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Relaxation by Slow Motional Processes. Effect of Molecular Rotations in Pure Quadrupole Resonance*

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Slow motional processes for which there is no motional narrowing can be important in spin-lattice relaxation. These relaxation mechanisms cannot be treated by perturbation theory. It is shown that the relaxation times are directly proportional to the motional correlation times. It is suggested that they can be used very effectively to measure the rate of motional processes in solids. A theory of the direct effect of molecular rotations on longitudinal spin relaxation in pure quadrupole resonance is described. The theory is applied to the N^{14} resonance in hexamethylene tetramine. Measurement of the longitudinal relaxation times in this molecule were carried out by a steady-state pulse method, and the rotational correlation times were determined. The results are in agreement with previous nmr measurements.

IN a recent note[1] the authors have pointed out that slow molecular rotations can have a very large direct effect on the logitudinal relaxation times in pure quadrupole resonance (pqr). It was shown that the measurement of these relaxation times can be used to determine the rate of rotation. The purpose of this paper is to discuss in detail the theory of the relaxation processes and the experimental techniques used.

We discuss the general problem of longitudinal relaxation by slow motional processes, develop a theory of pqr relaxation by molecular rotations and describe measurements of the longitudinal relaxation in the N^{14} pqr of hexamethylene tetramine (HMT).

The effect of random motional processes on nuclear magnetic resonance (nmr) is well understood.[2] In particular, the effect of hindered rotations and diffusion in solids on the line shape and spin-lattice relaxation time has been studied.[3] It is in fact well known that nmr can be used very effectively to measure the rate of such processes. The study of longitudinal relaxation (T_1) in pqr has tended to concentrate on the effects of vibrations.[4,5] Motional processes have so far received relatively little attention. The only detailed studies[6,7] deal with the effect of rotations on the linewidth.

In 1953 Ayant, Buyle-Budin, and Lurcat[6] pointed out that one should expect a line broadening in pqr when the direction of the field gradient changes rapidly between definite directions in space. Their argument was based on the uncertainty principle. Later Ayant[7] was able to calculate the expected line broadening in certain cases. Simultaneously Buyle-Budin[8] measured the linewidths of the *Cl* quadrupole resonance lines in a number of materials. His results agree very well with the theory of Ayant. Dodgen and Ragle[9] observed the large effect of molecular rotations on the pqr frequency and linewidth. Recently such observations[10] have led Woessner and Gutowsky[11] to study the temperature dependence of longitudinal relaxation times in *Cl* pqr in a number of materials. In several cases they observed rapid exponential temperature changes. To explain these effects Woessner and Gutowsky developed a theory of the effect of the rotation of remote molecular groups (e.g., methyl groups) on the pqr longitudinal relaxation time. They also mention the existence of a direct effect of the rotations on the relaxation time. Tatsuzaki *et al*,[12] and more recently Tokuhiro[13] have also observed line broadening which they attribute to a change in T_1 because of molecular rotations.

The usual approach to longitudinal (spin-lattice) relaxation uses perturbation theory. Following the classical work of Bloembergen, Purcell, and Pound[2] (BPP), the spin Hamiltonian is divided into a secular part (H_0) and a fluctuating nonsecular perturbation (H_1). One calculates the transition probabilities between the states of H_0 induced by the perturbation H_1. This approach is always justified in the motional-narrowing limit, i.e., when the observed transition frequencies are indeed the frequencies of H_0. This is certainly the more common situation and probably the only one of practical interest when H_1 is small compared to H_0. When the time dependence of H_1 can be described by a single correlation time (τ) BPP theory gives the well-known result

$$\frac{1}{T_1}\sim\frac{\tau}{\omega_0^2\tau^2+1}\omega_1^2, \qquad (1)$$

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* Based in part on part of a Ph.D. thesis to be submitted by A. Tzalmona to the Feinberg Graduate School of the Weizmann Institute of Science.

[1] S. Alexander and A. Tzalmona, Phys. Rev. Letters **13**, 546 (1964).

[2] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[3] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950). See also A. Abragam, *Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961), Chap. 10.

[4] H. Bayer, Z. Physik **130**, 227 (1951).

[5] J. Van Kronendonk, Physica **20**, 781 (1945).

[6] Y. Ayant, M. Buyle-Budin, and F. Lurcat, Compt. Rend. **236**, 800 (1953).

[7] Y. Ayant, Ann. Phys. (Paris) **10**, 487 (1955).

[8] M. Buyle-Budin, Ann. Phys. (Paris) **10**, 533 (1955).

[9] H. W. Dodgen and J. L. Ragle, J. Chem. Phys. **25**, 376 (1956). J. L. Ragle, J. Phys. Chem. **63**, 395 (1959).

[10] H. S. Gutowsky and D. W. McCall, J. Chem. Phys. **32**, 440 (1960).

[11] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **39**, 440 (1963).

[12] I. Tatsuzaki and Y. Yokozawa, J. Phys. Soc. Japan **12**, 802 (1957).

[13] T. Tokuhiro, J. Chem. Phys. **41**, 438 (1964).

where ω_0 and ω_1 are typical frequencies of H_0 and H_1, respectively.

When there is no motional narrowing, i.e.,

$$\omega_1\tau \gg 1\,; \tag{2}$$

the observed resonance frequencies are the frequencies of the total Hamiltonian (H_0+H_1) and not the frequencies of the secular part (H_0). In this case the details of the motional process become important.

Consider first a uniform motional process. The Hamiltonian changes slowly and one has

$$d(H_0+H_1)/dt \sim H_1/\tau \tag{3}$$

at all times. The inequality (2) then assures that the nuclear-spin wave functions $(\psi(t))$ follow the changes in the Hamiltonian adiabatically. A nucleus in a given eigenstate of H_0+H_1 stays in the same eigenstate and the energy

$$E(t)=\langle\psi(t)^\dagger|H_0+H_1(t)|\psi(t)\rangle \tag{4}$$

does not change appreciably. The changes in the wave function induced by H_1 are those required to keep the nucleus in the *same* state for a changing Hamiltonian. They do not contribute to the nuclear spin-lattice relaxation. Real thermal transitions only result because the wave function cannot quite follow the Hamiltonian and there is therefore a finite probability of transitions to different eigenstates of H_0+H_1. These transitions are induced directly by the *time dependence* of H_1 $(1/\tau)$[14] and therefore

$$\frac{1}{T_1}\sim\frac{\tau}{(\omega_0+\omega_1)^2\tau^2+1}\left(\frac{1}{\tau}\right)^2 \sim\frac{1}{(\omega_0+\omega_1)^2\tau^3}\,, \tag{5}$$

where we have used (2). As expected this is smaller than the BPP result (1) for slow rotations.

The situation is altogether different when the motion is nonuniform and consists of rapid transitions between positions of relative equilibrium. The changes in the Hamiltonian can then become very rapid momentarily and the nuclei cannot follow them. When the jumps are very rapid

$$d(H_0+H_1)/dt \gg (\omega_0+\omega_1)^2\,, \tag{6}$$

one can use the sudden approximation. The nuclear-spin wave function stays constant during the jump while the Hamiltonian changes. The probability of a transition to an eigenstate with a different energy is determined by the overlap between an eigenfunction of the initial Hamiltonian and an eigenfunction of the new total Hamiltonian with a different energy. When H_1 is small $(\omega_1/\omega_0 \ll 1)$ the overlap is of the order ω_1/ω_0 and therefore

$$\frac{1}{T_1}\sim\left(\frac{\omega_1}{\omega_0}\right)^2\frac{1}{\tau}\,. \tag{7}$$

This is identical to the slow-motion limit of the BPP expression (1).

