

# MOLECULAR STRUCTURE DETERMINATION BY NMR SPECTROSCOPY

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## ABSTRACT

The spin Hamiltonian giving rise to the energy levels of a system of nuclei in a partially oriented molecule is described. The splittings in the n.m.r. spectra are mainly due to the direct dipolar interactions of the nuclei, and their measurement is therefore capable of giving relative distances between magnetic nuclei. The limitations to the utility of this method of structure determination are considered, including the various effects of non-rigidity, anisotropy in the indirect spin-coupling tensor and the complexity of the spectra. An application to the determination of metal-hydrogen distances in transition-metal hydrides is described.

Nuclear magnetic resonance spectroscopy provides important qualitative information about molecular structure, and has frequently been used to distinguish between two or more postulated structures. However, it is also possible to obtain by n.m.r. quantitative information about structures—that is, to measure bond lengths and angles. This is done through measurement of the direct dipolar coupling of nuclei with spins of one-half, for this coupling is determined by the relative positions of the nuclei. In what follows I shall show how the high-resolution spectra of partially oriented molecules, as in a molecular beam or in an anisotropic liquid, may be used to obtain relative bond lengths, and emphasis will be placed upon the limitations of this particular technique.

## THE SPIN HAMILTONIAN FOR THE NMR OF PARTIALLY ORIENTED MOLECULES

High-resolution nuclear magnetic resonance frequencies associated with nuclei of spin  $I = \frac{1}{2}$  are dependent on two types of molecular constants: the shielding tensor  $\sigma^{(i)}$  of nucleus  $i$  and the coupling tensor  $\mathbf{T}^{(ij)} + \mathbf{J}^{(ij)}$  linking the spins  $\mathbf{I}^{(i)}$  and  $\mathbf{I}^{(j)}$  of nuclei  $i$  and  $j$ . The associated Hamiltonian may be written in the usual notation (in Hertz) as

$$\mathcal{H} = -(2\pi)^{-1} B_z \sum_i \gamma^{(i)} (I_z^{(i)} - \overline{\sigma_{\alpha z}^{(i)}} I_\alpha^{(i)}) + \sum_{i < j} (\overline{T_{\alpha\beta}^{(ij)}} + \overline{J_{\alpha\beta}^{(ij)}}) I_\alpha^{(i)} I_\beta^{(j)} \quad (1)$$

where the tensor summation convention is used (a repeated Greek suffix denotes a sum over all three Cartesian components). The spin-coupling tensor consists of the traceless symmetric direct dipolar interaction  $\mathbf{T}^{(ij)}$  and

the component  $\mathbf{J}^{(ij)}$  involving the indirect interaction of the nuclear spins  $\mathbf{I}^{(i)}$  and  $\mathbf{I}^{(j)}$  via the electrons.

$$T_{\alpha\beta}^{(ij)} = \frac{\mu_0 \hbar}{4\pi 2\pi} \frac{\gamma^{(i)}\gamma^{(j)}}{r_{ij}^5} (\overline{r_{ij}^2} \delta_{\alpha\beta} - 3\overline{r_{ij\alpha}r_{ij\beta}}) \quad (2)$$

where  $\mathbf{r}_{ij}$  is the vector from nucleus  $j$  to nucleus  $i$  and  $\mu_0/4\pi = 10^{-7} \text{ J C}^{-2} \text{ s}^2 \text{ m}^{-1} = 1 \text{ e.m.u.}$ . The bars over  $\overline{\sigma^{(i)}}$ ,  $\overline{\mathbf{T}^{(ij)}}$  and  $\overline{\mathbf{J}^{(ij)}}$  in equation (1) indicate average quantities—that is, the tensor components are statistically averaged over a time of the order of the appropriate nuclear spin lifetimes.

Actually there is also a term in  $\mathcal{H}$  which is quadratic in the nuclear spin  $\mathbf{I}^{(i)}$ . It arises from the second-order nuclear-spin interaction with the electrons. However, for  $I_z^{(i)} = \frac{1}{2}$  this term is independent of  $I_z^{(i)}$  and it does not contribute to the spectrum.

In an isotropic fluid

$$\overline{\sigma_{\alpha\alpha}^{(i)}} = \frac{1}{3} \overline{\sigma_{\gamma\gamma}^{(i)}} \delta_{\alpha\alpha} = \overline{\sigma^{(i)}} \delta_{\alpha\alpha} \quad (3)$$

$$\overline{T_{\alpha\beta}^{(ij)}} = \frac{1}{3} \overline{T_{\gamma\gamma}^{(ij)}} \delta_{\alpha\beta} = 0 \quad (4)$$

$$\overline{J_{\alpha\beta}^{(ij)}} = \frac{1}{3} \overline{J_{\gamma\gamma}^{(ij)}} \delta_{\alpha\beta} = \overline{J^{(ij)}} \delta_{\alpha\beta} \quad (5)$$

and equation (1) reduces to the usual n.m.r. Hamiltonian

$$\mathcal{H}_0 = -(2\pi)^{-1} B_z \sum_i \gamma^{(i)} (1 - \overline{\sigma^{(i)}}) I_z^{(i)} + \sum_{i < j} \overline{J^{(ij)}} \mathbf{I}^{(i)} \cdot \mathbf{I}^{(j)} \quad (6)$$

