

## ON THE EXISTENCE OF NUCLEAR MAGNETIC RESONANCE RELAXATION BY SPIN-ROTATIONAL INTERACTIONS IN THE SOLID

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*Abstract:* The temperature and frequency dependences of the nuclear spin-lattice relaxation times have been measured for a series of nearly spherical molecules both in the solid and in the liquid state, using a pulse technique. The same anomalous behaviour which was found before in  $SF_6$ ,  $SeF_6$  and  $TeF_6$  is now shown to occur in  $MoF_6$ ,  $WF_6$ ,  $UF_6$  and solid white phosphorus in a certain temperature range. The results seem to indicate that spin-rotational interactions do operate in a relatively large number of molecular solids and liquids and open the possibility of studying correlation functions for the angular velocity of molecules in the solid by NMR techniques.

### 1. Introduction

The modern theory of relaxation processes as developed by Kubo<sup>1)</sup> relates the relaxation time $\llcorner$  of a non-equilibrium system to »correlation times« of statistical fluctuations in the equilibrium system. The magnetic spin-lattice relaxation rate,  $T_1^{-1}$ , in particular is a macroscopic transport coefficient which describes the return of the component of magnetization  $\langle M_z \rangle$  along the Zeeman field to its equilibrium value  $M_0$ . It can be expressed in terms of a time correlation function for fluctuations of  $M_z$  in an equilibrium ensemble. In the field of nuclear magnetic resonance the most important interactions the fluctuations of which lead to nuclear spin-lattice relaxation are the magnetic dipolar interaction, the electric quadrupolar interaction and the spin-rotation interaction.

In molecular solids and liquids the dipolar interaction can be divided into an intra-molecular part, which is determined by interactions between nuclear magnetic dipolar moments within a given molecule and an inter-molecular part, which is determined by interactions between magnetic dipole moments in different molecules. In hexafluoride molecules which are the main subject of this study, the relaxation rate due to intermolecular dipolar interactions is small as compared to the intra-molecular one. For rigid molecules the distance between the magnetic dipole moments within a molecule is fixed and the thermal fluctuations hence vary the dipolar interaction energy of such a molecule in an external magnetic field  $H_0$  only because of changes in the angle  $\Phi$ , which the line joining a pair of spins makes with the applied field  $H_0$ . Thus the main part of the dipolar interactions transforms under rotations of the molecules as a spherical harmonic of second rank,  $Y_2^m(\Omega)$ , and the relaxation rate,  $R_d = 1/T_{1 \text{ intra } d}$ , depends on the power spectrum

$$J(\omega) = K_2 \int_{-\infty}^{+\infty} G_2(\tau) e^{-i\omega\tau} d\tau \quad (1)$$

of the equilibrium ensemble average of the correlation function of  $Y_2^m(\Omega)$ ,

$$G_d(\tau_d) = \langle Y_2^m(t) Y_2^m(t + \tau_d) \rangle \quad (2)$$

at the nuclear Larmor frequency  $\omega_L$  and  $2\omega_L$ . Hence the dipolar contribution to the nuclear spin relaxation rate,  $T_{1 \text{ intra } d}$ , gives information about the changes in the angular orientation of the molecules. The same statement holds for the electric quadrupole interaction which arises if the nuclear spin is larger than 1/2. The interaction is with the built in electric field gradient tensor of the molecule which transforms under molecular rotation in case of a spherically symmetric molecule in the same way as the intramolecular dipolar contribution. Since all the nuclei which we will investigate in this study have a spin 1/2, we will not discuss this term any longer.

The spin-rotation interaction arises because of the interaction of the nuclear magnetic dipole moment with the magnetic field produced by the rotation of the molecule containing the nucleus. If the molecule has an angular velocity it corresponds to a rotating charge system and hence produces a magnetic field at the site of the nucleus which is modulated if the angular velocity changes with time. The spin-rotational interaction hence transforms as the rotational angular momentum and its contribution to the nuclear spin-lattice relaxation rate depends on the power spectrum of the correlation function of the components of the angular momentum

$$G_{SR}(\tau_{SR}) = \langle I_z(t) I_z(t + \tau_{SR}) \rangle. \quad (3)$$

Whereas the dipolar contribution to the relaxation rate involves the correlation function for the molecular angular position, the spin-rotational contribution involves the correlation function for the molecular angular velocity. The characteristic times  $\tau_d$  and  $\tau_{SR}$  for the loss of these two types of correlation may be quite different and the relation between them depends on the nature of the involved random process. In particular it depends on whether the rotation is to be regarded as quantized or as a classical random walk problem.

For an interrupted quantized rotation, the correlation time  $\tau_{SR}$  must vary in the same way as  $\tau_d$  and one expects that the spin-rotational contribution to the relaxation rate  $T_{1,SR}^{-1}$  varies with temperature in the same way as the dipolar one,  $T_{1d}^{-1}$ . This situation<sup>2)</sup> seems to be realized in gases ( $\tau_{SR} \sim \tau_d$ ).

