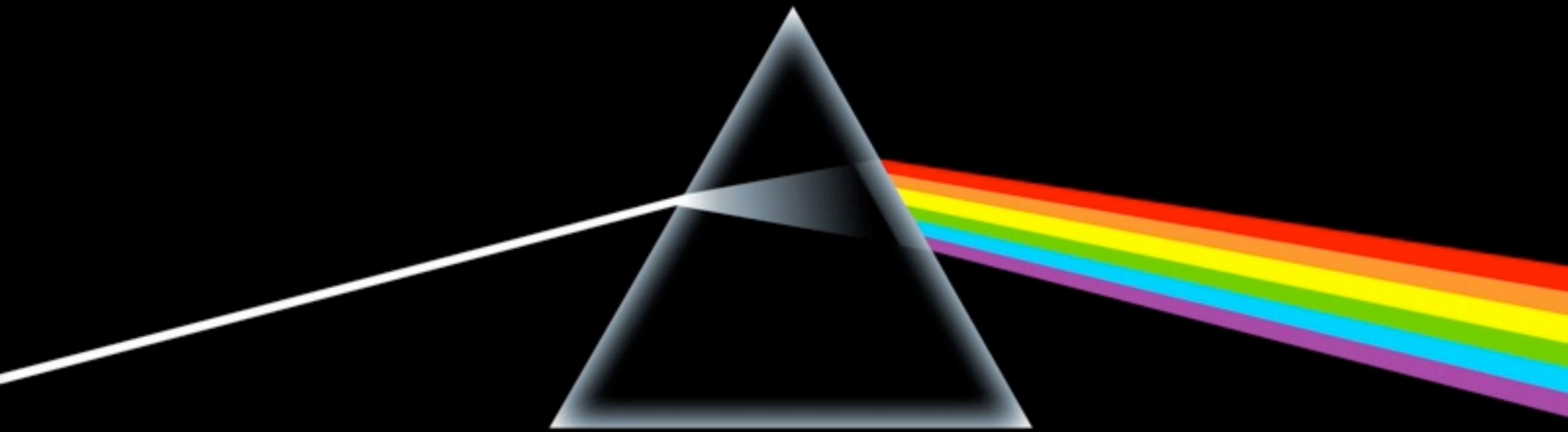


# Unit One Part 9: nuclear magnetic resonance spectroscopy



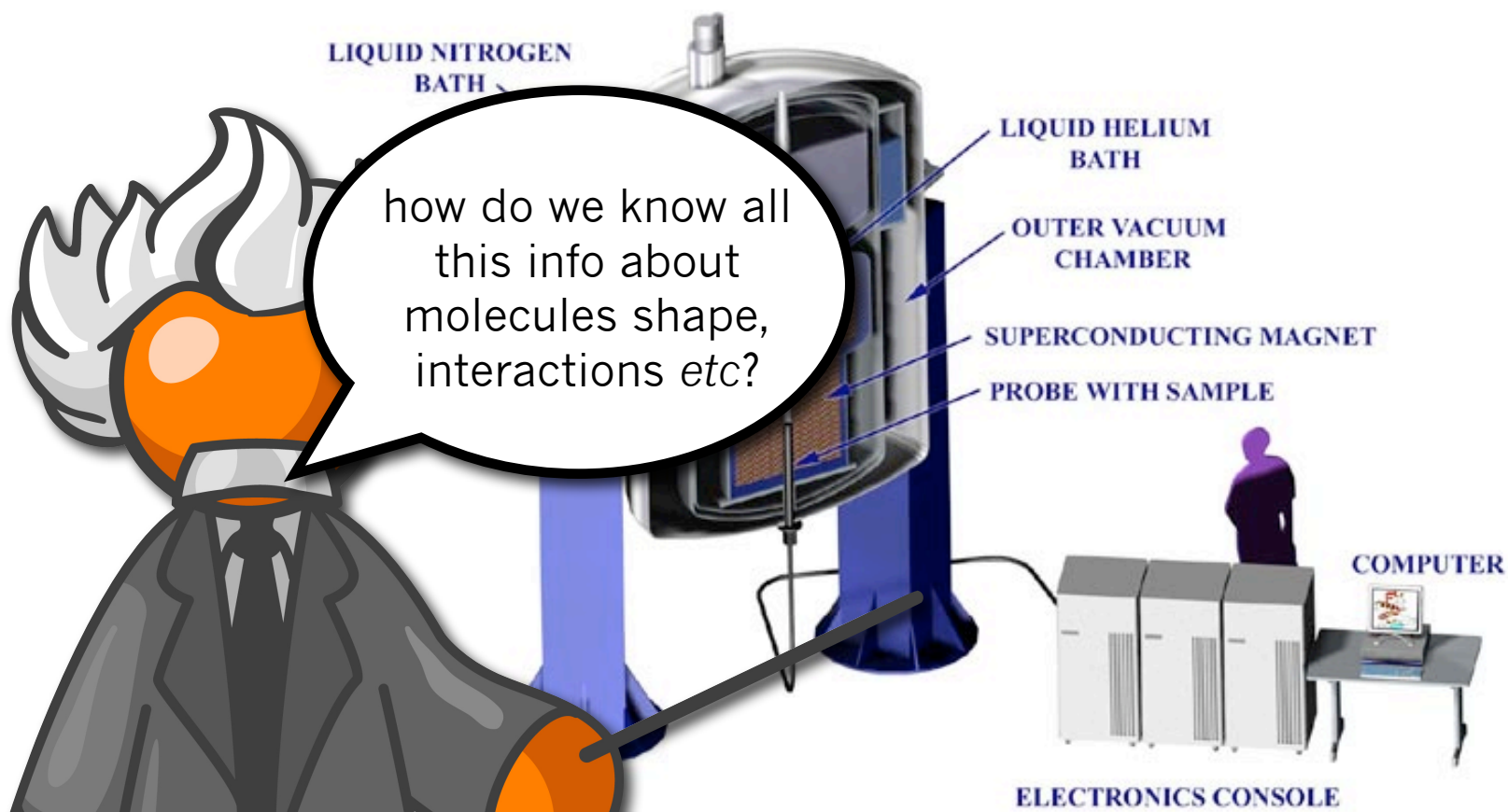
# Unit One

# Part 9

nmr spectroscopy

**equivalent** hydrogens

**integral** vs. number of hydrogens



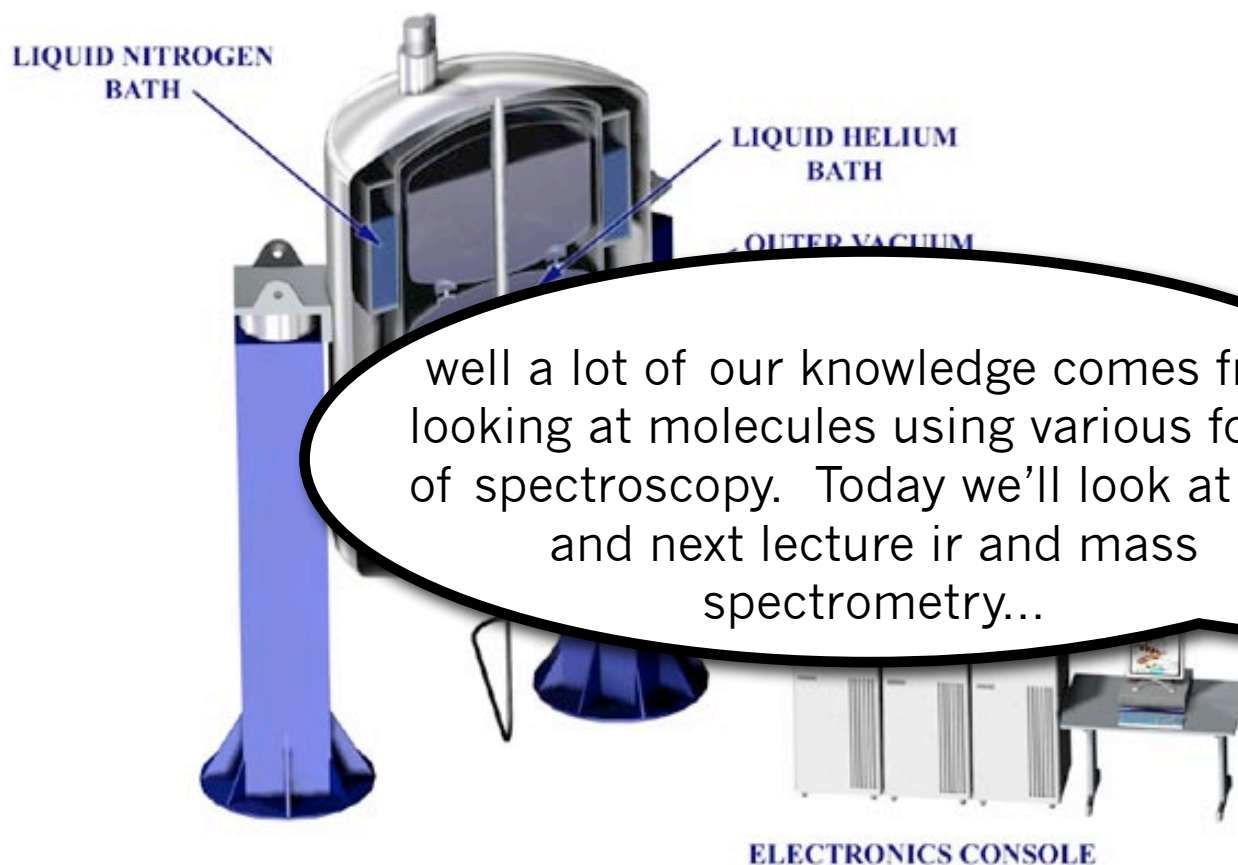
# Unit One

# Part 9

nmr spectroscopy

**equivalent** hydrogens

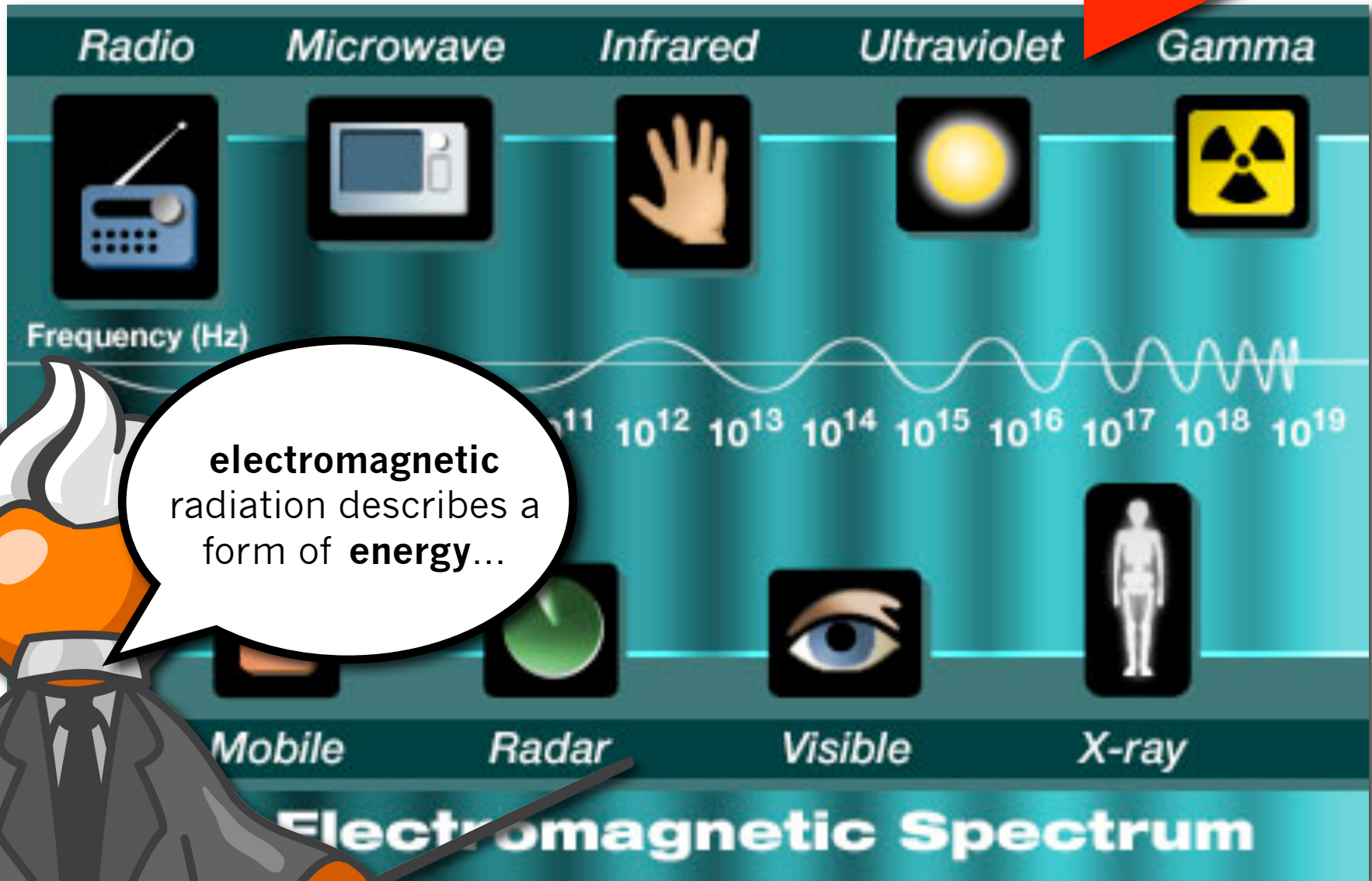
**integral** vs. number of hydrogens



well a lot of our knowledge comes from looking at molecules using various forms of spectroscopy. Today we'll look at nmr and next lecture ir and mass spectrometry...

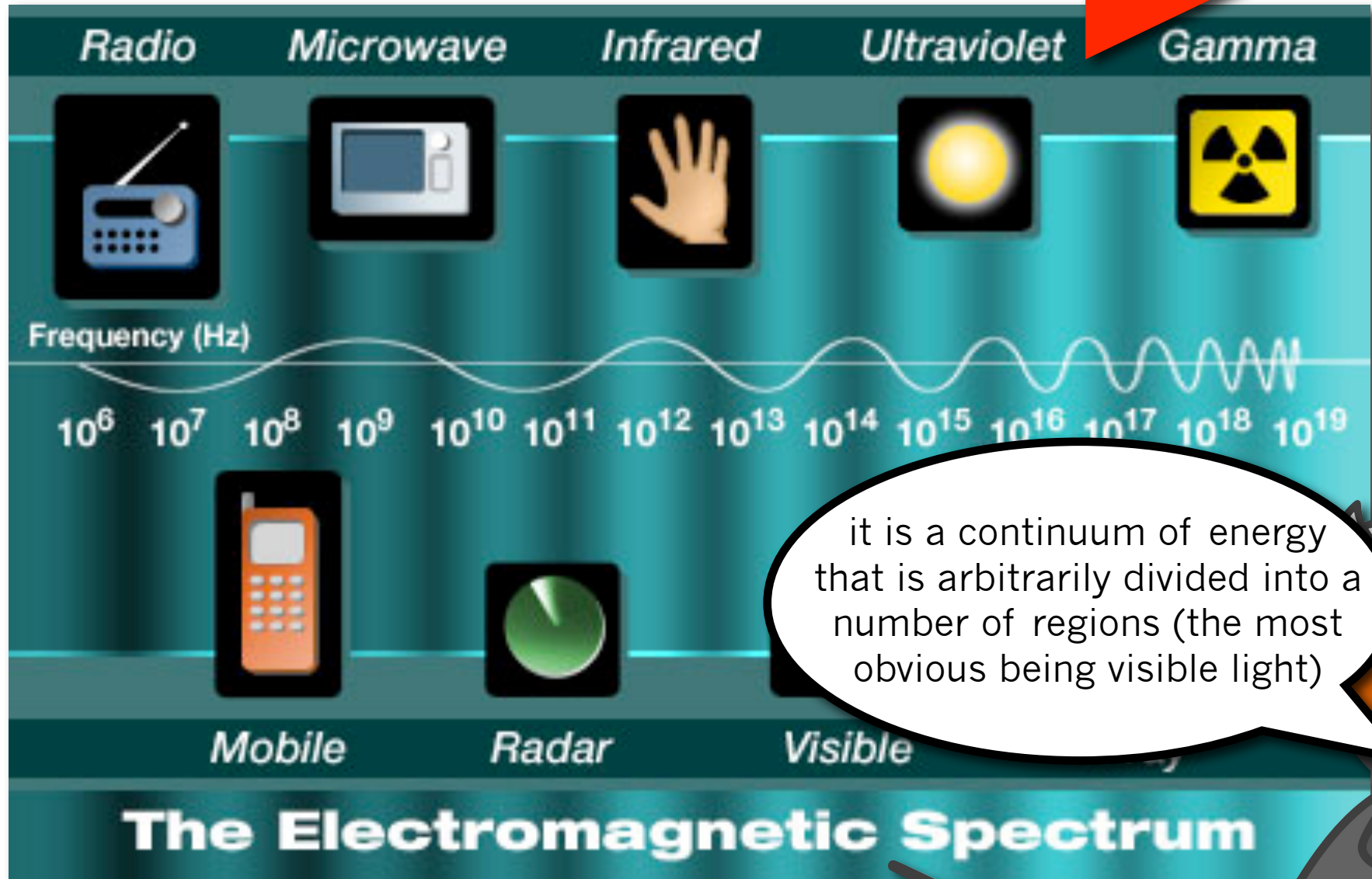


# ENERGY



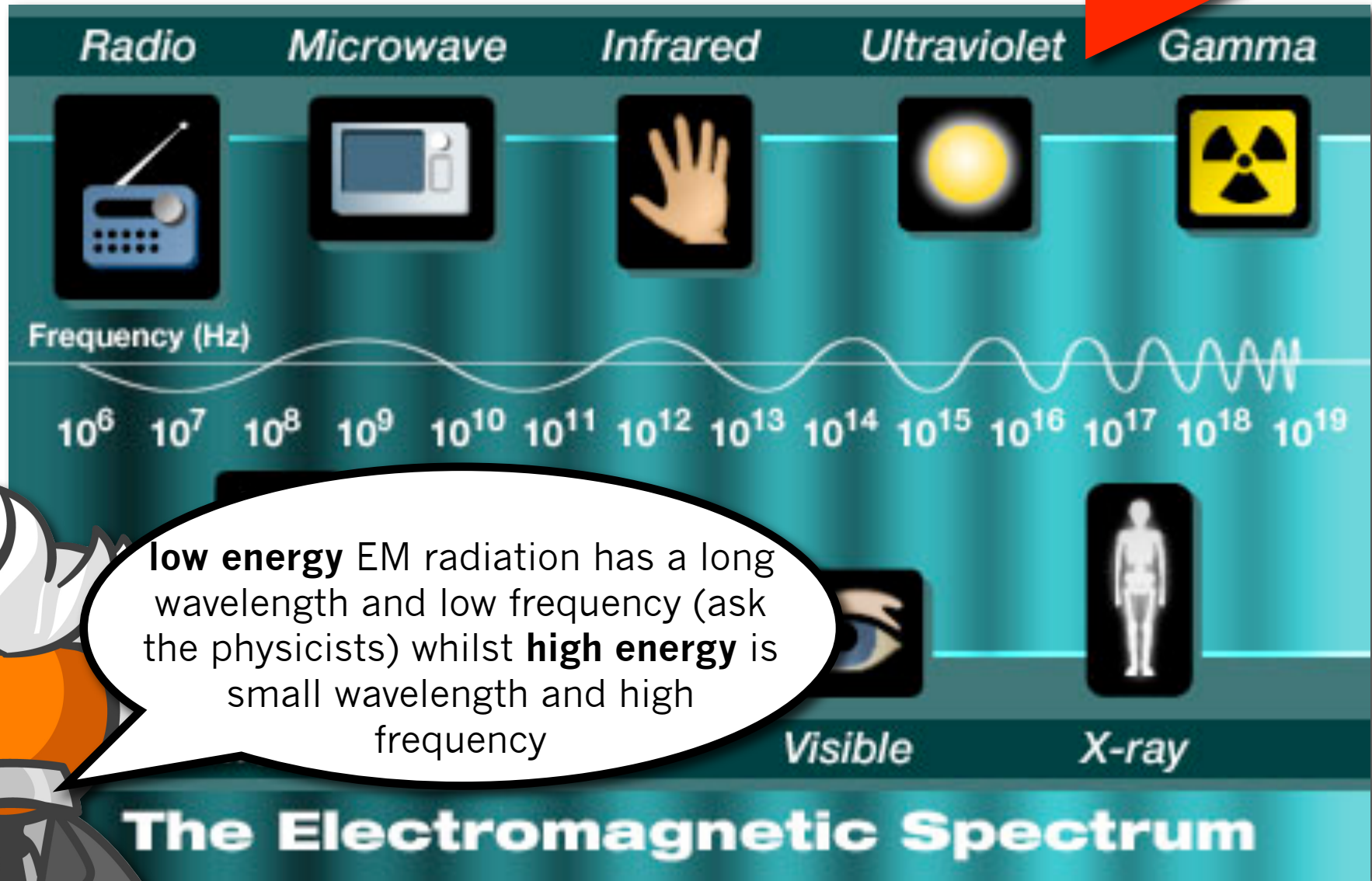
electromagnetic radiation describes a form of **energy**...

# ENERGY

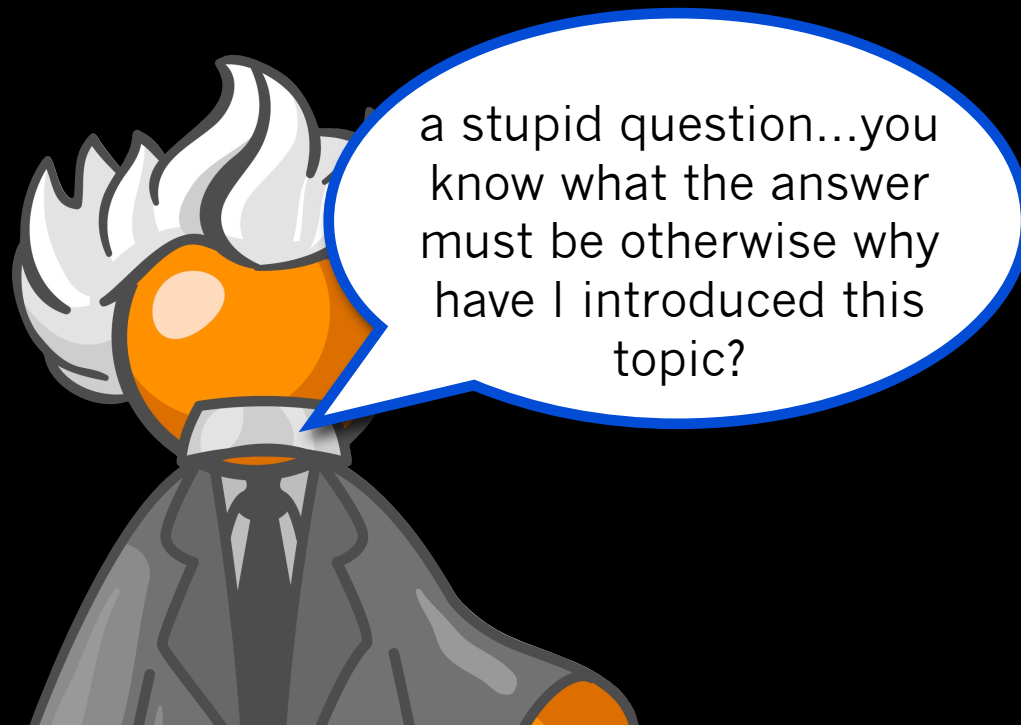


it is a continuum of energy that is arbitrarily divided into a number of regions (the most obvious being visible light)

# ENERGY



# can **electromagnetic radiation** interact with **molecules**?




a stupid question...you know what the answer must be otherwise why have I introduced this topic?



