NUCLEAR MAGNETIC RESONANCE AND NUCLEAR SPIN SYMMETRY IN MOLECULAR SOLIDS

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ABSTRACT

The small amount of experimental evidence indicating the importance of nuclear permutation symmetry in solids composed of polyatomic molecules is reviewed. In the case of methane and its deuterated modifications, heat capacity, spectroscopic and nmr measurements have each played an important role, while in solids having CH_3 groups the only significant experiments have involved nmr. Some basic relationships between nuclear spin symmetry and quantum mechanical tunnelling in solids are discussed and various methods of measuring tunnelling frequencies are reviewed and proposed.

1. INTRODUCTION

In order to understand the properties of solid H_2 or D_2, it is essential to take into account the symmetry properties of the molecule with respect to permutation of its two nuclei; i.e. if the two nuclei are labelled 1 and 2 respectively, and the molecular wave function written as $\psi(1, 2)$, then the permutation symmetry requirement is that

$$\psi(1, 2) = \pm\psi(2, 1) \tag{1}$$

with the + and − signs holding for D_2 and H_2, respectively, since the deuterons obey Bose–Einstein statistics while the protons obey Fermi–Dirac statistics. In the ground electronic and vibrational states of H_2 or D_2, which are the only states of importance in the solid, $\psi(1, 2)$ may be written as a superposition of products of rotational wave functions $\phi_{\alpha j}(1, 2)$ and spin wave functions $\chi_{\alpha i}(1, 2)$, which are separately even or odd with respect to the permutation operation

$$\psi(1, 2) = \sum_{\alpha} a_{\alpha ij}\phi_{\alpha j}(1, 2)\,\chi_{\alpha i}(1, 2) \tag{2}$$

such that each term in equation 2 satisfies equation 1 with positive or negative sign appropriate to the molecule. In equation 2, α is a 'nuclear spin symmetry' quantum number which takes on only two values + and − for diatomic molecules, while i and j label the nuclear spin and molecular rotational quantum numbers, respectively.

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Although the role of nuclear spin symmetry in solid H_2 and D_2 is very well understood, the same cannot be said of solids composed of polyatomic molecules. My purpose in this talk is to review in terms of a simple physical picture the small amount of experimental evidence for nuclear spin symmetry being of importance in *at least* a few polyatomic molecular solids. I also wish to discuss some ways in which nmr should help to elucidate the role of nuclear spin symmetry in a wider range of molecular solids than has been studied up to now.

2. A COMPARISON OF NUCLEAR SPIN SYMMETRY IN DIATOMIC AND POLYATOMIC MOLECULES

The well developed intuition which most physical scientists have about the influence of permutation symmetry on the properties of homonuclear diatomic molecules is based on the fact that the *permutation* operation is equivalent to the *parity* operation in the ground electronic states of these molecules. An important consequence of the equivalence of the parity and permutation operations is that the wave functions of an *isolated* diatomic molecule can be classified *rigorously* according to its nuclear spin symmetry quantum number. The reason for this is that the molecular hyperfine interactions, being invariant with respect to the parity operation, do not couple states corresponding to $\alpha = +$ and $-$. For example, the well known classification of the states of H_2 and D_2 is as follows:

Species	α	$i = I, M_I$	$j = J, M_J$
ortho-H_2	+	$I = 1$	odd J
para-H_2	−	$I = 0$	even J
ortho-D_2	+	$I = 0, 2$	even J
para-D_2	−	$I = 1$	odd J

When *two* hydrogen molecules interact, the *inhomogeneous* magnetic field produced by the nuclei of each of the molecules at the positions of the nuclei of the other molecules mixes the α + and − states thus making it possible for conversion to take place between states of different nuclear spin symmetry. However, the conversion proceeds very slowly. In H_2 gas at NTP the time constant for conversion is of the order of a year, while in H_2 solid it is about 100 hours. Because of these long time constants, it is possible to study the thermodynamic and other properties of hydrogen containing arbitrary amounts of the *ortho*- and *para*-species[1]. In recent years, great progress has been made in the elucidation of the properties of solid H_2 and D_2, mainly because techniques have been developed to produce samples containing nearly 100% *ortho*-H_2 or *para*-D_2. At low temperatures these solids, which are composed of hydrogen molecules in the $J = 1$ state, undergo an order–disorder phase transition. The low temperature, ordered phase is one in which the molecular orientations are arranged in a 4-sublattice structure, which has only recently been determined unambiguously[2]. One motivation for studying the properties of pure *ortho*-H_2 or *para*-D_2 solids is that the low

