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Peter A. Beckmann

Bryn Mawr College, pbeckman@brynmawr.edu

Myer Bloom

E. Elliott Burnell

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Deuteron Zeeman relaxation of CD₄ in the isotropic liquid, the liquid crystalline, and the solid state of several substances

Peter A. Beckmann^{a)}

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1W5, Canada

Myer Bloom

Department of Physics, University of British Columbia, Vancouver, British Columbia, V6T 1W5, Canada

E. Elliott Burnell

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1W5, Canada

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Measurement of deuteron Zeeman relaxation rates of CD₄ dissolved in benzene, hexane, and the liquid crystals MBBA, EBBA, and Merck ZLI-1132 and in pure CD₄ gas as a function of temperature at 30.7 and 61.4 MHz shows that the CD₄ is uniformly dispersed in the liquid solvents but resides in gas pockets when the solvents are in the solid state. Effects of centrifugal distortion were observed in the gas phase. The relaxation rate was found to be nearly independent of solvent, temperature, and pressure for the methane-liquid mixtures. This result is explained in terms of the extended diffusion model for the combined effects of free molecular rotation and collisions on the spectral density of quadrupolar interactions when the collisional and mean free rotational periods are of the same order of magnitude. It can also be interpreted in terms of the Fokker-Planck-Langevin model for rotational Brownian motion.

INTRODUCTION

Methane is an ideal molecule for studying fundamental molecular processes using nuclear magnetic resonance (NMR). The methane molecule is small and highly symmetric and a great deal is known about its electronic, vibrational, and rotational structure. NMR studies in pure CH₄ and its four deuterated analogs have yielded considerable information concerning fundamental intermolecular interactions and collisional processes under a variety of conditions, including the following three examples: (1) The NMR properties of solid methane at low temperatures are very sensitive to subtle effects associated with the permutation symmetry of the nuclear spins and the rotational tunneling of the molecules.¹ (2) The small NMR splittings observed in methane and its deuterated analogs dissolved in nematic liquid crystals provide information on the general nature of the average molecular fields in anisotropic fluids.² (3) Nuclear spin relaxation in methane gas provides information on collisional cross sections for molecular reorientation and on details of the spin-rotation, nuclear quadrupole, and the *intra*-molecular nuclear dipole-dipole interactions.³⁻⁶

The present study began as an empirical study of nuclear (deuteron) spin relaxation of CD₄ dissolved in various isotropic and anisotropic liquids in order to explore how the molecular reorientation rates of small molecules in solution are influenced by the orientational order of the solvent. To our surprise, the observed relaxation rates were all virtually identical and independent of temperature and pressure.

The main purpose of this paper is to present these experimental results and to explain the observed insensitivity of the relaxation rates in liquid solutions to the detailed molecular properties of the liquids. We are led by these results to focus our attention on the combined influence of free mo-

lecular rotation and collision induced molecular reorientation on the correlation function of the *intramolecular* quadrupolar interactions which are responsible for the deuteron spin relaxation in CD₄. Since the quadrupole coupling constant is known, it is possible to show from the universal value of the relaxation rate in all of the liquids studied that the collision frequency in all these liquids is, coincidentally, close to the average rotational frequency of CD₄. Under these conditions, we shall show that the spectral density of the quadrupolar interactions responsible for deuteron spin relaxation in CD₄ is only weakly dependent on the collision frequency thus accounting for the universal behavior observed in liquid solution.

In contrast to the results in liquid solutions, when the solvent is in the solid phase the CD₄ relaxation does depend on pressure. In addition, the relaxation rates are equal to those measured for the pure gas at the same pressure and temperature. Although we shall refer to these solid samples as solid solutions, they are in fact not homogeneous.

THE EXPERIMENT

Samples were made by dissolving CD₄ gas in benzene, hexane, *N-p*-methoxybenzylidene-*p'*-*n*-butylaniline (MBBA), *N-p*-ethoxybenzylidene-*p'*-*n*-butylaniline (EBBA), and Merck ZLI 1132, a mixture of three phenylcyclohexanes and one biphenylcyclohexane (1132). The liquids were well degassed on a vacuum line with many freeze-pump-thaw cycles. The CD₄ gas (99 at. % D) was obtained from Merck, Sharp, and Dohme and was used without purification. Samples using MBBA, EBBA, and 1132 as solvents were made by condensing 18 atm of CD₄ gas at room temperature above the solvent. Samples of benzene and hexane were made with CD₄ pressures of 15 atm and one benzene sample was made with a CD₄ pressure of 1.0 atm. In all samples, the ratio of the volume of the CD₄ gas to that of the

^{a)} On leave, 1984-1985, from the Department of Physics, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010.

liquid solvent or solid solvent plus dissolved CD₄ was about four to one. In addition, four gas samples were made with pressures of 6, 1, 0.5, and 0.1 atm CD₄ at room temperature. All pressures are accurate to $\pm 20\%$.

The deuteron magnetic resonance spectra and the deuteron Zeeman relaxation rates were measured on three Bruker nuclear magnetic resonance spectrometers: a WH-400 operating at 61.4 MHz, a CXP-200 operating at 30.7 MHz, and a considerably modernized BKR-322s operating at 30.7 MHz. To accommodate the long sample tubes, saddle coil inserts were constructed for the high-power, broadband probes used with the high-power CXP and BKR spectrometers. A standard high-resolution probe was used with the relatively low-power WH-400 spectrometer. Temperature was varied and controlled using either nitrogen gas (initially at 77 K) or air. Temperatures are known to ± 5 K for the benzene and hexane samples and to ± 1 K for the liquid crystalline samples where the observed quadrupolar splittings provide internal thermometry. The temperature gradient along the sample varied between 1 and 3 K depending on the size of the sample.