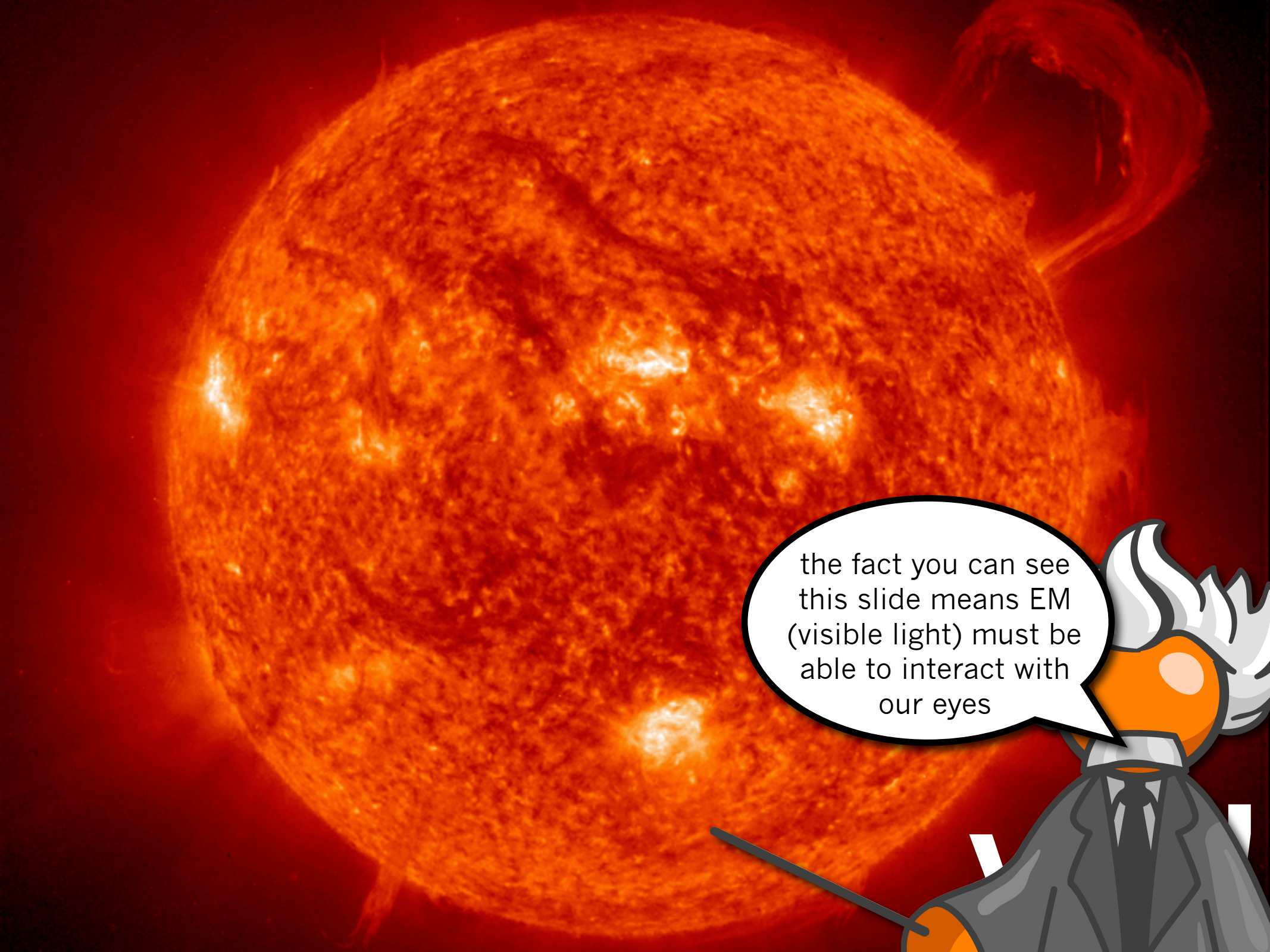
**yes!**



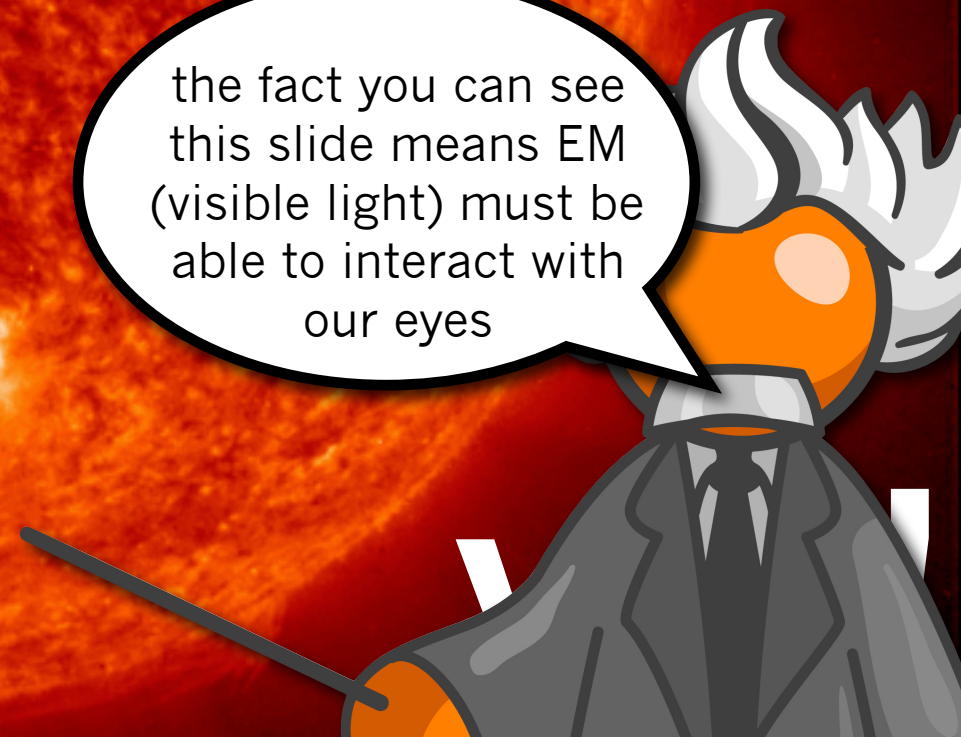


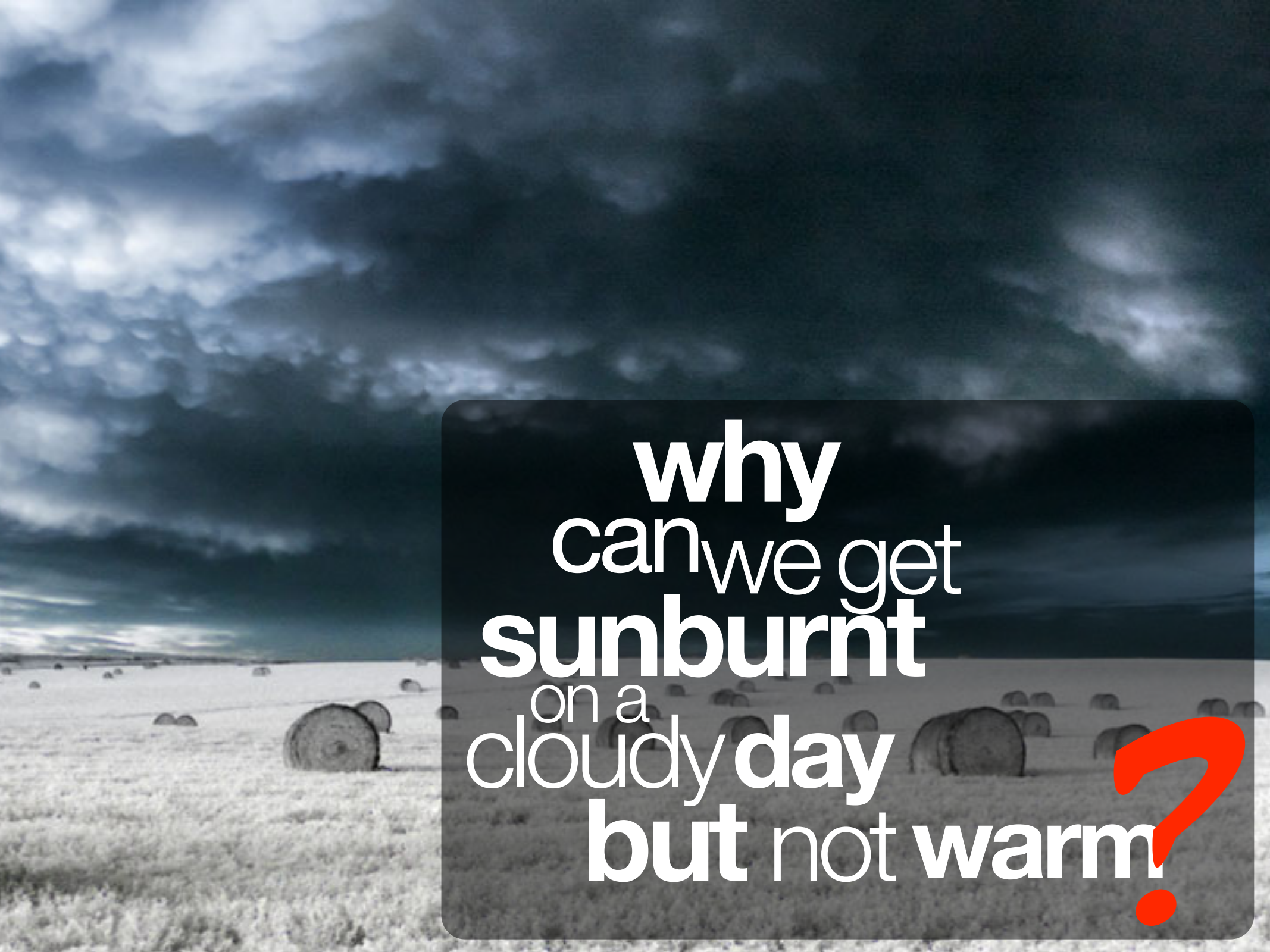
sunburn...simple  
interaction of energy  
and molecules...

**yes!**



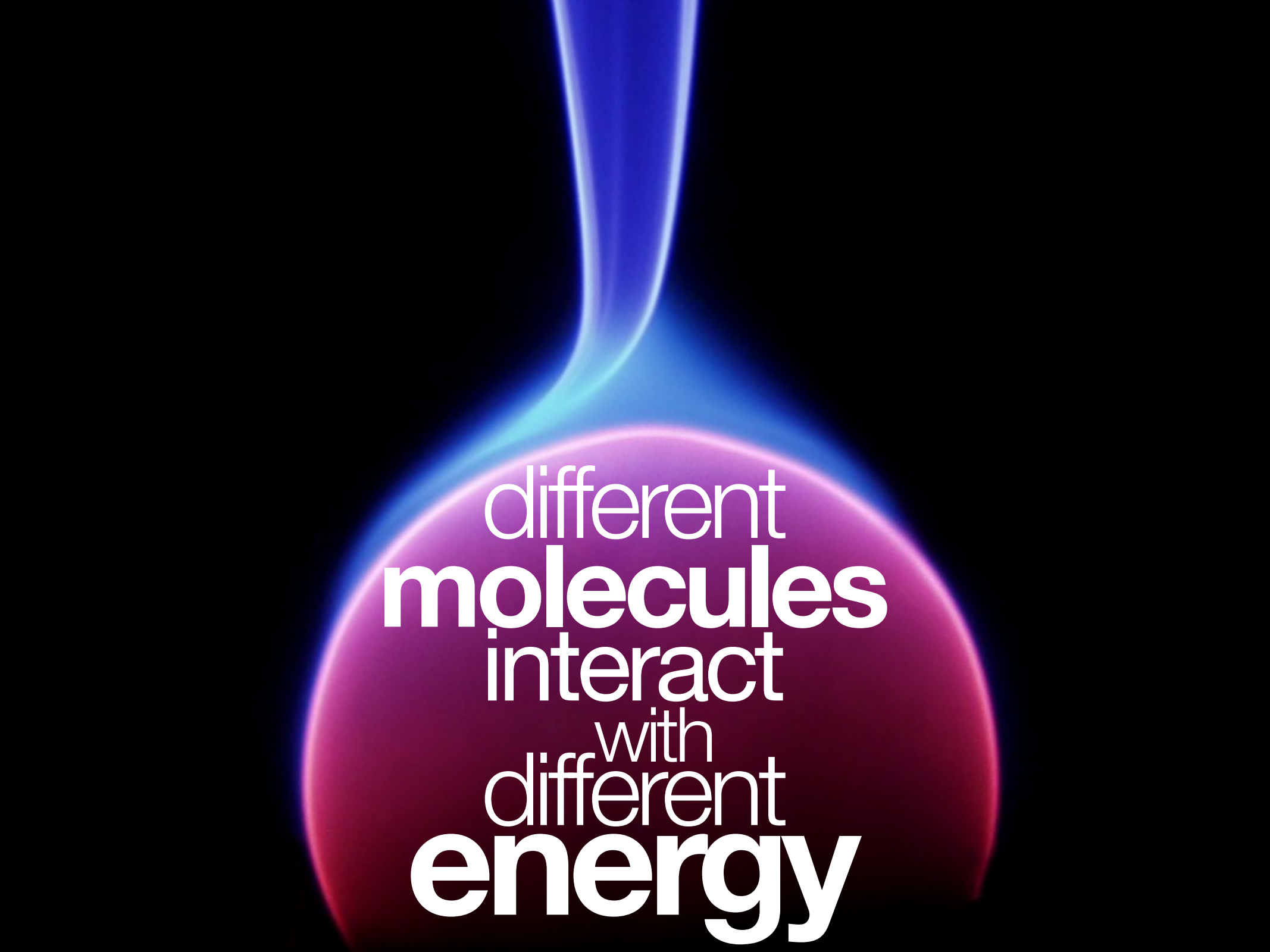
the fact you can see  
this slide means EM  
(visible light) must be  
able to interact with  
our eyes



A photograph of a field with several large round hay bales scattered across it. The sky is filled with heavy, dark, grey clouds, suggesting an overcast or stormy day. The overall tone is somewhat somber due to the dark sky.

**why**  
can we get  
**sunburnt**  
on a  
cloudy day  
**but not warm?**



A glowing blue and purple energy stream flows from the top center of the frame, tapering as it descends into a large, glowing purple sphere. The sphere has a gradient from light purple at the top to dark purple at the bottom. The text is centered within the sphere.

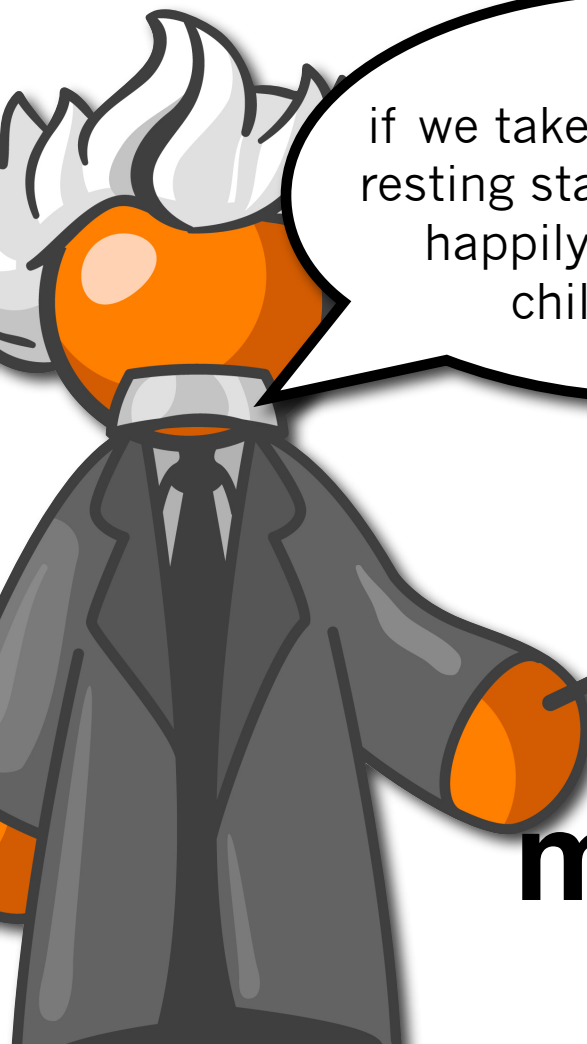
different  
**molecules**  
interact  
with  
different  
**energy**



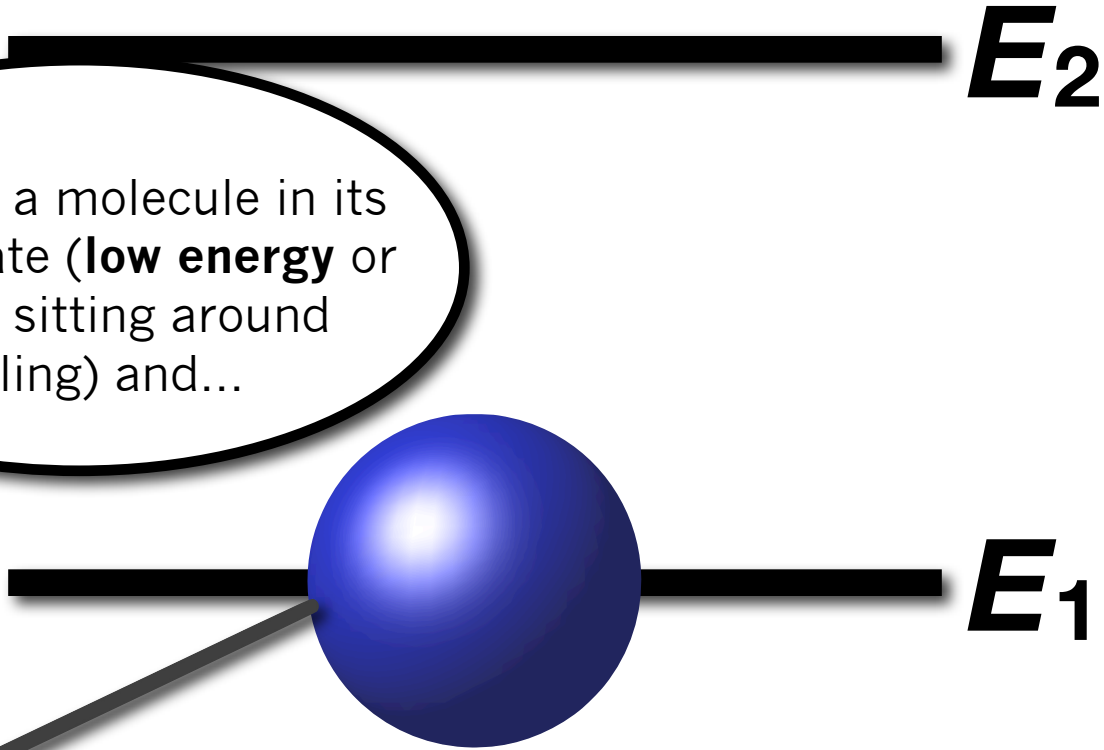
...water in clouds blocks infrared energy (which makes us hot) but does not block ultraviolet energy (which burns us)

different  
molecules  
act  
different  
energy

so how do  
we **use** this?



if we take a molecule in its resting state (**low energy** or happily sitting around chilling) and...



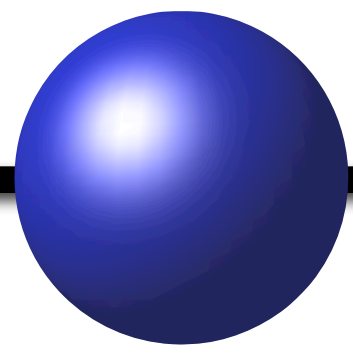
**molecule in energy state  $E_1$**



...irradiate the molecule with energy some will be absorbed causing the molecule...

$E_2$

absorption of energy

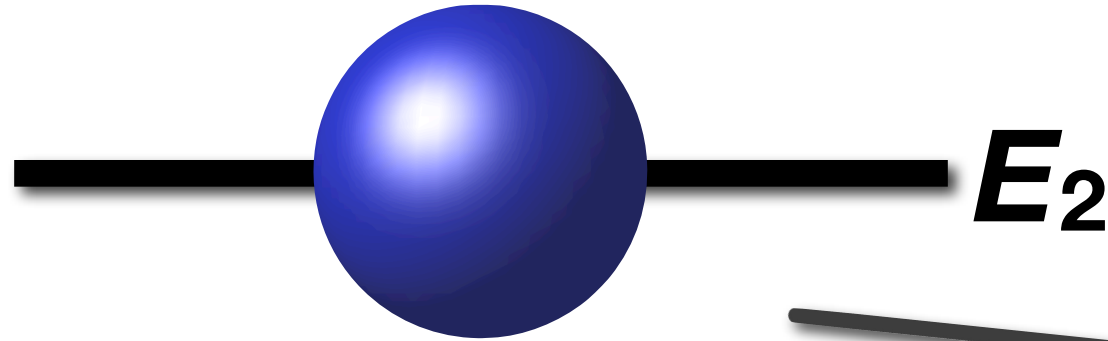


$E_1$

molecule in energy state  $E_1$



...to become excited or to rise to a higher energy level...

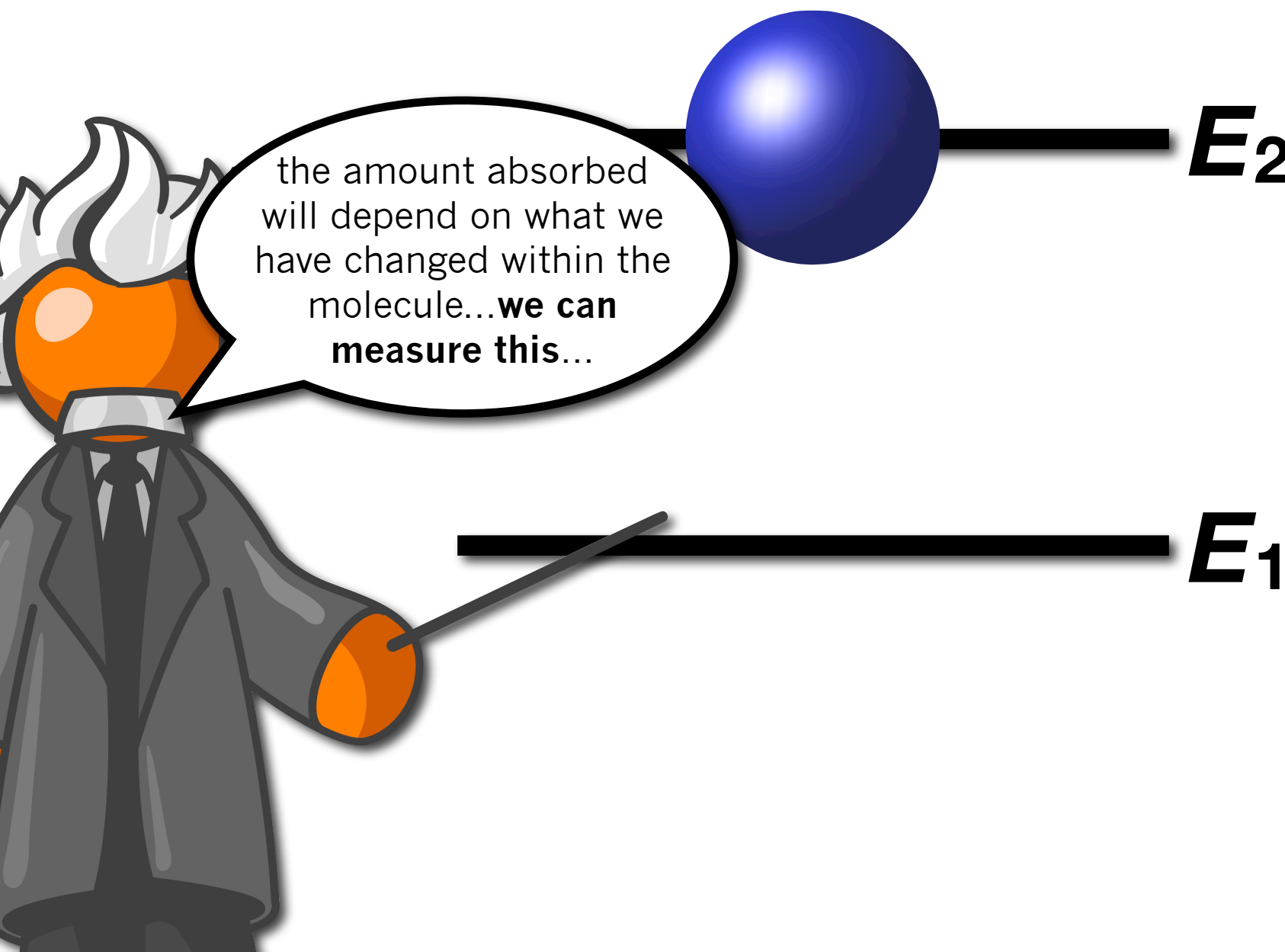


absorption of energy



molecule in energy state  $E_1$

# molecule in energy state $E_2$ or 'excited'



the amount absorbed will depend on what we have changed within the molecule...**we can measure this...**

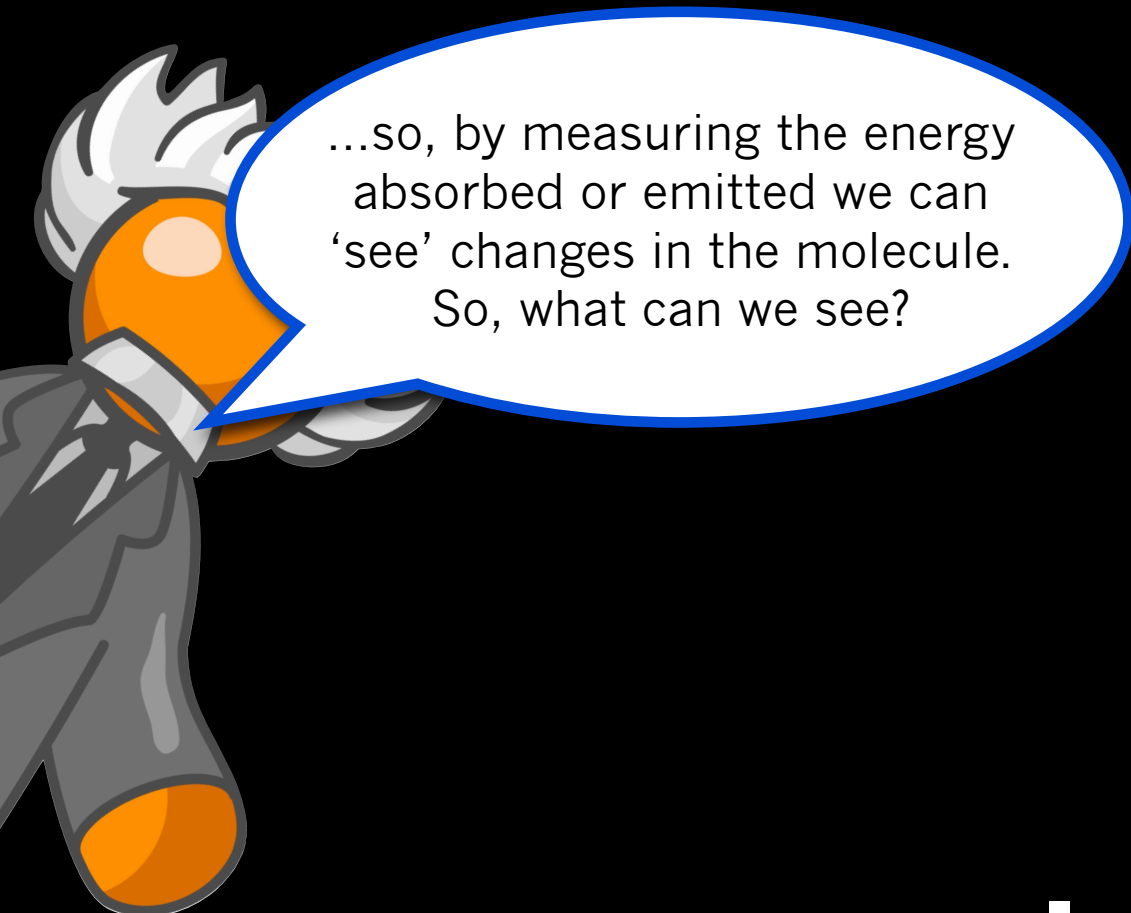
$E_2$

$E_1$

# molecule in energy state $E_2$ or 'excited'

eventually the molecule will relax and emit energy as it returns to its resting state...**we can measure this energy** as well...

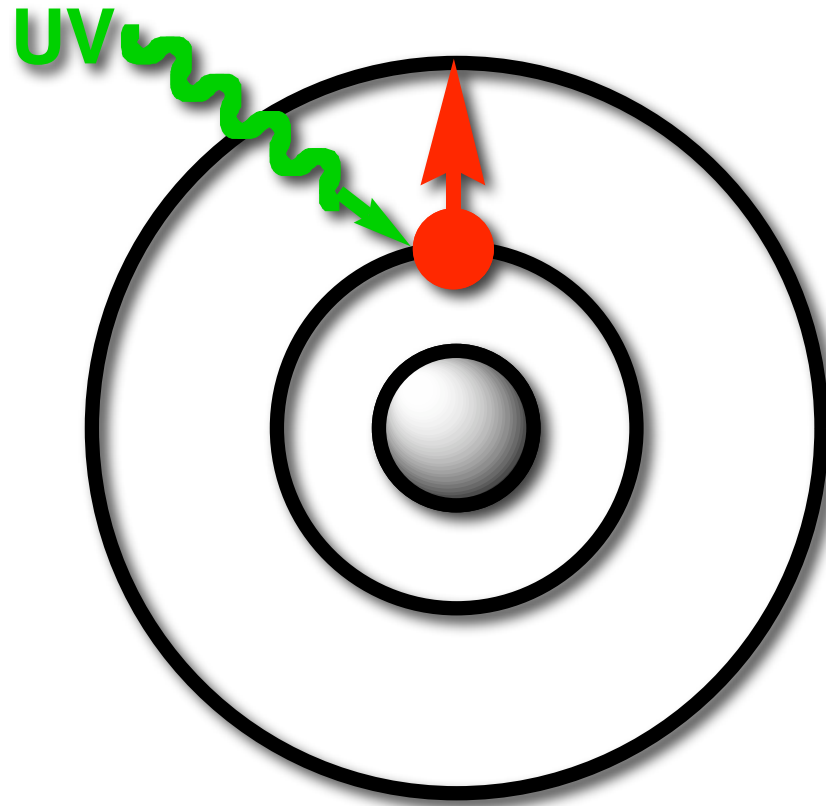




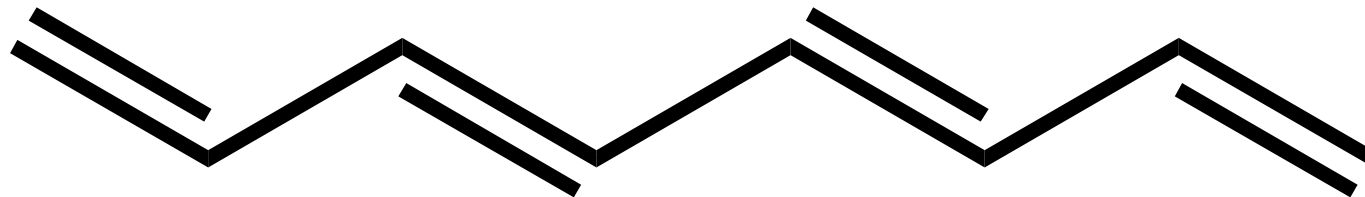
...so, by measuring the energy absorbed or emitted we can 'see' changes in the molecule.  
So, what can we see?

what part of the  
**molecule** is effected?