When H_1 is large it is of course necessary to calculate the overlap more carefully. It should approach unity when a major part of the Hamiltonian participates in the motion and one therefore expects

$$1/T_1 \sim 1/\tau \tag{8}$$

in this limit.

Rotations in solids are very effective in causing pqr relaxation because the motion consists of fast jumps between equilibrium positions and is accompanied by large changes in the quadrupolar Hamiltonian. Our general considerations can of course apply to various other cases when a large part of the spin Hamiltonian participates in a motional process. The motional process could, for example, be diffusion. One would also expect very similar relaxation processes in nuclear magnetic resonance in magnetic materials where the motional process could be electronic relaxation or atomic diffusion.

In Sec. II of this paper we discuss the theory of the effect of slow molecular rotations on the longitudinal relaxation times in pure quadrupole resonance. The theory is applied to some special cases and in particular to the pqr of N^{14} in hexamethylene tetramine (HMT) which we have studied experimentally. We also discuss an example which is related to the effect of slow electronic relaxation on nuclear magnetic resonance.

To measure longitudinal relaxation times we used a steady-state pulse technique. This technique is described in Sec. III.

Section IV discusses measurements of the longitudinal relaxation in the pqr of N^{14} in hexamethylene tetramine (HMT) from 77 to 327°K. The N^{14} pqr in this molecule was first observed by Watkins and Pound[15] who also measured T_1 at room temperature and at 77°K. Recently, Smith[16] has studied molecular rotations in this material using proton nmr. Our results show that the N^{14} longitudinal relaxation is dominated by molecular rotations above 250°K. The rotational correlation times calculated from our measurements are in good agreement with the results of Smith, and it seems certain that the two techniques measure the same physical effect.

II. RELAXATION OF THE NUCLEAR SPIN POLARIZATION BY SLOW MOLECULAR ROTATIONS

A. Magnetic Resonance with Random Reversals of the Field

It is illuminating to start by discussing a simple example suggested by Abragam.[17] A nucleus of spin $\frac{1}{2}$ is placed in a magnetic field of magnitude H_0 which reverses its direction by a random thermal process

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[14] See also Appendix A for a more detailed discussion of a specific example.

[15] G. D. Watkins and R. V. Pound, Phys. Rev. **85**, 1062 (1951).

[16] G. W. Smith, J. Chem. Phys. **36**, 3081 (1962).

[17] A. Abragam, *Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961), Chap. X, pp. 477–479.

with a correlation time τ. What is the effect of these reversals on the nuclear magnetization?

The problem is obviously closely related to that of the effect of electronic relaxation on nmr in magnetic materials and to the effects of diffusion in antiferromagnets.

There are two Hamiltonians:

$$H_a=\gamma H_0(\mathbf{I}\cdot\mathbf{a}) \tag{9a}$$

and

$$H_b=\gamma H_0(\mathbf{I}\cdot\mathbf{b}), \tag{9b}$$

where γ and $\mathbf{I}$ are the nuclear gyromagnetic ratio and vector spin operator, respectively, and $\mathbf{a}$ and $\mathbf{b}$ are unit vectors along the two directions of the magnetic field. The nucleus feels the Hamiltonian H_a when the field points along $\mathbf{a}$ and H_b when the field has the direction $\mathbf{b}$. As the magnetic field reverses its directions one has

$$\mathbf{a}=-\mathbf{b}. \tag{10}$$

H_a has two eigenstates $|+\frac{1}{2}\rangle_a$ and $|-\frac{1}{2}\rangle_a$ with eigenvalues $+\frac{1}{2}\gamma H_0$ and $-\frac{1}{2}\gamma H_0$, respectively. Similarly H_b has the eigenstates $|\pm\frac{1}{2}\rangle_b$ with eigenvalues $\pm\frac{1}{2}\gamma H_0$. In this simple case one obviously has the relationship:

$$|\pm\tfrac{1}{2}\rangle_a=|\mp\tfrac{1}{2}\rangle_b \tag{11}$$

between the two sets of eigenstates. If the field reverses rapidly

$$d\gamma H_0/dt\gg(\gamma H_0)^2, \tag{12}$$

the nuclear wave function cannot change during the reversal. As a result nuclei in state $|+\frac{1}{2}\rangle_a$ go only into $|-\frac{1}{2}\rangle_b$:

$$n_a^{+1/2}\rightleftarrows n_b^{-1/2} \tag{13a}$$

and similarly

$$n_a^{-1/2}\rightleftarrows n_b^{+1/2}, \tag{13b}$$

where $n_{a,b}^{\pm1/2}$ are the populations in the respective states. One can therefore write the rate equations for the populations in a

$$\begin{aligned} dn_a^{1/2}/dt&=p_a{}^{1/2}{}_b{}^{-1/2}n_b^{-1/2}-p_b{}^{-1/2}{}_a{}^{1/2}n_a^{1/2},\\ dn_a^{-1/2}/dt&=p_a{}^{-1/2}{}_b{}^{1/2}n_b^{1/2}-p_b{}^{1/2}{}_a{}^{-1/2}n_a^{-1/2}, \end{aligned} \tag{14}$$

and similar equations for b. It is obvious from the symmetry of the problem that the transition probabilities are symmetric so that

$$\begin{aligned} p_a{}^{1/2}{}_b{}^{-1/2}&=p_b{}^{1/2}{}_a{}^{-1/2}=p^{1/2,-1/2},\\ p_a{}^{-1/2}{}_b{}^{1/2}&=p_b{}^{-1/2}{}_a{}^{1/2}=p^{-1/2,1/2}. \end{aligned} \tag{15}$$

$p^{1/2-1/2}$ is the transition probability for field reversal when the nucleus goes from the low-energy state $|-\frac{1}{2}\rangle$ to the high-energy state $|+\frac{1}{2}\rangle$ and $p^{-1/2\,1/2}$ describes the reverse transition. For a thermal process there is obviously a Boltzmann factor between these two probabilities. The magnetic field is more likely to reverse when the reversal is favored by its interaction with the nucleus. We could, e.g., write:

$$\begin{aligned} p^{1/2-1/2}&=(1/\tau)e^{-\gamma H_0/2kT},\\ p^{-1/2\,1/2}&=(1/\tau)e^{+\gamma H_0/2kT}, \end{aligned} \tag{16}$$

where $1/\tau$ would be the transition probability of the *field* if the nuclear energy did not change.

Substituting (16) in (14) and subtracting the thermal equilibrium populations $\langle n^{\pm1/2}\rangle_{\mathrm{eq}}$ one gets in the high-temperature approximation

$$\begin{aligned} \frac{dn_a^{+1/2}}{dt}&=\frac{1}{\tau}\left[(n_b^{-1/2}-\langle n^{-1/2}\rangle_{\mathrm{eq}})-(n_a^{1/2}-\langle n^{1/2}\rangle_{\mathrm{eq}})\right],\\ \frac{dn_a^{-1/2}}{dt}&=\frac{1}{\tau}\left[(n_b^{1/2}-\langle n^{1/2}\rangle_{\mathrm{eq}})-(n_a^{-1/2}-\langle n^{-1/2}\rangle_{\mathrm{eq}})\right]. \end{aligned} \tag{17}$$

For the magnetizations

$$M_{a,b}=\tfrac{1}{2}\gamma(n_{a,b}^{-1/2}-n_{a,b}^{1/2}), \tag{18}$$

this gives:

$$\begin{aligned} \frac{dM_a}{dt}&=-\frac{2}{\tau}(M_a-M_0)+\frac{1}{\tau}(M_a-M_b),\\ \frac{dM_b}{dt}&=-\frac{2}{\tau}(M_b-M_0)+\frac{1}{\tau}(M_b-M_a), \end{aligned} \tag{19}$$

where M_0 is the thermal equilibrium magnetization.