In condensed matter, on the other hand the situation is much less clear. If one assumes that the molecular motion is adequately described by the rotational diffusion equation, the decays of the correlation functions of  $Y_2^m[\Omega(t)]$  and  $I(t)$  are exponential with correlation times  $\tau_d$  and  $\tau_{SR}$ :

$$G_d(\tau) = \text{Re} \langle Y_2^m[\Omega(t)] Y_2^m[\Omega(t + \tau)] \rangle = \langle |Y_2^m(\Omega)|^2 \rangle g_d(\tau_d) = \frac{1}{4\pi} e^{-\tau/\tau_d}, \quad (4)$$

$$G_{SR}(\tau) = \langle I(t) I(t + \tau) \rangle = \langle I(I + 1) \rangle g_{SR}(\tau) = \langle I(I + 1) \rangle e^{-\tau/\tau_{SR}}, \quad (5)$$

where  $\tau_{SR} \ll \tau_d$ , since the angular velocity is changed in every »collision« whereas many steps are required to accumulate an appreciable change in orientation. Here »Re« means »the real part of« and  $\langle \rangle$  stands for the ensemble average. For spherical top molecules with a moment of inertia  $\mathcal{J}$ , Hubbard<sup>3)</sup> showed that  $\tau_d$  and  $\tau_{SR}$  are related by

$$\tau_d \cdot \tau_{SR} = \mathcal{J}/6 kT, \quad (6)$$

so that  $\tau_{SR}$  increases with increasing temperature whereas  $\tau_d$  - which is given by the Arrhenius equation  $\tau_d = \tau_0 e^{E/kT}$  - decreases as expected for a thermally activated process. The intramolecular dipolar  $(1/T_1)_d$  and the spin-rotational  $(1/T_1)_{SR}$  contribution to the total spin-lattice relaxation rate

$$\frac{1}{T_1} = R = R_d + R_{SR} = \left( \frac{1}{T_1} \right)_{\text{intra } d} + \left( \frac{1}{T_1} \right)_{SR} \quad (7)$$

thus exhibit a different dependence on temperature. In case that both fluctuation rates,  $\tau_d^{-1}$  and  $\tau_{SR}^{-1}$  are larger than the nuclear Larmor frequency,  $\omega_L$ , one finds in the rotational diffusion model

$$R_d = \left( \frac{1}{T_1} \right)_{\text{intra } d} = \frac{3}{2} \hbar^2 \gamma^4 \left( \sum r_{ij}^{-6} \right) \tau_d, \quad (8)$$

and

$$R_{SR} = \left( \frac{1}{T_1} \right)_{SR} = \frac{2}{3} \left( \frac{1}{2} \mathcal{J}_0 kT \right) (2 C_{\parallel}^2 + C_{\perp}^2) \tau_{SR}, \quad (9)$$

where  $r_{ij}$  is the distance between the nuclei  $i$  and  $j$  within the molecule under consideration, and  $C_{\parallel}$  and  $C_{\perp}$  are the two independent principal values of the spin-rotation tensor with all other symbols having their usual significance. In the above case  $(T_1)_{\text{intra } d}$  increases and  $(T_1)_{SR}$  decreases with increasing temperature, with both contributions being in the limit  $\omega_L \tau \ll 1$  independent of the nuclear Larmor frequency.

Hence the product of these two contributions is independent of temperature<sup>3,9)</sup>

$$T_{1 SR} \cdot T_{1 \text{ intra } d} = C, \quad (10)$$

and there is a maximum in  $T_1$  at which

$$T_{1 SR} = T_{1 \text{ intra } d} = 2 T_1, \quad (11)$$

so that  $C$  can be found.

Whereas in gases the spin-rotational interaction is known to operate and the modulation of this interaction by molecular collisions is in many cases rate determining for NMR relaxation, it was generally assumed until recently that anisotropic interactions completely quench the molecular rotational magnetic moment in the condensed phases. Spin-rotational interactions were thus supposed to vanish in both liquids and solids. Gutowsky<sup>4)</sup> was the first to point out that this is not always the case with liquids and the authors of the present paper recently<sup>5)</sup> suggested that spin-rotational interactions do operate in some molecular solids as well and represent in a certain temperature range the dominant NMR spin-lattice relaxation mechanism.

In this paper we present further experimental evidence for the existence of anomalies in the temperature dependence of the nuclear spin-lattice relaxation times in various molecular solids which we believe to be due to spin-rotational interactions. A critical discussion of other possible relaxation mechanisms is as well added.

