

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 Kubo¹⁾ relates the «relaxation time» 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 Φ , 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 ω_L and $2\omega_L$. Hence the dipolar contribution to the nuclear spin relaxation rate, T_1 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 τ_d and τ_{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 τ_{SR} must vary in the same way as τ_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 situation²⁾ 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 τ_d and τ_{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} , Hubbard³⁾ showed that τ_d and τ_{SR} are related by

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

so that τ_{SR} increases with increasing temperature whereas τ_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, τ_d^{-1} and τ_{SR}^{-1} are larger than the nuclear Larmor frequency, ω_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

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

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^{2,3)}

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

and there is a maximum in T_1 at which

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

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. Gutowsky⁴⁾ was the first to point out that this is not always the case with liquids and the authors of the present paper recently⁵⁾ 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_6 , SeF_6 , TeF_6 , UF_6 , MoF_6 and WF_6 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 time⁶⁾, T_1^r , was as well determined by applying a 90° pulse followed by a pulse of length τ 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 τ :

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

The second moments of the ^{19}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 ^{19}F magnetic resonance absorption spectra of SF_6 , SeF_6 and TeF_6 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 Gauss² 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 (10^4 – 10^5 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_6 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

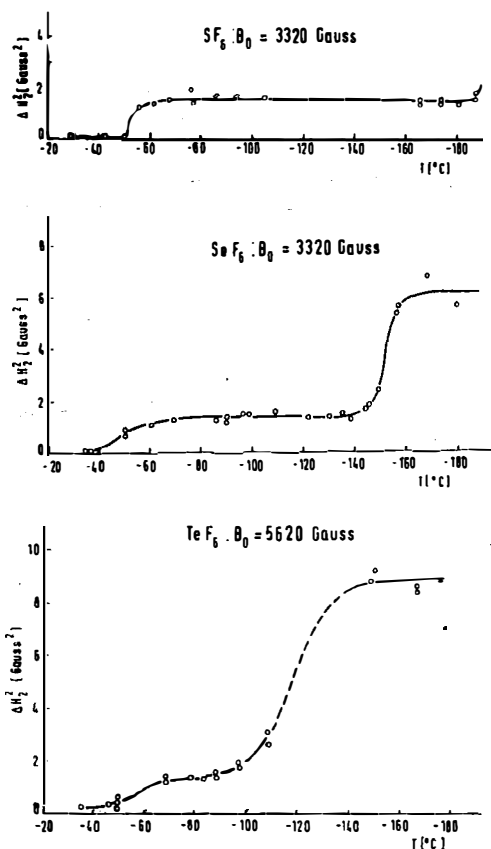


Fig. 1. Second moments of the ^{19}F nuclear magnetic resonance absorption line of SF_6 , SeF_6 and TeF_6 as a function of temperature.

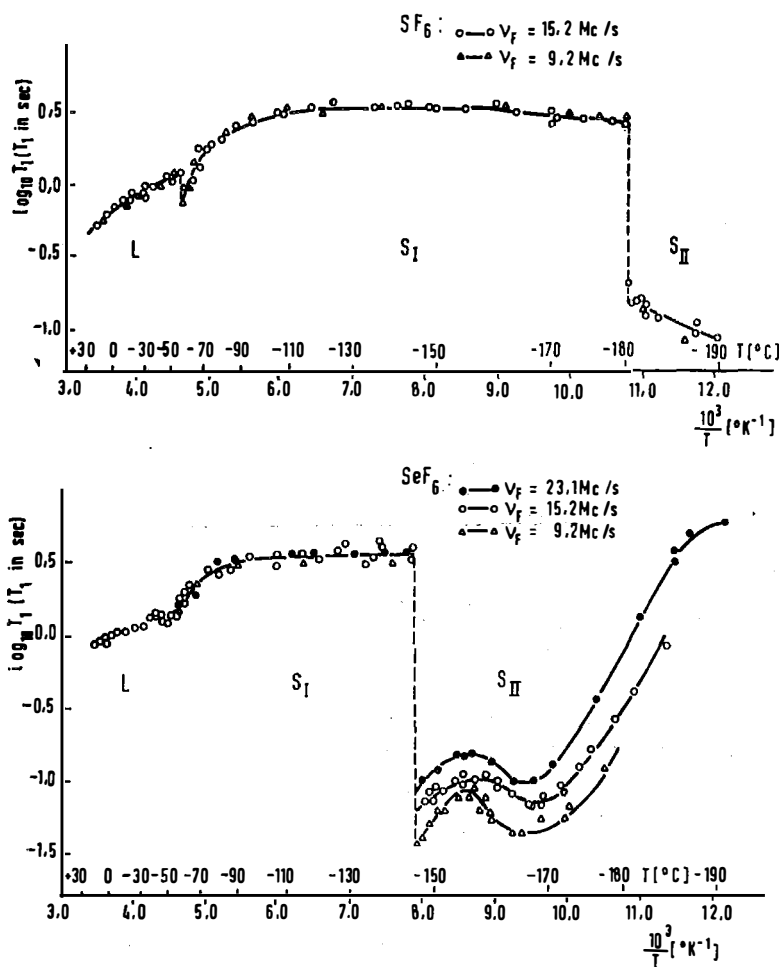
to the anisotropy of the chemical shift tensor, which can be in case of hexafluoride molecules at fields normally used in NMR experiments still larger than the dipolar contribution⁷⁾. For the case of an axially symmetric screening tensor $\sigma = (\sigma_{\perp} \sigma_{\perp} \sigma_{\parallel})$ one finds⁹⁾