It is thus seen that we have a very efficient spin-lattice relaxation mechanism

$$1/T_1=2/\tau \tag{20}$$

and also cross relaxation between the magnetizations in a and b. The latter obviously became important only when M_a and M_b are affected differently by external perturbations.

B. General Considerations of the Relaxation Mechanism

The rotation of a molecule or molecular group in a crystal consists of transitions between a discrete number of equilibrium positions. The relation between these equilibrium positions is in most cases clear from geometric considerations. They are separated by high potential barriers. As a result the molecular motion is characterized by two distinct and essentially independent times. These are the residence time near the potential minima (τ_r) and the transition time between them (τ_t). Clearly

$$\tau_r\gg\tau_t, \tag{21}$$

so that one never observes the molecule during the transition (i.e., in intermediate positions).

The molecular rotation affects the quadrupole resonance directly when the field gradients seen by a definite nucleus are changed by the molecular rotation. The most important effect, for our purposes, is the rotation of the field gradients in space. The magnitude of the gradients is usually similar for the different positions but their principal axes have different orientations. We are interested in the slow-rotation case where the nonsecular part of the quadrupole Hamiltonian contributes to the observed frequencies. We therefore assume that the molecule stays for a long time at its equilibrium positions; i.e.,

$$\omega_Q\tau_r \gg 1\,, \tag{22}$$

where ω_Q is a typical transition frequency. The nuclear polarization[18] is then changed only by the fast transitions between equilibrium positions.

There are two possibilities:

When

$$\omega_Q\tau_t \gg 1\,, \tag{23}$$

the transition is essentially adiabatic. A nucleus which was in a definite eigenstate of the local Hamiltonian $H_{\nu'}$ before the rotation will mainly end up in the corresponding eigenstate of the new, rotated, Hamiltonian (H_ν). When this happens there is no change in the nuclear polarization. There is, however, a small probability for a real transition in which the spin polarization changes. One can show (see Appendix A) that

$$|P_i^{\nu'} - P_f^{\nu}| \sim P_i^{\nu'}/\omega_Q^2\tau_t^2\,, \tag{24}$$

where $P_i^{\nu'}$ and P_f^{ν} are the nuclear spin polarizations at site ν' before the jump and at ν after the jump, respectively. The probability per unit time that a jump occurs is obviously $1/\tau_r$. One therefore has for the longitudinal relaxation time (T_1)

$$T_1 \sim \omega_Q^2\tau_t^2\tau_r\,. \tag{25}$$

The proportionality factor in (25) depends on the details of the transition process.

The situation is much simpler when τ_t is sufficiently short so that

$$\omega_Q\tau_t \ll 1\,, \tag{26}$$

the transition can then be treated as sudden, i.e., the Hamiltonian changes but the nuclear-spin wave function remains unchanged. As a result the effect on the polarization can be calculated from simple geometrical considerations. Essentially the nucleus reaches the new position (ν) in an eigenstate of the *old* Hamiltonian ($H_{\nu'}$), for example, the state $|\beta\rangle_{\nu'}$. This state can be described by a linear combination of the eigenstates ($|\alpha\rangle_\nu$) of the new Hamiltonian (H_ν).

$$|\beta\rangle_{\nu'} = \sum_\alpha u_{\beta^{\nu'}\alpha^{\nu}}|\alpha\rangle_\nu\,, \tag{27}$$

where the $u_{\beta^{\nu'}\alpha^{\nu}}$ are the elements of a unitary transformation matrix. The probability of finding the nucleus after the jump in any new eigenstate ($|\alpha\rangle_\nu$) is simply given by the square of its coefficient in this expansion ($|u_{\beta^{\nu'}\alpha^{\nu}}|^2$). For a thermal process these probabilities should be weighted by the proper thermal factors. We can thus set up the rate equations for the populations in the spin states and calculate the longitudinal relaxation times.

It is important to realize that both in case (23) and in case (26) the relaxation process is nonresonant. As the "static" Hamiltonian itself is changing one cannot consider the transitions as induced by the Fourier component at the resonance frequency of a time-dependent perturbation. Among other things this is reflected in the fact that there is no minimum of the relaxation times when $\omega_Q\tau_t \sim 1$.

In practice it seems that the "slow" jump case (23) has little practical interest for molecular rotations. One would expect the transition time (τ_t) to be of the same order as the time a molecule spends in a state near the top of the barrier and therefore

$$\tau_t/\tau_r \sim e^{-\Delta E/kT}\,, \tag{28}$$

which makes τ_t very short for the portential barriers usually encountered. We discuss the "slow" jump case briefly in Appendix A.

For fast jumps our considerations are sufficiently detailed to get a complete description of the effect of rotations on the resonance. The most convenient general procedure is probably to apply a density-matrix formalism. The problem is formally very similar to that of exchange in high-resolution nuclear magnetic resonance[19] and can be treated in the same way. This would give both the longitudinal relaxation and the effect on the linewidth. Here we are only interested in longitudinal relaxation and it is therefore sufficient to set up the rate equations for the populations in the various eigenstates.

C. The Rate Equations

We can now set up the rate equations for the occupation number of the eigenstates at the different sites, e.g., the occupation n_{α^ν} of the state $|\alpha\rangle_\nu$:

$$\frac{dn_{\alpha^\nu}}{dt} = \sum_{\nu'}\sum_{\beta}\left(p_{\alpha^\nu\beta^{\nu'}}n_{\beta^{\nu'}} - p_{\beta^{\nu'}\alpha^\nu}n_{\alpha^\nu}\right), \tag{29}$$

where the summation is over all the alternative sites (ν') which are directly interchanged with ν by molecular rotation and over all eigenstates $|\beta\rangle_{\nu'}$ of the local Hamiltonians at these sites ($H_{\nu'}$). The $|\alpha\rangle_\nu$ and $|\beta\rangle_{\nu'}$ are related by a unitary transformation with elements $u_{\beta^{\nu'}\alpha^{\nu}}$ (27). For fast jumps the transition probabilities $p_{\alpha^\nu\beta^{\nu'}}$ in Eq. (29) are

$$\begin{aligned} p_{\alpha^\nu\beta^{\nu'}} &= w_{\nu\nu'}|u_{\alpha^\nu\beta^{\nu'}}|^2 e^{(E_\beta - E_\alpha)/2kT}\,,\\ p_{\beta^{\nu'}\alpha^\nu} &= w_{\nu'\nu}|u_{\beta^{\nu'}\alpha^\nu}|^2 e^{-(E_\beta - E_\alpha)/2kT}\,, \end{aligned} \tag{30}$$

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[18] The intensity of a pqr signal is proportional to the difference in population between the two relevant energy levels (or doublets). Throughout this paper we use the term nuclear spin polarization (P) to describe this quantity. This usage is not quite accurate but stresses the analogy with nuclear magnetic resonance.

