

## Spin–spin and spinlattice contributions to the rotating frame relaxation of $^1\text{H}$ in L alanine

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# Spin-spin and spin-lattice contributions to the rotating frame relaxation of $^{13}\text{C}$ in *L*-alanine

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The spin-lattice relaxation times in both the Zeeman ( $T_1^C$ ) and rotating ( $T_{1\rho}^C$ ) frames were determined for three chemically distinct carbon atoms ( $^{13}\text{C}$ ) in polycrystalline *L*-alanine by combining crosspolarization and magic angle spinning techniques together with proton decoupling. The spin-lattice and spin-spin contributions to the experimentally measured  $T_{1\rho}^C$  could be separated by an experiment in which the  $^{13}\text{C}$  spin-locking field was varied. The spin-lattice contributions ( $T_{1\rho}^C$ ), which contain motional information, were determined to be 21.7, 23.4, and 138 ms for the  $\text{C}_\alpha$ ,  $\text{CH}_3$ , and  $\text{COO}^-$  carbons, respectively. The spin-spin contribution ( $T_{CH}^D$ ) was found to be exponential, namely,  $(T_{CH}^D)^{-1} \propto \exp(-2\pi\nu_{\text{CH}}\tau_D)$  in the low  $^{13}\text{C}$  spin-locking field. Therefore, the assumption of a Lorentzian correlation function for the proton dipolar fluctuations is adequate for *L*-alanine. Furthermore, the proton dipolar correlation times  $\tau_D$  were found to be the same ( $31 \pm 1 \mu\text{s}$ ) for all three carbons in *L*-alanine. The spin-lattice relaxation times in the Zeeman frame  $T_1^C$  were determined to be 4.0 s, 38 ms, and 13 s for the  $\text{C}_\alpha$ ,  $\text{CH}_3$ , and  $\text{COO}^-$  carbons, respectively. The experimental values of  $T_{1\rho}^C$  and  $T_1^C$  can be explained quantitatively by considering the internal rotations of the methyl and amino groups.

## I. INTRODUCTION

Spin-lattice relaxation time measurements for individual rare nuclei in different chemical environments in solids became plausible because of recent developments in high resolution NMR techniques.<sup>1-4</sup> These techniques include crosspolarization (CP) and dipolar decoupling, together with magic angle spinning (MAS), when desired. By using these newer experimental techniques, it has been possible to observe NMR resonances from  $^{13}\text{C}$  nuclei in natural abundance in organic compounds. In Fig. 1 is shown a thermodynamic scheme which provides a satisfactory model for the various spin-lattice and spin-spin relaxation processes which occur in a molecule such as *L*-alanine when subjected to the conditions of the experiments described later. The different possible relaxation processes of interest to us which occur in this system are labeled in Fig. 1 by the symbols  $T_1^C$ ,  $T_{1\rho}^C$ ,  $T_{1D}$ , and  $T_{CH}^D$ . The  $^{13}\text{C}$  spin-lattice relaxation time in the rotating frame ( $T_{1\rho}^C$ ) is of particular interest, as it can, in principle, provide information about slow molecular motion in solids.

The interpretation of  $T_{1\rho}^C$  (the experimentally observed relaxation time for the decay of rotating frame  $^{13}\text{C}$  magnetization), however, is not as simple in solids as in liquids, since the nucleus being studied in the solid experiences fluctuations of the local field caused not only by molecular motions but also by the spin fluctuations of other more abundant nuclei due to their mutual static dipolar interactions. As McArthur, Hahn, and Walstedt (MHW)<sup>5</sup> first showed in the case of  $\text{CaF}_2$ , the spin fluctuations of the abundant nuclei can be well represented by a Lorentzian correlation function. This initial proposal by MHW was further substantiated by rigorous calculations by Demco, Tegenfeldt, and Waugh (DTW)<sup>6</sup> for  $\text{CaF}_2$ , and experimentally by Pines and Shattuck<sup>7</sup> and Stokes and Ailion,<sup>8</sup> for relatively simple

crystals, such as Li metal, LiF, and adamantane.

Recently, a considerable interest has developed in studying molecular motions in solid synthetic polymers, for which  $T_{1\rho}^C$  measurements using the modern solid state high resolution NMR techniques seem to be appropriate.<sup>9-14</sup> Thus, Schaefer *et al.*,<sup>9,10</sup> Veeman *et al.*,<sup>11</sup> and Garroway *et al.*<sup>12-14</sup> have examined the  $^{13}\text{C}$  relaxation behavior in the rotating frame of several synthetic polymers. In most cases, the spin-spin process is found to play an important role in the relaxation of the  $^{13}\text{C}$  spin-lock magnetization.<sup>11-14</sup> In particular, Garroway *et al.* have shown from the spin-lock field dependence of  $T_{1\rho}^C$  that a Lorentzian correlation function for the proton dipolar fluctuation can adequately describe the rate of dissipation of the  $^{13}\text{C}$  spin-lock Zeeman energy to the proton dipolar reservoir. However, quantitative separation of the two contributions (spin-spin and spin-lattice processes) was insufficient in these studies, partly due to the complex nature of the molecular motions.