RESULTS

The NMR spectrum of CD₄ dissolved in an isotropic liquid is a single line. When the solvent is in the nematic state the CD₄ deuteron spectrum is dominated by a quadrupolar doublet. Spectra⁷ along with a thorough discussion concerning the details of the quadrupolar, dipolar, and scalar couplings observed in the spherical top CD₄ in nematic phases⁷⁻⁹ are presented elsewhere. The temperature dependence of the quadrupolar splittings for CD₄ in EBBA is shown in Fig. 1. Typical spectra for CD₄ in MBBA, as well as the temperature dependence of the quadrupolar splittings are also given elsewhere.^{10,11}

When the solvent is in the solid state the spectrum of CD₄ is a single line whose $\Delta\nu$ is determined by magnet inhomogeneity. This was poor at low temperatures, ranging from 10 to 100 Hz. Hence it is not possible to determine a spin-spin relaxation rate from the linewidth. However, it is clear that $\Delta\nu$ is orders of magnitude less than a typical solid

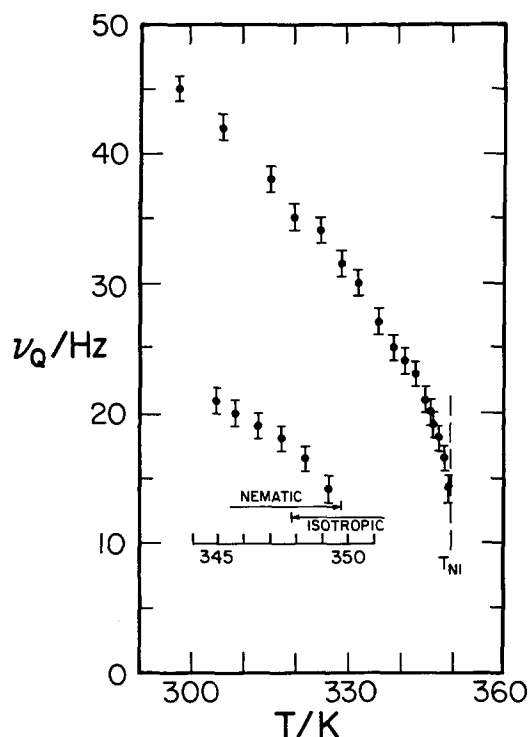


FIG. 1. Solute CD₄ deuteron quadrupolar splitting ν_Q vs temperature T for CD₄ in EBBA. The inset shows the two-phase region, due predominantly to temperature inhomogeneity, on an expanded scale.

line and that CD₄ is undergoing rapid fluid-like motion.

Deuteron Zeeman relaxation rates $R = T_1^{-1}$ of the solute CD₄ were measured at 30.7 and 61.4 MHz as a function of temperature T in three states of the solvents: solid S , nematic N , and isotropic liquid I as indicated in Table I. Relaxation measurements were also performed on the gas. R was measured using the usual inversion recovery pulse sequence with a relaxation delay of $\geq 8 T_1$. Appropriate phase cycling was used to reduce systematic errors. The R vs T results for the S , N , and I samples are presented in Figs. 2 and 3. For the long T_1 values, the experiments took between 4 and 24 h depending on signal to noise. The error bars in the figures are liberal estimates.

TABLE I. Experimental and theoretical parameters.

Sample No.	Solvent	CD ₄ P/atm	Range of T/K	Solvent state ^a	Range of R/s ⁻¹	Range of τ_θ /ps ^b	Range of ω_R^{-1} /ps	Range of $\omega_R \tau_\theta$ ^b
I	benzene	15 \pm 3	280-340	<i>I</i>	0.050-0.060	0.10-0.13	0.15-0.17	0.59-0.87
II	benzene	1.0 \pm 0.2	315-355	<i>I</i>	0.050-0.10	0.10-0.21	0.15-0.16	0.63-1.4
III	hexane	15 \pm 3	315-355	<i>I</i>	0.050-0.060	0.10-0.13	0.15-0.16	0.63-0.87
IV	MBBA	18 \pm 4	320-380	<i>I</i>	0.050-0.075	0.10-0.16	0.15-0.16	0.63-1.1
V	EBBA	18 \pm 4	360	<i>I</i>	0.057-0.065	0.12-0.14	0.15	0.80-0.93
VI	1132	18 \pm 4	360	<i>I</i>	0.053-0.066	0.11-0.14	0.15	0.73-0.93
IV	MBBA	18 \pm 4	280-340	<i>N</i>	0.060-0.095	0.13-0.20	0.15-0.17	0.87-1.3
V	EBBA	18 \pm 4	295-345	<i>N</i>	0.056-0.072	0.12-0.15	0.15-0.16	0.80-0.94
VI	1132	18 \pm 4	295-345	<i>N</i>	0.050-0.090	0.10-0.25	0.15-0.16	0.63-1.7
I	benzene	15 \pm 3	180-240	<i>S</i>	0.48 -0.56	1.0 -1.2	0.18-0.21	4.8-6.7
II	benzene	1.0 \pm 0.2	154-240	<i>S</i>	3.0-12	6.3-25	0.18-0.23	27-139
IV	MBBA	18 \pm 4	200-260	<i>S</i>	0.38-0.41	0.79-0.85	0.18-0.20	4.0-4.7

^a *I* = isotropic liquid, *N* = nematic, *S* = solid.

