Relaxation and Relaxation Times

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Outline

- Basic principles about spin-lattice ($T_1$) and spin-spin ($T_2$) relaxations
  --- Relaxation dynamics, Bloch equations, etc.
- $T_1$ and $T_2$ relaxation mechanisms
- Experimental determination of $T_1$ and $T_2$
- Brief introduction to the rotating frame
  spin-lattice relaxation $T_{1\rho}$
Basic principles of magnetic relaxations

Review of First-order rate kinetics

\[ A \xrightarrow{k} B \]

\[ \frac{d[A]}{dt} = -k[A] \]

\[ \ln[A] = -kt + C \]

\[ [A] = [A]_0 e^{-kt} \]

Similarly

\[ n \xrightarrow{\frac{1}{T_1}} n_{eq} \]

\[ \frac{dn}{dt} = \frac{1}{T_1} (n_{eq} - n) \]

\[ n = n_{eq} (1 - e^{-t/T_1}) \]

k: rate constant of the first order process

n: macroscopic magnetization of spins

\( T_1 \) does not depend on the initial state or the extent of perturbation, it depends only on the relative change in the amplitude.
Basic principles of magnetic relaxations

$T_1$ is governed by fluctuating magnetic or electric fields at the Larmor frequency of the nucleus. These fluctuations can arise from other nuclear spins, unpaired electron spins, electric moments of the molecules as a whole, etc.

$T_2$ is governed by fluctuations at low frequencies in addition to those at the Larmor frequency, hence $T_2 \leq T_1$. 
Bloch equations

Block generated a series of expressions that account for observed dynamics of the macroscopic magnetization.

\[ \frac{d\vec{M}(t)}{dt} = \gamma \vec{M}(t) \times \vec{B}(t) \]

Setting \( \vec{B} = (0,0,B_0) \)

Leads to the Block equations without relaxation

\[ \frac{dM_x}{dt} = M_y \gamma B_0 = \omega_0 M_y \]
\[ \frac{dM_y}{dt} = -M_x \gamma B_0 = \omega_0 M_x \]
\[ \frac{dM_z}{dt} = 0 \]

Now, if we consider the rotating field \( B_1 \) which is in the xy plane, with frequency \( \omega \), the above equations can be modified as:

\[ \frac{dM_x}{dt} = \gamma [M_y B_0 - M_z (B_1)_y] \]
\[ \frac{dM_y}{dt} = -\gamma [M_x B_0 + M_z (B_1)_x] \]
\[ \frac{dM_z}{dt} = \gamma [M_x (B_1)_y - M_y (B_1)_x] \]

Where \((B_1)_x\) and \((B_1)_y\) are the components of \( B_1 \) along the x and y axes and are given by

\[ (B_1)_y = -B_1 \sin \omega t \]
\[ (B_1)_x = B_1 \cos \omega t \]
Bloch equations

Further more, if we consider the relaxation of the magnetization along x, y, and z directions,

\[
\begin{align*}
\frac{dM_x}{dt} &= -\frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= -\frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= -\frac{M_z - M_0}{T_1}
\end{align*}
\]

Upon adding these terms to the previous equations, we obtain the complete Bloch equations:

\[
\begin{align*}
\frac{dM_x}{dt} &= \gamma[M_y B_0 + M_z B_1 \sin \omega t] - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= -\gamma[M_x B_0 - M_z B_1 \cos \omega t] - \frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= -\gamma[M_x B_1 \sin \omega t + M_y B_1 \cos \omega t] - \frac{M_z - M_0}{T_1}
\end{align*}
\]

Note that Bloch equations imply first-order relaxation, which means that the recovery from perturbation is single-exponential.
**Bloch equations**

The above Bloch equations were based on the laboratory reference frame, however, if we change the reference frame into rotating frame, we can easily see the significance of these equations in experimental terms.

In the rotating frame, both $B_0$ and $B_1$ are fixed

\[ M_x = u \cos \omega t - v \sin \omega t \]
\[ M_y = -u \sin \omega t - v \cos \omega t \]

$u$ and $v$ are rotating frame components, which are along and perpendicular to $B_1$, respectively.

\[
\frac{dM_x}{dt} = \gamma [M_y B_0 + M_z B_1 \sin \omega t] - \frac{M_x}{T_2}
\]
\[
\frac{dM_y}{dt} = -\gamma [M_x B_0 - M_z B_1 \cos \omega t] - \frac{M_y}{T_2}
\]
\[
\frac{dM_z}{dt} = -\gamma [M_x B_1 \sin \omega t + M_y B_1 \cos \omega t] - \frac{M_z - M_0}{T_1}
\]

We can see from the last equation that changes in the energy of the spin system are associated only with $v$, the out-of-phase component.
Bloch equations

Notice that in the rotating frame, the Bloch equations are dealing with a steady state in which \( u, v \) and \( M_z \) are constant with time \( t \).

