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# **A test of the theories of magnetic resonance and the study of liquids by this method**

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## *Résumé.*

On présente une revue critique de la théorie de la résonance magnétique nucléaire dans son application aux liquides. Une vérification générale des théories est établie, étant donné plusieurs généralisations, pour un liquide typique, le bromure d'isobutyle. Le fait de s'éloigner d'un liquide typique introduit certains effets qui sont étudiés pour le glycerol, les hauts polymères et certaines molécules longues. On démontre que dans certains cas, comme pour le toluène liquide, il existe des relaxations distinctes pour les différents noyaux de la molécule; ceci fournit des renseignements très détaillés sur le mouvement thermique moléculaire. Nous montrons également que la résonance électronique de radicaux libres en solution peut se présenter comme une méthode puissante d'étude de l'état liquide.

I should like to take up in more detail a number of points dealt with, necessarily rather briefly, by Professor Giulotto in his general lecture at this Conference on magnetic resonance relaxation in liquids.

It so happens that the work done on liquids over the past few years by my group illustrates both the development of the use of magnetic resonance in the study of liquids and the critical testing and consequent modification of the theories of magnetic resonance. Perhaps you will excuse me therefore if I draw almost exclusively on results obtained in my own laboratory in order to illustrate the points I wish to make.

Consider first the more general results of the theories which will serve as convenient matters for test. Assume for the moment that the thermal motions are adequately described by a motional correlation frequency  $\nu_c$ .

1. When  $\nu_c$  is small ( $\ll \nu_{r.c}$ , defined below) the line is broad.  $T_2$  is short and may be represented by  $T_{2r.l}$  in first approximation. The shape and width of the line is calculable from nuclear spacings, etc.  $T_1$  should be long.

2. As  $\nu_c$  increases  $T_1$  should become shorter.  $T_{2\ r.l}$  should not be affected until  $\nu_c \simeq \nu_{r.l}$  where  $\nu_{r.l}$  is the rigid lattice line width in terms of frequency.  $T_2$  then begins to increase.
3. For  $\nu_c > \nu_{r.l}$  the line should become Lorentzian in shape and we should find  $T_2 \propto \nu_c$ .  $T_1$  falls towards a minimum.
4. For  $\nu_c \simeq \nu_r$ , where  $\nu_r$  is the Larmor frequency,  $T_1$  should have a minimum value  $T_{1\ min}$  which should be calculable from  $T_{2\ r.l}$  with certain reservations.
5. At the minimum of  $T_1$  we should find  $T_1/T_2 \approx 2$ .
6. For  $\nu_c \gg \nu_r$  we should find  $T_1 = T_2 \propto \nu_c$ .

Such behaviour has not been observed in entirety in one liquid for a number of reasons. It is fair to say nevertheless that all the above theoretical predictions are very largely confirmed. A particular difficulty is that it is not possible in a real liquid to vary  $\nu_c$  over a sufficient range (say 10 c/s to  $10^{10}$  c/s) without altering other things and so the interpretation immediately becomes more complex. Another source of difficulty is that in most liquids we have complex interactions between nuclei and complex motions of nuclei which are far from adequately described by a single parameter  $\nu_c$ . Furthermore in order to test the theory we need *independent* evidence of the value of  $\nu_c$  and this is rarely available.

The major requirements of a suitable liquid for our purposes are therefore:

1.  $\nu_c$  should be known and variable over a wide range. At present this forces us to choose liquids composed of polar molecules since  $\nu_c$ , with certain reservations, can be deduced from  $\nu_D$ , the dielectric critical frequency. The wide variation of  $\nu_c$  can in practise only be obtained by using liquids which supercool readily. Ordinary liquids which do not supercool provide a range of  $\nu_c$  from about  $10^8$  to  $10^{12}$  c/s. Thus we do not usually get the interesting region where  $\nu_c \simeq \nu_r$  since  $\nu_r$  is usually about  $10^7$  c/s. With readily supercooled liquids  $\nu_c$  may fall with temperature to about  $10^{-2}$  c/s. Below this care is required because such liquids become glassy.
2. The molecules should be of simple shape and should not have strong interactions with each other e.g. hydrogen bonds and should not have internal flexibility.