In an anisotropic fluid, as in a strong uniform electric field or in a nematic liquid crystalline medium, the effective Hamiltonian becomes<sup>1-3</sup>

$$\begin{aligned} \mathcal{H}_{\text{eff.}} = \mathcal{H}_0 + (2\pi)^{-1} B_z \sum_i \gamma^{(i)} (\overline{\sigma_{zz}^{(i)}} - \overline{\sigma^{(i)}}) I_z^{(i)} \\ + \sum_{i < j} (\overline{T_{zz}^{(ij)}} + \overline{J_{zz}^{(ij)}} - J^{(ij)}) (\frac{3}{2} I_z^{(i)} I_z^{(j)} - \frac{1}{2} \mathbf{I}^{(i)} \cdot \mathbf{I}^{(j)}) \quad (7) \end{aligned}$$

Equation (7) is exact if the alignment is parallel to the magnetic field  $B_z$ ; if it is not, it is a good approximation provided  $\mathcal{H} - \mathcal{H}_0$  is small compared with the Zeeman splittings.

The major contributor to the anisotropic coupling constant  $\overline{T_{zz}^{(ij)}} + \overline{J_{zz}^{(ij)}} - J^{(ij)}$  is normally the direct dipolar interaction  $\overline{T_{zz}^{(ij)}}$  proportional to the inverse cube of the separation of the nuclei. This is the basis of structural determinations by this technique. From equation (2)

$$\overline{T_{zz}^{(ij)}} = -\frac{\mu_0 \hbar}{4\pi \pi} \gamma^{(i)} \gamma^{(j)} \overline{(\frac{3}{2} \cos^2 \theta_{ij} - \frac{1}{2}) r_{ij}^{-3}} \quad (8)$$

where  $\theta_{ij}$  is the angle between the internuclear vector  $\mathbf{r}_{ij}$  and the direction of the magnetic field.

In the case of a linear molecule in a  $^1\Sigma$  state and in the particular rotational state  $\psi_{JM}$ , where  $J = 0, 1, 2, \dots$  and  $J \geq M \geq -J$ ,

$$\begin{aligned} \overline{T_{zz}^{(ij)}} &= \langle \psi_{JM} | T_{zz}^{(ij)} | \psi_{JM} \rangle \\ &= -\frac{\mu_0 \hbar}{4\pi \pi} \gamma^{(i)} \gamma^{(j)} (r_{ij}^{-3})_J \frac{J^2 + J - 3M^2}{(2J - 1)(2J + 3)} \quad (9) \end{aligned}$$

The splitting resulting from this interaction was measured in  $H_2$  in the state  $J = 1$  by Ramsey and his collaborators<sup>4</sup> using molecular-beam resonance spectroscopy; and since the splitting actually depends on  $\overline{T_{zz}^{(ij)}} + \overline{J_{zz}^{(ij)}} - J^{(ij)}$  rather than  $\overline{T_{zz}^{(ij)}}$ , the measurement<sup>4</sup> gives

$$\left[ \frac{\mu_0 \hbar}{4\pi \pi} \gamma_H^2 (r^{-3})_{J=1} - \frac{2}{3} (J_{\parallel} - J_{\perp}) \right] = 576.71 \pm 0.24 \text{ kHz}$$

Hence, if  $(r^{-3})_{J=1} = 0.355 \ 56 \text{ a.u.}^5$ ,  $J_{\parallel} - J_{\perp} = -350 \pm 360 \text{ Hz}$  for  $H_2$ . It would be worthwhile repeating this experiment in the hope of obtaining a more accurate value for the anisotropy in  $\mathbf{J}$  for  $H_2$ .

If the molecule partially orients in a uniaxial constraint as a rigid body, equation (8) simplifies to

$$\overline{T_{zz}^{(ij)}} = -\frac{\mu_0 \hbar}{4\pi \pi} \gamma^{(i)} \gamma^{(j)} S^{(ij)} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) \langle r_{ij}^{-3} \rangle \quad (10)$$

where the angular brackets  $\langle \dots \rangle$  denote an average over the vibrational motion and  $\Omega$  is the angle between the constraint and the magnetic field ( $\Omega = 0$  and  $\frac{3}{2} \cos^2 \Omega - \frac{1}{2} = 1$  if the magnetic field causes the constraint, as in a nematic liquid crystal medium), and

$$S^{(ij)} = \frac{3}{2} \overline{\cos^2 \phi_{ij}} - \frac{1}{2}$$

is the mean value of the second Legendre polynomial of the cosine of the angle  $\phi_{ij}$  between the internuclear vector  $\mathbf{r}_{ij}$  and the constraint;  $S^{(ij)}$  is a particular element of the molecular alignment matrix  $S_{\alpha\beta}$  introduced by Saupe<sup>2</sup>:

