Molecular Motion in Liquid Toluene from a Study of ^{13}C and ^{2}D Relaxation Times

H. W. Spiess, D. Schweitzer, and U. Haeberlen

Max-Planck-Institut, 6900 Heidelberg, Jahn-Straße 29, W. Germany

The ^{13}C nuclear spin-lattice relaxation times for ring and methyl carbons in liquid toluene were studied from $-95°$C to $+60°$C at frequencies of 14 and 61 MHz. Data were taken for protonated as well as deuterated toluene. The results were analyzed in terms of three relaxation mechanisms: intramolecular dipole–dipole coupling, spin–rotation interaction, and anisotropic chemical shift. The last mechanism gives a significant contribution only to the relaxation rate of the ring carbons of the deuterated species at 61 MHz and low temperatures. A tentative value of $\Delta\sigma = 295$ ppm is obtained in this case. In order to separate the contributions of the dipole–dipole and spin–rotation interactions the ^{13}C data are compared with deuteron relaxation times. Comparison of the ^{13}C data in the protonated and deuterated form of toluene shows that the correlation times for the ring differ by 20% and an even larger effect of isotopic substitution is found for the methyl group. It is demonstrated that the fast internal motion of the methyl group cannot be studied quantitatively using deuteron or ^{13}C intramolecular dipole–dipole relaxation rates alone because of the sensitivity of the results to the angle, ϑ, the Z-axis of the electric field gradient, or the internuclear vector, respectively, forms with the C_3 axis. Analysis of the relaxation rates due to spin–rotation interaction yields τ_J (internal), the correlation time of angular momentum of the internal motion directly. The correlation time of reorientation τ_c (internal) is calculated from τ_J (internal) using Gordon's extended diffusion model which is applied to a symmetric rotor with a fixed axis. It is found that both τ_J (internal) and τ_c (internal) are of the same magnitude as the correlation time of the free rotor. The ratio of correlation times of the overall and internal reorientation ranges from approximately 200 at the melting point to approximately 13 at $+60°$.

I. INTRODUCTION

The study of spin–lattice relaxation times (T_1) yields valuable information about molecular motion. Most of the work reported so far (*1*) has been done on proton NMR. For protons, however, both intra- and intermolecular dipole–dipole interactions give major contributions to the relaxation rate. For ^{13}C, on the other hand, the intermolecular dipole–dipole interaction can be safely neglected for carbons directly bound to a hydrogen atom (*2*). Another relaxation mechanism which has been demonstrated to give important contributions to the relaxation rate of ^{13}C is the spin–rotation interaction (*3–7*). Finally, in high magnetic fields of more than 30 kg relaxation through anisotropic chemical shift may be significant (*4*).

One purpose of this study is to investigate the relative importance of these mechanisms in protonated and deuterated compounds. Another important aspect arises from the fact that all three mechanisms that contribute to the ^{13}C relaxation rate arise predominantly from intramolecular coupling and therefore allow a detailed study of

molecular reorientation. In that respect, ^{13}C relaxation times yield information similar to that from relaxation times of nuclei with spin $I > 1/2$ (e.g., ^2D), where the intramolecular quadrupole coupling often provides the dominant relaxation mechanism.

An advantage of studying ^{13}C relaxation times arises from the fact that this can be done for the protonated and deuterated species of the same compound and the effect of isotopic substitution on correlation times can be investigated. Such effects are often tacitly ignored in substitution studies (8). Moreover, for strongly anisotropic motion such as the internal rotation of the methyl group in liquid toluene, the study of ^2D relaxation does not give very reliable values for the correlation time of the fast motion as pointed out by Allerhand (9). However, for a rapidly rotating CH_3 group relaxation through spin–rotation interaction becomes dominant for ^{13}C, and therefore ^{13}C relaxation times contain more reliable information about the internal motion.

II. EXPERIMENTAL

All data were taken with a Bruker pulse spectrometer operating at 14, 30, and 61 MHz and a Siemens superconducting magnet. The NMR probes and measurement procedure for $T_1 > 5$ sec have been described before (2). For $T_1 < 5$ sec the standard $180°$-τ-$90°$ sequence was used. The homogeneity of the magnet is such that the resonance frequencies of the individual ring ^{13}C atoms in toluene cannot be resolved. By using commercial samples of toluene $C_6H_5CH_3$ and $C_6D_5CD_3$ we measured an average over the different ring positions. For studying the methyl carbon, 60% enriched samples were prepared in this laboratory. At 14 MHz the signal to noise ratio of the ring ^{13}C in natural abundance was well below unity especially at the high end of our temperature range. Signal averaging techniques become very inefficient when T_1 is very long as, e.g. in $C_6D_5CD_3$. In such cases we did not employ our standard pulse sequence (2) $90°$-τ-$90°$-τ_1-$180°$ where the echo amplitude is taken as a measure of the recovery of the Z-magnetization within the variable time τ and $\tau_1 \ll \tau$ (minimum) is kept constant. Instead we used a $90°$-τ-$90°$-τ_1-$180°$-$(2\tau_1$-$180°)_N$ sequence. The N echo peaks were digitized, stored in a computer memory and added. Usually we choose $N = 64$ and $\tau_1 = 2$ msec. For $2N\tau_1 \ll T_2 \ll T_1$ the signal-to-noise ratio obtained by that technique in a single shot is as high as after accumulating the amplitude of N echoes in the standard sequence which would require a prohibitively long time. The stability requirements of the whole set up are as high as for typical Carr–Purcell T_2 measurements (10). Before applying this technique to the samples with ^{13}C in natural abundance, the adjustments were, of course, thoroughly tested with an enriched sample with high signal-to-noise ratio and known T_1.

Because of the relatively poor homogeneity of the magnet, ^1H and ^2D relaxation times for the ring and the methyl group were determined from partially deuterated samples, $C_6H_5CD_3$ and $C_6D_5CH_3$. The ^2D relaxation times were also determined from measurements on a fully deuterated sample. All samples were carefully degassed and sealed.

III. RESULTS

The ^{13}C data are summarized in Fig. 1. For the methyl carbons in $C_6H_5CH_3$ no frequency dependence of T_1 was found between 14 and 61 MHz. This is also the case for deuterated toluene at temperatures above $-80°C$. For the ring carbon of the

deuterated species, however, we found a marked increase of the rate with applied field revealing a large contribution of relaxation through anisotropic chemical shift.

