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High Resolution Proton Magnetic Resonance in Water and the Concept of Hydrogen Bonding

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The proton magnetic resonance spectrum of liquid water is commonly employed as a reference standard for high resolution proton resonance spectra in other compounds. The development of a thermally insulated "head" containing the transmitter and receiver coils has made possible the study of proton resonance in gaseous water. A liquid water sample of quantity corresponding to about ten atmospheres pressure when vaporized was contained in the conventional slender Pyrex glass tube, previously evacuated and sealed off. The sample tube was heated in an electric furnace to cause complete volatilization of the liquid and was then rapidly transferred to the Dewar vessel insert of a thirty megacycle nuclear magnetic resonance spectrometer. The signal to noise ratio was adequate to demonstrate an appreciable line breadth (of the order of five cycles per second) for the proton resonance. Most interesting was the displacement relative to liquid water. The average of fifteen measurements yielded a figure of 150 cycles per second, the proton resonance in the vapor state falling at the higher magnetic field.

The author had previously demonstrated*) a similar effect in the case of gaseous and liquid ammonia, the proton resonance in the gas falling at higher magnetic field, with a displacement of some 50 cycles per second at a frequency of 30 megacycles. The explanation offered for the present results is precisely that previously proposed, namely that so-called "Hydrogen bonding" is merely close classical electrostatic interaction between molecular electric dipoles. The considerably greater effect observed for water is due to the fact that the permanent electric dipole moment of water molecules is considerably greater than that of ammonia.

*) R. A. Ogg, Jr., J. Chem. Physics, **22**, 560 (1954).

It should be noticed that the 150 cycles per second shift observed for a simple phase transition is greater than the usual magnitudes of "chemical shift" associated with differences in chemical structure. For purpose of relating nuclear magnetic resonance spectra to molecular structure, the vapor state is ideal. In the accompanying letter by Mr. P. DIEHL, it is seen, that the widely held concepts about the "classical" case of ethyl alcohol are due to the previous restriction of the experimental studies of the proton magnetic resonance spectrum to the pure liquid. The above results with water would suggest that (in comparison with the vapor) the spectrum is strongly distorted by electrostatic interaction in the pure liquid. This appears to be in fact the case. The author wishes to acknowledge the assistance of Dr. J. SHOOLERY of Varian Associates, Palo Alto, California, in the experimental work. Financial support of the Research Corporation and of the National Science Foundation is gratefully acknowledged.
