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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 ν_c.

1. When ν_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 ν_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 ν_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 ν_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 ν_c. Furthermore in order to test the theory we need *independent* evidence of the value of ν_c and this is rarely available.

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

1. ν_c should be known and variable over a wide range. At present this forces us to choose liquids composed of polar molecules since ν_c, with certain reservations, can be deduced from ν_D, the dielectric critical frequency. The wide variation of ν_c can in practise only be obtained by using liquids which supercool readily. Ordinary liquids which do not supercool provide a range of ν_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 ν_r is usually about 10^7 c/s. With readily supercooled liquids ν_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 ($(CH_3)_2\,CHCH_2\,Br$), 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 the published articles for details [1, 2] and discuss only certain important points. For isobutyl bromide ν_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 ν_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 ν_c deduced from proton magnetic resonance are compared with ν_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 ν_c at low temperatures. There is also a difficulty due to an

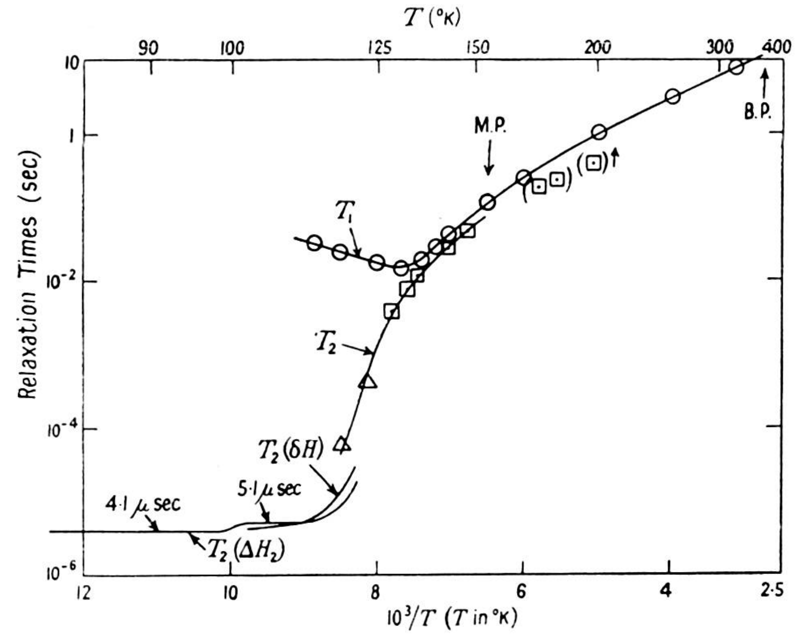

Fig. 1.

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

internal motion (of a 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] ($CH_2OH . CHOH . CH_2OH$). We have here an awkward shape of molecule and intermolecular hydrogen bonding but ν_c is

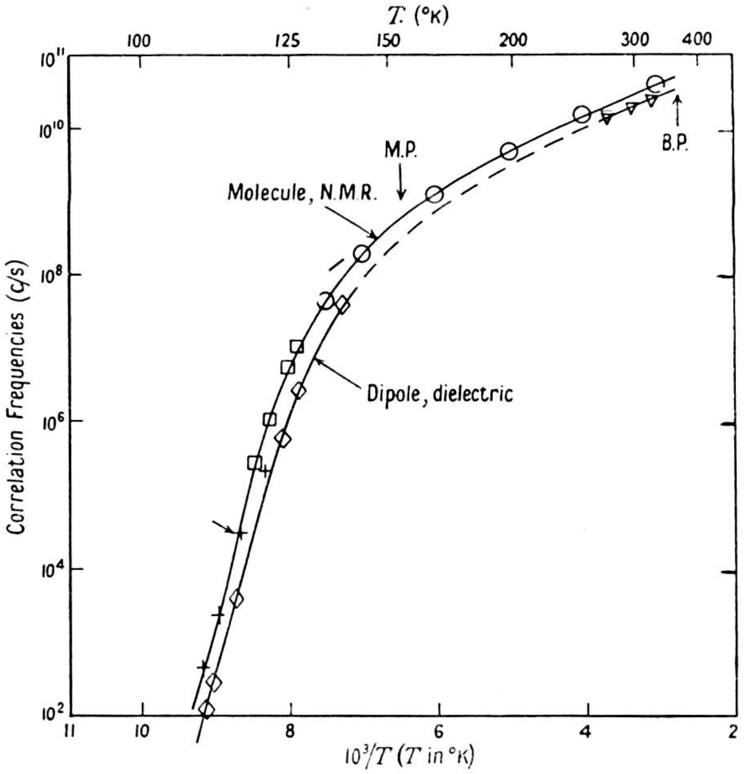

Fig. 2.

A comparison of ν_c (called Molecule NMR) and ν_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 ν_c. Moreover it is found that ν_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 —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 ν_c's and different interactions and given nuclei may even have complex motions with different parts of the motion associated with different ν_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 this to result from multiple interactions between nuclei associated with different ν_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.

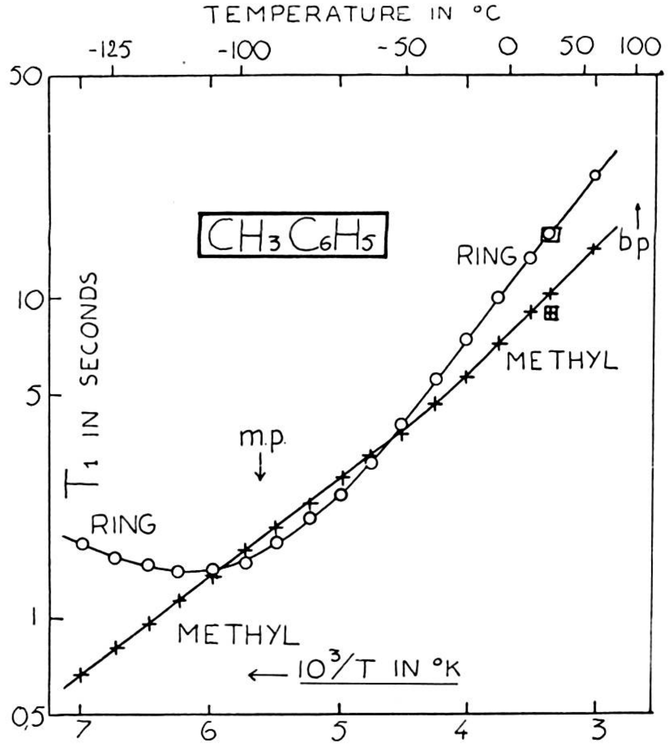

Fig. 3.

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

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 ν_D refers to the motion of the C-Br vector and ν_c to that of the protons. This coincidence of ν_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 (ε'' (ν)) 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 waggling 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 δ 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 ν_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 peroxylamine 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 ν_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.

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