temperature phase is very similar to antiferromagnetism. Solid hydrogen has advantages over most antiferromagnets, i.e. (1) the H_2 molecule is sufficiently simple that the intermolecular potential should be calculable from first principles[1], (2) the relative *ortho-* and *para*-concentrations can be easily varied in a controlled manner, thus providing well-defined alloys to study the influence of the anisotropic potentials in disordered systems.

In polyatomic systems such as CH_3 or CH_4, the real rotations which permute the protons are those rotations which are symmetry operations of the molecule. Thus, the properly symmetrized or antisymmetrized wave functions for polyatomic molecules, which correspond to equation 2, involve indices α associated with the irreducible representations of the group of rotations which satisfy the symmetry of the molecule. Unlike the case of diatomic molecules, however, there is no fundamental reason preventing the molecular hyperfine interactions from coupling states of different nuclear spin symmetry. Thus, even for an isolated molecule, states of different α are mixed[3, 4]. For free molecules, the states of different α are usually separated by energies much larger than the molecular hyperfine interaction so that the index α is, to first approximation, a reasonably good quantum number. Under certain conditions, the same remark may also be made of molecular solids. The extent to which the nuclear spin symmetry quantum number α is well-defined for individual molecules in a molecular solid should have a large influence on the observable properties of the solid at low temperatures, as we shall now discuss.

3. AN EXAMPLE—THE NUCLEAR SPIN WAVE FUNCTIONS OF A CH_3 GROUP IN A POTENTIAL HAVING C_3 SYMMETRY

In this case, the index α takes on values A, E_1 and E_2 corresponding to the three irreducible representations of the C_3 group. The low energy states of torsional oscillation in the 3-fold potential $\phi_{A,n}$ and $\phi_{E,n}$ are linear combinations of the three wave functions ϕ_{an}, ϕ_{bn} and ϕ_{cn} which transform among themselves under 120° rotations about the C_3 axis and the spin wave functions are denoted by χ_{A,IM_I} and χ_{E,IM_I} with $I = \frac{3}{2}$ for $\alpha = A$ and $I = \frac{1}{2}$ for $\alpha = E_1$ or E_2. The explicit wave functions for the 3-spin system may be written as follows[3, 5]

$$\psi(123) = \sum_{\alpha;\, n;\, I,\, M_I} a_{\alpha n I M_I} \phi_{\alpha,n} \chi_{\alpha,\, IM_I} \tag{3}$$

where

$$\phi_{A,n} = \frac{1}{\sqrt{3}} [\phi_{an} + \phi_{bn} + \phi_{cn}] \tag{4}$$

$$\phi_{E_1(E_2),n} = \frac{1}{\sqrt{3}} [\phi_{an} + e^{(\pm)(2\pi i/3)} \phi_{bn} + e^{(\mp)(2\pi i/3)} \phi_{cn}]$$

and writing the nuclear spin wave functions in terms of the $|M_1 M_2 M_3\rangle$ representation for protons labelled 1, 2 and 3, respectively, with $M = +\frac{1}{2}$ and $-\frac{1}{2}$ being denoted by + and −, respectively, we have

$$\chi_{A,\frac{3}{2}\frac{3}{2}} = |+++\rangle$$

$$\chi_{A,\frac{3}{2},\frac{1}{2}} = \frac{1}{\sqrt{3}}[|-++\rangle + |+-+\rangle + |++-\rangle], \text{ etc.} \tag{5}$$

$$\chi_{E_1(E_2),\frac{1}{2}\frac{1}{2}} = \frac{1}{\sqrt{3}}[|-++\rangle + e^{(\mp)(2\pi i/3)}|+-+\rangle + e^{(\pm)(2\pi i/3)}|++-\rangle], \text{ etc.}$$

