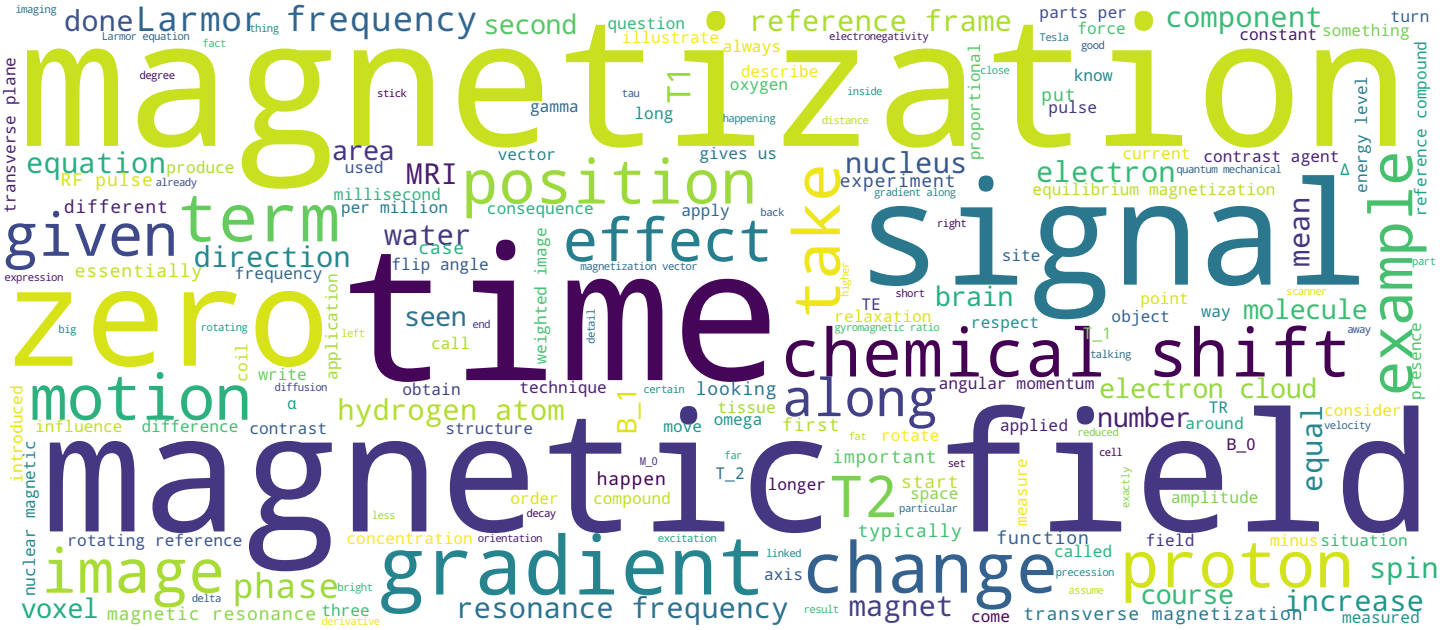
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

