The theoretical results indicate ready acid- and base-catalyzed rearrangements of all three quinonoid forms **1–3** to 7,8-dihydropterin at neutral pH, in agreement with experiment.[2] The quinonoid forms are predicted to be $\sim$26 kcal/mol higher in energy than 7,8-dihydropterin.

The reduction mechanism most consistent with the theoretical results involves preprotonation of quinonoid dihydropterin to form the cation **7** followed by hydride ion transfer to N5 to form directly the most stable N3(*H*) 5,6,7,8-tetrahydropterin. However, for the DHPR enzymic reduction, hydride ion transfer from NADH to N5 as the initial step to form the enzyme-stabilized tetrahydropterin anions **15** or **16** is also a possibility.

Registry No. 1 (R = H), 98482-79-2; **1** (R = CH₃), 83650-48-0; **2** (R = H), 98482-81-6; **2** (R = CH₃), 83650-46-8; **3** (R = H), 98482-80-5; **3** (R = CH₃), 98482-90-7; **4** (R = H), 98482-89-4; **5** (R = H), 98482-82-7; **5** (R = CH₃), 98509-13-8; **6** (R = H), 98509-14-9; **7** (R = H), 98482-84-9; **8** (R = H), 98482-83-8; **9** (R = H), 98482-85-0; **10** (R = H), 98482-86-1; **11** (R = H), 98482-87-2; **12** (R = H), 98482-88-3; **15** (R = H), 98482-93-0; **16** (R = H), 98482-92-9; **17** (R = H), 98482-91-8; dihydropteritine reductase, 9074-11-7.

Cartesian Correlation Times for NMR AX₂ Spin Systems

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Abstract: The spectral densities derived from the analysis of NMR relaxation in AX₂ spin systems are reexpressed in a Cartesian tensor basis. Four orientational correlation times are derived from the Cartesian spectral densities. For rigid spherical, symmetric, and asymmetric tops, abiding by a rotational diffusion model appropriate to the symmetry, there are one, two, and three distinct correlation times, respectively. Flexible molecules require more than three correlation times to describe the rotational dynamics. The Cartesian correlation times are model independent and provide a convenient reduced form for reporting experimental data.

In recent years dipolar spin relaxation has been used to study the dynamics of molecules in condensed phases. At first the relaxation behavior was observed for several pairs of dipolar coupled spins whose orientations in the molecule are linearly independent.[1] Later, as the relaxation behavior of several coupled spins became well understood,[2,3] coupled spin systems such as AX₂ (e.g., an ¹³CH₂ group) became useful probes of the dynamics.[4–10]

There is a wealth of information available in the relaxation of even a simple coupled spin system. The dipolar relaxation of an AX₂ spin system is characterized by four spectral densities, $J_{AX,AX}$, $J_{AX,AX'}$, $J_{AX,XX'}$, and $J_{XX',XX'}$ (where pairs of subscripts refer to a particular dipole–dipole interaction). Other contributions to the relaxation are treated as random magnetic fields. For molecules that rotate as rigid bodies and that obey a rotational diffusion equation, the NMR spectral densities yield the principal components of the diffusion tensor and an angle, specifying the geometry of the spin system. This kind of interpretation for rigid molecules is not possible for flexible molecules. The dynamics of nonrigid molecules are complex and can be represented by several models.[11–15] Because of this complexity, it is desirable that the dynamical information obtained from the NMR relaxation measurements is not biased toward any model. Such a model-free representation facilitates the comparison of the predictions of theory with experimental data.

In this paper, we convert the dipolar spectral densities describing AX₂ relaxation to a Cartesian basis, yielding orientational correlation times that have a simple physical interpretation and that can be compared directly with theory of molecular dynamics in fluids. As a simple illustration, the orientational correlation times for a rigid asymmetric top are calculated and discussed.