^b These numbers have been computed using the value $eV_{zz}Q/h = 168$ kHz. We believe that this value represents an approximate lower bound to the vibrationally averaged value of the quadrupole coupling constant. An upper bound is set by the equilibrium value of 189 kHz (Refs. 2 and 9). This upper bound would give values of τ_θ and $\omega_R \tau_\theta$ that are 21% smaller than those reported.

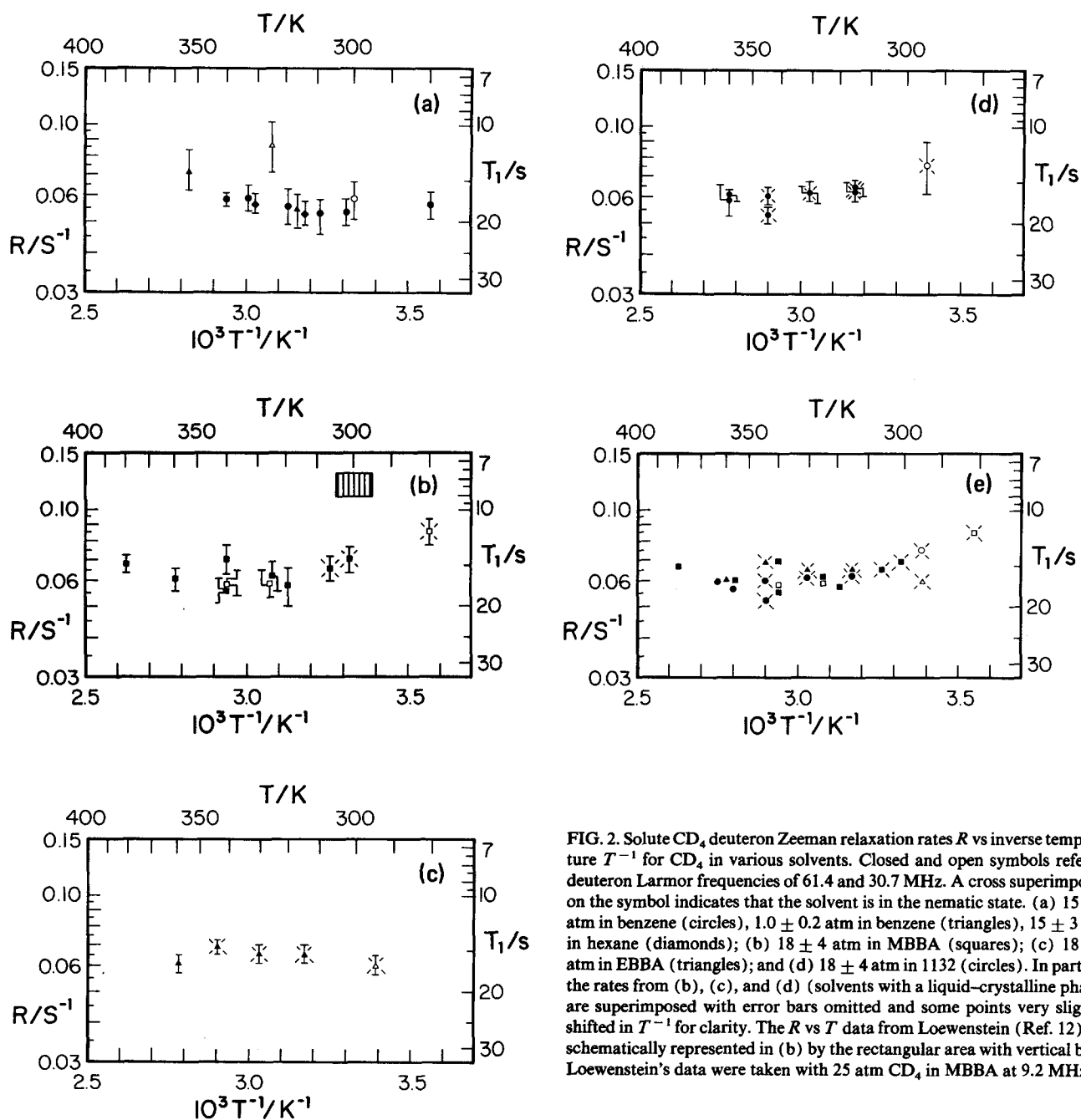


FIG. 2. Solute CD₄ deuteron Zeeman relaxation rates R vs inverse temperature T^{-1} for CD₄ in various solvents. Closed and open symbols refer to deuteron Larmor frequencies of 61.4 and 30.7 MHz. A cross superimposed on the symbol indicates that the solvent is in the nematic state. (a) 15 ± 3 atm in benzene (circles), 1.0 ± 0.2 atm in benzene (triangles), 15 ± 3 atm in hexane (diamonds); (b) 18 ± 4 atm in MBBA (squares); (c) 18 ± 4 atm in EBBA (triangles); and (d) 18 ± 4 atm in 1132 (circles). In part (e) the rates from (b), (c), and (d) (solvents with a liquid-crystalline phase) are superimposed with error bars omitted and some points very slightly shifted in T^{-1} for clarity. The R vs T data from Loewenstein (Ref. 12) are schematically represented in (b) by the rectangular area with vertical bars. Loewenstein's data were taken with 25 atm CD₄ in MBBA at 9.2 MHz.