The degeneracy of the torsional oscillation states corresponding to a given value of n is removed by an amount $\hbar\omega_t$ due to tunnelling of the CH_3 groups associated with the overlap of the ϕ_{an}, ϕ_{bn} and ϕ_{cn} wave functions[3, 5]. The energy levels of a CH_3 group in the ground state of torsional oscillation is illustrated schematically in *Figure 1*. The influence of a magnetic field is included in the diagram. It should be emphasized that while the degeneracy of the torsional oscillation energy levels is three for $\omega_t = 0$ and $H_0 = 0$, that of three spin $\frac{1}{2}$ nuclei is $2^3 = 8$. This degeneracy would be *lower* in a potential having symmetry *lower* than that of the molecule. Similarly, the ground state of torsional oscillation of a spinless tetrahedron in a potential having tetra-

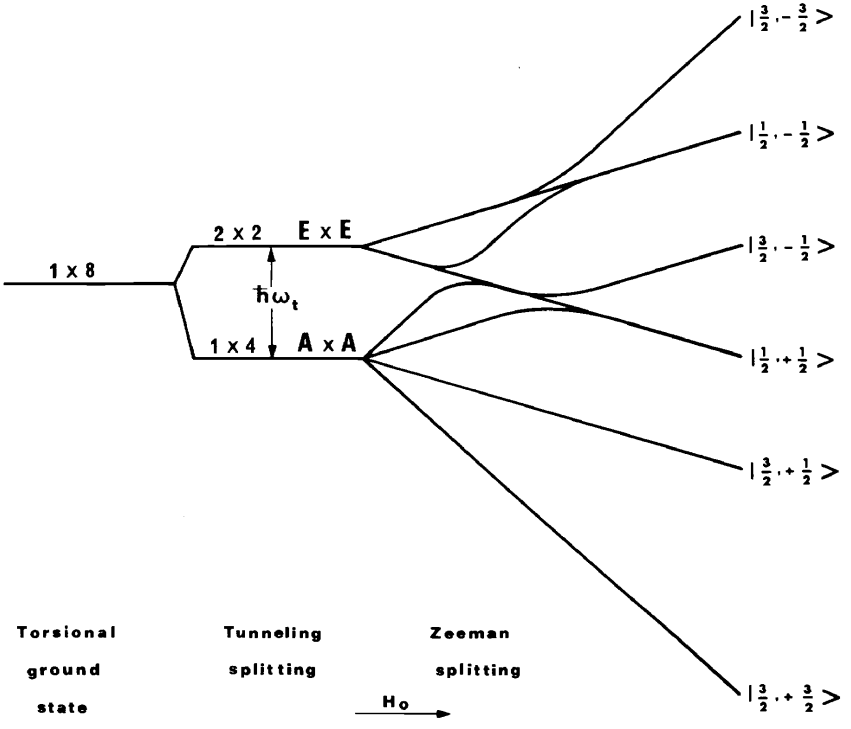

Figure 1. Schematic energy level diagram of the ground state of torsional oscillation of a three-spin system such as CH_3 in a potential having C_3 symmetry. The degeneracies and symmetry assignments are indicated. The high-field assignments of the angular momentum quantum number $|I, M_I\rangle$ are indicated on the diagram.

hedral symmetry would have 12-fold degeneracy in the absence of tunnelling and for $H_0 = 0$, while CH_4 or NH_4^+ in a tetrahedral field has a degeneracy of $2^4 = 16$. In the case of tetrahedral symmetry, there are two tunnelling frequencies associated with rotations about the C_2 and C_3 symmetry axes, respectively. The energy levels in zero magnetic field for the ground state of torsional oscillation of a CH_4 molecule in a potential having tetrahedral and trigonal symmetry[6], respectively, are shown in *Figure 2* below.