## 2. Experimental Considerations

A high pressure technique was used in the preparation of the SF<sub>6</sub>, SeF<sub>6</sub>, TeF<sub>6</sub>, UF<sub>6</sub>, MoF<sub>6</sub> and WF<sub>6</sub> samples. In order to prevent decomposition all samples were sublimed into carefully evacuated Pyrex tubes, sealed off and stored at liquid nitrogen temperatures. The purity of the samples was checked by chemical analysis and magnetic susceptibility measurements. The nuclear spin-lattice relaxation time  $T_1$  along the static magnetic field  $H_0$  was measured by spin echo methods. A 90° — 90° pulse sequence was used and the amplitude of the free induction decay  $M$ , following the second pulse, was measured as a function of the time  $t$  between the pulses, so that

$$M(t) = M(\infty) [1 - \exp(-t/T_1)]. \quad (12)$$

In a few selected cases, the rotating frame spin-lattice relaxation time<sup>6)</sup>,  $T_1^r$ , was as well determined by applying a 90° pulse followed by a pulse of length  $\tau$  which was phase shifted by 90° in order to lie along the magnetization. The amplitude  $M^r(\tau)$  of the free induction decay following the second pulse was measured as a function of  $\tau$ :

$$M^r(\tau) = M^r(0) \exp(-\tau/T_1^r). \quad (13)$$

The second moments of the <sup>19</sup>F magnetic resonance absorption spectra were determined by continuous wave methods on a broad line NMR spectrometer.

## 3. Results and Discussion

### 3.1. Second Moment

The dependences of the second moments of the <sup>19</sup>F magnetic resonance absorption spectra of SF<sub>6</sub>, SeF<sub>6</sub> and TeF<sub>6</sub> on temperature are presented in Fig. 1. Three different regions are apparent. In the liquid phase, rapid molecular diffusion and rotation are averaging out both the intramolecular and the inter-molecular dipolar interactions and the observed second moment is close to zero. In the solid phase I, the second moment is between 1 and 2 Gauss<sup>2</sup> indicating a high degree of reorientational freedom, but diffusion has effectively ceased as far as the second moment is concerned. The intramolecular contribution to the second moment is effectively averaged out by rotation of the octahedra about more than one axis at a rate which is large as compared to the rigid lattice line width (10<sup>4</sup>-10<sup>5</sup> c/s), but a large part of the inter-molecular contribution still persists demonstrating that the correlation frequency for diffusion is smaller than the rigid lattice line width. This conclusion is supported by relaxation time measurements in the rotating frame in SF<sub>6</sub> where the  $T_1^r$  values seem to be dominated by slow diffusion.

In the low temperature solid phase II, the second moment increases by a factor of 3 to 5, indicating a gradual freezing in of the rotational degrees of freedom. The value of the second moments starts to approach the rigid lattice value which is a sum of the dipolar rigid lattice contribution,  $M_{2, D-D}$  and the contribution due

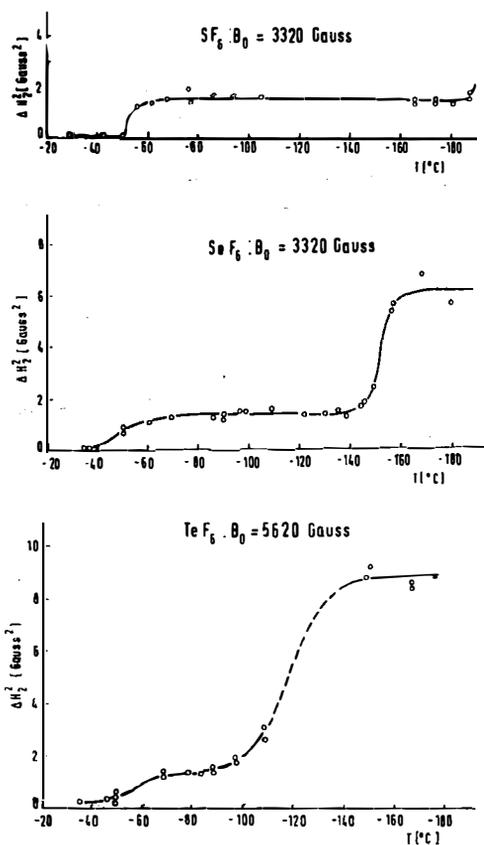


Fig. 1. Second moments of the  $^{19}F$  nuclear magnetic resonance absorption line of  $SF_6$ ,  $SeF_6$  and  $TeF_6$  as a function of temperature.

