Measurement of spin–lattice relaxation times of $^{13}$C in organic solids

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Abstract

A transient nuclear Overhauser effect (NOE) makes measurements of the $^{13}$C spin–lattice relaxation times in organic solids complicated. Extended Solomon equations are applied in order to describe $^{13}$C spin–lattice relaxation with $^1$H r.f. field irradiation. Spin–lattice relaxation under r.f. irradiation is shown to be generally a triple-exponential process, but it can be reduced to be single-exponential under stronger r.f. field irradiation as well as in the absence of $^1$H initial magnetizations. Based on numerical calculations, the difference between spin–lattice relaxation curves obeying $T_{1c}^{C} < T_{1h}^{H}$ and those obeying $T_{1c}^{C} > T_{1h}^{H}$ is clearly indicated. The methyl group resonances in solid-state t-valine are examined, and the experimental results agree well with the theoretical results. © 1997 Elsevier Science B.V.

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1. Introduction

The $^{13}$C spin–lattice relaxation times of different groups in organic solids are generally very different from one another because these spins are dilute, while spin–lattice relaxation times for the $^1$H spins often do not show significant differences due to efficient spin diffusion. In most cases, spin–lattice relaxation times of $^{13}$C in the solid state are longer than those of $^1$H, i.e. $T_{1c}^{C} > T_{1h}^{H}$. For groups displaying rapid motion (e.g. the methyl CH$_3$ group rotating fast about its C$_3$ axis) in organic solids as well as mobile regions in solid polymers, however, it is possible that the spin–lattice relaxation times of $^{13}$C are shorter than or almost equal to those of $^1$H, i.e. $T_{1c}^{C} \leq T_{1h}^{H}$ [1–5]. Spin–lattice relaxation in solids is also known to be anisotropic since it is caused by anisotropic motion [6–8].

The spin–lattice relaxation times of $^{13}$C in various magnetically inequivalent sites in organic solids may be measured by means of their CPMAS high-resolution spectra. The difficulty is that $T_{1c}^{C}$ in organic solids is usually very long, e.g. a few seconds or even longer; consequently, it is not practical to incorporate a high-power decoupling field (50 kHz or stronger) during the recovery period of $^{13}$C magnetization. Without high-power $^1$H decoupling and in the case of $T_{1c}^{C} \leq T_{1h}^{H}$, as shown previously [1–5], the contribution of a transient nuclear Overhauser effect (NOE) is highly evident and the courses of the $^{13}$C

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spin–lattice relaxation are very unusual, i.e. multiexponential. As a result, traditional determinations of $T_1^C$ may lead to unreliable values due to the carbon atoms in inequivalent sites having varying motions.

A feasible approach to acquiring all the spin–lattice relaxation times is to make proton resonances saturate during the $T_1^C$ measurements by using r.f. irradiation that is very weak in comparison with the decoupling r.f. field. Experimentally, a weak r.f. field can be conveniently applied by using a train of 90° pulses with equal intervals. This approach has been discussed by some authors [1–5]. McDowell and co-workers [1] first detailed the fact that $^{13}$C magnetization decays exponentially with a time constant $T_1^C$ by completely saturating the protons. They employed preferably a phase alternating pulse sequence, subtracting the $^{13}$C magnetizations from each other. In this way, they also showed that in a solid-state experiment the observed decay of the $^{13}$C magnetization may be approximated as a single-exponential process even when the protons are not irradiated. Instead of using the inversion–recovery pulse sequence, Findlay and Harris [2,3] proposed a pulse sequence suitable for the case where the spectra are complex, with overlapping peaks from carbon atoms with short and long longitudinal relaxation times.

In this paper, the steady-state properties of a spin system irradiated by an r.f. field are analyzed. It is shown that it is necessary to distinguish the steady state from the saturated state and the equilibrium state of the spin system. By using extended Solomon equations [9] instead of Solomon equations [10], we endeavour to give a consistent description of the measurement of spin–lattice relaxation times in organic solids, with emphasis placed on a theoretical analysis and an experimental demonstration of the effects of a transient NOE and weak irradiation on the $T_1^C$ measurements.

