

1.3: How does the population difference in NMR compare to the difference between electronic ground and excited states?

Up to this point in our discussion, the theory of NMR seems similar to that for other common spectroscopic methods. However there are some differences that should be considered. For example in UV-visible absorption spectroscopy, which occurs as a result of electronic transitions, at room temperature essentially all of the molecules will be in the ground electronic state because the energy difference between the ground and excited states is large. However, in NMR the difference in energy in the two spin states is very small, therefore the population difference is also small (about 1 in 10,000 for ^1H in an 11.74 T magnetic field). Because this population difference is the source of our signal, NMR is inherently a less sensitive technique than many other spectroscopic methods.

Let's think now about the energy difference between the nuclear spin states in NMR. Do you recall the relationship between energy and frequency? Say we are interested in a compound with an absorption maximum at a wavelength, λ , of 600 nm. What would be the frequency, ν , of the light absorbed?

The frequency of light absorbed is inversely proportional to the wavelength as shown in the equation below, where c is the speed of light, 3.0×10^8 m/s.

$$\nu = \frac{c}{\lambda} \quad (1.3.1)$$

Therefore, light with a wavelength of 600 nm has a frequency of 5×10^{14} Hz (cycles per second). The energy, E , of this light is directly proportional to the product of its frequency and Planck's constant (h), 6.626×10^{-34} J·s.

$$E = h\nu \quad (1.3.2)$$

Our 600 nm light has an energy of 3.31×10^{-19} J. The energy of the light absorbed by our molecule roughly corresponds to the energy difference between the ground and excited electronic states of our molecule. How does the energy absorbed in NMR compare with this value? We already indicated that we expect the energy difference between the ground and excited spin states in NMR to be much less than for absorption of visible light. We can calculate the energy of the NMR transition using Equation 2.1 for a particular nucleus in a given magnetic field strength. Let's do this calculation for the protons (hydrogen nuclei) in a sample placed in an 11.74 T magnet, using the value of γ for hydrogen (normally referred to as proton) in Table 1. We can now calculate the energy difference of the spin states, as in Equation 1.3.3.

$$\Delta E = \frac{26.75222127 \times 10^7 \text{ rad} \cdot \text{s}^{-1} \text{T}^{-1} \times 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 11.74 \text{ T}}{2\pi} = 1.054 \times 10^{-25} \text{ J} \quad (1.3.3)$$

This energy may not seem like it is that much less than the energy of our visible absorption transition at 600 nm, after all the numbers only differ by a factor of 10^6 . However, if we think about the thermal energy of our sample in terms of kT ($1.38066 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \times 298 \text{ K} = 4.11 \times 10^{-21} \text{ J}$) we can see that the thermal energy of our sample is about 100 fold less than the energy of the visible absorption of 600 nm light but is about 10,000 times greater than the energy of our proton NMR transition. This is why there is only a very small difference in population between the ground and excited states in NMR.

Having compared the energies of these two spectroscopic methods we might now ask how do the frequency and wavelength in NMR compare with our 600 nm light? We can calculate the NMR frequency, known as the Larmor frequency, using Equation 1.3.4

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi} \quad (1.3.4)$$

For our example of protons in an 11.74 T magnetic field, ν is 500×10^6 Hz or 500 MHz. This is in the radio frequency range of the electromagnetic spectrum. It is common to refer to NMR instruments by the frequency of protons in the magnetic field associated with a given spectrometer, therefore a spectrometer with an 11.74 T magnet is referred to as a 500 MHz instrument.

? Exercise 1.3.3

Calculate the wavelength of electromagnetic radiation corresponding to a frequency of 500 MHz.

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