3. The nuclear magnetic interactions should be few and simple, or simplifiable.

In view of these remarks you may well be surprised when I say that liquid isobutyl bromide ( $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$ ), which we have studied extensively, offers a rather nice test of all the major results of the theory quoted above. For this and the other substances discussed below I refer you to

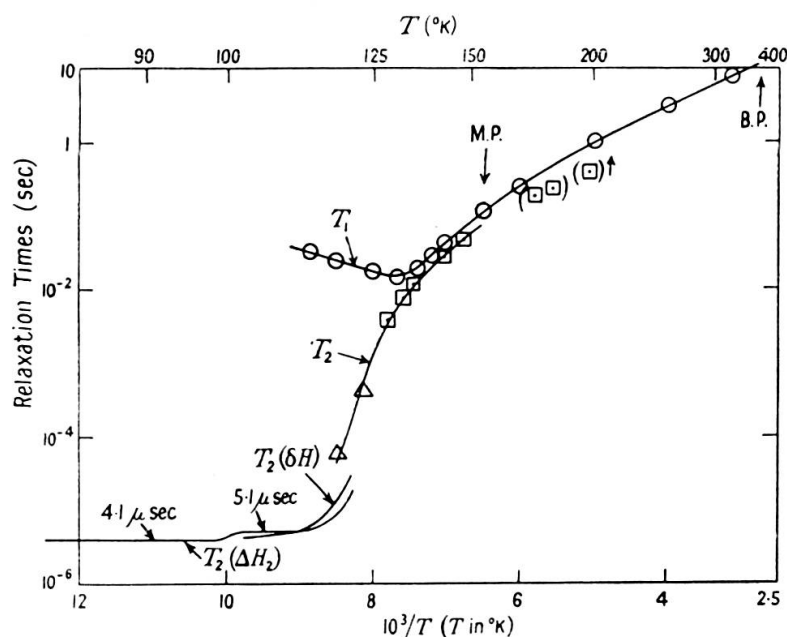


Fig. 1.

$T_1$  and  $T_2$  for iso butyl bromide as a function of temperature (from ref. 2).

the published articles for details [1, 2] and discuss only certain important points. For isobutyl bromide  $\nu_D$  is known in the radio frequency and microwave regions. We shall assume that  $\nu_c \simeq 3\nu_D$  for the present general discussion [3]. The variation of  $T_1$  and  $T_2$  with temperature (i.e. with  $\nu_c$  among other things) is shown in figure 1. We note in particular that  $T_1$  has a minimum at which  $T_1/T_2 = 2.2$  and  $T_1 \simeq T_2$  at high temperatures. The values of  $\nu_c$  deduced from proton magnetic resonance are compared with  $\nu_D$  in figure 2 and we see that the relation  $\nu_c \simeq 3\nu_D$  is quite well obeyed over a very wide range. We have, however, already had to allow one generalisation of the theory, a continuous distribution of correlation frequencies  $\nu_c$  at low temperatures. There is also a difficulty due to an

internal motion (of a  $\text{CH}_3$  group) to be faced. Nevertheless we may regard this result as very encouraging in accepting the method of interpretation.

Let us now depart appreciably from our ideal liquid and look at the results for glycerol [4] ( $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$ ). We have here an awkward shape of molecule and intermolecular hydrogen bonding but  $\nu_c$  is

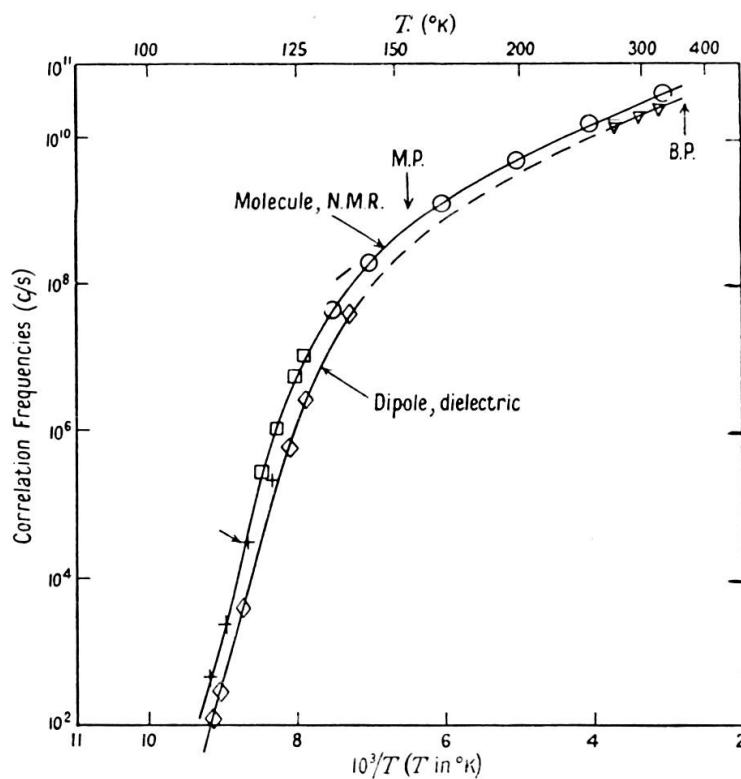


Fig. 2.