$$S_{\alpha\beta} = \frac{3}{2} \overline{\cos \phi_{\alpha} \cos \phi_{\beta}} - \frac{1}{2} \quad (11)$$

where  $\phi_{\alpha}$  is the angle between the  $\alpha$ -axis fixed in the molecule and the space-fixed constraint. The matrix  $\mathbf{S}$  is traceless and symmetric and in general requires five numbers to specify it. Symmetry may reduce this number<sup>†</sup>; for example, for a molecule with a three-fold or higher axis of symmetry only one  $S$ -parameter is independent and the  $\mathbf{S}$ -matrix takes the form

$$\mathbf{S} = \begin{pmatrix} -\frac{1}{2}S & 0 & 0 \\ 0 & -\frac{1}{2}S & 0 \\ 0 & 0 & S \end{pmatrix} \quad (12)$$

where  $S = S_{33}$  is the mean value of the second Legendre polynomial of the cosine of the angle between the constraint and the major symmetry axis of the molecule. For an isotropic system all the  $S$ -parameters are zero and if the 3-axis is completely oriented  $S_{33} = 1$ .

The alignment  $S^{(ij)}$  of the internuclear vector  $\mathbf{r}_{ij}$  can be expressed in terms of the  $\mathbf{S}$ -matrix by the following equations:

<sup>†</sup> The actual number of  $S$ -parameters is the same as the number of independent quadrupole moments  $\Theta_{\alpha\beta}$  given for various symmetries in Table 1 of reference 5a. If the molecule adopts different conformations, and spends sufficient time in each to be oriented in the anisotropic medium, appropriate  $S$ -parameters must be assigned to each conformation.

$$S^{(ij)} = S_{\alpha\beta} \cos \beta_\alpha^{(ij)} \cos \beta_\beta^{(ij)} \quad (13)$$

$$= \frac{2}{3} S_{\alpha\beta} \left( \frac{3}{2} \cos \beta_\alpha^{(ij)} \cos \beta_\beta^{(ij)} - \frac{1}{2} \delta_{\alpha\beta} \right) \quad (14)$$

$$= S_{33} \left( \frac{3}{2} \cos^2 \beta_3^{(ij)} - \frac{1}{2} \right) + \frac{1}{2} (S_{11} - S_{22}) (\cos^2 \beta_1^{(ij)} - \cos^2 \beta_2^{(ij)}) \\ + 2S_{12} \cos \beta_1^{(ij)} \cos \beta_2^{(ij)} + 2S_{23} \cos \beta_2^{(ij)} \cos \beta_3^{(ij)} + 2S_{31} \cos \beta_3^{(ij)} \cos \beta_1^{(ij)} \quad (15)$$

where  $\beta_\alpha^{(ij)}$  is the angle between  $\mathbf{r}_{ij}$  and the molecule-fixed  $\alpha$ -axis. The Cartesian molecule-fixed axes 1, 2, 3 may be chosen to suit the particular symmetry; for example, the 3-axis is conveniently assigned to the major rotational axis, such as the CF bond in  $\text{CH}_3\text{F}$  or perpendicular to the ring in  $\text{C}_6\text{H}_6$ .

From equations (2) and (11) (or 10 and 13)

$$\overline{T_{zz}^{(ij)}} = T_{\alpha\beta}^{(ij)} \overline{\cos \phi_\alpha \cos \phi_\beta} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) \\ = \frac{2}{3} T_{\alpha\beta}^{(ij)} S_{\alpha\beta} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) = - \frac{\mu_0 \hbar}{4\pi \pi} \gamma^{(i)} \gamma^{(j)} S_{\alpha\beta} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) \\ \times \langle r_{ij}^{-3} \cos \beta_\alpha^{(ij)} \cos \beta_\beta^{(ij)} \rangle \quad (16)$$

The general spin Hamiltonian for molecules containing nuclei of spin  $\frac{1}{2}$  and which align as rigid bodies may be written as

$$\mathcal{H}_{\text{eff.}} = \mathcal{H}_0 + \frac{2}{3} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) S_{\alpha\beta} \left[ (2\pi)^{-1} B_z \sum_i \gamma^{(i)} \sigma_{\alpha\beta}^{(i)} I_z^{(i)} \right. \\ \left. + \sum_{i < j} (T_{\alpha\beta}^{(ij)} + J_{\alpha\beta}^{(ij)}) \left( \frac{3}{2} I_z^{(i)} I_z^{(j)} - \frac{1}{2} \mathbf{I}^{(i)} \cdot \mathbf{I}^{(j)} \right) \right] \quad (17)$$