Relationship of Spectral Densities to Cartesian Correlation Times

The dipolar Hamiltonian for a pair of spins, *ij*, is:[16]

$$H^{ij}(t) = \frac{\gamma_i\gamma_j\hbar}{r_{ij}^3}\left\{(\vec{I}^i\cdot\vec{I}^j) - \frac{3}{r_{ij}^2}(\vec{I}^i\cdot\vec{r}_{ij})(\vec{I}^j\cdot\vec{r}_{ij})\right\} \quad (1)$$

where γ_i is the magnetogyric ratio of spin *i*, $\vec{r}_{ij}$ the internuclear vector connecting *i* and *j*, and $\vec{I}^i$ the spin operator. Equation 1 can be rewritten as

$$H^{ij}(t) = \frac{\gamma_i\gamma_j\hbar}{r_{ij}^3}(\vec{I}^i\cdot\tilde{D}_{ij}\cdot\vec{I}^j) \quad (2)$$

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where

$$\tilde{D}_{ij} = \tilde{\Pi} - \frac{3}{r_{ij}^2}(\vec{r}_{ij}\vec{r}_{ij}) \qquad (3)$$

and $\tilde{\Pi}$ is the unit dyadic. If the dipolar Hamiltonian is expressed in an irreducible spherical basis, then H^{ij} becomes[2]

$$H^{ij}(t) = \frac{\gamma_i\gamma_j\hbar}{r_{ij}^3}\left(\frac{6\pi}{5}\right)^{1/2}\sum_m V_2^m(ij)Y_2^{-m}(\Phi_{ij}(t)) \qquad (4)$$

where the V_2^m are irreducible spin tensor elements and the $Y_2^m(\Phi)$ are second-order spherical harmonics of polar angles Φ. The application of Redfield–Bloch theory[17] and the use of the Hubbard relationships for orientational correlation functions[18] allows one to describe spin relaxation in terms of spectral densities defined by:

$$J_{ijkl}(\omega) = \frac{\gamma_i\gamma_j\gamma_k\gamma_l\hbar^2}{r_{ij}^3 r_{kl}^3}\frac{6\pi}{5}\int_0^\infty \langle Y_2^0(\Phi_{ij}^{lab}(0))Y_2^0(\Phi_{kl}^{lab}(t))\rangle e^{-i\omega t}\,dt \qquad (5)$$

Space is isotropic for normal fluids in the absence of external fields. Even though space is isotropic, eq 5 measures the orientation of the vectors $\vec{r}_{ij}$ and $\vec{r}_{kl}$ with respect to the laboratory z axis. One can take advantage of the rotational invariance of the system arising from the isotropy of the fluid by making the replacement

$$\langle Y_2^0(\Phi_{ij}(0))Y_2^0(\Phi_{kl}(t))\rangle = \frac{1}{5}\sum_m\langle Y_2^m(\Phi_{ij}(0))Y_2^m(\Phi_{kl}(t))\rangle =$$

$$\frac{1}{4\pi}\langle P_2(\hat{r}_{ij}\cdot\hat{r}_{kl}(t))\rangle \qquad (6)$$

where $\hat{r}_{ij}$ and $\hat{r}_{kl}(t)$ are the unit vectors directed along the $\vec{r}_{ij}$ and $\vec{r}_{kl}(t)$ directions, respectively, and P_2 is the second-rank Legendre polynomial. The final equality in eq 6 follows from the spherical harmonic addition theorem. Equation 6 is useful becasue the time correlation function of P_2 can be related to the time correlation function of Cartesian tensors. Toward this end, consider the traceless second-rank tensor, $\tilde{T}_{ab}$, constructed from the unit vectors $\hat{a}$ and $\hat{b}$:

$$\tilde{T}_{ab} = \tfrac{1}{2}(\hat{a}\hat{b} + \hat{b}\hat{a}) - \tfrac{1}{3}\tilde{\Pi}(\hat{a}\cdot\hat{b}) \qquad (7)$$

In terms of the $\tilde{T}$ tensors we can write

$$\langle P_2(\hat{r}_{ij}\cdot\hat{r}_{kl}(t))\rangle = \tfrac{3}{2}\langle \tilde{T}_{ij,ij}:\tilde{T}_{kl,kl}(t)\rangle \qquad (8)$$

where ij or kl denote unit vectors aligned along the given dipole. The double dot notation stands for the inner product of the two tensors. Now eq 5 becomes

$$J_{ijkl}(\omega) = \tfrac{9}{20}K\int_0^\infty dt\, e^{-i\omega t}\langle \tilde{T}_{ij,ij}:\tilde{T}_{kl,kl}(t)\rangle \qquad (9)$$

where $K = \gamma_i\gamma_j\gamma_k\gamma_l\hbar^2/r_{ij}^3 r_{kl}^3$.

