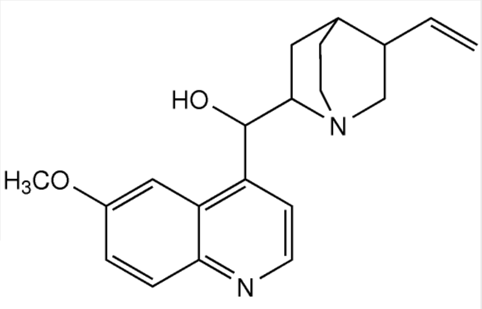
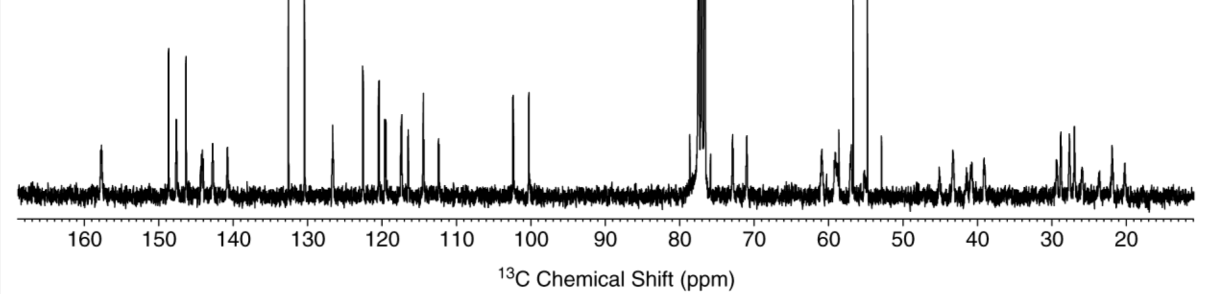
The NMR Spectrum - ^{13}C

Spin-Spin Coupling – ^{13}C NMR

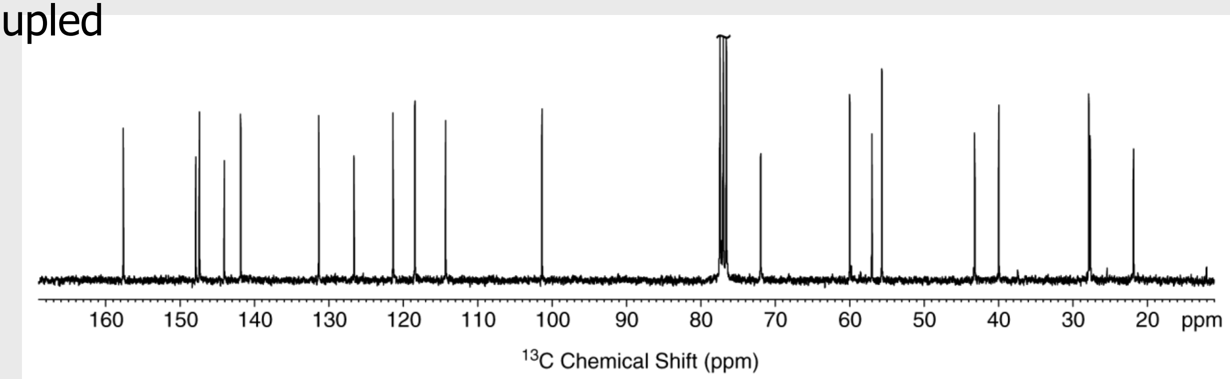
A comparison of two ^{13}C NMR Spectra



^{1}H Coupled (undecoupled)