If there are nuclei with spin  $I \geq 1$ , there is an important additional term in the Hamiltonian that varies quadratically with the nuclear spin  $\mathbf{I}^{(i)}$ .<sup>6</sup> This is dependent on the nuclear quadrupole coupling constant  $e^2 q^{(i)} Q^{(i)}$  and on the 'pseudo-quadrupole' interaction proportional to  $\gamma^{(i)2}$  and determined by the second-order nuclear magnetic hyperfine interaction. Both terms contribute to the coefficient of  $[3I_z^{(i)2} - I^{(i)}(I^{(i)} + 1)]$  in the spin Hamiltonian and they cannot easily be separated. However, the quadrupole coupling is normally dominant<sup>7</sup> and observed splittings in anisotropic n.m.r. spectra can usually safely be attributed to  $e^2 q^{(i)} Q^{(i)}$ .<sup>8</sup> The extra term to be added to the general Hamiltonian (1) is

$$\Delta \mathcal{H} = \frac{1}{2} \sum_i \left( \overline{K_{\alpha\beta}^{(i)}} + \frac{e^2 \overline{q_{\alpha\beta}^{(i)} Q^{(i)}}}{2I^{(i)}(2I^{(i)} - 1)} \right) (I_\alpha^{(i)} I_\beta^{(i)} + I_\beta^{(i)} I_\alpha^{(i)}) \quad (18)$$

In an isotropic fluid this degenerates into

$$\Delta \mathcal{H}_0 = \sum_i K^{(i)} I^{(i)}(I^{(i)} + 1) \quad (19)$$

where  $K^{(i)} = \frac{1}{3} K_{\alpha\alpha}^{(i)}$ , but this does not affect the spectra. In a uniaxial medium the appropriate contribution when the resultant splittings are small compared with the Zeeman splittings is

$$\Delta \mathcal{H}_{\text{eff.}} = \Delta \mathcal{H}_0 + \sum_i \left( \overline{K_{zz}^{(i)}} - K^{(i)} + \frac{e^2 \overline{q_{zz}^{(i)} Q^{(i)}}}{2I^{(i)}(2I^{(i)} - 1)} \right) \left[ \frac{3}{2} I_z^{(i)2} - \frac{1}{2} I^{(i)}(I^{(i)} + 1) \right] \quad (20)$$

Thus, for a single magnetic nucleus with  $I^{(i)} = 1$ , the levels  $I_z^{(i)} = \pm 1$  are raised from  $\mp (2\pi)^{-1} \gamma^{(i)} (1 - \sigma_{zz}^{(i)}) B_z$  by  $\frac{1}{2}(K_{zz}^{(i)} - K^{(i)} + \frac{1}{2}e^2 q_{\alpha\beta}^{(i)} Q^{(i)})$  and the level  $I_z^{(i)} = 0$  is lowered by twice this amount; the selection rule  $\Delta I_z^{(i)} = \pm 1$  produces a doublet with a spacing of  $\frac{3}{2}(K_{zz}^{(i)} - K^{(i)} + \frac{1}{2}e^2 q_{\alpha\beta}^{(i)} Q^{(i)})$ . If the molecule aligns as a rigid body,

$$\Delta \mathcal{H}_{\text{eff.}} = \Delta \mathcal{H}_0 + \frac{2}{3} \left( \frac{3}{2} \cos^2 \Omega - \frac{1}{2} \right) S_{\alpha\beta} \sum_i \left[ K_{\alpha\beta}^{(i)} + \frac{e^2 q_{\alpha\beta}^{(i)} Q^{(i)}}{2I^{(i)}(2I^{(i)} - 1)} \right] \times \left[ \frac{3}{2} I_z^{(i)2} - \frac{1}{2} I^{(i)}(I^{(i)} + 1) \right] \quad (21)$$

## THE EFFECTS OF NON-RIGIDITY

If the molecules do not orient as rigid rotators, then equations (10), (13) and (17) are inappropriate and it is necessary to return to equation (7). The anisotropic medium may be considered to have two effects on the molecular parameters  $\overline{T_{zz}^{(ij)}}$ ,  $\overline{J_{zz}^{(ij)}}$  and  $J^{(ij)}$ —there is the effect of *orientation* of the molecular axes considered in the previous section, and the effect of *distortion* arising from the change in geometrical structure (and for  $\overline{J_{zz}^{(ij)}}$  and  $J^{(ij)}$  the change in electronic structure) induced by the anisotropic environment. Both effects are dependent on the molecule and the solvent. Fortunately, many molecules are nearly rigid, so that distortion effects are often small.

The tetrahedral molecule  $\text{CH}_4$  exhibits a small splitting in its proton magnetic resonance spectrum in a nematic phase<sup>9</sup>, and this is presumably due to distortion, since in a regular tetrahedron  $\overline{T_{zz}^{(ij)}} + \overline{J_{zz}^{(ij)}} - J^{(ij)}$  is identically zero. Also, deuteron quadrupole splittings of 10–20 Hz have been observed in  $\text{CD}_4$ <sup>9</sup>. A 1:2:1 triplet is observed in tetramethyl silane (TMS) and in neopentane in nematic solvents<sup>10</sup>; the splitting varies with the temperature (the splitting is larger at lower temperatures, which indicates that vibrational excitation is not responsible) and solvent, and the separation of the lines in TMS is in the range 4–15 Hz<sup>10, 11</sup>.