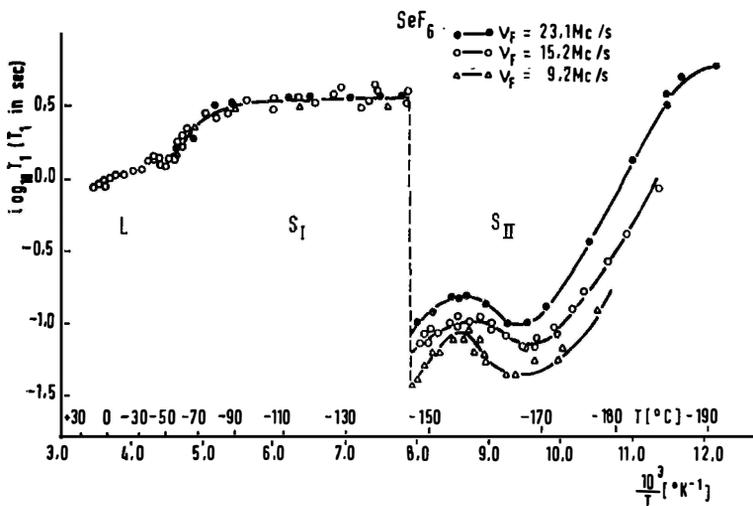
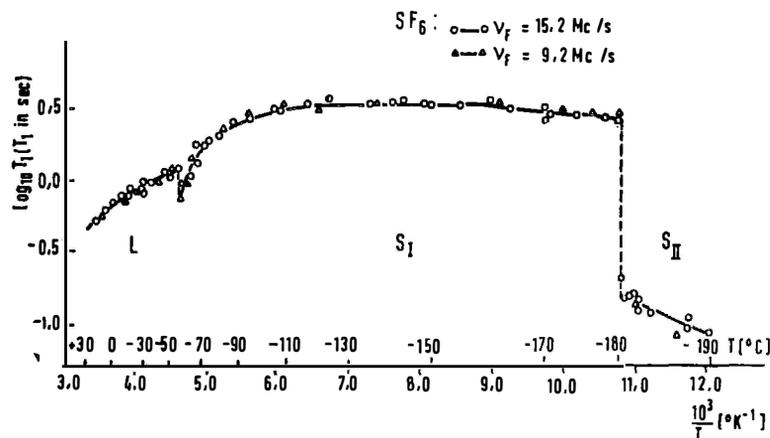
to the anisotropy of the chemical shift tensor, which can be in case of hexafluoride molecules at fields normally used in NMR experiments still larger than the dipolar contribution<sup>7)</sup>. For the case of an axially symmetric screening tensor  $\sigma = (\sigma_{\perp} \sigma_{\perp} \sigma_{\parallel})$  one finds<sup>9)</sup>

$$M_2 = M_{2, D-D} + (4/45) H_0^2 |\sigma_{\parallel} - \sigma_{\perp}|^2, \quad (14)$$

and the two contributions can be separated by studying the field dependence of  $M_2$  as this has been done in ref.<sup>7)</sup>

A similar temperature dependence of  $M_2$  is exhibited by  $\text{WF}_6$  and  $\text{MoF}_6$ , where however the solid phase I region is much narrower<sup>7)</sup>. In  $\text{UF}_6$ , this region does not exist at all and the solid phase I goes over directly to the liquid phase<sup>7)</sup>.

Whereas practically nothing is known about the crystal structure of solid  $\text{SF}_6$ ,  $\text{TeF}_6$  and  $\text{SeF}_6$ , one knows that the low temperature form (solid phase II) of  $\text{WF}_6$  and  $\text{MoF}_6$  is a close packed orthorhombic lattice with space group  $D_{2h}^{16}$  which makes a solid-solid transition to a less dense body centered cubic lattice<sup>8)</sup> (solid phase I) at higher temperatures. Transition entropy data<sup>8)</sup> suggest - in agreement with the present NMR results - that this phase change is connected with the onset of some kind of general rotation. The present data seem to show that the solid-solid transitions in  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$  are very similar to the ones found in  $\text{WF}_6$  and  $\text{MoF}_6$ .



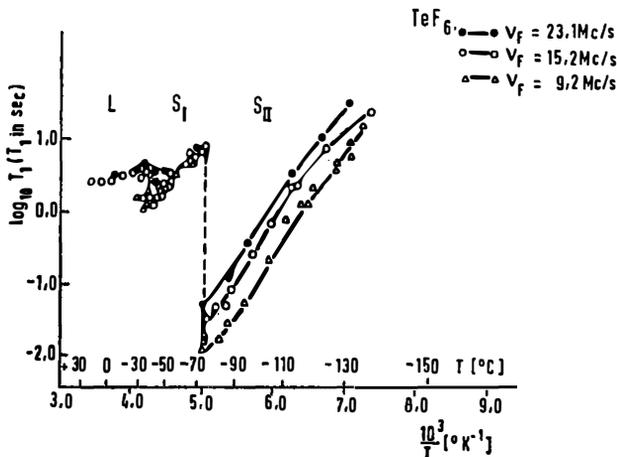


Fig. 2. Temperature dependences of the  $^{19}\text{F}$  spin-lattice relaxation times in  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$ .

### 3.2. Spin-Lattice Relaxation

The temperature dependences of the  $^{19}\text{F}$  spin-lattice relaxation times ( $T_1$ ) of  $\text{SF}_6$ ,  $\text{SeF}_6$ ,  $\text{TeF}_6$ ,  $\text{MoF}_6$ ,  $\text{WF}_6$  and  $\text{UF}_6$  are presented in Figures 2 and 3. Except for the case of  $\text{UF}_6$  (where solid phase I is absent) three different  $T_1$  regions are apparent: the liquid, the solid phase I (S I) and the low temperature solid phase II (S II).