The results in Figs. 2 and 3 are summarized in the sixth column of Table I. It is convenient to divide the results into two groups: solvent in a liquid state and solvent in the solid state. In the first nine rows of Table I where the solvent is in either the nematic (N) or isotropic liquid (I) state, R is generally between 0.05 and 0.07 s^{-1} . The benzene and hexane samples may have a slightly smaller R than the MBBA, EBBA, and 1132 samples in the vicinity of 310 K but other than that there is little reason to distinguish between the different solvents and between the two Larmor frequencies. Of special note is that there is little or no temperature dependence in R . Also there is no difference between the 1 and 15 atm samples of benzene. The single high R at 31 MHz for the low-pressure benzene sample [Fig. 2(a)] is considered an experimental anomaly: S/N was low and the experiment took 15 h on the CXP. Even though great care was taken to

rule out systematic errors it is impossible to consider all possible sources of such errors on commercial multifrequency spectrometers when S/N is very low and R very small (i.e., very long repetition periods). The second group in Table I is the last three rows where the solvent is in the solid (S) state. The R vs T values are shown in Fig. 3. Here there is a marked dependence on CD₄ pressure.

Loewenstein has measured R vs T at 9.2 MHz in a sample with about 25 atm pressure of CD₄ in MBBA.¹² The five values of R when the MBBA is nematic are schematically represented by the rectangular region with vertical bars in Fig. 2(b). These R values are more than twice the values found in the present 18 atm pressure sample. We do not understand the discrepancy between Loewenstein's and our results. However, effects such as paramagnetic impurities serve to increase R and smaller R values are normally con-

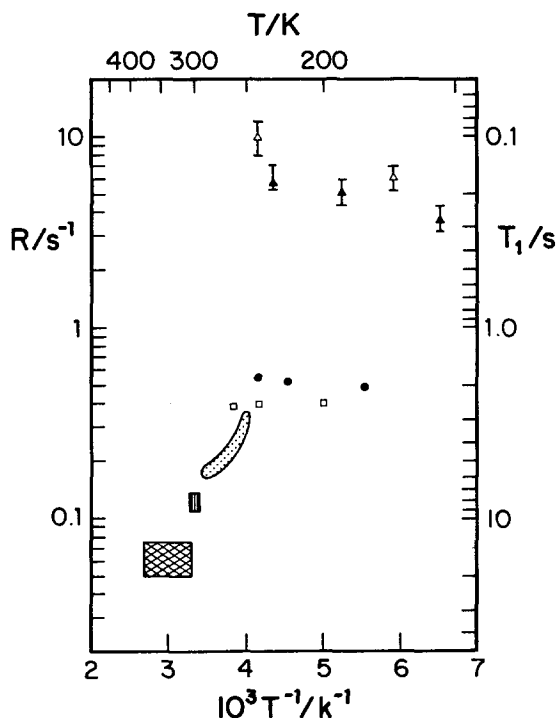


FIG. 3. Solute CD₄ deuteron Zeeman relaxation rates R vs inverse temperature T^{-1} in the solid state of the solvents: MBBA with a CD₄ room-temperature pressure of $P = 18 \pm 4$ atm (squares); benzene with $P = 15 \pm 3$ atm (circles); and benzene with $P = 1.0 \pm 0.2$ atm (triangles). Closed and open symbols refer to deuteron Larmor frequencies of 61.4 and 30.7 MHz. Where no error bars are shown, the uncertainties are within the size of the symbols. The R vs T^{-1} when the solvents are in the liquid state (Fig. 2) are shown schematically by the crosshatched region. Loewenstein's liquid values are shown by the rectangular area with vertical bars and his solid values by the dot filled region (Ref. 12).

sidered more reliable. Loewenstein's data are reproduced in Fig. 3. Also in Fig. 3 are Loewenstein's R vs T data when the solvent is in the solid state, represented by the dot-filled region.

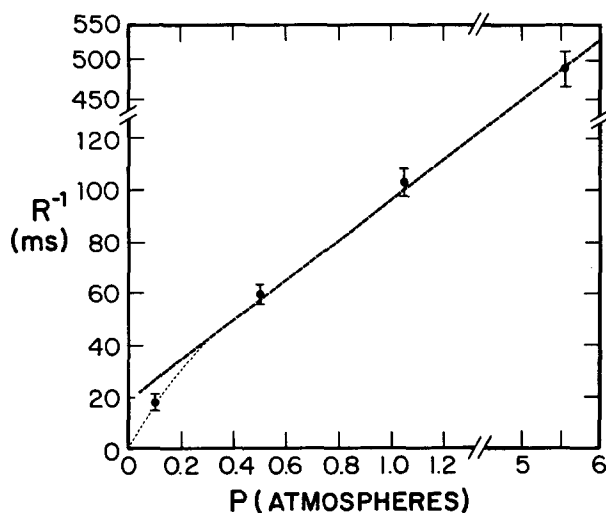


FIG. 4. Deuteron Zeeman relaxation time R^{-1} vs pressure P for CD₄ gas at $T = 295$ K. The dashed line is the fit to Eq. (12) and the dotted line is drawn to guide the eye.

Relaxation measurements have also been performed at 295 K on gaseous CD₄ at four densities. The results are presented in Fig. 4.