2. Theory

2.1. Spin–lattice relaxation processes of $^{13}$C described by the Solomon equations

It is known [1–5] that spin–lattice relaxation processes of $^{13}$C in organic solids can be described by the Solomon equations [10]. Let us suppose that $^{13}$C is I and $^1$H is S. For this heteronuclear two-spin system, the Solomon equations can be written

$$\frac{d\langle I_z \rangle(t)}{dt} = -\rho_1 [\langle I_z \rangle(t) - \langle I_z \rangle^{eq}]$$

$$- \sigma_{IS} [\langle S_z \rangle(t) - \langle S_z \rangle^{eq}]$$

$$\frac{d\langle S_z \rangle(t)}{dt} = -\rho_\sigma [\langle I_z \rangle(t) - \langle I_z \rangle^{eq}]$$

$$- \rho_s [\langle S_z \rangle(t) - \langle S_z \rangle^{eq}]$$

where $\langle I_z \rangle(t)$ and $\langle S_z \rangle(t)$ are the expectation values of the spin operators $I_z$ and $S_z$ at an arbitrary time $t$, $\langle I_z \rangle^{eq}$ and $\langle S_z \rangle^{eq}$ are the expectation values at equilibrium. $\rho_1$ and $\rho_s$ are the longitudinal relaxation rates of the two spins I and S, respectively, and $\rho_{IS}$ and $\sigma_{IS}$ are the cross-relaxation rates between two coupled spins I and S.

Note that for a heteronuclear spin system, the cross-relaxation rate $\sigma_{IS}$ is not equal to $\sigma_{SI}$, and in the case concerned, the cross-relaxation rate $\sigma_{SI}$ from dilute spins I ($^{13}$C) to abundant spins S ($^1$H) is too small to be noticed. If $\sigma_{IS}$ is negligible, analytical solutions of the Solomon equations with the initial magnetizations $\langle I_z \rangle(0)$ and $\langle S_z \rangle(0)$ can be obtained as follows

$$\langle I_z \rangle(t) = \langle I_z \rangle(0) - \langle I_z \rangle^{eq}$$

$$+ \frac{\sigma_{IS}}{\rho_1 - \rho_s} [\langle S_z \rangle(0) - \langle S_z \rangle^{eq}] e^{-\rho_1 t}$$

$$- \frac{\sigma_{IS}}{\rho_1 - \rho_s} [\langle S_z \rangle(0) - \langle S_z \rangle^{eq}] e^{-\rho_s t} + \langle I_z \rangle^{eq}$$

$$\langle S_z \rangle(t) = \langle S_z \rangle(0) - \langle S_z \rangle^{eq} e^{-\rho_s t} + \langle S_z \rangle^{eq}$$

(3)

We can see from Eq. (3) that the evolution of the $^{13}$C magnetization is a double-exponential process. Furthermore, Eq. (3) can be rewritten in the form

$$\langle I_z \rangle(t) = \langle I_z \rangle(0) - \langle I_z \rangle^{eq} e^{-\rho_1 t}$$

$$+ \frac{\sigma_{IS}}{\rho_1 - \rho_s} [\langle S_z \rangle^{eq} - \langle S_z \rangle(0)]$$

$$\times (e^{-\rho_s t} - e^{-\rho_1 t}) + \langle I_z \rangle^{eq}$$

(5)

where the second term results from cross-relaxation.
If there was no cross-relaxation, Eq. (5) would be reduced to
\[
\langle I_z \rangle(t) = \langle I_z \rangle(0) + \langle I_z \rangle^{eq} e^{-\rho_1 t} + \langle I_z \rangle^{eq}
\]
which is the well-known expression for an isolated spin system. It can be seen clearly that the cross-relaxation term is dependent on the proton initial magnetization, but its magnitude is always positive; the effect of cross-relaxation on the evolution of the \(^13\text{C}\) magnetization becomes very obvious and leads to "bumps" on the recovery curves (see below) when the rare spins relax faster than the abundant spins. Therefore, spin–lattice relaxation processes of \(^13\text{C}\) in organic solids will obviously contain a contribution from a transient NOE under \(\rho_1 \geq \rho_5\).