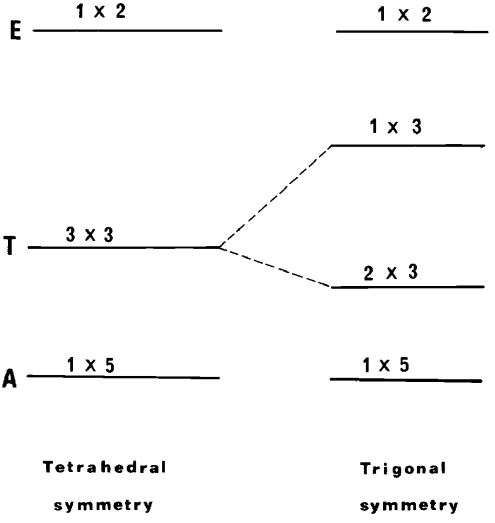

Figure 2. Schematic energy level diagram of the ground state of torsional oscillation of a tetrahedral 4-spin system such as CH_4 in potentials having tetrahedral and trigonal symmetry, respectively, with zero applied magnetic field.

Returning again to *Figure 1* for the energy levels of the lowest state of torsional oscillation of a CH_3 group, we see that in the low field limit ($\omega_0 = \gamma H_0 \ll \omega_t$) and in the high field limit ($\omega_0 \gg \omega_t$), the states are characterized to first order in the ratio of the dipolar interaction energy to $\hbar\omega_t$ or $\hbar\omega_0$ by a nuclear spin symmetry quantum number. However, in the regions of $\omega_0 \simeq \omega_t$ and $2\omega_0 \simeq \omega_t$, the 'cross-over regions', states of A and E nuclear spin symmetry which differ in their magnetic quantum number by $\Delta M_I = 1$ or 2, respectively, are mixed by the *intra*molecular dipolar interactions so that nuclear spin symmetry is not well defined in these regions. Note that only one of the two degenerate states is affected in this way.

4. MEASUREMENT OF TUNNELLING SPLITTINGS

For purposes of our discussion, we shall take as the fundamental experimental problem to be solved in the elucidation of nuclear spin symmetry in molecular solids, the detection and measurement of the energy differences associated with 'tunnelling' of a molecular group between different equivalent orientations. It should, of course, be kept in mind that the single-molecule picture, in terms of which the tunnelling frequencies have been defined, is

probably an oversimplification for many molecular solids. However, in view of the scarcity of experimental data at this time, it seems worthwhile reviewing the methods of obtaining information on the parameters associated with even a crude model such as this one.

A. Direct nmr methods

It should be possible to measure the tunnelling splittings directly using nmr techniques, although no such measurement has yet been reported. Since the *intra*molecular dipolar interactions couple states of different nuclear spin symmetry, the nmr spectrum of a 3-spin system such as that illustrated schematically in *Figure 1* should include two satellites at the frequencies $\omega_0 \pm \omega_t$ in addition to the usual type of resonance line centred at ω_0. When the tunnelling frequency is much larger than the frequency associated with the *intra*molecular dipolar interactions, or more precisely when $\omega_t^2 \gg M_2$, where M_2 is the contribution of the *intra*molecular dipolar interactions to the second moment of the nmr absorption line, the ratio of the intensity of the satellites to the main absorption line is bM_2/ω_t^2, where $b < 1$. (Note that the contribution of the satellite to the second moment of the nmr line is independent of ω_t as it should be according to van Vleck[7]). Therefore, under ordinary circumstances, the satellites are expected to be very weak ($M_2 \ll \omega_t^2$) or nonexistent ($M_2 \gg \omega_t^2$). It may be that very weak satellites could be detected using the methods of double resonance developed by Hahn and others[8] thus giving a direct measure of ω_t. Alternatively, a search could be made for the anticipated doubling of the resonance lines in the vicinity of the 'cross-over regions' ($\omega_0 \simeq \omega_t$, $2\omega_0 \simeq \omega_t$) when one of the E states is mixed with an A state.

B. Thermodynamic methods—heat capacity and nuclear magnetization measurements

Heat capacity. Molecular splittings such as $\hbar\omega_t$ can be determined from measurements of heat capacity as a function of temperature in the temperature range near $\hbar\omega_t/k$. Furthermore, by extrapolating the entropy versus temperature curve to the absolute zero of temperature, the residual entropy so obtained gives a reliable measure of the number of molecular states which are separated by energies much less than the lowest temperature reached in the experiment.

