

CARBON-13 RELAXATION MECHANISMS AND MOTIONAL STUDIES

IN SELECTED HALOMETHANE MOLECULES

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Introduction

The carbon-13 relaxation rates of several symmetric top halomethane species, CH_3I [1], CClBr_3 [2], CHBr_3 [3] and three others that have been shown to be quasi-symmetric top, CH_2Br_2 [4,5], CH_2Cl_2 [6], CH_2I_2 [7] were determined. These results were evaluated at two field strengths, 2.1 and 4.7 Tesla, at UNC-Wilmington and East Carolina University, respectively, and at an identical set of temperatures at each site. With these data and several theoretical models we were able to determine, or calculate, the contributions for all plausible relaxation modes.

Stokes-Einstein-Debye (SED) [8,9] theory of rotational diffusion and several variants to characterize the anisotropic reorientation of spheroids were also used to investigate for goodness of fit for hydrodynamically controlled rotational motion. In the hydrodynamic model, terms called "stick" and "slip" that attempt to describe the involvement of probe molecules and the solvent are exploited. The stick limit is normally encountered where the solute molecular radius is much larger than that of the solvent, while the slip condition is approached as solvent radius nears or exceeds that of the solute molecule. The J-extended diffusion model is used to determine inertial properties of rotational diffusion

[4] from J-diffusion to free rotation of the molecule.

Separation of R_1^{SC} from R_1^{tot} allowed calculation of $T_{1\text{Br}}^{\text{Q}}$ for Br and $^1J_{\text{C-Br}}$ for CClBr_3 , CH_2Br_2 , and CHBr_3 by use of plots of derived T_1^{SC} vs. $\Delta\omega^2$.

Experimental Section

Separation of Relaxation Mechanisms

T_1 values were obtained by the inversion recovery method using $(M_o, \cos\theta, T_1)$, a three parameter fit for magnetization, $M(\tau)$, as shown below.

$$M(\tau) = M_o[1 - (1 - \cos\theta)\exp(-\tau/T_1)] \quad (1)$$

Partitioning of relaxation rates into contributions by specific mechanisms was generally made with the following set of relationships in mind: When present, contribution to the relaxation rate by the scalar mechanism of the "second kind" (SC) is greater at 2.1 T than at 4.7 T while the reverse will be true for chemical shift anisotropy (CSA). Relaxation is more efficient at higher temperatures for SC while it is less so for CSA. Dipole-dipole (DD) relaxation is more rapid at lower temperatures while that of spin-rotation (SR) is less. These contributions

can be summed as follows where R_1^{tot} is the experimental rate of relaxation:

$$\frac{1}{T_1^{\text{tot}}} = R_1^{\text{tot}} = \frac{1}{T_1^{\text{DD}}} + \frac{1}{T_1^{\text{SR}}} + \frac{1}{T_1^{\text{CSA}}} + \frac{1}{T_1^{\text{SC}}} =$$

$$R_1^{\text{DD}} + R_1^{\text{SR}} + R_1^{\text{CSA}} + R_1^{\text{SC}} \quad (2)$$

Integration of the C^{13} signals with and without decoupling (pulse delay set to a full 10 T_1 [10]) for the protonated species, CH_3I , CH_2I_2 , CHBr_3 , CH_2Br_2 , and CH_2Cl_2 permitted determination of NOE values, η , and allowed direct calculation of the H contribution to R_1^{DD} [10] by the following relationship.

$$R_1^{\text{DD}}(C-H) = (\eta R_1)/1.988 \quad (3)$$

The evaluation of $\tau_c(C-H)$ [11] follows immediately from equation (4).

$$\tau_c(C-H) = (\gamma_C^2 \gamma_H^2 h^2 / 2\pi^2 r_{CH}^6) R_1^{\text{DD}}(C-H) \quad (4)$$

The dipole-dipole contribution to C from Br can then be calculated from the relationship below [12].

$$R_1^{\text{DD}}(C-H)/R_1^{\text{DD}}(C-Br) =$$

$$\frac{5(\gamma_{Br})^2 (r_{CH})^6 \tau_c(C-Br)}{(\gamma_H)^2 (r_{CBr})^6 \tau_c(C-H)} \quad (5)$$

A value for the quadrupole coupling constant, $(2\pi e^2 Qq/h)$, or T_1^Q for Br allows a calculation of $\tau_c(C-Br)$ in equation (6) [13] or (7) [14] respectively.

$$R_1^Q = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(\frac{2\pi e^2 Qq}{h} \right)^2 \tau_c \quad (6)$$

$$R_1^{\text{SC}} = \frac{4\pi^2 f^2}{3} S(S+1) \frac{T_1^S}{1+(\omega_I - \omega_S)^2 (T_1^S)^2} \quad (7)$$

R_1^{DD} subtracted from R_1^{tot} leaves R_1^{other} to be partitioned among the other contributions. The correlation time, τ_c , that was acquired from $R_1^{\text{DD}}(C-H)$ can be used in calculating R_1^{CSA} by

equation (8) [12] if σ_{per} and σ_{par} , the perpendicular and parallel components of the shielding tensor, are known.