We now discuss a simple theoretical model of a tetrahedral molecule such as  $\text{CH}_4$  in a uniaxial environment<sup>12</sup>. Four positions are considered in which the nuclei A, B, C and D occupy the unique position of  $\text{H}_A$  in Figure 1. Then if  $l$  is the undistorted inter-proton distance,

$$l_{\text{AB}} = \sqrt{\frac{3}{2}} l \sin \left( \frac{\theta + \delta}{2} \right) \approx l \left( 1 + \frac{\delta}{2\sqrt{2}} \right)$$

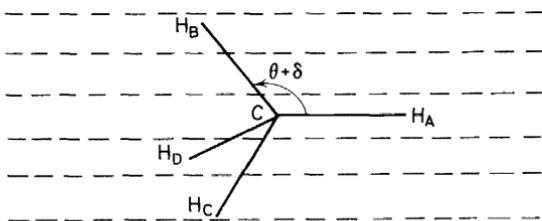


Figure 1. Distortion of a  $\text{CH}_4$  molecule by a uniaxial environment. The bond lengths are assumed to be constant, while the angle  $\text{H}_A\text{C H}_B = \text{H}_A\text{C H}_C = \text{H}_A\text{C H}_D$  is increased by  $\delta$  from the tetrahedral value of  $\theta = -\cos^{-1}(\frac{1}{3})$

$$l_{BC} = l_{CD} = l_{DB} = \frac{3}{2\sqrt{2}} l \sin(\theta + \delta) \approx l \left(1 - \frac{\delta}{2\sqrt{2}}\right)$$

where the approximations are valid for small  $\delta$ . From equation (2)

$$T_{zz}^{(AB)} = -\frac{\mu_0 \hbar \gamma^2}{4\pi 2\pi l_{AB}^3} \left[ 3 \sin^2\left(\frac{\theta + \delta}{2}\right) - 1 \right] \approx -\frac{\mu_0 \hbar \gamma^2}{4\pi 2\pi l^3} \left(1 + \frac{\delta}{2\sqrt{2}}\right) \quad (22)$$

$$T_{zz}^{(BC)} = T_{zz}^{(CD)} = T_{zz}^{(DB)} = \frac{\mu_0 \hbar \gamma^2}{4\pi 2\pi l_{BC}^3} \approx \frac{\mu_0 \hbar \gamma^2}{4\pi 2\pi l^3} \left(1 + \frac{3\delta}{2\sqrt{2}}\right) \quad (23)$$

The nuclei move rapidly between the different positions, yielding an average dipolar coupling

$$\overline{T_{zz}^{(j)}} = \frac{1}{2}(T_{zz}^{(AB)} + T_{zz}^{(BC)}) \approx \frac{\mu_0 \hbar \gamma^2 \delta}{4\pi 2\pi l^3 2\sqrt{2}} = L\delta \quad (24)$$

which vanishes, as it should, for  $\delta = 0$ . For  $\text{CH}_4$  the coupling constant  $L = 7.5 \text{ kHz rad}^{-1} = 130 \text{ Hz deg}^{-1}$ . If anisotropy in the indirect spin coupling is neglected, the effective Hamiltonian is

$$\begin{aligned} \mathcal{H}_{\text{eff.}} = & -(2\pi)^{-1} \gamma(1 - \sigma) B_z \sum_i I_z^{(i)} + J \sum_{i < j} \mathbf{I}^{(i)} \cdot \mathbf{I}^{(j)} \\ & + L\delta \sum_{i < j} \left(\frac{3}{2} I_z^{(i)} I_z^{(j)} - \frac{1}{2} \mathbf{I}^{(i)} \cdot \mathbf{I}^{(j)}\right) \quad (25) \end{aligned}$$

The isotropic  $J$ -coupling does not contribute to the spectrum which consists of a 1:3:3:1 quartet with a line separation of  $\frac{3}{2}L\delta$ , or 195 Hz per degree of distortion of  $\text{CH}_4$ . Thus a very small distortion ( $\delta \approx 10^{-2}$  deg) leads to a detectable splitting in  $\text{CH}_4$ .

Dipolar splittings in  $^{13}\text{CH}_4$  or nuclear quadrupole splittings in  $\text{CD}_4$  may be larger, but they may not be unambiguously interpreted in terms of a distortion, since there may be a solvent effect on the spin-coupling constant  $J_{\text{CH}}$  and the uniaxial environment itself may produce a small electric field gradient<sup>12</sup>.

The distortion effect considered above reflects the coupling of the rotational motion of the molecule in the uniaxial environment with the internal vibrations<sup>10, 13</sup>—it is a fundamental difficulty with this particular technique for determining bond lengths and angles in molecules. Fortunately, the difficulty is not severe in many rigid molecules which align significantly and thereby produce large dipolar splittings. However, from the evidence of tetramethylsilane it seems that it would be prudent to allow for a distortion contribution to proton splittings of up to 15 Hz—the actual magnitude is dependent on the deformability of the molecule and on the distance between the nuclei. The effect may be more important in methyl fluoride than in cyclopropane, and a possible reason for this has been given by Lucas<sup>14</sup>.

