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The Equivalence of the Two Theories of the Nematic Mesophase When Applied to Magnetic Resonance Experiments

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Abstract—The use of nematic liquid crystals as solvents in magnetic resonance experiments provides a potential source of information about the anisotropic interactions. To utilize this potential it is necessary to employ some model of the nematic mesophase in order to describe the ordering of the solute. Both the swarm and the distortion theory have been applied to the problem and in this paper it is shown that they lead to isomathematical conclusions.

1. Introduction

Although the magnetic resonance spectra of solutes in normal solvents contain a wealth of information, all knowledge of anisotropic interactions is lost because the molecules tumble isotropically. Saupe and Englert [1] were the first to use nematic liquid crystals [2] as solvents in high resolution nuclear magnetic resonance. They found that although the molecular motion is sufficiently rapid to average out intermolecular interactions, *it is anistropic.* The analysis of nuclear magnetic resonance spectra of solutes in a nematic mesophase has led to the measurement of relative bond lengths,[3] bond angles,[3] chemical shift tensors [4] and quadrupole tensors [5] as well as the signs of the indirect spin–spin coupling constants.[6]

Following Saupe and Englert's original note Carrington and Luckhurst [7] showed that nematic liquid crystals could also be used

to align free radicals and so produce dramatic changes in their electron resonance spectra. These solvents may be used to great advantage in the electron resonance study of free radicals. Indeed the signs of coupling constants and spin densities have been determined [7, 8] by using these solvents and we can measure the anisotropic hyperfine [9] and g tensors [8, 10] from the position of the lines in a spectrum. In many cases it is also possible to distinguish between stable mono- and biradicals.[11]

These two types of magnetic resonance experiment demonstrate the anisotropic nature of the motion of the solute but to obtain a quantitative analysis of the results we must have a theory with which to describe the extent and direction of this anisotropy. In order to develop the theory we need some model for the nematic mesophase; unfortunately since the discovery of liquid crystals there has been considerable controversy as to their structure. [2 p.76, 12] Two theories have been proposed; on the one hand there is the distortion theory due to Zocher [13] and this model has been used as the basis to interpret all of the nuclear magnetic resonance work. On the other hand, there is Bose's swarm theory [14] which has been used to explain the majority of the electron resonance results. This sharp division with respect to the use of the two models is largely fortuitous for as we shall show both models lead to isomathematical interpretations. Although in the next section our remarks will pertain to electron resonance we shall see that the conclusions are equally valid for nuclear resonance.

2. The Problem

It is not particularly illuminating to develop the theory in its most general form and instead we shall consider the case of a radical with an anisotropic g tensor, g_{ab}, containing a single magnetic nucleus with an anisotropic hyperfine tensor, A_{ab}. The spin Hamiltonian for the radical in a given orientation is

$$\mathscr{H} = \beta H_\alpha g_{\alpha\beta} S_\beta + I_\alpha A_{\alpha\beta} S_\beta, \tag{2.1}$$

where we have adopted the tensor convention of implied summation over repeated subscripts and the space fixed axes are denoted by

x, y and z (N.B. we denote a general space axis by a Greek subscript). When the radical moves rapidly the quantities $g_{\alpha\beta}$ and $A_{\alpha\beta}$ fluctuate with time and to determine the time independent Hamiltonian, $\langle \mathscr{H} \rangle$, we must take a time or ensemble average. In finding these averages it is convenient to transform the tensors from the space fixed axis system to a molecular axis system $a, b, c \ldots$ so that the direction cosines are the only time dependent quantities and

$$\langle \mathscr{H} \rangle = \langle l_{\alpha a} l_{\beta b} \rangle \beta g_{ab} H_\alpha S_\beta + \langle l_{\alpha a} l_{\beta b} \rangle A_{ab} I_\alpha S_\beta. \tag{2.2}$$

When the molecular motion is isotropic it is easy to show that

$$\langle l_{\alpha a} l_{\beta b} \rangle = \delta_{\alpha\beta} \delta_{ab}/3, \tag{2.3}$$

and if we use the magnetic field to define the z axis then

$$\mathscr{H}^I = g\beta H S_z + aI.S, \tag{2.4}$$

where $g = g_{aa}/3$ and $a = A_{aa}/3$. If the motion is not isotropic the problem is to choose a model for the molecular environment with which to evaluate these averages.