In liquid  $\text{SF}_6$ , the  $T_1$  results agree with the ones of Hubbard and Hackleman<sup>9)</sup>. Here, as well as in all other above mentioned compounds, the relaxation times are frequency independent and slowly *increase* with *decreasing* temperature, contrary to what one would expect from the simple BPP theory<sup>10)</sup>, which was until recently supposed to be quite adequate for liquids and disordered solids. Hubbard<sup>9)</sup> suggested that the anomalous temperature dependence in liquid  $\text{SF}_6$  demonstrates that spin-rotational interactions - as given by eq. (9) - are dominant whereas Bloom<sup>11)</sup> expressed some reservations about the validity of the rotational diffusion model and proposed that intramolecular dipolar interactions modulated by fast diffusion in the weak anisotropic interaction limit (WAIL) might as well explain the observed anomaly. The interesting thing, revealed by this investigation, is, however, that the same anomalous increase of  $T_1$  with decreasing temperature is preserved in the solid phase I even more than  $100^\circ$  below the melting point, thus making it hard to believe that diffusion modulated interactions could be responsible for the anomalous behaviour of  $T_1$ . After a small initial drop on going from the liquid to the solid, the relaxation times increase with decreasing  $T$  until in  $\text{SF}_6$  and  $\text{SeF}_6$  a flat maximum is reached. In  $\text{SeF}_6$  the plateau extends till the solid-solid transition point, whereas in  $\text{SF}_6$   $T_1$  starts to decrease with decreasing  $T$  in the region between  $-150^\circ$  and  $-180^\circ\text{C}$ . In  $\text{TeF}_6$ ,  $\text{MoF}_6$  and  $\text{WF}_6$ , the solid-solid phase transition apparently occurs before the maximum in  $T_1$  is reached. In all investigated compounds  $T_1$  does not depend on frequency in this temperature

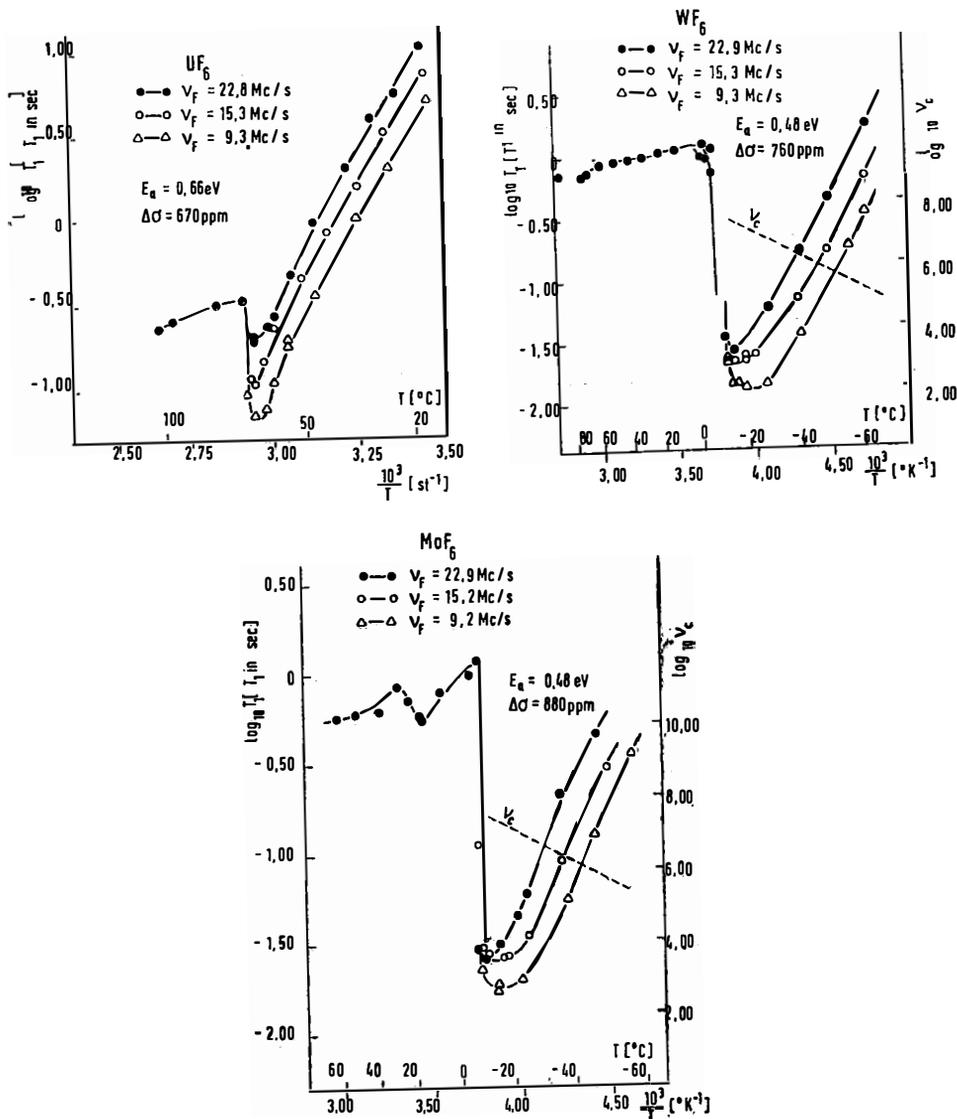


Fig. 3. Temperature dependences of the  $^{19}\text{F}$  spin-lattice relaxation times and correlation frequencies in  $\text{UF}_6$ , and  $\text{WF}_6$ ,  $\text{MoF}_6$ .