2.2. Paradox in the usual description of steady-state NOE experiments

Steady-state NOE experiments [11] are usually described by the Solomon equations also. Assuming that \(\langle I_z \rangle^{SS}\) and \(\langle S_z \rangle^{SS}\) are the expectation values of the spin operators \(I_z\) and \(S_z\), respectively, at the steady state. On completely saturating the spin \(S\) by applying a strong r.f. field, we have

\[
\langle S_z \rangle^{SS} = 0
\]

Inserting Eq. (7) into Eq. (1) leads to

\[
\frac{\langle I_z \rangle^{SS} - \langle I_z \rangle^{eq}}{\langle I_z \rangle^{eq}} = \frac{\sigma_{IS} \langle S_z \rangle^{eq}}{\rho_1}
\]

The steady-state NOE enhancement factor can thus be obtained

\[
\eta = \frac{\langle I_z \rangle^{SS} - \langle I_z \rangle^{eq}}{\langle I_z \rangle^{eq}} = \frac{\sigma_{IS} \langle S_z \rangle^{eq}}{\rho_1} \frac{\gamma_S}{\rho_1}
\]

However, Boulat and Bodenhausen [9] have recently pointed out that there occurs a paradox in such a widely accepted theoretical description by the Solomon equations, i.e. the Solomon equations do not allow one to obtain a consistent picture of the expectation values of the various magnetization components.

2.3. Equilibrium state, saturated state and steady state

In fact, it may be necessary to distinguish between the steady state and the saturated state of a spin system irradiated by an r.f. field. First, consider the case of a single spin system described by the Bloch equations

\[
\frac{d\langle S_z \rangle}{dt} = -\rho_5 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq}
\]

\[
\frac{d\langle S_z \rangle}{dt} = \omega_1 \langle S_z \rangle^{eq} - \rho_5 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq}
\]

\[
\frac{d\langle S_z \rangle}{dt} = \Delta \omega \langle S_z \rangle^{eq} - \rho_5 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq} - \omega_1 \langle S_z \rangle^{eq}
\]

where \(\langle S_z \rangle^{eq}\) and \(\langle S_z \rangle^{SS}\) denote the expectation values of the spin operators \(S_z\) and \(S_z\), respectively, \(\rho_5\) is the transverse relaxation rate of a spin \(S\), \(\Delta \omega = \omega_0 - \omega\) off-resonance, \(\omega_0 = -\gamma B_1\) is the r.f. field strength, and the r.f. field is applied along the \(y\) axis. It is not difficult to obtain the steady-state solutions as follows

\[
\langle S_z \rangle^{SS} = \frac{\rho_5 \rho_5 \omega_1}{\rho_5(\Delta \omega^2 + \rho_5^2)} + \rho_5 \omega_1 \langle S_z \rangle^{eq}
\]

\[
\langle S_z \rangle^{SS} = \frac{\rho_5 \Delta \omega \omega_1}{\rho_5(\Delta \omega^2 + \rho_5^2)} + \rho_5 \omega_1 \langle S_z \rangle^{eq}
\]

\[
\langle S_z \rangle^{SS} = \frac{\rho_5(\Delta \omega^2 + \rho_5^2)}{\rho_5(\Delta \omega^2 + \rho_5^2)} + \rho_5 \omega_1 \langle S_z \rangle^{eq}
\]

One can see that as the r.f. field increases, all the steady-state expectation values gradually become small, but they approach zero at different speeds, i.e.

\[
\lim_{\omega_1 \to \infty} \langle S_z \rangle^{SS} = 0 \quad (i = x, y, z)
\]

\[
\lim_{\omega_1 \to \infty} \omega_1 \langle S_z \rangle^{SS} \neq 0 \quad (i = x, y) \quad \lim_{\omega_1 \to \infty} \omega_1 \langle S_z \rangle^{SS} = 0
\]