# ultraviolet-visible (UV)

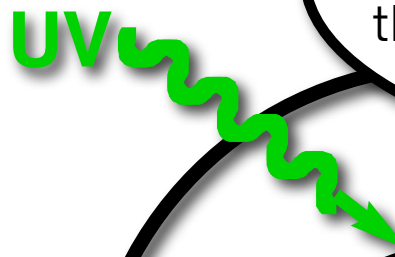


**excites an electron**

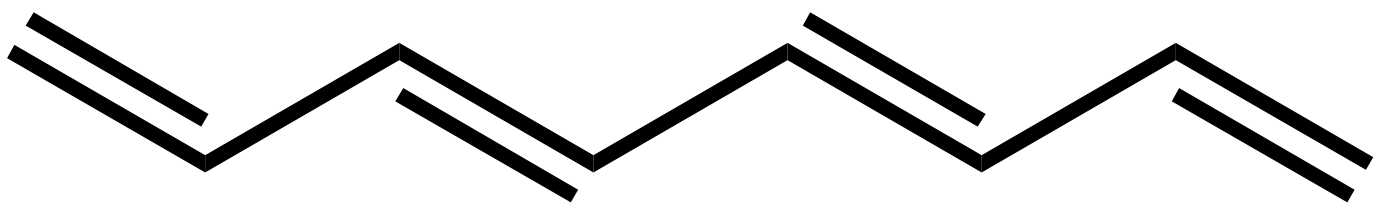


# ultraviolet

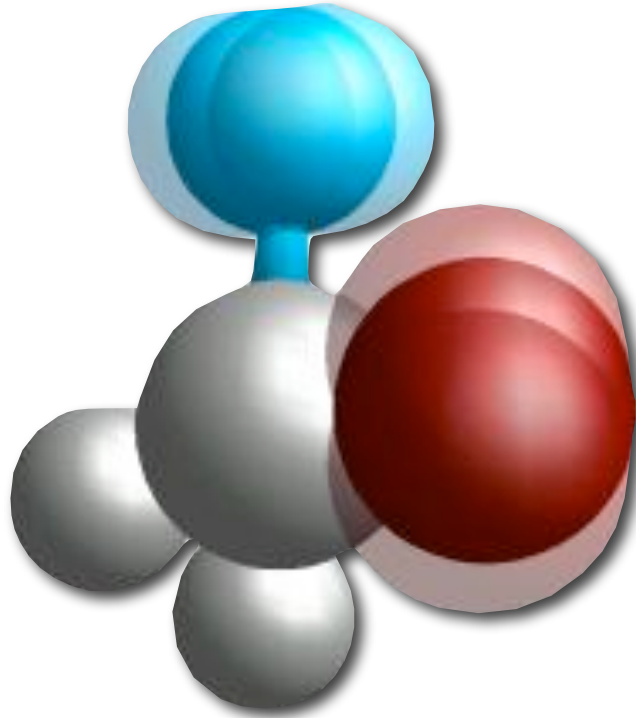
high energy UV radiation can excite an electron between orbitals ...this tells us about the conjugation within the molecule (multiple bonds separated by one single bond)



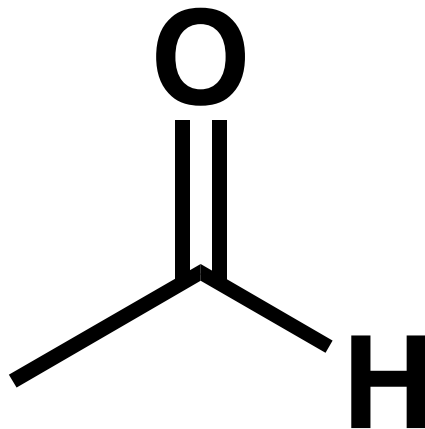
# excites an electron




# infrared (IR)



## vibrates bonds

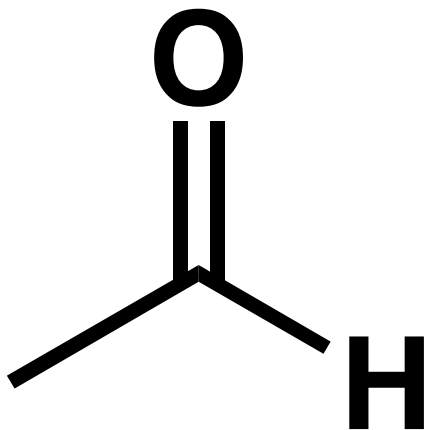


# infrared (IR)



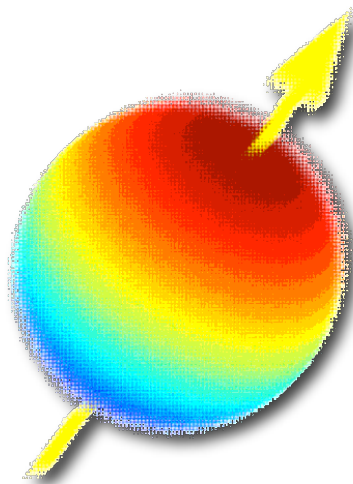
IR has slightly less energy and alters the vibration of bonds within a molecule...this can tell us about the functional groups within that molecule

**vibrates bonds**

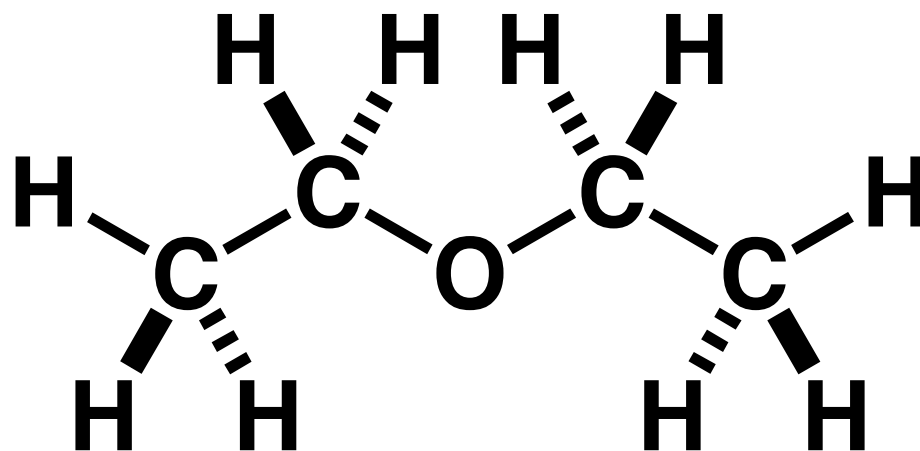




# nuclear magnetic resonance (NMR)



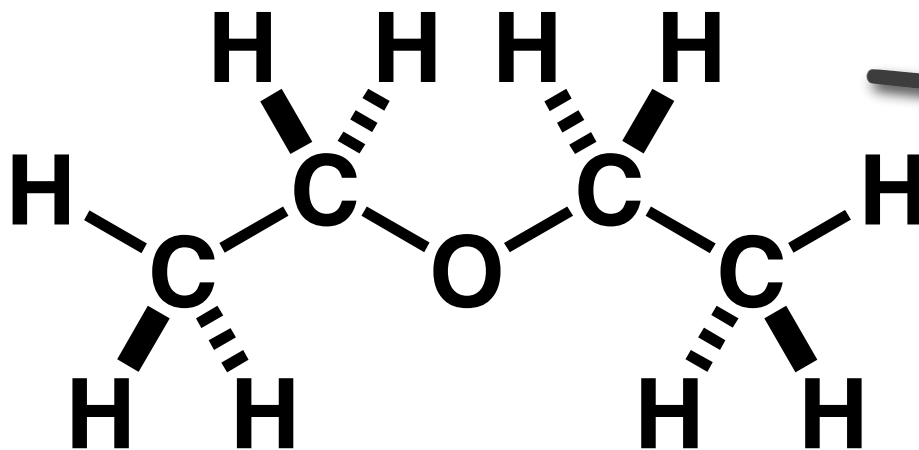
## C-H framework




# nuclear magnetic resonance (NMR)

NMR uses low energy radio waves to alter the spin of the nucleus of certain atoms... this can give us a lot of useful information about the position of C and H within the molecule. It is by far the most useful form of spectroscopy we routinely use


## C-H framework



what is **nmr**?

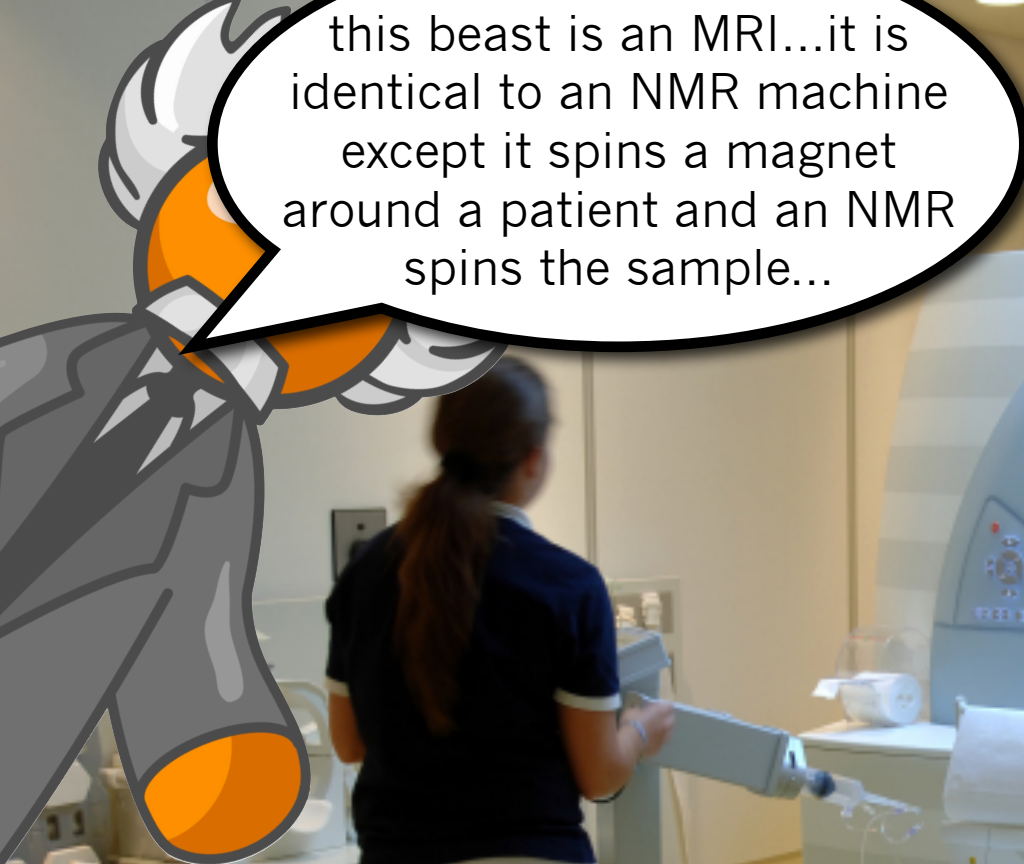
A close-up portrait of actor Hugh Laurie, looking directly at the camera with a serious expression. He has short, dark hair and a light beard. He is wearing a dark suit jacket over a light blue collared shirt. In the top left corner, there is a cartoon speech bubble with a grey and orange character holding a megaphone. The speech bubble contains the text: "I guess most of you know the character House? and for those of you that have watched it you might recognise...".

I guess most of you know the character House? and for those of you that have watched it you might recognise...



...the use of MRI to  
diagnose a variety of  
ailments...

# magnetic resonance imaging



this beast is an MRI...it is identical to an NMR machine except it spins a magnet around a patient and an NMR spins the sample...



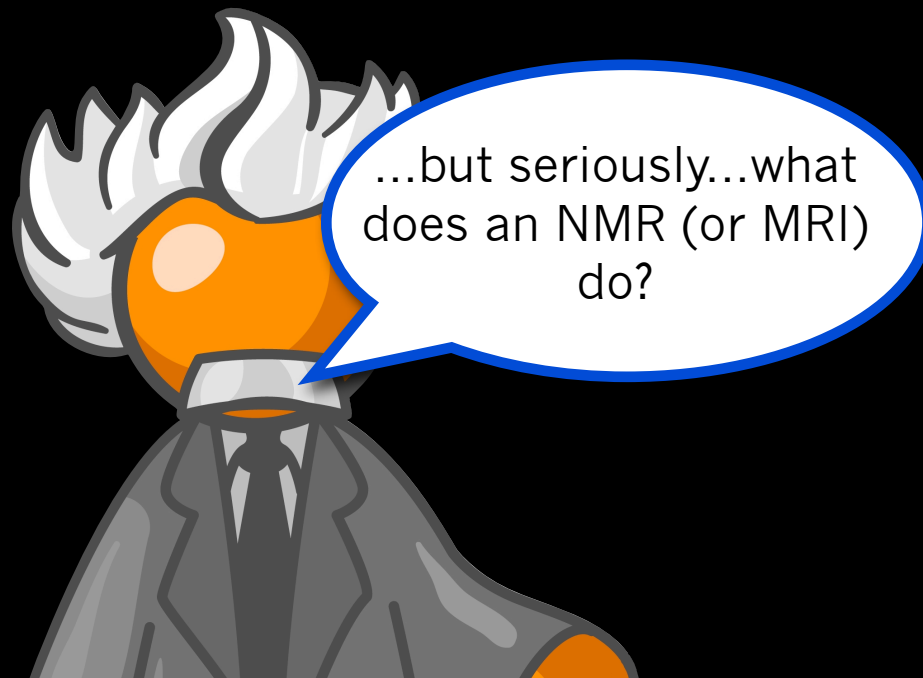
I guess it's called MRI and not NMR as no patient would allow a doctor to insert them in a machine with the word "nuclear" in the title

LINK

Photo: Industrial Light and Magic

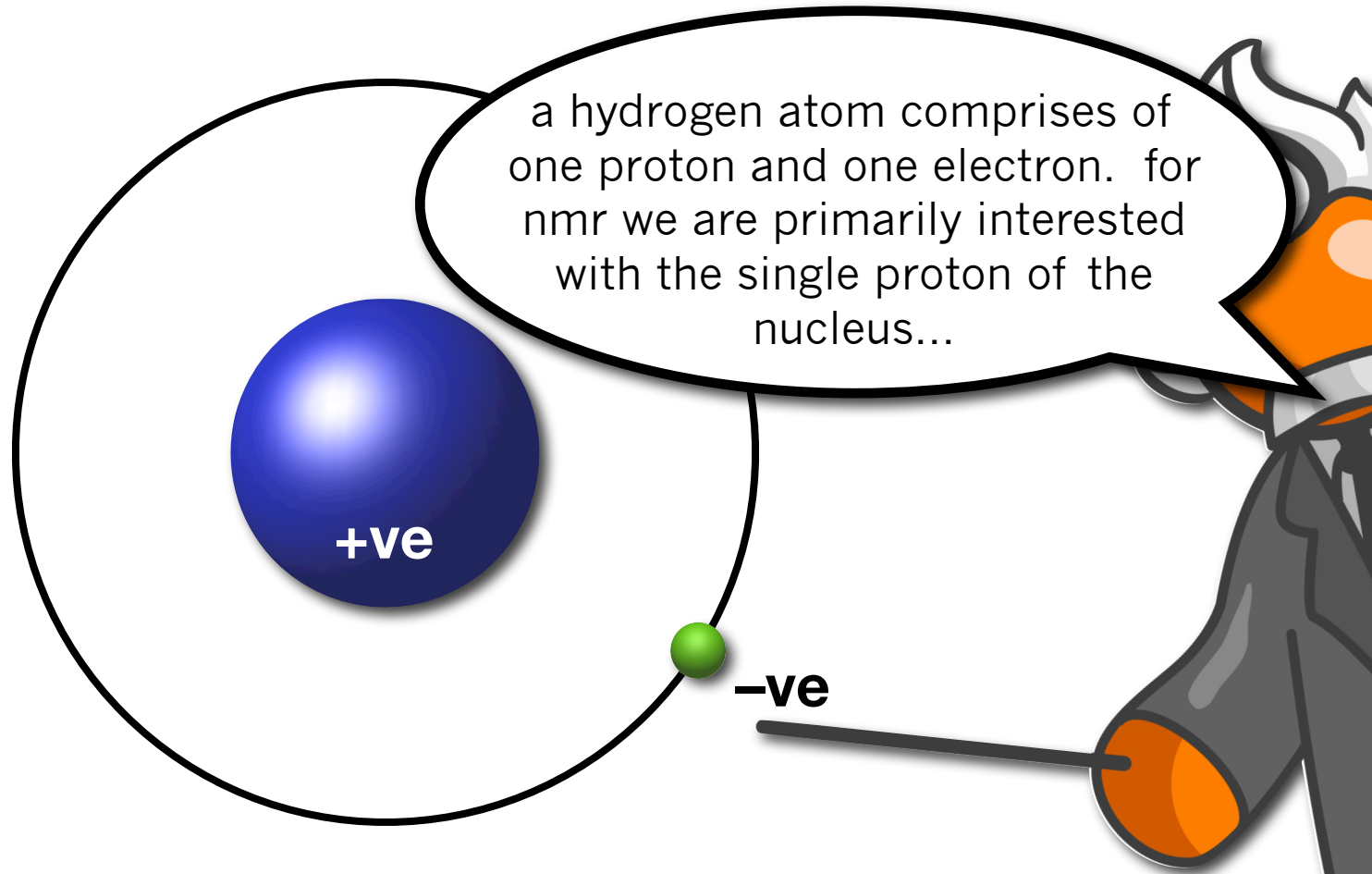
DRILL

so what **is** nmr?



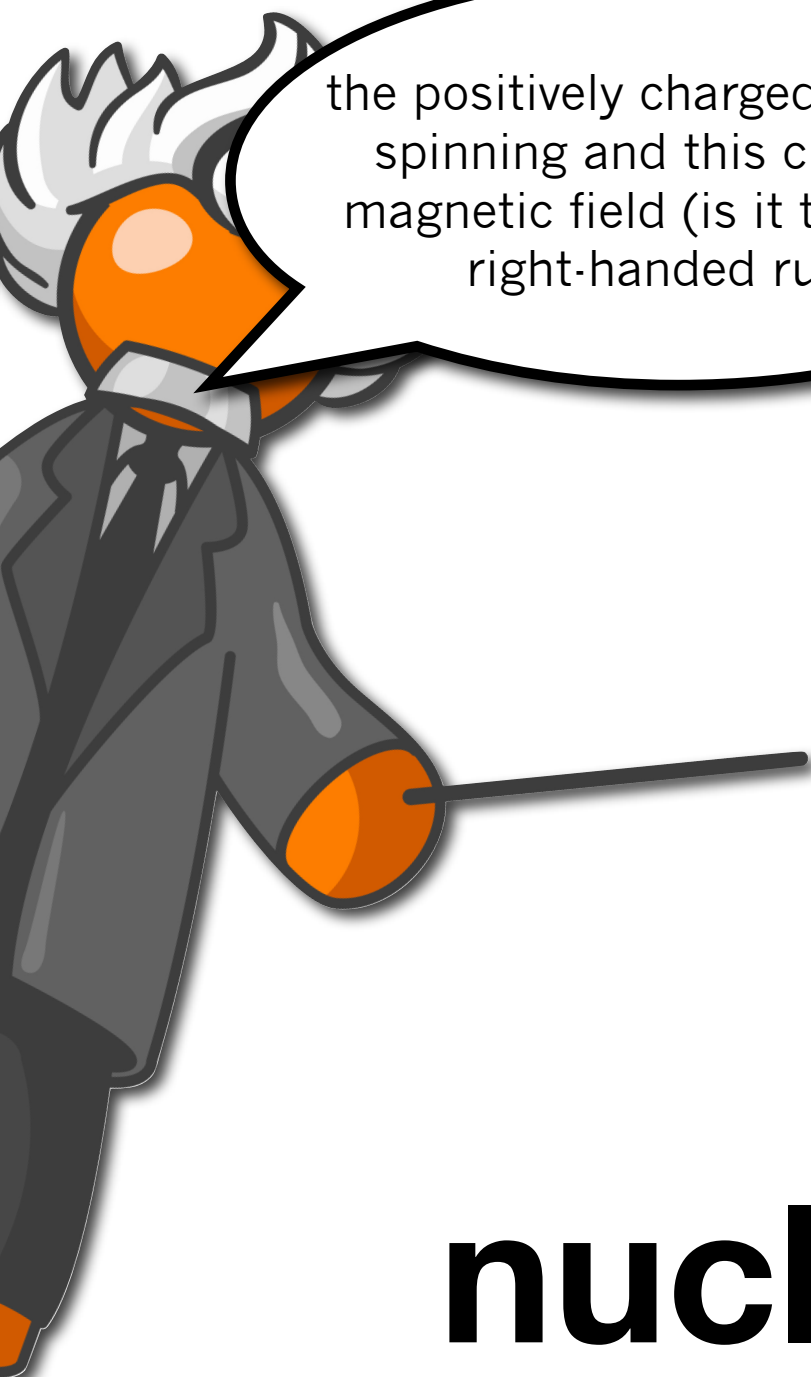


# hydrogen

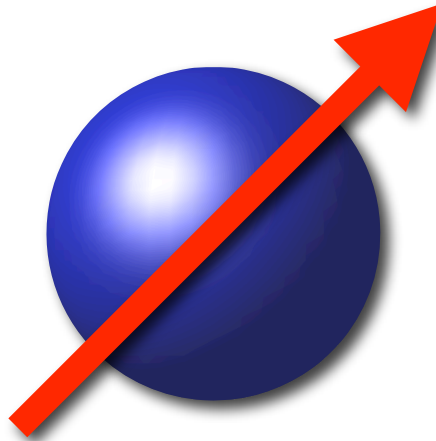


atom

# hydrogen



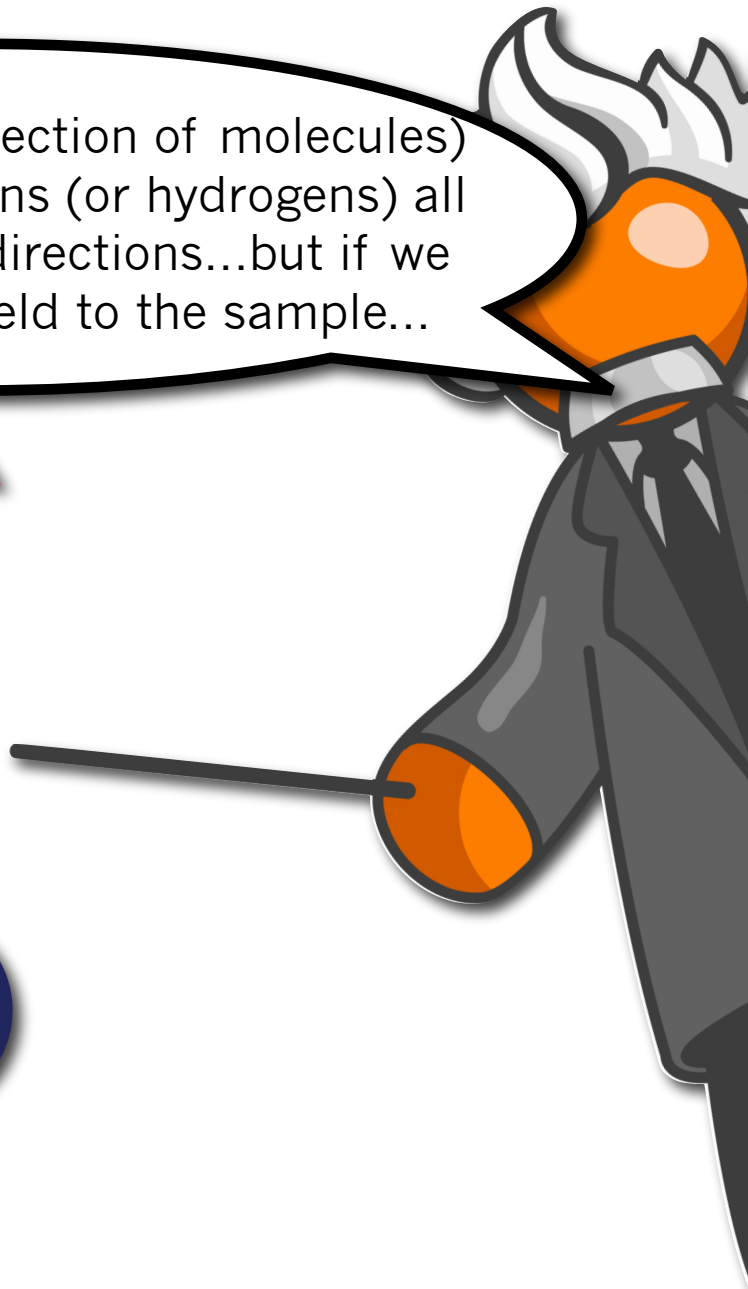
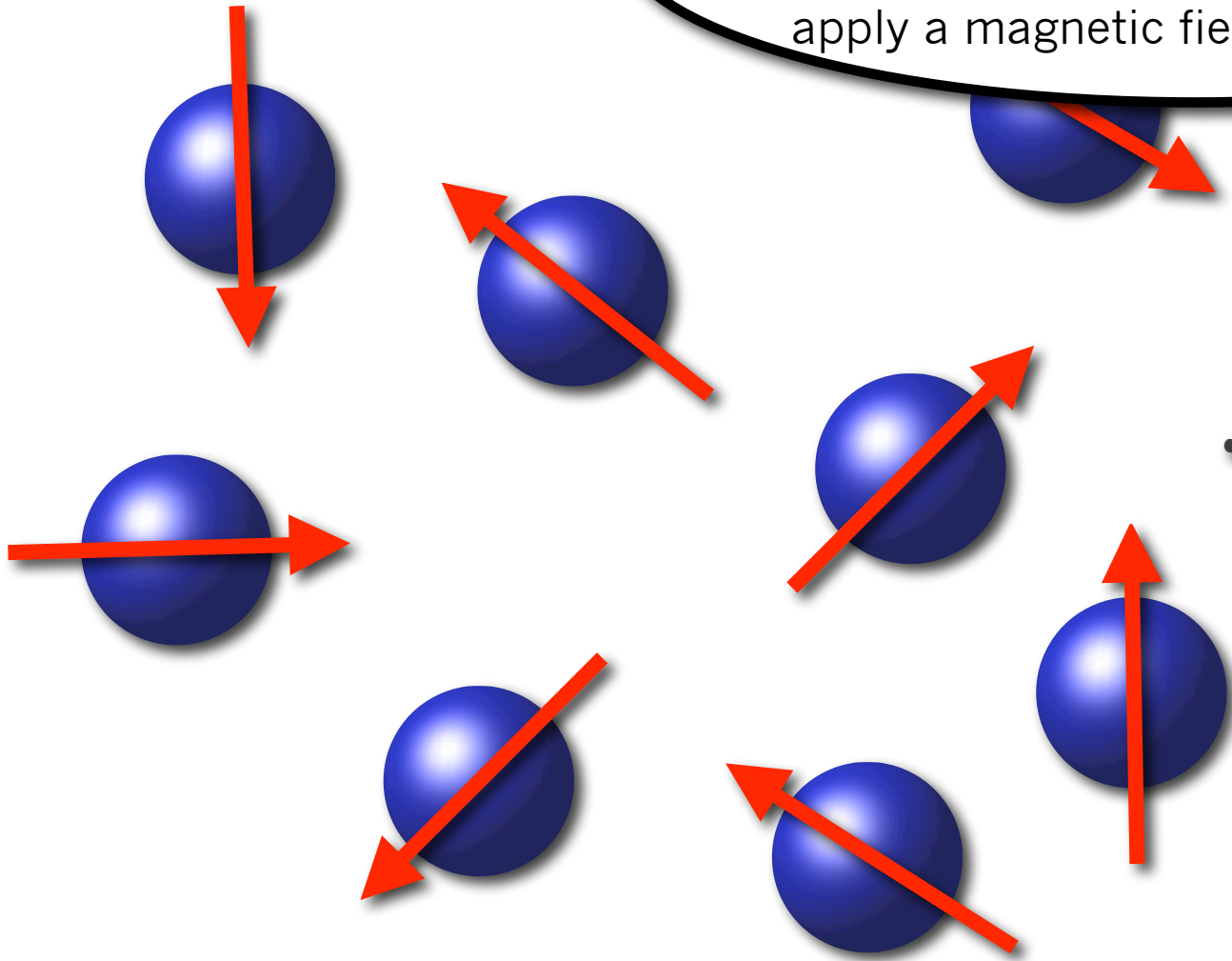
the positively charged proton is spinning and this creates a magnetic field (is it the left or right-handed rule?)



