Spin-lattice Relaxation in Solid Phosphorus Trichloride and Phosphorus Oxychloride

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The ^{31}P spin-lattice relaxation time, T_1, has been measured at 9 MHz in solid PCl_3 and $POCl_3$ at temperatures covering a range of about 70°C from the melting points.

The phosphorus spin-lattice relaxation for these solids is believed to be controlled by the intramolecular dipolar interaction. T_1 is calculated assuming both isotropic rotational diffusion and hindered rotation about the C_3 axis. For a powder sample the effect of a hindered rotation is to retard the relaxation relative to an isotropic reorientation.

The T_1 data are discussed in terms of possible molecular motions in the solids. It is argued that the rotations of the PCl_3 and $POCl_3$ molecules take place preferentially about the C_3 axis. The rate of motion in these solids, represented by a molecular correlation time, is of the order 10^{-7} to 10^{-8} sec.

In a previous paper [1] the ^{31}P spin-lattice relaxation times for liquid PCl_3 and $POCl_3$ were found to be mainly controlled by the spin-rotation interaction modulated by Brownian motion of the molecules. For super-cooled PCl_3 the contribution from the dipolar interaction also became important. The ^{31}P relaxation time, $T_{1\varrho}$, in the rotating frame, for liquid PCl_3 was, however, explained by modulation of the scalar interaction.[2]

The object of the present work is to study the molecular motions in solid PCl_3 and $POCl_3$ and to discuss the various interactions that might contribute to the nuclear spin-lattice relaxation. The most important mechanism in the relaxation of the ^{31}P nucleus certainly arises from the dipolar coupling. This, then illustrates how different types of interactions can be studied for the same molecules by changing the experimental conditions.

PCl_3 and $POCl_3$ belong to the symmetric-top molecules. Previous investigations of the structure of these molecules are mainly based on microwave spectroscopy and electron diffraction methods.[3,4] No pertinent data on the static and dynamical structure in the solid are, to the author's knowledge, available. There is, in particular, no information about possible phase transitions.

1. EXPERIMENTAL

Phosphorus trichloride and phosphorus oxychloride were obtained commercially. The liquids were redistilled two times successively on a closed vacuum line to obtain further purification. While still under vacuum, the purified samples were degassed four times by the freeze-pump-thaw technique, and then distilled into NMR glass phials and sealed under vacuum.

The T_1 times were measured at a resonance frequency of 9 MHz using a $90° - \tau - 90°$ pulse technique. The magnetization is proportional to the initial magnetization of the induction signal following the first 90° pulse. The poor signal-to-noise ratio made it necessary to apply the second 90° pulse at a series of different τ values to improve the accuracy of T_1. The slope of the straight line semilog plot of the difference between the equilibrium magnetization and the recovered magnetization as a function of τ, yielded T_1. The temperature was regulated to within 1°C using a nitrogen gas flow technique.

2. THEORY

The magnetic interactions between the nuclei and the 'lattice' are randomly modulated by the atomic and molecular motions in crystals, giving rise to fluctuating magnetic fields. These fields again induce transitions between the nuclear energy levels thus causing spin-lattice relaxation in the solid.

A great deal of work has been done during the past decade in applying the nuclear magnetic resonance method to the study of molecular motion in solids.[5] Theoretical calculations of T_1 in solids are often based on liquid models for the molecular motion. This is a crude approximation for many solids even though the relaxation is often fairly insensitive to the nature of the motion.

The following evaluation of the spin-lattice relaxation time, T_1, for dipolar interaction, is based on the Redfield theory.[6] The first expression obtained for T_1 is not restricted to a specific model. However, to proceed further, one has to adapt a particular model for the molecular motion. It is at this stage one gains specific information about the nature of the molecular motion.