All of the ^{13}C-T_1 data show a more or less pronounced curvature when plotted logarithmically vs $1/T$ suggesting that different relaxation mechanisms contribute to T_1. Relaxation through anisotropic chemical shift can be separated most unambiguously because its rate $1/T_1^{CS}$ is proportional to the square of the resonance frequency (11).
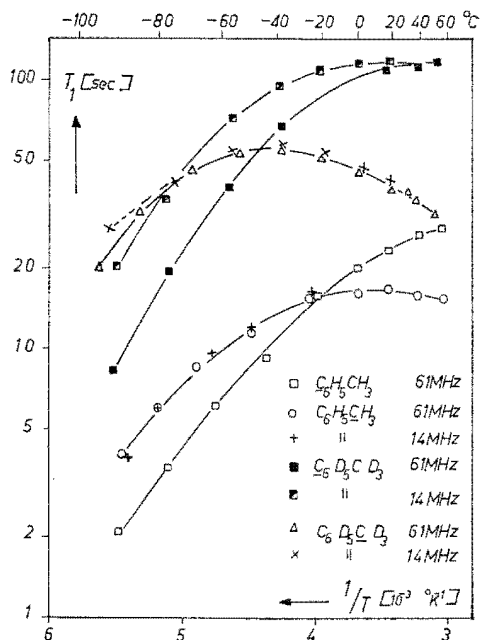

FIG. 1. ^{13}C spin–lattice relaxation times in protonated and deuterated toluene. The carbons studied are underlined.

Such a separation can be done for the ring carbons in $C_6D_3CD_5$ and the result is shown among others in Fig. 3.

The question then arises how to separate the relaxation rates due to intramolecular dipole–dipole coupling ($1/T_1^{DD}$) and due to spin–rotation interaction ($1/T_1^{SR}$). In the following we treat ring and methyl carbons separately.

1. Ring Carbons

For the ring carbons of the *deuterated* compound we make use of the deuteron relaxation data. Deuteron relaxation times in toluene have been reported recently in two papers (12, 13). In both cases, however, data were taken only above −45°C. Therefore, we have determined the relaxation times for both ring and methyl deuterons down to the melting point as shown in Fig. 2. Good agreement was obtained with previous work (12, 13). The data for fully deuterated and partially deuterated toluene differ by less than 10%.

We assume as usual that the Z-axis of the electric field gradient tensor lies approximately along the C–D bond direction and that the asymmetry parameter is $\eta \approx 0$. We

also note that the quadrupolar relaxation rate does not depend strongly on η *(11)*. This means that our conclusions are not affected if η is different from zero. The intramolecular dipole–dipole interaction of ^{13}C with the covalently bound deuteron accounts for more than 90% of the total dipolar relaxation rate. This follows simply from intra- and intermolecular atomic distances *(2)*. This means that the relevant directions for the couplings that relax ^{13}C and ^2D, respectively, are identical. An important consequence
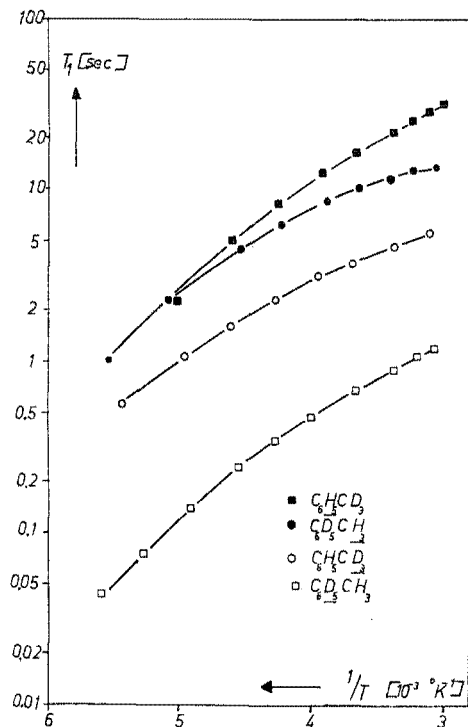

FIG. 2. Proton and deuteron relaxation times in partially deuterated toluene.

of this is that in both cases the effective correlation times reflect the *same average* over the anisotropic motion of the molecule. Moreover, we observe the same average over the different ring positions in both cases.[1] At the lower end of our temperature range the T_1 curves for ^{13}C and ^2D are parallel. This may be taken as a confirmation of the assumptions used.

We, therefore, separate the three relaxation rates that contribute to T_1 for the ring carbons of deuterated toluene in the following way: We extrapolate to zero frequency as described above and determine $1/T_1^{CS}$ on one hand and the sum $1/T_1^{DD} + 1/T_1^{SR}$ on the other. For the lowest temperature studied $1/T_1^{SR}$ can be neglected and the total relaxation rate is given by $1/T_1^{DD}$. Comparison with the deuteron data yields:

$$^{13}C T_1^{DD} = 400 \, ^1D T_1^Q \qquad [1]$$

[1] The quaternary carbon in the ring will have a much longer relaxation time and thus will not contribute appreciably to the observed signal under the conditions used to measure T_1.

at the lowest temperatures. We then assume that Eq. [1] holds for the entire temperature region studied. The result is shown in Fig. 3. Now we can also examine the product $1/T_1^{SR} \cdot 1/T_1^{DD}$ as is suggested by diffusion theory (14). We find that this product decreases monotonically as we increase the temperature, the deviation from the mean value being less than 15%. If diffusion theory applies, then T_1, as a function of temperature, is maximum if $T_1^{DD} = T_1^{SR}$. Our mean value of the product agrees remarkably well with the one obtained from the maximum T_1 using the assumption $T_1^{DD} = T_1^{SR}$.
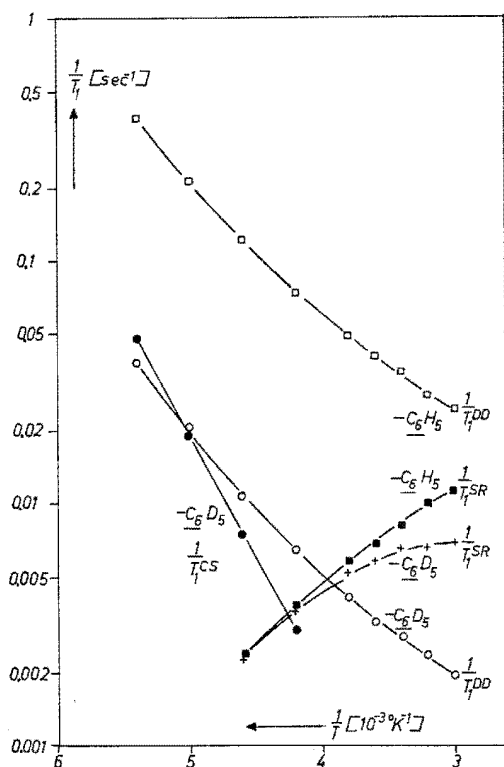

