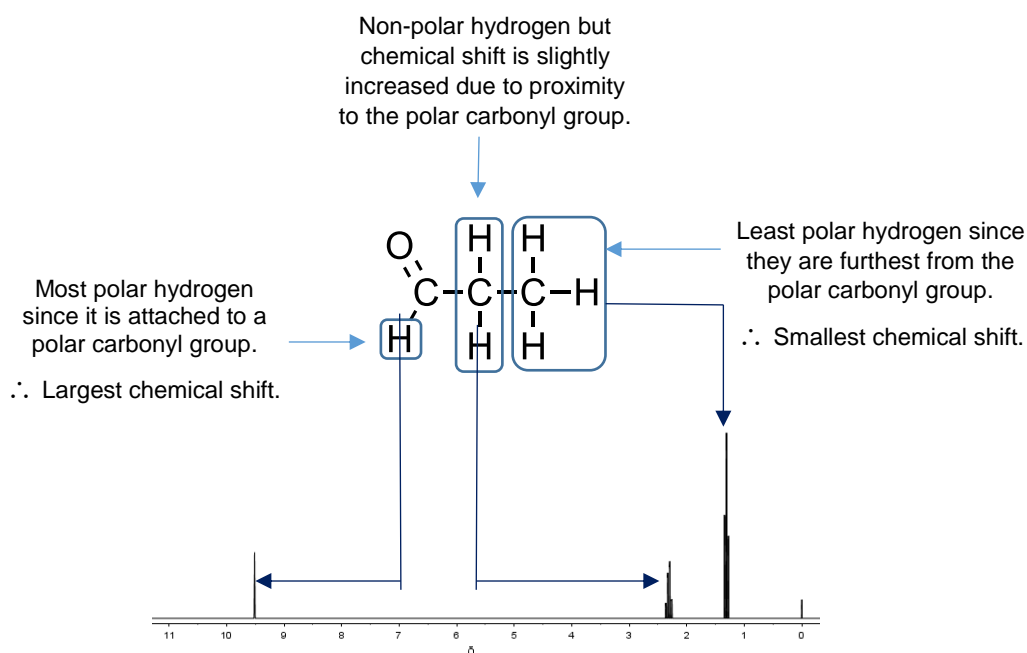
### Example:

Below is the high resolution spectrum for propionaldehyde. Identify which hydrogen produced each of the peaks in the spectrum (without using the data booklet).



### Solution

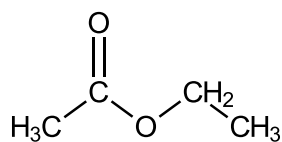
The most polar hydrogen environment will have the highest chemical shift, the least polar will have the smallest chemical shift.



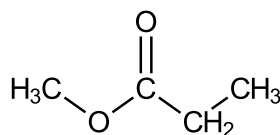
## SPLITTING

A peak will split according to how many non-equivalent hydrogen are on the neighbouring atoms (n+1 rule).

As an example, consider two isomers of an ester with the formula  $C_4H_8O_2$ .



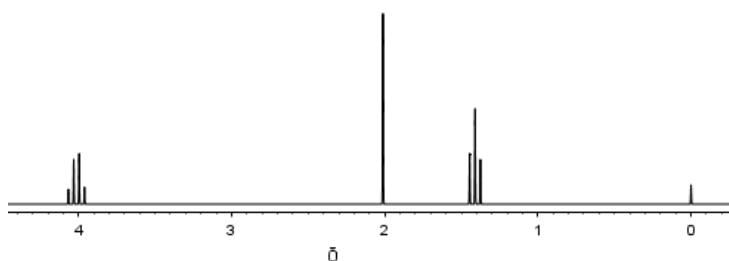
**Ester 1**



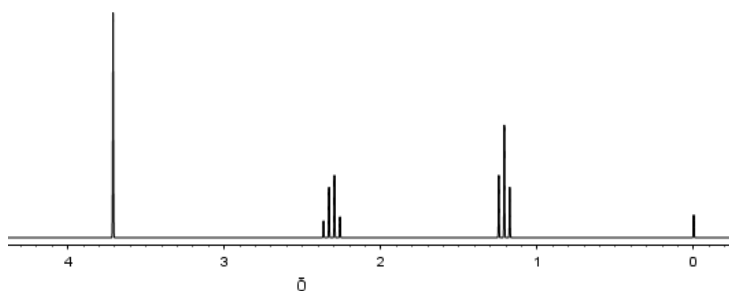
**Ester 2**

Match the esters to the spectra shown below.

**Spectrum 1:**



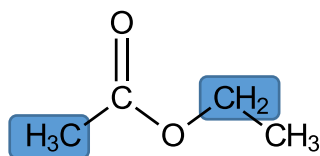
**Spectrum 2:**



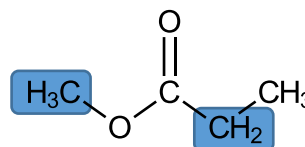
**Solution**

### Step 1:

Identify the peaks produced by the hydrogen environments on both sides of the ester link. Since ester links occur in the middle of a hydrocarbon chain, there are always two peaks the spectrum due to the hydrogen on either side of the link.