**nucleus spins**

# sample

in a molecule (or collection of molecules) we have lots of protons (or hydrogens) all spinning in various directions...but if we apply a magnetic field to the sample...



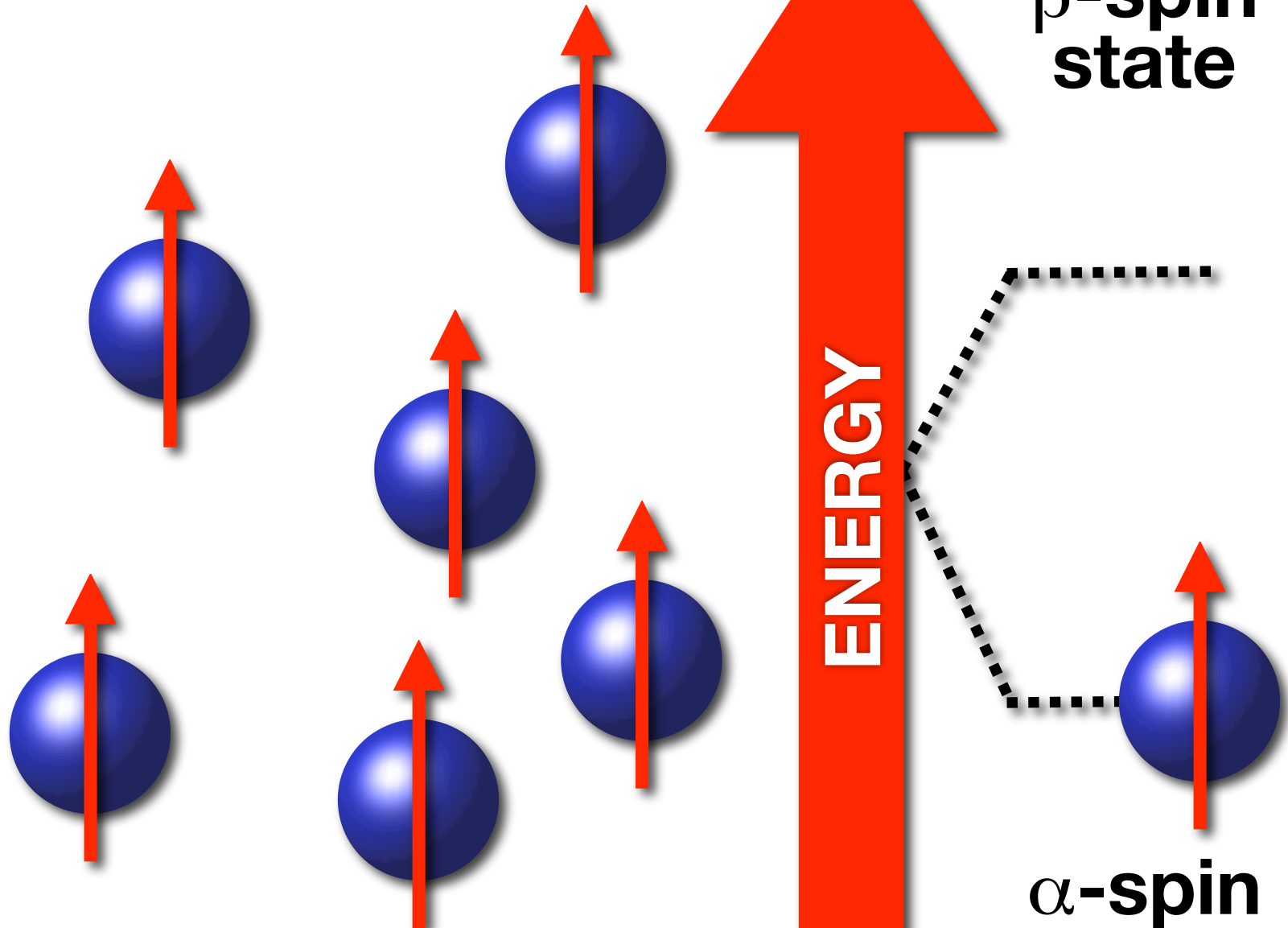
# random orientation

# sample



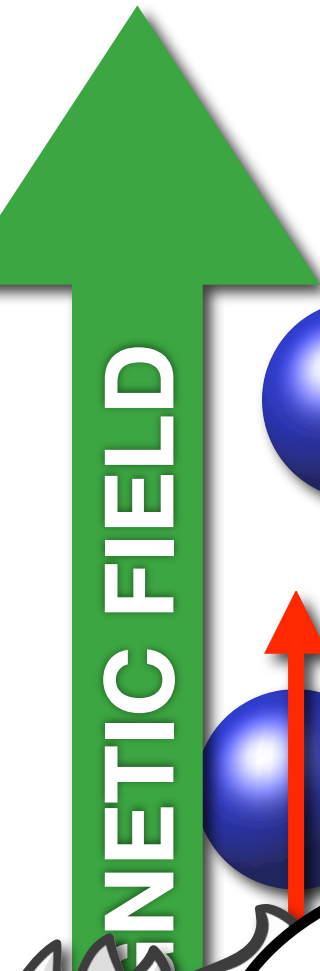
$\beta$ -spin state

$\alpha$ -spin state



# aligned

# sample

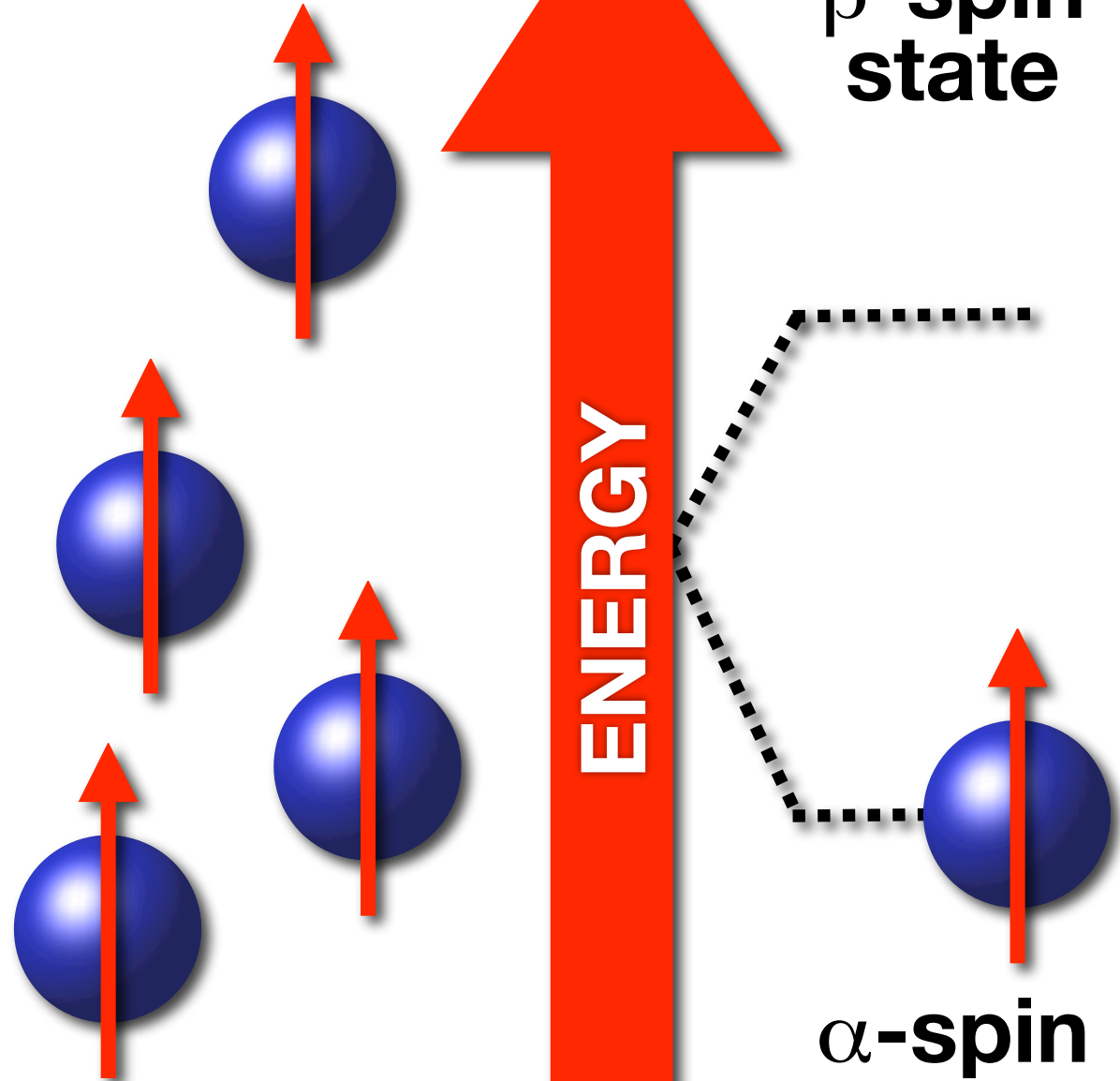
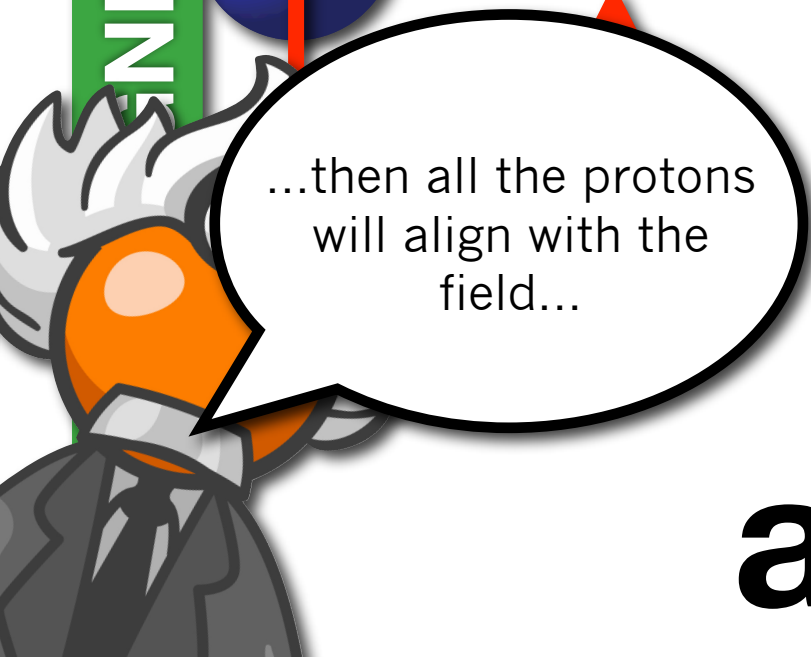


$\beta$ -spin state

$\alpha$ -spin state

...then all the protons will align with the field...

# aligned



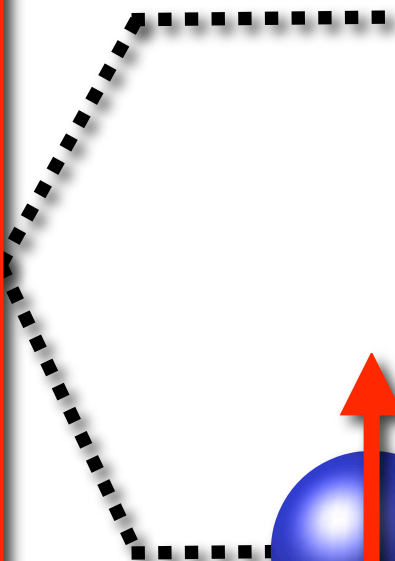
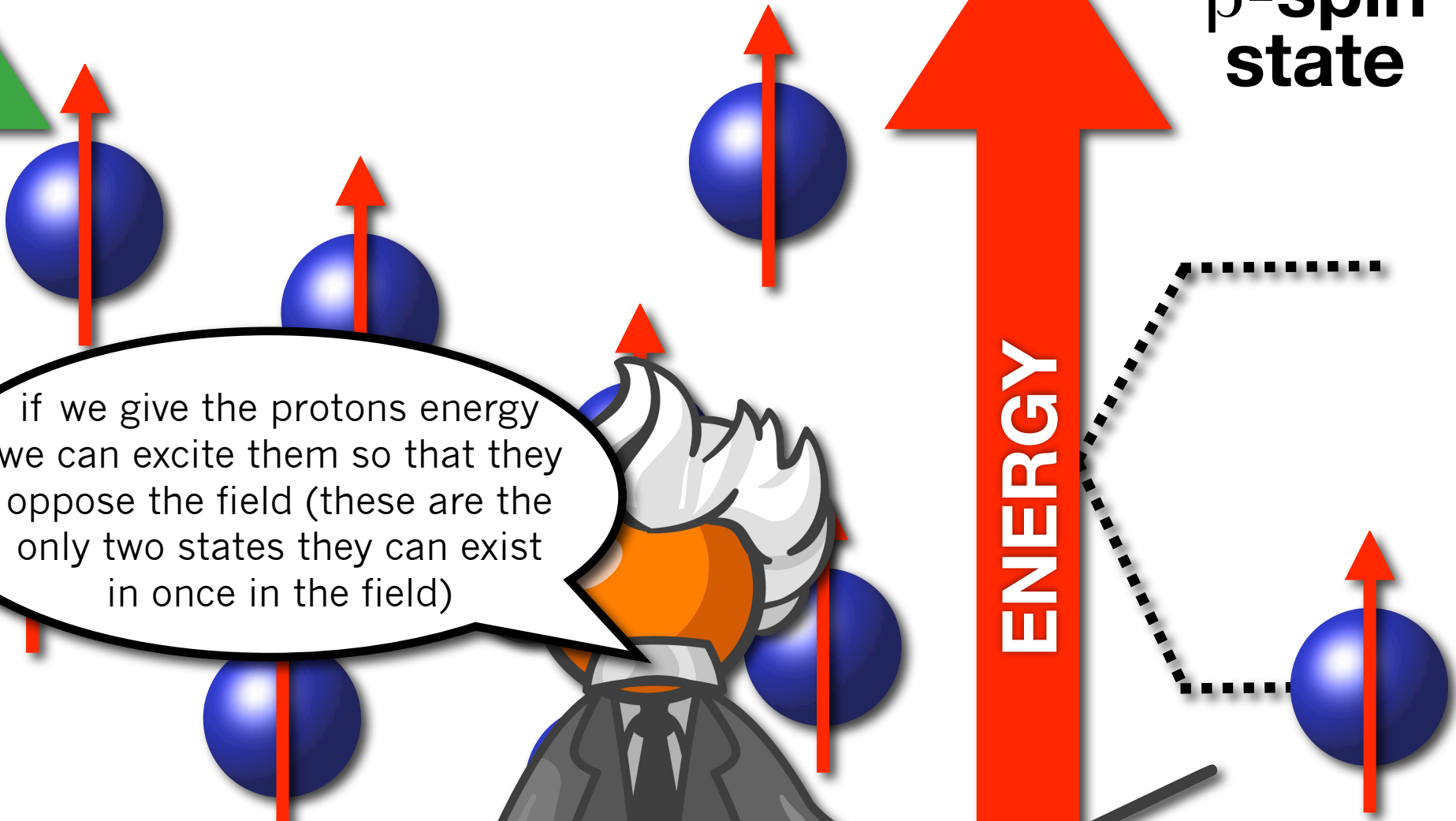
# sample



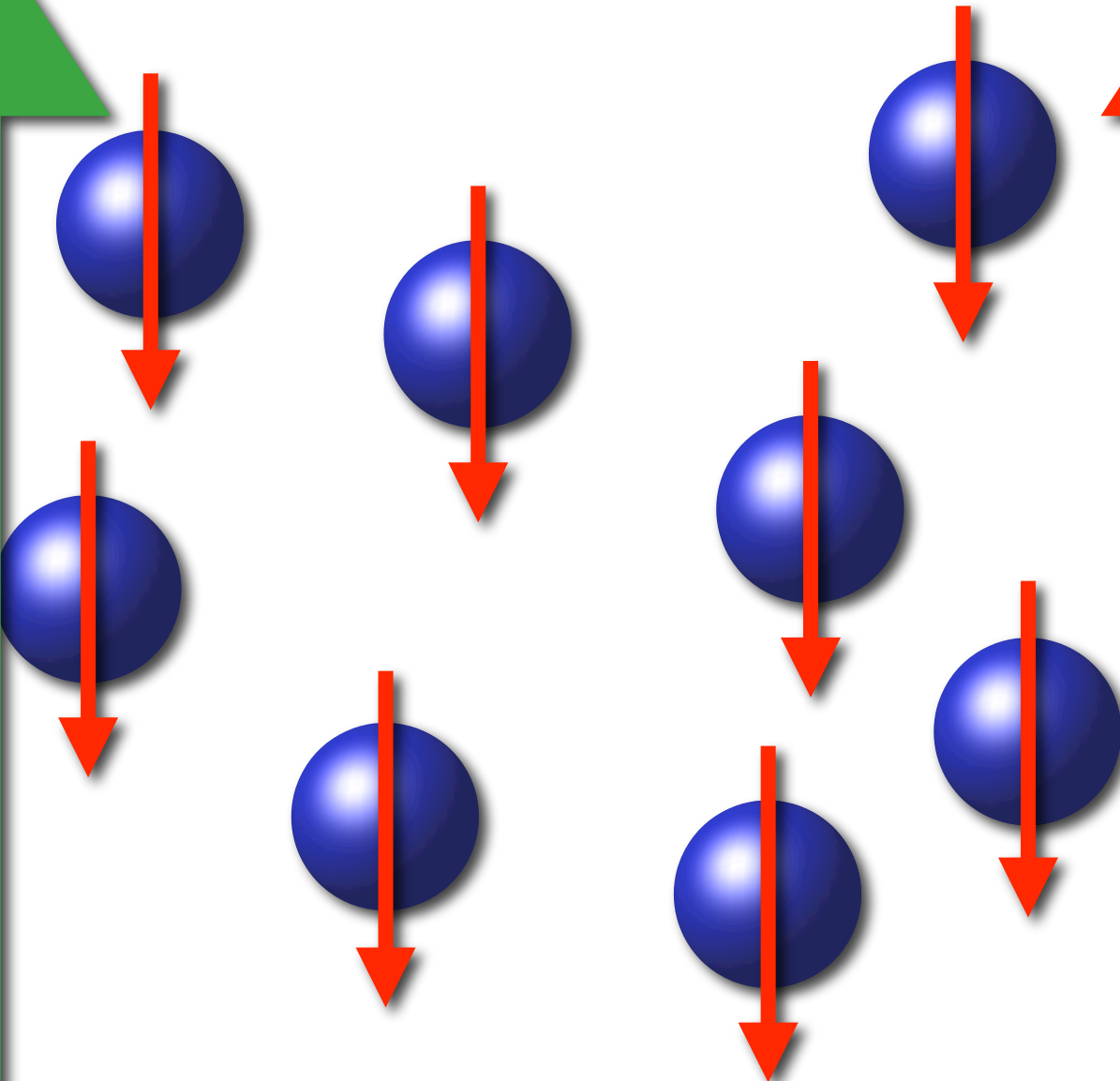
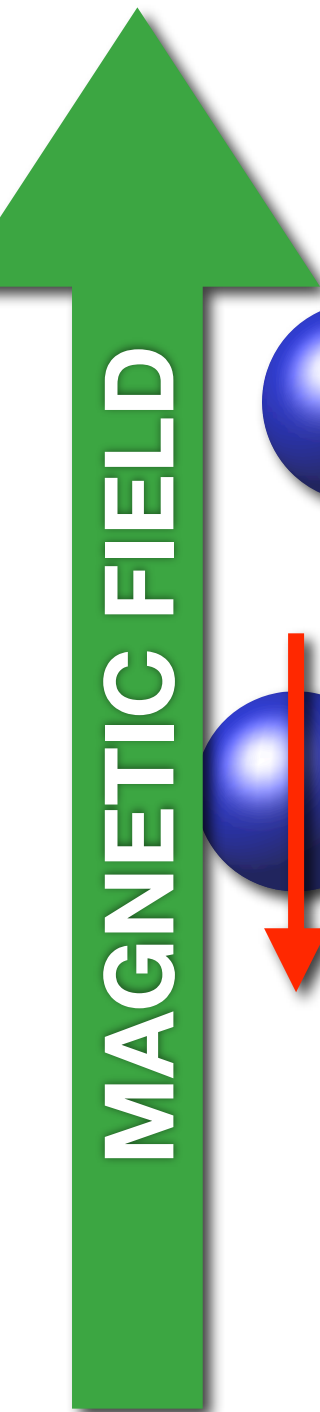
$\beta$ -spin state

$\alpha$ -spin state

if we give the protons energy we can excite them so that they oppose the field (these are the only two states they can exist in once in the field)



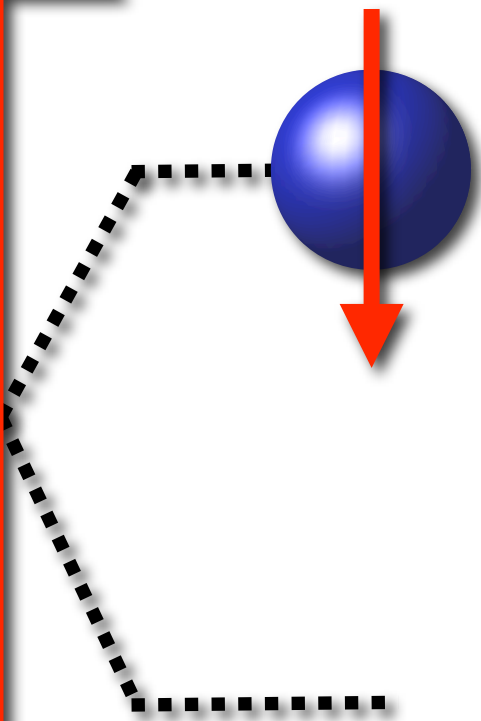
# sample



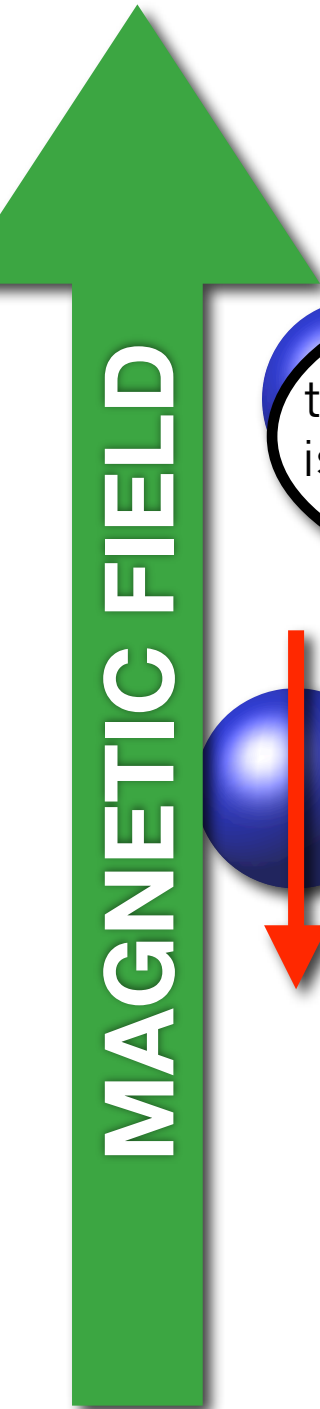
$\beta$ -spin state

$\alpha$ -spin state

# excited



# sample



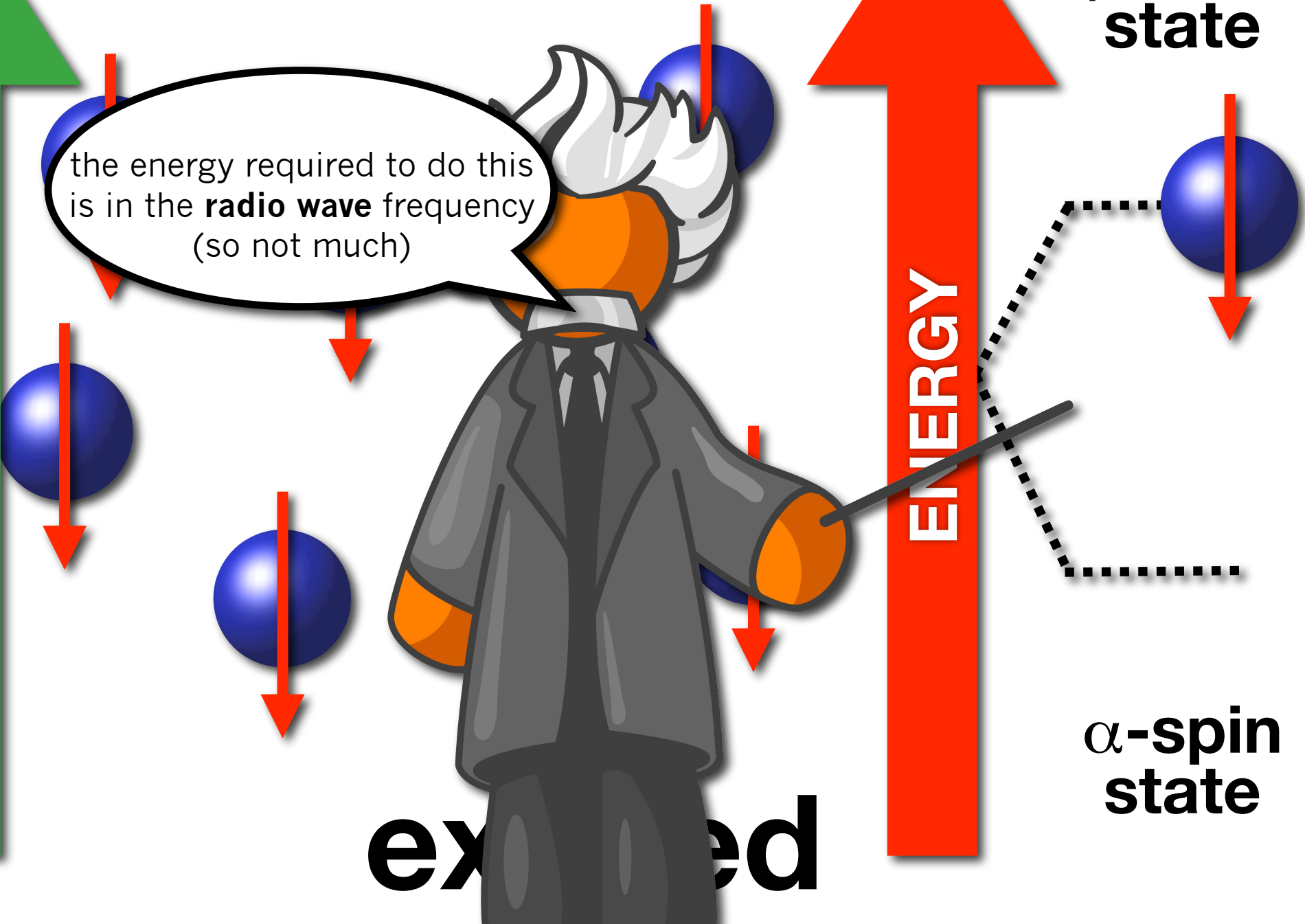
the energy required to do this is in the **radio wave** frequency (so not much)