FIG. 3. ^{13}C dipolar and spin–rotational relaxation rates for the ring carbons in protonated and deuterated toluene. Also shown is $1/T_1^{CS}$ due to relaxation through anisotropic chemical shift in $C_6D_5CD_3$.

For the *protonated* compound we have to use a different approach for separating the two contributions because of different correlation times for protonated and deuterated species as will be discussed in detail below. We make use of the product $1/T_1^{DD} \cdot 1/T_1^{SR}$. We extrapolate our ^{13}C data for the protonated ring to a maximum $T_1 = 30$ sec. From this we determine the product of the individual rates using the assumption $T_1^{DD} = T_1^{SR}$. We then assume the same scaled temperature dependence of this product as we found for the deuterated ring. Since the total rate is given by the sum of the individual rates, $1/T_1^{DD}$ and $1/T_1^{SR}$ can then both be determined as functions of temperatures and the results are shown in Fig. 3.

2. Methyl Carbons

For the methyl carbons the procedure follows the same line. Again T_1^{PD} should be proportional to the deuteron relaxation time for the same reasons as outlined above for the ring. The contribution of the spin–rotation interaction in $C_6D_5CD_3$ at the lowest temperatures was estimated as 10 % of the total rate by extrapolating the high temperature branch of the T_1 curve (see Fig. 1). We then find

$$^{13}CT_1^{PD} = 65\,^{2D}T_1^Q. \qquad [2]$$

From this the separate contributions to T_1 were determined as shown in Fig. 4. Again the product of the two rates decreases with increasing temperature, the deviation from
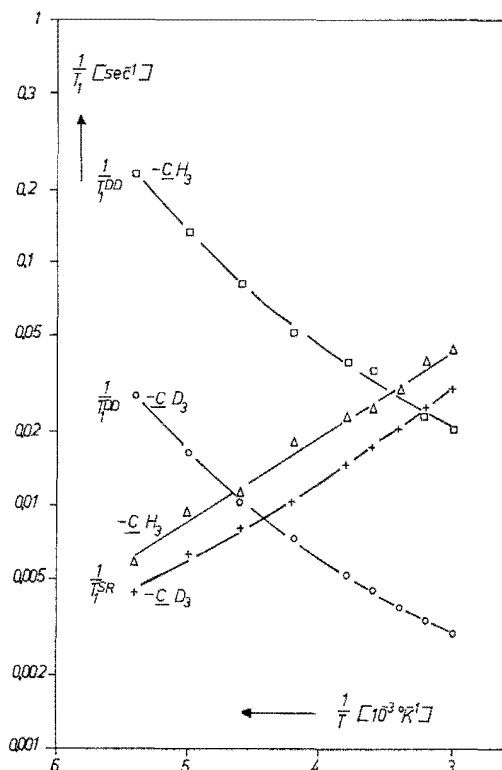

FIG. 4. ^{13}C dipolar and spin–rotational relaxation rates for the methyl carbon in protonated and deuterated toluene.

the mean value being less than 7 % and the mean value is the same as is found from the maximum T_1. The procedure to separate the two contributions to T_1 of the protonated species was the same as described above for the ring carbons and the results are shown in Fig. 4.

IV. DISCUSSION

1. Ring Carbons

a. Dipole–dipole coupling. The intramolecular dipole–dipole relaxation rate of ^{13}C in those five positions where a proton or deuteron is directly bound to the carbon is given by (11) (see also (2))

$$1/T_1^{PD} = (4/3)\,\gamma_{^{13}C}^2\,\gamma_S^2\,\hbar S(S+1)\,r_{C-H}^{-6}\,\tau_c, \qquad [3]$$

where S stands for proton or deuteron. Assuming equal correlation times τ_c and internuclear distances r_{C-H} for the protonated and deuterated molecules, we obtain a "scale factor":

$$R_{HD} \equiv \frac{T_1^{DD}(C-D)}{T_1^{DD}(C-H)} = 15.9 \qquad [4]$$

which should convert the ^{13}C dipolar relaxation times of the protonated and deuterated form of any molecule. Inspection of Fig. 3 shows that this scale factor is found experimentally to be approximately 11 instead of 15.9. A similar discrepancy was noticed by Olivson and Lippmaa (6) in other molecules. Taking into account that the average C–H distance appears to be 0.009 Å greater than the average C–D distance (15), the theoretical scale factor reduces to 15.15 for aromatic compounds. A further reduction of the discrepancy is obtained by realizing that the ^{13}C Z-magnetization does not relax with a single time constant as we tacitly assumed so far, but rather with two time constants. This is a consequence of the heteronuclear relaxation mechanism in which the partner spins to the ^{13}C, protons or deuterons, do not possess an independent infinitely fast relaxation path. This effect is negligible for the deuterated compound, but not for the protonated one, because the proton relaxation times are only about three times as short as the ^{13}C relaxation times. The accuracy of our data is not good enough to warrant an attempt to extract two time constants, but from the known ratios of $^{1H}T_1/^{13C}T_1$ we may infer that our graphical T_1 determination from the usual log-plot of the directly measured data yields T_1 which is about 10% longer than the value one *would* obtain if $^{1H}T_1/^{13C}T_1$ *was* very small.