region, so that  $\omega^2 \tau^2 \ll 1$ . If dipolar interactions were to dominate the relaxation process and the classical BPP theory<sup>10)</sup> would be applicable, the condition  $\omega^2 \tau_d^2 \ll 1$  would lead to

$$(1/T_1)_d = C_1 \cdot \tau_d, \quad (15)$$

and since

$$\tau_d = \tau_d^0 \exp(E/kT), \quad (16)$$

the relaxation time should decrease with decreasing temperature contrary to observation. Spin-rotation interactions, on the other hand, offer a plausible explanation for this anomaly. The combination of eq. (9) with eq. (6) yields within the rotational diffusion model a spin-rotational contribution to the relaxation time of the form

$$(1/T_1)_{SR} = C_2/\tau_d, \quad (17)$$

so that the resulting expression for  $T_1$ ,

$$T_1 = \frac{\tau_d}{C_2 + C_1 (\tau_d)^2}, \quad (18)$$

as obtained from expression (7), qualitatively reproduces the experimental plots of  $T_1$  versus inverse temperature in SI, except at lowest  $T$ , where  $C_2$  seems to become temperature dependent. Since no theory of spin-rotational interactions exists as yet for solids (Hubbard's<sup>9)</sup> rotational diffusion model was originally developed for liquids), one should not ascribe too much significance to the numerical values of the constants occurring in eq. (18). It is perhaps nevertheless worthwhile to mention, that a typical value of  $\tau_d$  at the  $T_1$  maximum is  $10^{-10}$  s and of  $C_2$ ,  $10^{-11}$  s. A careful analysis of other possible relaxation mechanisms and, particularly, the one suggested by Bloom<sup>12)</sup>, has to be made before one can be sure that the above explanation is unique.

On going to solid phase II,  $T_1$  discontinuously decreases by two orders of magnitude and dipolar interactions become rate determining for spin-lattice relaxation, as can be seen from the pronounced frequency dependence of  $T_1$  and the occurrence of dipolar NPP minima in  $T_1$ , which indicate that  $\tau_d$  is now of the order of  $\omega_L^{-1}$ . The solid-solid transition is thus connected with a discontinuous increase in  $\tau_d$  in agreement with the second moment and transition entropy data. The occurrence of more than one minimum in the  $T$ -dependence of  $T_1$  in SeF<sub>6</sub> further indicates that rotations about the  $C_4$  and the  $C_2$  axis do not have the same  $\tau_d$ , so that the dipolar intramolecular relaxation rate is a sum of contributions

$$\left(\frac{1}{T_1}\right)_{\text{intra } d, i} = B_i \left[ \frac{\tau_{d, i}}{1 + \omega_L^2 \tau_{d, i}^2} + \frac{4 \tau_{d, i}}{1 + 4 \omega_L^2 \tau_{d, i}^2} \right], \quad (19)$$

with  $B_i$  being proportional to the intramolecular dipolar second moment, and  $\tau_{d, i}$  being the dipolar correlation time for rotation of the hexafluoride octahedron about the  $C_i$  axis. From the plots of  $1/T_1$  versus the inverse square of the Larmor frequency, the anisotropy ( $\sigma_{\parallel} - \sigma_{\perp}$ ) contribution to the relaxation rate can be determined. This contribution is relatively small and cannot influence our conclusions concerning the relaxation rate in SI.

It should be pointed out that the above mentioned anomalous behaviour of  $T_1$  in the liquid phase and the high temperature solid is not at all limited to hexafluorides only. An exactly analogous behaviour was observed by Resing<sup>12)</sup> in solid white phosphorus (Fig. 4) in the high temperature  $\alpha$ -phase and in the liquid phase, whereas the low temperature  $\beta$ -phase showed again a typical BPP minimum.

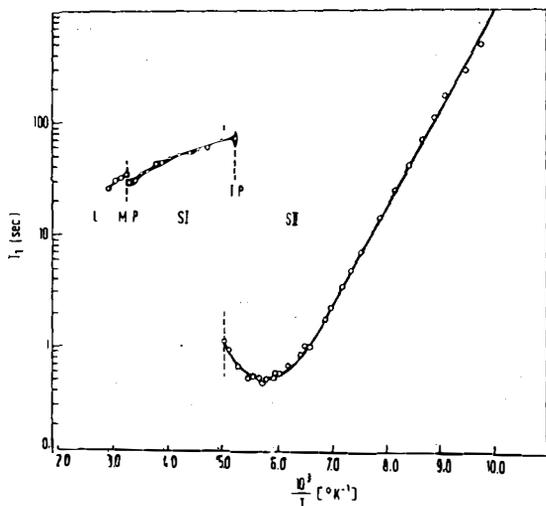


Fig. 4. Temperature dependence of the  $^{31}\text{P}$  spin-lattice relaxation time in white phosphorus <sup>13)</sup>

### 3.3. Possible Relaxation Mechanisms

The above results show that intramolecular dipolar interactions modulated by hindered rotations of the hexafluoride octahedra, dominate the nuclear spin-lattice relaxation process at low temperatures in the S II phase. The classical BPP theory seems to work quite well in this region.