In pure nuclear quadrupole resonance the dipolar coupling of integer spins (S) to neighbouring like and unlike spins (I) is reduced or quenched at low field if the quadrupole interaction $\mathscr{H}_Q$, is significantly asymmetric.[7] The dipolar coupling is, however, fully restored in the limit of high applied magnetic fields. The states $\pm m_S$ of $\mathscr{H}_Q$ are double degenerate in an axial symmetric field gradient $(\eta = 0)$. The asymmetry term in η will, however, lift this degeneracy for integer spins and cause a dipolar field quenching. However, if S is half-integer the initially degenerate states $\pm m_S$ differ at least by an odd integer and the asymmetry term will not introduce a further lift of degeneracy and thus not give rise to dipolar quenching.[7] For like spins S, and at low field, the effect of the dipolar quenching would, however, have to be taken into account in an exact evaluation of T_1. This is, however, a difficult problem which is not treated in the present paper. At any rate, the evaluated expression for T_1 will in this paper only be applied to a case where S is half-integer. The following evaluation of T_1 is therefore based on the assumption that both the I and S spins are quantized along the direction of the static field. The general theory due to Redfield and Abragam [6] can then be used.

The total Hamiltonian for a pair of dipolar coupled nuclei with spin quantum numbers I and S in a static field along the z-axis, is given by [6]

$$\hbar \mathscr{H} = \hbar \mathscr{H}_0 + \hbar \mathscr{H}_1 \qquad (1)$$

where the Zeeman Hamiltonian is

$$\mathscr{H}_0 = \omega_I I_z + \omega_S S_z \qquad (2)$$

ω_I and ω_S are the Larmor angular frequencies for the I and S spins, respectively. The dipolar interaction can be written [6]

$$\mathscr{H}_1 = \sum_q F^q A^q \qquad (3)$$

where the random operators F^q are functions of the relative positions of the two spins and are related to the normalized spherical harmonics $Y_l^m (\theta,\phi) \equiv Y_l^m (\Omega)$ by

$$F^0 = -\frac{1}{r^3} \left(\frac{16\pi}{5}\right)^{\frac{1}{2}} Y_2^{\,0}(\Omega); F^1 = \frac{1}{r^3}\left(\frac{8\pi}{15}\right)^{\frac{1}{2}} Y_2^{\,1}(\Omega); F^2 = \frac{1}{r^3}\left(\frac{32\pi}{15}\right)^{\frac{1}{2}} Y_2^{\,2}(\Omega) \qquad (4)$$

where r, θ and ϕ are the usual polar coordinates. The A^q are the well known operators acting on the spin variables.[6]

When there is interaction between unlike spins, the recovery of the longitudinal magnetization following a 90° pulse is not a simple exponential with a single relaxation time. The relaxation of two spins I and S is governed by a pair of coupled differential equations for their expectation values. The equation for the time variation of $\langle I_z \rangle$ reads[1,6]

$$\frac{\mathrm{d}\langle I_z \rangle}{\mathrm{d}t} = -\alpha \left(\langle I_z \rangle - \langle I_0 \rangle\right) - \beta \left(\langle S_z \rangle - \langle S_0 \rangle\right) \qquad (5)$$

with a similar equation for the S nucleus. α and β are relaxation rates which will be given as they arise. In cases where the relaxation of the S nucleus is controlled by a strong quadrupole interaction, and is thus very effective, the last term of eqn. (5) can be neglected. The recovery of $\langle I_z \rangle$ is then exponential with a spin-lattice relaxation rate $\alpha = 1/T_1$.

If the intramolecular dipole interaction is the only relaxing mechanism contributing to T_1, then

$$\frac{1}{T_1} = (\gamma_I \gamma_S \hbar)^2 S(S+1) \left[\frac{1}{12} J^0(\omega_I - \omega_S) + \frac{3}{2} J^1 (\omega_I) + \frac{3}{4} J^2 (\omega_I + \omega_S)\right] \qquad (6)$$

where the spectral density is given by the Fourier transform of the auto-correlation function [6]

$$G^q(\tau) = \overline{F^q(t)\overline{F^q(t+\tau)}} \qquad (7)$$

and where the random functions F^q are defined by eqn. (4). The bar means the average over a statistical ensemble. The arguments of the spectral density follow from the fact that the A^q are transformed into the interaction representation

$$\exp(i\mathscr{H}_0 t) A^q \exp(-i\mathscr{H}_0 t) = \sum_p A_p^{\,q} \exp(i\omega_p^{\,q} t) \qquad (8)$$

under the evaluation of eqn. (6), where, for instance,

$$\exp(i\mathcal{H}_0 t)\, I_+ S_- \exp(-i\mathcal{H}_0 t) = \exp[i(\omega_I - \omega_S)]I_+ S_- \tag{9}$$