# 10.3 Distinguishing the signal based on chemistry

## Fundamentals of Biomedical Imaging

Prof. Rolf Gruetter



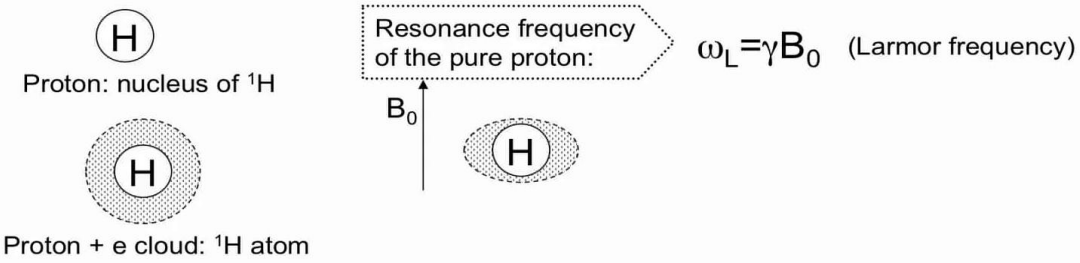
**Search MOOC**

**Video**

EPFL

## 10-3. What role does the chemical environment play?

Chemical shift: Effect of $B_0$ on e-cloud



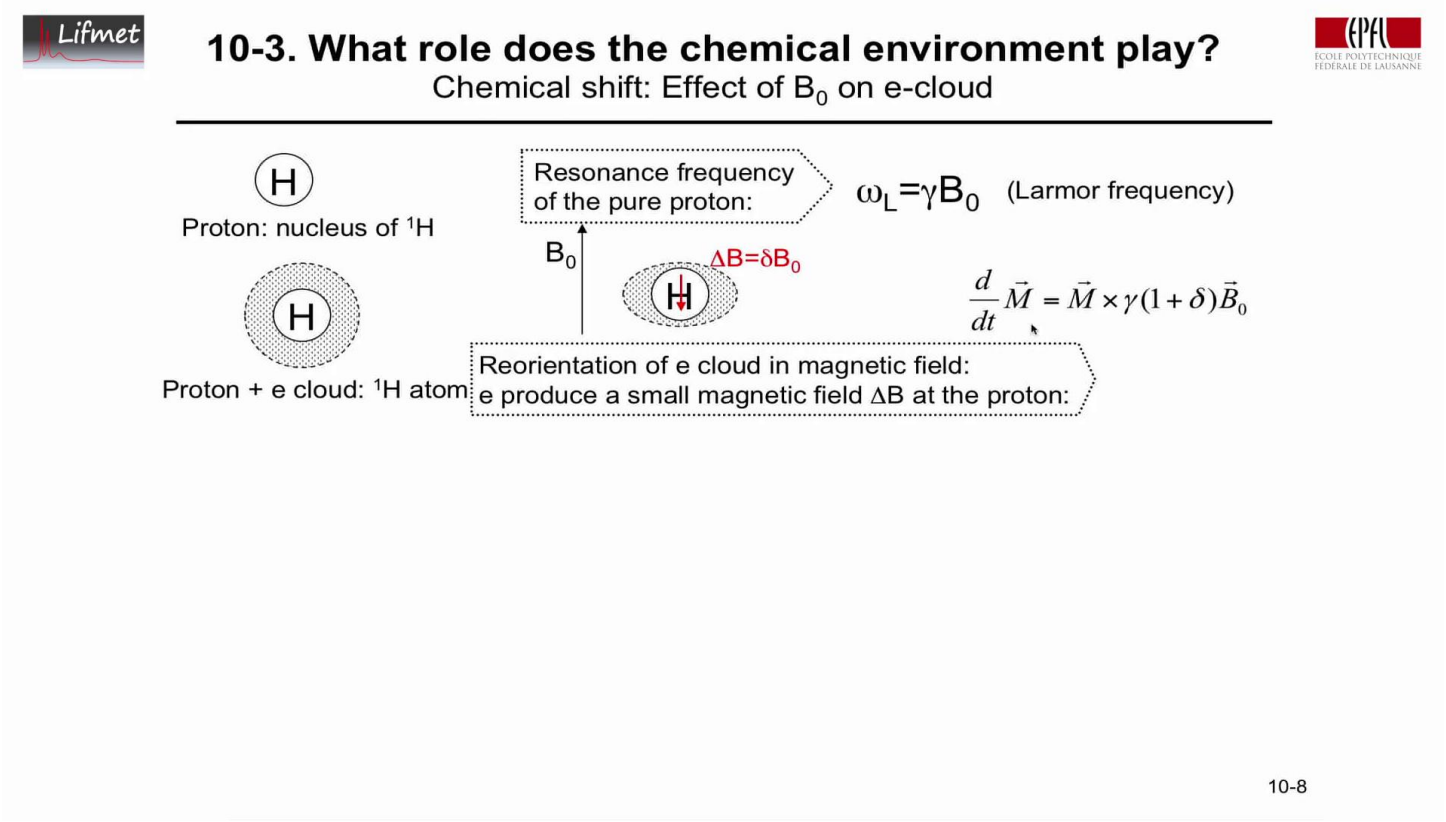

10-8

Okay, now we're talking about nuclear magnetic resonance here. We're talking about a nuclear property, so how can we from a nuclear property deduce chemical information? And the question is, how does chemical environment influence the nuclear magnetic resonance effect? So let's start out with the nucleus of the proton of the hydrogen atom H1, that's the proton. That's a single lone proton. This proton typically if you take a isolated hydrogen atom is surrounded by an electron, so there's an electron cloud surrounding that nucleus here, and it's nice and symmetric. For the resonance frequency of the pure proton, that is the procession frequency, we have the Larmor frequency, which is *gamma (γ) B zero* so that is the Larmor frequency that we have dealt with so far. Now if we have our hydrogen atom in a magnetic field *B zero* what now happens is a distortion, a very small distortion of the electron cloud. I will not go into the details of the quantum mechanical explanation of how this electron cloud is distorted but you can rationalize this simply by the fact that the electron which swirls around the nucleus around the proton, that electron, its flight pattern is most likely influenced by the presence of an external magnetic field.

Notes

Summary

0m 04s




Think of it this way, if it happens to fly parallel to be zero, there's no influence of the magnetic field if it flies perpendicular to *B zero* there's a maximal influence. What the consequence of this is that the electron cloud is deformed, it changes ever so slightly its shape. As a result of that, a small magnetic field due to the electron is being introduced. This magnetic field, we'll call it here *delta (Δ) B*, this magnetic field is proportioned to *B zero* with proportionality constant Δ here. So the presence of the electron around the nucleus in the magnetic field leads to an alteration of the magnetic field at the site of the nucleus. So this small change in the magnetic field *B zero* at the position of the proton leads to a multifield expression for the procession. Here's the Larmor equation and now we don't have $\gamma$ *B zero* but we have $\gamma$ *(1 + Δ )* That is the equation of motion that describes the behavior of the magnetization and as a consequence, the Larmor frequency is now the procession frequency which is $\gamma$ *B zero* times this is now changed and is given by the Larmor frequency times *(1 + Δ)*.