The first indication that nuclear spin symmetry plays a role in polyatomic molecular solids seems to have been given by the specific heat measurements of Morrison *et al.*[9] on CH_4. They noticed that the time required to establish thermodynamic equilibrium became quite long below about 8 K, which made it necessary to use unconventional methods to determine the heat capacity in that temperature range. In spite of this difficulty, however, Morrison *et al.* were able to show that the residual entropy of solid CH_4 as determined by measurements down to about 6 K was 4.93 ± 0.10 cal K^{-1} $mole^{-1}$, which is definitely less than the value of $R \log 16 = 5.51$ cal K^{-1} $mole^{-1}$ associated with the 16-fold degeneracy of the ground state of torsional oscillation of CH_4. Guided by the example of H_2 and D_2, Morrison *et al.* attempted to explain their results under the assumption that no conversion took place between the $A(I = 2)$, $T(I = 1)$ and $E(I = 0)$ spin symmetry

species of CH_4 in the low temperature solid over the time of their experiments. Their ingenious proposal for obtaining a residual entropy less than $R \log 16$ *even without conversion* was that the onset of a low-temperature phase transition in CH_4 near 8 K gives rise to a trigonal contribution to the effective crystal field at the molecular positions thus removing the degeneracy of the ground state of the T-species, as indicated in *Figure 2*. This conjecture does, in fact, give the experimentally observed residual entropy of the CH_4 system within experimental error. We now know, as will be shown below, that conversion between the different nuclear spin symmetry species in CH_4 cannot be neglected even in samples containing a negligible amount of paramagnetic impurities. The basic reason for this is that the *intra*molecular dipolar interactions do couple the different nuclear spin symmetry species, thus mixing them and allowing phonon-assisted transitions between them to take place. Nevertheless, the energy-level diagram proposed by Morrison *et al.* is still adequate to account for the small amount of experimental data available on solid CH_4 at this time.

Nuclear magnetization. The equilibrium nuclear magnetization of a system of N CH_4 molecules is adequately approximated by Curie's law at temperatures such that $kT \gg \hbar\omega_0$

$$M_0 = \frac{N\gamma^2\hbar^2 H_0 \langle I(I+1)\rangle}{3kT} \tag{6}$$

where $\langle I(I+1)\rangle$ is the mean squared value of the nuclear angular momentum per molecule which takes on the values of 6, 2 and 0 for the A, T and E spin symmetry species, respectively. Therefore, denoting the fractional populations of the A, T and E species by P_A, P_T and P_E, respectively, we have

$$\langle I(I+1)\rangle = 6P_A + 2P_E \tag{7}$$

Measurements of the nuclear magnetization, therefore, give information on the populations of the different nuclear spin symmetry states. At high temperatures, $P_A : P_T : P_E = 5:9:2$ and equation 7 gives $\langle I(I+1)\rangle = 3$, which is the same as obtained for four uncorrelated spins, i.e. $\langle I(I+1)\rangle = 4.\frac{1}{2}.\frac{3}{2} = 3$. At very low temperatures, it is anticipated that $P_A \gg P_T, P_E$ at equilibrium so that $\langle I(I+1)\rangle \simeq 6$. Therefore, an increase in M_0 by a factor of two over that given by a $1/T$ law is expected at low temperatures.

The first qualitative observation of such an increase was noted by Wolf and Whitney[10] on the basis of an increase in the proton magnetic resonance signal over a period of a few hours after their sample had been cooled down to 4.2 K. Later, Hopkins *et al.*[11] reported an increase in signal after cooling to 4.2 K by almost a factor of 2 over a period of 24 hours. They interpreted this result to indicate that the conversion of CH_4 into the A species was almost complete at 4.2 K. Such a result would imply that the separation of the ground states of the A and the T spin symmetry species was greater than 4.2 K. This striking result led us to do a more reliable type of measurement in our laboratory, namely to measure the ratio of the proton and ^{13}C free induction signals in a methane sample containing 53 per cent $^{13}CH_4$. The result obtained[12] was that $\langle I(I+1)\rangle = 3.73 \pm 0.18$ at 4.2 K with a time constant for conversion between nuclear spin symmetry species of the order