Even if this is taken into account there still remains a marked difference between the theoretical and experimental scale factor. One, of course, could argue that T_1 found in the deuterated compound is shortened by paramagnetic impurities. This can be excluded by comparing ^{13}C and ^2D relaxation times. Using the value of 193 kHz for the quadrupole coupling constant of the ring deuterons (17) we calculate

$$^{13C}T_1^{DD} = 385 \, ^{2D}T_1^Q. \qquad [1a]$$

Comparison of Eqs. [1] and [1a] shows that the experimental data agree remarkably well with the prediction obtained from the known quadrupole coupling constant and internuclear distance.

As a consequence the ^{13}C data for the protonated and deuterated ring can only be explained by allowing for a difference in correlation time. Values for the correlation times τ_c obtained from the ^{13}C dipolar relaxation rates are shown in Fig. 5. It is seen that τ_c for the protonated and deuterated ring differ by about 20%. The plots of τ_c for $-C_6H_5$ and $-C_6D_5$ are almost parallel so that the difference at a given temperature cannot be explained by a difference in activation energy. It should be mentioned that the change in correlation time on isotopic substitution is approximately equal to the change of the mean moment of inertia Θ of the phenyl ring.

From this one is tempted to the following speculation: In the diffusion model the correlation times of angular reorientation τ_c and angular momentum τ_j for a spherical molecule are related by (14)

$$\tau_c \cdot \tau_j = \Theta/6kT. \qquad [5]$$

If we assume Eq. [5] to be valid with a mean value of Θ, then our data suggest that only τ_c is changed on isotopic substitution, whereas τ_j is the same for protonated and deuterated samples.

   b. Spin–rotation interaction. As seen from Fig. 3 the contribution of the spin–rotation interaction to the relaxation rate is by no means negligible for the ring carbons at the higher temperatures. Straight extrapolation of the low temperature data, however, grossly overestimates $1/T_1^{SR}$. A detailed analysis does not seem to be advisable since
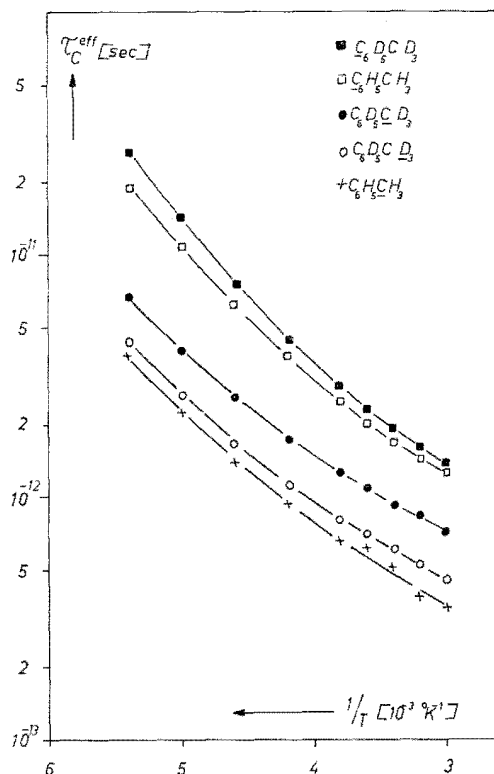

FIG. 5. Effective correlation times obtained from dipolar relaxation of ^{13}C and quadrupolar relaxation of ^{2}D for ring and methyl group in protonated and deuterated toluene.

neither the principal axis system nor the mean values of the spin–rotation interaction tensor are known.

   c. Anisotropic chemical shift. The complete orientation of the principal axis system of the chemical shift tensor for the ring carbons is not yet known (see, however, the last paragraph of this section). Therefore, it is difficult to estimate the effective correlation time for relaxation through anisotropic chemical shift. High resolution ^{13}C relaxation data for toluene at room temperatures (*18*) show that T_1 is equal for ortho and meta carbons and 27 % lower for the para carbons. This means that the effective correlation times at least for different directions within the plane of the ring differ only relatively little. In benzene the rotation about the sixfold axis is about three times as fast as about an axis in the plane (*19*). The anisotropy of the motion of the phenyl ring in toluene is

expected to be smaller. Nevertheless we tentatively use the effective correlation time found from the dipolar rate in order to calculate the anisotropy of the chemical shift of the ring carbons in toluene noting that the correct value of τ_c^{eff} for the chemical shift relaxation is probably larger because of the anisotropy of the motion as outlined above. We then obtain $\Delta\sigma = 295$ ppm which should serve as an upper limit for the shift anisotropy.[2] This value is larger than found in solid benzene (20, 21) at temperatures where the benzene ring is rapidly rotating about its sixfold axis. Since the value quoted (20, 21) $\Delta\sigma = 180$ ppm is an average over this motion our value appears to be not unreasonable. Since the completion of this work $\Delta\sigma$ has been determined for the ring carbons of toluene in the solid (21). The values obtained, $\sigma_{33} - \sigma_{11} = 225$ ppm and $\sigma_{33} - \sigma_{22} = 138$ ppm also represent averages over the different ring positions. The most shielded σ component is found for the magnetic field perpendicular to the ring. This supports our statement that the value we obtained from the relaxation data serves as an upper limit for the anisotropy of the chemical shift.

2. Methyl Carbons

a. Dipole–dipole coupling. The relaxation rate due to the intramolecular dipole–dipole coupling of ^{13}C with the protons or deuterons of the methyl group can be calculated to a very good approximation by treating the interaction with each proton (or deuteron) separately and adding the rates (11, 22). Then again the relevant directions for the intramolecular dipole–dipole relaxation of ^{13}C and of the quadrupole relaxation of ^{2}D should almost coincide. However, using the known internuclear distance and the quadrupole coupling constant of 165 kHz (17) we get from ^{13}C and ^{2}D relaxation rates greatly different values for the effective correlation time τ_c^{eff} for the deuterated methyl group as shown in Fig. 5. The effective correlation time for the methyl group is considerably shorter than that for the ring at a given temperature indicating that the methyl group rotates rapidly about its threefold axis at the temperatures studied. In order to calculate τ_c^{eff} in terms of τ_c (ring) and τ_c (internal) let us consider for simplicity a symmetric top and let us further assume that the diffusion model can be employed. Expressions for the effective correlation time in that case have been given by several authors (see e.g., 9, 23, 24)

$$\tau_c^{\text{eff}} = \tau_{c\perp}[1 - (3(\rho - 1)/(5 + \rho))\sin^2\vartheta(1 - (3(\rho - 1)/2(2\rho + 1))\sin^2\vartheta)] \qquad [6]$$