$\beta$ -spin state

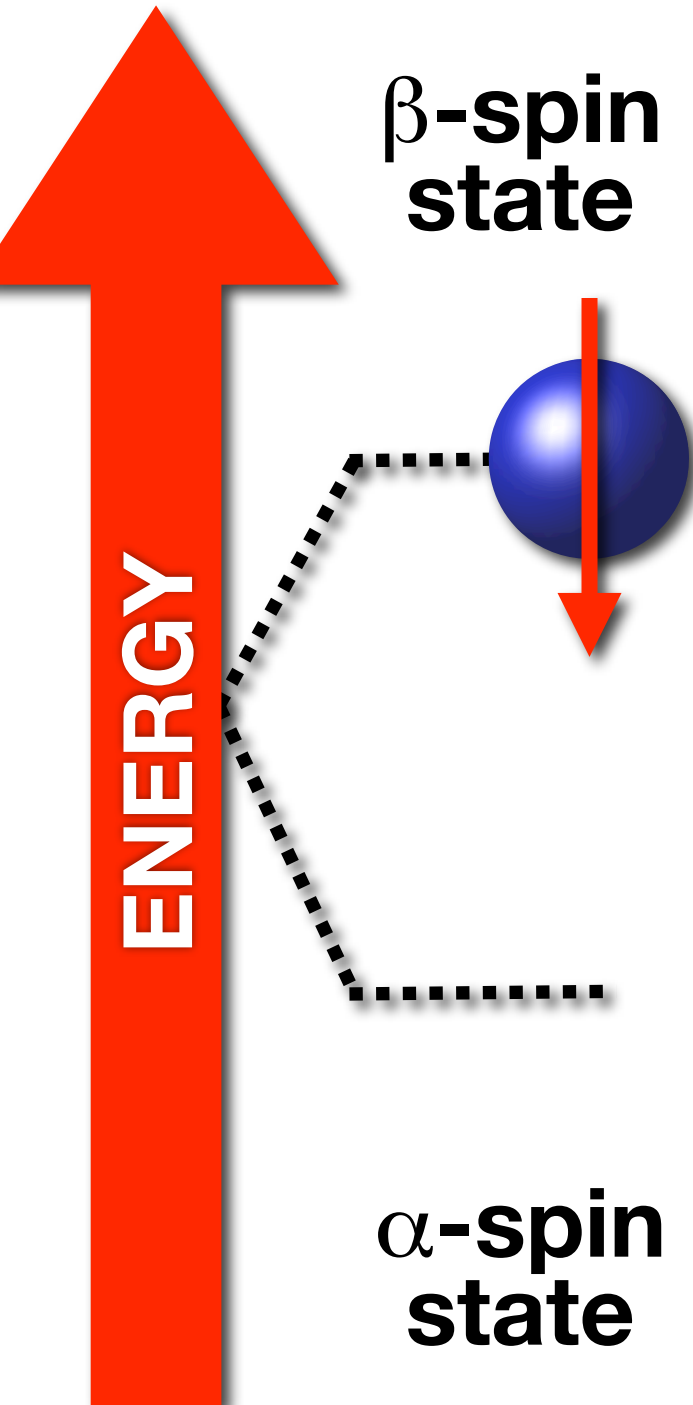
$\alpha$ -spin state

excited





# sample



take away the energy source and the protons will relax (become aligned with the field once more)

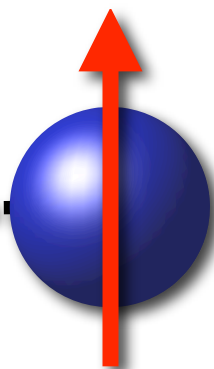
# relaxes



# sample



$\beta$ -spin state



$\alpha$ -spin state



record energy emitted

when they do this they emit energy as a radio wave...which we can measure

relaxes



# sample

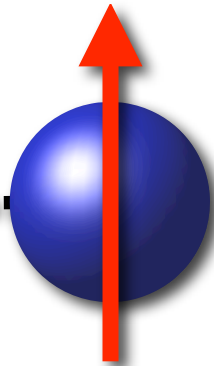


$\beta$ -spin  
state



record energy  
emitted

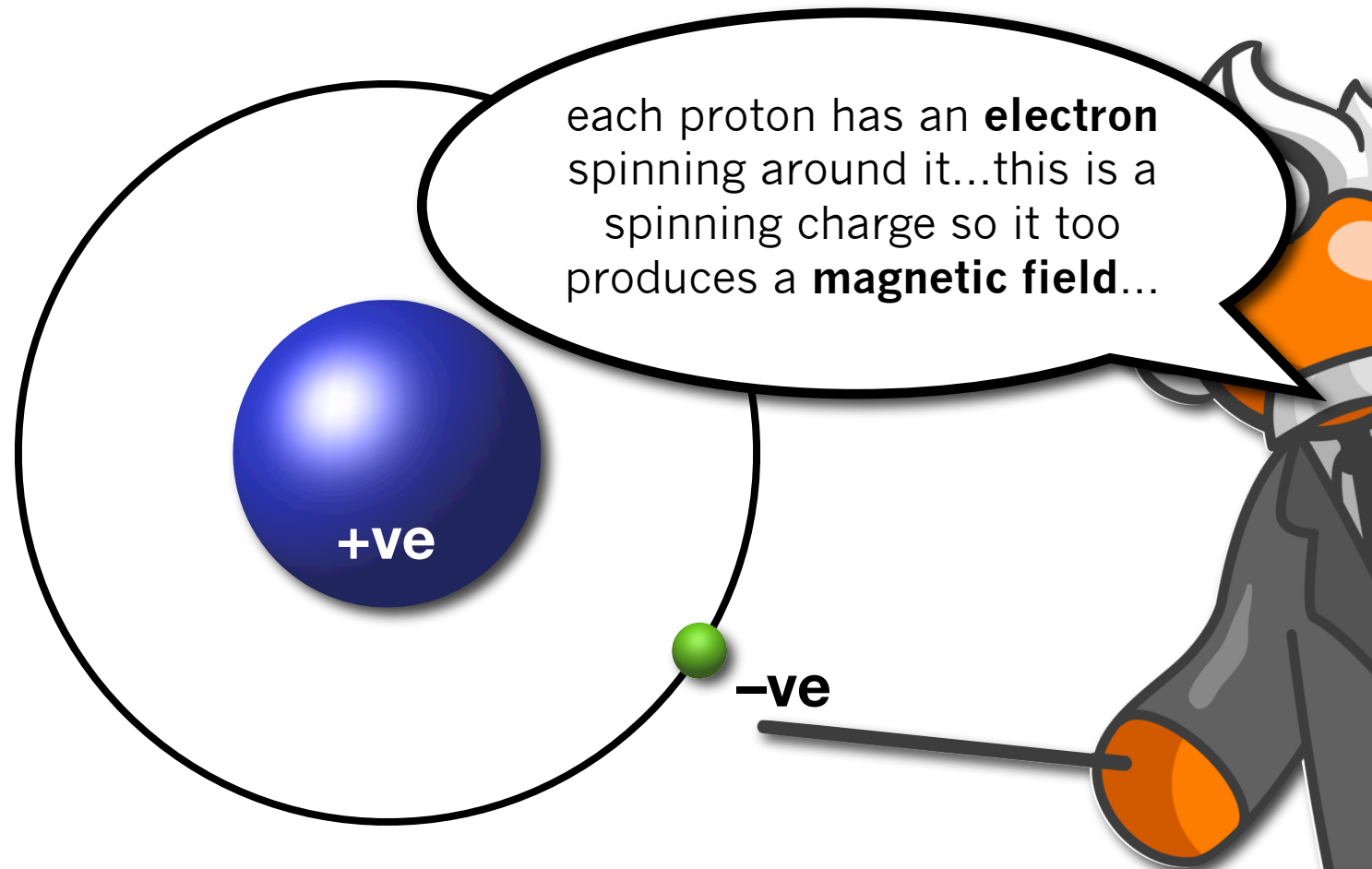
$\alpha$ -spin  
state



now, the cool bit is...  
the amount of energy they will  
emit depends on the **strength of  
the magnetic field** that they  
experience...

# relaxes

# hydrogen



# atom

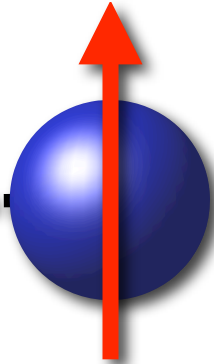
# sample



$\beta$ -spin  
state



record energy  
emitted

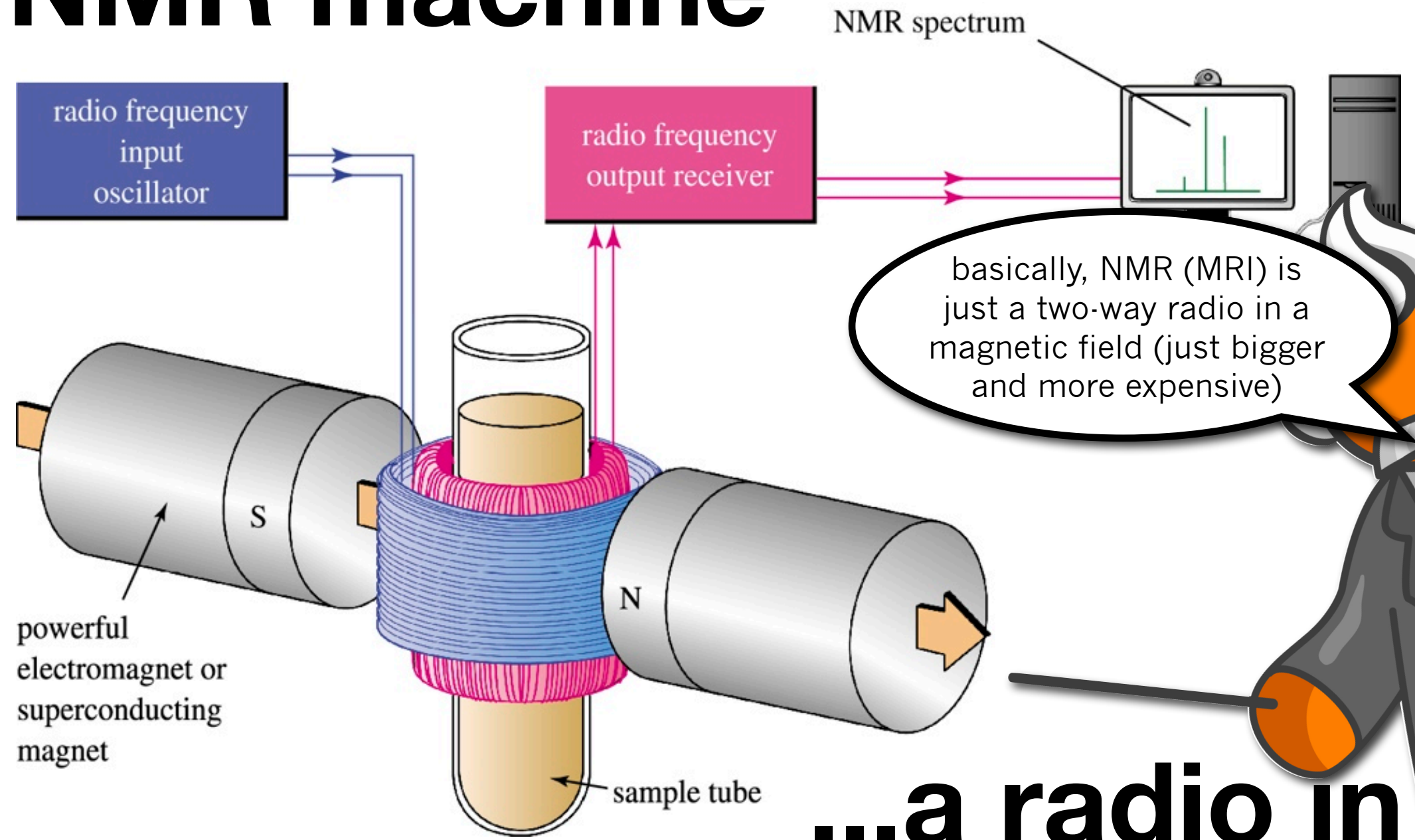


$\alpha$ -spin  
state

...so, the amount of energy emitted is influenced by the electrons around the proton or **the chemical environment**. As bonds are electrons we now have information about bonds / structure of the molecule

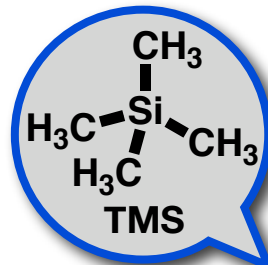
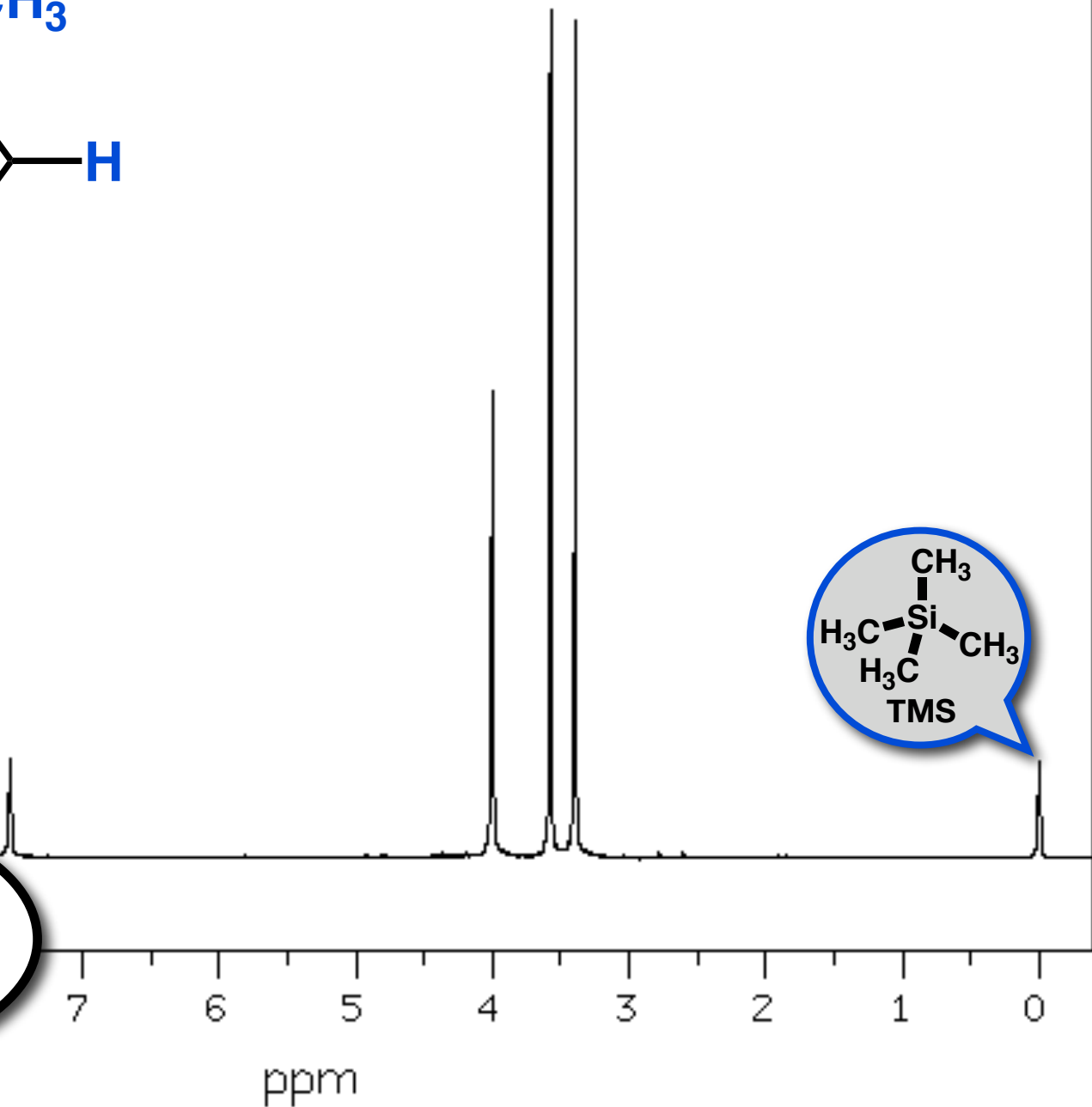
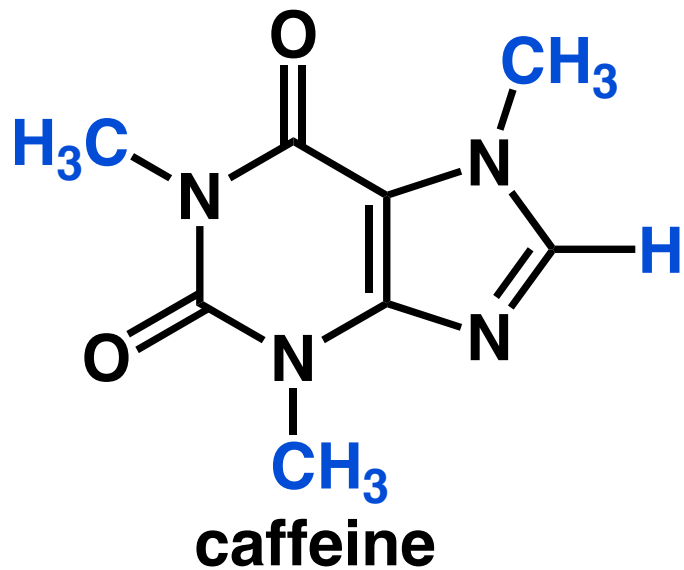
# relaxes

# NMR machine



**...a radio in a magnet...**

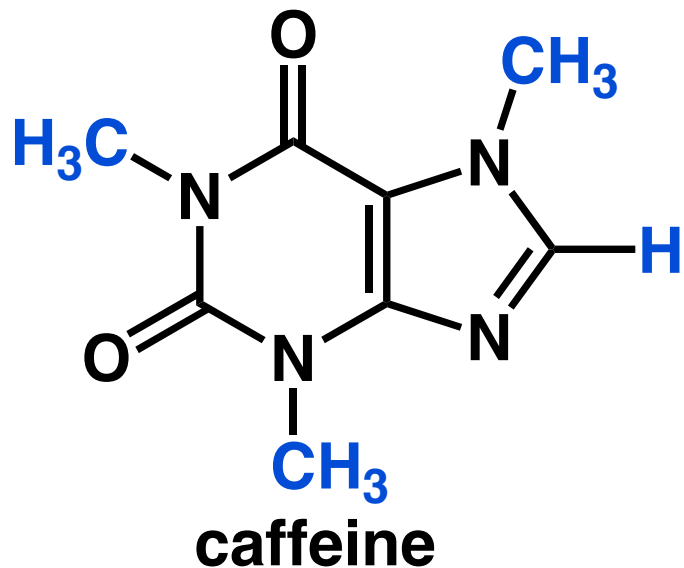
so what does the  
nmr tell us?



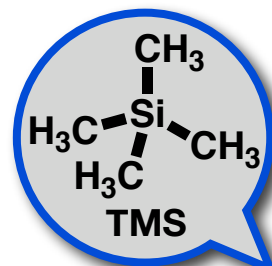
NMR tells us about the individual H in a molecule...

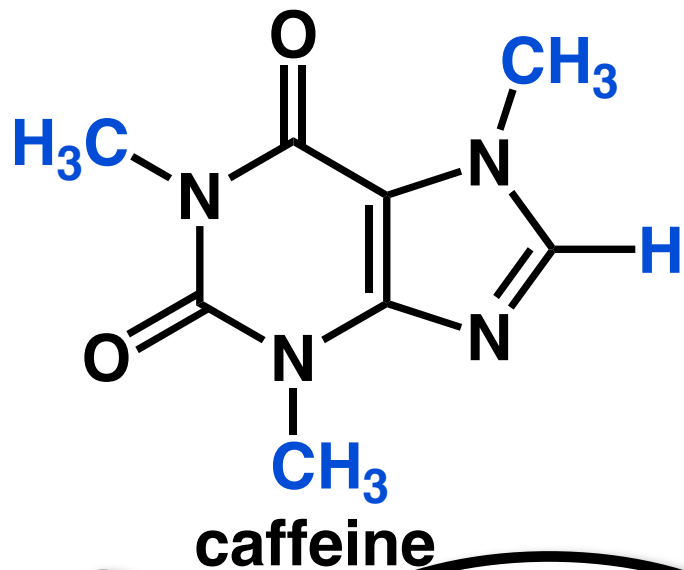




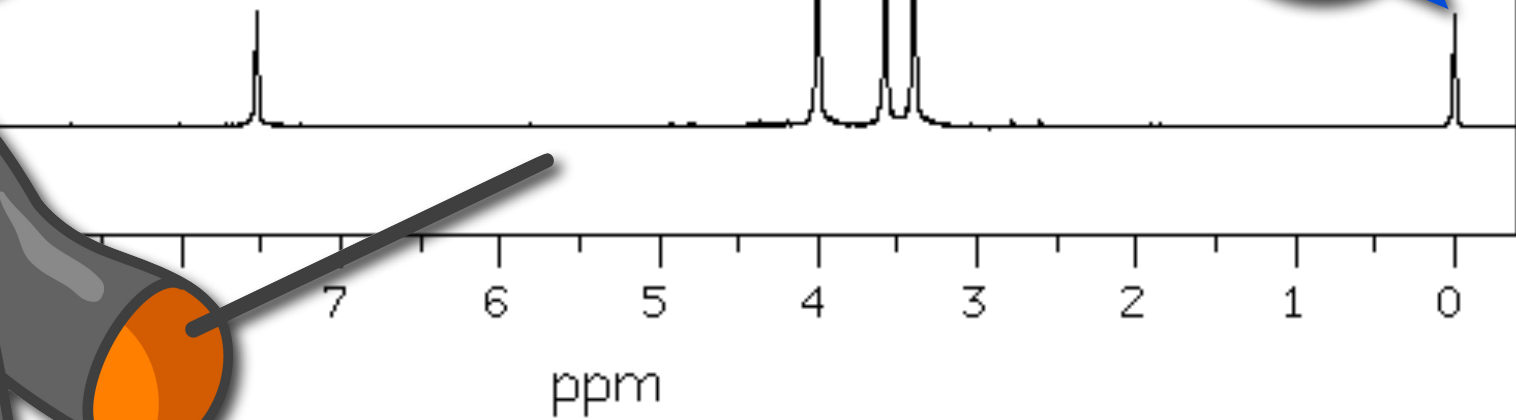
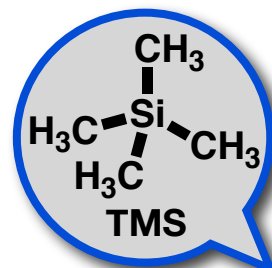


in caffeine there are **four** different kinds of H (or proton) depending on where they are...



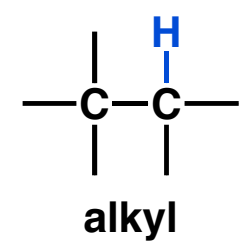
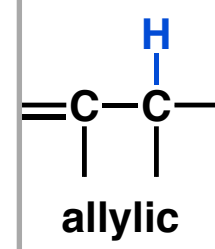
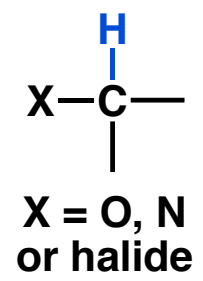
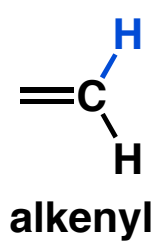
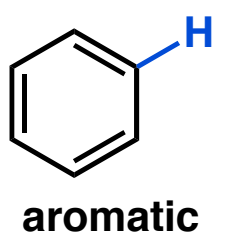


so the NMR spectrum has **four** peaks...one for each kind of H



deshielded

shielded



8

6

4

2

0

low

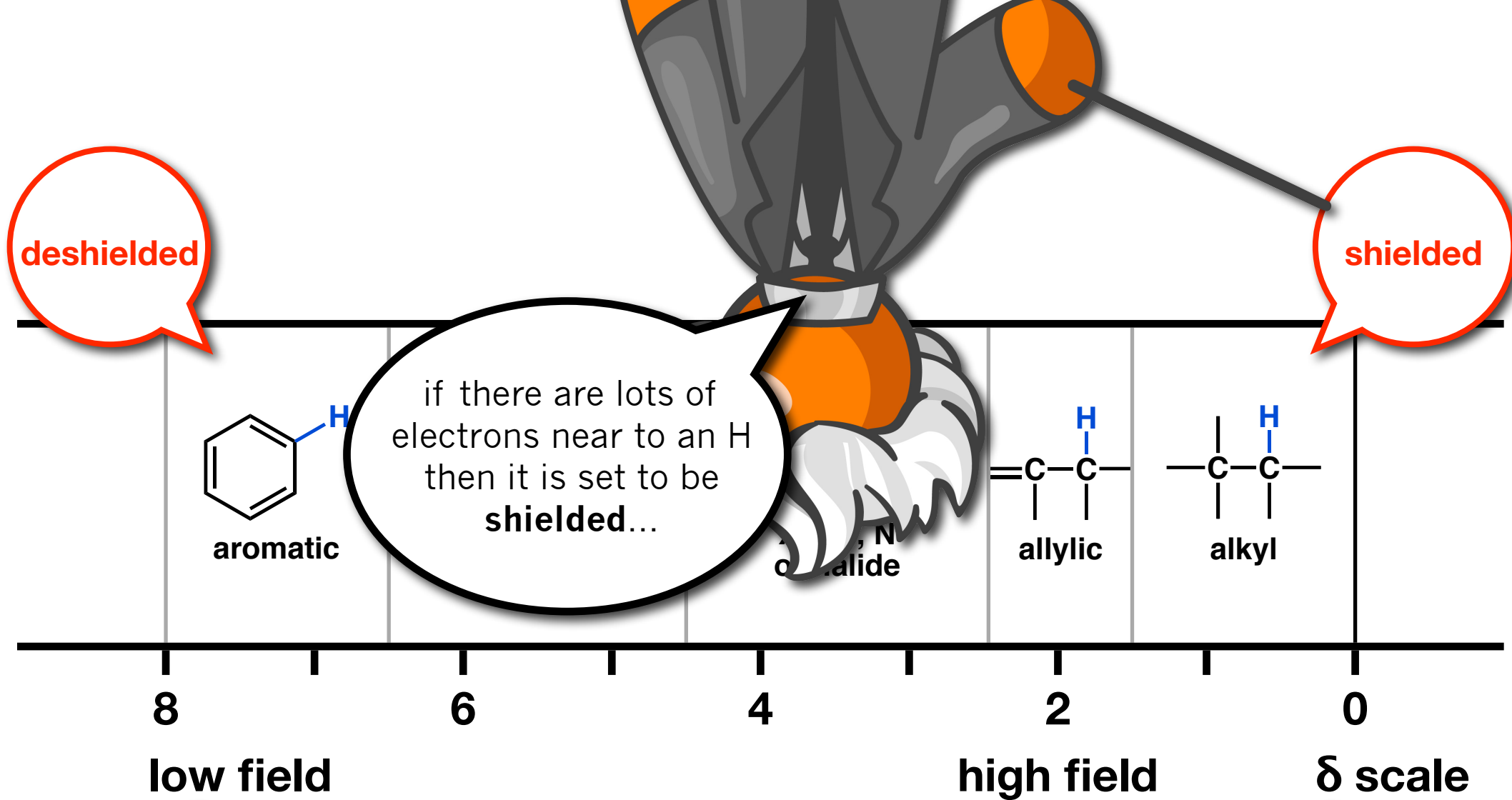
high field

$\delta$  scale

we can predict roughly where a peak will be found in the H NMR spectrum as it is related to the concentration of electrons near each H

high electron density





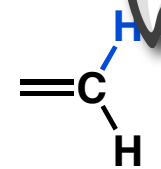
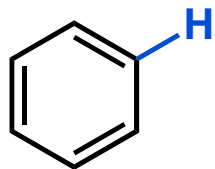
low electron density

high electron density

deshielded

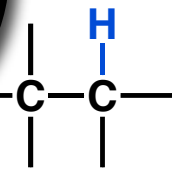
shielded

if there aren't many electrons near the H it is deshielded...