Consequently, a single spin system under r.f. field irradiation will approach a steady state which is characterized by the three steady-state expectation values \(\langle S_z \rangle^{SS}\) \((i = x, y, z)\). Not only is this steady state different from the equilibrium state without r.f. field irradiation because of \(\langle S_z \rangle^{SS} \neq 0\) and \(\langle S_z \rangle^{SS} \neq \langle S_z \rangle^{eq}\), but it is also generally not the saturated state due to \(\langle S_z \rangle^{SS} \neq 0\) unless the r.f. field is sufficiently strong.
Now, we turn to the Solomon equations for a coupled spin system. If \( \delta^2 = \rho_1 \rho_S - \sigma_{IS} \sigma_{SI} \neq 0 \), we can readily write their steady-state solutions

\[
\langle I_z \rangle^{SS} = \langle I_z \rangle^{eq} \tag{18}
\]

\[
\langle S_z \rangle^{SS} = \langle S_z \rangle^{eq} \tag{19}
\]

Therefore, the steady state described by the Solomon equations is not the saturated state because of \( \langle I_z \rangle^{SS} \neq 0 \) and \( \langle S_z \rangle^{SS} \neq 0 \), but the equilibrium state in the absence of r.f. field irradiation. Strictly speaking, the Solomon equations are unable to describe the case where r.f. irradiation is present, such as steady-state NOE experiments [11] and longitudinal relaxation processes of coupled spin systems manipulated by an r.f. field [1–5].

2.4. The extended Solomon equations and their steady-state solutions

In order to overcome this contradiction, Boulat and Bodenhausen [9] have shown that it is necessary to supplement the two Solomon equations (i.e. Eq. (1) and (2)) with a third differential equation which describes the time dependence of the transverse component of the S spin magnetization. Without loss of generality, we assume that the r.f. field lies along the y axis. Combining Eq. (1) and (2) with Eq. (10)–(12), we have

\[
\frac{d\langle I_z \rangle(t)}{dt} = -\rho_1 [\langle I_z \rangle(t) - \langle I_z \rangle^{eq}] - \sigma_{IS} [\langle S_z \rangle(t) - \langle S_z \rangle^{eq}] \tag{20}
\]

\[
\frac{d\langle S_z \rangle(t)}{dt} = -\sigma_S [\langle I_z \rangle(t) - \langle I_z \rangle^{eq}] - \rho_S [\langle S_z \rangle(t) - \langle S_z \rangle^{eq}] - \omega_1 \langle S_z \rangle(t) \tag{21}
\]

\[
\frac{d\langle S_x \rangle(t)}{dt} = \omega_1 \langle S_z \rangle(t) - \rho_S \langle S_y \rangle(t) - \Delta \omega \langle S_z \rangle(t) \tag{22}
\]

\[
\frac{d\langle S_y \rangle(t)}{dt} = \Delta \omega \langle S_z \rangle(t) - \rho_S \langle S_x \rangle(t) \tag{23}
\]

It is due to the presence of off-resonance that we have supplemented two differential equations for describing the transverse components of the S spin magnetization. Apparently, if \( \sigma_{SI} = \sigma_{IS} \) and \( \Delta \omega = 0 \), Eq. (20)–(22) are reduced to those proposed by Boulat and Bodenhausen [9], while Eq. (23) is isolated from the former equations.

It should be pointed out that extension of the Solomon equations has also been noted recently by many authors [12–14]: in so-called Z spectroscopy [12,13], especially, four or even six coupled equations are needed where the off-resonance effect is always considered and two coupled spins may be irradiated simultaneously.

The extended Solomon equations can provide a consistent and more general description of the experiments with r.f. field irradiation, and their steady-state solutions can be written as

\[
\langle I_z \rangle^{SS} - \langle I_z \rangle^{eq} = \frac{\sigma_{IS} \rho_S^2 \omega_1^2}{\delta^2 (\Delta \omega^2 + \rho_S^2)} + \rho_1 \rho_S^2 \omega_1^2 \langle S_z \rangle^{eq} \tag{24}
\]

\[
\langle S_z \rangle^{SS} = \frac{\delta^2 (\Delta \omega^2 + \rho_S^2)}{\delta^2 (\Delta \omega^2 + \rho_S^2)} + \rho_1 \rho_S^2 \omega_1^2 \langle S_z \rangle^{eq} \tag{25}
\]