3. The Distortion Theory

The essential concept of this theory is that the orientation of the molecules in the nematic mesophase changes continuously throughout the bulk fluid. The application of a strong magnetic field causes the molecules to adopt a configuration in which their long axes tend to be parallel to the magnetic field. In general the addition of solutes to the solvent does not destroy this alignment and because of solute–solvent interactions the motion of the solute is anisotropic. The situation is analogous to the alignment of dipolar molecules by an electric field. However, the degree of alignment produced by the magnetic field with a nematic liquid crystal is much greater than an electric field and so it was necessary to extend the perturbation treatment given by Buckingham and Pople.[15]

Saupe[16] was the first to develop the theory for liquid crystals implicitly using the distortion theory; he chose to describe the average orientation of the solute by an ordering matrix S_{ab}. Since then the theory has been rewritten first by Snyder[17] who describes

the orientation by a probability distribution function whilst Glarum and Marshall[8] have chosen to use the average value of spherical harmonics. Because each theory starts from the same model their results are readily related and we shall therefore sketch Saupe's original treatment of the problem.

Because of the invariance with respect to reversing the direction of each of the space fixed axes terms with $\alpha \neq \beta$ vanish. We are only interested then in the average value of $l_{\alpha a} l_{\alpha b}$, in fact we require the three averages $\langle l_{za} l_{zb} \rangle$, $\langle l_{xa} l_{xb} \rangle$ and $\langle l_{ya} l_{yb} \rangle$. The values of $\langle l_{xa} l_{xb} \rangle$ and $\langle l_{ya} l_{yb} \rangle$ are equal because of the axial symmetry of the system about the magnetic field and because the properties of direction cosines are such that

$$\langle l_{\alpha a} l_{\alpha b} \rangle = \delta_{ab}, \tag{3.1}$$

then

$$\langle l_{xa} l_{xb} \rangle = \frac{\delta_{ab} - \langle l_{za} l_{zb} \rangle}{2}. \tag{3.2}$$

Let us define a quantity S_{ab} where

$$S_{ab} = \frac{3\langle l_{za} l_{zb} \rangle - \delta_{ab}}{2}, \tag{3.3}$$

then

$$\langle l_{za} l_{zb} \rangle = \frac{\delta_{ab} + 2S_{ab}}{3}, \tag{3.4}$$

and

$$\langle l_{xa} l_{xb} \rangle = \langle l_{ya} l_{yb} \rangle = \frac{\delta_{ab} - S_{ab}}{3}. \tag{3.5}$$

If we substitute these averages into equation (2.2) and use the formula for the isotropic Hamiltonian we find

$$\langle \mathscr{H} \rangle = \mathscr{H}^I + \tfrac{2}{3} g_{ab} S_{ab} \beta H S_z + \tfrac{2}{3} A_{ab} S_{ab} I_z S_z - \\ - \frac{A_{ab}}{3} S_{ab} [I_x S_x + I_y S_y]. \tag{3.6}$$

The properties of the ordering matrix, S_{ab}, have been derived in detail by Saupe and so we shall not discuss them here.