For the sake of simplicity in this derivation, two indexes are used or autocorrelation functions and all four indexes imply a cross-correlation term. Also, only the zero frequency (frequency independent or extreme narrowing limit) reduced spectral densities are considered:

$$\hat{J}_{ijkl} \equiv \frac{20}{9K}J_{ijkl}(\omega = 0) = \int_0^\infty dt\,\langle \tilde{T}_{ij,ij}:\tilde{T}_{kl,kl}(t)\rangle \qquad (10)$$

The Cartesian tensors, $\tilde{T}_{ab}$, have been introduced since the $\tilde{T}$ obey a particularly simple algebra and express model-independent correlation times in terms of an intuitve Cartesian basis set. To obtain these quantities from the measured spectral densities, the coordinate system shown in Figure 1 is used. Here, the x axis is the twofold symmetry axis of the AX_2 group: the y axis is directed along the X–X′ vector (pointing out of the plane), and

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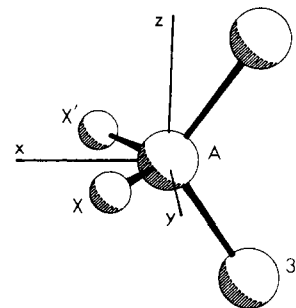(18) Hubbard, P. S. *Phys. Rev.* **1969**, *180*, 319.

Figure 1. Orientation of the AX_2 spin system in the Cartesian coordinate system.

$e_z = e_x \times e_y$. Using this coordinate system, we find that

$$\hat{r}_{XX'} = \hat{e}_y \qquad (11a)$$

$$\hat{r}_{AX} = \alpha\hat{e}_x + \beta\hat{e}_y \qquad (11b)$$

$$\hat{r}_{AX'} = \alpha\hat{e}_x - \beta\hat{e}_y \qquad (11c)$$

with $\alpha = \cos\theta/2$, $\beta = \sin\theta/2$, and θ is the XAX′ bond angle. Substitution of unit vectors lying along the x, y, and z axes into eq 7 leads to five independent Cartesian tensors ($\tilde{T}_{xx}$, $\tilde{T}_{yy}$, $\tilde{T}_{xy}$, $\tilde{T}_{xz}$, and $\tilde{T}_{yz}$). A sixth member, $\tilde{T}_{zz}$, is not independent of $\tilde{T}_{xx}$ and $\tilde{T}_{yy}$ as these three terms always sum to zero. In our case $\tilde{T}_{AX,AX}$, $\tilde{T}_{AX',AX'}$, and $\tilde{T}_{XX',XX'}$ do not have any z components, and this allows the expansion to be done in terms of $\tilde{T}_{xx}$, $\tilde{T}_{yy}$, and $\tilde{T}_{xy}$ alone.

Consequently, the tensors for the dipolar interactions are given in terms of the following Cartesian basis set:

$$\tilde{T}_{XX'} = \tilde{T}_{yy} \qquad (12a)$$

$$\tilde{T}_{AX} = \alpha^2\tilde{T}_{xx} + \beta^2\tilde{T}_{yy} + 2\alpha\beta\tilde{T}_{xy} \qquad (12b)$$

$$\tilde{T}_{AX'} = \alpha^2\tilde{T}_{xx} + \beta^2\tilde{T}_{yy} - 2\alpha\beta\tilde{T}_{xy} \qquad (12c)$$

To derive the Cartesian $\hat{J}$'s in terms of the dipolar $\hat{J}$'s, a number of identities are useful. The $\tilde{T}$ tensor is traceless and therefore

$$\tilde{T}_{xx} + \tilde{T}_{yy} + \tilde{T}_{zz} = 0 \qquad (13)$$

Time reversal symmetry further requires that

$$\langle \tilde{T}_{\alpha\beta}:\tilde{T}_{\gamma\delta}(t)\rangle = \langle \tilde{T}_{\gamma\delta}:\tilde{T}_{\alpha\beta}(t)\rangle \qquad (14)$$