In the present work, we have studied the relaxation of the  $^{13}\text{C}$  magnetization in the rotating frame  $T_{1\rho}^C$  for the amino acid *L*-alanine with a view of separating the spin-spin  $T_{CH}^D$  and spin-lattice  $T_{1\rho}^C$  contributions to the relaxation. *L*-alanine was chosen as a representative amino acid because its crystal structure is known,<sup>15</sup> and the molecular motions in the solid compound are known from proton  $T_1$  measurements.<sup>16</sup> Special attention was paid to the differential relaxation behavior of the three chemically nonequivalent carbon atoms of *L*-alanine whose resonances are separately observable under MAS.<sup>17</sup> The  $T_{1\rho}^C$  data, combined with an independent measurement of  $T_1^C$  values for chemically distinct carbon atoms should be potentially useful for the understanding of local motions in more complex biological systems, e.g., proteins.

## II. EXPERIMENTAL

Polycrystalline *L*-alanine was obtained from the Aldrich Chemical Co. All the NMR experiments were

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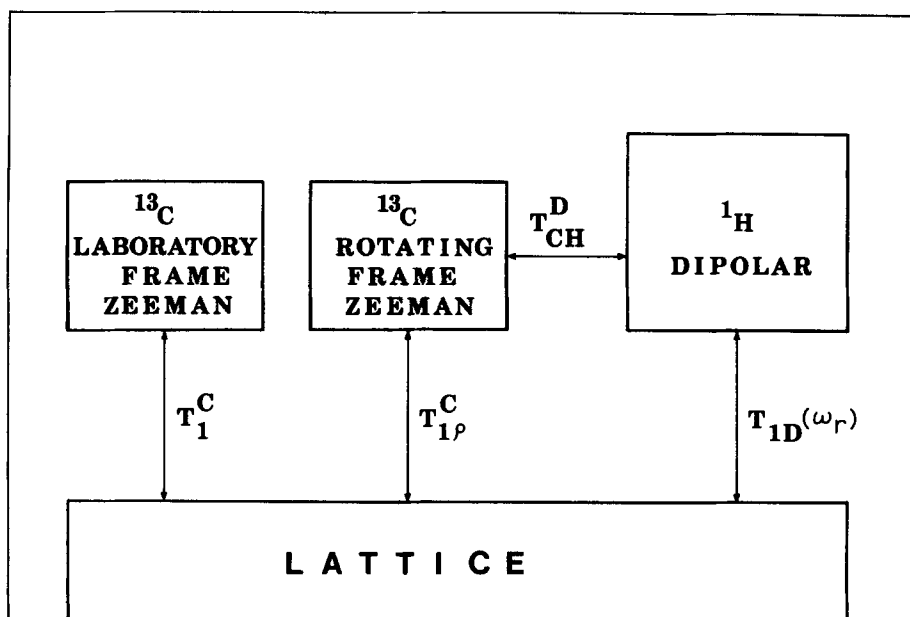


FIG. 1. A thermodynamic model for  $^{13}\text{C}$  relaxation experiment in the Zeeman and rotating frames.  $T_1^C$  and  $T_{1\rho}^C$  are the spin-lattice relaxation times in the laboratory and rotating frames for  $^{13}\text{C}$  nuclei, respectively.  $T_{1D}$  is the dipolar spin-lattice relaxation time and is determined primarily by the relaxation of the protons.  $T_{CH}^D$  is the crossrelaxation time for a particular carbon atom.

performed on a Bruker CXP-200 FT NMR spectrometer operating at 200 MHz for protons and 50.3 MHz for carbon-13, equipped with a probe for magic angle spinning. A Delrin spinner was used at the spinning frequency of 4.5 kHz for the  $T_{1\rho}^{C*}$  and  $T_1^C$  measurements, and a deuterated plexiglas spinner was used for the proton  $T_{1D}$  measurements. The spinning frequency of the deuterated plexiglas spinner was 3.8 kHz. All the  $^{13}\text{C}$  relaxation experiments were carried out at room temperature (291 K).

For the  $T_{1\rho}^{C*}$  measurements, a combination of pulse sequences shown in Figs. 2(a) and 2(b) was employed. First,  $^{13}\text{C}$  magnetization was obtained by crosspolarization with protons in the rotating frame under Hartmann-Hahn conditions. Then the proton rf field was cut off for variable time  $\tau$  while the  $^{13}\text{C}$  spin-locking rf field ( $H_{1C}$ ) was held stationary at a chosen amplitude. The  $^{13}\text{C}$  free induction decay signal (FID) was accumulated under high power proton decoupling and then Fourier transformed. The decay of the individual  $^{13}\text{C}$  signals as a function of  $\tau$  gives the observed  $T_{1\rho}^{C*}$  values. The mixing time of 500  $\mu\text{s}$  and proton decoupling time of 25 ms were chosen to give a maximum signal-to-noise ratio. The experiment was repeated for different  $\nu_{1C}$  values in the range of 20–60 kHz ( $\nu_{1C} = \gamma_C H_{1C} / 2\pi$ ).

