4.8: Proton Exchange in Ammonia and Ammonium Ions

A number of interesting exchange experiments of other kinds have been done with nitrogen compounds. Only one sharp proton resonance has been observed lipX2 for ammonia-water mixtures, as would be anticipated for a rapidly exchanging system. Extremely anhydrous liquid ammonia or gaseous ammonia gives a triplet resonance pattern with all of the peaks being the same height (see Fig. 4-14).[11,12] This pattern arises from spin-spin coupling between the protons and the 14N nucleus, which has a spin of 1 and hence the magnetic quantum numbers +1, 0, -1, which are equally probable. The line at the lowest field represents the proton resonance absorption of those ammonia molecules having nitrogen with a magnetic quantum number +1, while the center and high-field lines correspond to the nitrogen nuclei with magnetic quantum numbers 0 and -1, respectively.

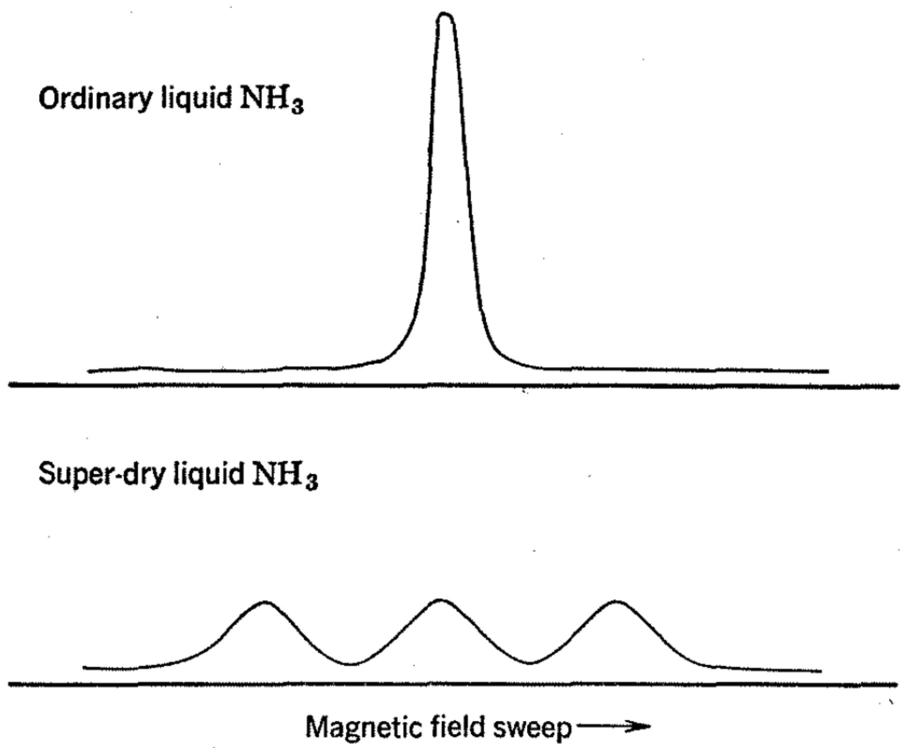

Fig. 4-14. Proton resonance spectrum of ordinary liquid ammonia and superdry ammonia as prepared by Ogg.[11]

In the presence of water or minute amounts of amide ion, exchange of hydrogens between ammonia molecules is extremely rapid, so that the spin-spin splitting is washed out when the mean lifetime of a proton on any given nitrogen is substantially less than 0.007 sec. In aqueous solution, exchange is so rapid between ammonia and water molecules that separate 0-H and N-H resonances are not obtained and only a single average proton resonance is obtained. Similar results are obtained with ammonium nitrate solutions in water containing enough additional ammonia to make the solution nearly neutral. Under these circumstances, ammonium ions, ammonia, and water exchange protons with one another sufficiently rapidly to give only a single line. A startling change takes place on the acidification of such solutions with nitric acid.[13] As is seen in Fig. 4-15, a triplet pattern appears which corresponds to the three possible spin orientations of the 14N nuclei and there is an additional large single proton resonance, that of water. This result proves that water is singularly ineffective in removing protons from ammonium ions while ammonia is extremely effective. Similar observations[14] have been made for methylammonium ion, the spectrum of which in acidic solution is shown in Fig. 4-16. The broad N-H resonances which contrast to the sharp lines observed for ammonium ion result from quadrupole effects as will be discussed later and not from intermediate proton exchange rates, because further addition of acid does not cause the lines to sharpen. It is possible to obtain the exchange rate constants by observations of line-shape changes with temperature or pH. The kinetics and mechanisms of such processes have been studied in detail by Grunwald and coworkers.[15]

11 R. A. Ogg, Jr., J. Chem. Phys., 22, 560 (1954).

12 H. S. Gutowsky and S. Fujiwara, J. Chem. Phys., 22, 1782 (1954).

13 R. A. Ogg, Jr., Discussions Faraday Soc., 215 (1954).

14 J. D. Roberts, J. Am. Chem. Soc., 78, 4495 (1956).

15 E. Grunwald, A. Loewenstein, and S. Meiboom, J. Chem. Phys., 27, 630 (1957).