The third useful relationship follows from the implied symmetry of the AX_2 spin system wherein the motion of the AX vector is assumed to be equivalent to the motion of the AX′ vector on the NMR time scale appropriate to spin relaxation. Under these conditions ($J_{AX} = J_{AX'}$), the cross term between $\tilde{T}_{xy}$ and $\alpha^2\tilde{T}_{xx} + \beta^2\tilde{T}_{yy}$ must vanish. To confirm this statement, consider the following argument. From eq 10 and 12, we have that

$$\hat{J}_{AX} - \hat{J}_{AX'} = 2\langle(\alpha^2\tilde{T}_{xx} + \beta^2\tilde{T}_{yy}):\tilde{T}_{xy}(t)\rangle \equiv 0 \qquad (15a)$$

As $\beta^2 = 1 - \alpha^2$, then

$$\alpha^2(\langle(\tilde{T}_{xx} = \tilde{T}_{yy}):\tilde{T}_{xy}(t)\rangle) + \langle\tilde{T}_{yy}:\tilde{T}_{xy}(t)\rangle = 0 \qquad (15b)$$

But eq 15b can hold for an arbitrary α only if both terms on the left side of eq 15b are zero and so,

$$\langle\tilde{T}_{xx}:\tilde{T}_{xy}(t)\rangle - \langle\tilde{T}_{yy}:\tilde{T}_{xy}(t)\rangle = \langle\tilde{T}_{zz}:\tilde{T}_{xy}(t)\rangle = 0 \qquad (16)$$

The last equality follows directly from the first two equalities and eq 13. Using the definition given in eq 12a–c along with eq 14 and 16, we find that

$$\hat{J}_{AX} = \alpha^4\hat{J}_{xx} + \beta^4\hat{J}_{yy} + 2\alpha^2\beta^2\hat{J}_{xx,yy} + 4\alpha^2\beta^2\hat{J}_{xy} \qquad (17a)$$

$$\hat{J}_{AX,AX'} = \alpha^4\hat{J}_{xx} + \beta^4\hat{J}_{yy} + 2\alpha^2\beta^2\hat{J}_{xx,yy} - 4\alpha^2\beta^2\hat{J}_{xy} \qquad (17b)$$

$$\hat{J}_{AX,XX'} = \alpha^2\hat{J}_{xx} + \beta^2\hat{J}_{yy} \qquad (17c)$$

$$\hat{J}_{XX'} = \hat{J}_{yy} \qquad (17d)$$

having defined

$$\hat{J}_{yy} = \int_0^\infty dt \, \langle \tilde{T}_{yy} : \tilde{T}_{yy}(t) \rangle; \ \hat{J}_{xx} = \int_0^\infty dt \, \langle \tilde{T}_{xx} : \tilde{T}_{xx}(t) \rangle;$$

$$\hat{J}_{xy} = \int_0^\infty dt \, \langle \tilde{T}_{xy} : \tilde{T}_{xy}(t) \rangle; \ \text{and} \ \hat{J}_{xx,yy} = \int_0^\infty dt \, c \langle \tilde{T}_{xx} : \tilde{T}_{yy}(t) \rangle$$

No other unique Cartesian power densities contribute to the dipolar power densities in AX$_2$ relaxation but, of course, the various Cartesian power densities may be expanded in terms of other nonunique power densities. Of the four Cartesian $\hat{J}$'s, only one, $\hat{J}_{xx,yy}$, is a cross term. The other three, J_{xx}, J_{yy}, and J_{xy}, are autocorrelation functions. Employing eq 13 to expand $\langle \tilde{T}_{zz} : \tilde{T}_{zz}(t) \rangle$, $\hat{J}_{xx,yy}$ may be related to correlation functions following involving only single tensor operators:

$$\langle \tilde{T}_{xx} : \tilde{T}_{yy}(t) \rangle = \tfrac{1}{2} \{ \langle \tilde{T}_{zz} : \tilde{T}_{zz}(t) \rangle - \langle \tilde{T}_{xx} : \tilde{T}_{xx}(t) \rangle - \langle \tilde{T}_{yy} : \tilde{T}_{yy}(t) \rangle \} \tag{18a}$$