A more straightforward effect of non-rigidity reflects the vibrational averaging in equations (10) and (16). A full account requires a knowledge not only of the harmonic force field but also of the cubic anharmonic constants; in  $\text{H}_2$  the anharmonic contribution to  $\langle r^{-3} \rangle = \langle (r_e + \Delta r)^{-3} \rangle$  is larger than the harmonic and  $\langle r^{-3} \rangle = 0.982(r_e^{-3})^{1, 15}$ . Anharmonic force fields are not,

in general, available for polyatomic molecules, so that vibrational corrections cannot easily be made. However, Lucas<sup>15</sup> has shown that if a vibrationally averaged structure is available, harmonic corrections alone suffice. He has explained apparent inconsistencies between the structures of cyclopropane determined by nematic-phase n.m.r. and by electron diffraction<sup>14</sup>. However, with methyl fluoride and 1,1-difluoroethene vibrational 'corrections' apparently increase the inconsistencies<sup>15, 17</sup>. Thus in CH<sub>3</sub>F, if a reasonable H—H separation is chosen, and the observed  $T_{zz}^{(HH)}$  used to obtain the unique orientation parameter *S*, then a C—F bond length and HCH angle may be deduced from  $T_{zz}^{(CF)}$  and  $T_{zz}^{(CH)}$ ; the calculated value of  $T_{zz}^{(HF)}$  is then 1.011 times the experimental result if no allowance is made for vibrations, and this factor increases to 1.017 when vibrational 'corrections' are incorporated<sup>15</sup>. It has been suggested that this discrepancy may arise from anisotropy in the indirect couplings,  $J_{zz}^{(ij)} - J^{(ij)}$ <sup>18</sup>, or from solvent-induced changes in  $J^{(ij)}$ <sup>16</sup>. However, it may be due to the coupling of orientational and vibrational motion at a rate of 250 s<sup>-1</sup> at 0°C and with an activation energy of 45.6 kJ

Nuclear magnetic resonance studies of non-rigid molecules in nematic solvents can provide useful information about the internal motion. Two cases may be distinguished. The first involves motion which is rapid compared with the time required for a molecule to reorient in the uniaxial environment, and this is interpreted by employing an averaged molecular symmetry. Thus in CH<sub>3</sub>CH<sub>2</sub>F the rapid rotation of the CH<sub>3</sub> group effectively introduces a plane of symmetry—thus restricting the number of independent *S*-parameters to three<sup>19</sup>. The second case is associated with motion which is fast compared with the inverse dipolar coupling constant but slow compared with the time required to orient in the anisotropic medium; it is then, in general, necessary to employ different *S*-parameters for each conformation. In the case of cyclooctatetraene n.m.r. studies have been made over the range -35° to 170°C in various nematic media<sup>20</sup>, and the results show that the molecule has a symmetrical tub (*D*<sub>2d</sub>) conformation in which there is an internal 'bond-shift' motion at a rate of 250 s<sup>-1</sup> at 0°C and with an activation energy of 45.6 kJ mol<sup>-1</sup>; inversion of the tub presumably also occurs, but as it leaves the dipolar interactions unchanged, it does not affect the spectrum<sup>20</sup>.

The nematic-phase spectrum of  $\pi$ -cyclobutadienyliron-tricarbonyl [ $\pi$ -C<sub>4</sub>H<sub>4</sub>Fe(CO)<sub>3</sub>] enriched with <sup>13</sup>CO proves that the  $\pi$ -C<sub>4</sub>H<sub>4</sub> group rotates with respect to the rest of the molecule<sup>21</sup>. Non-rigidity has also been detected and studied in  $\pi$ -cyclopentadienyltricarbonyltungsten hydride [ $\pi$ -C<sub>5</sub>H<sub>5</sub>WH(CO)<sub>3</sub>]<sup>22</sup> and nickel(IV)-bis-1,2-dithiolate [Ni(S<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>]<sup>23</sup> in which the dipolar couplings  $T_{zz}^{(13)}$  and  $T_{zz}^{(14)}$  (see Figure 2) are found to be

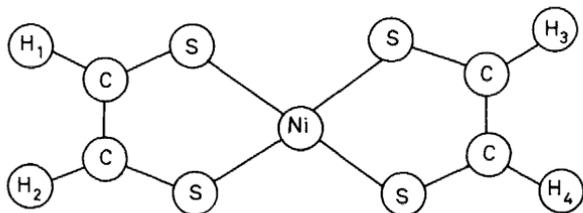


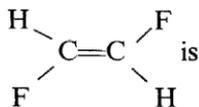
Figure 2. The structure of nickel(IV)-bis-1,2-dithiolate. The direct proton coupling constants  $T_{zz}^{(13)}$  and  $T_{zz}^{(14)}$  are equal, which indicates internal rotation of the ligands, since the pseudotetrahedral *D*<sub>2d</sub> symmetry is excluded by the need for more than one orientation parameter

equal at a variety of temperatures, which indicates an intramolecular rotation of one dithiolate ligand with respect to the other, since changes in the spectra with temperature demonstrate the need for more than one independent orientation parameter; the rotation is slow compared with the time required to orient in the nematic phase<sup>2,3</sup>.

