2/2 Great work!

CH-314 Structural Analysis
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Jigsaw 2B

Hore Section 2.3. Origin of chemical shifts

1. **The lowest energy electronic transitions in alkanes and alkenes are approximately 10 eV and 8 eV, respectively. Predict whether saturated (sp^3) or unsaturated (sp^2) ^{13}C nuclei have larger chemical shifts. Assume the paramagnetic contribution is the dominant contribution. Justify the assumptions made in this exercise.**

The lowest-energy electronic transitions occur at approximately 10eV for alkanes and (eV for alkenes. If the paramagnetic contribution σ_p dominates, it follows that:

$$\sigma_p \propto -\frac{1}{\Delta}\langle\frac{1}{r^3}\rangle$$

With Δ *the energy gap between ground and excited electronic states.*

As such, a smaller Δ gives a larger magnitude of σ_p. Since the total shielding is:

$$\sigma = \sigma_d + \sigma_p$$

Since σ_p is negative the overall σ is smaller. The chemical shift is related by the following equation:

$$\delta \approx 10^6(\sigma_{ref} - \sigma)$$

So, a smaller σ results in a larger δ. Since alkenes (sp2) have the smaller energy gap compared to alkanes (sp3), the σ_p will have a higher magnitude. Therefore, sp2 ^{13}C nuclei exhibit larger chemical shifts than sp3 ^{13}C nuclei.

2. **[From lecture] ^1H has a gyromagnetic ratio of 2.68×10^8 rad·s^{-1}T^{-1}.**

   a. **What are the relative populations of the α and β spin states of a proton in a 11.7 T spectrometer, at both room temperature and −150°C? The equation for the Boltzmann distribution is given below, where $k = 1.381 \times 10^{-23}$ J/K. Hint: Use the Larmor frequency to determine the energy difference.**

$$\mathbf{\frac{N_\beta}{N_\alpha} = exp\left(-\frac{\Delta E}{kT}\right)}$$

The Larmor frequency:

$$\omega_0 = -\gamma B_0 = 2.68 \cdot 10^8 \cdot 11.7 = 3.1356 \cdot 10^9\, rad \cdot s^{-1}$$

The energy difference between spin states is thus:

$$\Delta E = \hbar\omega = 1.05457 \cdot 10^{-34} \cdot 3.1356 \cdot 10^9 \approx 3.307 \cdot 10^{-25} J$$

We can now use the Boltzmann distribution at 298K (RT):

$$\frac{\mathrm{N}_\beta}{\mathrm{N}_\alpha} = \exp\left(-\frac{\Delta\,\mathrm{E}}{\mathrm{kT}}\right) = exp\left(-\frac{3.307 \cdot 10^{-25}}{1.381 \cdot 10^{-23} \cdot 298}\right) \approx 0.9999$$

And at -150 ºC:

$$\frac{\mathrm{N}_\beta}{\mathrm{N}_\alpha} = exp\left(-\frac{\Delta\,\mathrm{E}}{\mathrm{kT}}\right) = exp\left(-\frac{3.307 \cdot 10^{-25}}{1.381 \cdot 10^{-23} \cdot 123.15}\right) \approx 0.9998$$

So, in both vases $N_\beta$is very close to N_α. There is only a tiny excess of the lower energy α state.

b. **Based only on the answers to the previous question (i.e., ignoring changes in state of the sample, equipment logistics, etc.), which of these two temperatures would you choose to run an experiment? Why?**

The preferred temperature to perform an experiment would be -150°C, since the population difference between the α and β spin states increases according to the Boltzmann distribution, as seen in 2.a. A larger difference between N_α and N_β corresponds to a higher polarization:

$$P = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \tanh\left(\frac{\Delta E}{2kT}\right)$$

This higher polarization increases the net magnetization of the sample, resulting in a stronger and therefore better NMR signal.

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1. The lowest energy electronic transitions in alkanes and alkenes are approximately 10 eV and 8 eV, respectively. Predict whether saturated (sp^3) or unsaturated (sp^2) ^{13}C nuclei have larger chemical shifts. Assume the paramagnetic contribution is the dominant contribution. Justify the assumptions made in this exercise.