[19] J. Kaplan, J. Chem. Phys. **29**, 462 (1958); S. Alexander, *ibid.* **37**, 967 (1962).

where we have chosen a symmetric form for the nuclear Boltzmann factors ($e^{(E_\beta-E_\alpha)/2kT}$) and $w_{\nu\nu'}$ is the transition probability of the *molecule* from a position in which a given nucleus is at ν' to a position in which it is at ν when no change in the nuclear spin energy occurs. When the molecule has different energies for ν (E_ν) and ν' ($E_{\nu'}$) one obviously has

$$w_{\nu\nu'}/w_{\nu'\nu}=e^{-(E_\nu-E_{\nu'})/kT}. \tag{31}$$

The transformation matrices $U^{\nu\nu'}$ can be calculated easily if one knows the structure of the eigenstates of H_ν and the angles between the principal axis of the field gradients at ν and ν'. For cylindrically symmetric gradients they reduce to the Wigner **D** matrices.[20] It is obvious from the definition of the U that

$$U^{\nu\nu'}\cdot U^{\nu'\nu}=1$$

and therefore from unitarity

$$|u_{\alpha^\nu\beta^{\nu'}}|^2=|u_{\beta^{\nu'}\alpha^\nu}|^2. \tag{32}$$

It should be noted that there are in general no selection rules for the transition probabilities ($|u_{\alpha^\nu\beta^{\nu'}}|^2$; $p_{\alpha^\nu\beta^{\nu'}}$). In particular one is *not* restricted to transitions with $\Delta m=\pm1$ and $\Delta m=\pm2$.

Equations (29) and (30) describe the whole effect of the rotations on $n_\alpha{}^\nu$. As in the magnetic case there are two types of relaxation effects. The first is proper spin-lattice relaxation which depends on the deviation of the occupation numbers from thermal equilibrium. The second effect describes the transfer of polarization from ν' to ν and is therefore a sort of cross relaxation between the different sites. It is convenient to rewrite (29) in a form which exhibits this clearly.

As usual we start by subtracting the thermal equilibrium solutions $\langle n_\alpha{}^\nu\rangle_{\rm eq}$. Using (30) and (32) this gives

$$\frac{d(n_\alpha{}^\nu-\langle n_\alpha{}^\nu\rangle_{\rm eq})}{dt}=\sum_{\nu',\beta}|u_{\alpha^\nu\beta^{\nu'}}|^2 \times(w_{\nu\nu'}(n_\beta{}^{\nu'}-\langle n_\beta{}^{\nu'}\rangle_{\rm eq})-w_{\nu'\nu}(n_\alpha{}^\nu-\langle n_\alpha{}^\nu\rangle_{\rm eq})) \tag{33}$$

to first order in $\hbar\omega_Q/kT$. To separate the cross relaxation terms we shall assume that the energies of the local Hamiltonians (H_ν; $H_{\nu'}$) are similar. There is then a simple correspondence between the states at ν ($|\beta\rangle_\nu$) and at ν' ($|\beta\rangle_{\nu'}$). One can then add and subtract a term

$$\sum_{\nu',\beta}w_{\nu'\nu}|u_{\alpha^\nu\beta^{\nu'}}|^2(n_\beta{}^\nu-\langle n_\beta{}^\nu\rangle_{\rm eq}) \tag{34}$$

to the right-hand side of Eq. (33) and rewrite the rate equations in a different form:

$$\begin{aligned}\frac{d(n_\alpha{}^\nu-\langle n_\alpha{}^\nu\rangle_{\rm eq})}{dt}&=\sum_{\nu'\beta}|u_{\alpha^\nu\beta^{\nu'}}|^2(w_{\nu\nu'}n_\beta{}^{\nu'}-w_{\nu'\nu}n_\beta{}^\nu)\\&\quad-\sum_\beta\Big(\sum_{\nu'}w_{\nu'\nu}|u_{\alpha^\nu\beta^{\nu'}}|^2\Big)\\&\quad\times\big((n_\alpha{}^\nu-n_\beta{}^\nu)-(\langle n_\alpha{}^\nu\rangle_{\rm eq}-\langle n_\beta{}^\nu\rangle_{\rm eq})\big),\end{aligned} \tag{35}$$

when one remembers that $w_{\nu\nu'}\langle n_\beta{}^{\nu'}\rangle_{\rm eq}=w_{\nu'\nu}\langle n_\beta{}^\nu\rangle_{\rm eq}$, because of detailed balance, even when $w_{\nu\nu'}\neq w_{\nu'\nu}$.

The first term on the right-hand side of (35) describes the transfer of spin polarization between ν and ν'. It is effective only when the populations at ν and at ν' have been *disturbed* in different ways. The second term can be regarded as spin-lattice relaxation of the nuclei at ν.

So far our discussion has been quite general and is valid for cases where the molecule has different energies for different orientations ($w_{\nu\nu'}\neq w_{\nu'\nu}$) and for nuclei of arbitrary spin. In a pqr experiment we are concerned with the polarization connected with a definite transition, i.e., with the population difference between a definite pair of levels (or Kramers doublets). The relaxation equations for such a polarization can be found from (35) when p^ν is expressed in terms of the $n_\alpha{}^\nu$. It can be seen from (35) that the resulting equations will always involve the polarizations at the other sites ($P^{\nu'}$). When there is more than one pqr transition the populations in energy levels which are not connected with the observed transition will also appear. It is obvious that the solution of such a system of coupled equations cannot be described by a single relaxation time (T_1). Instead one has a series of relaxation and cross relaxation times for the different polarizations. We will show below that the problem may not be as serious as it appears and can be solved completely in simple cases. Quite generally it is, however, clear from (35) that all the relaxation rates are simply proportional to the $w_{\nu\nu'}$. The temperature dependence of the $w_{\nu\nu'}$ can therefore be determined from the over-all behavior of the system. For symmetric molecules one frequently has situations where all positions (ν) have the same energy and there is only one relevant type of transition. One then has:

$$w_{\nu\nu'}=w_{\nu'\nu}=1/\tau \tag{36}$$

for all transitions which appear in (35). In this case all the relaxation times are proportional to τ.

D. Nuclei of Spin 1 and Spin $\frac{3}{2}$ with Cylindrical Symmetry

In both cases there is only one pqr transition and the calculation is particularly simple.

For spin 1 the polarization (P^ν) can be written:

$$P^\nu=n_1{}^\nu+n_{-1}{}^\nu-2n_0{}^\nu, \tag{37}$$

where we have chosen eigenstates of the component of the nuclear-spin vector operator (**I**) along the local cylindrical axis (z_ν) to describe the spin states.

Similarly for spin $\frac{3}{2}$:

$$P^\nu=n_{3/2}{}^\nu+n_{-3/2}{}^\nu-n_{1/2}{}^\nu-n_{-1/2}{}^\nu. \tag{38}$$

One could now use (35) to derive the rate equations for P^ν. It turns out, however, that in these two cases there is a much simpler way to derive the result.

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[20] E. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 166–169.