One can often assume a correlation function that, on general physical grounds, has about the correct behaviour. If the reorientation of the coupled spins can be described by a diffusion equation an exponential correlation function results.[6]

In that case one obtains

$$J^q(\omega) = \int G(\tau) e^{-i\omega\tau}\, d\tau = \frac{1}{r^6}\,\frac{\tau_d}{1 + \omega^2 \tau_d{}^2} \times k \tag{10}$$

where $k = 8/5,\ 4/15,\ 16/15$ for $q = 0,\ 1,$ and 2, respectively, and τ_d is the correlation time for the motion of the internuclear vectors of the dipolar coupling.

The above equations require that the average over the motion of the perturbing Hamiltonian $\mathcal{H}_1$, defined by eqn. (3) vanishes. This condition is not fulfilled if the motion of the nuclear pair is a hindered rotation since not all $Y_2{}^m$ average to zero over the motion. The remedy is then to include the average of the dipolar interaction into the Zeeman Hamiltonian, viz.[6,8,9]

$$\hbar\mathcal{H} = \hbar E + \hbar\mathcal{H}_1{}'(t) \tag{11}$$

where

$$E = \mathcal{H}_0 + \langle\mathcal{H}_1\rangle_{Av};\quad \mathcal{H}_1{}'(t) = \mathcal{H}_1(t) - \langle\mathcal{H}_1\rangle_{Av} \tag{12}$$

However, since $\langle\mathcal{H}_1\rangle_{Av}$ does not commute with $\mathcal{H}_0$, the redefined Hamiltonian E, is no longer diagonal in the same representation as $\mathcal{H}_0$. In a proper representation the so-called Redfield equation, on which the theory above is based, will in general contain more nonsecular terms than before since any degenerate levels will be split by energies of the order $\langle\mathcal{H}_1\rangle_{Av}$. For an isolated pair of coupled spins no more nonsecular terms are introduced by $\langle\mathcal{H}_1\rangle_{Av}$. Eqn. (6) can then still be used provided that the correlation function is redefined to read [10]

$$G^q(\tau) = \langle F^q(t)F^q(t+\tau)\rangle_{Av} - \langle F^q(t)\rangle_{Av}{}^2 \tag{13}$$

Let the nuclear pair belong to a molecule with a C_3 symmetry axis, for instance one $P - Cl$ pair of phosphorus trichloride. For the calculation of the various correlation functions one assumes successively uncorrelated rotations of $\pm 2\pi/3$ about the C_3-axis [8-10] occurring at average jump rates ν. The variation of $F^q(t)$ is then considered as a Markov jump among three equiprobable values f_k labelled from 1 to 3 corresponding to the three equivalent positions of the three nuclei. It then follows that the correlation function (13) takes the form [10]

$$G(t) = \tfrac{1}{9}[3\sum_{k=1}^{3}|f_k|^2 - |\sum_{k=1}^{3} f_k|^2]\, \exp\left(-|t|/\tau_c\right) \tag{14}$$

where $\tau_c = 2\nu^{-1}/3$.

In crystal powders the axes of rotation are randomly distributed over the sphere of directions. The average for a powder sample is then found by averaging over the solid angle $d\Omega$. This is most easily done by using the relation between the components of spherical harmonics in two coordinate systems S_1 and S_2. [9,11]

$$Y_l^k(\Omega_1) = \sum_{k'=-l}^{l} D_{kk'}^l{}^*(\alpha\beta\gamma) Y_l^{k'}(\Omega_2) \tag{15}$$

where α, β, and γ are the Euler angles of S_2 with respect to S_1 and $D_{kk'}^l$ are the elements of a rotation matrix. It then follows that

$$\int Y_2^k(\Omega_1) \; Y_2^{k'}{}^*(\Omega_2) \mathrm{d}\Omega = D_{kk'}^2{}^* \; (\alpha\beta\gamma) \tag{16}$$