$$R_1^{\text{CSA}} = \frac{2}{15} \gamma^2 H_0^2 (\sigma_{\text{par}} - \sigma_{\text{per}})^2 \tau_c$$

$$= \frac{8}{15} \pi^2 v^2 (\sigma_{\text{par}} - \sigma_{\text{per}})^2 \tau_c \quad (8)$$

A classic case for relaxation by the CSA mode was that of CH_3I [1]. We found that the CSA component to relaxation was significant since R_1^{tot} was much greater at 4.7 T than at 2.1 T and that this value decreased with an increase in temperature. Using the relationship

$$R_1^{\text{tot}} = R_1^{\text{DD}} + R_1^{\text{SR}} + R_1^{\text{CSA}} = R_1' + R_1^{\text{CSA}}$$

$$= R_1' + kv^2 \quad (9)$$

we utilized the fact that the variance in R_1^{tot} going from 2.1 to 4.7 T must be due to the CSA mechanism since the SR mechanism is independent of field strength. A plot of R_1^{tot} vs. v^2 at 303K has at the intercept $R_1^{\text{tot}} = R_1'$ and at this point the contribution of R_1^{CSA} to the value of R_1^{tot} vanishes. These results show the R_1^{CSA} contributions at 303K of 7.52×10^{-3} ($T_1^{\text{CSA}} = 133\text{s}$) at 4.7 T and 1.52×10^{-3} ($T_1^{\text{CSA}} = 659\text{s}$) at 2.1 T.

The $\tau_c(C-H)$ values were also employed in conjunction with the J-extended diffusion theory computer program by McClung to calculate τ_J , and its reduced form, τ_J^* , for symmetric tops [15, 16, 17]. The equation for R_1^{SR} is as follows [12]:

$$R_1^{\text{SR}} = (2\pi I k T / h^2) C_{\text{eff}}^2 \tau_J \quad (10)$$

A second program written by McClung relates R_1^{SR} to τ_J . This program requires values for I_x, I_z, τ_J and the spin-rotation tensor components, C_x and C_z , which are not generally available. These spin-rotation components can be approximated by the method of Flygare [18], which uses the facts that $\sigma_p(^{13}\text{CO}) = -259.5$ ppm and $\delta(^{13}\text{CO}) = -182.2$ ppm, and that the

difference between $\Delta\sigma_P$ and $\Delta\delta$ for ^{13}CO and the particular halomethane of interest, for instance, ($\Delta\sigma_P \equiv \sigma_P(\text{halomethane}) - \sigma_P(\text{CO})$, etc.) are the same. In general one must assume that $\Delta\sigma$ is zero. In this manner the relationship $I_z C_z \approx I_x C_x$ holds if $\Delta\sigma$ is small compared to σ_P .

Scalar relaxation of the "second kind" is expected to be a prevalent relaxation mechanism in the Br bearing halomethanes. It is predominantly the ^{79}Br isotope instead of ^{81}Br that makes the greatest contribution to relaxation of C-13 [19, 20]. This is due to the fact that the $(\omega_I - \omega_S)$ term in equation (7) is smaller for ^{79}Br . Scalar coupling is greater at 2.1 T than at 4.7 T since the $\Delta\omega$ term is smaller in the lower magnetic field. R_1^{SC} also increases with temperature. A plot of $\Delta\omega^2$ vs. T_1^{SC} gives

$$T_{1\text{Br}}^{\text{O}} = \sqrt{m/b} \quad (11)$$

and

$$J = \sqrt{T_{1\text{Br}}^{\text{O}} / (N(2/3)S(S+1)m)} \quad (12)$$

where m and b are the slope and intercept, and N is the number of Br atoms attached to the halomethane carbon atom.

Rotational Motion

In the limit of extreme narrowing, the small-step diffusion theory [13, 21, 22] predicts the relationship between τ_c and the diffusion constants D_x and D_z in a symmetric top environment by the following equation [4]

$$\tau_c = \frac{0.25(3\cos^2\theta-1)^2}{6D_x} + \frac{3\sin^2\theta\cos^2\theta}{5D_x+D_z} + \frac{0.75\sin^4\theta}{2D_x+4D_z} \quad (13)$$

where θ is the angle between the reorienting vector and the unique axis of rotation. This is the axis with the lowest moment of inertia. For example, this is the C_3 axis in CH_3I , but not in CHBr_3 , where the C-H vector is at 90° to this unique axis.

We have applied the J-extended diffusion theory of Gordon [23], as expanded to symmet-

ric tops by McClung [15, 16], an inertial model, to generate τ_J values using our previously determined $\tau_c(\text{C-H})$, or τ_c , parameters. In this model molecules undergo a period of free rotation generating angular momentum, then upon hard molecular collision randomize both magnitude and direction of this vector. In the small-step diffusion limit, $\tau_J \ll \tau_c$. Here the reduced correlation time, τ_J^* , is found to obey the following equation:

$$\tau_J^* = \tau_J \left(\frac{kT}{I} \right)^{\frac{1}{2}} \ll 1 \quad (14)$$

In addition, under these conditions, the rotational diffusion constants, D_z and D_x of equation (13) are related to τ_J by

$$D_z = \frac{kT}{I_z} \tau_J \quad \text{and} \quad D_x = \frac{kT}{I_x} \tau_J \quad (15)$$

In the inertial model $\tau_J \approx \tau_c$. The period of time for rotation through 1 radian, τ_f , as determined by the equipartition principle is given as [24]:

$$\tau_f = \left(\frac{I}{kT} \right)^{\frac{1}{2}} \quad (16)$$

Thus one is able to follow with this program by McClung the limits from small-step diffusion to free rotation where the rotations are inertially controlled.