For successful measurements at high  $H_1$  fields, careful tuning of the probe and the circuits and long duty cycles were essential. Since the accuracy of the  $^{13}\text{C}$  spin-locking field  $H_{1C}$  was particularly important in the present experiment, the magnitude of  $H_{1C}$  was determined directly under exactly the condition of each  $T_{1\rho}^{C*}$  measurement in the following way: Since the  $\text{CH}_3$  carbon atom of *L*-alanine has a very short  $T_1^C$  value, its signal can be recorded with a good signal-to-noise ratio in a relatively short time without utilizing crosspolarization with protons. Thus, the intensity of the  $\text{CH}_3$  carbon NMR signal was recorded as a function of the duration of a single  $^{13}\text{C}$  resonance excitation pulse, under proton decoupling, with exactly the  $H_{1C}$  field

strength used for each  $T_{1\rho}^{C*}$  experiment. The reciprocal of the pulse duration necessary to produce a  $360^\circ$  flip of the magnetization was taken as  $\nu_{1C}$ .

For the  $T_1^C$  measurements, a combination of the pulse sequences shown in Figs. 2(a) and 2(c) was employed. The  $^{13}\text{C}$  magnetization obtained by crosspolarization was subsequently flipped  $90^\circ$  to lie along the  $H_0$  direction using a  $^{13}\text{C}$   $90^\circ$  pulse in the  $y$  direction. After a variable time  $\tau$  a  $90^\circ$  pulse was applied

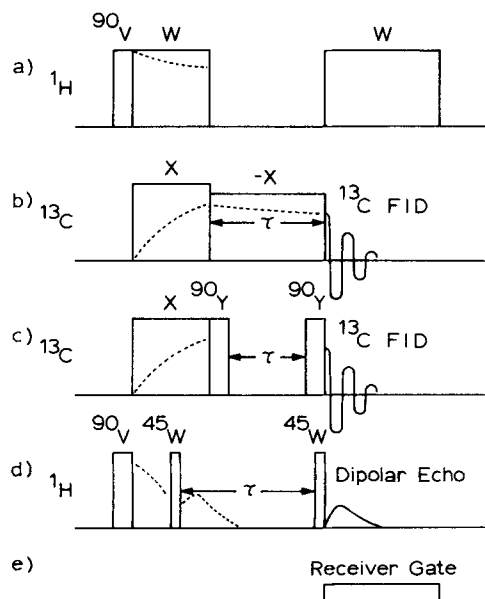


FIG. 2. Pulse sequences employed for the determination of relaxation times. (a) and (b); Measurement of  $T_{1\rho}^{C*}$ . The mixing time was 500  $\mu\text{s}$ , and the applied rf fields were, respectively, 10 and 40 G for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei during crosspolarization. (a) and (c); Measurement of  $T_1^C$ . (d); Jeener-Broekaert pulse sequence for the measurement of proton  $T_{1D}$ . (e); Receiver gate opened for 25 ms for the measurement of  $T_{1\rho}^{C*}$  and  $T_1^C$ .

again in the  $y$  direction. Subsequently, the FID signal was acquired during proton decoupling and then Fourier transformed. The intensities for the three carbon signals were plotted as a function of  $\tau$  to yield  $T_1^C$  values. The proton dipolar spin-lattice relaxation times  $T_{1D}$  were measured with stationary and spinning samples by using the Jeener-Broekaert pulse sequence<sup>18</sup> shown in Fig. 2(d).

### III. THEORETICAL

The features of the  $T_{1D}^{C*}$  experiments are present in a thermodynamic scheme depicted in Fig. 1. This is similar to the scheme by MHW<sup>5</sup> and later modified by VanderHart and Garroway.<sup>12</sup> The carbon-13 rotating frame Zeeman system is coupled with the lattice system and with the proton dipolar reservoir by the relaxation times  $T_{1D}^C$  and  $T_{CH}^D$ , respectively. The proton dipolar order relaxes to the lattice with the relaxation time  $T_{1D}$ . Therefore, the experimentally observed  $T_{1D}^{C*}$  does not reflect the true  $T_{1D}^C$  value, but includes effects depending on the relative magnitudes of  $T_{1D}^C$ ,  $T_{CH}^D$ , and  $T_{1D}$ , and the heat capacity of the proton dipolar reservoir.<sup>12</sup>

The relaxation time  $T_{1D}$  is determined by molecular motion in a stationary sample. In a spinning sample, however,  $T_{1D}$  decreases since the proton spins are not able to follow adiabatically the apparent motion of the local dipolar fields, and dissipate rapidly. For a polycrystalline specimen rotation at an angular frequency  $\Omega$ , with the rotation axis perpendicular to  $H_0$ ,  $T_{1D}$  can be expressed as<sup>19</sup>

$$(T_{1D})^{-1} = (1/2)\pi 3\Omega^2 \tau_D', \quad (1)$$

where  $\tau_D' = (3/M_{HH}^{(2)})^{1/2}$  is the dipolar fluctuation time, and  $M_{HH}^{(2)}$  is the Van Vleck proton-proton second moment.