The equation above will be applied to the particular case when $\alpha = \gamma = 0$ and β represents the angle between two directions Ω_1 and Ω_2, that is, the angle between two pairs of spins pointing in the directions labelled 1 and 2. By using eqns. (14) and (16) the various correlation functions and corresponding spectral densities are easily evaluated.[12] The spin-lattice relaxation time, averaged over a powder sample, for a pair of spins undergoing restricted rotation, then follows from eqn. (6). However, when the A^q are transformed into the interaction representation, E should replace $\mathscr{H}_0$ in eqn. (8). Since $\langle\mathscr{H}_1\rangle_{\mathrm{Av}}$ is a small perturbation, however, one gets significant contributions to $J_q(\omega)$ for very nearly the same frequencies as when $\langle\mathscr{H}_1\rangle_{\mathrm{Av}} = 0$.

It follows from eqn. (14) that the effect of the hindered rotation relative to isotropic reorientation, is to retard the relaxation.[8,9]

3. RESULTS AND INTERPRETATION

The experimental ^{31}P spin-lattice relaxation times as a function of reciprocal temperature, for solid phosphorus trichloride and phosphorus oxychloride, are shown in Figs. 1 and 2. The variation of T_1 for PCl_3 is linear within experimental error while the variation of T_1 for $POCl_3$ is linear well below the melting point but appears to approach a minimum when melting intervenes. At $-93°C$ $POCl_3$ had a T_1 of about 1500 sec (off graph).

The ^{31}P spin-lattice relaxation times for liquid PCl_3 and $POCl_3$ were found to be mainly controlled by the dipolar and spin rotation interactions.[1] Furthermore, the intermolecular dipolar contribution was quite small compared to the intramolecular term. In these solids the contribution from the spin-rotation interaction will certainly be negligible. The line widths were broad and appeared to change only slightly in the temperature range studied. It can therefore be concluded that the spin-lattice relaxation in the two solids, is controlled by the intramolecular dipolar interaction modulated by molecular reorientation.

One may speculate about the nature of the motion occurring in solid PCl_3 and $POCl_3$. The symmetry of the molecules naturally suggests a hindered rotation about the C_3 axis.[13] But a more general reorientation is also possible at temperatures not too far below the melting points. In solid AsF_3 an intramolecular dipolar interaction modulated by isotropic reorientation, accounted very well for the experimental data.[14] It was found that a triad rotation occurs in solid NF_3 at temperatures below the first-order transition point at 57°K, but that a more general reorientation and diffusion occur at higher temperatures.[13,15] In a relaxation study of metal hexafluorides it was concluded that the rotations of molecules occur preferentially about a single C_3 axis in UF_6
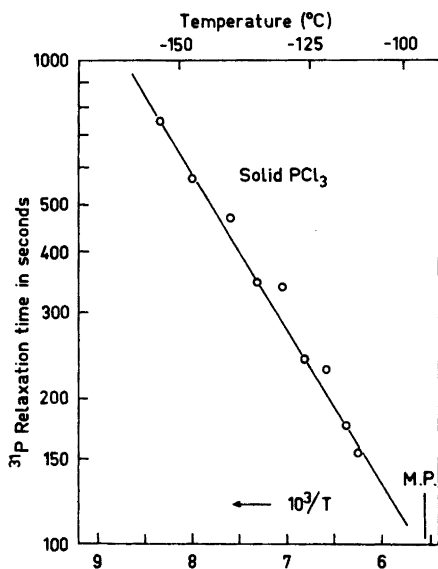
Fig. 1. Phosphorus spin-lattice relaxation time in solid PCl_3 at 9 MHz. M.P. indicates the melting point.
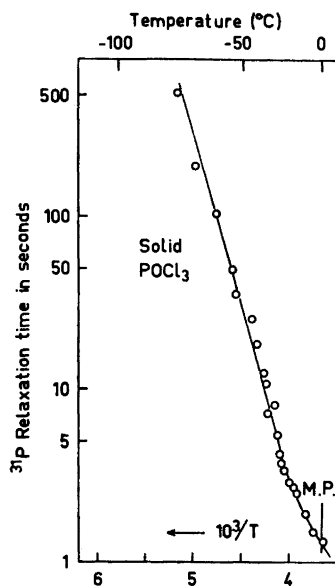

Fig. 2. Phosphorus spin-lattice relaxation time in solid $POCl_3$ at 9 MHz. M.P. indicates the melting point.

whilst the rotations are quasi-isotropic in MoF_6.[10] The P_4 tetrahedra were, however, found to undergo general reorientation above 130°K.[16] All counted, it appears to be difficult to draw any definite conclusions concerning the motions occurring in solid PCl_3 and $POCl_3$ from knowledge about the motions of similar systems.