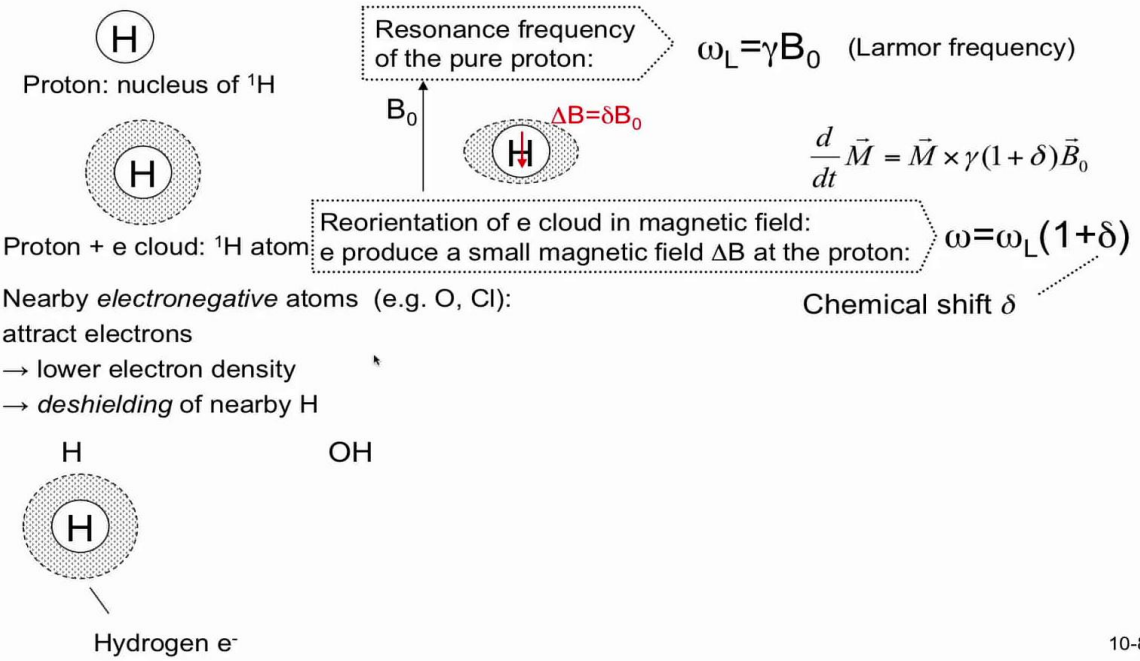
Notes

Summary

1m 36s

# 10-3. What role does the chemical environment play?

## Chemical shift: Effect of $B_0$ on e-cloud

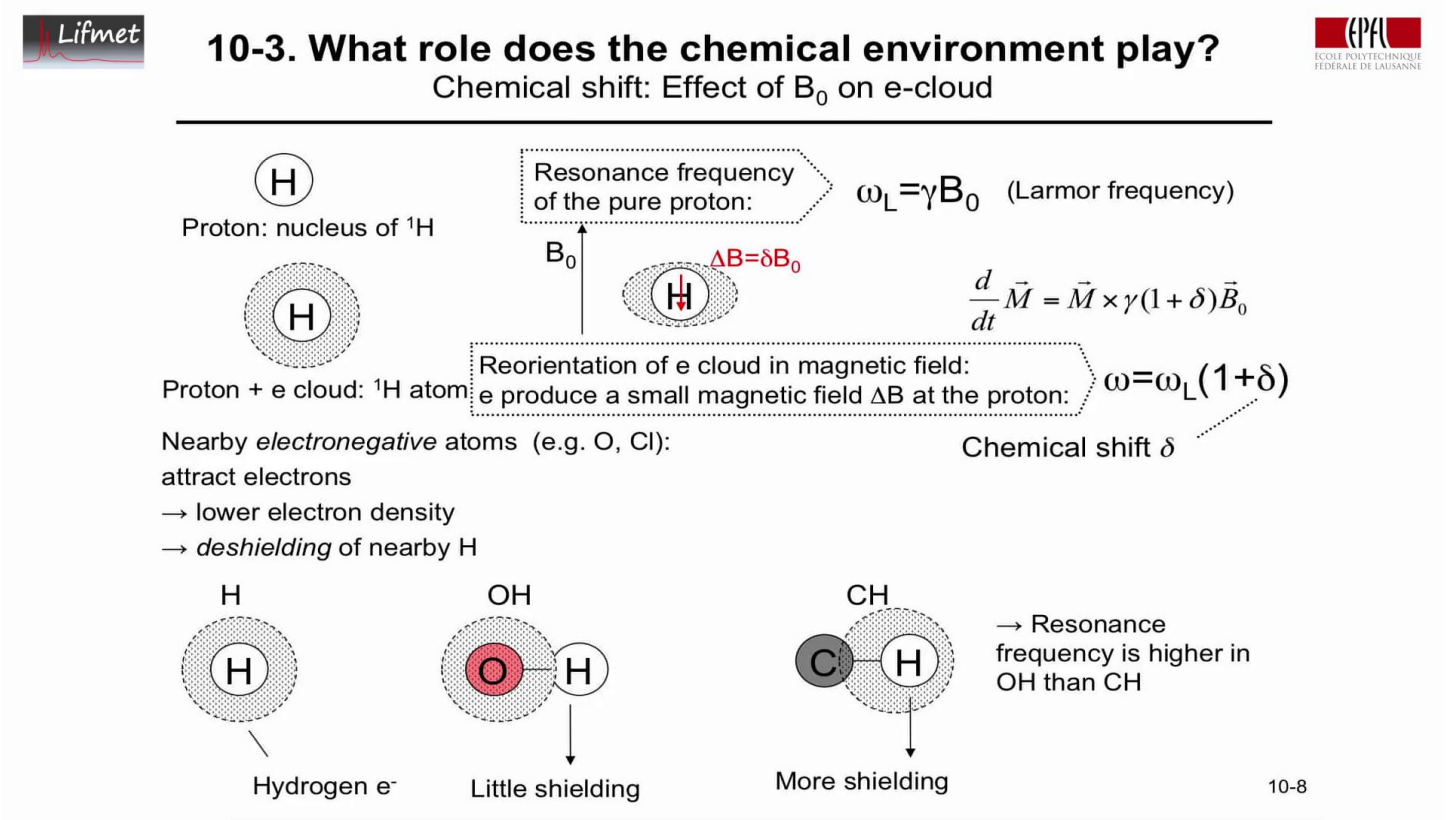



And this Δ is called the chemical shift, short for chemical shift of the Larmor frequency. The sign here is not important for the further understanding whether we put a +Δ or - Δ. What is important here is that based on the presence of the electron, the proton magnetization will no longer process exactly at the Larmor frequency. Now let's think about if we have this hydrogen atom close to a nearby electronegative atom such as oxygen or chloride. These electronegative atoms attract the electrons. They produce therefore a reduced electron density at the site of the proton and therefore a so-called deshielding of the nearby hydrogen nuclei of the protons. That means we have less of an effect of the electrons on the resonance frequency. So I'll illustrate this here with an example. First we'll take the normal hydrogen isolated hydrogen atom. Here's the hydrogen electron. Everything is as we have described here. If we now have nearby an oxygen so we'll look at a hydrogen nucleus in a OH, which is part of an OH bond, we have the electronegative oxygen and now for convenience I have drawn a simplified distribution of the electron cloud that belongs to the hydrogen atom.

Notes

Summary

3m 08s




And essentially because oxygen's electronegative, the probability that the electron is swirling around the hydrogen is much reduced and most of the electron is actually at the site of the oxygen. So what this means now is if we put the OH group into a magnetic field, there's little shielding from the electron so there's little modification of the magnetic field at the site of the nucleus of the hydrogen atom here at the proton. Consider a third example. This is a CH bond, so we have the carbon here. Carbon is less electronegative so it starts to pull the electron cloud off the hydrogen electron over to it but not as much as the OH, which is here. And so as a result, there's a stronger effect of the presence of the electron on the changing magnetic fields. So there's more shielding and a stronger shielding of the magnetic field, this *ΔB*, this figure. So as a consequence, the resonance frequency of the nucleus of the hydrogen atom of the proton is higher in an OH bond than it is in a CH bond. So I'll stick with this qualitative description because it helps us qualitatively understand what's happening, the strictly quantum mechanical beneath your calculations trying to predict based on molecular [inaudible] of chemical shifts.