THEORETICAL CONSIDERATIONS

The deuteron relaxation rate for isotropically reorienting CD₄ molecules in the short correlation time regime can be expressed in the following simple form¹³:

$$1/T_1 = 1/T_2 = R = (3\pi^2/2)(eV_{zz}Q/h)^2 j(0), \quad (1)$$

where $eV_{zz}Q/h$ is the quadrupolar coupling constant of the deuterons in CD₄. Recent experiments on deuterated methanes dissolved in nematic solvents give a value of 189 ± 3 kHz for $(eV_{zz}Q/h)^{eq}$, the quadrupolar coupling constant for the equilibrium geometry for CD₄.^{2,9} The value averaged over molecular vibrations will be somewhat lower. In this paper we shall use the commonly accepted experimental value for hydrocarbons of 168 kHz.¹⁴ Early NMR relaxation experiments of gaseous CD₄ indicated a value between 130 and 200 kHz.⁶ The quantity $j(0)$ is the reduced spectral density of the quadrupolar interactions at zero frequency, i.e., $\tau_\theta \equiv j(0)$ has the dimension of time and is the area under the reduced $[g(0) = 1]$ correlation function of $Y_{2m}[\Omega(t)]$ associated with the orientation $\Omega(t)$ of a particular CD bond in a CD₄ molecule:

$$\tau_\theta \equiv j(0) = \int_0^\infty g(t) dt. \quad (2)$$

In liquid-crystal solvents, methane exhibits anisotropic couplings⁷ and there is a small correction term in Eq. (1).^{15,16} This term can be ignored since its effect is to change Eq. (1) by a fractional amount of order S_{CD} , where S_{CD} ($\sim 10^{-4}$ for CD₄) is the order parameter for a CD bond.

The time dependence of $g(t)$ is influenced both by free rotation and by collision induced reorientation of the CD₄ molecules. The short correlation time regime in a Zeeman relaxation study corresponds to $\omega_0 \tau_\theta \ll 1$, where ω_0 is the deuteron Larmor angular frequency. We shall now consider three models which relate τ_θ to dynamical molecular processes.

Model A. Assumption that the processes of free molecular rotation and molecular reorientation due to collisions are independent of each other. In this "strong collision model,"

$$g(t) = [g(t)]_R [g(t)]_C, \quad (3)$$

where the subscripts R and C refer to free rotation and collisions. In this model it is assumed that the mean time τ_C between collisions which randomize the molecular orientation is given by

$$\tau_C = \int_0^\infty [g(t)]_C dt. \quad (4)$$

The rotation is governed by the moment of inertia, $I_0 = 1.1 \times 10^{-46}$ kg m², of CD₄ and is conveniently expressed in terms of the rotational parameter Ω_R or T_R defined by

$$\hbar \Omega_R \equiv k T_R \equiv \hbar^2 / 2I_0. \quad (5)$$

Neglecting effects associated with permutation symmetry of the four deuterons in CD₄,^{3,4} the rotational correlation

function may be shown to be well approximated by Eq. (A13) of Bloom *et al.*⁶ At high temperatures ($T \gg T_R = 3.7$ K) this equation yields the following expression for the reduced rotational correlation function:

$$[g(t)]_R = 1/5 \int_0^\infty dJ P_J \sum_{n=-2}^{+2} \times \cos\{2nJ[1 + (n+1)/2J]\Omega_R t\}, \quad (6)$$

where, for a spherical top in the high-temperature approximation,

$$P_J = (2J+1)^2 \exp[-J(J+1)T_R/T] / \int_0^\infty (2J+1)^2 \times \exp[-J(J+1)T_R/T] dJ. \quad (7)$$

The five values of the index n arise from nonzero matrix elements of $Y_{2m}[\Omega(t)]$ for $\Delta J = 0$ ($n = 0$), $\Delta J = \pm 1$ ($n = \pm 1$), and $\Delta J = \pm 2$ ($n = \pm 2$),⁶ and their frequency factors $2nJ\Omega_R$ correspond to the (high-temperature approximation) Q ($\Delta J = 0$), P,R ($\Delta J = \pm 1$), and O,S ($\Delta J = \pm 2$) branches of the rotational Raman spectrum of CD₄ molecules.¹⁷ The integrals in Eq. (6) evaluated at high J (i.e., $J \gg 1$) give

$$[g(t)]_R = 1/5 \sum_{n=-2}^{+2} (1 - n^2\omega_R^2 t^2) \exp(-n^2\omega_R^2 t^2/2), \quad (8)$$

where

$$\omega_R = (kT/I_0)^{1/2} \quad (9)$$

defines the free rotation parameter ω_R . A plot of $[g(t)]_R$ vs t is shown in Fig. 5. The areas above and below $[g(t)]_R = 0.2$ indicated by cross hatching in this plot are equal and are associated with the oscillatory nature of the contributions of the $n = \pm 1, \pm 2$ terms to $[g(t)]_R$.

For a given $[g(t)]_C$ the relationship between τ_θ and τ_C is given by Eqs. (2), (3), (4), and (8). For the limiting case $\omega_R\tau_C \ll 1$ (strong friction limit) $\tau_\theta = \tau_C$ and for $\omega_R\tau_C \gg 1$ (weak friction limit) $\tau_\theta = \tau_C/5$, independent of the choice of $[g(t)]_C$. The passage from the strong to the weak friction limit ($\omega_R\tau_C \sim 1$) is illustrated in Fig. 6 for $[g(t)]_C = \exp(-t/\tau_C)$. As may be seen the variation of τ_θ with τ_C is linear in the strong and weak friction limits but is a more slowly varying function of τ_C in the intermediate region because the area under the correlation function vs time curve is a slowly varying function of τ_C under those conditions.