The spin-spin relaxation between the proton dipolar and carbon-13 rotating frame Zeeman system ( $T_{CH}^D$ ) is caused by the proton spin fluctuation, modulating the proton carbon dipolar interaction. The correlation function of the proton spin fluctuation is assumed to be Lorentzian and hence the spectral density can be expressed as an exponential function<sup>5</sup> as follows:

$$J_D(\omega) = (1/2)\pi \tau_D \exp(-\omega \tau_D), \quad (2)$$

where  $\tau_D$  is the correlation time of the dipolar fluctuation given by<sup>8</sup>

$$(\tau_D)^{-2} = KM_{HH}^{(2)}/9. \quad (3)$$

Here,  $K$  is a geometric factor involving both the proton-proton and the proton carbon dipolar interactions. The value of  $T_{CH}^D$  at an effective spin-locking field  $2\pi\nu_{eC}$  =  $\gamma_C H_{eC}$  can be expressed as

$$(T_{CH}^D)^{-1} = \sin^2 \theta M_{CH}^{(2)} J_D(\omega_{eC}), \\ = (1/2)\pi \sin^2 \theta M_{CH}^{(2)} \tau_D \exp(-2\pi\nu_{eC} \tau_D), \quad (4)$$

where  $\theta$  is the off-resonance angle given by  $\tan \theta = H_{1C}/(H_{0C} - \omega_{1C}/\gamma_C)$  and  $M_{CH}^{(2)}$  is the second moment of the carbon nucleus, in question, due to the surrounding protons.

As mentioned above,  $T_{1D}$  is a function of the spinning frequency and when a sample spins at a frequency of

several kHz, the  $T_{1D}$  value becomes less than 100  $\mu$ s. In that case, the condition  $T_{CH}^D \gg T_{1D}$  is well satisfied. Therefore, the  $^{13}\text{C}$  rotating frame magnetization will be depleted through two independent pathways, either through  $T_{1D}^C$  to the lattice, or by relaxation, via  $T_{CH}^D$ , to the proton dipolar reservoir which always attains a common spin temperature with the lattice due to the short relaxation time  $T_{1D}$  when the sample is spinning. Consequently, in the  $T_{1D}^C$  experiment for the spinning sample, the observed relaxation time  $T_{1D}^{C*}$  may be assumed to be given by<sup>12</sup>

$$(T_{1D}^{C*})^{-1} = (T_{CH}^D)^{-1} + (T_{1D}^C)^{-1}. \quad (5)$$

In *L*-alanine, the molecular motions which contribute to  $T_{1D}^C$  and  $T_{1D}^C$  are the rotations of the  $\text{NH}_3^+$  and  $\text{CH}_3$  groups. The rotational correlation times of the  $\text{NH}_3^+$  and  $\text{CH}_3$  groups are known from proton  $T_1$  measurements<sup>16</sup> to be  $1.4 \times 10^{-7}$  and  $1.6 \times 10^{-9}$  s, respectively, at the room temperature. Therefore,  $\omega_{1C}^2 \tau_C^2 \ll 1$  holds for the present experiment ( $\nu_{1C} < 60$  kHz), which makes  $T_{1D}^C$  independent of  $\nu_{1C}$ . It is clear that  $T_{CH}^D$  is exponentially dependent, and  $T_{1D}^C$  is constant for the variable  $\nu_{1C}$ , as long as  $\nu_{1C}$  is small. The variation of  $T_{1D}^{C*}$  with  $\nu_{1C}$  dependence can, therefore, be analyzed using a nonlinear least-squares fit to the function [Eq. (6)] which arises from Eqs. (4) and (5),

$$(T_{1D}^{C*} \sin^2 \theta)^{-1} = P_1 \exp(P_2 \nu_{eC}) + P_3, \quad (6)$$

$P_i$  are the parameters to be deduced by the least-square fitting and are as follows:  $P_1 = (1/2)\pi \tau_D M_{CH}^{(2)}$ ,  $P_2 = -2\pi \tau_D$ , and  $P_3 = (T_{1D}^C)^{-1}$ . After the  $P_i$  are determined, the values of  $M_{CH}^{(2)}$ ,  $\tau_D$ , and  $T_{1D}^C$  are obtained.

