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13C NMR Chemical Shift

Transcript

00:00:00:00 - 00:00:18:28
Dr.Jessie Key: Hello again, Dr. Jessie Key here, in this video, we'll examine chemical shift in terms of carbon NMR. The electrons which surround all nuclei are charged particles that produce their own local magnetic field, opposing an externally applied magnetic field.

00:00:18:28 - 00:00:49:79
Dr.Jessie Key: This is called ‘diamagnetism’. Because these local magnetic fields produced by the electrons oppose the externally applied magnetic field, the actual field felt by nuclei is less than the applied field, we call this “shielding”. We can represent this mathematically with the equation, B effective equals B applied minus B local (Beffective = Bapplied - Blocal).

00:00:49:92 - 00:01:37:00
Dr.Jessie Key: Alternatively, we can represent this visually with the image at the bottom of the slide, which shows that the shielding magnetic field from the electrons shown in blue reduces the applied magnetic field from the magnet in red to give the effective field experienced shown in green. Since shielding reduces the strength of the applied field, it results in a smaller difference in energy between Alpha and Beta spin states of nuclei. Therefore, nuclei will release different amounts of energy to relax from the higher energy Beta state to the lower energy Alpha state depending on the amount of electron density present shielding them.

00:01:37:18 - 00:02:08:17
Dr.Jessie Key: We relate these differences in signal energies detected in terms of chemical shift. The chemical shift Delta is the location of a signal in an NMR spectrum relative to the reference material tetramethlysilane (TMS). The unit used to express chemical shift is the part-per-million (ppm), where where 1 ppm represents 1 part per million of the NMR spectrometer’s operating frequency.

00:02:08:21 - 00:02:39:30
Dr.Jessie Key: Tetramethylsilane (TMS) is therefore always assigned a ppm value of 0. The use of the chemical shift system allows for differences in spectrometer operating frequency, as the chemical shift value for a given sample will remain the same no matter what NMR

operating frequency is used. NMR spectra are plots of intensity of radio frequency absorption vs. chemical shift (in ppm).

00:02:39:30 - 00:03:16:70
Dr.Jessie Key: Most carbon 13 (13C) NMR spectra span from around 220 ppm to 0 ppm, which is a much broader range than proton NMR, which typically spans from about 14 to 0 ppm. Historically, the terms downfield and upfield were often used as relative terms to describe the position of a signal in a spectrum. These terms originate from the first NMR instruments, which analyze samples by holding radio frequencies constant and swept from low to high magnetic field strength.

00:03:16:70 - 00:03:45:87
Dr.Jessie Key: While this instrumental design was made obsolete in the 1960's by the development of modern Fourier-Transform NMR, the terms ‘Downfield’ and ‘Upfield’ are still frequently used. IUPAC recommends that these terms should no longer be used and most modern chemists would instead use the terms ‘Deshielded’ and ‘Shielded’ to relate relative signal position. One of the main factors affecting chemical shift is induction.

00:03:45:87 - 00:04:08:73
Dr.Jessie Key: Nuclei can be deshielded by nearby electronegative atoms, with higher chemical shift value seen as neighbouring atom electronegativity increases. Here we can compare dibromomethane with a chemical shift of 19.2 and dichloromethane with a chemical shift of 53.5.

00:04:09:39 - 00:04:31:33
Dr.Jessie Key: Induction is also additive, (but not-linearly), where additional electronegative atoms can further deshield a given carbon. In this example, we can see that chloromethane has a chemical shift of 28.7 ppm, while dichloromethane has a chemical shift of 53.5 ppm,

00:04:31:33 - 00:04:50:88
Dr.Jessie Key: trichloromethane or (chloroform) has a chemical shift of 77.3 ppm. Induction is distance dependent with the effects greatest at close proximity and trailing off to insignificant levels after 2-3 carbons.

00:04:50:88 - 00:05:04:19
Dr.Jessie Key: Here we have the molecule propan-1-ol or propanol. The electronegative hydroxyl group deshields the carbon is attached to the most with a chemical shift of 64.3 ppm.

00:05:04:19 - 00:05:15:95
Dr.Jessie Key: The next closest carbon is deshielded less at a chemical shift of 25.9 ppm and the furthest carbon has the least deshielding with a chemical shift of 10.3 ppm.

00:05:15:95 - 00:05:34:28

Dr.Jessie Key: Chemical shift is also affected by the diamagnetic effects of nearby Pi electron systems. For example, Pi electrons in aromatic rings and triple bonds circulate generating their own local magnetic fields. This is known as diamagnetic anisotropy.

00:05:34:28 - 00:06:21:14
Dr.Jessie Key: As a result, most sp two (sp2) and sp hybridized carbons are significantly more deshielded than sp three (sp3) carbons. The chemical shifts of many carbon types are categorized into regions of the spectrum, they tend to be found, as shown below in a correlation table. We can broadly generalize a carbon NMR correlation table into three regions: sp two (sp2) hybridized carbons like carbonyls and aromatics 220-100 ppm, sp hybridized carbons like nitriles and alkynes from around 130-75 ppm, and sp hybridized carbons from around 90 to 0 ppm.

00:06:22:52 - 00:06:55:61
Dr.Jessie Key: Let's take a look at an example to help get a feel for the chemical shift regions, below is the carbon NMR of ethyl anisate with each signal's carbon labelled. Looking at the structure of ethyl anisate, we can see that it contains sp two (sp2) hybridized carbons in its aromatic ring and its ester. As well, it has sp three (sp3) hybridized carbons in the methyl and ethyl groups attached to the ether and ester, respectively.

00:06:55:61 - 00:07:24:03
Dr.Jessie Key: I suggest reading an NMR spectrum from left to right, just like reading a book in English. We can see in the sp two (sp2) hybridized region, the carbons labeled one through five are visible from around 170 ppm to 110 ppm. Notice, the ester carbon is the most shielded in the spectrum, this is quite common as carbonyl carbons are typically found between about 220-160 ppm.

00:07:24:03 - 00:08:04:67
Dr.Jessie Key: Next, the aromatic ring carbons can be seen, it can be hard to definitively identify each individual aromatic carbon by chemical shift alone with the knowledge we have now, but we can make some educated guesses. The more intense signals of three and five should correspond to the symmetrical aromatic carbons bearing hydrogens - remember, Nuclear Overhauser effect enhancement and symmetry will make these carbons present a stronger intensity signal. Carbons two and four should belong to the carbons bearing the ether and ester substituents, with the ether-bearing carbon labelled 2 being more deshielded by being directly attached to an electronegative oxygen.

00:08:04:93 - 00:08:32:21
Dr.Jessie Key: The sp three hybridized carbons we can identify based upon their relative deshielding. Carbons labeled six and seven are beside electronegative atoms, which deshields them, putting them up around 50-60 ppm. Finally, the carbon labeled eight is the most shielded at around 14 ppm as it is an sp three (sp3) hybridized carbon slightly farther away from electronegative atoms.