In spectroscopic terms, the passage from the strong to the weak friction limit can be understood in terms of the widths of the rotational lines becoming smaller as τ_C increases. In the weak friction limit, the $J \neq 0$ rotational Raman lines contribute negligibly to the low-frequency spectral density.

Model B. Assumption that collisions change the angular momentum of the molecules and that the molecules rotate freely between collisions: This "extended diffusion model" was first developed for diatomic molecules by Gordon.¹⁸ The model assumes that the duration of a single collision is $\ll 2\pi/\omega_R$. In this model τ_C is the mean time between collisions which either randomize both the magnitude and the orientation of the angular momentum of the molecule (J

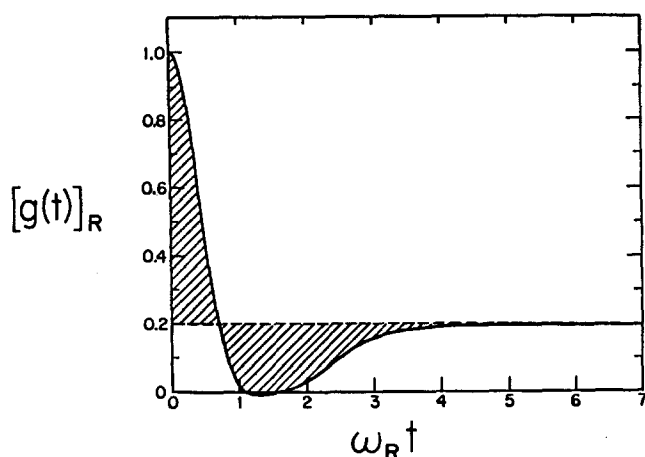


FIG. 5. The correlation function $[g(t)]_R$ vs $\omega_R t$ for freely rotating spherical top molecules in the classical limit. The shaded regions above and below $[g(t)]_R = 0.2$ have equal areas.

diffusion) or only its orientation (M diffusion). Unlike model A, the orientation of the molecule is not changed by the collision but evolves after the collision. The extended diffusion model has been applied to spherical top molecules by McClung¹⁹ who was written a comprehensive review²⁰ of the application of the extended diffusion models to the interpretation of various spectroscopic measurements of molecular reorientation in fluids. The result of McClung's analysis for J diffusion is that τ_θ is given by

$$\tau_\theta^{(2)} \equiv \tau_\theta \equiv j(0) = \tau_C X / (1 - X), \quad (10)$$

where

$$X = 4/(5\pi^{1/2}) \sum_{n=-2}^{+2} \int_0^\infty dx x^2 \exp(-x^2) / (1 + 2n^2\omega_R^2\tau_C^2 x^2). \quad (11)$$

Numerical calculations of Eq. (10) are plotted in Fig. 6 as $\omega_R\tau_\theta$ vs $\omega_R\tau_C$. As noted by McClung,¹⁹ this extended J -diffusion model gives the value $\tau_\theta = \tau_C/4$ in the weak friction limit. A striking feature of this plot is that τ_θ is predicted to go through a minimum corresponding to $\omega_R\tau_\theta \sim 0.65$ in

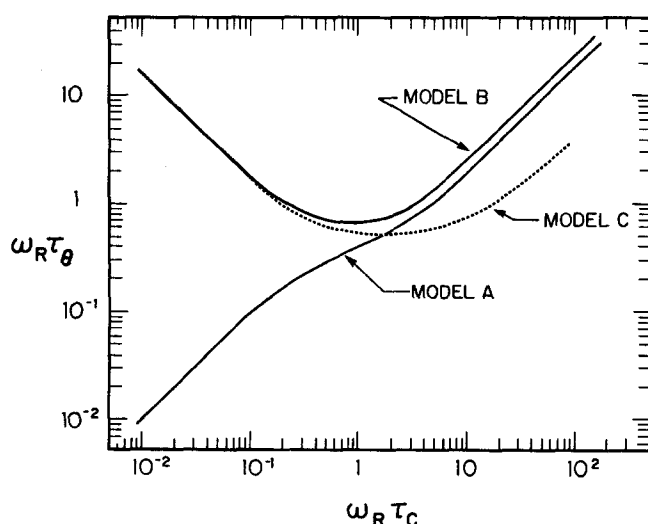


FIG. 6. $\omega_R\tau_\theta$ vs $\omega_R\tau_C$ for models A (strong collision), B (extended J diffusion), and C (Fokker-Planck-Langevin).