X = O, N or halide

allylic



8

6

4

2

0

low field

high field

$\delta$  scale

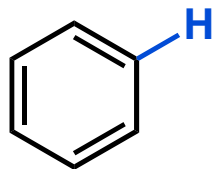
low electron density

high electron density

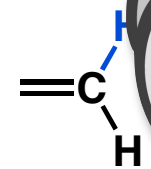
electron withdrawing groups pull electrons away causing objects to be deshielded and once again...

deshielded

shielded

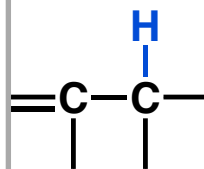


aromatic

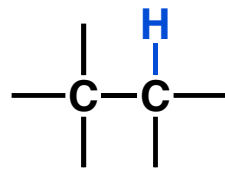


alkenyl

X = O, N or halide



allylic



alkyl

8

6

4

2

0

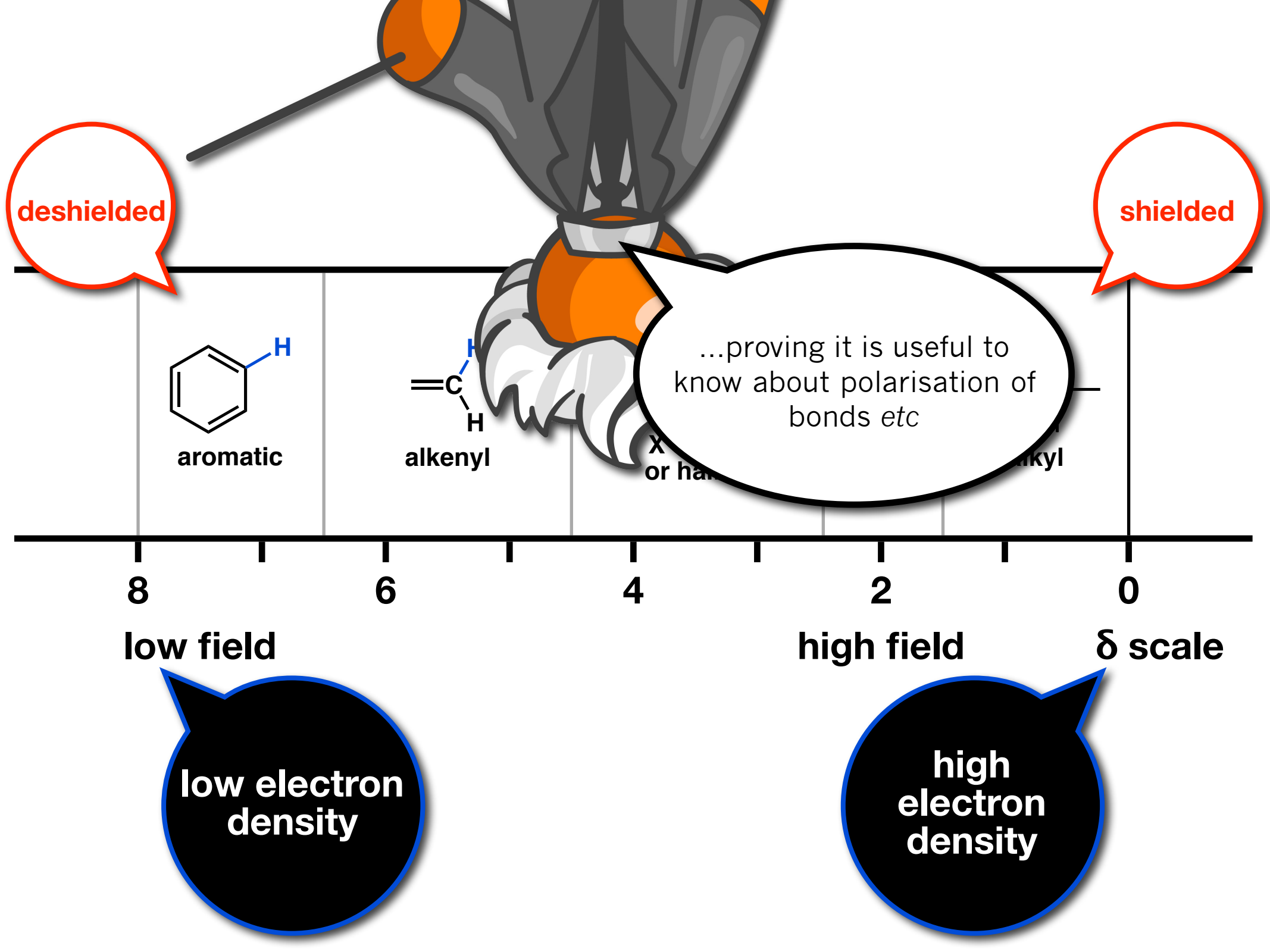
low field

high field

$\delta$  scale

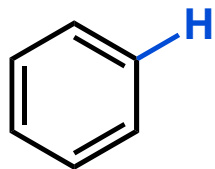
low electron density

high electron density

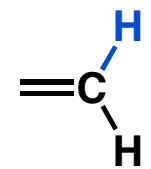


deshielded

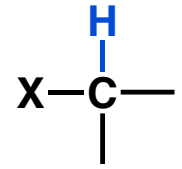
shielded



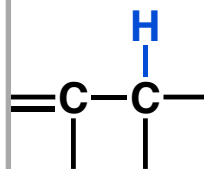
aromatic



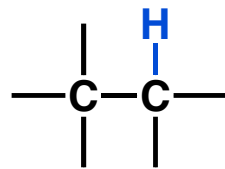
alkenyl



X = O, N  
or halide



allylic



alkyl

8

6

4

2

0

low field

high field

$\delta$  scale

low electron density

high electron density



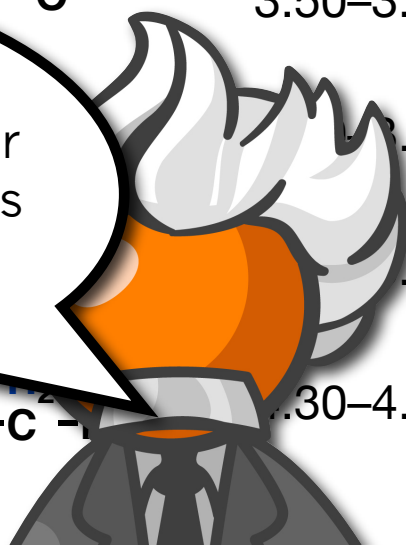
# correlation table

Type of hydrogen	$\delta$ (ppm)	Type of hydrogen	$\delta$ (ppm)	Type of hydrogen	$\delta$ (ppm)
$\text{C}-\text{CH}_3$	0.70–1.30	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Ph}$	2.60	$\text{C}=\text{CH}_2$	4.60–5.00
$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{C}$	1.20–1.35	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{I}$	3.10–3.30	$\text{C}-\underset{\text{H}}{\text{C}}=\text{C}$	5.20–5.70
$\begin{array}{c} \text{C} \\   \\ \text{C}-\underset{\text{H}}{\text{C}}-\text{C} \end{array}$	1.40–1.65	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Br}$	3.40	$-\text{CHCl}_2$	5.80–5.90
$\text{H}_3\text{C}-\text{C}=\text{C}$	1.60–1.90	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Cl}$	3.50	$\text{Ph}-\text{H}$	6.60–8.00
$\begin{array}{c} \text{H}_3\text{C}-\text{C}=\text{O} \\   \end{array}$	2.10–2.60	$\text{H}_2\text{C}-\text{O}-$	3.50–3.80	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{H} \end{array}$	9.50–9.70
$\text{H}_3\text{C}-\text{N} \begin{array}{l} / \\ \backslash \end{array}$	2.10–3.00	$\text{H}_3\text{C}-\text{O}-$	3.50–3.80	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{OH} \end{array}$	10.00–13.00
$\text{Ph}-\text{CH}_3$	2.20–2.50	$\text{Ar}-\text{OH}$	4.00–8.00	$\text{R}-\text{OH}$	0.50–5.50
$-\text{C}\equiv\text{C}-\text{H}$	2.40–2.70	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{F}$	4.30–4.40		

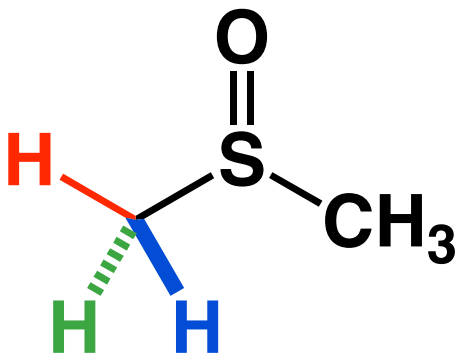
# correlation table

Type of hydrogen	$\delta$ (ppm)	Type of hydrogen	$\delta$ (ppm)	Type of hydrogen	$\delta$ (ppm)
$\text{C}-\text{CH}_3$	0.70–1.30	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Ph}$	2.60	$\text{C}=\text{CH}_2$	4.60–5.00
$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{C}$	1.20–1.35	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{I}$	3.10–3.30	$\text{C}-\underset{\text{H}}{\text{C}}=\text{C}$	5.20–5.70
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C} \\   \\ \text{H} \end{array}$	1.40–1.65	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Br}$	3.40	$-\text{CHCl}_2$	5.80–5.90
$\text{H}_3\text{C}-\text{C}=\text{C}$	1.60–1.90	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{Cl}$	3.50	$\text{Ph}-\text{H}$	6.60–8.00
$\text{H}_3\text{C}-\underset{ }{\text{C}}=\text{O}$	2.10–2.25	$\text{H}_2\text{C}-\text{O}-$	3.50–3.80	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{H} \end{array}$	9.50–9.70
$\text{H}_3\text{C}-\text{C}-\text{O}-$	3.70–3.80	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{O}-$	3.80–4.00	$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{C}-\text{OH} \end{array}$	10.00–13.00
$\text{Ph}-\text{H}$	6.60–8.00	$\text{C}-\overset{\text{H}_2}{\text{C}}-\text{N}-$	3.30–4.40	$\text{R}-\text{OH}$	0.50–5.50
$-\text{C}\equiv\text{C}-\text{H}$	2.10–2.30				

shows where we would expect to find peaks in our NMR data...you will always be given a table like this for your exams...



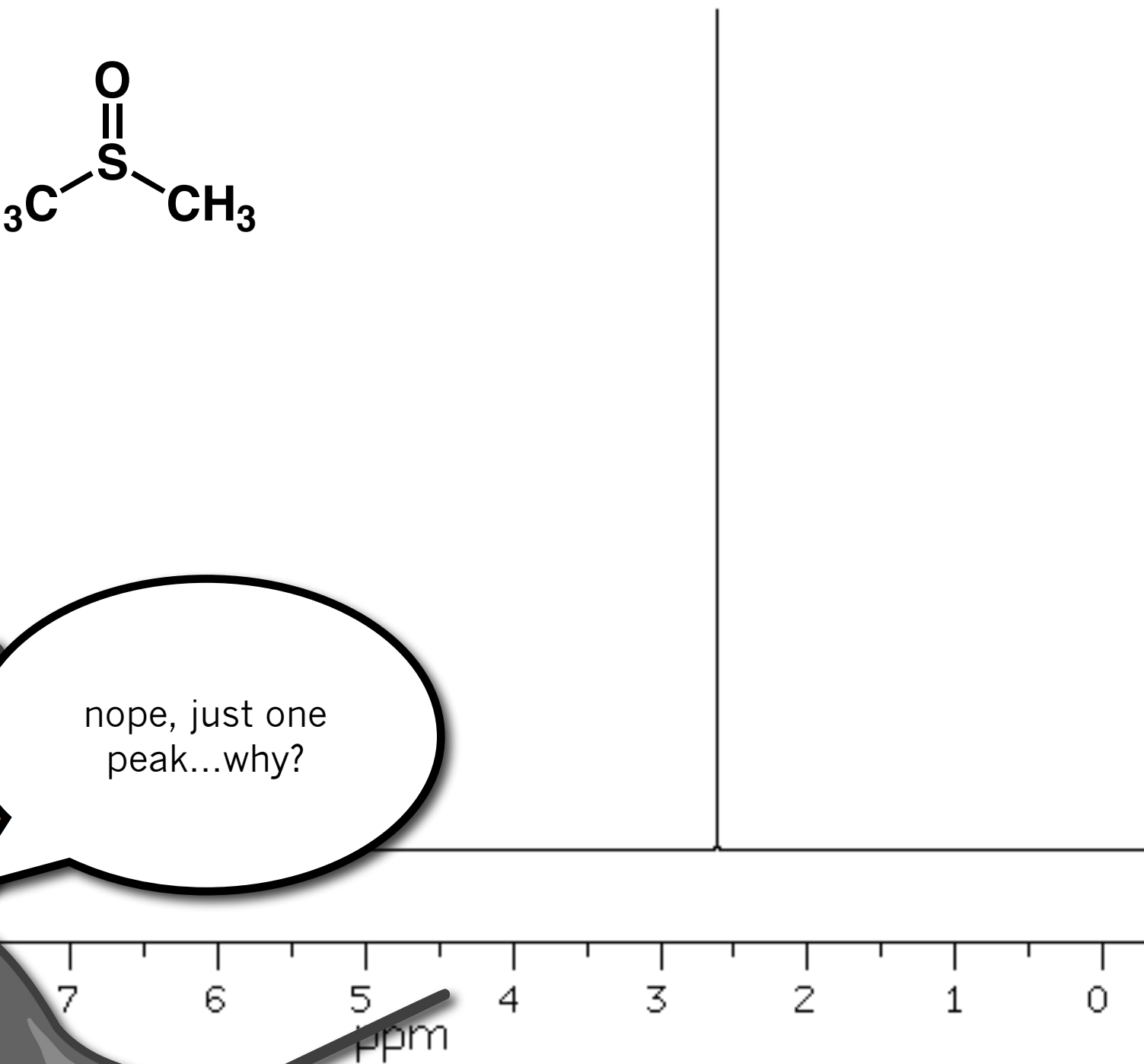
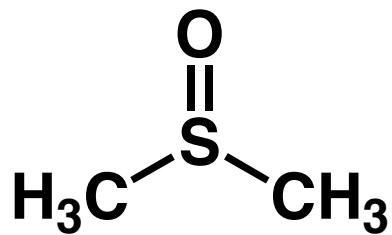
# chemically equivalent hydrogen




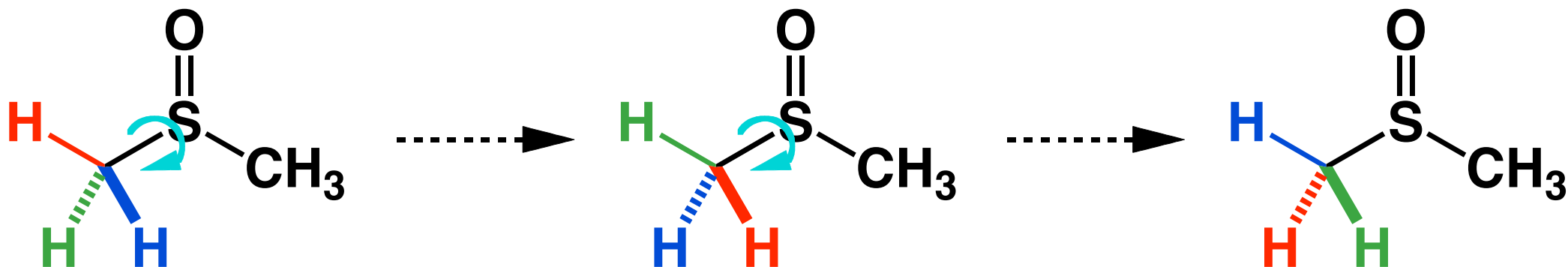
this is DMSO  
(dimethylsulfoxide)...it has  
**six** hydrogen atoms...do  
we see **six** peaks?



# chemically equivalent hydrogen

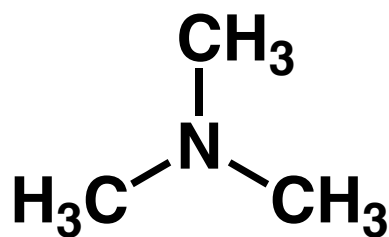


# chemically equivalent hydrogen



all the hydrogens are **chemically equivalent**...if we rotate the C-C bond we see we can put each H in exactly the same place...so we can not tell them apart and neither can the nmr. They are identical

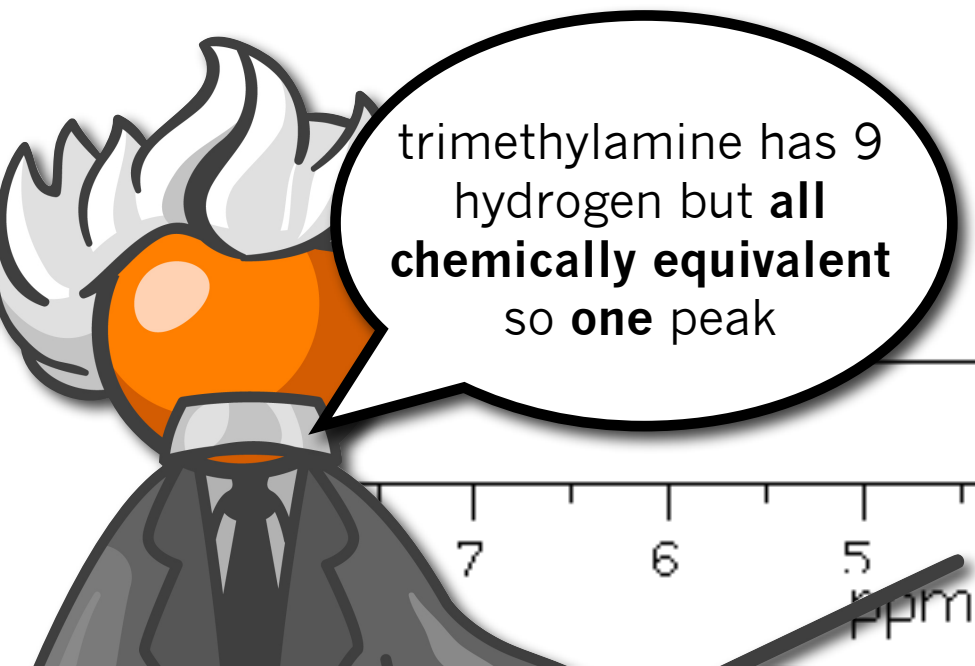
# chemically equivalent hydrogen



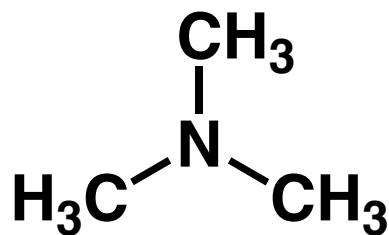
trimethylamine has 9 hydrogen but **all chemically equivalent** so **one** peak

7 6 5 4 3 2 1 0

ppm



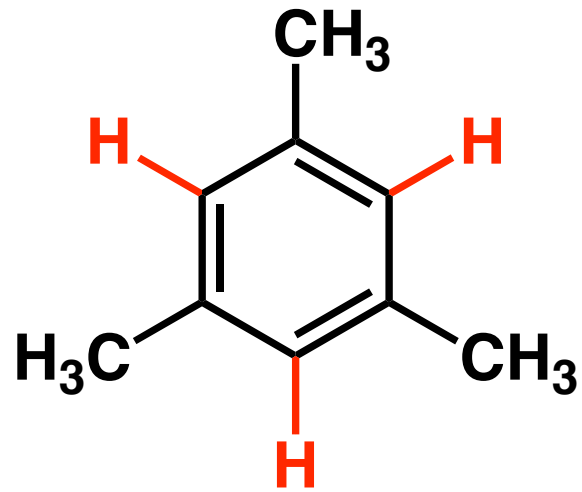
# chemically equivalent hydrogen



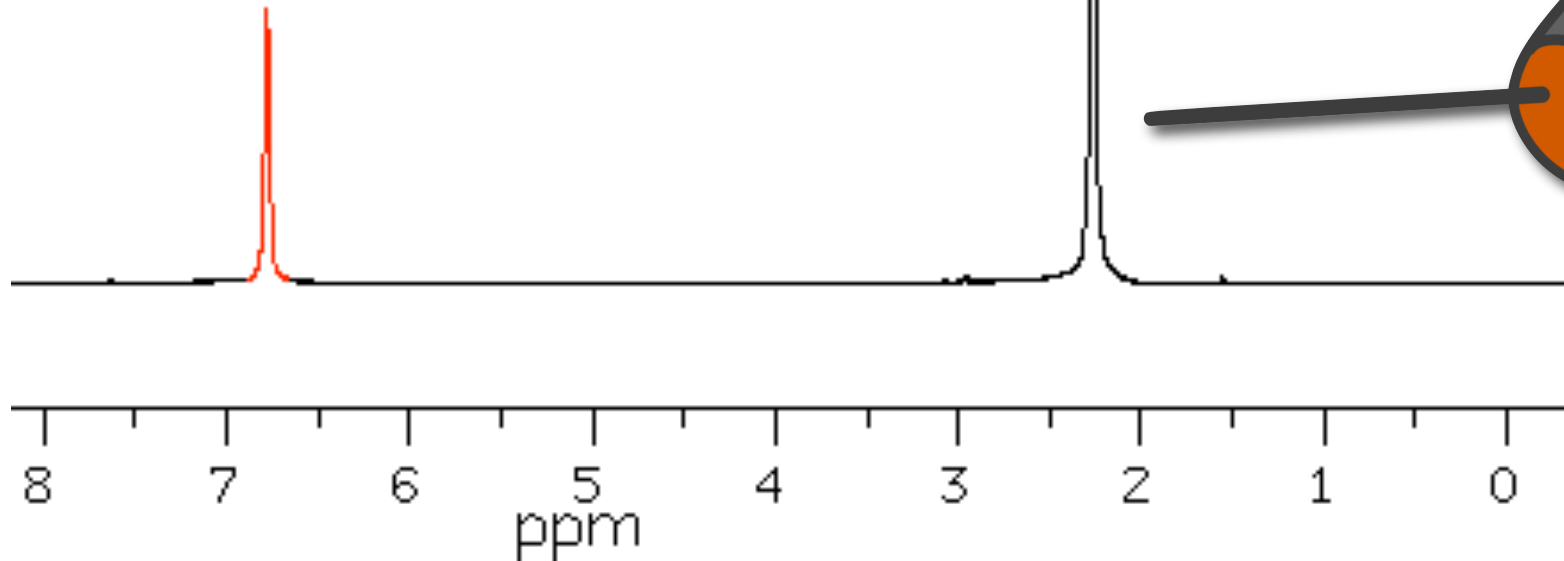
the peak is slightly shifted compared to DMSO as N does not pull the electrons towards it as much as the S=O group



# two chemical environments

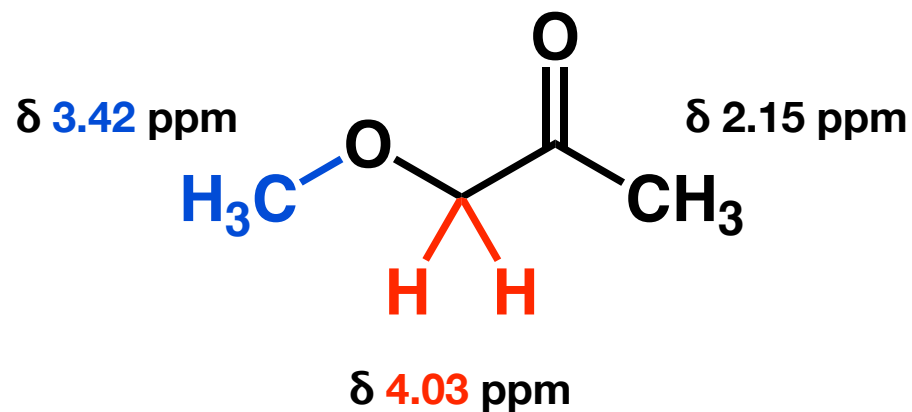


mesityl has **two** peaks as it has **one set** of H attached to the aromatic ring and **one set** attached to methyl groups