4. The Swarm Theory

In this theory the molecules are said to form aggregates containing large numbers of molecules with their long axes parallel; these swarms are surrounded by molecules moving isotropically. The model is similar to an isotropic solution of colloidal particles but with an essential difference, namely, that the molecules in the swarms are exchanging rapidly with those in the isotropic fluid.[18] The application of a magnetic field aligns the swarms, to a certain extent, with their long axes parallel to the magnetic field. A solute will be partitioned between the two regions of the mesophase and when the radical is in the isotropic region its Hamiltonian will simply be that given by equation (2.4). Because of the alignment of the clusters there is a partial ordering of the solute in these clusters and we can best describe this with an ordering matrix S^A_{ab}. The Hamiltonian, $\mathscr{H}^A$, for the radical in the swarm is given by equation (3.6) but with S_{ab} replaced by S^A_{ab}. Since the rate of exchange between the two regions is rapid[7] the time averaged Hamiltonian is

$$\langle \mathscr{H} \rangle = (1-x)\mathscr{H}^I + x\mathscr{H}^A, \tag{4.1}$$

where x is the mole fraction of the solute in a cluster. By combining this equation with (3.6) we find

$$\langle \mathscr{H} \rangle = \mathscr{H}^I + \tfrac{2}{3}xS^A_{ab}g_{ab}\beta HS_z + \tfrac{2}{3}xS^A_{ab}I_zS_z - \frac{x}{3}S^A_{ab}A_{ab}[I_xS_x + I_yS_y]. \tag{4.2}$$

The form of the average Hamiltonian is clearly the same for both models of the nematic mesophase but with the ordering matrix S_{ab} of the distortion theory equated with xS^A_{ab} of the swarm theory. In principle our task is complete although we have only proved the equivalence of the two theories when applied to a single radical this conclusion holds for all magnetic resonance experiments because the positions of the lines in a spectrum depend on the value of $\langle l_{\alpha a} l_{\beta b} \rangle$ and this has been shown to be the same in both theories. In practice when the swarm theory is employed it is customary to make more assumptions about the orientation of the solute in a

swarm. The reason for this is that the distortion theory contains five independent parameters, the S_{ab}, whereas the general form of the swarm theory contains six, the S_{ab}^{A} and the mole fraction x. We shall now consider two examples of planar radicals where it is possible to reduce the number of parameters and still retain the equivalence of the theories.

5. Two Examples

It is convenient to persist in the use of electron resonance for the introduction of examples from nuclear magnetic resonance does not present us with any new concepts.

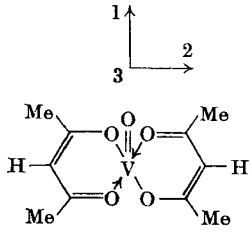

Figure 1. The structure and axis system for vanadyl acetylacetonate.

We begin with vanadyl acetylacetonate the structure of which is shown in Fig. 1. The unpaired electron interacts exclusively with the vanadium nucleus and to a good approximation both the g and the vanadium hyperfine tensors are cylindrically symmetric about an axis perpendicular to the molecular plane.[19] The Hamiltonian for the complex in the nematic mesophase is given by equation (4.2) and our problem is to evaluate the S_{ab}^{A}. Measurements on nematic mesophases in magnetic fields suggest that saturation occurs at field strengths of about 1 kilogauss.[20] According to the swarm theory this means that for fields normally used in magnetic resonance the clusters are completely aligned with their long axes parallel to the field. It is reasonable to assume that when a planar solute such as vanadyl acetylacetonate is in a cluster the field will be parallel to the molecular plane and so the value of S_{33}^{A} is simply $-\frac{1}{2}$.

Because the g and hyperfine tensors are diagonal in the axis system 1, 2, 3 given in Fig. 1

$$S^A_{ab} g_{ab} = S^A_{11} g_{11} + S^A_{22} g_{22} + S^A_{33} g_{33}, \tag{5.1}$$

and since the ordering matrix is traceless [16]

$$S^A_{ab} g_{ab} = \tfrac{3}{2} g'_\perp, \tag{5.2}$$

and similarly

$$S^A_{ab} A_{ab} = \tfrac{3}{2} A'_\perp, \tag{5.3}$$

where the prime indicates the anisotropic component of a tensor. Substitution of these results into equation (4.2) gives us the average Hamiltonian

$$\langle \mathscr{H} \rangle = \mathscr{H}^I + x g'_\perp \beta H S_Z + x A'_\perp I_Z S_Z - \frac{x}{2} A'_\perp [I_x S_x + I_y S_y]. \tag{5.4}$$