This is not the case for the liquid and the S I phase where spin-rotational interactions seem to be an important relaxation mechanism. Other possible relaxation mechanisms are:

- (i) relaxation by paramagnetic impurities,
- (ii) dipolar relaxation due to slow cooperative rotation,
- (iii) diffusion modulated dipolar relaxation in the weak anisotropic interaction limit (WAIL).

The flat plateau in the  $T_1$  vs.  $1/T$  plot in the S I phase of  $\text{SF}_6$  and  $\text{SeF}_6$  is certainly in accord with what one would expect if relaxation by paramagnetic impurities<sup>12)</sup> would be rate determining. The fact that samples of different origin yield the same  $T_1$ , and that the low temperature  $T_1$  (in the S II phase of  $\text{TeF}_6$  and white phosphorus) is much longer than the maximum S I or liquid phase relaxation time, on the other hand is hard to understand on this basis. The convincing argument against this mechanism, however, is that it cannot explain the detailed form of the  $T$ -dependence of  $T_1$ : in  $\text{SF}_6$ , in particular,  $T_1$  first increases with decreasing  $T$  up to 60 degrees below the melting point, then remains constant, and finally decreases, whereas relaxation by paramagnetic impurities would yield only a flat plateau. Therefore the anomalous decrease of  $T_1$  with  $T$  cannot be attributed to relaxation by paramagnetic impurities.

Dipolar relaxation due to slow cooperative rotation can be as well disregarded as the rate determining relaxation mechanism. Whereas it is true that such a mechanism may reproduce the observed  $T$ -dependence of  $T_1$  in the limit  $\omega^2 \tau^2 \gg 1$  (eq. 19), it also predicts a strong frequency dependence of  $T_1$  which has not been observed.

The WAIL model of Bloom<sup>11)</sup>, on the other hand, - which was proposed as a criticism of the rotational diffusion model - may reproduce both the temperature and frequency dependence of  $T_1$  without requiring the existence of spin-rotational interactions, provided that certain requirements as to the strength of the intermolecular forces and the diffusion rate are fulfilled. This conditions seem to be met in the liquid but not in the solid. The argument goes as follows<sup>17)</sup>:

In the weak anisotropic interaction limit, the unperturbed molecular energy levels are the eigenvalues of the Schrödinger equation,

$$(H_{J_i} + H_{C_i}) \psi_{n_i} = \hbar \omega(n_i) \psi_{n_i}, \quad (20)$$

with  $H_{C_i}$  standing for the »crystal field«, and  $H_{J_i}$  for the rotational kinetic energy term. The correlation function for any single-molecule operator  $O_i(t)$  is for an equilibrium ensemble obtained as

$$\begin{aligned} G(\tau) &= \text{Re} \sum_{n_i, n_i'} P_{n_i} \langle n_i | O_i(t) | n_i' \rangle \langle n_i' | O_i(t + \tau) | n_i \rangle = \\ &= \left\{ \sum_{n_i, n_i'} P_{n_i} |\langle n_i | O_i | n_i' \rangle|^2 \right\} g(\tau), \end{aligned} \quad (21)$$

where  $g(\tau)$  is the »reduced correlation function«, which has been introduced in eq. (4) and whose value at  $\tau = 0$  is unity, and where

$$P_{n_i} = \frac{\exp(-\hbar \omega(n_i)/kT)}{\sum_{n_i} \exp(-\hbar \omega(n_i)/kT)}. \quad (22)$$

It should be noted that for a spherically symmetric crystal field  $H_C$ ,  $g_{SR}(\infty) = 1$  for  $O_i = J_i$  (since  $J_i$  is diagonal in  $|n_i\rangle$ ), whereas for a large enough  $H_C$  of sufficiently low symmetry,  $g(\infty) = 0$  since  $J_i$  is completely »quenched«. For  $O_i = Y_2^m(\mathcal{D}_i)$ , on the other hand, one gets in this last case  $g_a(\infty) = 1$  (since the molecules are rigidly »oriented«), whereas  $g_a(\infty) = 0.2$  for the case of freely rotating spherical tops<sup>11)</sup>.

The presence of weak anisotropic intermolecular interactions results in molecular reorientations which produce a decay of  $g(\tau)$ . Bloom<sup>11)</sup> assumes that this decay is gaussian at long times

$$g(\tau) = g(\infty) \exp(-1/2 \omega_A^2 \tau^2), \quad (23)$$

where  $\hbar \omega_A$  is the effective strength of the intermolecular interactions.