A comparison of  $\nu_c$  (called Molecule NMR) and  $\nu_D$  (called Dipole, dielectric) for iso butyl bromide over a wide temperature range (from ref. 2).

still variable over a wide range. In this case we also find a minimum in  $T_1$  but at the minimum  $T_1/T_2 = 3.8$  i.e. significantly greater than 2. This and the behaviour at lower temperatures we believe to be due again to distributions over  $\nu_c$ . Moreover it is found that  $\nu_c$  is less than  $3\nu_D$  by a factor varying between 3 and 9. This difference I believe is real and shows that the dipoles (mainly  $-\text{OH}$ ) move faster than the skeleton of the molecule to which most of the protons are attached. We therefore see that different nuclei may have different  $\nu_c$ 's and different interactions and given nuclei may even have complex motions with different parts of the motion associated with different  $\nu_c$ 's.

Suppose we now pass to an extreme case and take a very long molecule i.e. a liquid polymer. Such a case is polyisobutylene (PIB) or polydimethyl siloxane. Here we find [5, 6] minima of  $T_1$  but  $T_1/T_2$  at the minimum of  $T_1$  is 100 for PIB and 1,300 for the silicone. Further, above the minimum of  $T_1$  we find  $T_2 \ll T_1$  and that the line is not Lorentzian in shape. I believe

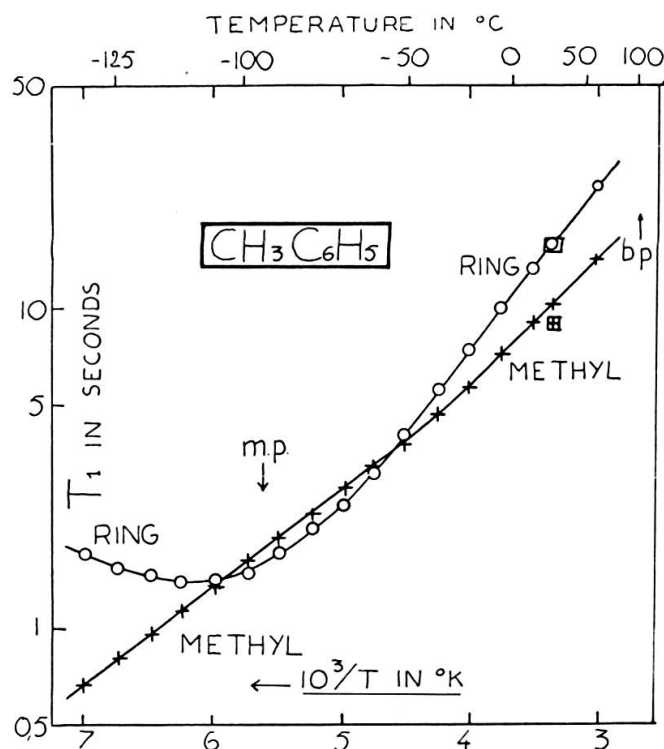


Fig. 3.

For liquid toluene the  $T_1$ 's for the ring and methyl protons differ and behave differently with temperature (from ref. 8).

this to result from multiple interactions between nuclei associated with different  $\nu_c$ 's. In this case the nuclei can interact with adjacent ones on the same chain and between chains. It so happens that at certain temperatures the former interaction has  $\nu_c \gg \nu_r$  and the latter  $\nu_c \ll \nu_r$  and then the line although narrow (say 1 mG) has the characteristics of a broad line i.e. not Lorentzian and  $T_2 < T_1$ . We have suggested [6] that these may be called narrow broad lines.

For moderately long molecules the situation is less complex and we find [7] for instance in n-octyl bromide that  $\nu_c \simeq 3\nu_D$ . However it should be borne in mind that  $\nu_D$  refers to the motion of the C-Br vector and  $\nu_c$  to that of the protons. This coincidence of  $\nu_c$  and  $3\nu_D$  is not trivial. We

find [7] for n-octyl alcohol  $\nu_c/3\nu_D \simeq 15$  i.e. the motion of —OH is slower than that of the other protons. A closer inspection of the dielectric loss ( $\epsilon''(\nu)$ ) shows that besides the principal absorption region there is a weaker one at a higher frequency. For this one has  $\nu_c/3\nu_D \simeq 1$ . This leads therefore to the picture of the octyl alcohol molecules with wagging tails but held to some extent at the heads presumably by hydrogen bonding of the OH groups. Nevertheless the OH groups are moved a bit by the tails and so show some dielectric absorption at the higher frequency.