Let us see what result the ordering matrix would have given us. We must again evaluate $S_{ab} g_{ab}$ and $S_{ab} A_{ab}$; using the molecular axis system 1, 2 and 3 we have

$$S_{ab} g_{ab} = S_{33} g_\parallel + (S_{11} + S_{22}) g_\perp, \tag{5.5}$$

and so

$$S_{ab} g_{ab} = -3 S_{33} g'_\perp, \tag{5.6}$$

and similarly

$$S_{ab} A_{ab} = -3 S_{33} A'_\perp. \tag{5.7}$$

Substitution of these results into equation (3.6) gives

$$\langle \mathscr{H} \rangle = \mathscr{H}^I - 2 S_{33} g'_\perp \beta H S_z - 2 S_{33} A'_\perp I_z S_z + S_{33} A'_\perp [I_x S_x + I_y S_y], \tag{5.8}$$

which is identical in form to equation (5.4) but with $-2S_{33}$ replaced by x.

In the previous example we were concerned with a radical whose tensors had cylindrical symmetry and we now consider the peri-naphthenyl radical [8] whose shape is cylindrically symmetric. A glance at the formula in Fig. 2 tells us that there are many magnetic nuclei present, however, the only effect this has on the equations is to necessitate a summation sign in equation (3.6) and (4.2). Again

we must evaluate $S^A_{ab} g_{ab}$ and the $S^A_{ab} A^i_{ab}$. When the radical is in a swarm the magnetic field will be parallel to the molecular plane but there will be no other preferred orientation of any molecular axis within the swarm. The ordering matrix is therefore cyclindrically symmetric with $S^A_{33} = \frac{1}{2}$ and $S^A_{11} = S^A_{22} = -\frac{1}{4}$. Substitution of these three numbers into the modified form of equation (4.2) gives

$$\langle \mathscr{H} \rangle = \mathscr{H}^I - x g'_{33} \beta H S_Z + \sum_i \left\{ -\frac{x}{2} A^i_{33} I^i_Z S_Z + \frac{x A^i_{33}}{4} [I^i_x S_x + I^i_y S_y] \right\}. \tag{5.9}$$

As we might expect we obtain an entirely analogous equation using the ordering matrix. The symmetry of the radical dictates

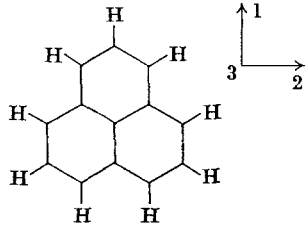

Figure 2. The structure and axis system for the perinaphthenyl radical.

that in the axis system 1, 2, 3 the ordering matrix S_{ab} is also diagonal and cylindrically symmetric with

$$S_{11} = S_{22} = -\frac{S_{33}}{2}, \tag{5.10}$$

and so

$$S_{ab} g_{ab} = \tfrac{3}{2} S_{33} g'_{33}, \tag{5.11}$$

and

$$S_{ab} A^i_{ab} = \tfrac{3}{2} S_{33} A'^i_{33}. \tag{5.12}$$

Inclusion of these results into the modified equation (3.6) gives a Hamiltonian identical to (5.9) but with $-2S_{33}$ instead of x.

Conclusions

The distortion theory describes the orientation of a solute by the ordering matrix whilst the important quantity in the swarm theory

is the mole fraction of the solute in the swarms. Mathematically the interpretations of magnetic resonance experiments provided by the general form of either theory are equivalent. In practice it is usual to make more assumptions about the orientation of the solute in a cluster in order to reduce the number of parameters but even then the two theories give the same result. Provided the molecular motion is rapid the choice of which theory one should use to interpret *magnetic* resonance experiments would seem to be largely a question of taste.

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