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

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

A similar temperature dependence of M_2 is exhibited by WF_6 and MoF_6 , where however the solid phase I region is much narrower⁷⁾. In UF_6 , this region does not exist at all and the solid phase I goes over directly to the liquid phase⁷⁾.

Whereas practically nothing is known about the crystal structure of solid SF_6 , TeF_6 and SeF_6 , one knows that the low temperature form (solid phase II) of WF_6 and 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 lattice⁸⁾ (solid phase I) at higher temperatures. Transition entropy data⁸⁾ 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 SF_6 , SeF_6 and TeF_6 are very similar to the ones found in WF_6 and MoF_6 .



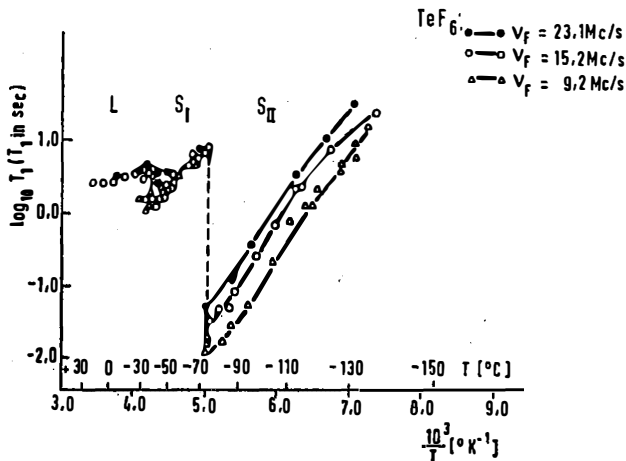


Fig. 2. Temperature dependences of the ^{19}F spin-lattice relaxation times in SF_6 , SeF_6 and TeF_6 .

3.2. Spin-Lattice Relaxation

The temperature dependences of the ^{19}F spin-lattice relaxation times (T_1) of SF_6 , SeF_6 , TeF_6 , MoF_6 , WF_6 and UF_6 are presented in Figures 2 and 3. Except for the case of 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 SF_6 , the T_1 results agree with the ones of Hubbard and Hackleman⁹⁾. 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 theory¹⁰⁾, which was until recently supposed to be quite adequate for liquids and disordered solids. Hubbard⁹⁾ suggested that the anomalous temperature dependence in liquid SF_6 demonstrates that spin-rotational interactions - as given by eq. (9) - are dominant whereas Bloom¹¹⁾ 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° 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 SF_6 and SeF_6 a flat maximum is reached. In SeF_6 the plateau extends till the solid-solid transition point, whereas in SF_6 T_1 starts to decrease with decreasing T in the region between -150° and -180°C . In TeF_6 , MoF_6 and 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

