

CHAPTER II

THEORY



2.1 Spin-lattice Relaxation in Liquids

Spin-lattice relaxation is a process in which energy is exchanged between the nuclear-spin system and the lattice, tending to bring the system to a common temperature. The approach to equilibrium is exponential, the time constant of the process, T_1 , being inversely proportional to the probability of transition between the nuclear magnetic energy levels brought about by interaction with the lattice. The general formula for the spin-lattice relaxation due to molecular rotation and diffusion through the dipole-dipole interaction in the case of identical particles is written⁵.

$$\frac{1}{T_1} = \frac{3\gamma^4 \hbar^2}{2} I(I+1) \left[J_1(\omega) + J_2(2\omega) \right] \dots (2.1)$$

where γ is the gyromagnetic ratio and $J(\omega)$ represents the spectral density.

The intensity $J(\omega)$ of the Fourier spectra of the functions of the position coordinates²

$$F_0 = \sum_{ij} (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3$$

$$F_1 = \sum_{ij} \sin \theta_{ij} \cos \theta_{ij} e^{i\phi_{ij}} / r_{ij}^3 \dots (2.2)$$

$$F_2 = \sum_{ij} \sin^2 \theta_{ij} e^{2i\varphi_{ij}} / r_{ij}^3$$

is defined by the equations

$$\begin{aligned} \left\langle \sum_j \left| (1 - 3 \cos^2 \theta_{ij}(t)) r_{ij}^{-3}(t) \right|^2 \right\rangle_{av} &= \int_{-\infty}^{\infty} J_0(\omega) d\omega \\ \left\langle \sum_j \left| \sin \theta_{ij}(t) \cos \theta_{ij}(t) e^{i\varphi_{ij}(t)} r_{ij}^{-3}(t) \right|^2 \right\rangle_{av} &= \int_{-\infty}^{\infty} J_1(\omega) d\omega \quad \dots\dots (2.3) \\ \left\langle \sum_j \left| \sin^2 \theta_{ij}(t) e^{2i\varphi_{ij}(t)} r_{ij}^{-3}(t) \right|^2 \right\rangle_{av} &= \int_{-\infty}^{\infty} J_2(\omega) d\omega \end{aligned}$$

In liquids, the function F will vary in a random fashion with time, as the particles containing the magnetic nuclei take part in Brownian motion. The correlation function of $F(t)$ is introduced as

$$\langle F(t) F^*(t + \tau) \rangle_{av} = G(\tau)$$

It is assumed that $G(\tau)$ is an even function of τ and independent of t , and that it is a real function. It may be assumed also that $G(\tau)$ approaches zero for sufficiently large values of τ . The relation between the Fourier spectrum of a function F and the correlation function of F gives the following relationship for the spectral density,

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{i\omega\tau} d\tau \quad \dots\dots (2.4)$$

We assume the form of $G(\tau)$ as

$$G(\tau) = \langle F(t) F^*(t) \rangle_{av} e^{-K|\tau|/\tau_c} \quad \dots\dots (2.6)$$

The time τ_c is a characteristic of the random motion, and it is called the correlation time. From (2.5) and (2.6) it is found, for each of the three J's, that

$$J(\omega) = \langle F(t) F^*(t) \rangle_{av} 2 \tau_c (1 + \omega^2 \tau_c^2)^{-1} \quad \dots(2.7)$$

In water, the interactions responsible for the spin-lattice relaxation are due to intramolecular interactions inside a molecule and interactions between the spins of different molecules.

2.1.1 Rotation

In the interior of a molecule, the variation of dipolar coupling of a spin arises almost completely from the rotation of the molecule. The variation of the distance between the spin due to vibration and also the contribution from the neighbor molecules can be neglected because they are relatively much smaller. It has been supposed, that the rotation of a molecule can be compared to that of a rigid sphere of radius a in a medium of viscosity η . The orientation of the vector connecting the two protons would vary randomly with no direction preferred. The functions F_1 , and F_2 would be given by

$$F_1 = \sin \theta \cos \theta e^{i\varphi} b^{-3} \quad \dots\dots(2.8)$$

$$F_2 = \sin^2 \theta e^{2i\varphi} b^{-3}$$

where b is the interproton distance. It would follow that

$$\langle F_1(t) F_1^*(t) \rangle_{av} = 2/15 b^3 \dots\dots\dots(2.9)$$

$$\langle F_2(t) F_2^*(t) \rangle_{av} = 8/15 b^3$$

Substituting (2.9) in (2.6) and using (2.1), the spin - lattice relaxation time due to rotation may be given by

$$\left(\frac{1}{T_1} \right)_{rot} = \frac{2}{5} \gamma^4 \frac{\hbar^2}{b^6} I(I+1) \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] \dots(2.10)$$

The time τ_c is obtained from the Debye theory of dielectric dispersion in liquid where $\tau_c = 4 \pi \eta a^3 / 3kT$

It is assumed that $\omega \tau_c \ll 1$, and that for water $I = \frac{1}{2}$.