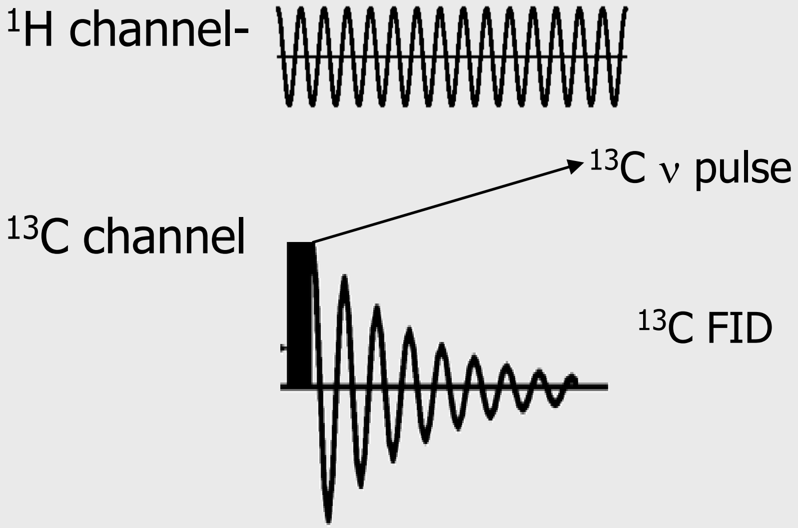
^{1}H Decoupled



Proton Decoupled ^{13}C NMR

6. To simplify the ^{13}C spectrum, and to increase the intensity of the observed signals, a decoupler is used to remove the spin effects of the ^{1}H nucleis

7. A second RF generator irradiates at the ^{1}H resonance frequency causing the saturation – effectively averaging all their spin states to zero



Nuclear Overhauser Effect (NOE)

1. A phenomenon observed with proton-decoupled ^{13}C-NMR is that the intensity of the signal for a given ^{13}C increases versus the proton-coupled spectrum roughly proportional to the number of protons attached

2. The degree of this signal enhancement is called the Nuclear Overhauser Enhancement (NOE) and is a heteronuclear effect

6. This effect is general, and appears anytime when one of two types of atoms is irradiated, while the spectrum of the other is observed

   In this case, while the ^{1}H population is irradiated to saturation, the ^{13}C is observed

Nuclear Overhauser Effect (NOE)

4. The effect can be a positive or negative one, but for the case of 1H-13C, the effect is positive

5. The maximum enhancement is given by:

$$\mathrm{nOe}_{\mathrm{max}} = \frac{1\,(\gamma_{\text{irradiated}})}{2\,(\gamma_{\text{observed}})}$$

This value is what is added to the observed intensity in the coupled spectrum to give the intensity observed in the decoupled spectrum:

$$\text{total predicted intensity} = 1 + \mathrm{NOE}_{\mathrm{max}}$$

Nuclear Overhauser Effect (NOE)

6. For ^{1}H – ^{13}C, nOe = ½ (267.5/67.28) = 1.988

7. This indicates a maximum enhancement of almost 200% is possible

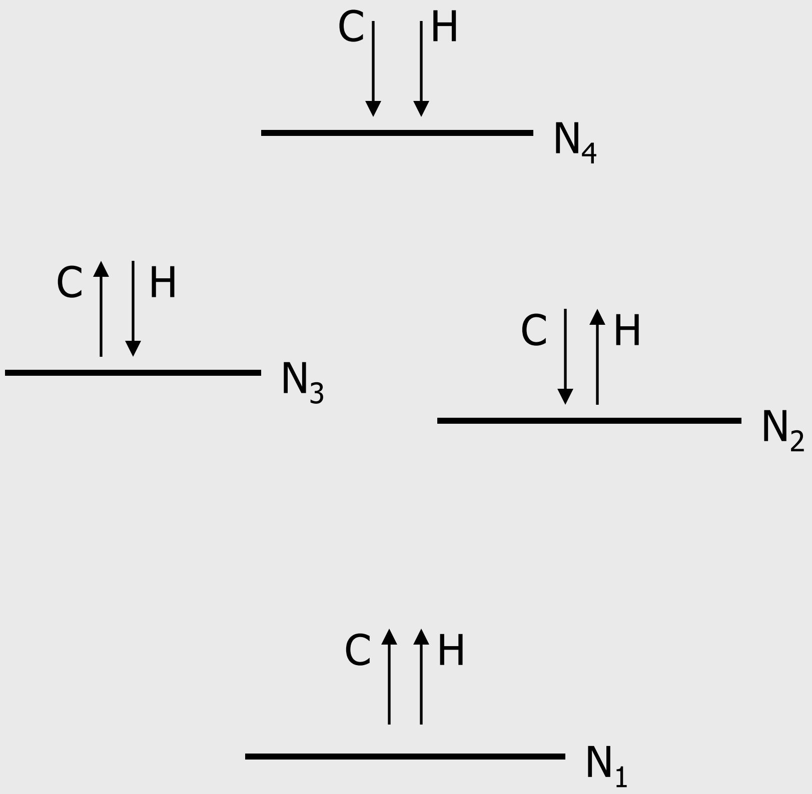
8. NOE operates in both directions – ^{13}C nuclei (if decoupled) would enhance the signal of ^{1}H – however, this signal would be weak due to the low prevelance of ^{13}C