Solve Bloch equations at rotating frame, we obtain:

\[
\begin{align*}
    u &= M_0 \frac{\gamma B_1 T_2^2 (\omega_0 - \omega)}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 B_1^2 T_1 T_2} \\
    v &= -M_0 \frac{\gamma B_1 T_2}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 B_1^2 T_1 T_2} \\
    M_z &= M_0 \frac{1 + T_2^2 (\omega_0 - \omega)^2}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 B_1^2 T_1 T_2}
\end{align*}
\]

At the center of the peak, when \( \omega_0 - \omega = 0 \), the signal height is proportional to \( \gamma B_1 T_2 \).

And so the peak width at half-maximum can be easily calculated:

\[
\Delta \omega = \frac{2}{T_2}
\]

or

\[
\Delta v = \frac{1}{\pi T_2}
\]

When \( \gamma^2 B_1^2 T_1 T_2 \ll 1 \), the absorption or “v” mode is proportional to \( \gamma B_1 T_2 / [1 + T_2^2 (\omega_0 - \omega)^2] \).

This describes what is known as lorentzian line shape.
**T$_1$ and T$_2$ relaxation mechanisms**

The observed relaxation processes are sum of many different rates attributable to individual mechanisms:

$$\frac{1}{T_n} = \frac{1}{T_{n}^{DD}} + \frac{1}{T_{n}^{Q}} + \frac{1}{T_{n}^{SC}} + \frac{1}{T_{n}^{CSA}} + \frac{1}{T_{n}^{P}} + \frac{1}{T_{n}^{SR}}$$

$n = 1$ or $2$

DD = nuclear dipole-dipole relaxation

Q = electric quadrupolar relaxation

SC = scalar relaxation

CSA = Chemical shift anisotropy relaxation

P = paramagnetic relaxation

SR = spin-rotation relaxation

Usually, DD contribution decrease with increasing temperature. The SR contribution, however, has the opposite dependence. The CSA contribution increases with the square of the magnetic field. Q, SC, and P contribution present only under special circumstances.
**T₁ and T₂ relaxation mechanisms --- dipolar-dipolar relaxation**

For the like-nucleus, such as protons being relaxed by other protons:

\[
\frac{1}{T_{1}^{DDL}} = \frac{1}{5} \gamma^4 \hbar^2 I(I + 1) \sum r_i^{-6} \left( \frac{2}{1 + \omega^2 \tau_r^2} + \frac{8}{1 + 4\omega^2 \tau_r^2} \right) \tau_r \\
\frac{1}{T_{2}^{DDL}} = \frac{1}{5} \gamma^4 \hbar^2 I(I + 1) \sum r_i^{-6} \left( 3 + \frac{5}{1 + \omega^2 \tau_r^2} + \frac{2}{1 + 4\omega^2 \tau_r^2} \right) \tau_r
\]

\( \gamma \) = gyro magnetic ratio (rad/(sec. Gauss))
\( \hbar = \text{h}/2\pi \)
\( I = \) spin quantum number
\( r_i = \) internuclear distance (cm) to the \( i \)th proton
\( \omega = \) resonance or Larmor frequency (rad/s)
\( \tau_r = \) rotational correlation time, in seconds

In the extreme narrowing limit, \( \omega \tau_r << 1 \),

\[
\frac{1}{T_{1}^{DDL}} = \frac{1}{T_{2}^{DDL}} = 2\gamma^4 \hbar^2 I(I + 1) \sum r_i^{-6} \tau_r
\]

For the unlike-nucleus, such as \(^{13}\text{C} \) (S) being relaxed by neighboring protons (I):

\[
\frac{1}{T_{1}^{DDU}} = \frac{1}{15} \gamma_S^2 \gamma^2 \hbar^2 I_I(I_I + 1) \sum r_{IS}^{-6} \cdot Z \cdot \tau_r \\
\frac{1}{T_{2}^{DDU}} = \frac{1}{15} \gamma_S^2 \gamma^2 \hbar^2 I_I(I_I + 1) \sum r_{IS}^{-6} \cdot Y \cdot \tau_r
\]