of an hour. This result has since been confirmed in laboratories at Louvain[13], the University of Washington[14] and Saclay[15]. The temperature dependence of $\langle I(I+1)\rangle$ has also been measured from high temperatures down to about 1.5 K by Piott[14] and in the liquid helium range by Glättli[15] (see also the experiments of Runolfsson and Mango[16]), and their results are consistent with a crystal field having trigonal symmetry and a spacing of about 1 K between the six-fold degenerate ground state of the T species and the five-fold degenerate ground state of the A species. Clearly, it would be interesting to extend these measurements to lower temperatures.

Nuclear magnetization measurements have also been carried out in SiH_4 at low temperatures by Jones and Montgomery[17], who observed no departure from a T^{-1} temperature dependence down to 4.2 K. This result indicates that the separation of the ground states of the different spin symmetry species of SiH_4 is much less than for CH_4 as would be expected if the crystal field acting on SiH_4 is much greater than for CH_4.

Unfortunately, we do not have sufficient time here to discuss in detail the interesting subject of the phase changes in solid methane and its deuterated modifications, in connection with which extensive heat capacity[18] and T_1 measurements[19] have been made. We shall also omit, with regret, any discussion of recent results on conversion among nuclear spin symmetry states in the deuterated modifications of methane at low temperatures[20]. Each modification of methane, with the *possible* exception of CH_4 about which some controversy still exists[9, 11], is known to undergo two phase transitions in the solid. The fact that two phase transitions should occur can be understood in terms of a molecular field model due to James and Keenan[21] which is based on interactions between the octupole moments of the charge distributions of neighbouring methane molecules. James and Keenan's classical treatment has been extended to include quantum mechanical effects on the angular momentum by Yamamoto[22] and his coworkers, and has been reformulated more recently by Alexander[23] in such a way as to take advantage of the crystal and molecular symmetry.

C. Indirect nmr methods

Analysis of the temperature and frequency dependence of the second moment M_2 and spin–lattice relaxation time T_1 is capable of giving useful information on nuclear spin symmetry states even at high temperatures, i.e. $kT \gg \hbar\omega_t$. The most elegant and clear-cut use of M_2 and T_1 to obtain such information has been made by Allen and his collaborators[5, 24, 25] on systems containing CH_3 groups. (Mention should also be made here of the important work on esr by Freed[3]). In classical systems, T_1 undergoes a characteristic minimum at a temperature at which the correlation time τ_c for molecular reorientation is of the order of the Larmor period. When the temperature is lowered to the region where $\tau_c \sim M_2^{-\frac{1}{2}}$, the observed nmr line is usually observed to broaden. However, this does not happen in systems such that $\omega_t^2 \gg M_2$ since the satellite lines at $\omega_0 \pm \omega_t$, which make an appreciable contribution to M_2 but are not normally observed, are not strongly influenced by τ_c. In addition, the temperature dependence of T_1 when $\omega_t^2 \gg M_2$ is unusual[24] and involves a mechanism not present for classical systems. As discussed in detail elsewhere[25, 26], the effect of phonon-

assisted transitions between different states of torsional oscillation, in conjunction with the fact that the order of the A and E levels in the first excited torsional oscillation states is inverted from that shown for the ground state in *Figure 1*, is to give rise to a frequency modulation of that part of the dipolar interaction which couples different nuclear spin symmetry states. This frequency modulation is probably responsible for spin–lattice relaxation at low temperatures in many systems.