where ρ is the ratio of the correlation times of reorientation perpendicular and parallel to the symmetry axis ($\rho = \tau_{c\perp}/\tau_{c\parallel}$) and ϑ is the angle between the molecular vector of interest (e.g., a bond direction) and the symmetry axis. Allerhand (9) has pointed out that ρ cannot be determined accurately from this formula if $\rho \gg 1$ because small uncertainties in $\tau_{c\perp}$ and τ_c^{eff} will affect ρ drastically. Such uncertainties are unavoidable because the quadrupole coupling constant cannot be determined directly in the liquid. In Fig. 6 the ratio $\tau_c^{\text{eff}}/\tau_{c\perp}$ is plotted vs the angle ϑ. In the case of dipolar relaxation of ^{13}C or quadrupolar relaxation of ^{2}D in a rotating methyl group, ϑ is approximately equal to the tetrahedral angle. It is easily verified from Eq. [6] and is also seen from Fig. 6 that for $\rho \to \infty$ $d\tau_c^{\text{eff}}/d\vartheta$ has a maximum for $\vartheta = 109°$. This has the following two important consequences.

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[2] The expression for the relaxation rate due to anisotropic chemical shift (11) shows that is it not sensitive against the asymmetry parameter η.

First, in order to derive values of ρ for a rapidly rotating methyl group ($\rho \gg 1$) from quadrupole or dipole relaxation data one has to know not only the values of the quadrupole coupling constant (or the internuclear distance) with extremely high accuracy but also the angle between the Z-axis of the field gradient (or the internuclear vector) and the axis of symmetry.

Second, if the Z-axis of the field gradient is tilted by only a few degrees from the internuclear vector, the effective correlation times for quadrupole relaxation and dipole–dipole relaxation are significantly different.
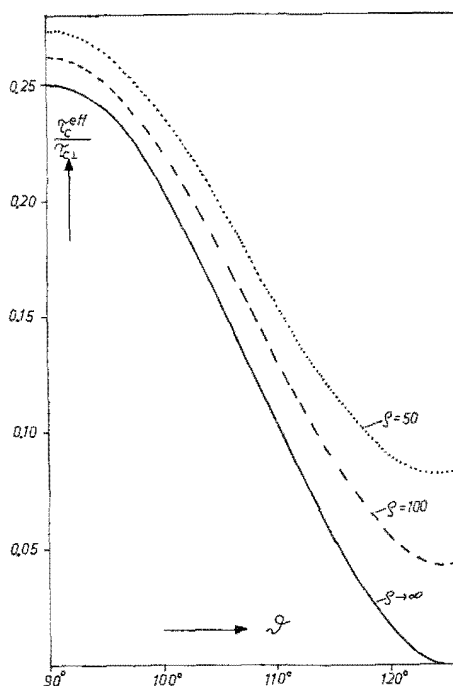

FIG. 6. Ratio of correlation times $\tau_c^{eff}/\tau_{c\perp}$ of a rapidly rotating symmetric rotor as obtained from Eq. [6]. For a definition of ρ and ϑ see text.

In our case of the methyl group in toluene we find at the lowest temperatures, for which the diffusion model is expected to provide a reasonable description, a value of 1.56 for the ratio of effective correlation times obtained from ^{13}C and ^{2}D data, respectively. For $\rho \gg 1$ (which is the case, as will be shown below) this ratio can be explained if the Z-axis of the field gradient differs by only 4.4° from the internuclear vector. This minimum deviation is obtained for $\vartheta_{C-D} = 107.3°$ and $\vartheta_{Z\text{-axis}} = 111.7°$. Such a deviation of the Z-axis from the bond direction is not unreasonable and has indeed been observed in HDO (25). We do not claim that from our relaxation data we can determine this angle of deviation accurately, but our data clearly are evidence that the Z-axis of the field gradient at the deuteron site in the methyl group of toluene does not coincide with the C–D internuclear vector.

It is also clear from this discussion that the fast internal rotation of the methyl group in toluene cannot be studied quantitatively by deuteron relaxation measurements alone.

It is shown in the next section that relaxation by spin–rotation interaction provides a much better means to study fast internal motions.

b. Spin–rotation interaction. Schmidt and Chan (*26*) showed that the contribution to the spin–rotational relaxation rate due to the overall rotation of the toluene molecule is negligible for the temperatures studied. In order to calculate the ^{13}C spin relaxation rate due to the *internal rotation* of the methyl group we assume that the axis of rotation remains fixed in space for a time that is long compared with the time between collisions
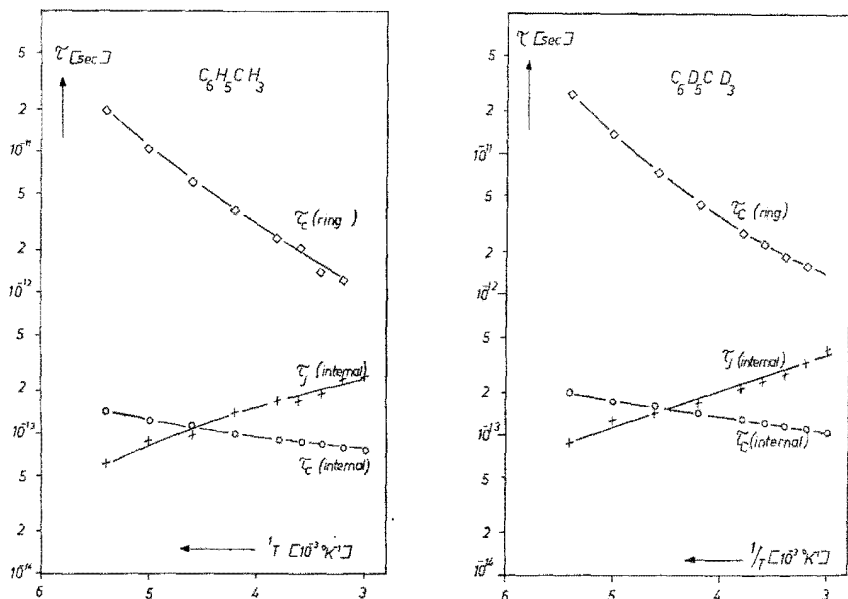