\[
\langle S_x \rangle^{SS} = \frac{\rho_1 \rho_S \omega_1}{\delta^2 (\Delta \omega^2 + \rho_S^2)} + \rho_1 \rho_S \omega_1 \langle S_z \rangle^{eq} \tag{26}
\]

\[
\langle S_y \rangle^{SS} = \frac{\delta^2 \Delta \omega \omega_1}{\delta^2 (\Delta \omega^2 + \rho_S^2)} + \rho_1 \rho_S \omega_1 \langle S_z \rangle^{eq} \tag{27}
\]

where Eq. (24) is the expectation value of the spin I at equilibrium, and Eq. (25)–(27) are those of the spin S. When \( \omega_1 \to \infty \), Eq. (24) is reduced to Eq. (8), while Eq. (25)–(27) obey Eq. (16) and (17).

The steady-state NOE enhancement factor can thus be expressed by

\[
\eta' = \frac{\langle I_z \rangle^{SS} - \langle I_z \rangle^{eq}}{\langle I_z \rangle^{eq}} = \frac{\gamma_S \sigma_{IS} \rho_S^2 \omega_1^2}{\gamma_1 \delta^2 (\Delta \omega^2 + \rho_S^2)} + \rho_1 \rho_S \omega_1 \quad \tag{28}
\]
If $\Delta \omega = 0$, 

$$
\eta' = \frac{\gamma_S \sigma_{IS} \omega^2}{\gamma_1 \delta^2 \rho_S^2 + \rho_1 \omega^2} = \frac{\rho_1 \omega^2}{\delta^2 \rho_S^2 + \rho_1 \omega^2} 
$$

(29)

According to Eq. (28) and (29), not only does the steady-state NOE enhancement factor $\eta'$ depend on the relaxation parameters $\rho_1$ and $\sigma_{IS}$ of the observed spin I, but it also depends on the relaxation parameters $\rho_S$, $\sigma_{SI}$, and $\rho_S^2$ of the irradiated spin S, the off-resonance $\Delta \omega$, and the r.f. field strength $\omega_1$. Clearly, we have 

$$
\lim_{\omega_1 \to 2} \eta' = \eta 
$$

(30)

Therefore, the normal results (Eq. (7)–(9)) are only for a limiting situation. In our previous paper [5], we have studied both theoretically and experimentally the dependence of the steady-state NOE enhancement factor on the r.f. field strength.

2.5. Analytical solutions of the extended Solomon equations

Suppose that the applied r.f. field is on resonance, i.e. $\Delta \omega = 0$. The extended Solomon equations can thus be written

$$
d\langle I_x \rangle(t) \over dt = -\rho_1 \langle I_x \rangle(t) - \langle I_x \rangle^{eq} 
$$

$$
- \sigma_{IS} \langle S_y \rangle(t) - \langle S_y \rangle^{eq} 
$$

(31)

$$
d\langle S_y \rangle(t) \over dt = -\sigma_{SI} \langle I_x \rangle(t) - \langle I_x \rangle^{eq} 
$$

$$
- \rho_S \langle S_y \rangle(t) - \langle S_y \rangle^{eq} - \omega_1 \langle S_y \rangle(t) 
$$

(32)

$$
d\langle S_z \rangle(t) \over dt = \omega_1 \langle S_z \rangle(t) - \rho_S^2 \langle S_z \rangle(t) 
$$

(33)

The analytical solutions of these extended Solomon equations are generally cumbersome. If these differential equations have three unequal real eigenvalues, the corresponding analytical solutions are triple-exponential. For the situation concerned, as mentioned above, the cross-relaxation rate $\sigma_{SI}$ is so small as to be negligible. Using this approximation, analytical solutions of the extended Solomon equations with initial magnetizations $\langle I_x \rangle(0), \langle S_y \rangle(0)$, and $\langle S_z \rangle(0)$ can easily be obtained, and the results are

$$
\langle I_x \rangle(t) = 1 - \frac{A \sigma_{IS}}{\alpha + \rho_1} \frac{\langle I_x \rangle^{eq}}{\beta + \rho_1} - \langle I_x \rangle^{SS} 
$$

$$
= \frac{A \sigma_{IS}}{\alpha + \rho_1} e^{\alpha t} - \frac{B \sigma_{IS}}{\beta + \rho_1} e^{\beta t} + \langle I_x \rangle^{SS} 
$$