D. Level-crossing experiments (a proposal)

A simple experiment has been proposed recently[26] to measure ω_t for systems in which the energy levels of states of different nuclear spin symmetry can be made to cross by the application of a magnetic field. We shall discuss the proposed experiment specifically for systems such as CH_3 which have the type of energy level diagram shown in *Figure 1* in which level crossing occurs at $\omega_0 = \omega_t$ and $2\omega_0 = \omega_t$. For such systems, T_1 is usually extremely long at low temperatures. Furthermore, the mechanism for spin–lattice relaxation is the same as that responsible for conversion between nuclear spin symmetry species[25, 26]. Normally, after applying a magnetic field H_0 to such a system, it is necessary to wait a time comparable with T_1 before a nuclear magnetic resonance signal can be observed. Suppose, however, that the system is allowed to come to equilibrium in zero magnetic field *before* applying the field. Then if ω_t is not very much less than ω_0 (so as to give an appreciable initial population difference between the A and E spin symmetry species) and if ω_t is not so large as to preclude the possibility of attaining the condition $2\omega_0 > \omega_t$ in the available magnetic fields, the effect of turning on the field *adiabatically* is to induce a nuclear magnetization at high fields. The subsequent observation of an nmr signal after times $\ll T_1$ would therefore establish an upper limit for ω_t. The magnitude of the signal enables one to estimate ω_t after which it would be a simple matter to devise experiments to measure the actual field at which the level-crossing occurs with more precision.

There are really two types of adiabatic conditions required here. One is that of quantum mechanical adiabaticity, i.e. in which the field is varied sufficiently *slowly* that a molecule in a state $|I, M_I\rangle = |\frac{3}{2}, -\frac{3}{2}\rangle$ in low fields changes its state to $|\frac{1}{2}, \frac{1}{2}\rangle$ as the field is varied through the region $2\omega_0 \simeq \omega_t$ (see *Figure 1*) and then changes its state to $|\frac{3}{2}, -\frac{1}{2}\rangle$ as the field is varied through $\omega_0 \simeq \omega_t$. This condition is satisfied if the nuclei precess many times in the '*intra*molecular field' H_i during the time $H_i/(\mathrm{d}H_0/\mathrm{d}t)$ taken for the field to be swept through the cross-over region, i.e. the adiabatic condition is

$$\frac{\mathrm{d}H_0}{\mathrm{d}t} \ll \gamma H_i^2$$

Since, for protons $H_i \gtrsim 1$ gauss and $\gamma \simeq 2.9 \times 10^4$ e.m.u., this requires that $\mathrm{d}H_0/\mathrm{d}t \ll 3 \times 10^4$ gauss s^{-1}, *a condition which is difficult to violate* with large magnets. The second type of adiabatic condition, the thermodynamic one of thermal isolation, requires that the field be applied in a time much shorter than T_1. Since the values of T_1 in pure solids containing CH_3 groups at the temperatures of liquid helium can be many minutes[24], this condition is also easy to satisfy for practical cases.

It is easy to show that the ratio of the magnetization obtained by adiabatic magnetization to a high field of a CH_3 system initially in equilibrium in zero field to the magnetization obtained at equilibrium in the high field H_0 is given by $\omega_t/3\omega_0$, where $\omega_0 = \gamma H_0$. Since the attainable signal-to-noise ratio at low temperatures for typical proton resonance is quite high, it should be possible to measure ω_t over a wide range of values up to about $10^9\ s^{-1}$. Values of ω_t for CH_3 groups in solids are expected to range up to about $10^8\ s^{-1}$, but no direct measurements have yet been made on such systems. Practically nothing is known about other prospective systems such as NH_4^+, SiH_4 but there is a good chance that many solids will exhibit tunnelling splittings in the radiofrequency range and thus be amenable to investigation by means of level-crossing experiments.

E. Spectroscopic techniques

We have not had time here to discuss all possible methods of investigating nuclear spin symmetry states. For those systems such as methane having relatively large energy separations between energy levels of the different species, the methods of infrared and Raman spectroscopy are extremely powerful, as has already been demonstrated experimentally[27, 28]. It remains to be seen whether spectroscopic methods will be able to make a significant contribution to the study of nuclear spin symmetry states of those polyatomic solids in which the energy differences of interest are extremely small.