From (2.9) it follows that

$$\begin{aligned} \left(\frac{1}{T_1} \right)_{rot} &= \frac{3}{2} \frac{\gamma^4 \hbar^2 \tau_c}{b^6} \\ &= \frac{2 \pi \gamma^4 \hbar^2 \eta a^3}{b^6 k T} \dots\dots\dots(2.11) \end{aligned}$$



2.1.2 Translation

Now the contribution to the spin-lattice relaxation process of the intermolecular protons will be considered. The fluctuation in the local field arising from neighboring fields is mainly caused by their translational motion. Let us calculate τ_c for the molecule in a spherical shell between r and $r + dr$. The centre of the shell is located at, and moves with, the molecule containing the proton i . A reasonable choice for τ_c is the time

it takes the molecule j to move a distance r in any direction from its original position on the shell, for in that time the field at the proton i , due to j , will have changed considerably. The relation of motion i and j is simply diffusion, and can be described most directly by means of the diffusion coefficient D of the liquid.

From the theory of Brownian motion, the mean square displacement of a particle is⁶

$$\bar{x}^2 = 2 k T \tau_c / \beta \quad \dots\dots (2.12)$$

From Stokes formula $\beta = 6 \pi \eta a$ with the diffusion constant $D = kT/\beta$, the value for the correlation time is,

$$\tau_c = \bar{x}^2 / 2D = r^2 / 12 D \quad \dots\dots (2.13)$$

where r is the relative displacement of two particles in any direction. The angular functions, $\langle F(t) F^*(t) \rangle_{av}$ are averaged as before and then, treating the molecules as independent, we sum the effects of all neighbors by integrating over the volume from the radius of closest approach, $r = 2a$, to infinity. Also we keep $\omega \tau_c \ll 1$

We have for the relaxation time due to the neighbors,

$$\begin{aligned} \left(\frac{1}{T_1} \right)_{trans} &= \frac{3}{2} \frac{4 \pi^2 N_o}{2a} \int_{2a}^{\infty} \frac{1}{r^6} \cdot \frac{r^2}{12D} \cdot 4 \pi r^2 dr \\ &= \frac{\pi}{4} \frac{4 \pi^2 N_o}{aD} = \frac{3}{2} \frac{\pi^2 \hbar^2 N_o \eta}{k T} \quad \dots\dots (2.14) \end{aligned}$$

For more rigorous calculation, accounting for detail angular distribution, the result is⁵

$$\left(\frac{1}{T_1} \right) = \frac{\pi \gamma^4 \hbar^2 N_0}{5 aD}$$

where N_0 is the number of molecule per cm^3 .

2.2. The Effect of Alternating Magnetic Field⁷

When an alternating magnetic field is applied perpendicular to the static field $\vec{H}_0 = \hat{k} H_0$, we can write the equation of motion.

$$\frac{d\vec{\mu}}{dt} = \vec{\mu} \times \gamma \left[\vec{H}_0 + \vec{H}_1(t) \right] \quad \dots\dots\dots(2.15)$$

By using a coordinate system that rotates about the z-direction at frequency ω_z , and by taking H_1 along the x-axis with resonance $\omega_z + \gamma H_0 \cong 0$, and $\omega_z = -\omega$, we get

$$\frac{S\vec{\mu}}{St} = \vec{\mu} \times \gamma \left[(H_0 - \frac{\omega}{\gamma}) \hat{k} + H_1 \hat{i} \right] \quad \dots\dots\dots(2.16)$$

$$= \vec{\mu} \times \vec{H}_{\text{eff}} \quad \dots\dots\dots(2.17)$$

$$\text{where } \vec{H}_{\text{eff}} = \hat{k} (H_0 - \frac{\omega}{\gamma}) + H_1 \hat{i} \quad \dots\dots\dots(2.18)$$

Equation (2.17) states that in the rotating frame, the magnetic moment acts as though it effectively experienced a static magnetic field H_{eff} . The magnetic moment therefore precesses in a cone of fixed angle about the direction of H_{eff} at an angular frequency γH_{eff} .

At resonance frequency we have $\omega = \gamma H_0$ and the effective field is simply $H_1 \hat{i}$. A magnetic moment which is parallel to the static field initially will then precess in the $y - z$ plane. If we were to turn on H_1 for a short time, t_w , the magnetic moment would precess through an angle $\theta = \gamma H_1 t_w$.

If t_w were chosen such that $\theta = \pi$, the pulse would simply invert the magnetic moment. Such a pulse is referred to as a "180° pulse". If $\theta = \frac{\pi}{2}$ (90° degree pulse), the magnetic moment is turned from the z -direction to the y -direction.

2.3 The Principle of Spin Echo^{8,9}

The nmr spin-echo technique was introduced by Hahn¹⁰ in 1950, and Carr and Purcell¹¹ in 1954 to give more convenient ways of measuring T_1 and T_2 .

The rf pulse is applied perpendicular to the static field H_0 . H_1 is larger than the field inhomogeneity over the sample (ΔH). The pulse time t_w is short compared to the time $(\gamma \Delta H)^{-1}$ in which the nuclei precess out of phase due to the field inhomogeneity.

The 90° pulse at time $t = 0$ changes the orientation of the resultant magnetic moment vector of each volume element of the specimen, and a nuclear induction signal is obtained from each as it precesses freely, decaying with different precessional frequency the precessing magnetic moments and the nuclear induction signals rapidly out of phase in a time $(\gamma \Delta H)^{-1}$. The 180°

pulse at time t is applied, and the volume elements are rotated by 180° in the opposite direction, so that the faster volume elements are behind the slower volume elements. After another time t , they find themselves again in phase and thus produce a net magnetization. The construction magnetization induced an "echo" signal in the receiver coil. The phenomenon is called a "spin-echo".