FIG. 7. Correlation times of angular momentum τ_j and of angular reorientation τ_c for the internal motion of the protonated and deuterated methyl group in toluene. Also shown are the effective correlation times for the ring.

of the methyl group. It is then easily shown (*27*) that the relaxation rate due to the spin–internal-rotation is given by

$$1/T_1^{SR} = (2/3)\, C_\parallel^2\, \Theta k T \tau_j \quad \text{(internal)} \qquad [7]$$

where the correlation time τ_j of the angular momentum $\mathscr{J}$ is defined by

$$\tau_j = \int_0^\infty \frac{\langle \mathscr{J}(t)\, \mathscr{J}(0)\rangle}{\langle \mathscr{J}(0)\, \mathscr{J}(0)\rangle}\, dt.$$

$C_\parallel$ is the spin–rotation constant and Θ the moment of inertia of the methyl group alone. $C_\parallel$ is equal to the ^{13}C spin–rotation constant in methane which is not known experimentally. It can be calculated from the known value in ^{13}CO and the isotropic chemical shift of $^{13}CH_4$ relative to ^{13}CO (for details see e.g., Refs. (*4*) and (*26*)). One then finds $C_\parallel/2\pi = -17.3$ kHz (see also Ref. (*26*)) for CH_3 and $C_\parallel/2\pi = -8.65$ kHz for CD_3.

From the measured relaxation rates $1/T_1^{SR}$ (see Fig. 4) one obtains immediately τ_j as a function of temperature for both CH_3 and CD_3 as shown among others in Fig. 7.

Comparison of the values found for τ_j with the time τ_f the free rotor takes to reorient through one radian, $\tau_f = (\Theta/kT)^{1/2}$ shows that τ_j and τ_f are of about the same magnitude in our temperature range. Thus the Debye diffusion model cannot be employed to calculate the reorientational correlation time τ_c of the methyl group from τ_j. A general relation between τ_c and τ_j is obtained by using Gordon's extended diffusion model (28) which has been applied to spherical molecules by McClung (29). His results have recently been shown to give good agreement with correlation times obtained from NMR
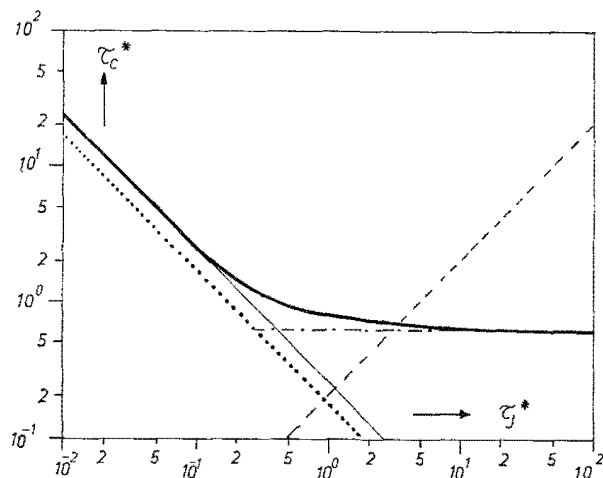

FIG. 8. Theoretical correlation times for a symmetric rotor with fixed axis ———, extended diffusion model; ——— Debye model; —·—·— perturbed free rotor model. For comparison · · · ·, Debye — and – – –, perturbed free rotor model for a spherical rotor.

relaxation times in the quasispherical molecule ClO_3F (30), in a case where the deviations from the Debye model are significant.

The extended diffusion model removes the restriction of small angle diffusive steps and therefore both the Debye diffusion model and the perturbed free rotor model are included as special cases. For convenience one defines the reduced correlation times (28)

$$\tau_j^* = \bar{\omega}\tau_j; \qquad \tau_c^* = \bar{\omega}\tau_c$$

with

$$\bar{\omega} = 1/\tau_f = (kT/\Theta)^{1/2}. \qquad [9]$$

For $\tau_j^* \ll 1$ the Debye model and for $\tau_j^* \gg 1$ the perturbed free rotor model are appropriate.

In our case of the internal rotation of the methyl group in liquid toluene τ_j^* ranges from 0.42 at low temperatures to 2.4 at higher temperatures, thus neither of the simple models can be used. In the Appendix McClung's treatment is modified for the case of a rotating methyl group whose axis is fixed in space for a time that is long compared with the time between collisions. The result is shown in Fig. 8 where τ_c^* is plotted vs τ_j^*. For $\tau_j^* \ll 1$ we obtain $\tau_c^* \propto 1/\tau_j^*$ as in the Debye model, whereas for $\tau_j^* \gg 1$ we get $\tau_c^* = $ const, i.e., $\tau_c \propto \tau_f$ contrary to the perturbed free rotor model which gives $\tau_c^* \propto \tau_j^*$. This is to be expected because for our one-dimensional rotor we ask for a reorientational correlation time depending on the *speed* of the internal rotation, whereas in the

perturbed free rotor model an average over the M substrates of J is taken. This average is dominated by the $M = 0$ term and largely independent of how fast the molecule rotates Therefore, in the perturbed free rotor model τ_c also answers essentially the question of how fast the angular momentum changes.

It is seen from Fig. 8 that in our case both τ_J^* and τ_c^* are close to unity in the entire temperature region studied. Using Fig. 8 we can finally obtain τ_c from τ_J determined experimentally and the results are shown in Fig. 7. The values of τ_J and τ_c are determined independently for the CH_3 and CD_3 groups. We find that the *ratio* for both correlation times is independent of temperature with mean values of 1.40 and 1.43 for τ_J and τ_c, respectively. This is remarkably close to $(\Theta_{CD_3}/\Theta_{CH_3})^{1/2} = (2)^{1/2}$, as is to be expected because both τ_J and τ_c are close to τ_f and thus proportional to $(\Theta/kT)^{1/2}$. It should be noted that this is an independent check of our method of separating the various contributions to the total relaxation rate.