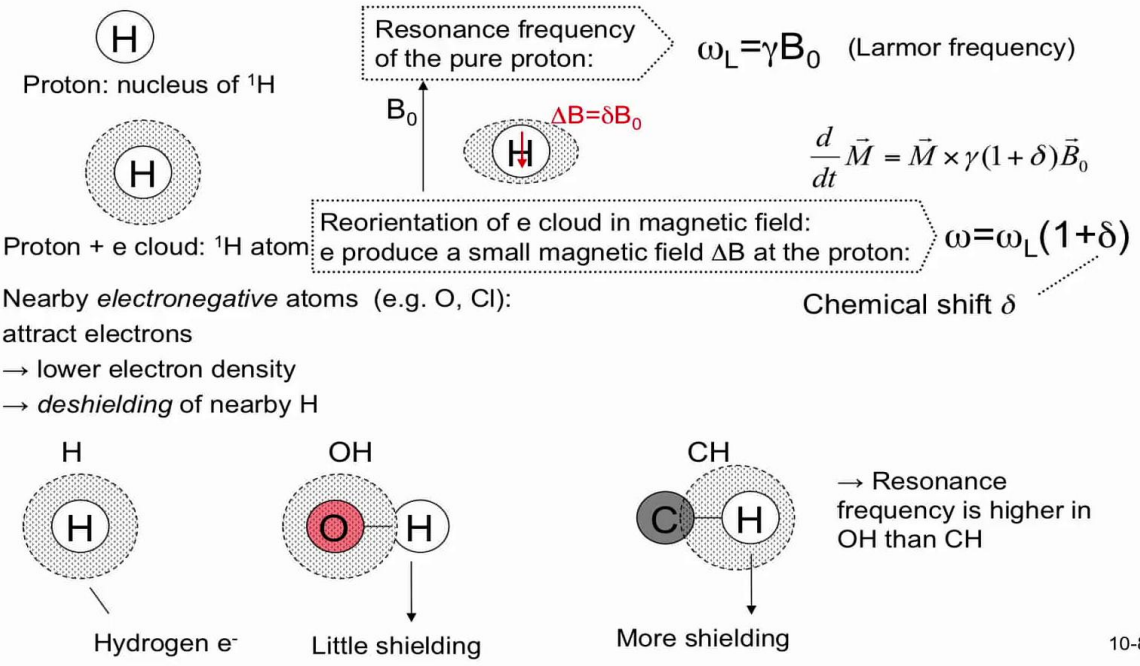
Notes

Summary

4m 47s

## 10-3. What role does the chemical environment play?

Chemical shift: Effect of $B_0$ on e-cloud




They are qualitatively very good but they are not sufficient in explaining all the details that one sees. So we will stick with this qualitative argument here that electronegativity, that is the distribution of the electron clouds has an influence on the resonance frequency, and therefore through the change in resonance frequency with this nuclear magnetic resonancy effect, one is able to sense the chemical environment.

Notes

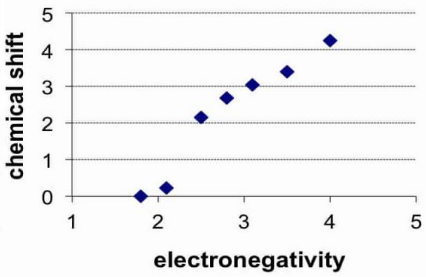
Summary

6m 16s

## How is chemical shift δ linked to electronegativity ?

Example: Protons

| Compound, $CH_3X$ | $CH_3F$ | $CH_3OH$ | $CH_3Cl$ | $CH_3Br$ | $CH_3I$ | $CH_4$ | $(CH_3)_4Si$ |
|---|---|---|---|---|---|---|---|
| X | F | O | Cl | Br | I | H | Si |
| Electronegativity of X | 4.0 | 3.5 | 3.1 | 2.8 | 2.5 | 2.1 | 1.8 |
| Chemical shift, δ / ppm | 4.26 | 3.4 | 3.05 | 2.68 | 2.16 | 0.23 | 0 |




*0 ppm* is defined by resonance frequency of reference compound $\omega_L^{ref}$
(e.g. tetramethylsilane (TMS) for $^1H$)

10-9

So how is this chemical shift of the resonance frequency or chemical shift Δ linked to electron negativity. And I've taken here a table, we're looking at compounds CH3X where X is fluoride, oxygen, chloride, bromide, iodine, hydrogen or silicone. In these molecules, one has determined the electronegativity precisely and also the chemical shift of the proton resonance frequency. Taking this table and plotting electronegativity on the x axis versus the chemical shift on the y axis, we actually see a fairly nice at least monotonous relationship between electronegativity and chemical shift. This compound is a little bit different from the others, but this is a very nice strong correlation between chemical shift and electronegativity. Now chemical shift is not measured in Hertz but it's measured in parts per million. And parts per million here is not a measure of the number of molecules present and it's not an absolute measure. It's actually measured with respect to a reference compound. For protons, tetramethylsilane is one compound or TMS, and here it is the reference compound so this is set to zero.

Notes

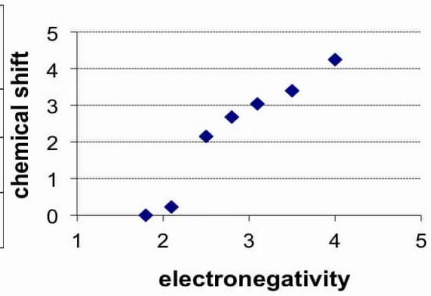
Summary

6m 44s

## How is chemical shift δ linked to electronegativity ?

Example: Protons

| Compound, $CH_3X$ | $CH_3F$ | $CH_3OH$ | $CH_3Cl$ | $CH_3Br$ | $CH_3I$ | $CH_4$ | $(CH_3)_4Si$ |
|---|---|---|---|---|---|---|---|
| X | F | O | Cl | Br | I | H | Si |
| Electronegativity of X | 4.0 | 3.5 | 3.1 | 2.8 | 2.5 | 2.1 | 1.8 |
| Chemical shift, δ / ppm | 4.26 | 3.4 | 3.05 | 2.68 | 2.16 | 0.23 | 0 |