In the absence of any other motion, the spectral density of fluctuations at the nuclear Larmor frequency  $\omega_L$  is

$$J(\omega_L) = \int_{-\infty}^{+\infty} g(\tau) e^{-i\omega_L \tau} d\tau = g(\infty) \cdot \exp(-\omega_0^2/2\omega_A^2) \cdot \sqrt{2\pi}/\omega_A, \quad (24)$$

and the intramolecular dipolar  $R_d = (1/T_1)_{\text{intram. } d}$ , and spin-rotational  $R_{SR} = (1/T_1)_{SR}$  relaxation rates are obtained as

$$R_d = K_d \cdot g_d(\infty) \exp(-\omega_0^2/2\omega_A^2) \cdot \sqrt{2\pi}/\omega_A, \quad (25)$$

$$R_{SR} = K_{SR} \cdot g_{SR}(\infty) \exp(-\omega_0^2/2\omega_A^2) \cdot \sqrt{2\pi}/\omega_A, \quad (26)$$

with  $K_d$  being temperature independent, and  $K_{SR}$  being proportional to temperature. If  $\omega_0 \ll \omega_A$ ,  $R_d$  is temperature and frequency independent in contrast to the classical BPP theory, whereas  $R_{SR}$  increases with increasing temperature in qualitative agreement with the rotational diffusion model and expressions (9) and (17). To reproduce the experimental  $T_1$  vs. inverse temperature plots in the S I phase one has to take into account both  $R_d$  and  $R_{SR}$ , similarly as in the rotational diffusion model (eq. 18).

If one now allows for translational diffusion of molecules with a correlation time  $\tau_0$  one finds, following Moriya<sup>13</sup>,

$$R_d(\omega_A \tau_0) = R_d F(\omega_A \tau_0), \quad (27)$$

where

$$F(x) = (2/\pi)^{1/2} \exp(x^2) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \cdot \frac{x^{2n}}{x + n/x} \quad (28)$$

is practically constant for large  $x$ , but rapidly increases with decreasing  $x$  if  $x$  is smaller than one. If now  $\omega_A \tau_0 < 1$ , and at the same time  $\omega_L \ll \omega_A$ , one may explain the increase of the frequency independent  $T_1$  with decreasing temperature (and a consequently increasing  $\tau_0$ ) in terms of  $R_d(\omega_A \tau_0)$  only, without invoking the existence of spin-rotational interactions. This situation may well be realized in the liquid state, where  $\tau_0$  is of the order of  $10^{-10}$  sec. For liquid  $\text{SF}_6$ , in particular, Bloom showed<sup>11</sup>) that taking into account diffusion, one may explain the temperature dependence of  $T_1$  by choosing  $\omega_A = 6.4 \cdot 10^{10} \text{ s}^{-1}$  and  $K_d = 1.15 \cdot 10^{10} \text{ s}^{-2}$ . This interpretation is of course not unique and does not mean that spin-rotational interactions are really absent in liquid  $\text{SF}_6$ , but it represents an interesting alternative to the rotational diffusion model.

It seems, however, that this interpretation does not work for the solid S I phase. Second moment data seem to show that  $\tau_0$  is longer than  $10^{-4}$  s, so that  $\omega_A$  should be less than  $10^4$  c/s in order to reproduce the observed temperature dependence. In such a case, however,  $\omega_L$  is larger than  $\omega_A$ , and equations (25) and (27) predict a strong frequency dependence of  $T_1$ , which has not been observed. In order to explain the experimental data in the solid, one thus has to introduce spin-rotational interactions not only in the classical rotational diffusion model, but in the WAIL model as well.

#### 4. Conclusion

Spin-lattice relaxation time measurements show that an anomalous increase of the frequency independent  $T_1$  with decreasing temperature occurs in a number of molecular solids and liquids. The only plausible explanation for this anomaly appears to be the spin-rotation interaction. The above results thus seem to throw

new light on reorientations in disordered solids and open the possibility of studying correlation functions for the angular velocity of molecules not only in gases and liquids but in the solids as well.

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## O EGZISTENCIJI REZONANTNE NUKLEARNE MAGNETSKE RELAKSAKCIJE POMOČU SPIN-ROTACIONIH MEĐUDJELOVANJA U ČVRSTOM TIJELU

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### Sadržaj

Sa impulsnim nuklearnim magnetnim rezonantnim spektrometrom izmerene su temperaturne i frekventne zavisnosti longitudinalnih relaksacionih vremena spin-rešetka u nizu gotovo sferno simetričnih molekula kako u čvrstoj tako i u tečnoj fazi. Na osnovu rezultata može se zaključiti da je spin-rotaciona interakcija dominantan relaksacioni mehanizam u srazmerno velikom broju molekula kako u čvrstom tako i u tečnom stanju, što daje mogućnost izučavanja korelacionih funkcija za uglovnu brzinu molekula metodama NMR-a.