At the other extreme, molecular shape instead of inertial effects may dictate the mode of rotational diffusion of a molecular species. Extension of the SED theory to prolate and oblate spheroids has produced many equations as boundary conditions for stick and slip rotational motion are considered for D_x and D_z . For instance, Perrin [25] was able to show a relationship between the Stokes diffusion constant, D_S , by solving the Navier-Stokes equation assuming a stick boundary condition.

$$D_i = \frac{1}{f_{p,i}} D_S = \frac{1}{f_{p,i}} \frac{kT}{8\pi r^3 \eta} \quad (17)$$

The factors $f_{p,x}$ and $f_{p,z}$ are functions of $\rho = b/a$ (<1 for a prolate and >1 for oblate spheroid). The

average molecular radius is used for r and the bulk viscosity for η .

Hu and Zwanzig [26] tackled the rotational diffusion problem by assessing the fact that the Perrin values, using the stick boundary condition, did not fit the experimental work well. They instead assumed a slip boundary condition in solving the Navier-Stokes equation. A separate value for a friction coefficient, ξ^* , was obtained and tabulated for each axis ratio for prolate and oblate spheroids. Under this treatment, motion parallel to the top axis would experience no tangential stress and would have the motion of a free rotor.

$$\tau_z^{fr} = \frac{41\pi}{180} \left(\frac{I_z}{kT} \right)^{\frac{1}{2}} \quad \text{and} \quad D_z^{fr} = \frac{1}{6\xi_z^{fr}} \quad (18)$$

There would be some solvent displacement possible about the x-axis for perpendicular rotational motion. The expression used here is

$$D_x = \frac{\rho^2}{f_{HZ}} D_S \quad (19)$$

where in our work $f_{HZ} = \xi^*/8$.

Gillen [27] and Griffiths [28] note that the D_x motion in some molecules is diffusionally controlled and as such may be treated by the Gierer-Wirtz microviscosity model [29]. The parallel motion, D_z , is treated in the slip boundary conditions, as essentially frictionless rotation.

$$D_x = \frac{1}{f_{GW}} \left(\frac{kT}{8\pi a^3 \eta} \right) \quad (20)$$

The Gierer-Wirtz factor, f_{GW} , is 0.1633 for neat liquids.

Tanabe [30, 31] has extended the Hynes, Kapral, Weinberg (HKW) model [32] to include nonspherical molecules in solution and in neat form.

$$D_i = \frac{1}{f_{pi}} D_S \left(1 + \frac{3\eta}{\beta + \alpha\eta} \right) \quad (21)$$

The α factor is zero for D_z but is fitted to a Hu-Zwanzig coefficient for D_x since even in the

case of slip ($\beta=0$) there is a finite friction coefficient.

Results

In CH_2Br_2 [4, 5] and CHBr_3 [3], DD and SC of the second kind were shown to be the important relaxation modes. The dipolar contribution to R_1 fell off as the temperature was raised, while the scalar coupling rate increased. There was a larger value for R_1 at any particular temperature at 2.1 T than found at 4.7 T. R_1^{SR} and R_1^{CSA} were calculated and found to be negligible. The dipole-dipole relaxation contribution from Br to C-13 was calculated by equation (5) and was much less than the experimental error. In CClBr_3 [3] the relaxation results were clearly scalar.

Average values of $^1J_{\text{CBr}}$ and $T_{1\text{Br}}^0$ for CClBr_3 , CH_2Br_2 , and CHBr_3 are respectively: 75 Hz and 4.3×10^{-6} ; 53 Hz and 4.3×10^{-6} ; 49.7 Hz and 8.03×10^{-7} .

The rotational diffusional motion of CH_2Br_2 and CHBr_3 as treated by the several models above, matches very closely that predicted by the J-extended diffusion model.

The trend towards faster relaxation rates in CH_3I [1] at 4.7 T compared to 2.1 furnishes positive evidence for the importance of CSA rather than SC in this molecular species. SR and DD are also found to be significant.

The approach taken here was that of Gillen [27] and Griffiths [28]. Motion about the top axis in CH_3I fit closely the Gierer-Wirtz microviscosity model with an average difference of less than 1% compared to experimental results. The excellent correlation indicates that the tumbling motion is hindered by viscous drag while the motion about the top axis is dominated by inertial effects.

The modes of relaxation in CH_2I_2 [7] were as follows: DD; the dominant mechanism, SR; a very small contribution, and SC; about 18% at all temperatures.

The J-extended diffusion model was a good predictor of rotational motion for both CH_2I_2 and CH_2Cl_2 [4,6].

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