(34)

$$
\langle S_y \rangle(t) = \langle S_y \rangle^{eq} + \langle S_y \rangle^{SS} 
$$

(35)

$$
\langle S_z \rangle(t) = \frac{A \omega_1}{\alpha + \rho_S} e^{\alpha t} + \frac{B \omega_1}{\beta + \rho_S} e^{\beta t} + \langle S_z \rangle^{SS} 
$$

(36)

where

$$
\alpha, \beta = 1/2 \left\{ - (\rho_S + \rho_S^2) 
$$

$$
\pm \left\{ \left( \rho_S - \rho_S^2 \right)^2 - 4 \omega_1^2 \right\}^{1/2} \right\} 
$$

(37)

$$
A = \frac{1}{\alpha - \beta} \left\{ \langle S_y \rangle(0) - \langle S_y \rangle^{eq} \right\} 
$$

$$
- \omega_1 \left\{ \langle S_y \rangle(0) - \langle S_y \rangle^{SS} \right\} 
$$

(38)

$$
B = \frac{1}{\alpha - \beta} \left\{ - (\beta + \rho_S) \langle S_y \rangle(0) - \langle S_y \rangle^{SS} \right\} 
$$

$$
+ \omega_1 \left\{ \langle S_y \rangle(0) - \langle S_y \rangle^{SS} \right\} 
$$

(39)

$$
A + B = \langle S_y \rangle(0) - \langle S_y \rangle^{SS} 
$$

(40)

$$
\langle I_x \rangle^{SS} = (1 + \eta') \langle I_x \rangle^{eq} 
$$

(41)

$$
\langle S_y \rangle^{SS} = \frac{\rho_S \omega_1}{\omega_1^2 + \rho_S \rho_S^2} \langle S_y \rangle^{eq} 
$$

(42)

$$
\langle S_z \rangle^{SS} = \frac{\rho_S \omega_1}{\omega_1^2 + \rho_S \rho_S^2} \langle S_z \rangle^{eq} 
$$

(43)

$$
\eta' = \eta \frac{\omega_1}{\rho_S \rho_S^2 + \omega_1} 
$$

(44)

Since $\rho_S^2 \gg \rho_S$ (i.e. $T_2^I \ll T_1^I$) in the solid state, and $\rho_S^2 \gg \omega_1$ in our experiments (see below), $\alpha$ and $\beta$ are two unequal negative numbers. From Eq. (34), we can see readily that $^{13}C$ spin–lattice relaxation is a triple-exponential course of three relaxation rates $\rho_1, -\alpha$ and $-\beta$. 

It is shown by Eq. (34)–(36) that the spin system will approach the steady state in a sufficiently long irradiation time. Eq. (41)–(43) are their corresponding steady-state solutions. Obviously, the steady-state expectation values \( \langle S_x \rangle^{SS} \) and \( \langle S_z \rangle^{SS} \) may not vanish. Only when \( \omega_1 \) is strong enough (\( \omega_1 \to \infty \) from the viewpoint of mathematics), as was already pointed out by Boulat and Bodenhausen [9], \( \langle S_x \rangle^{SS} \to 0 \) and \( \langle S_z \rangle^{SS} \to 0 \). Therefore, the steady state is not equivalent to the saturated state, and the saturated state represents only an extreme situation.

On the assumption of the initial magnetizations \( \langle S_i \rangle(0) = \langle S_i \rangle(0) = 0 \), and the steady-state magnetizations \( \langle S_i \rangle^{SS} = \langle S_i \rangle^{SS} = 0 \), owing to a sufficiently strong r.f. irradiation, we have \( A = B = 0 \). Hence, Eq. (34) can be reduced to the usual result [1–5]

\[
\langle I_z \rangle(r) = \left[ \langle I_z \rangle(0) - \langle I_z \rangle^{SS} \right] e^{-\rho_1 r} + \langle I_z \rangle^{SS}
\]  

(45)

showing that the \(^{13}\text{C} \) spin–lattice relaxation is a single-exponential process with longitudinal relaxation rates \( \rho_1 \). Therefore, although the transient NOE complicates the measurement of \( T_1^C \), one can eliminate its effect on the \( T_1^C \) values as long as the proton resonances are saturated during the measurements by a sufficiently strong r.f. irradiation.