### ANISOTROPY IN THE INDIRECT SPIN-COUPLING TENSOR

Another problem associated with the interpretation of the n.m.r. spectra of partially oriented molecules is related to the presence of anisotropy in the indirect spin-coupling tensor  $\mathbf{J}^{(ij)}$  in the observed coupling constant  $\overline{T}_{zz}^{(ij)} + \overline{J}_{zz}^{(ij)} - J^{(ij)}$  (see equation 7). Inconsistencies have been noted in the observed coupling constants in molecules such as  $^{13}\text{CH}_3\text{F}$ <sup>15, 17, 18</sup>,  $\text{H}_2\text{C}=\text{CF}_2$ <sup>13, 17, 24, 25</sup> and  $\text{C}_6\text{F}_6$ <sup>26</sup>. Thus in  $\text{C}_6\text{F}_6$  the experimental coupling constants are in the ratio 1:0.187:0.134<sup>26</sup>, compared with  $1:3^{-\frac{1}{2}}:2^{-3}$  (i.e. 1:0.192:0.125) for a regular hexagon; this particular discrepancy is probably due to anisotropy in  $\mathbf{J}$  rather than to non-rigidity, since in  $\text{C}_6\text{H}_6$ , where the amplitude of nuclear motion is greater, the ratios are very close to those for a hexagon<sup>27, 28</sup>. Inconsistencies have also been noted between structures deduced for fluorine-containing molecules, e.g.  $\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$ <sup>29</sup>, by n.m.r. and other techniques.

Various approximate calculations of indirect spin-coupling tensors have been reported and references are given in the review by Bulthuis, Hilbers and MacLean<sup>30</sup>. Using a coupled Hartree-Fock procedure and INDO wave functions, Haigh and Sykes<sup>31</sup> have shown that anisotropy in  $\mathbf{J}^{(\text{HE})}$  can usually be neglected but that *trans* F-F indirect coupling may be markedly anisotropic. For *trans*-difluoroethene the indirect contribution to the observed F-F coupling constant  $\overline{T}_{zz}^{(\text{FF})} + \overline{J}_{zz}^{(\text{FF})} - J^{(\text{FF})}$  has been calculated to be about -5 per cent of the values observed in different nematic media<sup>32</sup>. The calcu-

lated  $\mathbf{J}$ -tensor for  is

$$\mathbf{J}^{(\text{FF})}/\text{Hz} = \begin{matrix} & \begin{matrix} 1 & 2 & 3 \end{matrix} \\ \begin{matrix} 1 \\ 2 \\ 3 \end{matrix} & \begin{pmatrix} -172.0 & -247.5 & 0 \\ -247.5 & -91.0 & 0 \\ 0 & 0 & -35.7 \end{pmatrix} \end{matrix} \quad (26)$$

where the 1-axis is parallel to the C—C bond and the 3-axis is perpendicular to the molecular plane. The orbital contribution dominates  $\mathbf{J}^{(\text{FF})}$ . In general,  $\mathbf{J}$  is a non-symmetric second-rank polar tensor and the equality of  $J_{12}$  and  $J_{21}$  in equation (26) is due to the retention of only one-centre matrix elements of the perturbation operators. If anisotropy in  $\mathbf{J}^{(\text{HH})}$  and  $\mathbf{J}^{(\text{HF})}$  is neglected, the calculated  $\mathbf{J}^{(\text{FF})}$  brings remarkable internal consistency to the four observed coupling constants.

## THE COMPLEXITY OF SPECTRA

If a molecule contains  $n$  nuclei of spin  $\frac{1}{2}$ , the resonance of each is, in general, split into  $2^{n-1}$  lines, so that the total number of lines in the spectrum is of the order of  $n2^{n-1}$ . This is 4 for  $n = 2$ , 192 for  $n = 6$ , 1024 for  $n = 8$  and 5120 for  $n = 10$ . Extensive overlapping of peaks occurs when  $n$  is more than about 8, thus limiting the applicability of the technique to small molecules. It is interesting to note that in principle a similar complexity should exist in isotropic n.m.r. spectra, since splittings arising from  $J^{(ij)}$  lead to the same number of lines; it is fortunate that indirect spin-coupling is of short range,  $J^{(ij)}$  being effectively zero for nuclei that are separated by more than about 10 atomic units. However,  $\overline{T_{zz}^{(ij)}}$  decreases only as the cube of the separation and is still 1.3 Hz for a proton pair separated by 50 atomic units ( $26.5 \times 10^{-10}$  m) and with an alignment  $S^{(\text{HH})}$  of 0.1. An escape from this limitation using deuterium substitution and decoupling has been provided by Hewitt, Meiboom and Snyder<sup>33</sup>. The deuterium nuclei are decoupled by irradiating at a frequency corresponding to a double-quantum  $\Delta I_z = \pm 2$  deuteron transition, i.e. at the central frequency in a symmetric spectrum. Hewitt *et al.* demonstrated the effects of varying the deuterium irradiation frequency and intensity in a series of experiments on partially deuterated cyclohexane in a nematic solvent and showed how the behaviour of the spectrum under frequency-offset can be used as an aid in assigning the spectrum<sup>33</sup>. This technique is clearly very promising; it will be interesting to discover how well it will work when applied to a molecule containing deuteriums having different chemical shifts.