9. Because NOE for ^{13}C – ^{1}H operates in the opposite direction (a rare nuclei always bound to an abundant one) it is a useful probe into structural assignments

10. The NOE effect is very short-ranged, falling off as $1/r^3$ the distance between the nuclei

Nuclear Overhauser Effect (NOE) – Origin of the effect

Observe the following energy diagram:



Here, we see an isolated two spin system between a single carbon and single hydrogen atom

The effects of coupling are left out for simplicty

Shown are the four combinations of spin states of these two nuclei, $N_{1\text{-}4}$

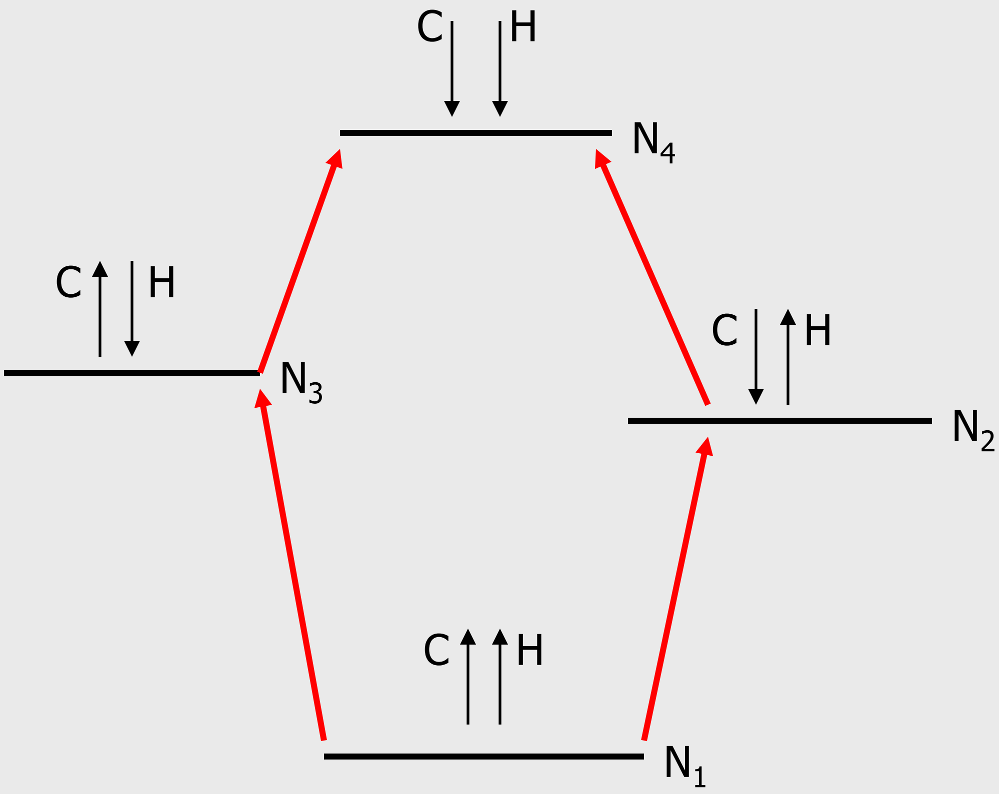
As expected, the two energy states where both are spin up or spin down are the lowest and highest energy states

The "mixed" states are roughly degenerate in energy

Nuclear Overhauser Effect (NOE) – Origin of the effect

Quantum mechanics dictates that allowed transitions involve only one change of spin at a time – single quantum transitions