One notes that in both cases P^ν is proportional to the thermal expectation value of the energy (H_ν) which has the simple operational form (for cylindrical symmetry)

$$H_\nu = A(3I_{z_\nu}^2 - \mathbf{I}^2). \tag{39}$$

We can therefore use the well-known transformation properties of the quantity on the right-hand side of (39). Whenever a nucleus leaves site ν all the polarization is lost. On the other hand, when a nucleus jumps from ν' to ν we only gain the projection of $P_{\nu'}$ on the direction z_ν, i.e.,

$$[\tfrac{1}{2}(3\cos^2\vartheta_{\nu\nu'} - 1)]P^{\nu'}, \tag{40}$$

where $\vartheta_{\nu\nu'}$ is the angle between z_ν and $z_{\nu'}$. We can therefore immediately write the rate equation corresponding to Eq. (33):

$$\frac{d(P^\nu - \langle P^\nu\rangle_{\mathrm{eq}})}{dt} = \sum_{\nu'} (w_{\nu\nu'}[\tfrac{1}{2}(3\cos^2\vartheta_{\nu\nu'} - 1)] \times (P^{\nu'} - \langle P^{\nu'}\rangle_{\mathrm{eq}}) - w_{\nu'\nu}(P^\nu - \langle P^\nu\rangle_{\mathrm{eq}})). \tag{41}$$

This can be rewritten in the more convenient form:

$$\frac{d(P^\nu - \langle P^\nu\rangle_{\mathrm{eq}})}{dt} = \sum_{\nu'} [\tfrac{1}{2}(3\cos^2\vartheta_{\nu\nu'} - 1)](w_{\nu\nu'}P^{\nu'} - w_{\nu'\nu}P^\nu) - \tfrac{3}{2}\sum_{\nu'} w_{\nu'\nu}(1 - \cos^2\vartheta_{\nu\nu'})(P^\nu - \langle P^\nu\rangle_{\mathrm{eq}}), \tag{42}$$

where the first term on the right-hand side is a cross relaxation term and the second one describes thermal spin-lattice relaxation. A direct calculation using Eqs. (35) and (37) or (38) leads to the same result.

Equation (1) of Ref. 1 is a special case of Eq. (42).

The simple derivation which led to (40) is only valid for nuclei of spin 1 or $\frac{3}{2}$ *and* cylindrically symmetrical field gradients. These are the only cases where the polarization observed in pqr is proportional to $(3I_z^2 - \mathbf{I}^2)$.

E. Longitudinal Relaxation in Hexamethylene Tetramine

In the case of HMT there are three conditions which greatly simplify the calculation:

(1) The molecule has tetrahedral symmetry so that all orientations and all transitions are equally probable.

(2) The field gradient has cylindrical symmetry.

(3) The nucleus (N^{14}) has spin 1.

We can therefore use Eq. (42). Moreover, because of the symmetry,

$$w_{\nu\nu'} = w_{\nu'\nu} = 1/\tau,$$
$$\langle P^\nu\rangle_{\mathrm{eq}} = \langle P^{\nu'}\rangle_{\mathrm{eq}} = P_0; \quad \cos\vartheta_{\nu\nu'} = -\tfrac{1}{3}, \tag{43}$$

for any two positions of the nucleus (ν and ν'). Thus Eq. (42) becomes

$$\frac{d(P^\nu - P_0)}{dt} = -\frac{1}{3\tau}\sum_{\nu'} (P^{\nu'} - P^\nu) - \frac{4}{\tau}(P^\nu - P_0). \tag{44}$$

The general solution of the four coupled Eqs. (44) has the form:

$$P^\nu(t) - P_0 = -Ae^{-4t/\tau} + B_\nu e^{-8t/3\tau}, \tag{45}$$

where

$$-A = \tfrac{1}{4}\sum_\nu (P^\nu(0) - P_0); \quad \sum_\nu B_\nu = 0. \tag{46}$$

The shorter relaxation time $(\frac{1}{4}\tau)$ thus describes the approach of the *total* nuclear polarization of a molecule to its thermal equilibrium value. The second term is due to cross relaxation between the P^ν at the different apexes. In a pqr experiment we never affect the nuclei at the four apexes in the same way. Both exponentials will therefore contribute to the observed relaxation rate.

III. STEADY-STATE PULSE METHOD FOR MEASURING LONGITUDINAL RELAXATION TIMES

Longitudinal relaxation times are best measured by pulse techniques. The accepted technique in pqr is to apply two 90° (i.e., maximum amplitude) pulses and to measure the ratio of the amplitudes of the two free precession signals as a function of the pulse spacing. We found this technique rather inconvenient mainly because one has to wait for a long time (compared to T_1) before one can repeat the measurement.

It is much more convenient experimentally to use a steady-state technique where the measured signals are repeated periodically. This also makes it easier to use a boxcar integrator. We therefore repeat the 90° pulses indefinitely with a fixed pulse separation. We measure the amplitude of the free precession signals after the pulses under these steady-state conditions. This amplitude obviously depends on the pulse separation and one can determine the longitudinal relaxation time from this dependence. This technique is applicable when $T_1 \gg T_2$. With our setup we could easily measure relaxation times between 10 sec and 1 msec.

The algebra involved in interpreting the experimental results is somewhat confusing and formally leads to integrals which cannot be evaluated in closed form. When the calculation is done properly it can however be seen that the interpretation of the results is quite simple. It seems useful to go through the calculations in detail.

We will first calculate the signal amplitude when the longitudinal relaxation is simply exponential. Clearly,

$$(P(t) - P_0) = (P(0) - P_0)e^{-t/T_1}, \tag{47}$$

where $P(t)$ is the nuclear spin polarization at time t and P_0 its thermal equilibrium value. On the other hand, one has the effect of the pulses:

$$P_f = P_i \cos\Psi, \tag{48}$$

where P_i is the spin polarization before the pulse, P_f the polarization after the pulse and Ψ can be regarded as a precession angle. For a cylindrically symmetric field gradient one has

$$\Psi=\Psi(\vartheta)=\alpha\sin\theta\,, \tag{49}$$

where ϑ is the angle between the rf field and the z axis of the electric-field gradient. The constant α depends on the rf level, pulse length, nuclear gyromagnetic ratio, and transition matrix element (see, e.g., Ref. 11).

Under steady-state conditions, P_i and P_f are also connected by the free relaxation equations:

$$(P_i-P_0)=(P_f-P_0)e^{-t_r/T_1}\,, \tag{50}$$

where t_r is the pulse separation. Combining Eqs. (48) and (50) gives

$$(P_i-P_0)=(P_i\cos\Psi-P_0)e^{-t_r/T_1}\,. \tag{51}$$

For a fixed angle ϑ the observed free precession signal after the pulse is proportional to

$$P_i\sin\Psi(\vartheta)\sin\vartheta\,. \tag{52}$$

In a powdered sample one therefore has for the signal (S)

$$S=S(t_r)=\int P_i(\vartheta,t_r)\sin\Psi\sin^2\vartheta d\vartheta d\phi \tag{53}$$

except for irrelevant proportionality factors. One could now solve Eq. (51) for P_i and substitute this in Eq. (53). The result is, however, simpler if one retains the implicit from (51) and integrates both sides. This gives

$$S-S_0=(\hat{S}-S_0)e^{-t_r/T_1}\,, \tag{54}$$

where S is the signal given by Eq. (53), S_0 the signal for zero repetition rate ($P_i=P_0$) and the correction term $\hat{S}$ is given by

$$\hat{S}=\int P_i\cos\Psi\sin\Psi\sin^2\vartheta d\vartheta d\phi$$

$$=\frac{1}{2}\int P_i\sin2\Psi\sin^2\vartheta d\vartheta d\phi\,. \tag{55}$$

$\hat{S}$ is thus half the signal one would obtain if one applied a pulse of amplitude 2α [see Eq. (49)]. For a definite direction (ϑ) one can cause $\hat{S}$ to vanish by choosing α so that $\Psi=\frac{1}{2}\pi$. This is not possible for all directions in a powdered sample. It is, however, clear physically that $\hat{S}$ is never going to be very large.

