

5.3: Proton N-H Resonance of Pyrrole. Double Resonance

Broadening of N-H proton resonance lines by quadrupole-induced relaxation has been observed with a number of types of nitrogen compounds. A particularly striking example is afforded by pyrrole. The NMR spectrum of pyrrole at room temperature shows no N-H line on casual inspection (see Fig. 5-3). The principal observed peaks are those of the C-H protons. However, very careful inspection of the spectrum shows a very broad peak to the low-field side of the C-H resonances, which rises only slightly above the base line. Apparently, the ^{14}N nucleus in pyrrole is undergoing relaxation at just the right rate to cause the protons attached to it to give the broadest possible line intermediate between the singlet and triplet patterns.

Any process which causes the N-H protons to "see" either a more slowly or more rapidly moving sequence of nitrogen magnetic quantum states will sharpen the resonance lines to give the triplet or singlet lines, respectively. As is seen in Fig. 5-3, this may be achieved by raising or lowering the temperature so as to change the rates of tumbling of the molecules and thus influence the effectiveness of the quadrupole relaxation of the nitrogen nucleus. As with pyrrolidine hydrochloride, lowering the temperature gives a sharpened single resonance, while raising the temperature causes a triplet pattern to appear. A given N-H proton of pyrrole can be exposed to a more rapid sequence of nitrogen magnetic quantum states by addition of potassium pyrrolate, which induces intermolecular proton exchange. As expected, exchange causes the N-H resonance line to sharpen.

By far the most elegant procedure for eliminating the magnetic relaxation effects of the ^{14}N nucleus is the "double-resonance" or "spindecoupling" technique. As applied by Shoolery² to pyrrole, this involves observing the proton spectrum in the normal way while subjecting the sample to a powerful rf field at the ^{14}N resonance frequency (2.9 Mc at 9400 gauss). The proton signal is detected with a narrow-bandwidth receiver, so that there is no pickup of the second oscillator frequency. The rf input at the ^{14}N frequency causes the nitrogen nuclei to change their magnetic quantum numbers rather more rapidly than is possible for quadrupole-induced relaxation alone. As a result, each N-H proton sees its nitrogen nucleus with the magnetic quantum numbers effectively averaged to zero and thus gives a sharpened N-H resonance (Fig. 5-4). Several other applications of double-resonance technique will be described in Sec. 5-5.

² Private communication from J. N. Shoolery.

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