Since the molecular motions which contribute to  $T_{1D}^C$  and  $T_{1D}^C$  are the anisotropic rotations of the amino and methyl groups about the  $\text{C}_\alpha\text{-NH}_3^+$  and the  $\text{C}_\alpha\text{-CH}_3$  bonds, respectively, both  $T_{1D}^C$  and  $T_{1D}^C$  values should, therefore, be anisotropic with respect to the angle which these rotation axes make with the  $H_0$  field.<sup>20</sup> For a polycrystalline sample, this would result in a distribution of  $T_{1D}^C$  or  $T_{1D}^C$  in the range of a factor of 2 or so.<sup>20</sup> This small variation in  $T_{1D}^C$  or  $T_{1D}^C$  would be averaged out by MAS, giving essentially a single relaxation time. The powder-averaged relaxation times may be obtained from the corresponding expressions in solution [Eqs. (7) and (8)] simply by putting the correlation time for the overall molecular tumbling equal to infinity; the resulting form for the spectral densities is given by Eq. (9),

$$(T_{1D}^C)^{-1} = (1/32) d^2 [4J_0(\omega_{1C}) + J_0(\omega_H - \omega_C) + 18J_1(\omega_C) \\ + 36J_1(\omega_H) + 9J_2(\omega_H + \omega_C)] \quad (\omega_{1C} \ll \omega_C, \omega_H) \quad (\text{Ref. 21}), \quad (7)$$

$$(T_{1D}^C)^{-1} = (1/16) d^2 [J_0(\omega_H - \omega_C) + 18J_1(\omega_C) + 9J_2(\omega_H + \omega_C)] \quad (\text{Ref. 22}), \quad (8)$$

with

$$J_m(\omega) = K_m \sum_i r_{CH_i}^{-6} N_i (3/4) (\sin^2 2\beta_i + \sin^4 \beta_i) \frac{2\tau_{ci}}{1 + \omega^2 \tau_{ci}^2}, \quad (9)$$

$$K_0 = (4/5), \quad K_1 = (2/15), \quad \text{and} \quad K_2 = (8/15).$$

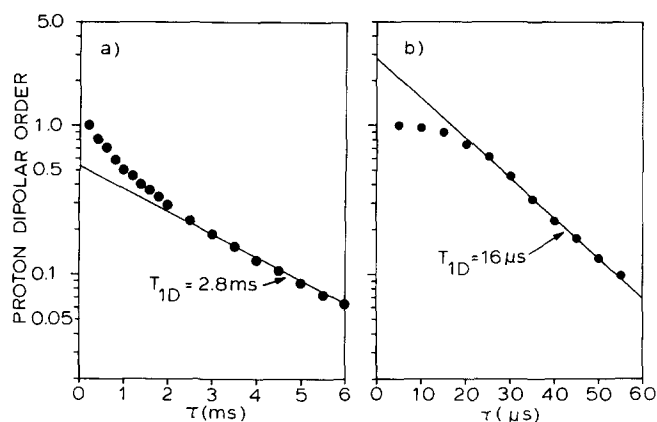


FIG. 3. Plots of the dipolar signal intensity decay as a function of the various time delays  $\tau$  between the two  $45^\circ$  pulses in the Jeener-Broekaert sequence. (a) Stationary sample. (b) Sample spun at the magic angle at a frequency of 3.8 kHz.

Here,  $d^2 = \gamma_C^2 \gamma_H^2 \hbar^2$ ,  $N_i$  is the number of equivalent protons undergoing rotation in the  $i$ th group, and  $\beta_i$  is the angle between the C-H vector and the axis of the  $i$ th group rotation which is axial symmetric with respect to the carbon atom in question.  $\tau_{ei}$  is the correlation time for the  $i$ th group rotation, and is defined according to the original definition by Woessner<sup>23</sup> [ $\tau_{ei} = (D_{rot})^{-1}$ ] for a model with random jumps between three equivalent positions.

Equation (9) is applicable to only those carbon atoms for which the group rotations are axially symmetric. Within a single molecule of *L*-alanine, the methyl group rotation is axially symmetric with respect to the  $\text{CH}_3$  carbon ( $\beta = 69.8^\circ$ ) and  $\text{C}_\alpha$  ( $\beta = 28.3^\circ$ ), but not to the  $\text{COO}^-$  ( $\beta = 20.8^\circ$ ) carbon. Likewise, the  $\text{NH}_3^+$  group rotation is axially symmetric with respect to  $\text{C}_\alpha$  ( $\beta = 27.9^\circ$ ), but not to the  $\text{CH}_3$  ( $\beta = 20.2^\circ$ ) and  $\text{COO}^-$  ( $\beta = 20.2^\circ$ ) carbons. Of course, none of the group rotations of neighboring alanine molecules are axially symmetric with respect to either of the three carbon atoms. For the calculation of  $T_{1\rho}^{C*}$  and  $T_1^C$ , we assumed all the group rotations are axially symmetric and the average C-H<sub>i</sub> distances are used.