*0 ppm* is defined by resonance frequency of reference compound $\omega_L^{ref}$
(e.g. tetramethylsilane (TMS) for $^1H$)

$$\delta=(\omega-\omega_L^{ref})10^6/\omega_L^{ref}$$

10-9

So the exact explanation here is the difference of the resonance frequency observed, relative to that of the reference compound, divided by the frequency of the reference compound, and that typically gives us numbers that are *10 ^ -6* or it's a parts per million effect, and someone multiplies by *10 ^ 6* to obtain a number which is something in the order of 1 to 10 or something like that. it's easier to write than constantly having to write *10 ^ -6* and that's why it's parts per million or ppm because we multiply here by *10 ^ 6* So there is no absolute measure here that this is zero is a convention where the zero is placed. What is important here is the relative relationship.

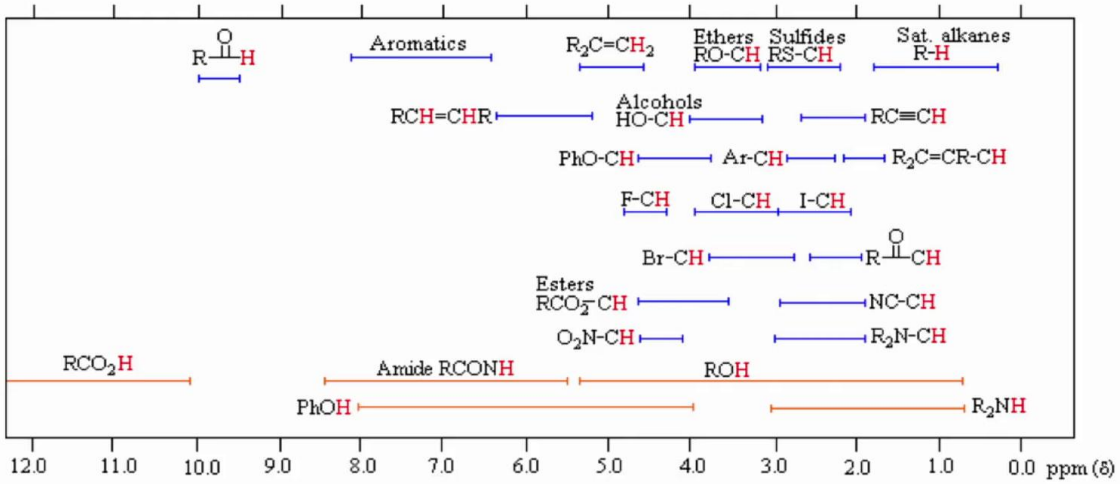
Notes

Summary

8m 01s

## How is chemical shift δ linked to electronegativity ?

Example: Protons



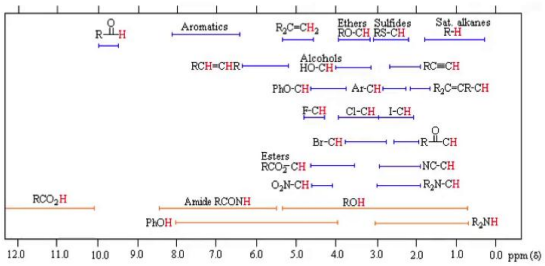

10-9

And so if one looks at the chemical shift of protons that's the nuclei of hydrogen in all sorts of different compounds, one knows roughly based on the type of chemical bond in which range the chemical shifts to appear. So we will not see this type OOH with a chemical shift over here. This is a high chemical shift here. This is all with respect to TMS, tetramethylsilane. So at what place in the spectrum, here the proton spectrum, the resonance frequency is observed tells us a lot already about the chemical compound under investigation.

Notes

Summary

8m 52s




**Nuclear Magnetic Resonance Spectroscopy**
http://slideplayer.nl/slide/2164537/

Notes

Summary

9m 40s