the vicinity of $\tau_C \sim \omega_R^{-1}$. This implies that as the molecular collision frequency is increased from low values (e.g., as in the dilute gas), the rate of molecular reorientation should increase, going through a maximum value where the collision frequency matches the average rotational frequency. This is a physically reasonable result. When $\omega_R \tau_C \gg 1$, the randomization of the angular momentum by each collision and the subsequent free rotation of the molecule through large angles between successive collisions results in a randomization of the molecular orientation during the time τ_C between successive collisions. On the other hand, when $\omega_R \tau_C \ll 1$, the molecules undergo only small rotations between successive collisions. Thus, the orientation of the molecule performs a random walk such that the mean squared rotation about a given axis in a time t is proportional to the number of collisions (t/τ_C) times the mean squared rotation angle $(\omega_R \tau_C)^2$ between successive collisions, i.e., $\langle \theta^2 \rangle_t \propto t/\tau_C \times (\omega_R \tau_C)^2 \propto t \tau_C$. Since $t = \tau_\theta$ for $\langle \theta^2 \rangle \sim 1$, $\tau_\theta \equiv \tau_\theta^{(2)} \propto \tau_C^{-1}$ in this regime. Detailed calculations give the result $\tau_\theta^{(2)} \tau_C = I_0/6kT$ appropriate to the Debye limit.^{19,21}

Model C. Assumption that molecules experience continuous intermolecular torques which produce only minute changes in angular velocity: An alternative and quite general treatment of rotational diffusion in dense fluids is provided by the Fokker-Planck-Langevin FPL model²² which has been further developed and compared with the extended diffusion and other models in a number of papers.²³⁻²⁶ Molecules in the FPL model experience continuous intermolecular torques which produce only minute changes in the angular velocity. The molecule is assumed to be an appropriately shaped solid object immersed in a continuous viscous fluid in which the intermolecular torques are proportional to the angular velocity. The model is based on a rotational Fokker-Planck equation for the angular momentum-orientation conditional probability density and a rotational Langevin equation for the angular velocity. The FPL model has been quite successful in the joint analysis of data from Raman and NMR measurements of pure CF₄ and of mixtures of CF₄ in Ar and Ne at high pressures.²⁵ In that work it was shown that the FPL model described the data much more accurately than the extended J -diffusion model (our model B).

Numerical calculations for the FPL model using the polynomial expansion of Eq. (4) and Table I of Ref. 24 for values of $\omega_R \tau_C < 2$ and estimated from Fig. 8 of Ref. 24 and Fig. 1 of Ref. 25 for $\omega_R \tau_C > 2$ are plotted in Fig. 6 as model C. As was the case for model B, a minimum is again predicted. One way of distinguishing between the extended diffusion and FPL models is that $\omega_R \tau_\theta$ is ~ 0.53 at the minimum in the FPL model, approximately 18% less than for the extended J -diffusion model (see Fig. 6). Also, as seen in Fig. 6, the plot of $\omega_R \tau_\theta$ vs $\omega_R \tau_C$ exhibits a much broader minimum in the FPL than in the extended J -diffusion model.

DISCUSSION

In order to interpret the results of the CD₄ relaxation measurements in liquid and solid solvents, it will be helpful to first examine the gas-phase measurements. On the basis of the gas-phase results, we shall show that the CD₄ molecules

reside in gas pockets for solvents in the solid state. By contrast, for each of the liquid solvents studied, τ_θ of CD₄ was found to be far too short to be explained in terms of gas pockets. In fact, we shall show that $\omega_R \tau_C$ is ~ 1 which represents the interesting regime between the strong and weak friction limits in which $j(0) = \tau_\theta$ is predicted to be relatively insensitive to τ_C . We believe that this is the underlying reason for the relative insensitivity of the relaxation rate in liquid solvents to the temperature and the chemical composition of the solvent.

Relaxation in CD₄ gas

The relaxation rate R in CD₄ gas can be expressed by Eqs. (1) and (2) so long as $\omega_0 \tau_\theta \ll 1$. The largest R in the gas samples in Fig. 4 is 56 s^{-1} at 0.1 atm which yields $\tau_\theta = 116 \text{ ps}$ and $\omega_0 \tau_\theta = 0.045$ at $\omega_0/2\pi = 61.4 \text{ MHz}$. A maximum in R will occur when $\omega_0 \tau_\theta \sim 1$. The relaxation cross sections for CH₄ and CD₄ are roughly equal.⁶ Therefore the values of τ_θ for these two molecules will be similar, and the maxima in the gas-phase values of R will occur at roughly the same pressure. For room temperature CH₄ gas at 30 MHz this pressure is 0.04 atm^{3,4}; the pressure at 61.4 MHz will be approximately 0.02 atm. Except for the 0.1 atm sample, our pressures are well above these values so that the short correlation time approximation is well satisfied. Since the gas pressures are sufficiently low that the weak friction limit also holds, the results of the theoretical section predict that $R \propto \tau_\theta \propto \tau_C$; τ_C , the mean time between collisions, is $\propto P^{-1}$, where P is the pressure. We find that over the range of pressures studied at 300 K, the plot of R^{-1} vs P is indeed linear but that the line does not pass through the origin. Our empirical fit to the experimental results in Fig. 4 is

$$R^{-1} = C(P + P_0), \quad (12)$$

where $P_0 = 0.23 \text{ atm}$ and $C = 0.0835 \text{ s}^{-1} \text{ atm}^{-1}$. The reason that the fit of Eq. (12) does not extrapolate to the origin is that the quadrupolar interaction is modulated by the centrifugal distortion (rotation-vibration) interaction which partially removes the $(2J + 1)^2$ degeneracy of each set of J states.^{3,4} Many of the populated rotational states at 300 K have centrifugal distortion splittings of the same order of magnitude as the collision induced reorientation frequency over the range of pressures studied in our experiments. Similar effects have been explored experimentally and theoretically in studies of proton Zeeman relaxation in CH₄ gas.^{3,4} The main difference between the CH₄ and CD₄ systems is that the relaxation in CH₄ is due to spin-rotation interactions while that in CD₄ is due to quadrupolar interactions. Examination of Figs. 3 and 4 in Ref. 3 shows that the plot of R^{-1} vs P in CH₄ is similar to our observations over the pressure range of 1 to 10 atm. Note that the difference between curves (B) and (D) of Fig. 4 of Ref. 3 is due to the centrifugal distortion terms. A detailed investigation of nuclear spin relaxation in CD₄ gas would involve a study over a wide range of densities and Larmor frequencies.