The allowed transitions are shown in red



Nuclear Overhauser Effect (NOE) – Origin of the effect

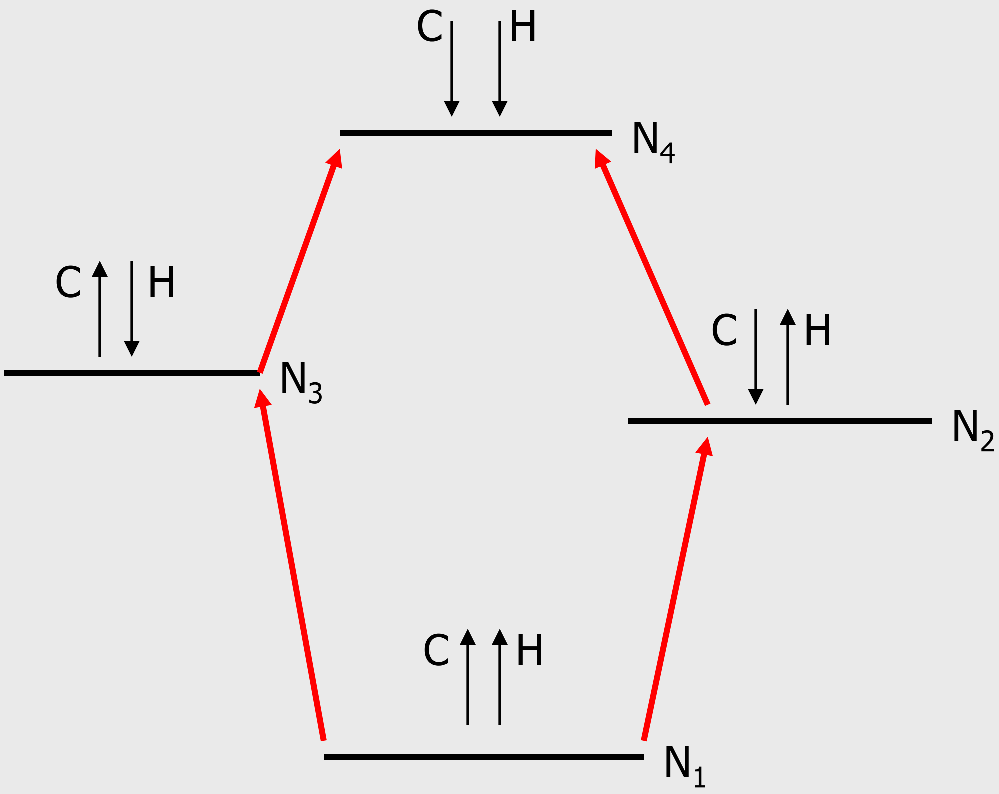
Let's set the equilibrium population of the two degenerate states to be **B**