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REFERENCES

[1] A. Brooks Harris, *Phys. Rev.* **B1**, 18881, **B2**, 3495 (1970). These articles include reviews of the present state of knowledge of the properties of solid hydrogen.
[2] W. N. Hardy, I. F. Silvera and J. P. McTague, *Phys. Rev. Lett.* **26**, 127 (1971).
[3] J. H. Freed, *J. Chem. Phys.* **43**, 1710 (1965).
[4] P. Yi, I. Ozier and C. H. Anderson, *Phys. Rev.* **165**, 92 (1968).
[5] P. S. Allen, *J. Chem. Phys.* **48**, 3031 (1968).
[6] T. Nagamiya, *Prog. Theor. Phys.* (*Kyoto*) **6**, 702 (1951).
[7] J. H. van Vleck, *Phys. Rev.* **74**, 1168 (1948).
[8] See e.g. M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids*. Oxford University Press (1970).
[9] J. H. Colwell, E. K. Gill and J. A. Morrison, *J. Chem. Phys.* **36**, 2223 (1962); **39**; 635 (1963).
[10] R. P. Wolf and W. M. Whitney, *Proceedings of the Ninth Conference on Low Temperature Physics*, page 1118. Plenum Press (1968).
[11] H. P. Hopkins Jr, P. L. Donoho and K. S. Pitzer, *J. Chem. Phys.* **47**, 864 (1967).
[12] K. P. Wong, J. D. Noble, M. Bloom and S. Alexander, *J. Mag. Res.* **1**, 55 (1969).
[13] P. van Hecke, P. Grobet and L. van Gerven, *Phys. Lett.* **33A**, 379 (1970). See also contributed paper at this conference.
[14] J. Piott, private communication, Ph.D. Thesis, University of Washington (1971).
[15] H. Glättli, private communication.
[16] O. Runolfsson and S. Mango, *Phys. Lett.* **28A**, 254 (1968).
[17] E. P. Jones and L. P. Montgomery, *Phys. Lett.* **35A**, 229 (1971).
[18] J. H. Colwell, E. K. Gill and J. A. Morrison, *J. Chem. Phys.* **42**, 3144 (1965).
[19] G. A. De Wit and M. Bloom, *Can. J. Phys.* **47**, 1195 (1965).

[20] J. H. Colwell, *J. Chem. Phys.* **51**, 3820 (1969).
[21] H. M. James and T. A. Keenan, *J. Chem. Phys.* **31**, 12 (1959).
[22] T. Yamamoto, *J. Chem. Phys.* **48**, 3193 (1968).
T. Yamamoto and Y. Kataoka, *Supp. Prog. Theor. Phys.* **46**, 383 (1970).
These are the first and eighth papers in a series.
[23] S. Alexander, private communication.
[24] P. S. Allen and A. Cowking, *J. Chem. Phys.* **47**, 4286 (1967); **49**, 789 (1968).
see also J. Haupt and W. Müller-Warmuth, *Zeits. f. Naturforsch.* **24***a*, 1066 (1969).
[25] P. S. Allen and S. Clough, *Phys. Rev. Lett.* **22**, 1351 (1969).
[26] P. S. Allen and M. Bloom, to be published.
[27] F. H. Frayer and G. E. Ewing, *J. Chem. Phys.* **48**, 781 (1968).
[28] C. Chapados and A. Cabana, *Chem. Phys. Lett.* **7**, 191 (1970).

Note added in Proof: Several papers directly related to the subject of this paper have appeared since the Symposium. They include the following:

D. Wallach, *J. Chem. Phys.* **54**, 4044 (1971).
J. Haupt, *Z. Naturforsch.* **A26**, 1578 (1971); *Phys. Lett.* **38A**, 389 (1972).
S. Clough, *J. Phys. C., Proc. Phys. Soc. London* **4**, 2180 (1971); see also, *ibid.* **5**, 518, 631 (1972).
C. Mottley, T. B. Cobb and C. S. Johnson, Jr., *J. Chem. Phys.* **55**, 5823 (1971).
H. Glättli, A. Sentz and M. Eisenkremer, *Phys. Rev. Lett.* **28**, 871 (1972).
E. P. Jones and M. Bloom, *Phys. Rev. Lett.* **28**, 1239 (1972).
A. Watton, A. R. Sharp, H. E. Petch and M. M. Pintar, *Phys. Rev.* **B5** (1972), in press.