\( Z = 2E + 6B + 12D \)
\( E = 1/[1 + (\omega_I - \omega_S)^2 \tau_r^2] \)
\( B = 1/(1 + \omega_S^2 \tau_r^2) \)
\( D = 1/[1 + (\omega_I + \omega_S)^2 \tau_r^2] \)
\( Y = 4 + Z/2 + 6C \)
\( C = 1/(1 + \omega_I^2 \tau_r^2) \)

In the extreme narrowing limit:

\[
\frac{1}{T_{1}^{DDU}} = \frac{1}{T_{2}^{DDU}} = \frac{4}{3} \gamma_S^2 \gamma^2 \hbar^2 I_I(I_I + 1) \sum r_{IS}^{-6} \tau_r
\]
T$_1$ and T$_2$ relaxation mechanisms --- electric quadrupole relaxation

Any nucleus having spin quantum number I greater than ½ is subject to electric quadrupole relaxation

\[
\frac{1}{T_1^Q} = \frac{3(2I+3)}{400 \cdot I^2(2I-1)} \left(\frac{e^2 Q q}{\hbar}\right)^2 (1 + \frac{\eta^2}{3}) Z_2 \cdot \tau_r
\]

\[
\frac{1}{T_2^Q} = \frac{3(2I+3)}{400 \cdot I^2(2I-1)} \left(\frac{e^2 Q q}{\hbar}\right)^2 (1 + \frac{\eta^2}{3}) Y_2 \cdot \tau_r
\]

\[Z_2 = 2B + 8D'
\]

\[Y_2 = 3 + 5B + 2D'
\]

\[B = \frac{1}{1 + \omega^2 \tau_r^2}
\]

\[D' = \frac{1}{1 + 4\omega^2 \tau_r^2}
\]

In the extreme narrowing limit, \( \omega \tau_r \ll 1 \),

\[
\frac{1}{T_1^Q} = \frac{1}{T_2^Q} = \frac{3(2I+3)}{40 \cdot I^2(2I-1)} \left(\frac{e^2 Q q}{\hbar}\right)^2 (1 + \frac{\eta^2}{3}) \tau_r
\]
**T₁ and T₂ relaxation mechanisms --- scalar relaxation**

When a nucleus is J-coupled to one or more nuclei, relaxation can occur if the coupling constant fluctuates ("first kind") or if the spin state of the coupled nucleus fluctuates ("second kind") at appropriate frequencies.

\[
\frac{1}{T_{1}^{sc}} = \frac{4}{3} \pi^2 I_i (I_i + 1) \sum_j j_i^2 \left( \frac{2\tau_2}{1 + (\omega_i - \omega_s)^2 \tau_2^2} \right)
\]

\[
\frac{1}{T_{2}^{sc}} = \frac{4}{3} \pi^2 I_i (I_i + 1) \sum_j j_i^2 \left( \tau_1 + \frac{\tau_2}{1 + (\omega_i - \omega_s)^2 \tau_2^2} \right)
\]

\[
\frac{1}{\tau_1} = \frac{1}{\tau_{exch}} + \frac{1}{T_{1I}}
\]

\[
\frac{1}{\tau_2} = \frac{1}{\tau_{exch}} + \frac{1}{T_{2I}}
\]

Scalar relaxation of first kind involves collapse of spin multiplets, the second kind usually (but not always involves spin coupling to a quadrupolar nucleus, the nucleus itself is relaxed efficiently through the quadrupolar mechanism.
T<sub>1</sub> and T<sub>2</sub> relaxation mechanisms --- chemical shift anisotropy

Anisotropy of the chemical shift can provide a fluctuating magnetic filed at a nucleus as the molecule tumbles, and it increases with the square of field strength.

\[
\frac{1}{T_{1}^{CSA}} = \frac{1}{45} \omega^2 (\Delta \sigma)^2 Z_3 \tau_r
\]

\[
\frac{1}{T_{2}^{CSA}} = \frac{1}{45} \omega^2 (\Delta \sigma)^2 Y_3 \tau_r
\]

\[
Z_3 = 6B
\]

\[
Y_3 = 4 + 3B
\]

\[
\Delta \sigma = \text{anisotropy in shielding}
\]

In the extreme narrowing limit,

\[
\frac{1}{T_{1}^{CSA}} = \frac{6}{45} \omega^2 (\Delta \sigma)^2 \tau_r
\]

\[
\frac{1}{T_{2}^{CSA}} = \frac{7}{45} \omega^2 (\Delta \sigma)^2 Y_3 \tau_r
\]