The N_1 level would be lower than **B** by a small amount, δ

The N_4 level would be higher than **B** by a the same amount, δ

The signal for a ^{13}C in this case would be proportional to δ at equilibrium

The two ^{13}C transitions are $N_1 - N_2$ and $N_3 - N_4$



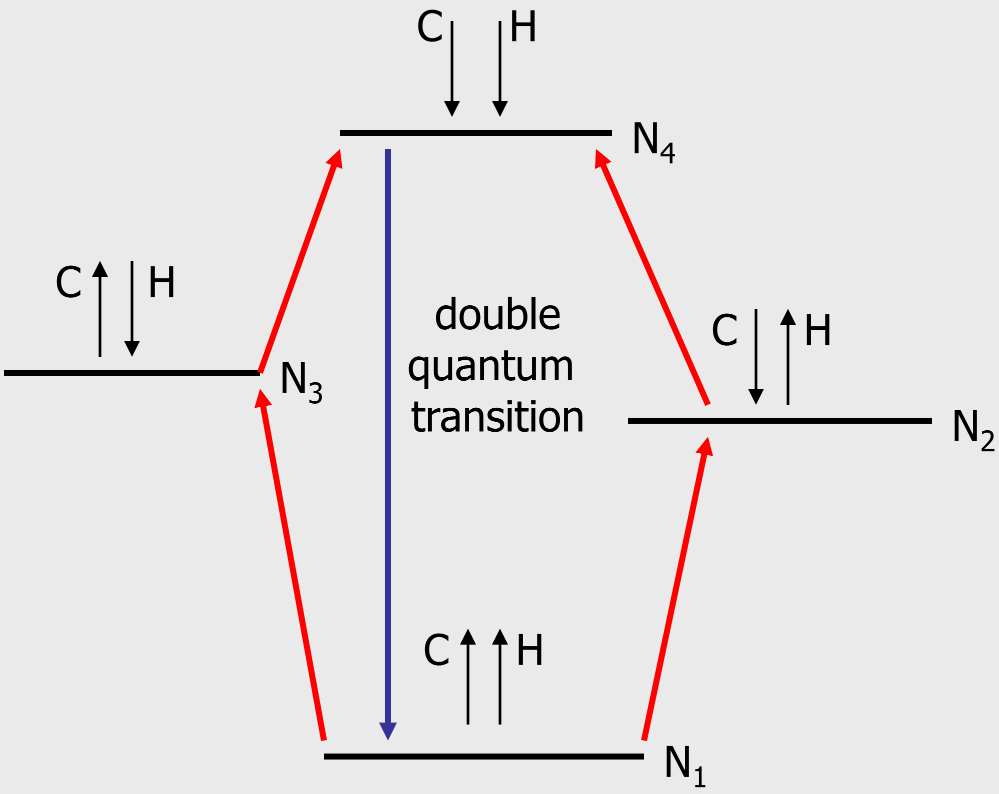
Nuclear Overhauser Effect (NOE) – Origin of the effect

When a decoupler is used, the 1H populations are disturbed from their equilibrium values

Relaxation processes restore these disturbed populations to their equilibrium values

One such process is a double-quantum transition, where both the C and H nuclei relax simultaneously (blue line)

This "leak" in the upper state enhances the population of the lower energy state for carbon – the excess population is larger – and the signal intensifies



Relaxation Processes

1. The generation of the FID from either ^{1}H or ^{13}C nuclei comes from the relaxation of the excess population from the excited to the ground equilibrium population in the magnetic field

2. There are two mechanisms for this relaxation:

3. T_1 process – called spin-lattice relaxation or longitudinal – here spins lose their energy by transferring it to the surroundings (lattice) as heat in the direction of the field

4. T_2 process – called spin-spin relaxation – here the spin is transferred to another nuclei in the plane in which the signal is detected

   It is an entropy process, and causes the signal of the proton population to *lose phase with the other excited nuclei*

Relaxation Processes

5. The importance of these two relaxation types is low for ^{1}H NMR, the relaxation times are generally fast, and any information from them is usually lost
6. ^{13}C has a long relaxation period – and the effect of T_2 type decay is pronounced for a nuclei such as a quaternary carbon which has no adjacent nuclei capable of transferring spin to
7. Ipso, quaternary and carbonyl carbons have low intensities due to this effect – since many hundreds of pulses are used to generate a ^{13}C spectrum, the delay between pulses is often short for time constraints
8. These carbons therefore do not decay effectively before the next pulse, weakening the signal

DEPT – Distortionless Enhancement by Polarization Transfer

1. This is the first advanced 1-D technique we will consider

2. As we just pointed out, the relaxation times for ^{13}C are strongly a factor of T_2 processes – where spin is transferred and the resulting signal shifts out of phase with what is being detected

3. If different pulse widths are applied in a ^{13}C determination, the resulting phase shift (and signal intensity) will be different depending on how many ^{1}H atoms the ^{13}C can transfer its spin to

4. In a typical DEPT experiment, a 45, 90 and 135 pulse are applied successively to the sample and the results compared to the original carbon spectrum