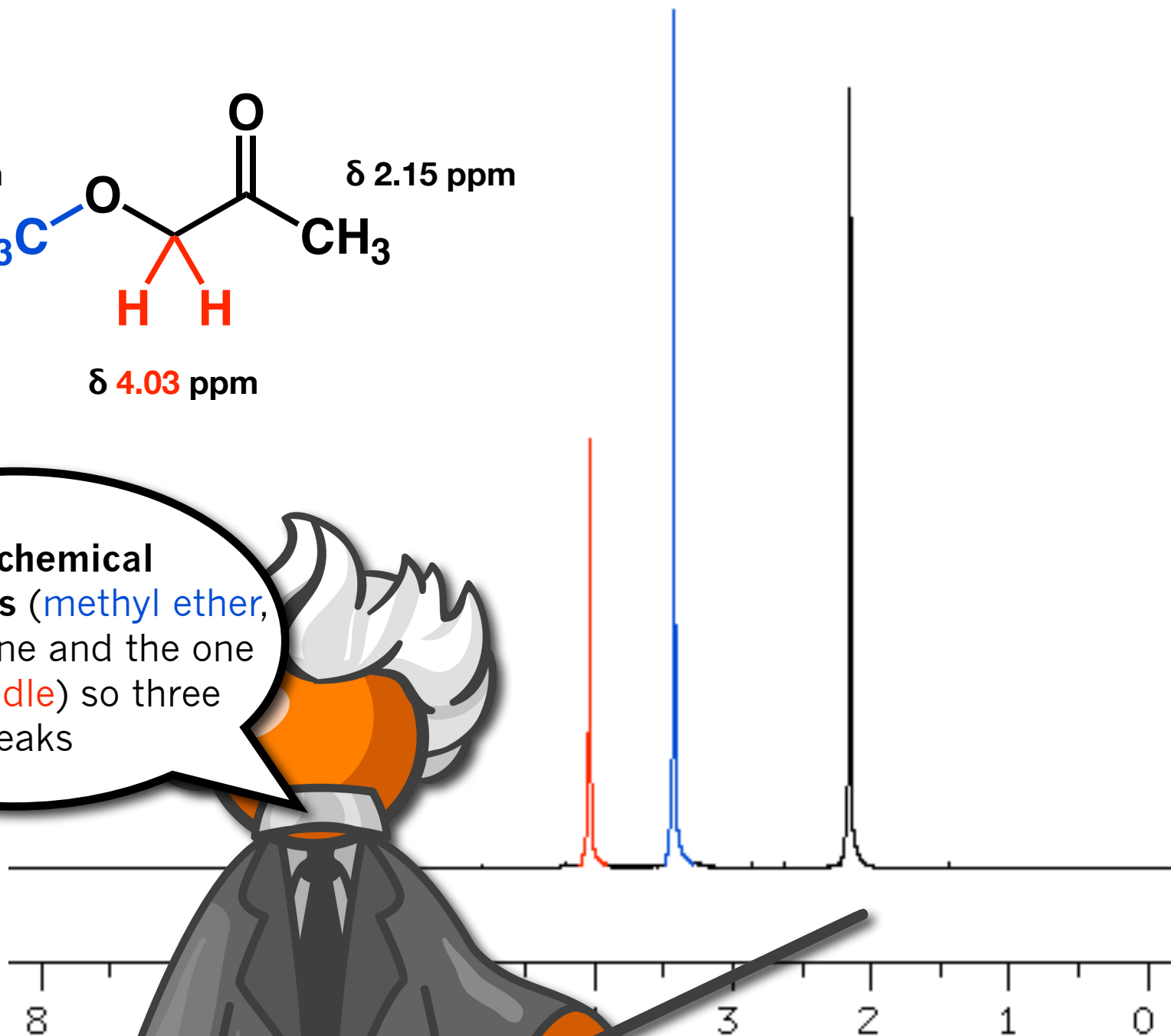




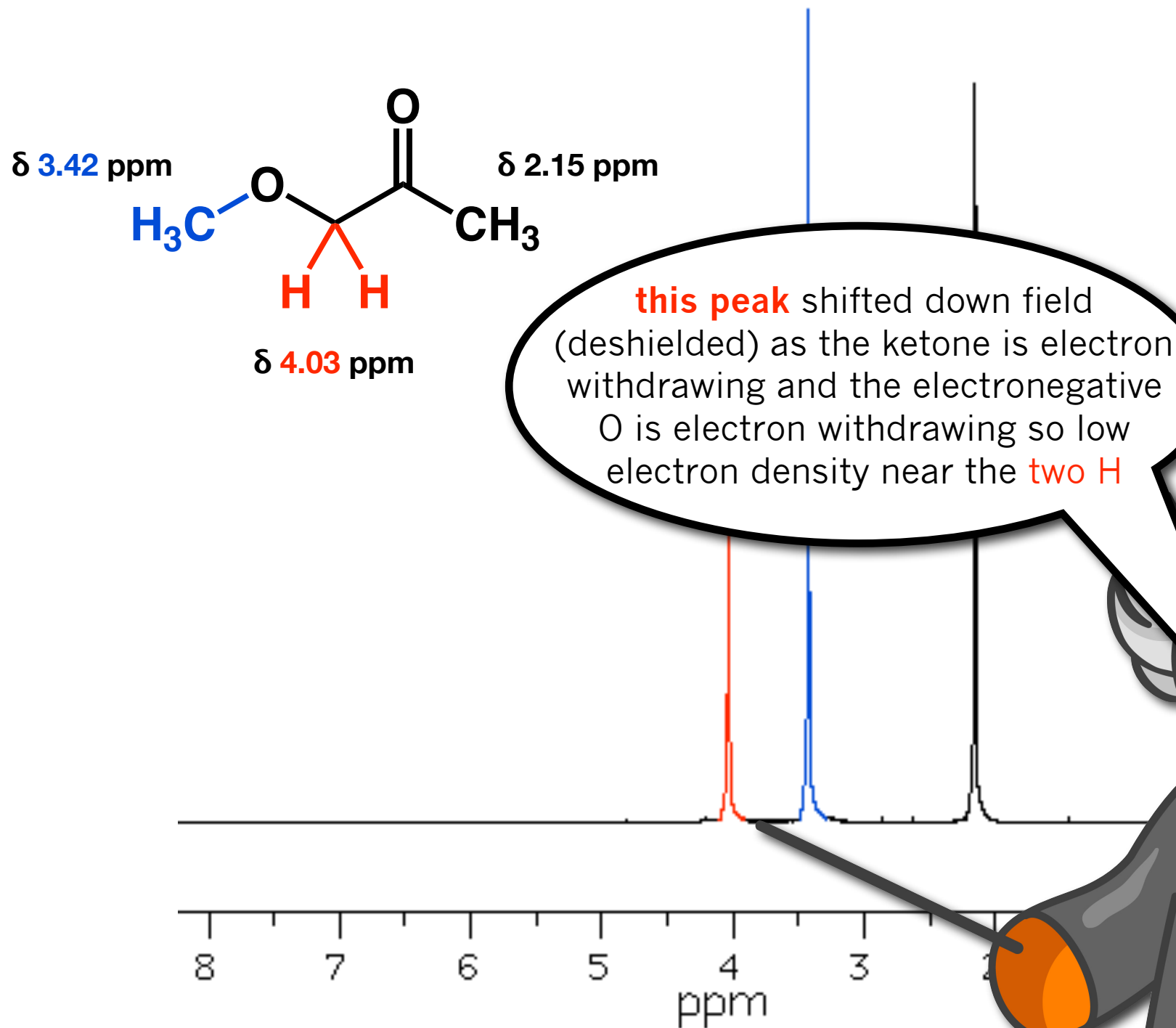
# three chemical environments



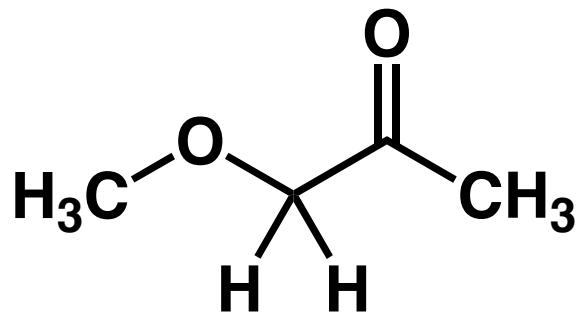
three chemical environments (methyl ether, methyl ketone and the one in the middle) so three peaks



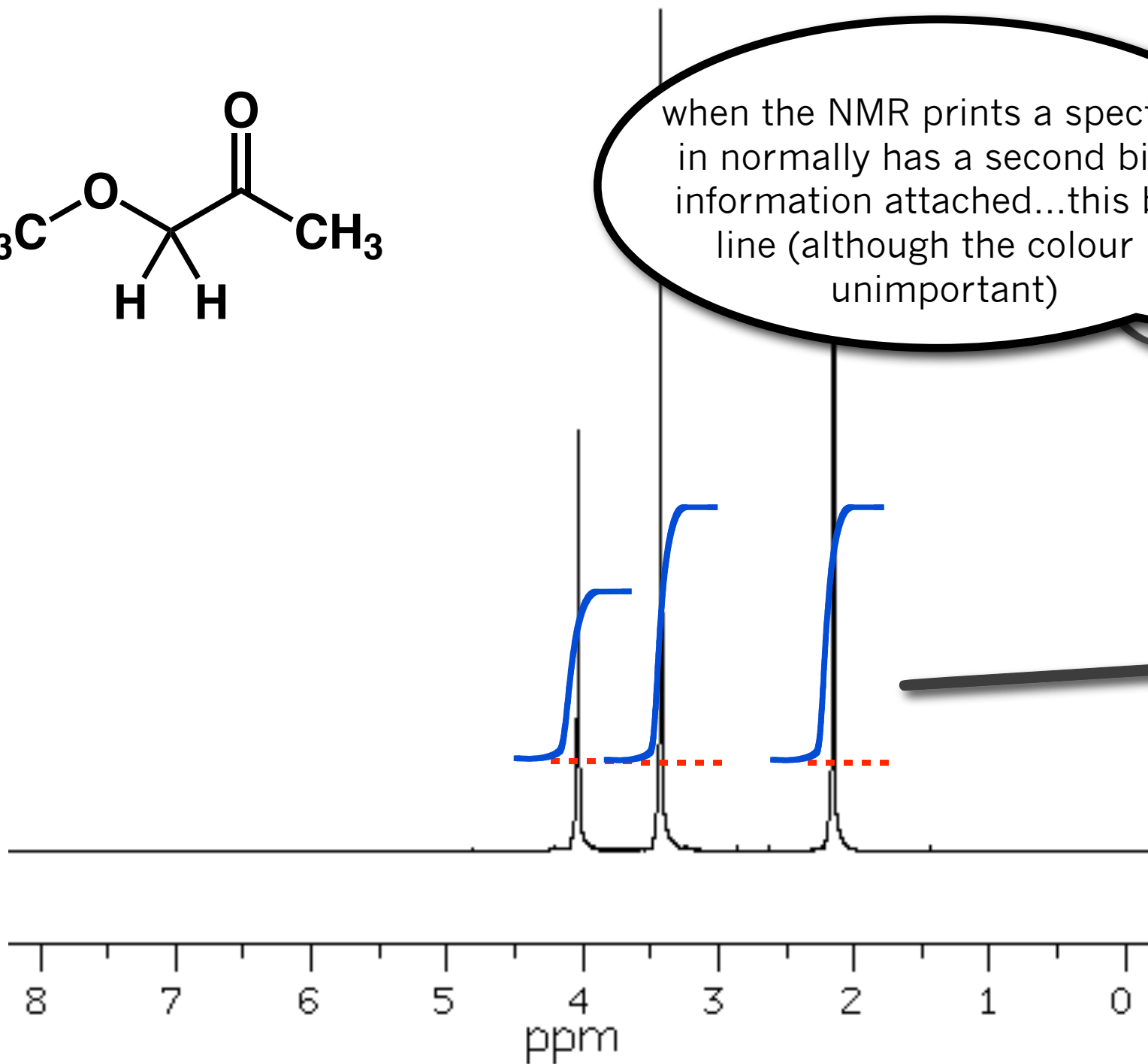
# three chemical environments



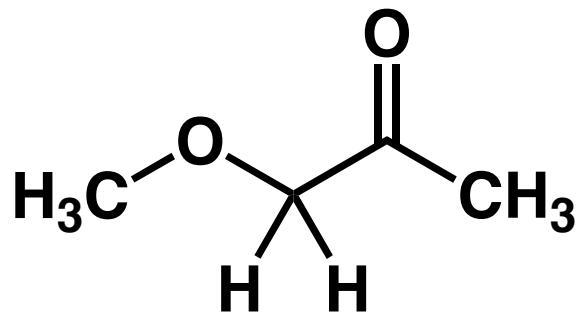
# integration (hydrogen counting)



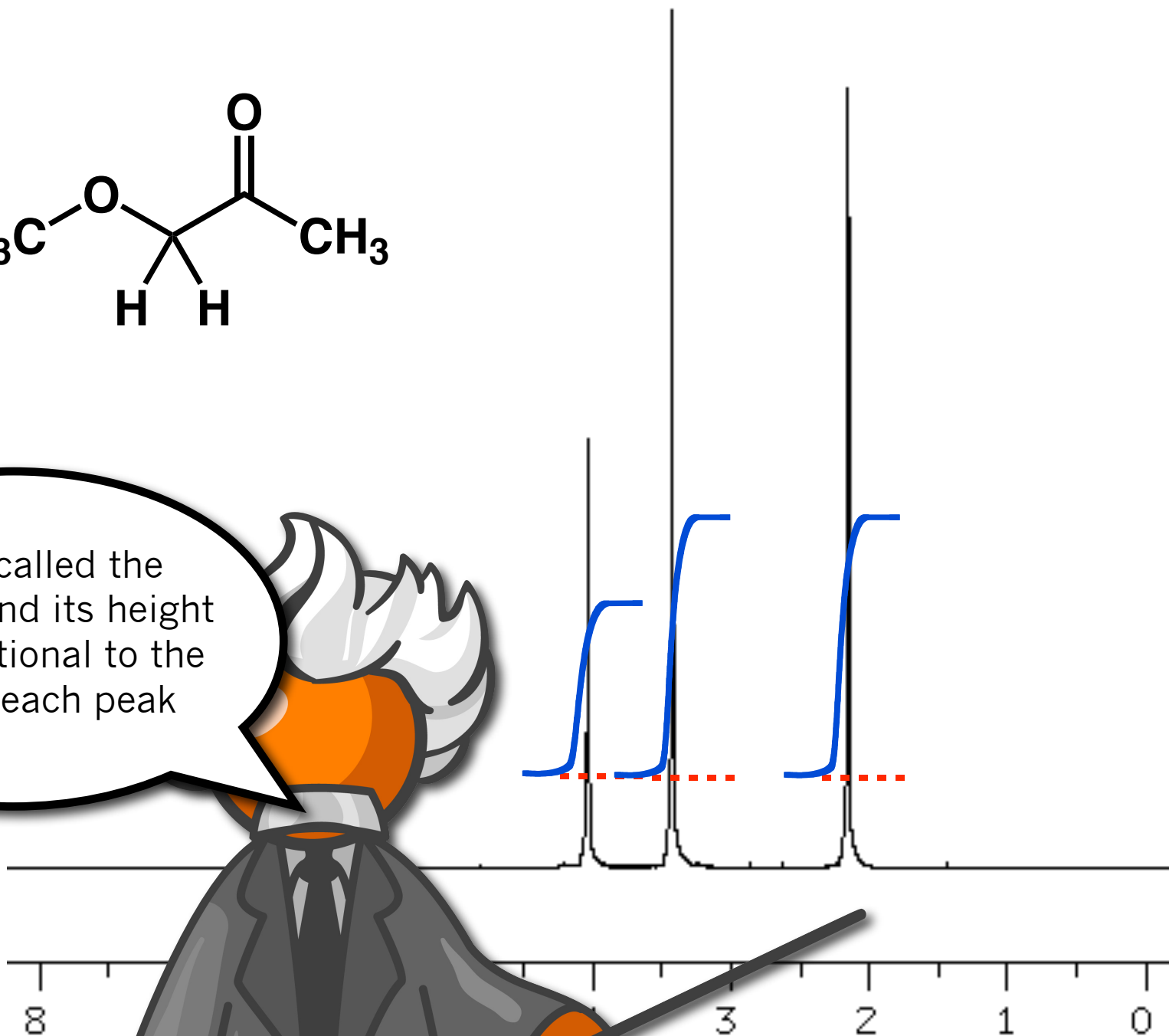
when the NMR prints a spectrum in normally has a second bit of information attached...this blue line (although the colour is unimportant)



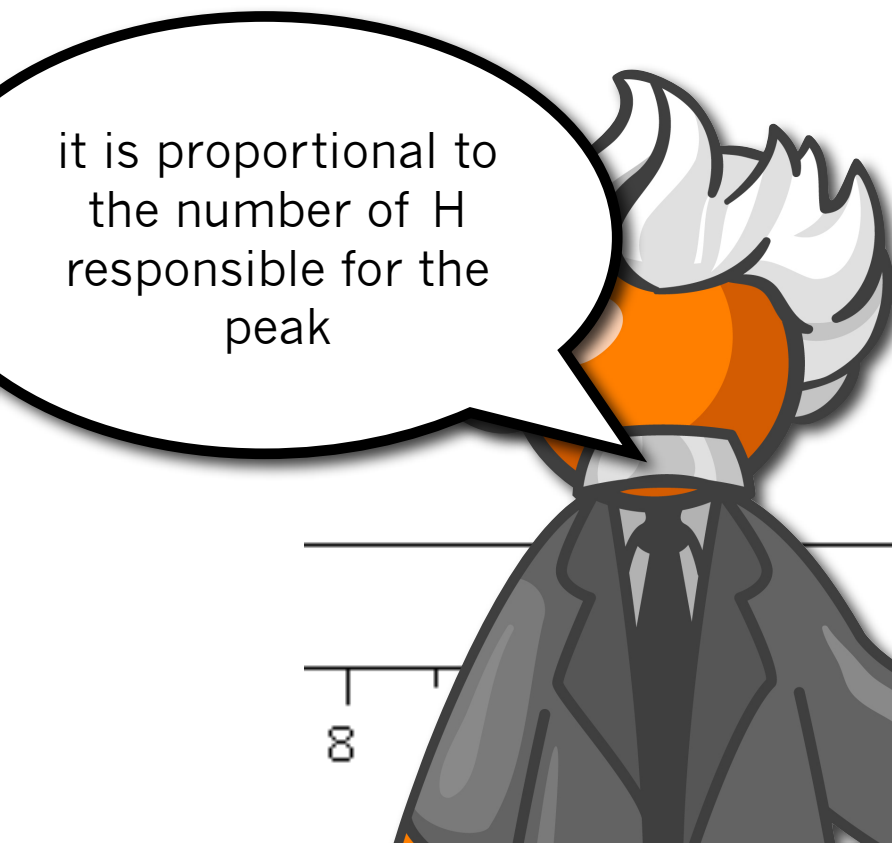
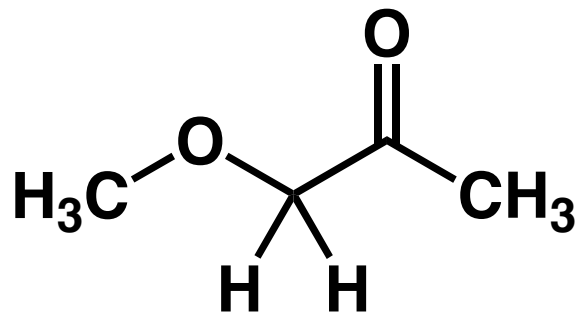
# integration (hydrogen counting)



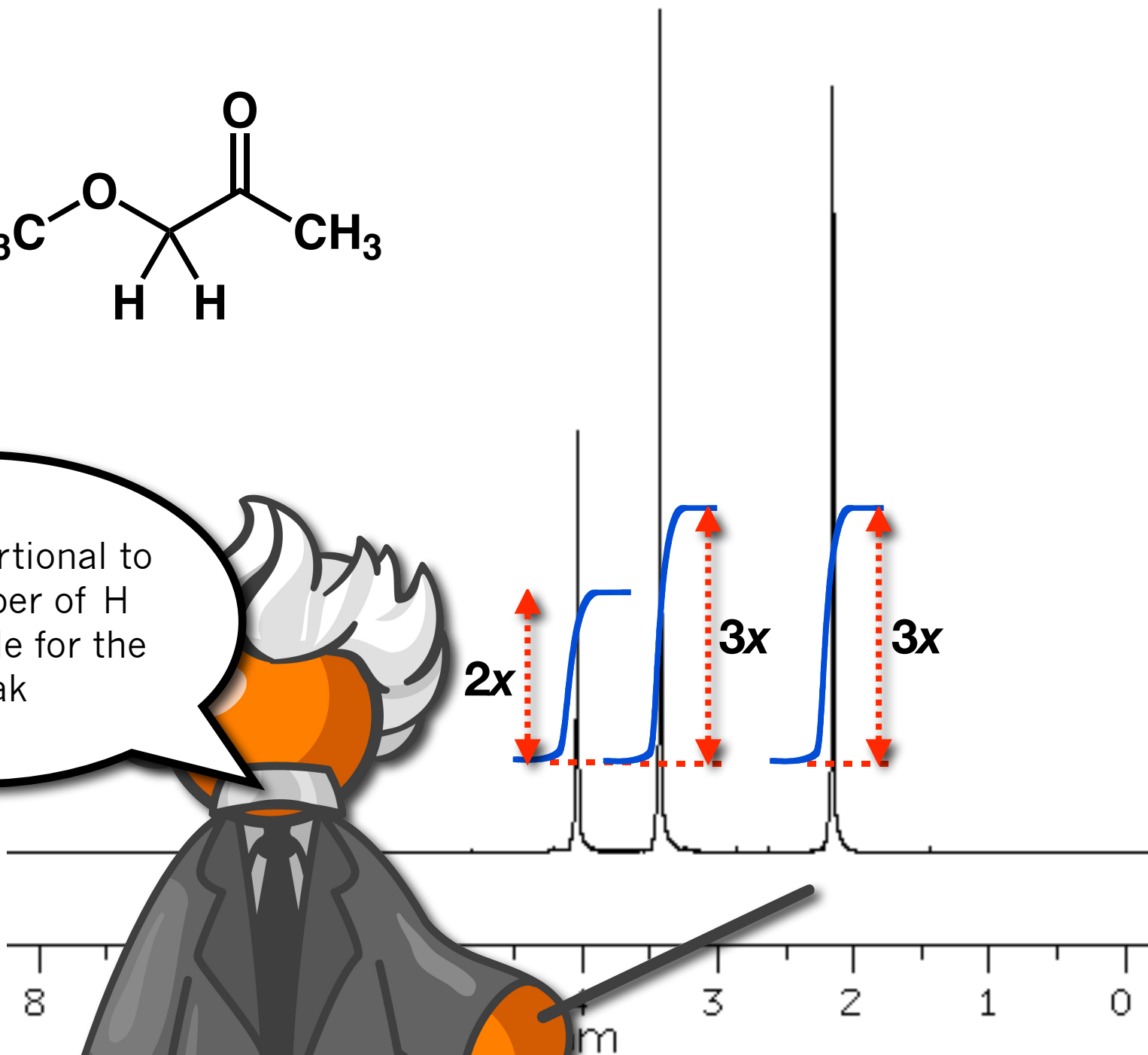
this is called the **integral** and its height is proportional to the area of each peak



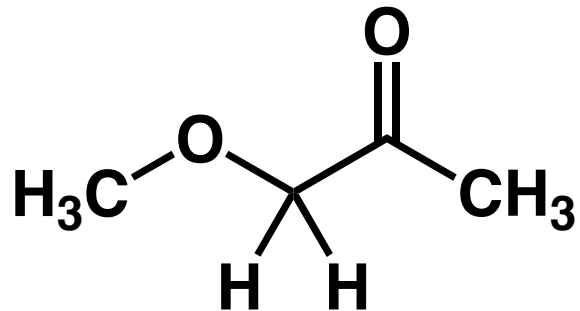
# integration (hydrogen counting)



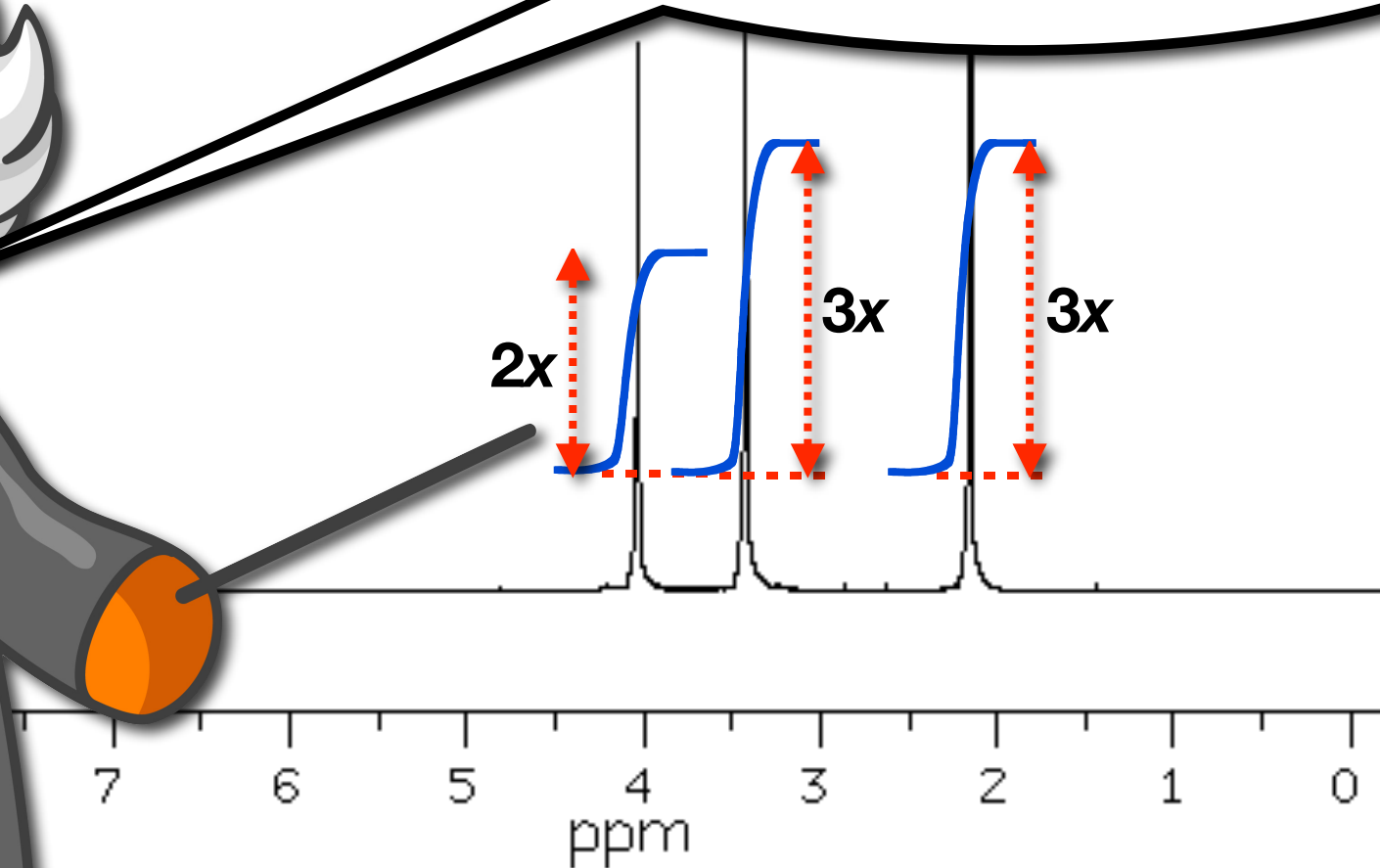
it is proportional to  
the number of H  
responsible for the  
peak



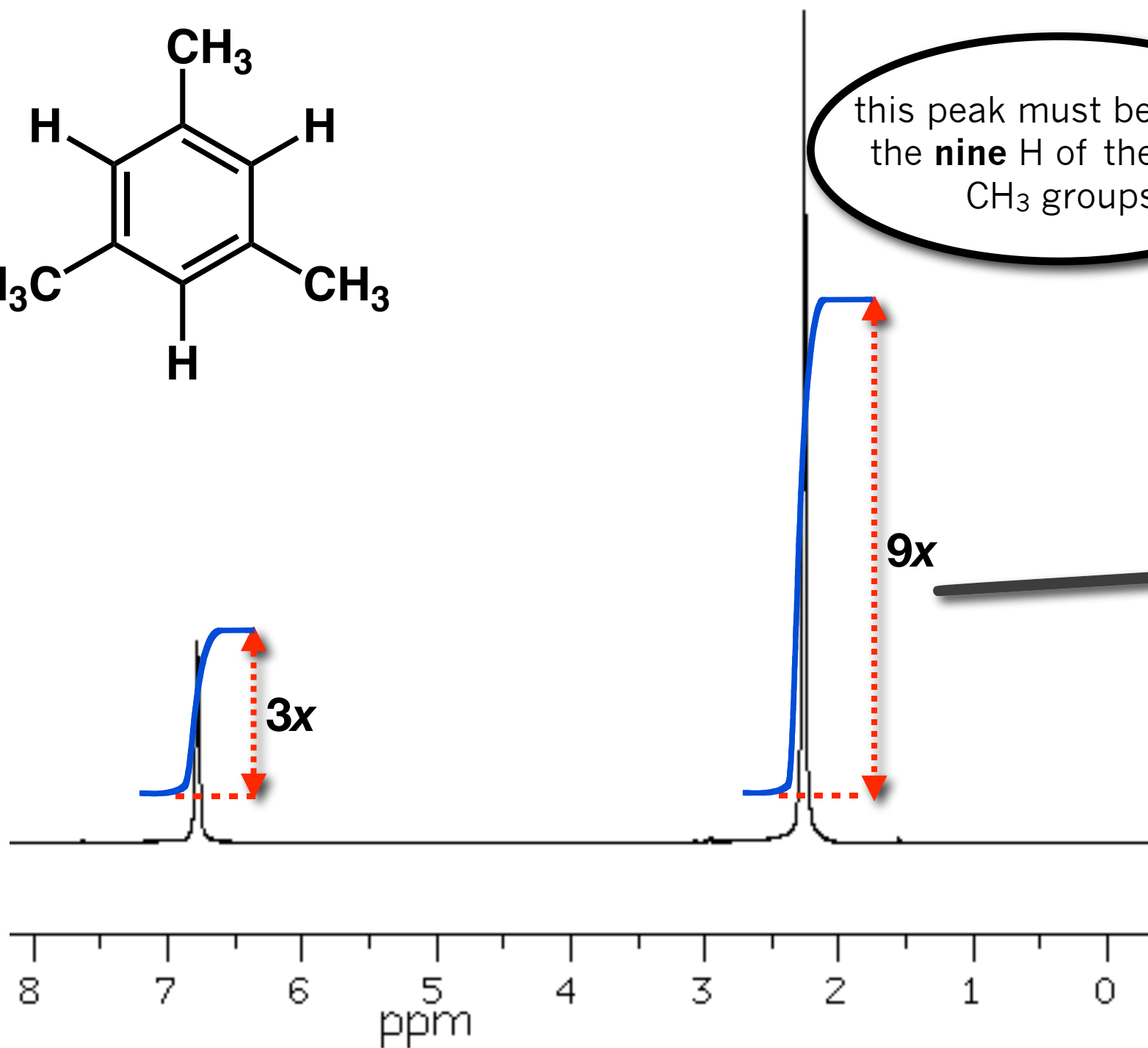
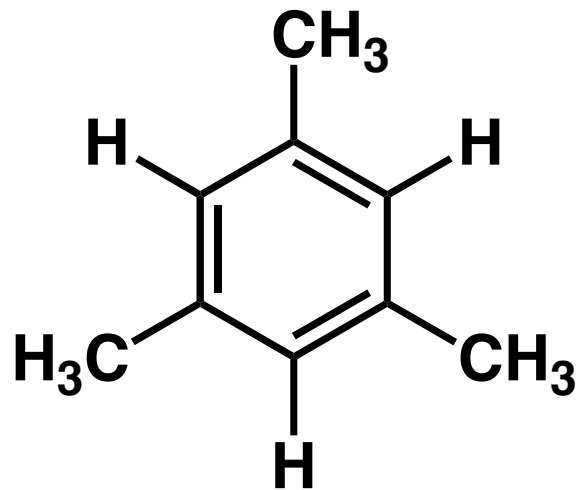
# integration (hydrogen counting)