One can rewrite Eq. (54) in the form:

$$(S_0-S)/S_0=(1-\hat{S}/S_0)e^{-t_r/T_1}\,, \tag{56}$$

the correction term on the right-hand side ($\hat{S}/S_0$) is small when $\alpha\sim\frac{1}{2}\pi$. It can be neglected if one restricts oneself to intermediate repetition rates so that

$$\hat{S}/S\ll1\,. \tag{57}$$

We have for example calculated that $\hat{S}/S_0\sim0.01$ for $\alpha=\frac{1}{2}\pi$ and $t_r/T_1=1$. This is completely negligible with standard experimental accuracy.

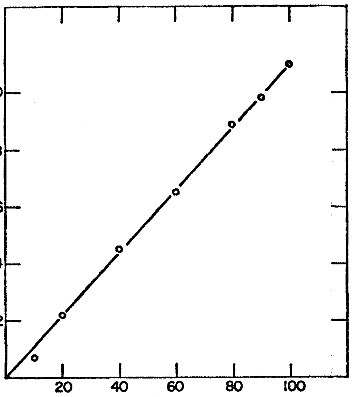

FIG. 1. Plot of the logarithm of the steady-state degree of saturation [$\ln((S_0-S)/S_0)$] as a function of the pulse separation (t_r) at 273°K. The deviations from linearity for large pulse separations are mainly due to experimental inaccuracy in determinations. For small separations, $\hat{S}/S\sim1$ and the correction terms in (56) become important.

One can therefore determine T_1 from the slope of a plot of $\ln(S_0-S)/S_0$ versus t_r. Such a plot can be seen in Fig. 1.

The interpretation is a little more complicated for the rotational relaxation mechanism discussed in Sec. II because of the cross relaxation terms. The behavior of $P-P_0$ cannot be described by a single exponential. This leads to rather complicated expressions for the signal. In practice one can, however, avoid much of the labor involved.

We will again discuss the case of HMT but similar arguments should be applicable fairly generally. The general solution of Eq. (44) has the form (45):

$$P^{\nu}-P_0=-Ae^{-4t/\tau}+B_\nu e^{-8t/3\tau}.$$

It is therefore immediately obvious that the expression for the signal $S(t_r)$ depends on t_r and τ only through the ratio t_r/τ. One can therefore write

$$(S_0-S)/S_0=F(t_r/\tau)\,, \tag{58}$$

where F depends only on t_r/τ as long as the pulse amplitude (α) is constant. This is in fact sufficient to determine an activation energy. For every temperature (T) one measures the repetition time $t_r(T)$ for which the ratio $(S_0(T)-S(T))/S_0(T)$ has a definite constant value, e.g.,

$$(S_0(T)-S(T))/S_0(T)=\tfrac{1}{3}\,. \tag{59}$$

It now follows from Eq. (58) that

$$t_r(T)=C\tau(T)\,, \tag{60}$$

where

$$F(C)=\tfrac{1}{3}\,. \tag{61}$$

The activation energy can thus be determined directly from $t_r(T)$ without calculating F.

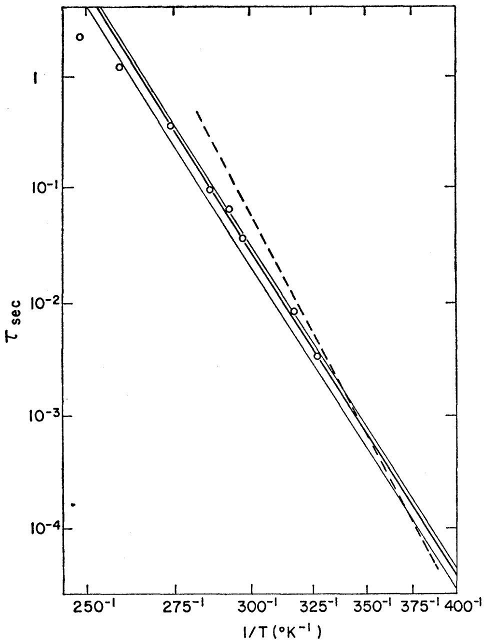

FIG. 2. Temperature dependence of the rotational correlation time of hexamethylene tetramine. The experimental points were obtained from our measurements using Eq. (68) and the heavy line is a least-squares fit to the six high-temperature points. The two light lines describe the limits on τ from Eq. (66). The results of Smith's (Ref. 16) nmr measurements (72) are described by a broken line.

One can also estimate the constant C fairly easily. It is clear from Eq. (45) that the behavior of P_ν is intermediate between that one would have for $T_1=\frac{1}{4}\tau$ and that $T_1=3\tau/8$, i.e., from (56):

$$e^{-4t_r/\tau}<F(t_r/\tau)<e^{-8t_r/3\tau} \tag{62}$$

at least when $\hat{S}/S\ll 1$. These are fairly narrow limits on a logarithmic plot (see Fig. 2) and for most purposes should be sufficient. In Appendix B we calculate F explicitly.

IV. EXPERIMENTAL TECHNIQUES AND RESULTS ON HEXAMETHYLENE TETRAMINE

A. Apparatus and Experimental Technique

The rf gate was essentially that developed by Blume[21] tuned to the frequencies of interest. Because of the small spin and moment of N^{14} we used very little damping on the tank circuit. Another modification we found useful was to feed the power into the tank circuit through a capacitive tap. This steps up the rf voltage and we could get voltages up to 2000 V peak to peak with the Type 5763 output tubes used by Blume and a power supply of 450 V dc. The gate is fed by a General Radio type 1001-A Standard signal generator, and amplified pulses from a Tektronix 163 pulse generator.

The receiver was a broad band amplifier consisting of 4 identical stages of 6AK5 tubes with a 6AL5 detector.[22] The only protection against overload was a pair of crossed diodes[23] across the anode load of the first stage. The recovery time of the amplifier depended on the damping of the tank circuit. With proper damping one could get down to 10 μsec. Because of the small signal of N^{14} we retained a high Q and the recovery time was in practice 40–50 μsec.

The detector was operated as a phase detector at the rf frequency by introducing leakage from the signal generator into the amplifier. With this arrangement the amplifier was very sensitive and most of the noise observed originated in the tank circuit. The pqr signals of HMT were observed directly on a Tektronix type 545 Oscilloscope with a signal to noise ratio of ~50 at liquid-nitrogen temperatures and 5–10 at room temperature.

Temperature control was achieved by a technique suggested by Abe.[24] The sample and coil were enclosed in a closed copper cylinder. At low temperatures the temperature was determined by the height of this cylinder above the liquid-nitrogen surface in a Dewar. Above room temperature we used a small heating element wound on a glass tube surrounding the copper cylinder. This arrangement guaranteed sufficient homogeneity of the sample temperature and we did not observe any line broadening due to temperature gradients. Temperatures were measured with a copper constantan thermocouple attached directly to the sample.

The material was a powdered sample of HMT supplied by Fluka.

B. Determination of T_1 in Hexamethylene Tetramine

The technique used for measuring the longitudinal relaxation was that described in Sec. III. The pulses were adjusted for maximum signal. In our setup these were pulses of ~50 μsec and ~1700 V peak to peak. The maximum signal adjustment is not sharp and the signal changes very little from 30 to 70 μsec. The exact value is, however, not critical for our purposes as long as one uses the same pulses at all temperatures.

For each temperature (T) the pulse separation (t_r) was varied to determine the value:

$$t_r(T)=t_{1/3} \tag{63}$$

for which

$$(S_0-S(t_{1/3}))/S_0=\tfrac{1}{3}. \tag{64}$$

The longitudinal relaxation time T_1 can then be determined from Eq. (56) neglecting $\hat{S}/S_0$. This gives

$$1.1\ T_1=t_{1/3}. \tag{65}$$

At most temperatures we only adjusted t_r carefully to determine the single value ($t_{1/3}$). At two temperatures

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[21] R. J. Blume, Rev. Sci. Instr. 32, 554 (1961).