So that:

\[
\frac{1}{T_{1}^{CSA}} \times \frac{1}{T_{2}^{CSA}} = \frac{6}{7}
\]

\[
T_2^{CSA} = \frac{6}{7} T_1^{CSA}
\]
$T_1$ and $T_2$ relaxation mechanisms --- paramagnetic relaxation

The equations for paramagnetic relaxation are basically identical to the “unlike” unpair dipole-dipole relaxation (through space) and scalar relaxation (through bond) equations. The electron-nuclear coupling constant $A$ is analogous to spin-spin coupling constant $J$.

\[
\frac{1}{T_1^p} = \frac{1}{15} \gamma^2 \chi g_{avg}^2 \beta^2 S(S+1)r_{sx}^{-6} \left( \frac{6\tau_{c1}}{1 + \omega_X^2 \tau_{c1}^2} + \frac{14\tau_{c2}}{1 + \omega_S^2 \tau_{c2}^2} \right) + \frac{S(S+1) \cdot A_{erg}^2}{3\hbar^2} \left( \frac{2T_{2e}}{1 + \omega_S^2 T_{2e}^2} \right)
\]

$X$ = the nucleus being observed

$S$ = the electrons causing relaxation

$g_{avg}$ = average electronic “g” factor (commonly 2~2.8)

$\beta = $ Bohr magneton = 9.274 erg Gauss$^{-1}$

$S$ = electron spin quantum number

$r = $ distance (cm) from the unpaired electrons to the x nucleus

$\tau_{cn} = $ the correlation time for the dipolar interaction, which is made up of contributions from $\tau_r$ and the electron spin relaxation times, $T_{1e}$ and $T_{2e}$

\[
\frac{1}{T_2^p} = \frac{1}{15} \gamma^2 \chi g_{avg}^2 \beta^2 S(S+1) r_{sx}^{-6} \left( 4\tau_c + \frac{3\tau_c}{1 + \omega_X^2 \tau_c^2} + \frac{13\tau_c}{1 + \omega_S^2 \tau_c^2} \right) + \frac{S(S+1) \cdot A_{erg}^2}{3\hbar^2} \left( \tau_e + \frac{T_e}{1 + \omega_S^2 T_e^2} \right)
\]

In most cases: $T_{1e} = T_{2e} = T_e$

so

$\tau_c = \tau_{c1} = \tau_{c2}$

$n = 10r2$
**$T_1$ and $T_2$ relaxation mechanisms --- spin-rotation relaxation**

As a molecule or a part of molecule rotates, the motion of electrons generates a current and a molecular magnetic moment. Molecular collisions cause this magnetic moment to fluctuate, proving a mechanism for nuclear relaxation. This mechanism is important for gases. The efficiency increase as increasing temperature.

\[
\frac{1}{T_{1SR}^1} = \frac{8\pi^2\Theta k T}{9\hbar^2} \left( \frac{(2C_\perp + C_\parallel)^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) + \frac{(2C_\perp + C_\parallel)^2 \tau_{jr}}{1 + \omega^2 \tau_{jr}^2} \\
\frac{1}{T_{2SR}^1} = \frac{4\pi^2\Theta k T}{9\hbar^2} \left( (2C_\perp + C_\parallel)^2 \tau_j + (2C_\perp + C_\parallel)^2 \tau_{jr} \right) \frac{1 + \omega^2 \tau_j^2}{1 + \omega^2 \tau_{jr}^2}
\]

$X = \text{moment of inertia of the molecule or group. } g\text{Å}^2$/mol

$k = \text{Boltzmann’s constant } = 1.38044 \times 10^{-16} \text{ erg/K}$

$T = \text{absolute temperature (K)}$

$C_\perp \text{ and } C_\parallel = \text{spin-rotation tensors describing the coupling of the nuclear and molecular angular momenta along perpendicular and parallel axes.}$

$\tau_j = \text{spin-rotation angular momentum correlation time in seconds, the average time a molecule spends in any given state of angular momentum}$

$\tau_r = \text{molecular reorientation correlation time in seconds} \quad \frac{1}{T_{1SR}^1} = \frac{1}{T_{2SR}^1} = \frac{8\pi^2\Theta k T}{3\hbar^2} (2C_\perp + C_\parallel)^2 \tau_j$