You may well have objected that in some of the cases cited above the behaviour of different protons is so different that they may well be considered as separate systems and so have different  $T_1$ 's and  $T_2$ 's. This is indeed so but only of course when the signals are separate (i.e. if  $\delta \gg 1/T_2$  where  $\delta$  is the chemical shift) otherwise cross relaxation makes the systems indistinguishable. It is possible to show that for the above systems and by the usual transient methods of measuring  $T_1$  (and  $T_2$ ) it is quite difficult to distinguish two or more sets of nuclei of the same type. We have recently developed a method [8] of measuring the  $T_1$ 's of different groups of nuclei and have confirmed and extended some earlier work [9] which showed that  $T_1$  indeed may differ substantially from group to group. The results for liquid toluene [8] are most striking and are shown in figure 3. There we see that the ring proton  $T_1$  has a minimum in the available temperature range and the methyl proton  $T_1$  does not! This means that the  $\nu_c$ 's appropriate to the interactions of the two sets of protons are very different and leads to a picture of the thermal motion of toluene molecules in liquid toluene which is much more complex than has hitherto been contemplated. We shall not discuss this here but merely mention that we find [10] similar substantial differences in many other liquids including the alcohols.

The question of whether  $T_1 = T_2$  for sufficiently high temperatures is of considerable current interest. From our work at high fields we find that  $T_2$  always rises, or would appear to rise to within at least  $\frac{1}{2}T_1$  so that the difference, if any, is not large, unless, as in polymer liquids, there is good reason for it to be otherwise. We have measured  $T_1$  and  $T_2$  in low fields [11] and think that it is not at all uncommon for  $T_2$  to be less than  $T_1$ , e.g. in water. However in our measurements there is the additional possibility of field dependent effects and there continue to be disquieting rumours of wall effects etc. causing  $T_2 < T_1$  [12]. The considerable difficulties in measuring  $T_2$  both accurately and in absence of r.f. field continue to confuse the issue and we shall not discuss it further.

Finally I should like to draw attention to the possibility of obtaining significant information about ordinary liquids from electron resonance. We have recently studied the electron resonance signal of the peroxyamine disulphonate negative ion in water and water/glycerol mixtures. We find [13] effects we believe to be due to the incomplete motional narrowing of the anisotropic hyperfine interaction of the electron in this radical and to the anisotropy of the  $g$  factor. The results correlate satisfactorily and in some detail with the known  $\nu_c$  values in the liquids. More recently we have been studying the signal from the diphenyl negative ion in solution. Here both anisotropic hyperfine interaction and exchange narrowing can both be related in some detail to molecular motion in the pure liquid (this elaborates pioneer work by Pake and Tuttle [14] and by Hausser [15]). It seems likely therefore that this method will provide another tool for the study of liquids.

To sum up, we see that the magnetic resonance methods are beginning to show exciting possibilities for a detailed study of what happens in liquids and will soon provide us with some rather detailed information which should be of extreme value in interpreting the behaviour of liquids in general. After all, the most important property of a liquid is the thermal agitation of its constituent particles. All transport processes, including for instance viscosity, depend largely on this as do indeed all properties of liquids to a greater or lesser extent.

## RÉFÉRENCES

1. POWLES, J. G. and J. A. E. KAIL, *Proc. Phys. Soc.*, **73**, 833, 1959.
  2. LUSZCZYNSKI, K. and J. G. POWLES, *Proc. Phys. Soc.*, **74**, 408, 1959.
  3. BLOEMBERGEN, N., E. M. PURCELL and R. V. POUND, *Phys. Rev.*, **73**, 679, 1948.
  4. LUSZCZYNSKI, K., J. A. E. KAIL and J. G. POWLES, *Proc. Phys. Soc.*, **75**, 243, 1960.
  5. POWLES, J. G. and K. LUSZCZYNSKI, *Physica*, **25**, 455, 1959.
  6. ——— and A. HARTLAND, *Nature*, **186**, 26, 1960.
  7. ——— and A. HARTLAND, *Proc. Phys. Soc.*, **75**, 617, 1960.
  8. ——— and D. J. NEALE, *Proc. Phys. Soc.*, awaiting publication.
  9. NEDERBRAGT, E. W. and C. A. REILLY, *J. Chem. Phys.*, **24**, 1110, 1956.
  10. POWLES, J. G. and D. J. NEALE, *Proc. Phys. Soc.*, submitted for publication.
  11. ——— and D. CUTLER, *Nature*, **184**, 1123, 1959.
  12. e.g. G. BONERA et al., this Conference.
  13. POWLES, J. G. and M. MOSLEY, *Proc. Phys. Soc.*, awaiting publication.
  14. PAKE, G. E. and T. R. TUTTLE, *Phys. Rev. Letters*, **3**, 423, 1959.
  15. HAUSSER, K. H., *Z. Naturforsch.*, **14a**, 425, 1959.
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