[22] W. G. Proctor (private communication).

[23] W. G. Clark, Rev. Sci. Instr. 35, 316 (1964).

[24] Y. Abe, J. Phys. Soc. Japan 18, 1804 (1963).

(273 and 297°K) more careful measurements over a wide range of values of t_r were done. The results at 273°K are shown in Fig. 1, where we plot $\ln((S_0-S)/S_0)$ as a function of t_r.

At the two lowest temperatures 77 and 150°K we used a different technique for measuring T_1. The signal was saturated by a series of pulses and the recovery of the polarization afterwards was measured directly.

The values of T_1 determined in this way, Eq. (65) are given in Table I, together with the pqr frequencies measured.

TABLE I. Longitudinal relaxation times (T_1) and pqr frequencies. T_1 was determined from Eq. (65)-($T_1=t_{1/3}/1.1$).

T°K	T_1 (sec)	f (kc/sec)
77°	17.0	3406.8
150°	4.2	3378.5
181°	1.8	3364.0
213°	1.2	3348.0
248°	0.64	3332.0
258°	0.35	3327.5
273°	0.10	3320.0
286°	0.027	3314.0
292.5°	0.018	3310.5
297°	0.010	3308.0
317°	0.0023	3297.5
327°	0.0009	3292.0

At low temperatures the longitudinal relaxation is dominated by vibrations and has approximately a T^2 temperature dependence.[4,5] This is shown in Fig. 3 where $1/T_1$ is plotted as a function of T^2.

The pqr frequency is almost linear in temperature over the whole temperature range covered (see Fig. 4). The temperature coefficient is −485 cps/°K.

C. Measurement of Molecular Rotations

Above ~250°K molecular rotations become important and T_1 changes very rapidly with temperature. We have shown in Sec. II that the longitudinal relaxation cannot be described by a single exponential in this region. The behavior is intermediate between that for $T_1=3\tau/8$ and that for $T_1=\frac{1}{4}\tau$. This gives for τ the limits:

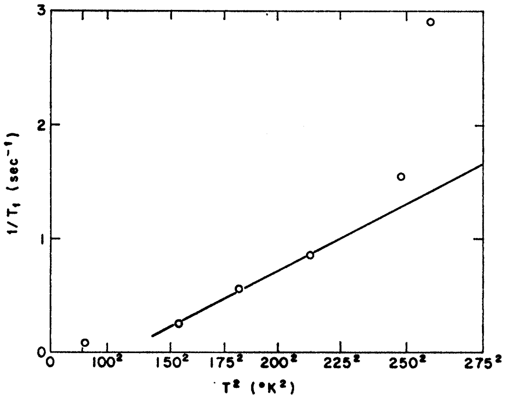

FIG. 3. Low-temperature results. $1/T_1$ is plotted as a function of T^2.

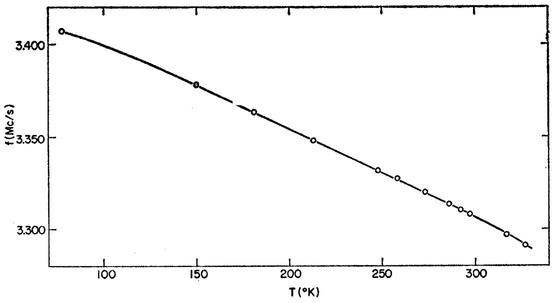

FIG. 4. pqr frequency of N^{14} in HMT as a function of temperature.

$$2.4t_{1/3}<\tau<3.6t_{1/3}. \qquad (66)$$

A more accurate result can be found if one uses the results of Appendix B. The calculation there shows that near $(S_0-S)/S_0=\frac{1}{3}$ one has

$$(S_0-S)/S_0=0.285e^{-8t_r/3\tau}+0.715e^{4t_r/\tau}, \qquad (67)$$

which gives with very good accuracy

$$\tau=3.3t_{1/3}. \qquad (68)$$

In Fig. 2 we have plotted $\ln\tau$ as a function of $1/T$. τ was determined from Eq. (68).[25] We also show the limiting values one would obtain from Eq. (66). It is clear from the figure that these limits are narrow enough for most purposes.

A least-squares fit of the six high-temperature points for which the vibrational relaxation can be neglected, gives

$$\nu_0=7.6\ 10^{12}\ \text{sec}^{-1},$$

$$\Delta E=15.6\ \text{kcal/mole}, \qquad (69)$$

where

$$1/\tau=\nu_0 e^{-\Delta E/RT}. \qquad (70)$$

It is of interest to relate our correlation time τ to the actual probabilities for a transition of the molecule between two different positions.

HMT is a tetrahedral molecule and therefore has 12 distinct but crystographically equivalent positions in the crystal. We have defined $1/\tau$ as the probability of a transition of the field gradient between two definite orientations, e.g., between its direction at 1 and that at 2 in Fig. 5. This is of course the transition probability of a nucleus at 1 into 2. There are three ways of doing this, namely: a rotation which keeps nucleus 3 fixed, a rotation which keeps nucleus 4 fixed and finally the rotation which permutes 1 with 2 and simultaneously 3 with 4. It seems reasonable to assume that the last type of rotation has a considerably higher potential barrier than the other two and is therefore

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[25] In Ref. 1 we used $\tau=3.5t_{1/3}$.

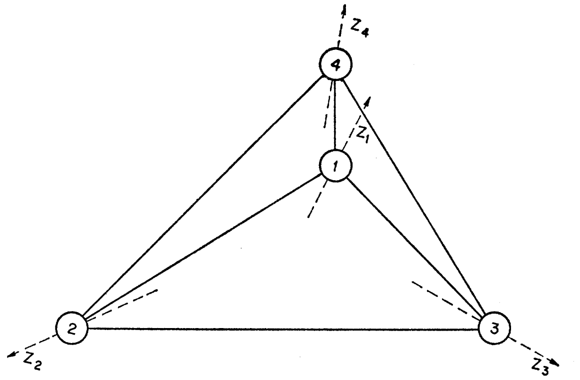

FIG. 5. Schematic description of the positions of the N^{14} nuclei in the tetrahedral molecule hexamethylene tetramine. The positions of the nuclei are numbered. The directions of the axis of the local field-gradient tensors (Z_r) are indicated by broken arrows.

unimportant. One then has

$$1/\tau=2/\tau_{\mathrm{mole}}, \qquad (71)$$

where $1/\tau_{\mathrm{mole}}$ is the *molecular* transition probability for a transition in which one apex of the tetraheder remains fixed.

Smith[16] has carried out a detailed investigation of the proton nmr in HMT. He was able to determine the correlation time for molecular rotations both from linewidth measurements and from measurements of T_1. He finds for the correlation frequency (ν_c)

$$\nu_c=7.5\ 10^{14}\ \mathrm{sec}^{-1},$$
$$\Delta E=18.7\ \mathrm{kcal/mole}, \qquad (72)$$

from linewidth measurements between 340 and 400°K. T_1 measurements between 320 and 440°K give[26]

$$\nu_c=8.6\ 10^{14}\ \mathrm{sec}^{-1},$$
$$\Delta E=17.9\ \mathrm{kcal/mole}. \qquad (73)$$

There is thus a considerable difference between the activation energies and frequency factors given by the two types of measurements.