Relaxation of CD₄ "dissolved" in solids

A true homogeneous solid solution would be expected to yield CD₄ relaxation rates that are similar to those found

in liquid solutions of equal pressure. Our results do not agree with this picture because the observed R values (Fig. 3) are far too large. However, if we assume that the solute CD₄ molecules reside in gas pockets in the solid, we can use our empirical fit to the gas-phase results [Eq. (12)] to compute R from the known gas densities. For all samples and all CD₄ pressures (1 to 18 atm) used, the resulting values, corrected for temperature using the ideal gas law, are within 25% of the values measured when the solvent is in the solid state. This is strong evidence that the CD₄ molecules do indeed exist in gas pockets. It is not possible to say anything precise about the size of these gas pockets on the basis of the current measurements since we have no information on the effects of wall collisions on the molecular orientation. However, the size of the pockets could be determined by spin-echo studies of bounded translational diffusion.²⁷

Relaxation of CD₄ dissolved in liquids

When the preceding analysis for gas pockets is applied to the R vs T results for the liquid state of the samples it implies pressures of hundreds of atmospheres of CD₄. This is orders of magnitude greater than the known pressure and implies that the CD₄ is not in gas pockets when the solvent is in the liquid state. Indeed this is consistent with the observation that both the 1 and 15 atm samples of CD₄ in benzene give essentially the same R vs T curve when the solvent is in the liquid state. This also suggests that whatever the unknown concentrations of CD₄ in the liquid state of the solvent, we can safely assume an infinite dilution limit.

The results of Fig. 2 indicate that R is a relatively insensitive function of temperature, pressure, and solvent. If such results were interpreted according to model A, they would imply a smaller variation of τ_C than can reasonably be expected for such a wide variation of physical conditions. By contrast, models B and C offer a reasonable explanation for the insensitivity of R providing that the experimental values of τ_θ are close to the $\omega_R \tau_\theta$ minimum, which corresponds to $(\omega_R \tau_\theta)_{\min} \sim 0.65$ for model B and ~ 0.53 for model C. Examination of Table I shows, indeed, that the range of values obtained for $\omega_R \tau_\theta$ from the measurement of R in each of the solvents has a lower bound above and in some cases equal to $(\omega_R \tau_\theta)_{\min} = 0.65$, within the experimental error of about 10%. It is interesting that, in some of the plots of R vs temperature in Fig. 2 [see especially Figs. 2(a), 2(b), and 2(e)], there are clear indications that R goes through a minimum as the temperature is changed. According to McClung's theory of the extended J -diffusion model (see Fig. 1 of Ref. 19 and Fig. 6 of this paper), the collision frequency at $(\omega_R \tau_\theta)_{\min} = 0.65$ corresponds to $\tau_C^{-1} = \omega_R$. For the extended M -diffusion model (Fig. 2 of Ref. 19), the value of $(\omega_R \tau_\theta)_{\min} \sim 1$. Therefore, our measurements are in agreement with the predictions of the J -diffusion model but not with those of the M -diffusion model.

As discussed in the theoretical section, the FPL model (model C) also predicts a minimum value for $\omega_R \tau_\theta$; in this case the minimum is broad and value is predicted to be about 18% lower than that for the extended J -diffusion model. As described in Table I, our present knowledge of the quadrupole coupling does not allow us to distinguish between the

FPL and the extended J -diffusion models. If the value of $(eV_{zz}Q/h)$ in Eq. (1) turns out to be close to the recently proposed value of $(eV_{zz}Q/h)^{\text{eq}} = 189$ kHz,^{2,9} it would strongly favor the FPL model.

It is interesting that the values of $R \sim 0.1$ s⁻¹ obtained in liquid CD₄ at temperatures close to $T = 100$ K²⁸ also yield a value of $\omega_R \tau_\theta \sim 0.67$ very close to $(\omega_R \tau_\theta)_{\min}$.

CONCLUDING REMARKS

On the basis of a study of the spin-lattice relaxation rates of the deuteron spins in CD₄ dissolved in the liquid and solid phases of several organic solvents, we conclude that the CD₄ molecules reside in gas pockets in the solids and are uniformly dispersed in the liquids. A quantitative analysis of our relaxation measurements provides a striking demonstration of the validity of either the extended J -diffusion model or the Fokker-Planck-Langevin model for molecular reorientation of CD₄ molecules dissolved in liquids. Both these models predict a minimum in the plot of relaxation rate vs collision frequency, i.e., a maximum in T_1 . Our measurements support this prediction and, within the experimental uncertainty of about 10%, yield the predicted value for R at the minimum. A better determination of the vibrationally averaged quadrupolar coupling constant for the deuteron in CD₄ will allow one to distinguish between the FPL and extended J -diffusion models using the experiments reported here. The results are not consistent with the extended M -diffusion model or with a strong collision model.

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