In the extreme narrowing limit,

$\tau_j \ll \tau_r,$

\[
\frac{1}{\tau_{jr}} = \frac{1}{\tau_j} + \frac{1}{\tau_r}
\]
Methods to measure relaxation times --- $T_1$ measurement

(a) non-selective inversion recovery;
(b) selective inversion recovery;
(c) non-selective saturation recovery;
(d) selective saturation recovery
(e) single-scan saturation recovery

Inversion recovery methods:

$$M_x(\tau) = \{M_z(0)\exp(-\tau/T_1) + M_0[1-\exp(-\tau/T_1)]\} \sin \beta$$

In the case of a perfect $\pi$ pulse, the initial magnetization $M_z(0) = -M_0$, it reduces to

$$M_x(\tau) = M_0[1-2\exp(-\tau/T_1)]\sin \beta$$

If $\beta = \pi/2$, the equation reduces further to

$$M_x(\tau) = M_0[1-2\exp(-\tau/T_1)]$$

Saturation recovery methods:

$$M_x(\tau) = M_0[1-\exp(-\tau/T_1)]\sin \beta$$

More efficient but less accurate
Methods to measure relaxation times --- $T_1$ measurement

By using monitoring pulse with small rotation angles $\beta$, it is possible to measure the entire $T_1$ recovery in a single experiment. (This can be achieve with the “single scan method” shown as the pulse sequence (e) in the above slide)

\[
M_z(n\tau) - M_\infty = (M_z(0) - M_0) \exp(-n\tau/T^*_1)
\]

$n\tau$ is the interval between the p-pulse and the $(n+1)$th monitoring pulse, and $T^*_1$ is an apparent relaxation time

\[
\frac{1}{T^*_1} = \frac{1}{T_1} - \frac{\ln \cos \beta}{\tau}
\]

$M_\infty$ is the steady state magnetization reached after a large number of $\beta$-pulse

\[
\frac{M_\infty}{M_0} = \frac{1 - \exp(-\tau/T_1)}{1 - \exp(-\tau/T_1) \cos \beta}
\]

If $\beta$ approach $\pi/2$, a steady state is reached too rapidly, while small angles give poor sensitivity. A reasonable compromise is $\beta=30^\circ$
Methods to measure relaxation times --- $T_2$ measurement

In favorable cases, the transverse relaxation time $T_2$ can be obtained simply by measuring the full line-width at half height

$$T_2^* = \frac{1}{\pi \Delta \nu (Hz)} = \frac{2}{\Delta \omega (rad)}$$

However, in the real case, the apparent decay rate $1/T_2^*$ is the sum of the nature relaxation rate $1/T_2$ and the inhomogeneous broadening contribution $1/T_2^+$
Pulse sequence (a) with single refocusing $\pi$ pulse is often referred to as “Carr-Purcell method A”. However, the amplitude of the echoes can be strongly **attenuated by translational diffusion through field gradients $g$**. This effect can be largely removed with the “Carr-Purcell method B” shown in (d), which employs $n$ refocusing pulses.

(a) Spin-echo sequence with a single refocusing pulse.
(b) Evolution of two magnetization vectors (isochromats), labelled F and S for “fast” and “slow”
(c) The phases of the isochromats as a function of time
(d) Spin-echo sequence with multiple refocusing
(e) Phases of two isochromats in the course of multiple refocusing.
Example-T1 measurement

Inversion recovery pulse sequence for measuring $T_1$

The inversion recovery ($T_1$) pulse sequence yields a signal of intensity

$$I_0 \left[ 1 - 2 \exp \left( \frac{\tau}{T_1} \right) \right]$$
Exponential decay curve

The CPMG (Carr-Purcell-Meiboom-Gill) ($T_2$) experiment yields a signal of intensity

$$I_0 \exp \left( -\frac{\tau}{T_2} \right)$$

$\tau$ is the total evolution time ($4n\Delta$).
Rotating frame spin-lattice relaxation $T_{1\rho}$

The rotating frame spin-lattice relaxation ($T_{1\rho}$) can be used to investigate chemical exchange with rates in the intermediate microsecond time scale.

$T_{1\rho}$ can be measured by a spin-locking experiment

The observed rotating-frame relaxation rate is also the sum of contributions from various relaxation mechanisms.

$T_{1\rho}$ can be obtained by fitting resonance intensities to the equation:

$$M_y(\tau) = M_0 \exp(-\tau/T_{1\rho}) + M'$$

$M'$ is a residual signal present at the long spin-locking time
References


Thank you for your attention!