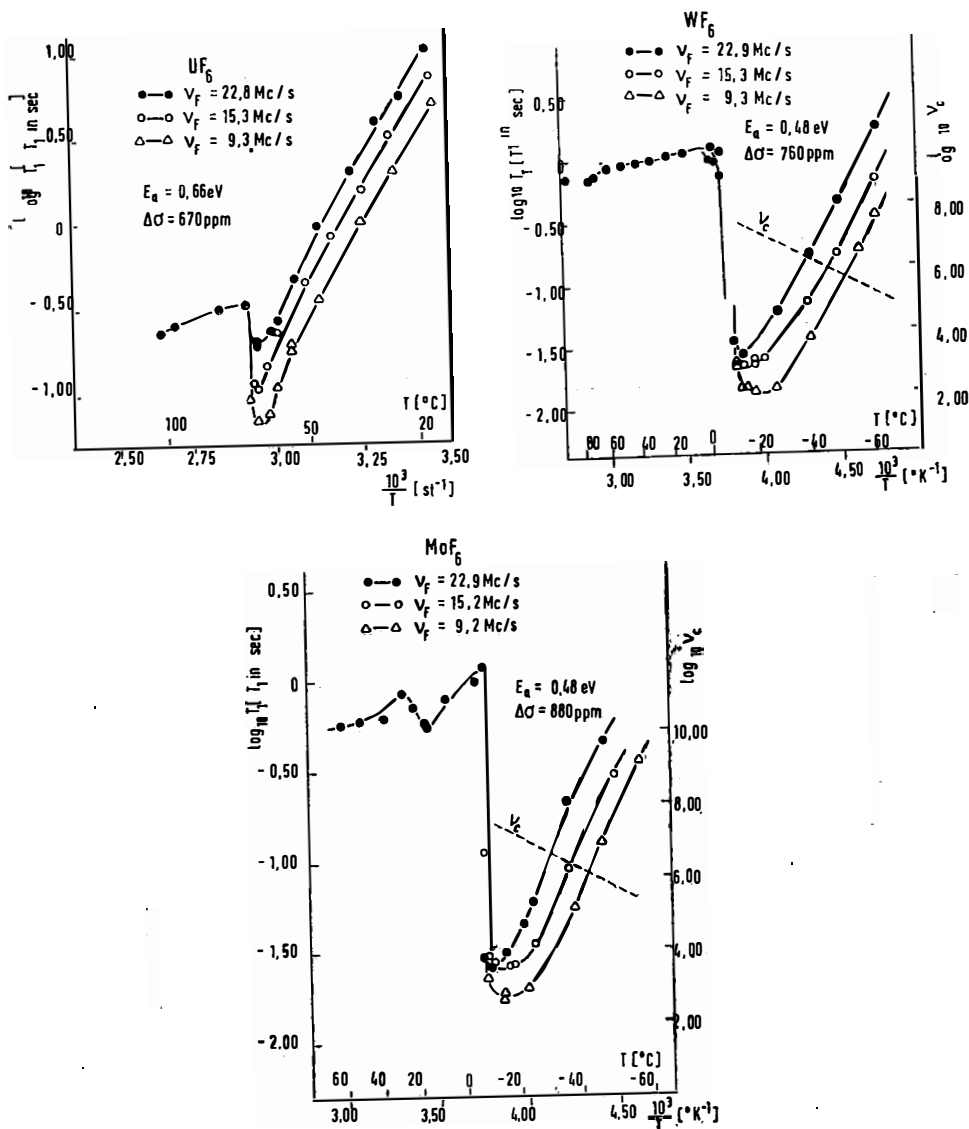


Fig. 3. Temperature dependences of the ^{19}F spin-lattice relaxation times and correlation frequencies in UF_6 , and WF_6 , MoF_6 .

region, so that $\omega^2 \tau^2 \ll 1$. If dipolar interactions were to dominate the relaxation process and the classical BPP theory¹⁰⁾ 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's⁹) 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 τ_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 Bloom¹²), 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 τ_d is now of the order of ω_L^{-1} . The solid-solid transition is thus connected with a discontinuous increase in τ_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_6 further indicates that rotations about the C_4 and the C_2 axis do not have the same τ_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 Resing¹²) in solid white phosphorus (Fig. 4) in the high temperature α -phase and in the liquid phase, whereas the low temperature β -phase showed again a typical BPP minimum.

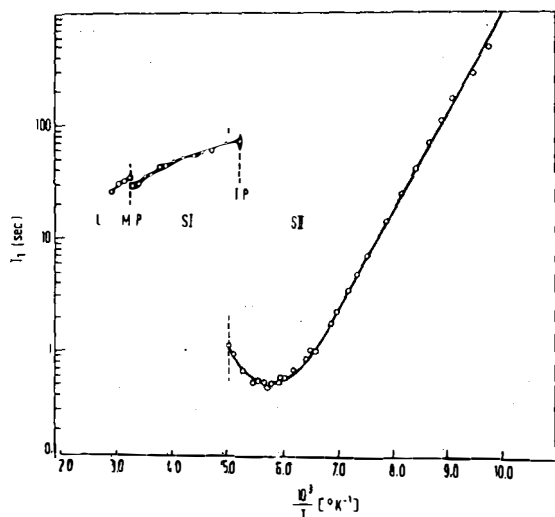


Fig. 4. Temperature dependence of the ^{31}P spin-lattice relaxation time in white phosphorus ¹²⁾

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 SF_6 and SeF_6 is certainly in accord with what one would expect if relaxation by paramagnetic impurities¹³⁾ 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 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 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 Bloom¹¹⁾, 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 follows¹⁷⁾:

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 $O_i = Y_2^m(\mathfrak{F}_i)$, 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 tops¹¹⁾.

The presence of weak anisotropic intermolecular interactions results in molecular reorientations which produce a decay of $g(\tau)$. Bloom¹¹⁾ 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 ω_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 $R_d = (1/T_1)_{\text{intra } d}$, 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 τ_0 one finds, following Moriya¹³,

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

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 τ_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 τ_0 is of the order of 10^{-10} sec. For liquid SF_6 , in particular, Bloom showed¹¹) 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 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 τ_0 is longer than 10^{-4} s , so that ω_A should be less than 10^4 c/s in order to reproduce the observed temperature dependence. In such a case, however, ω_L is larger than ω_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.