

Proton Magnetic Resonance Data on Ice

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In a recent Communication,¹ measurements of the chemical shift of ice have been reported. Ice at -12° is stated to show a line-width of about 1 kc./sec. (0.24 gauss) and a chemical shift of more than 6 p.p.m. upfield from liquid water at 0° . A high-resolution spectrometer was used for these measurements. On the other hand Kume,² using broad-line techniques, obtained a value of from 7.4 to 8.9 gauss (depending on the purity of the sample) for the line-width of ice at about the same temperature, in agreement with the earlier work of Bloembergen, Purcell, and Pound.³ To investigate this contradiction we have made n.m.r. measurements on ice and other proton-containing substances below their melting points.

A spectrum of ice obtained on a broad line spectrometer (Varian PA7) at -12° is shown in Figure 1. It is composed of a broad line and a narrow line. The width of the broad line (between

points of maximum slope) is 8.7 gauss. In this measurement the width of the narrow line is determined by the modulation used but a separate experiment showed it to be about 0.19 gauss (at half height). The proportion of the sample contributing to the narrow line part of the signal was estimated from measurements of the area under an overmodulated signal, using as standards, samples containing known amounts of water dispersed on solid surfaces. This proportion varied with temperature, with the purity of the sample and with its previous history, but for ice at -12° was between 0.2% and 0.4% of the total sample. The variation of the width of the broad line, and the proportion of sample in the narrow line, with temperature is shown in Figure 2 for a typical ice sample. Pulsed n.m.r. measurements were made

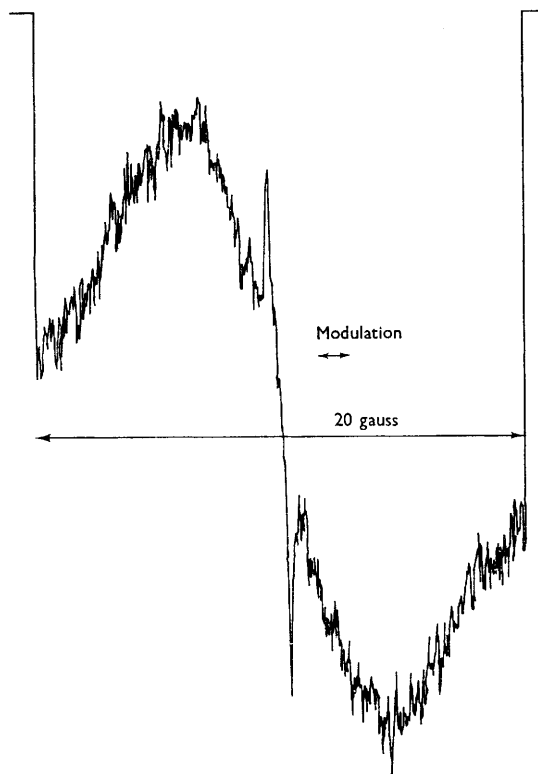


FIGURE 1. Wide-line n.m.r. spectrum of ice at -12° .

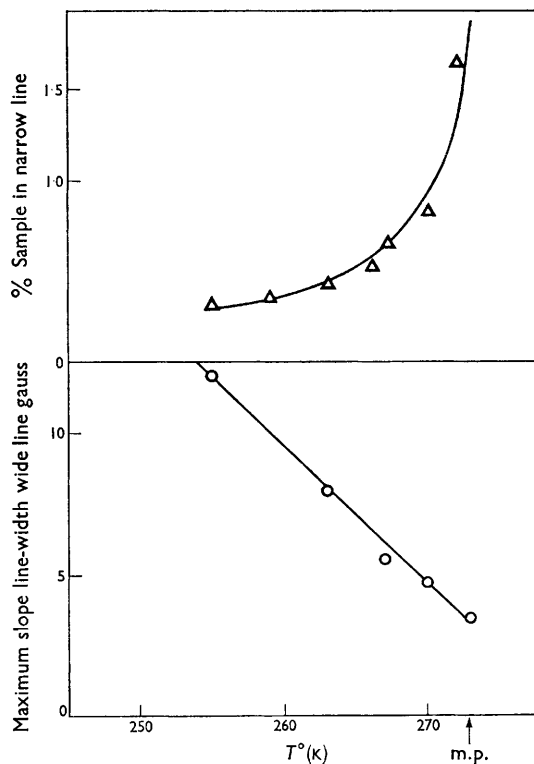


FIGURE 2. The variation with temperature of the amount of sample in the narrow-line component of ice and of the line-width of the broad-line component.

with a Bruker Physik B-KR-302 pulse spectrometer. These showed that the proton spin-spin relaxation time, T_2 , in ice at -12° calculated from the decay of transverse magnetisation following a 90° pulse, was between 5 and 10 microseconds ($T_1 \sim 15$ sec.). This corresponds with a line-width of the order of 10 gauss, and could not possibly be due to a proton resonance with a line width of 1 kc./sec. which would give a T_2 of not less than 300 microseconds.

It is clear that the bulk of the ice sample is in a state giving rise to the broad n.m.r. line. Its chemical shift remains unknown at present. The measurements of Akitt and Lilley might be on the narrow component ($> 0.5\%$ of the whole). It is suggested that this may be interstitial liquid of some kind, possibly water trapped between growing ice crystals, *i.e.*, water in ice capillaries, water on

crystal surfaces, or just possibly non-hydrogen-bonded water molecules in spaces in the ice lattice. (Faraday⁴ inferred that liquid water must exist on ice surfaces well below 0° . It is possible that n.m.r. now provides direct evidence for this.)

The presence of 'fine structure', *i.e.*, the existence of a narrow line as part of the broad line spectrum of solid organic substances has often been noted. Detailed studies have indicated that it is probably caused by mobile 'liquid' molecules at crystal boundaries or dislocations.^{5,6} High-resolution studies at 34° on dodecanoic acid (m.p. 44°) shows the presence of a narrow line which differs from that reported for ice in that it is narrower (150 c./sec. at half height) and that its chemical shift is, within experimental error, the same as observed for CH_2 protons in the liquid state.

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³ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 1948, **73**, 679.

⁴ M. Faraday, *Proc. Roy. Inst. Great Britain*, 1850.

⁵ J. Clifford, *Nature*, 1962, **195**, 568.

⁶ M. R. Barr, B. A. Durrell, and R. F. Grant, *Canad. J. Chem.*, 1963, **41**, 1188.