Another escape might be made through the use of slightly oriented molecules in which  $S$  is about  $2 \times 10^{-4}$ . Protons separated by more than 10 a.u. would then produce dipolar splittings less than 0.5 Hz, and observed splittings would arise only from nuclei which are close together, as in the isotropic case.

## THE METAL-HYDROGEN DISTANCE IN TRANSITION-METAL HYDRIDES

The difficulties in determining hydride proton positions in transition-metal hydrides are well known<sup>34</sup>. High-resolution n.m.r. spectra of partially oriented molecules offer an attractive route to these elusive bond lengths. We have applied the technique to a ruthenium hydride cluster,  $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CCH}_3$ <sup>35</sup>, and to its osmium analogue,  $\text{H}_3\text{Os}_3(\text{CO})_9\text{CCH}_3$ <sup>36</sup>. Their structures are illustrated in *Figure 3*. Since there is a threefold rotation axis (the 3-axis), only one  $S$ -parameter is required, and if the molecule orients as a rigid rotator,

$$\overline{T_{zz}^{(ij)}} = -\frac{\mu_0 \hbar}{4\pi \pi} \gamma^{(i)} \gamma^{(j)} \langle (\frac{3}{2} \cos^2 \beta_3^{(ij)} - \frac{1}{2}) r_{ij}^{-3} \rangle S_{33} \quad (27)$$

There are three independent H—H dipolar couplings,  $T_{\text{intra-CH}_3}$ ,  $T_{\text{intra-H}_3}$  and  $T_{\text{inter}}$ , and these may easily be deduced from the spectra (which are nearly first-order and are therefore two triplets of quartets) if indirect coupling between the methyl and hydride protons is negligible, since the indirect coupling of fully equivalent nuclei does not affect the spectrum when anisotropy in this coupling is negligible<sup>37-39</sup>. The intramethyl and intrahydride

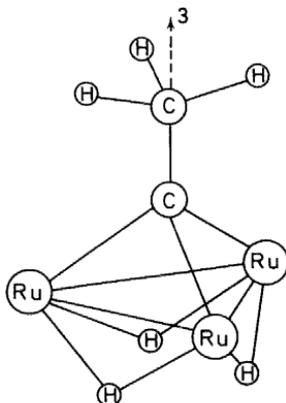


Figure 3. The structure of the ruthenium hydride cluster,  $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CCH}_3$ . Distances, taken from a single-crystal x-ray study<sup>40</sup>, are (in  $10^{-10}$  m)  $r_{\text{CC}} = 1.52$ ,  $r_{\text{RuC}} = 2.08$ ,  $r_{\text{RuRu}} = 2.84$ . The distance  $r_{\text{HH}}$  in the  $\text{CH}_3$  group was assumed to be 1.780 and the HCH angle taken to be tetrahedral. The n.m.r. spectrum<sup>35</sup> then gives  $r_{\text{HH}} = 2.486 \pm 0.004$  in the hydride group and the ratio  $T_{\text{inter}}/T_{\text{intra-CH}_3} = -0.1028 \pm 0.0010$  establishes a distance of  $4.115 \pm 0.020$  between the planes of the two  $\text{H}_3$  groups. The osmium complex has the same structure and bond lengths as the ruthenium compound<sup>36</sup>

dipolar couplings must be of the same sign, since the angle  $\beta_3$  in equation (27) is zero for both. The orientation parameter  $S_{33}$  was obtained from  $T_{\text{intra-CH}_3}$  and an assumed H—H separation in  $\text{CH}_3$  of  $1.780 \times 10^{-10}$  m. The separation of the three hydride protons and that of the two  $\text{H}_3$  planes can then be deduced from  $T_{\text{intra-H}_3}$  and  $T_{\text{inter}}$  (rapid rotation of the  $\text{CH}_3$  group is assumed). In order to determine the position of the hydride protons in relation to the three Ru or Os atoms, the positions of the metal and carbon atoms were taken to be those found in a single-crystal x-ray diffraction study of the Ru compound<sup>40</sup>; the unit cells of the Ru and Os compounds have the same dimensions<sup>36</sup>. The transition-metal-hydrogen bond length in both compounds is  $1.82 \times 10^{-10}$  m, the metal-hydrogen-metal angle  $103^\circ$  and the hydrogen-metal-hydrogen angle  $86^\circ$ .

In conclusion I want to draw attention to the fine reviews of this subject that have appeared in recent years. These have been listed in reference 30 and include those by Diehl and Khetrpal<sup>41</sup>, Luckhurst<sup>42</sup>, Meiboom and Snyder<sup>43</sup> and Bulthuis, Hilbers and MacLean<sup>30</sup>. In addition, I should like to express my warmest gratitude to my collaborators, including E. E. Burnell, C. A. de Lange, M. B. Dunn, A. J. Rest, D. Bailey and J. P. Yesinowski.

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