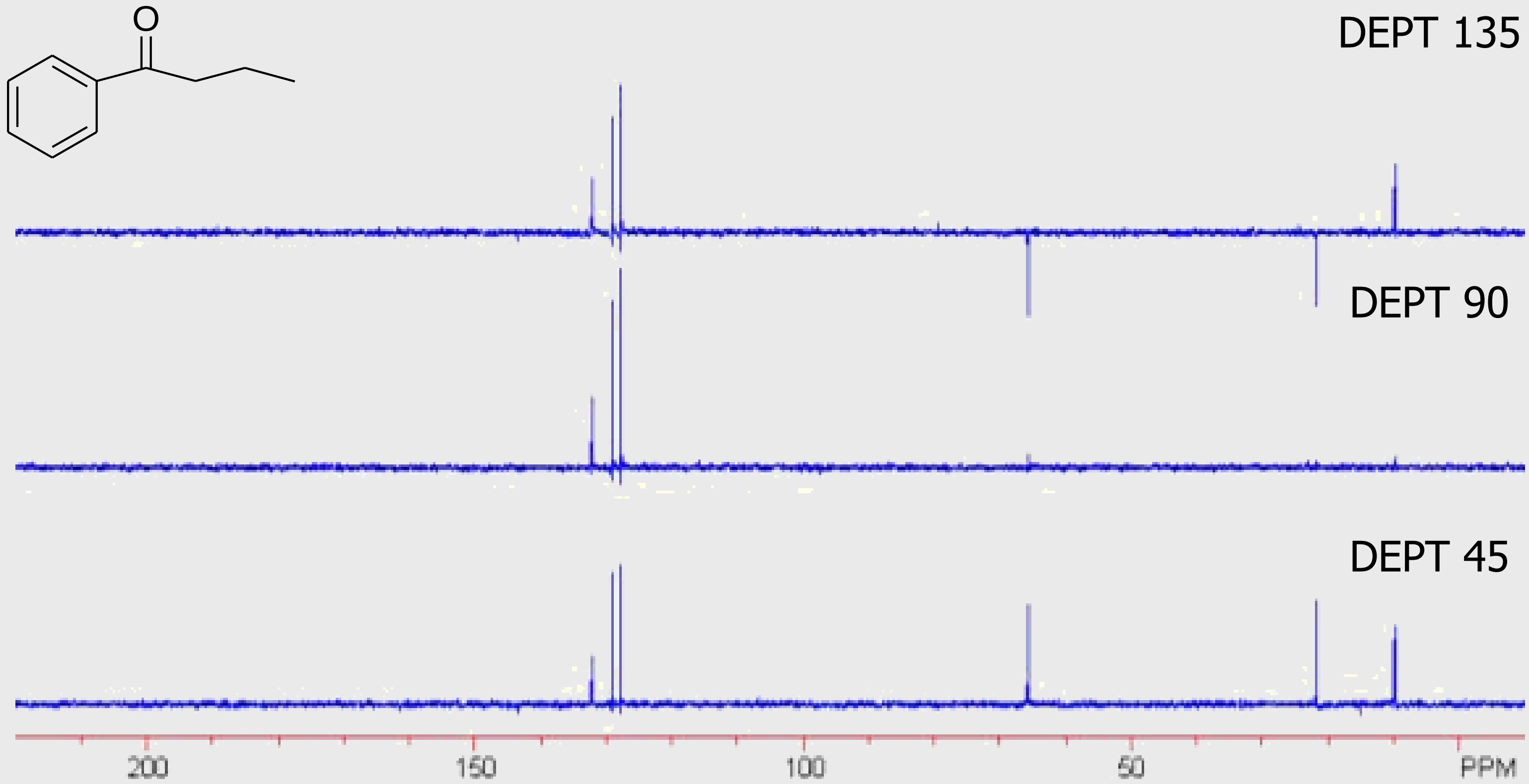
DEPT – Distortionless Enhancement by Polarization Transfer

5. At each pulse angle, a different effect is observed for quaternary, methine, methylene and methyl carbons:

DEPT Pulse Sequence	methyl	methylene	methine	quaternary
DEPT-45	Positive peak	Positive peak	Positive peak	Not observed
DEPT-90	No obs. peak	No obs. peak	Positive peak	Not observed
DEPT-135	Positive peak	Negative Peak	Positive Peak	Not observed

DEPT – Distortionless Enhancement by Polarization Transfer

6. The spectra are typically illustrated together to allow the operator to find the substitution of each carbon in the spectrum:



Integration

1. For reasons of long relaxation times, NOE, and low population abundance, ^{13}C spectra are not integrated
2. For ^{1}H NMR most nuclei relax in a second or two, the intensity of the signal is only proportional to the observation of the excess population
3. Relaxation times for ^{13}C are prohibitively long given the number of pulses needed to generate a spectrum – signal intensity, already low is more a factor of T_1, T_2 and NOE