2.6. Numerical calculations

In order to make the theoretical description directly comparable with the experimental results, we solved the extended Solomon equations numerically. Although cross-relaxation from the carbon atoms to the protons is very weak because of the low natural abundance of \(^{13}\text{C} \), and ignoring \( \sigma_{S1} \) gives a very good approximation, our numerical calculations still take into account the effects of \( \sigma_{S1} \). Therefore, the theoretical results obtained should be more reliable and exact. Theoretical relaxation curves for the spins I for a few typical longitudinal relaxation rates \( \rho_1 \) and \( \rho_S \) are given in Fig. 1, where curves (a) correspond to the case without r.f. irradiation and curves (b) and (c) correspond to the cases with two r.f. fields of strengths 10 Hz and 50 Hz, respectively. In the numerical computations, we assumed a transverse self-relaxation rate \( \rho_i = 100 \text{ s}^{-1} \), cross-relaxation rates \( \sigma_{IS} = 0.5 \rho_i \) and \( \sigma_{SI} = 0.02 \text{ s}^{-1} \), initial magnetizations \( \langle I_z \rangle(0) = -3 \langle I_z \rangle^{eq} \) and \( \langle S_i \rangle(0) = \langle S_i \rangle^{eq} / \langle I_z \rangle^{eq} = 4 \). The numerical results obtained by using these parameters would agree with our experimental results given below.

It is reasonable to consider the six groups of theoretical recovery curves in Fig. 1 as being those of six equivalent spins I (\(^{13}\text{C} \)). According to the curves, we can see clearly the effects of the transient NOE and the weak r.f. field irradiation on the spin–lattice relaxation processes. First of all, for the case without r.f. field irradiation (curves (a)), the curves obeying \( \rho_1 > \rho_S \) (left) are clearly different from those obeying \( \rho_1 < \rho_S \) (right). There is a very evident transient NOE in the former curves, but not in the latter curves. Of course, the situation in the absence of r.f. field irradiation can be described exactly by the Solomon equations [10]. We then observe the curves in the case with r.f. field irradiation (curves (b) and (c)). It has been shown theoretically and experimentally [5] that steady-state NOE
3. Experimental results and discussion

All the experiments were carried out on a Bruker MSL-400 spectrometer operating at 400.13 MHz for protons and 100.63 MHz for $^{13}$C at room temperature. The spinning rate was 3720 Hz. The sample was l-valine in the solid state. Its four resonant lines corresponding to two methyl carbon atoms were considered in this work since their spin–lattice relaxation times were shorter. The chemical shifts of these resonant lines were 22.1, 21.5, 19.5, and 19.2 ppm [15]. The pulse sequences used are shown in Fig. 2, and were composed of two parts, i.e. those of the CPMAS technique and those of the inversion–recovery (IR) method. A train of $90^\circ$ pulses with equal intervals was applied to the proton channel in the pulse sequence (b). If the interval of these $90^\circ$ pulses is $\tau$, the corresponding average r.f. field strength is $\bar{\omega}_f = 1/4\tau$ (Hz). In our experiments, we chose $\tau$ = 50 ms, 25 ms, 10 ms, and 5 ms, corresponding to average r.f. field strengths of 5 Hz, 10 Hz, 25 Hz, and 50 Hz, respectively, which are all much weaker than the applied decoupling field strengths (50 kHz).

The experimental curves are shown in Fig. 3, where the curves (●) correspond to the case without r.f. field irradiation, and the curves (○) and (×) correspond to the cases with average r.f. field strengths of 10 Hz and 50 Hz, respectively. Because the four relaxation curves corresponding to average r.f. field strengths of 5, 10, 25, and 50 Hz for each resonant line are almost overlapping, only two of them are plotted, confirming experimentally the fact that the differences among the spin–lattice relaxation processes with sufficiently strong r.f. irradiation is very small.