The T_1 measurements in the solid clearly show that some type of molecular motion occurs in both PCl_3 and $POCl_3$. However, no drastic changes in T_1 and T_2 were observed. First-order phase transitions are therefore not expected in the measured temperature ranges. The temperature dependence of the dielectric constants could give information about the reorientation of the molecular dipoles. No data on heat-capacities, phase transitions and dielectric constants are, however, reported for these solids.

The experimental T_1 relaxation times in PCl_3 and $POCl_3$ certainly correspond to values well below the minimum, that is $\omega_p \tau_d \gg 1$ and therefore $T_1 \alpha \tau_d$. If the correlation times follow the Arrhenius law, the activation energies can be obtained from the slopes of the experimental curves. This yields 1.5 kcal/mol and 9 kcal/mol for PCl_3 and $POCl_3$, respectively. The $POCl_3$ molecules are fairly tetrahedral and closer packed than the pyramidal PCl_3 molecules possessing lone electron pairs. The activation energy of only 1.5 kcal/mol for PCl_3 rules out the possibility of inversion. The spacious electron cloud constituting the lone pair, is naturally affected by neighbouring molecules and this might retard a general reorientation. This suggests that a C_3-rotation rather

than a general reorientation, is favoured in this molecule. A C_3-rotation also preserves the configurational order without requiring elaborately cooperative molecular motions. An activation energy of 9 kcal/mol for the more symmetrical and compact $POCl_3$ molecules could, however, correspond to a general reorientation. Such a motion, since it changes the direction of molecular dipoles, would probably give rise to a phase transition possible below the measured temperature range. No indication of a phase transition was, however, found in the measured temperature range. A crystal structure determination of $POBr_3$ has shown that the molecules are linked by weak intermolecular $Br \cdots O$ bridges.[17] Comparison of the Raman spectra of $POCl_3$ in the liquid and solid state indicates that intermolecular bonding is also present in $POCl_3$ crystals.[17] This would give rise to a higher activation energy for a C_3-rotation in the $POCl_3$ molecules because the motion would require breaking of intermolecular bonds. It is therefore expected that the reorientation of the $POCl_3$ molecules also occurs preferentially about the C_3 axis.

The expressions for the spin-lattice relaxation times given in last section, can now be applied to the PCl_3 and $POCl_3$ molecules. There are two isotopes of chlorine, ^{35}Cl and ^{37}Cl of approximately 75·% and 25 % abundance, respectively. The following possible types of molecule $P^{35}Cl_3$, $P^{35}Cl_2{}^{37}Cl$, $P^{35}Cl^{37}Cl_2$ and $P^{37}Cl_3$ are denoted as types, a, b, c, and d with relative abundances of about 27:27:9:1. In finding the rate of relaxation one should take into account these different types of molecule and also the different γ_{Cl} and ω_{Cl} of the two isotopic species.

If isotropic rotational diffusion of molecules is assumed, one obtains from eqns. (6) and (10) the following expression for T_1, for a molecule of type a possessing only one chlorine species.[1]

$$\frac{1}{T_1} = \frac{3(\gamma_P \gamma_{Cl} \hbar)^2}{2r^6_{P-Cl}} \left[\frac{1}{1 + (\omega_P - \omega_{Cl})^2 \tau_d^2} + \frac{3}{1 + \omega_P^2 \tau_d^2} + \frac{6}{1 + (\omega_P + \omega_{Cl})^2 \tau_d^2} \right] \tau_d \quad (17)$$

