One of the most startling developments in NMR spectroscopy since its inception has been the discovery of chemically induced dynamic nuclear polarization or CIDNP. An especially dramatic example is provided by irradiation of 3,3-dimethyl-2-butanone with ultraviolet light.

![3,3-dimethyl-2-butanone](image)

Prior to irradiation, the proton NMR spectrum (Figure 27-9a) shows the expected two peaks in the ratio 3:9. However, on irradiation, the spectrum changes drastically (Figure 27-9b). A host of new resonances appear, some inverted (which means emission of radio-frequency energy), and the intensity ratio of the peaks of the ketone itself changes to about 3:18. When the light is turned off, the spectrum rapidly changes to almost exactly its original form. After 20 minutes in the dark, there are no emission lines and only the faintest traces of resonances corresponding to the many resonances observed only after the light was turned on. Similar phenomena are observed in the NMR spectra of many other reacting systems, some induced by light, others not.

Figure 27-9: Observation of CIDNP-induced enhanced absorption and emission resonances produced by irradiation of 3,3-dimethyl-2-butanone (a) before irradiation and (b) during irradiation. (Courtesy of Professor H. Fischer.)

The CIDNP effect is a complicated one and we will not attempt to explain it in detail. It is observed exclusively for radical reactions. However, it is not expected for chain-propagation steps, but only for termination steps. Furthermore, chemically dissimilar radicals have to be involved at some stage in the reaction sequence. Let us now consider how these considerations apply to the irradiation of 3,3-dimethyl-2-butanone.

Absorption of light by a ketone can give several reactions, but an especially important one, which will be discussed in more detail in Chapter 28, is cleavage of \( \text{O=C-C=O} \) bonds to give radical pairs. For 3,3-dimethyl-2-butanone there
are two possible cleavage reactions of this type:

The heavy lines drawn over the radical pairs indicate that the radicals in the pairs are in close proximity to one another. Combination of the radicals in the pairs regenerates the ketone, whereas separation of the radicals can lead to formation of other products. The radicals in a pair can combine with each other only if the odd electron on one radical has its spin opposite to the spin of the odd electron on the other radical. This is necessary for formation of an electron-pair bond.

CIDNP arises because the radical combination products have nonequilibrium distributions of their proton magnetic states. How can nonequilibrium distributions arise? First, we must recognize that the radicals formed by irradiation of the ketone can have different proton magnetic states. For example, the methyl protons of any given \(\ce{CH_3CO} \cdot\) radical will be in one of the proton states: \(+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}; +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}; +\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\) states (8 in all; see Section 27-3).

The effect of the different proton magnetic states is to cause the two unpaired electrons of the radical pairs to become unpaired at different rates. In other words, \(\overline{\ce{R} \uparrow + \ce{R'} \downarrow}\) pairs produced by irradiation are converted to \(\overline{\ce{R} \uparrow + \ce{R'} \uparrow}\) at different rates, depending on the proton magnetic states of \(\ce{R} \uparrow\) and \(\ce{R'} \downarrow\). Thus, a particular pair of proton magnetic states for \(\ce{R} \uparrow\) and \(\ce{R'} \downarrow\) can favor radical-pair recombination over radical-pair separation while another pair of proton magnetic states for \(\ce{R} \uparrow\) and \(\ce{R'} \downarrow\) can favor separation over combination. The result is a “sorting” of proton magnetic states, some appearing preferentially in particular products and others appearing in other products. Thus one product may have more than the normal equilibrium value of a higher-energy magnetic state and hence will emit radio-frequency energy to get back to equilibrium, while another product may have an abnormally low concentration of the higher-energy magnetic states and hence exhibit an enhanced absorption intensity. Figure 27-9 shows that recombination of the radical pairs produced in photolysis of 3,3-dimethyl-2-butanone forms ketone with a higher-than-normal magnetic energy in the protons of the methyl group (reduced absorption) and lower-than-normal magnetic energy in the protons of the tert-butyl group (enhanced absorption).

The other CIDNP peaks in Figure 27-9b arise from reactions of the separated radicals first formed, and show both enhanced absorption and enhanced emission. You should try to identify the origin of each of the CIDNP resonances with the expected reaction products:
Because thermodynamic equilibrium usually is established between magnetic states of protons in a few seconds, the enhanced-absorption and enhanced-emission resonances disappear quickly when irradiation is stopped.

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