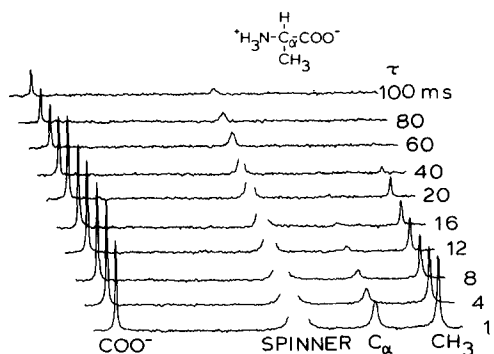


FIG. 4. CP-MAS  $^{13}\text{C}$  NMR spectra of polycrystalline *L*-alanine as a function of the  $^{13}\text{C}$  spin-locking time  $\tau$  at a  $^{13}\text{C}$  spin-locking field of  $\nu_{1C} = 40$  kHz.

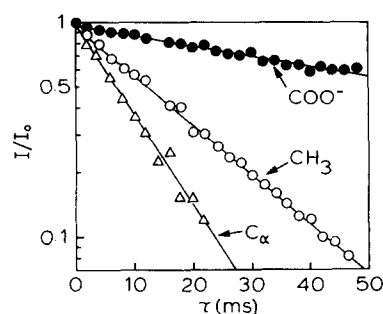


FIG. 5. Semilogarithmic plots of  $^{13}\text{C}$  NMR signal intensities for individual carbon atoms of polycrystalline *L*-alanine as a function of the  $^{13}\text{C}$  spin-locking time  $\tau$  at a  $^{13}\text{C}$  spin-locking field of  $\nu_{1C} = 40$  kHz.

#### IV. RESULTS

The experimental results for the decay of the dipolar order ( $T_{1D}$ )<sup>-1</sup> are shown in Figs. 3(a) and 3(b). Inspection of those figures shows that the  $T_{1D}$  value is greatly reduced by spinning the sample, i.e., from 2.8 ms for the case of the stationary sample to 16  $\mu$ s for the sample spinning at 3.8 kHz. The  $T_{1D}$  value deduced for the stationary sample is in good agreement with the result published by Emid *et al.*<sup>24</sup> Therefore, as mentioned in the previous section, Eq. (5) can be used to analyze the  $T_{1\rho}^{C*}$  data obtained with sample spinning.

Figure 4 shows the spectra obtained in the  $T_{1\rho}^{C*}$  experiment for *L*-alanine with the CP-MAS techniques; the spectra are shown as a function of the spin-locking period  $\tau$ . The corresponding semilogarithmic plots (Fig. 5) show single exponential decays, from which we deduce values of  $T_{1\rho}^{C*}$  for the individual carbon atoms by least-squares fitting. Such experiments were repeated for different values of the effective spin-locking

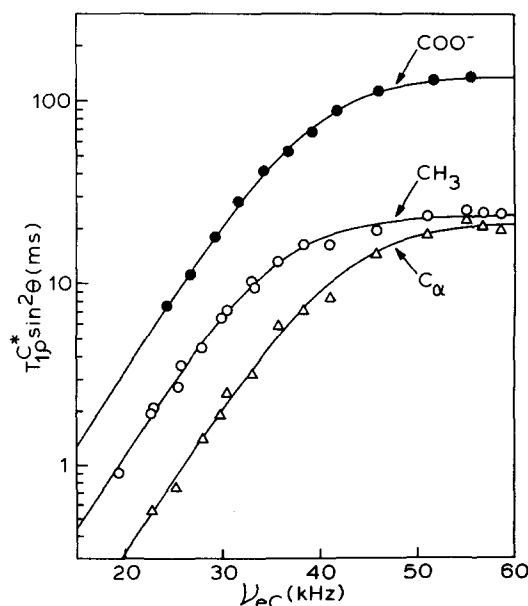


FIG. 6. Plots of the deduced  $T_{1\rho}^{C*} \sin^2 \theta$  values for individual carbons as a function of the effective  $^{13}\text{C}$  spin-locking field. The solid lines were obtained from the nonlinear least-squared fit to Eq. (6) (see the text).

TABLE I. Measured and calculated relaxation times and second moments for *L*-alanine.