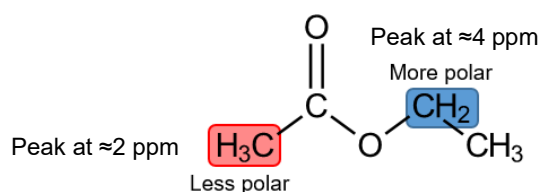


Ester 1

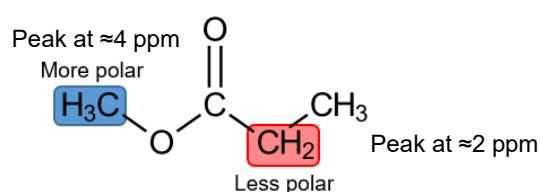


Ester 2

The hydrogen closest to the oxygen in the chain are in a more polar environment and will have a higher chemical shift of about 4 ppm. The hydrogen closest to the carbonyl (C=O) are in a less polar environment and will have a chemical shift of about 2 ppm.

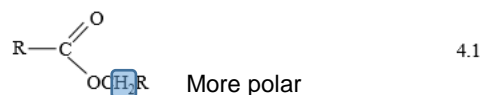


Ester 1

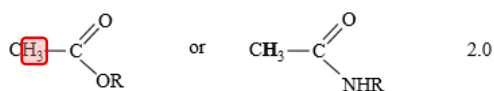


Ester 2

### From the data booklet:

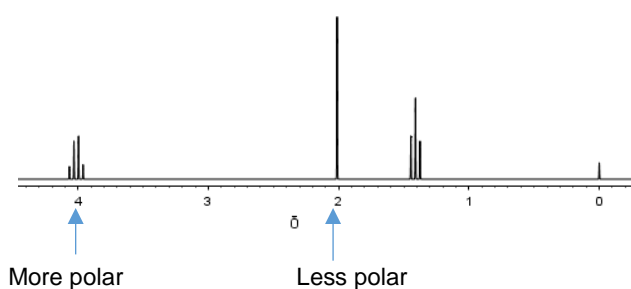


Less polar

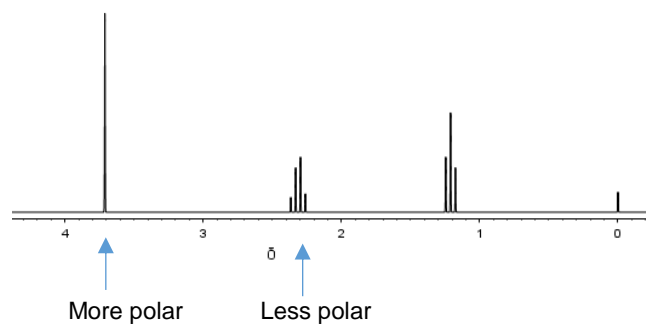


These peaks can now be identified on the spectra.

### Spectrum 1:



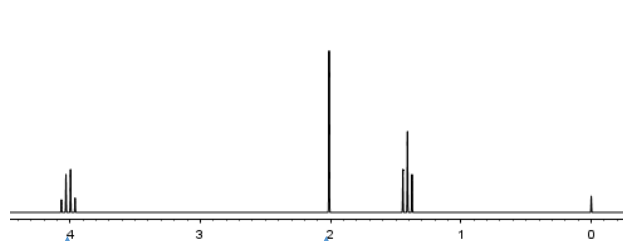
### Spectrum 2:



## Step 2:

Use the splitting patterns to assign each ester to a spectrum.

### Spectrum 1:



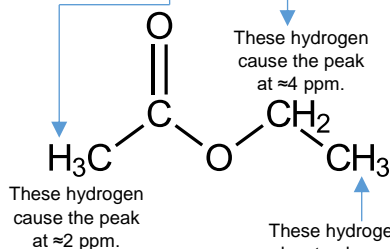
More polar

Less polar

This peak is due to the hydrogen on the most polar side of the ester link. Therefore, these hydrogen will be next to the oxygen in the carbon chain. Since the peak is split into a quartet, there are three hydrogen on the neighbouring atom.

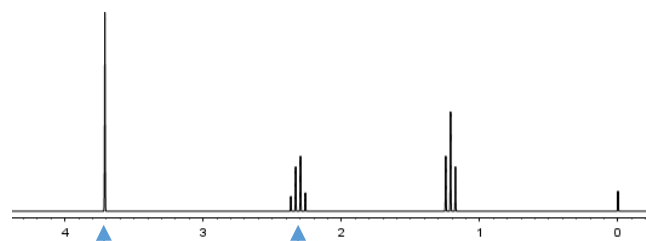
This peak is due to the hydrogen on the least polar side of the ester link. Therefore, these hydrogen will be next to the carbonyl (C=O). Since the peak is not split, there are no neighbouring hydrogen. Therefore, it must be a methyl group.

These hydrogen cause the peak at  $\approx 4$  ppm.



These hydrogen are in the least polar environment overall and produce the peak at  $\approx 1.5$  ppm. The peak is a triplet since there are two hydrogen on the neighbouring atom.

### Spectrum 2:



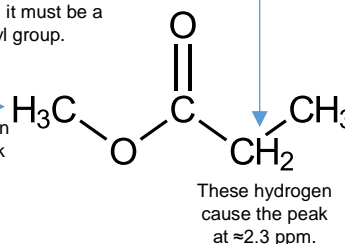
More polar

Less polar

This peak is due to the hydrogen on the most polar side of the ester link. Therefore, these hydrogen will be next to the oxygen in the carbon chain. Since the peak is not split, there are no neighbouring hydrogen. Therefore, it must be a methyl group.

This peak is due to the hydrogen on the least polar side of the ester link. Therefore, these hydrogen will be next to the carbonyl (C=O). Since the peak is split into a quartet, there are three hydrogen on the neighbouring atom.

These hydrogen cause the peak at  $\approx 3.7$  ppm.



These hydrogen are in the least polar environment overall and produce the peak at  $\approx 1.2$  ppm. The peak is a triplet since there are two hydrogen on the neighbouring atom.