Unsaturated sp^2 has a larger chemical shift because the electronegative hydrogens attract electron density from the carbons. This is justified by the paramagnetic shielding constant $\sigma_p \propto -\frac{1}{\Delta}\langle\frac{1}{R^3}\rangle$

$\Rightarrow$ smaller Δ, larger shielding constant

2. [From lecture] ^1H has a gyromagnetic ratio of 2.68×10^8 rad·$s^{-1}T^{-1}$.

   a. What are the relative populations of the α and β spin states of a proton in a 11.7 T spectrometer, at both room temperature and −150°C? The equation for the Boltzmann distribution is given below, where $k = 1.381 \times 10^{-23}$ J/K. Hint: Use the Larmor frequency to determine the energy difference.

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT}\right) \qquad w_0 = -B\gamma$$

Larmor frequency : $\nu_0 = -\frac{|\gamma| B_0}{2\pi}\overbrace{(1-\bar{\sigma})}^{\approx 1}$

$|\Delta E| = h\nu_0 = 6{,}63 \cdot 10^{-34}\,J \cdot s^{-1} \frac{-2{,}68 \cdot 10^8\,rad\,s^{-1}T^{-1} \cdot 11{,}7\,T}{2\pi} = 3{,}3 \cdot 10^{-25}\,J$

RT : $\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{3{,}3 \cdot 10^{-25}}{1{,}381 \cdot 10^{-23} \cdot 298{,}15}\right) = 0{,}99992$ At $-150°C \Rightarrow \frac{N_\beta}{N_\alpha} = 0{,}99981$

   b. Based only on the answers to the previous question (i.e., ignoring changes in state of the sample, equipment logistics, etc.), which of these two temperatures would you choose to run an experiment? Why?

Ignoring logistics, we would choose to run the experiment at -150°C, since there is more population spread out on the α and β spin states, meaning the spectra would have better resolution The noise is also proportional to $\sqrt{T}$, meaning there will be less noise at lower temperatures.

Resolution (separation between peaks) doesn't depend on the spin state population. Having a larger population difference means we have would get more signal, since NMR measures the transitions between spin states

2/2 Very nice!

1. Alkane sp^3 $\Delta = 10\,eV$ VS Alkene sp^2 $\Delta = 8\,eV$

- Assumpt° $\sigma = \sigma_d + \sigma_p \approx \sigma_p$, with $\sigma_p \propto -\frac{1}{\Delta}\langle\frac{1}{R^3}\rangle$
  Knowing that $\Delta(sp^3) > \Delta(sp^2)$, then $|\sigma_p|_{sp^3} < |\sigma_p|_{sp^2}$
  $\sigma_{sp^3} > \sigma_{sp_2}$

- From $\nu_{NMR} = \frac{\gamma B_0 (1-\sigma)}{2\pi}$, we get $\nu_{sp3} < \nu_{sp^2}$
- Converting into chemical shift with $\delta = 10^6 \frac{\nu - \nu_{ref}}{\nu_{ref}}$, it can be concluded that $\delta(sp^2) > \delta(sp^3)$.

- Justificat° of assumpt° made : no diamagnetic contribut°. Diamagnetic contribut° arises from e⁻ circulat° in atomic or molecular orbital. As this contribut° is fairly identical for C−C and C=C, it can be neglected.

2. a)

$$\omega_0 = \gamma B_0 = 3.14 \cdot 10^9 \text{ rad } s^{-1}$$

$$\Delta E = \hbar\omega_0 = 1.05 \cdot 10^{-34} \cdot 3.14 \cdot 10^9 \approx 3.304 \cdot 10^{-25} \text{ J}$$

At $T_1 = 298\,k$

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT_1}\right) = 0.9999197$$

At $T_2 = 123.15\,k$

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT_2}\right) = 0.9998056$$

$$N_\alpha + N_\beta = 1$$

$$\frac{N_\beta}{N_\alpha} = x \qquad N_\beta = x N_\alpha \rightarrow N_\alpha = \frac{1}{1+x} \qquad N_\beta = \frac{x}{1+x}$$

At 298 k $x = 0.9999197$ $N_\alpha \approx 0.5000201$ $N_\beta \approx 0.4999799$

At 123.15 k $x = 0.9998056$ $N_\alpha = 0.5000486$ $N_\beta \approx 0.4999514$

b)

At 298 k $N_\alpha - N_\beta \approx 4.02 \cdot 10^{-5}$

At 123.15 k $N_\alpha - N_\beta \approx 9.72 \cdot 10^{-5}$

Low temperature give higher signal intensity

We choose -150°c because the greater population difference yield a stronger NMR signal