Glancing at Fig. 3, we immediately distinguish the experimental curves corresponding to a chemical shift of 19.2 ppm from those corresponding to chemical shifts of 22.1, 21.5, and 19.5 ppm. The former agrees with the case shown on the right-hand side of Fig. 1, whose spin–lattice relaxation rates obey $\rho_1 < \rho_5$ or whose spin–lattice relaxation times obey $T_1^C$.
Table 1
The spin–lattice relaxation times $T_1^C$ (s) of the four methyl group resonances of L-valine in the solid state

<table>
<thead>
<tr>
<th>$\bar{\omega}_1$ (Hz)</th>
<th>22.1</th>
<th>21.5</th>
<th>19.5</th>
<th>19.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.39</td>
<td>0.30</td>
<td>0.24</td>
<td>2.56</td>
</tr>
<tr>
<td>10</td>
<td>0.39</td>
<td>0.30</td>
<td>0.18</td>
<td>2.49</td>
</tr>
<tr>
<td>25</td>
<td>0.39</td>
<td>0.29</td>
<td>0.15</td>
<td>2.40</td>
</tr>
<tr>
<td>50</td>
<td>0.38</td>
<td>0.29</td>
<td>0.15</td>
<td>2.45</td>
</tr>
</tbody>
</table>

$> T_1^{1H}$. This is the situation normally observed. The latter belongs to the case shown on the left-hand side of Fig. 1, whose spin–lattice relaxation rates satisfy $p_1 > p_2$ or whose spin–lattice relaxation times satisfy $T_1^C < T_1^{1H}$. Each of the two methyl carbon atoms of L-valine in solids has two resonant lines, and this multi structure can also be found for other amino acids [15]. It may originate in polymorphism and/or the presence of two inequivalent molecules in a unit cell. Therefore, the spin–lattice relaxations corresponding to the multiple lines for the same carbon atom may vary significantly due to the different local motions. Here, we notice an essential difference between the experimental curves corresponding to the chemical shifts of 19.5 and 19.2 ppm, but not between those corresponding to the chemical shifts of 22.1 and 21.5 ppm.

Based on the single-exponential model normally used, the $^{13}C$ longitudinal relaxation times under the different average r.f field strengths are listed in Table 1. Furthermore, the spin–lattice relaxation times $T_1^{1H}$ of solid-state L-valine have been measured, approximately amounting to 0.7 s for all protons [4]. As a result, we derive quantitatively the relation $T_1^C < T_1^{1H}$ for the resonant lines of the chemical shifts 22.1, 21.5, and 19.5 ppm and $T_1^C > T_1^{1H}$ for the resonant line of 19.2 ppm, which are well in agreement with the qualitative prediction. From Table 1, we can see that the values for the resonance at 19.5 ppm vary considerably with $\bar{\omega}_1$, whereas the others do not. In addition, we found that under proton r.f irradiation, the courses of spin–lattice relaxation for the resonances at 19.5 and 19.2 ppm exhibited a larger deviation from the single-exponential model than those at 22.1 and 21.5 ppm. This may arise from the experimental errors since the resonances at 19.5 and 19.2 ppm overlap considerably.

4. Conclusions

The $^{13}C$ spin–lattice relaxation processes in organic solids are multiexponential where there is an appreciable transient NOE. If the protons are not saturated during the measurements, it may be cumbersome to acquire the spin–lattice relaxation times $T_1^C$. Under certain experimental conditions, however, the $^{13}C$ relaxation processes can be reduced to be single-exponential and the relaxation times $T_1^C$ can be measured in the traditional way, including the pulse sequence and the data analysis procedure. It is known that details and intricate aspects of the relaxation are best pursued by resorting to more general tools such as the density matrix formalism combined with projection operator theory [16,17]. Nevertheless, it is always useful to provide a simpler though rougher description of a physical phenomenon. Being an approximation of the density matrix formalism, the extended Solomon equations [9] can reasonably describe the $^{13}C$ spin–lattice relaxation processes under r.f. field irradiation and analyze the weak effect of r.f. field irradiation on $^{13}C$ spin–lattice relaxation.

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References