Far away from the minimum on the frequency dependent side where $\omega_P \tau_d \gg 1$, eqn. (17) simplifies to

$$\frac{1}{T_1} = \frac{3(\gamma_P \gamma_{Cl} \hbar)^2}{2r^6_{P-Cl}} \left[\frac{1}{(\omega_P - \omega_{Cl})^2} + \frac{3}{\omega_P^2} + \frac{6}{(\omega_P + \omega_{Cl})^2} \right] \tau_d^{-1} \times f \quad (18)$$

where the suffix Cl refers to the ^{35}Cl isotope only, and the factor f takes into account the different types of molecule listed above; f is, respectively, 1, 0.90, 0.80, 0.70 for the molecules a, b, c, and d. Experimentally an average relaxation time is obtained for the mixture of the four different types of molecule. It is therefore reasonable to use the weighted average value $f = 0.92$. From eqn. (18) the following expression for T_1 is obtained

$$1/T_1 = 3.36 \times 10^{-7} \tau_d^{-1} r^{-6} \quad (19)$$

where the $P - Cl$ distance is measured in Ångström units. Inserting the values $r = 2.03$ Å and $r = 1.99$ Å for PCl_3 and $POCl_3$ respectively, [3,4] one obtains

$$1/T_{1 PCl_3} = 4.80 \times 10^{-8} \tau_d^{-1}; \; 1/T_{1 POCl_3} = 5.40 \times 10^{-8} \tau_d^{-1} \quad (20)$$

At the melting point for PCl_3 it follows from eqn. (20) that $\tau_d = 4.6 \times 10^{-7}$ sec since $T_1 \simeq 95$ sec. For $POCl_3$ $T_1 \simeq 1.4$ sec and thus $\tau_d = 7.6 \times 10^{-8}$ sec

at the melting point. From eqn. (17) it follows that T_1 has a minimum for $\omega_p \tau_d \simeq 0.9$ corresponding to $\tau_d = 1.6 \times 10^{-8}$ sec and $T_{1\ min} = 0.8$ sec for phosphorus oxychloride. This adds evidence to the assumption that T_1 actually is approaching a minimum in Fig. 2. Judging from the slope of the experimental curve, the minimum value is quite reasonable.

If, however, the molecular motion in the solid is a rotation along the C_3 axis T_1 is, according to last section, still given by eqns. (17) and (18) provided that the constants 1, 3, and 6 of the frequency dependent terms, are multiplied by factors d_0, d_1, and d_2, respectively, where

$$d_0 = 1 - \cos^2\beta; \ d_1 = 1 - \tfrac{1}{3}|2\cos^2\beta + \cos\beta|; \ d_2 = 1 - \tfrac{1}{3}|1 + \tfrac{1}{2}(1 + \cos\beta)^2| \qquad (21)$$

Since $\beta \simeq 102°$ for both molecules studied,[3,4] it follows that $d_0 = d_1 = 0.96$ and $d_2 = 0.57$. It is thus seen that the hindered rotation has an appreciable effect on the $J^2(\omega)$ term but a smaller effect on the two other terms. The final results is a retardation of about 28 % in T_1. Using eqns. (18) and (21) it is calculated that

$$1/T_{1PCl_3} = 3.76 \times 10^{-8} \ \tau_d^{-1}; \quad 1/T_{1POCl_3} = 4.23 \times 10^{-8} \ \tau_d^{-1} \qquad (22)$$

This gives $\tau_d = 3.6 \times 10^{-7}$ sec and $\tau_d = 5.9 \times 10^{-8}$ sec at the melting points of PCl_3 and $POCl_3$, respectively. Eqns. (17) and (21) also result in a minimum value of about 1.1 sec for T_1. The deviation of $T_{1\ min}$ calculated on basis of of the models above, is thus well above the experimental error. It can be seen from the experimental curve that the isotropic reorientation model gives the more reasonable $T_{1\ min}$ value for $POCl_3$.

A further interpretation of the T_1 data will have to await new data on the static and dynamical structure of PCl_3 and $POCl_3$.

It would have been interesting to measure T_1 at a different resonance frequency, particularly at a lower frequency where it might be possible to observe the T_1 minimum at least for $POCl_3$. More definite conclusions concerning the motion could then be drawn on the basis on the theory presented in this paper. The theory is of course applicable to any system possessing a C_3 axis of symmetry.

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