Parameters	C <sub>α</sub>	CH <sub>3</sub>	COO <sup>-</sup>
$T_{1\rho}^C(\text{obs})/\text{ms}$	21.7	23.4	138
$T_{1\rho}^C(\text{calc})^a$			
Contributions			
CH <sub>3</sub> group/ms	$2.4 \times 10^3$	25	$2.1 \times 10^4$
NH <sub>3</sub> <sup>+</sup> group/ms	50	$4.6 \times 10^2$	$4.7 \times 10^2$
Total/ms	49	24	$4.6 \times 10^2$
$T_1^C(\text{obs})/\text{s}$	4.0	0.038	13
$T_1^C(\text{calc})/\text{s}$			
Contributions			
CH <sub>3</sub> group/s	2.9	0.030	25
NH <sub>3</sub> <sup>+</sup> group/s	59	$5.4 \times 10^2$	$5.5 \times 10^2$
Total/s	2.8	0.030	24
$M_{\text{CH}}^{(2)}(\text{obs})/\text{Hz}^2$	$31.3 \times 10^8$	$9.52 \times 10^8$	$3.04 \times 10^8$
$M_{\text{CH}}^{(2)}(\text{calc})/\text{Hz}^2$	$44.9 \times 10^8$	$16.0 \times 10^8$	$2.20 \times 10^8$
$\tau_D(\text{obs})/\mu\text{s}$	30.7	32.1	31.2
$\tau_D(\text{calc})/\mu\text{s}$	34	34	34

<sup>a</sup>These values are calculated at  $\nu_{1C} = 50$  kHz.

fields in terms of  $\nu_{eC}$ . Figure 6 depicts the results of those measurements. In that figure we have plotted  $T_{1\rho}^{C*} \sin^2\theta$  instead of  $T_{1\rho}^{C*}$  to correct for any off-resonance effects. That is necessary because the <sup>13</sup>C carrier frequency applied was close to the CH<sub>3</sub> carbon resonance frequency, the C<sub>α</sub> and COO<sup>-</sup> carbon frequencies are slightly off resonance and are locked to different effective fields. Actually, the off-resonance frequencies were 2.32, 0.78, and 8.69 kHz for the C<sub>α</sub>, CH<sub>3</sub>, and COO<sup>-</sup> carbon atoms, respectively. Furthermore,  $\nu_{eC}$  was plotted as the abscissa rather than  $\nu_{1C}$ . The relaxation times  $T_{1\rho}^C$ , the second moment  $M_{\text{CH}}^{(2)}$ , and the correlation time of the dipolar fluctuation  $\tau_D$  are obtained by a nonlinear least-square fitting to Eq. (6), and summarized in Table I together with corresponding values obtained by calculation.

The results of  $T_1^C$  measurements in the laboratory frame, showed that these quantities were enormously different for the different carbon atoms as listed in Table I. The CH<sub>3</sub> carbon atom, in particular, is found to have a small  $T_1^C$  value.

## V. DISCUSSION

We see from Fig. 6 that the  $T_{1\rho}^{C*} \sin^2\theta$  values satisfy Eq. (6) for all the three carbons of *L*-alanine. This shows that the simple thermodynamic model depicted in Fig. 1 is applicable to the spin relaxation mechanism of the individual carbons of *L*-alanine. The result is also to our knowledge the first example showing a clear separation of  $T_{\text{CH}}^D$  and  $T_{1\rho}^C$  in a quantitative fashion. Several features of this example will be discussed below in more detail.

### A. The MAS effect

Since our measurements are done on a sample under the MAS condition where the spinning frequency is considerably larger than  $(T_{1\rho}^{C*})^{-1}$  itself, the measured values of  $T_{1\rho}^{C*}$  correspond to the powder average of  $T_{1\rho}^{C*}$ 's

for different crystal orientations. The MAS effect would not considerably change the  $T_{\text{CH}}^D$  or  $T_{1\rho}^C$  values, as the spinning frequency  $\nu_r$  is much less than  $(\tau_D)^{-1}$ , the dipolar fluctuation rate, and  $(\tau_c)^{-1}$ , the rate of rotation of the NH<sub>3</sub><sup>+</sup> or CH<sub>3</sub> groups, so that the spectral density for these fluctuations would not be altered appreciably. From the measurements with  $\nu_{1C} = 30$  and 51 kHz where  $T_{\text{CH}}^D$  and  $T_{1\rho}^C$  dominate, respectively, and a spinning frequency 2.4 kHz it is seen that the values of  $T_{1\rho}^{C*}$  have little dependency on the spinning frequency. On the other hand, the sample spinning has a marked effect on  $T_{1D}$ , the spin-lattice relaxation time of the proton dipolar order, as shown in Fig. 3.

### B. $\tau_D$ values

One of the interesting points of the present study is whether or not the spin-spin process ( $T_{\text{CH}}^D$ ) reflects its characteristic environment. In this context, it is interesting to see the surprisingly good agreement among the  $\tau_D$  values obtained from the slopes of the linear portions of the three curves of Fig. 6. On the other hand, the experimentally obtained second moments  $M_{\text{CH}}^{(2)}$  are different for each of the three carbon atoms as expected. Moreover, the time constant ( $\tau_D$ ) of the dipolar flip-flop correlation time of protons calculated from the proton second moment through Eq. (3), and  $K$  taken to be unity, yields values which are within 10% of the experimentally determined  $\tau_D$  for the three carbon atoms.