Finally, since the effective correlation time for the ring carbons and the correlation time for the internal motion of the methyl group have been determined independently, it is meaningful to compare these correlation times (see Fig. 7). Since the temperature dependence for τ_c (ring) is much stronger than that of τ_c (internal) the ratio ρ of the correlation times changes from approximately 200 close to the melting point to approximately 13 at +60°C.

c. Anisotropic chemical shift. For both the protonated and deuterated methyl carbon no measurable contribution to relaxation due to anisotropic chemical shift was found. Because of the rapid reorientation of the methyl group, one can only expect to observe the anisotropy of the chemical shift averaged over this rotation. $\Delta\sigma$ has recently been determined for the methyl carbon in toluene (21). The value found, $\Delta\sigma = 28$ ppm, is quite small compared with the anisotropy of the chemical shift for the ring carbons (see above). Since the relaxation rate due to the anisotropy of the chemical shift is proportional to $(\Delta\sigma)^2$, it is clear that for the methyl carbon in toluene this rate will be only a few per cent of the value found for the ring carbons in agreement with our data.

V. CONCLUSIONS

To summarize our results we can state the following.

1. It is clear that ^{13}C relaxation times give much more reliable information about the molecular motion than do proton relaxation data.

2. Relaxation through anisotropic chemical shift is unimportant for carbons directly bound to hydrogen even at 60 MHz. By deuteration it is possible, however, to measure the relaxation rate due to anisotropic chemical shift in favorable cases.

3. Correlation times in the protonated and deuterated form of the same compound differ significantly. This means that correlation times obtained from ^2D relaxation studies cannot be used without correction for the protonated compound. This difference in correlation times also casts some doubt on the method usually employed to determine the intramolecular dipole–dipole relaxation rate for protons by measuring the proton relaxation times in mixtures of protonated and deuterated compounds.

4. Determination of the ^{13}C relaxation rates due to spin–rotation interaction provides a much better means for a quantitative study of fast internal motion (e.g. of a methyl group) than do deuteron relaxation times that have mostly been studied so far.

APPENDIX

In the Debye diffusion model it is assumed that a molecule undergoes many changes in angular momentum before its orientation changes appreciably. Gordon (28) has removed this restriction of small angle diffusive steps in his extended diffusion model which he applied to linear molecules. McClung (29) later treated spherical molecules and in this appendix the extended diffusion model is applied to a symmetric rotor the axis of which is fixed in space.

By that model we intend to describe a methyl group that undergoes rapid internal reorientation. The methyl group is attached to a bulky remainder of the molecule. This means that the orientation of the threefold axis of the methyl group will not change during a time which is long compared with the time between collisions the methyl group undergoes during its internal reorientation. On the other hand because of the re-orientation of the molecule as a whole, the orientation of the C_3 axis is randomized in a time which is short compared with the time of observation in an NMR experiment.

In the extended diffusion model it is assumed that the times over which the torques act on the molecule are short compared with the average period of free rotation of the molecule. In Refs. (28) and (29) two cases are considered designated as J and M diffusion, respectively. In both models the molecular reorientation is assumed to take place by diffusive steps of arbitrary size. In the J diffusion model it is assumed that at the termination of each diffusive step both magnitude and direction of the angular velocity vector $\boldsymbol{\omega}$ are randomized, whereas only the direction of $\boldsymbol{\omega}$ is randomized in the M diffusion model, the magnitude remaining unchanged. Both models are not appro-priate for a rapidly rotating methyl group for which we propose a model in which the direction of $\boldsymbol{\omega}$ remains fixed and its magnitude is randomized at each step. The following treatment is a special case of reference (29) and notation is chosen accordingly.

We want to relate the angular momentum correlation time τ_j to the reorientational correlation time τ_c. τ_c can be expressed as the Fourier transform $K_m^{(2)}(\omega_0)$ at $\omega_0 = 0$ of the reorientational correlation function $G_m^{(2)}(t)$ which by definition is:

$$G_m^{(2)}(t) = \frac{\langle Y_{2m}^*[\Omega(t)] \, Y_{2m}[\Omega(0)] + Y_{2m}[\Omega(t)] \, Y_{2m}^*[\Omega(0)]\rangle}{2\langle|Y_{2m}[\Omega(0)]|^2\rangle} \qquad [A1]$$

where Y_{2m} is a second-order spherical harmonic and the set of angles $\Omega(0)$ and $\Omega(t)$ describe the orientation of a vector fixed in the molecule relative to the laboratory system at times zero and t, respectively. The angular brackets indicate that an equi-librium ensemble average is to be taken. We want to study the internal motion of the methyl group and, therefore, the vector we are concerned about is perpendicular to the C_3 axis of the methyl group. Without loss of generality we define a molecular coordinate system such that its Z-axis lies along the C_3 axis and the vector whose orientation as a function of time we want to specify lies along its X-axis. At time zero, at the beginning of the first diffusive step (29), this molecular axis system is related to the laboratory axes by an Eulerian transformation $\mathscr{D}^{(2)}[\xi, \eta, \chi]$. As the methyl group rotates during the diffusive process, the orientation of $\boldsymbol{\omega}$ remains fixed and ω, the magnitude of $\boldsymbol{\omega}$ will have positive and negative values. The linear transformation $U^{(2)}(n, t)$ that relates the laboratory and molecular axes at time t after n diffusive steps is then given by

$$U^{(2)}(n, t) = \mathscr{D}^{(2)}[\omega_n(t - t_{n-1}), 0, 0] \mathscr{D}^{(2)}\left[\sum_{i=1}^{n-1} \omega_i(t_i - t_{i-1}), 0, 0\right] \mathscr{D}^{(2)}[\xi, \eta, \chi] \quad [A2]$$

where $t_1, t_2, \cdots, t_{n-1}$, respectively, are the times at which the 1st, 2nd, ..., $(n-1)$-th diffusive step ended and $\omega_1, \omega_2, \cdots, \omega_n$ are the magnitudes of $\boldsymbol{\omega}$ during the 1st, 2nd, $\cdots$ n-th step (29). During the n-th step the spherical harmonics $Y_{2m}[\Omega(t)]$ transform as

$$Y_{2m}[\Omega(t)] = \sum_k Y_{2k}[\Omega_0]\, U_{km}^{(2)}(n, t), \tag{A3}$$

where Ω_0 represents the orientation angles of the molecular vector of interest in the *molecular* axes system. Then for our special case $Y_{20}[\Omega_0]$ is constant and $Y_{2\pm1}[\Omega_0]$ vanishes. Following McClung we now represent the reorientational function as