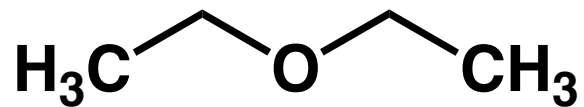
so without any knowledge of polarity (electron withdrawing groups) we know that this peak must be due to the central CH<sub>2</sub> as it is smaller than the other two peaks (which are caused by 3 H each)



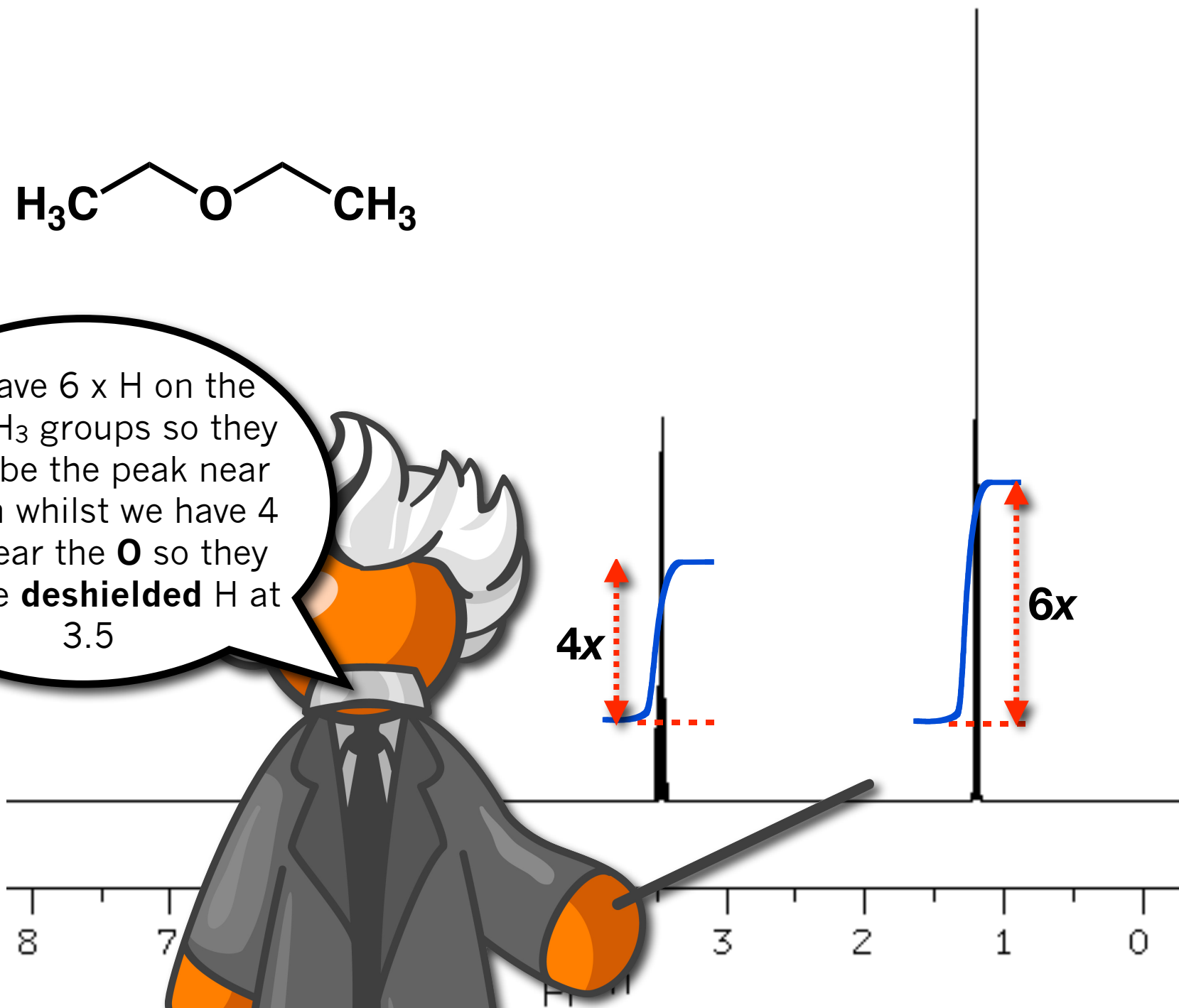
# integration (hydrogen counting)



# integration (hydrogen counting)

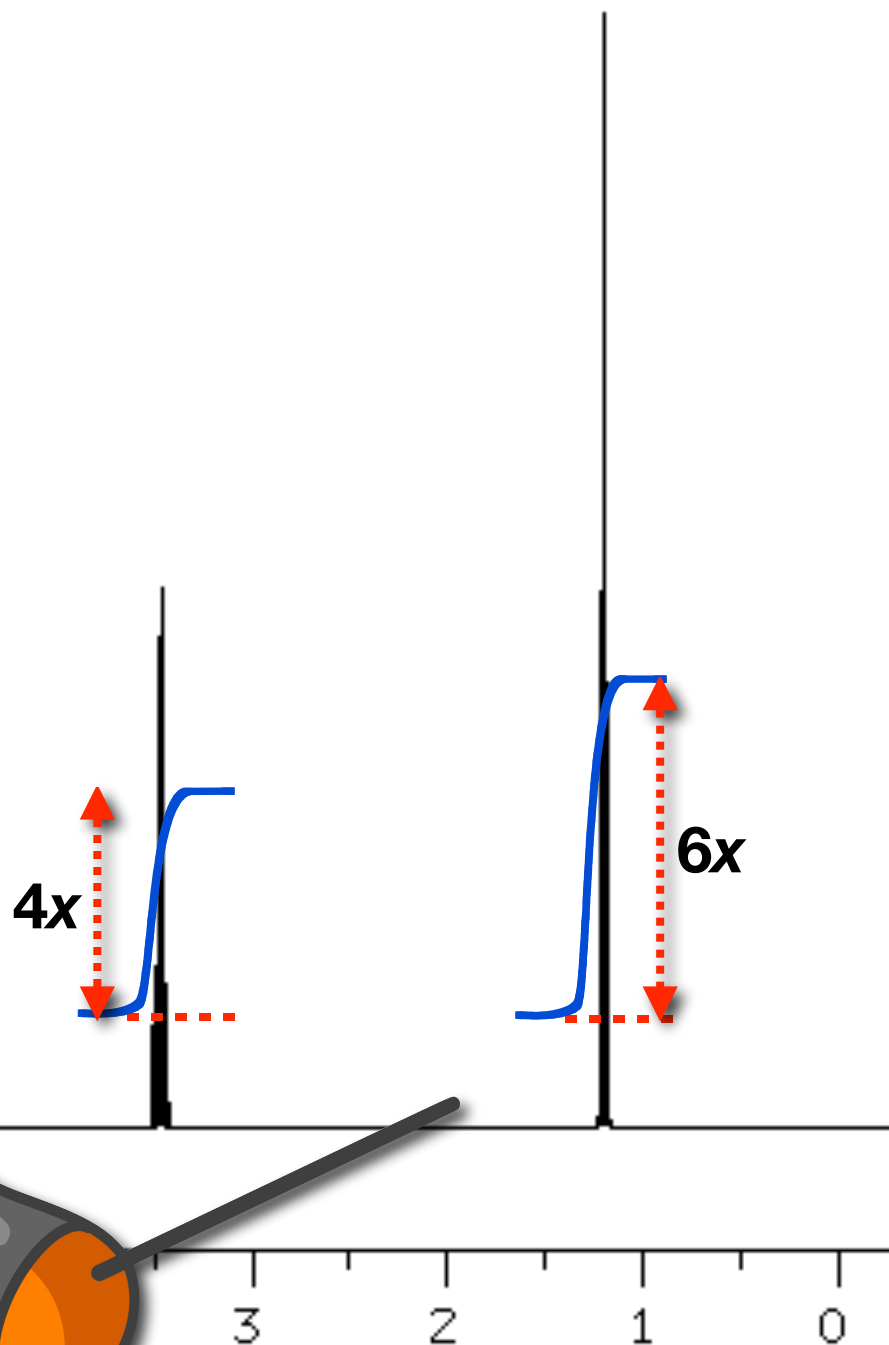
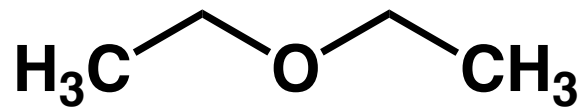


we have 6 x H on the two CH<sub>3</sub> groups so they must be the peak near 1 ppm whilst we have 4 x H near the **O** so they are the **deshielded** H at 3.5



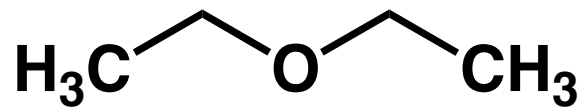


# integration (hydrogen counting)

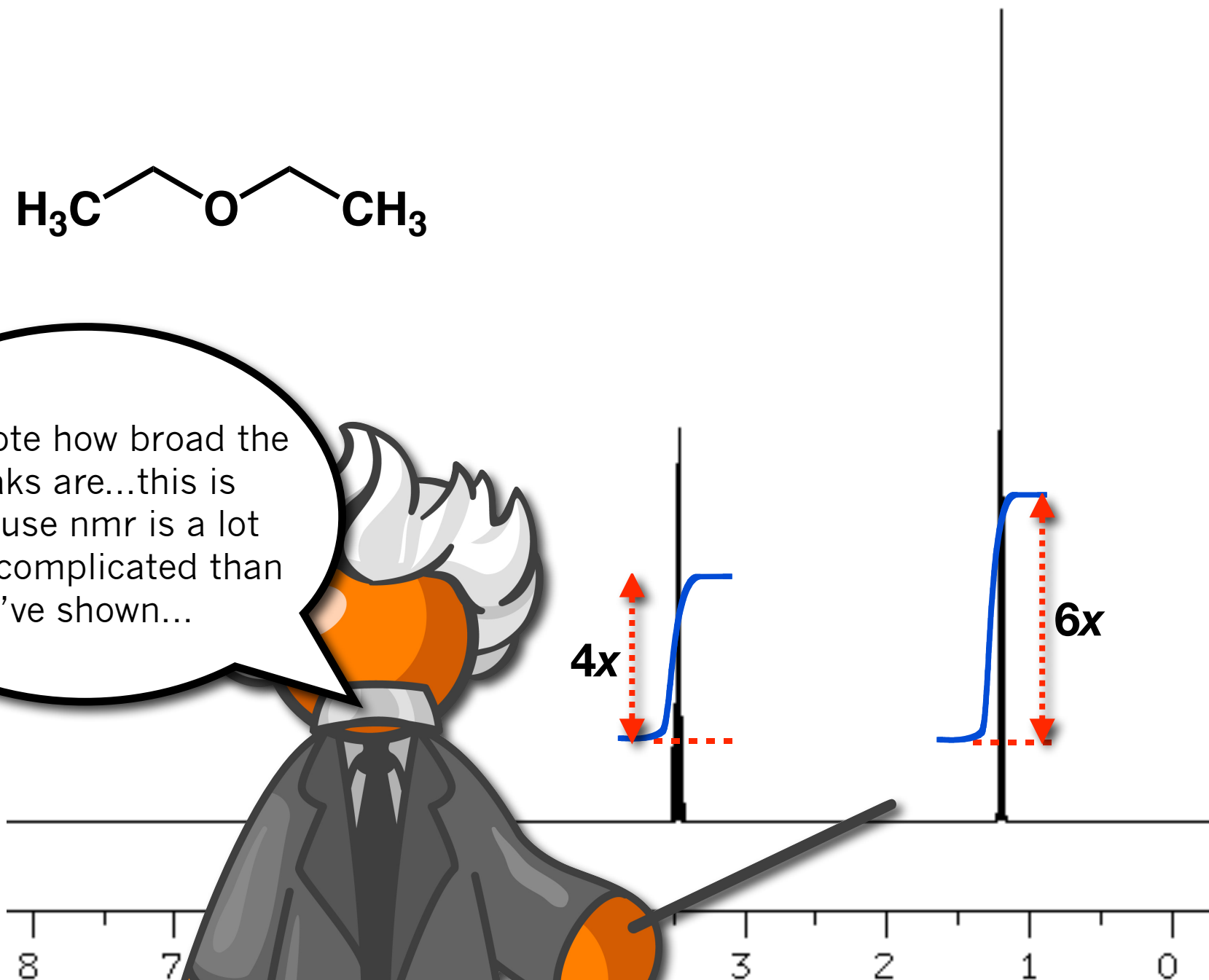


but note...it is only a ratio...ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) would give a very similar spectrum as the ratio 3:2 is the same as 6:4

# integration (hydrogen counting)



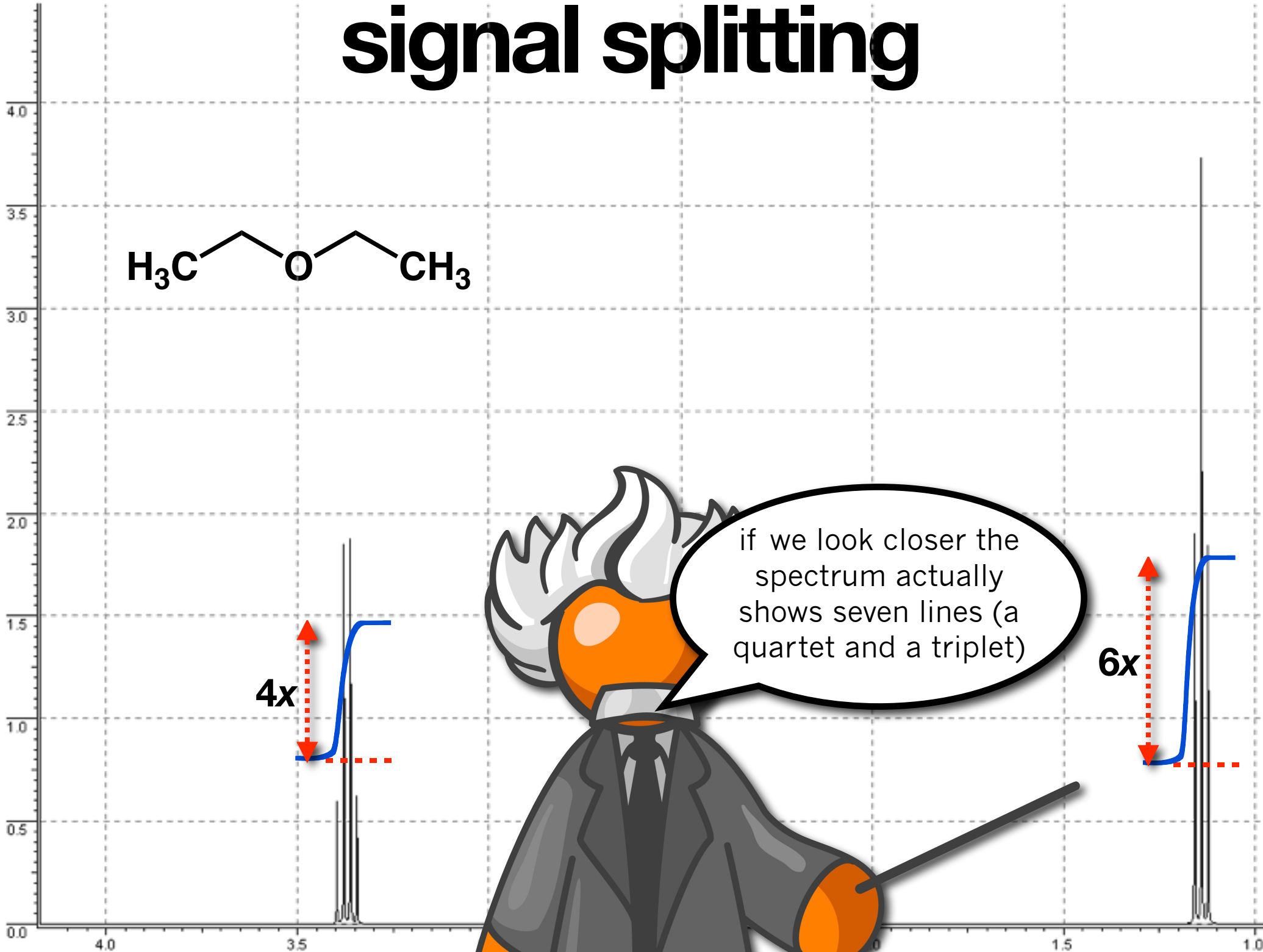
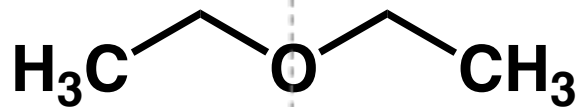
also note how broad the peaks are...this is because nmr is a lot more complicated than I've shown...



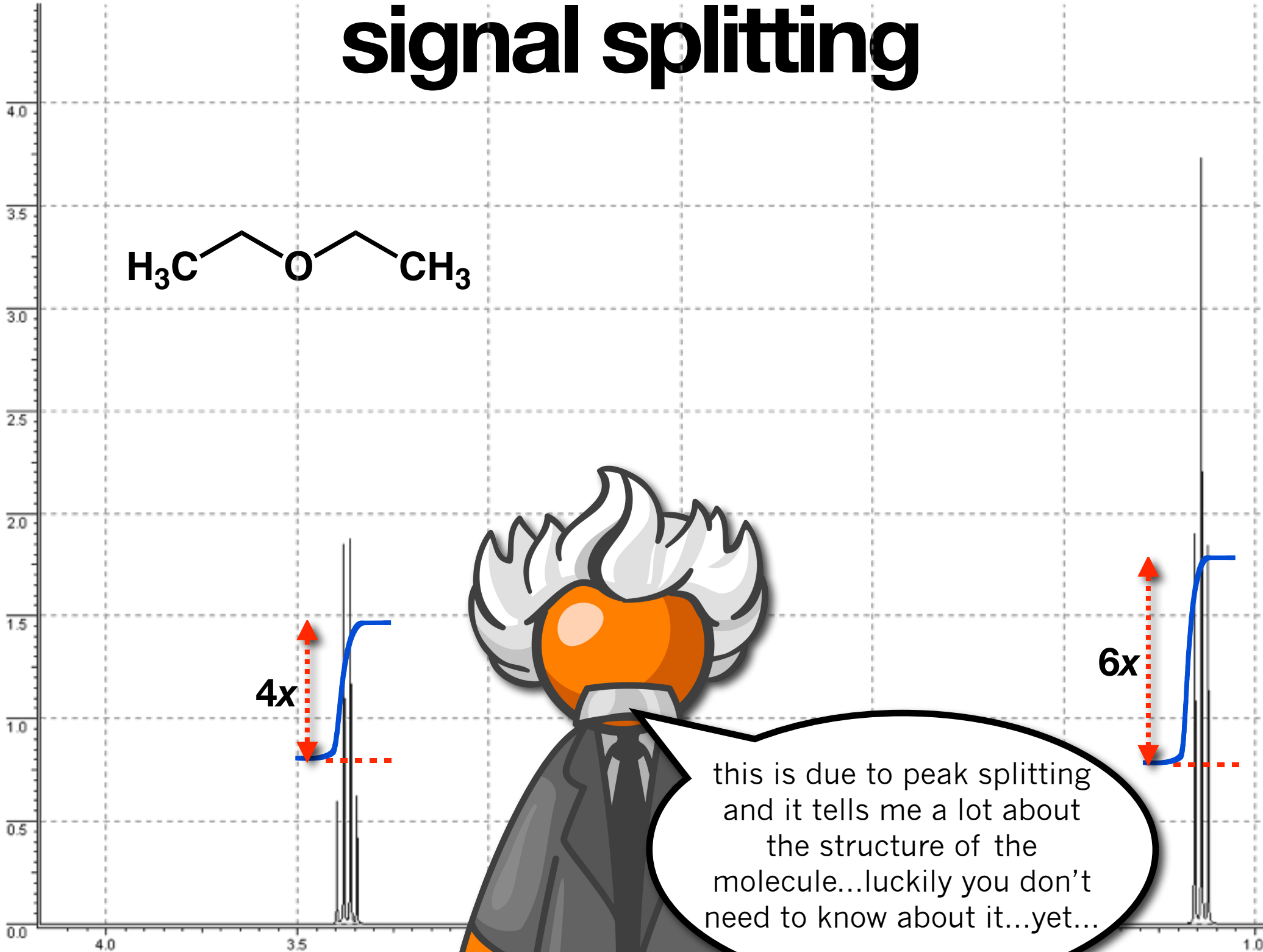
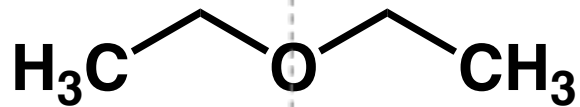
this is chemistry...

...it gets more complicated...

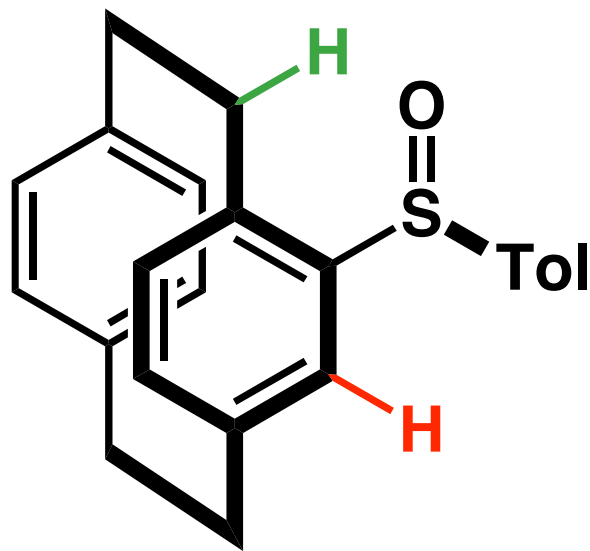
# signal splitting



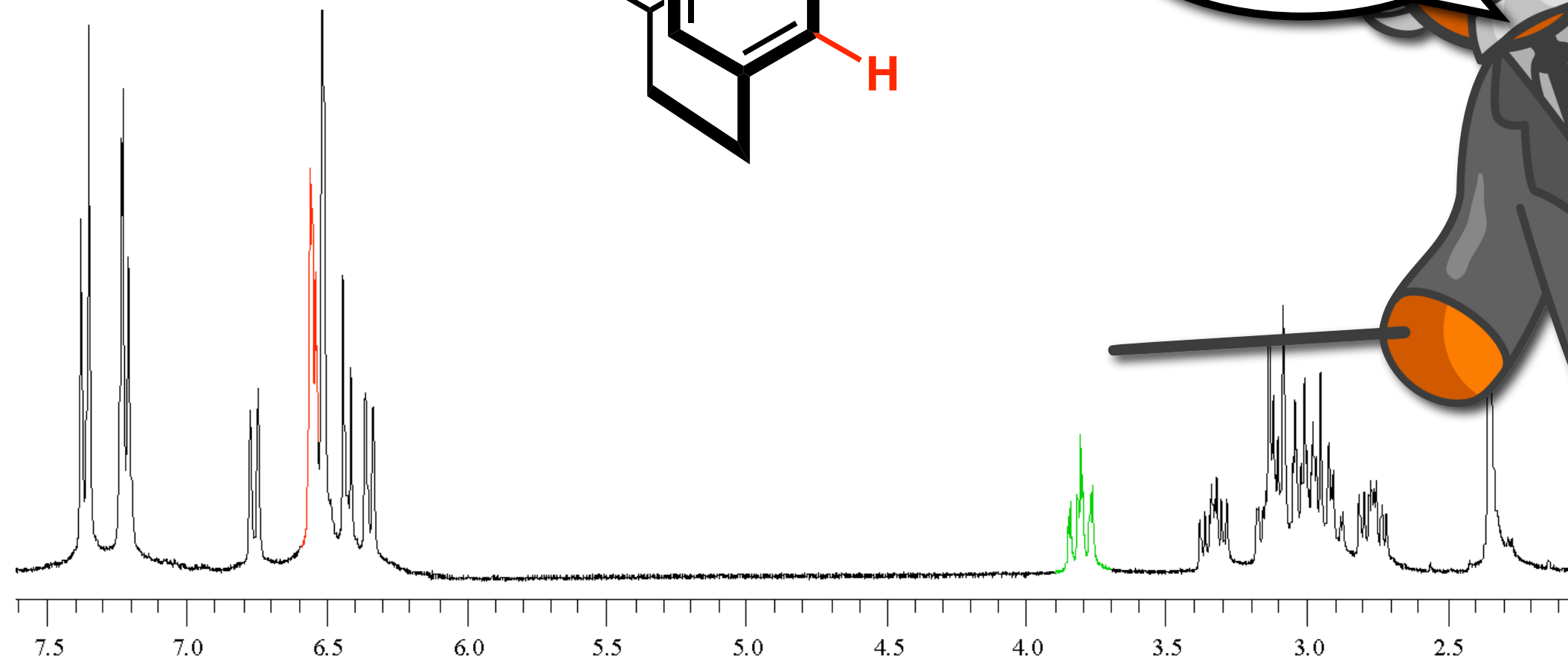
# signal splitting




# a real $^1\text{H}$ NMR spectrum



looks nasty but  
is very useful!



The background of the slide is a complex, abstract fractal pattern. It consists of numerous overlapping, swirling lines and circular motifs in shades of orange, red, and yellow, creating a sense of depth and movement. The pattern is dense and intricate, resembling a microscopic view of a biological structure or a complex mathematical fractal.

what have  
we **learnt?**

all about  
**NMR**