The above observations indicate that although the local proton environment of the three carbon atoms differ greatly from each other, and the protons of *L*-alanine are located in a complex manner in the crystal as compared to the cases of much simpler system such as CaF<sub>2</sub><sup>5</sup> or polyethylene,<sup>12</sup> the simple picture of crossrelaxation between the carbon atoms and the protons such that C-H dipolar interaction is modulated by a common dipolar fluctuation of protons appears to be valid, at least within the measured range of  $\nu_{eC}$ . This implies that the spin fluctuation spectrum may be considered uniform over the crystal, and "spin-diffusion inhibition"<sup>5</sup> does not seem to be appreciable for the  $T_{\text{CH}}^D$  process in this case.

Deviation from the exponential dependency of  $T_{\text{CH}}^D$  on  $\nu_{eC}$  might occur for different carbon nuclei at higher values of  $\nu_{eC}$ , i.e., where  $\nu_{eC}$  exceeds  $(\tau_D)^{-1}$ . However, such conditions cannot be observed in *L*-alanine, since above  $\nu_{eC} = 40 \sim 50$  kHz, the  $T_{1\rho}^C$  mechanism comes into play and predominates over the  $T_{\text{CH}}^D$  mechanism, thus rendering  $T_{\text{CH}}^D$  unmeasurable.

### C. $M_{\text{CH}}^{(2)}$ values

The experimental values of  $M_{\text{CH}}^{(2)}$  obtained by extrapolation of the linear portion of the curve shown in Fig. 6 to zero are widely different for the carbon atoms, reflecting the local proton magnetic environments for the three centers. Each of these values agrees well (within 70%) with the  $M_{\text{CH}}^{(2)}$  values calculated from the Van Vleck second moment formula. In view of the lack of experimental points at lower  $\nu_{eC}$  values, this agreement between experimental and calculated  $M_{\text{CH}}^{(2)}$  values is considered to be satisfactory.

#### D. $T_{1\rho}^C$ values

The saturation of  $T_{1\rho}^{C*}$  for the different carbon atoms in *L*-alanine as indicated in Fig. 6 shows that  $T_{1\rho}^C$  sets in at higher  $\nu_{ec}$  values and that the  $T_{1\rho}^{C*}$  values are independent of  $\nu_{ec}$  as expected from the theoretical expression of  $T_{1\rho}^C$  [Eq. (7)] for  $\omega_{1c}^2\tau_c^2 \ll 1$ . The  $T_{1\rho}^C$  values calculated from Eq. (7) using the  $\tau_c$  values for the rotations of the  $\text{NH}_3^+$  and  $\text{CH}_3$  groups obtained from the proton  $T_1$  measurements by Andrew *et al.*<sup>16</sup> (considering only the intramolecular CH dipolar interactions) predict the correct magnitude of  $T_{1\rho}^C$  obtained experimentally (Table I), thus giving an independent check of the results from proton  $T_1$  measurements.

Indeed, the agreement is excellent for the methyl carbon whose  $T_{1\rho}^C$  is determined almost solely from its own C-H dipolar interactions (see Table I). Less agreement is obtained for  $\text{C}_\alpha$  and  $\text{COO}^-$  carbons where the main contribution to the  $(T_{1\rho}^{C*})^{\text{calc}}$ ,  $s$  is from the intramolecular amino group rotation. The result indicates some intermolecular contribution to the relaxation of these carbons. The inclusion of an intermolecular contributions improves the agreement considerably. The agreement between the observed and the calculated  $T_{1\rho}^C$  values also shows that slow librational motion in the frequency range of  $\omega_{1c}/2\pi$  does not occur in solid *L*-alanine.

#### E. $T_1^C$ values

A further independent check on the rate of internal motions is provided from the  $T_1^C$  data (Table I). Here again, the agreement is satisfactory between the calculated and the observed  $T_1^C$  values for all the three carbons. In all cases the  $T_1^C$ 's arise wholly from contributions from the methyl group rotation and the contribution from the slowly rotating amino group is negligible. The fact that  $T_{1\rho}^C$  (23.4 ms) is fairly close to  $T_1^C$  (38 ms) for the methyl carbon is a direct consequence of rapidity of the methyl group rotation; in the extreme narrowing condition ( $\omega_c^2\tau_c^2 \ll 1$ ,  $\omega_H^2\tau_c^2 \ll 1$ ), we obtain  $T_{1\rho}^C \approx T_1^C$  from Eqs. (7) and (8). This fact also suggests that a transient Overhauser effect will occur through the crossrelaxation term<sup>25</sup> since the proton magnetization is not stationary after crosspolarization but relaxes with  $T_1^H \sim 0.5$  s.<sup>18</sup> On the other hand, the great differences between  $T_{1\rho}^C$  and  $T_1^C$  for the  $\text{C}_\alpha$ , and the  $\text{COO}^-$  carbons, are the result of the slow rate of rotation of the amino group which contributes significantly only to  $T_{1\rho}^C$ .

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