$$G_m^{(2)}(t) = \sum_{n=1}^{\infty} p(n, t)\, G_m^{(2)}(n, t), \tag{A4}$$

where $G_m^{(2)}(n, t)$ is the reorientational correlation function for the methyl group in its n-th diffusive step at time t, and $p(n, t)$ is the probability that it will be in its n-th diffusive step at time t. It is also assumed that $p(n, t)$ is given by a Poisson distribution

$$p(n, t) = (t/\tau_j)^{n-1} \exp(-t/\tau_j)/(n-1)!. \tag{A5}$$

The probability that between time zero and t, exactly $n-1$ collisions have taken place during the time intervals t_1 to $t_1 + dt_1$; t_2 to $t_2 + dt_2$, $\cdots$, t_{n-1} to $t_{n-1} + dt_{n-1}$ is given by $(n-1)!\, dt_1\, dt_2 \cdots dt_{n-1}/t^{n-1}$ (28, 29). Also the averages over $t_1, t_2, \cdots, t_{n-1}$ are independent of the averages over all other variables (29). Taking the average over the initial orientations, we get for the reorientational function in the n-th diffusive step (for details see reference (29)):

$$G_m^{(2)}(n, t) = \frac{(n-1)!}{2t^{n-1}} \int_0^t dt_{n-1} \int_0^{t_{n-1}} dt_{n-2} \cdots \int_0^{t_2} dt_1$$

$$\times \left\langle \sum_{\alpha=\pm2} D_{\alpha\alpha}^{(2)}[\omega_n(t - t_{n-1}), 0, 0]\, D_{\alpha\alpha}^{(2)}\left[\sum_{i=1}^{n-1} \omega_i(t_i - t_{i-1}), 0, 0\right] \right\rangle_\omega, \tag{A6}$$

where the brackets $\langle \cdots \rangle_\omega$ indicate that the ensemble average over the angular velocities is to be taken. From the special form of the Wigner matrices $\mathscr{D}^{(2)}[\alpha, 0, 0]$ it follows:

$$G_m^{(2)}(n, t) = \frac{(n-1)!}{t^{n-1}} \int_0^t dt_{n-1} \int_0^{t_{n-1}} dt_{n-2} \cdots \int_0^{t_2} dt_1$$

$$\times \left\langle \{\cos 2\omega_n(t - t_{n-1})\} \prod_{i=1}^{n-1} \cos 2\omega_i(t_i - t_{i-1}) \right\rangle_\omega. \tag{A7}$$

The terms containing $\sin 2\omega_i(t_i - t_{i-1})$ vanish. From this we obtain for the reorientational correlation function:

$$G_m^{(2)}(t) = \sum_{n=1}^{\infty} \frac{\exp(-t/\tau_j)}{\tau_j^{n-1}} \int_0^t dt_{n-1} \int_0^{t_{n-1}} dt_{n-2} \cdots \int_0^{t_2} dt_1$$

$$\times \left\langle \{\cos 2\omega_n(t - t_{n-1})\} \prod_{i=1}^{n-1} \cos 2\omega_i(t_i - t_{i-1}) \right\rangle_\omega. \tag{A8}$$

As shown in Ref. (29) it is convenient to consider the Fourier transform $K_m^{(2)}(\omega_0)$ of the reorientational correlation function directly. We are interested in the reorientational correlation time

$$\tau_c = K_m^{(2)}(0) = \int\limits_0^\infty dt\, G_m^{(2)}(t). \qquad [A9]$$

The orientation of the rotation axis of the methyl group is randomized independently of the internal motion on a much slower time scale as we mentioned above. This ensures that τ_c is independent of m. Inserting [A8] for $G_m^{(2)}(t)$ and inverting the order of integrations over time (29), we obtain:

$$K_m^{(2)}(0) = \sum_{n=1}^\infty \frac{1}{\tau_j^{n-1}} \int\limits_0^\infty dt_1 \exp(-t_1/\tau_j) \int\limits_0^\infty d(t_2 - t_1) \exp\left(\frac{-(t_2 - t_1)}{\tau_j}\right) \cdots \int\limits_0^\infty d(t - t_{n-1})$$

$$\times \exp\left(\frac{-(t - t_{n-1})}{\tau_j}\right) \left\langle \{\cos 2\omega_n(t - t_{n-1})\} \cdot \prod_{i=1}^{n-1} \cos 2\omega_i(t_i - t_{i-1}) \right\rangle_\omega, \qquad [A10]$$

which can be readily solved to give

$$K_m^{(2)}(0) = \sum_{n=1}^\infty \tau_j \prod_n \langle 1/(1 + \omega_n^2 \tau_j^2) \rangle_\omega. \qquad [A11]$$

For ω_n we assume a Maxwell distribution for the one dimensional rotor and obtain:

$$K_m^{(2)}(0) = \tau_j X/(1 - X), \qquad [A12]$$

where

$$X = (2/\pi)^{1/2}(1/\bar\omega) \int\limits_0^\infty \frac{\exp(-\omega^2/2\bar\omega^2)}{1 + 4\omega^2 \tau_j^2}\, d\omega \qquad [A13]$$

with $\bar\omega = (kT/\Theta)^{1/2}$. This result resembles the expression obtained by McClung for the J diffusion model where the three dimensional Maxwell distribution is used instead (29).

In the limiting case $\bar\omega\tau_j \ll 1$ (Debye limit) expression [A12] can be solved analytically in exactly the same way as described by McClung (29). The result is

$$\tau_c = 1/4\bar\omega^2 \tau_j, \qquad (\bar\omega\tau_j \ll 1) \qquad [A14]$$

which is similar to the result for the spherical molecule

$$\tau_c = 1/6\bar\omega^2 \tau_j.$$

For the perturbed free rotor limit ($\bar\omega\tau_j \gg 1$) the exponential in the integrand of Eq. [A13] can be replaced by 1 and we get

$$\tau_c = 1/4(2\pi)^{1/2} \cdot 1/\bar\omega, \qquad (\bar\omega\tau_j \gg 1). \qquad [A15]$$

For the intermediate cases the integral [A13] has to be solved numerically. A discussion of the results which are shown in Fig. 8 is given in the main text.

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