A detailed quantitative comparison is complicated by the fact that there is some arbitrariness in determining the absolute value of the rotational correlation time (τ_c) from nmr measurements. There is also a numerical factor between the correlation time for discrete jumps we measure and the correlation time for continuous rotations used in interpreting the nmr results. This factor could of course be calculated.

In Fig. 2 we have somewhat arbitrarily assumed[27]

$$1/\tau_c\sim\nu_c \qquad (74)$$

and Smith's results [Eq. (72)] are then represented by the broken line. It can be seen that there is then very good quantitative agreement between the absolute values of the correlation times determined by the two techniques but this is probably fortuitous. Our results for the absolute value of the correlation time are certainly more reliable because they do not involve any independent parameters. We believe that a comparison of the absolute values will only be justified if the arbitrariness in determining them from nmr can be removed. Smith[26] has apparently reached the same conclusions.

In determining the activation energy the accuracy of the nmr T_1 measurement is comparable to our accuracy. The difference between our value (15.6 kcal) and the nmr value (17.9 kcal) at higher temperatures may therefore be real and represent a charge of ΔE with temperature. This would not be very surprising. We believe however that the experimental evidence for such a charge is not very strong because the errors in determining ΔE are rather large in both cases.

In any case the agreement between the two independent measurements is quite satisfactory and it is clear that the two techniques measure the same dynamic process.

ACKNOWLEDGMENT

We would like to thank Dr. A. Szöke for helpful remarks on the manuscript.

APPENDIX A: RELAXATION BY SLOW JUMPS

As pointed out in Sec. II this case

$$\omega_Q\tau_t\gg1 \qquad (A1)$$

probably has little practical interest for molecular rotations. It may, however, be applicable to other physical processes. It is also, in a sense, intermediate between the usual magnetic resonance relaxation processes where one assumes continuous rotation and the discontinuous processes we investigate in Sec. II.

We want to calculate the change in the nuclear spin polarization because of a single rotational jump.

The nuclei feel a perturbation for a time τ_t and the Fourier component at the resonance frequency is therefore

$$\sim\tau_t/(\omega_Q^2\tau_t^2+1). \qquad (A2)$$

In general one would now multiply this by the square of the matrix element of the time-dependent perturbation. In our case the whole Hamiltonian (H_Q) is changing. We are interested in transitions with respect to the *changing* Hamiltonian H_Q. It is most convenient to transform to a (time-dependent) coordinate system in which H_Q is stationary. The changes in polarization in this frame are, in fact, the relaxation processes we are looking for.

Before a jump this H_Q coordinate system is, of course, fixed in space and after the jump it is a new rotated fixed system. During the jump it is, however,

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[26] G. W. Smith, J. Chem. Phys. (to be published).

[27] In fact Smith (Ref. 26) has pointed out that it seems more reasonable to set $1/\tau=\omega_c=2\pi\nu_c$ which does not give quantitative agreement.

a rotating system, in the usual sense, rotating with an angular frequency $\sim 2\pi/\tau_t$. One could thus say that the nuclei (in the H_Q system) feel an effective magnetic field

$$\sim 2\pi/\gamma\tau_t \tag{A3}$$

during the rotation. This field induces transitions relative to H_Q. The transition probability during the jump is therefore, from (A2) and (A3),

$$\frac{4\pi^2}{\tau_t^2}\frac{\tau_t}{\omega_Q^2\tau_t^2+1}\sim\frac{4\pi^2}{\omega_Q^2\tau_t^3}. \tag{A4}$$

This is essentially the result we gave in Eq. (5).

As this perturbation is only effective for a fraction τ_t/τ_r of the time one finally gets

$$\frac{1}{T_1}\sim\frac{4\pi^2}{\omega_Q^2\tau_t^2}\frac{1}{\tau_r}. \tag{A5}$$

The argument can of course be made more precise if one follows the behavior of the spin polarization in the rotating frame in detail. The calculation is exactly analogous to that one would use in describing the effect of a changing magnetic field on the nuclear magnetization.

This sort of calculation is not restricted to the slow jump limit. At least in principle it is possible to calculate the effect of arbitrary rates of rotation. For very fast jumps one could justify the sudden approximation in this way.

APPENDIX B: CALCULATION OF THE CORRELATION TIME FOR ROTATIONS (τ)

The solution of Eq. (44) was given in (45)

$$P^\nu(t)-P_0=-Ae^{-4t/\tau}+B_\nu e^{-8t/3\tau},$$

where

$$A=\tfrac{1}{4}\sum_{\nu=1}^{4}(P_0-P^\nu(0));\quad \sum_\nu B_\nu=0 \tag{B1}$$

and the summation is over all apexes of the tetraheder.

The effect of the pulses is of course described by (49) as before:

$$P_f^\nu=P_i^\nu\cos\Psi_\nu \tag{B2}$$

and therefore

$$P_f^\nu-P_0=P_i^\nu\cos\Psi_\nu-P_0=-A+B_\nu, \tag{B3}$$

$$P_i^\nu-P_0=-Ae^{-4t_r/\tau}+B_\nu e^{-8t_r/3\tau}. \tag{B4}$$

Elimination of B_ν gives

$$P_i^\nu-P_0=A(e^{-8t_r/3\tau}-e^{-4t_r/\tau})+(P_i^\nu\cos\Psi_\nu-P_0)e^{-8t_r/3\tau}. \tag{B5}$$

Integration of both sides now leads to the expression analogous to (56)

$$(S_0-S)/S_0=F(t_r/\tau)=(1-K)e^{-8t_r/3\tau}+Ke^{-4t_r/\tau}-(S/S_0)e^{-8t_r/3\tau}, \tag{B6}$$

where

$$S_0K=\int A(\vartheta,\phi)\sin\Psi\sin^2\vartheta d\vartheta d\phi. \tag{B7}$$

From the definition of A (B1) and (B5) one finds

$$A=P_0\sum_\nu\frac{1-\cos\Psi_\nu}{1-\cos\Psi_\nu e^{-8t_r/3\tau}}\Big/\sum_\nu\frac{1-\cos\Psi_\nu e^{-4t_r/\tau}}{1-\cos\Psi_\nu e^{-8t_r/3\tau}}. \tag{B8}$$

By definition A is the deviation of the average polarization of the molecule from its thermal equilibrium value (P_0), i.e.,

$$A=\tfrac{1}{4}\sum_\nu(P_0-P_f^\nu). \tag{B9}$$

This quantity is not sensitive to the direction and magnitude of the rf field as long as $\alpha\sim\frac{1}{2}\pi$. Roughly one could say that three directions in the tetrahedra are always approximately perpendicular to the rf field and therefore,

$$\Psi_\nu\sim\tfrac{1}{2}\pi \quad\text{and}\quad P_f^\nu\sim 0, \tag{B10}$$

independent of the repetition rate. The fourth direction is near the rf field ($\Psi_\nu\sim 0$) and therefore,

$$P_f^\nu\sim P_i^\nu. \tag{B11}$$

At moderate repetition rates this direction is not saturated and therefore,

$$A\sim\tfrac{3}{4}P_0. \tag{B12}$$

As the repetition rate is increased A slowly increases to P_0. One therefore expects K to be approximately constant

$$K\sim 0.75. \tag{B13}$$

We have evaluated K numerically [using (B7) and (B8)] for

$$\alpha=\tfrac{1}{2}\pi \quad\text{and}\quad 8t_r/3\tau=1$$

and found

$$K=0.715, \tag{B14}$$

which is the value used in the interpretation of our experimental results.