or

$$\hat{J}_{xx,yy} = \tfrac{1}{2}(\hat{J}_{zz} - \hat{J}_{xx} - \hat{J}_{yy}) \tag{18b}$$

where $\hat{J}_{zz} = \int_0^\infty dt \, \langle \tilde{T}_{zz} : \tilde{T}_{zz}(t) \rangle$. If we substitute eq 18b into (17a,b) and solve for the four remaining Cartesian tensors, then

$$\hat{J}_{yy} = \hat{J}_{XX'} \tag{19a}$$

$$\hat{J}_{zz} = \frac{1}{\alpha^4} \left\{ \tfrac{1}{2} \hat{J}_{AX} + \tfrac{1}{2} \hat{J}_{AX,AX'} + (\alpha^2 - \beta^2)^2 \hat{J}_{XX'} + 2(\alpha^2 - \beta^2) \hat{J}_{AX,XX'} \right\} \tag{19b}$$

$$\hat{J}_{xx} = \frac{1}{\alpha^4} \left\{ \tfrac{1}{2} \hat{J}_{AX} + \tfrac{1}{2} \hat{J}_{AX,AX'} + \beta^4 \hat{J}_{XX'} - 2\beta^2 \hat{J}_{AX,XX'} \right\} \tag{19c}$$

$$\hat{J}_{xy} = \frac{1}{8\alpha^2\beta^2} \{ \hat{J}_{AX} - \hat{J}_{AX,AX'} \} \tag{19d}$$

It will be useful later in our discussion to have an expression for $\hat{J}_{xx-yy} = \int_0^\infty dt \, \langle (\tilde{T}_{xx} - \tilde{T}_{yy}) : (\tilde{T}_{xx} - \tilde{T}_{yy})(t) \rangle$. From eq 18b and 19a–c, we obtain

$$\hat{J}_{xx-yy} = 2\hat{J}_{xx} + 2\hat{J}_{yy} - \hat{J}_{zz} \tag{19e}$$

The orientational correlation time is the zero frequency part of the normalized correlation functions associated with a particular vector or tensor in the molecule. Given the reduced spectral densities, $\hat{J}_{xx}$, $\hat{J}_{yy}$, $\hat{J}_{zz}$, $\hat{J}_{xy}$, and $\hat{J}_{xx-yy}$, the correlation times are

$$\tau_q \equiv \int_0^\infty dt \, \langle \tilde{T}_q : \tilde{T}_q(t) \rangle / \langle \tilde{T}_q : \tilde{T}_q \rangle = \hat{J}_q / \langle \tilde{T}_q : \tilde{T}_q \rangle \tag{20}$$

with normalization constants,

$$\langle \tilde{T}_q : \tilde{T}_q \rangle = \begin{cases} \tfrac{2}{3} & q = xx, yy, zz \\ \tfrac{1}{2} & q = xy, xz, yz \\ 2 & q = xx-zz, xx-yy, yy-zz \end{cases} \tag{21}$$

Although our primary intention is to apply the derived expressions for the correlation times to analyze the rotational dynamics of nonrigid molecules, it is useful to document properties of the correlation times for rigid molecules. We do so in the following section.

Interpretation of the Correlation Times for a Rigid Asymmetric Top

The above results may be compared with previous work on rigid asymmetric top molecules undergoing diffusion with a diffusion tensor diagonal in the chosen x, y, z coordinates.

Elsewhere the correlation times for the Cartesian tensors have been calculated.[19] Using similar techniques, one obtains:

$$\tau_{xx} = (4D_x + D_y + D_z)/12d \tag{22a}$$

$$\tau_{yy} = (4D_y + D_x + D_z)/12d \tag{22b}$$

$$\tau_{zz} = (4D_z + D_x + D_y)/12d \tag{22c}$$

$$\tau_{xy} = 1/(D_x + D_y + 4D_z) \tag{22d}$$

and

$$\tau_{xx-yy} = (D_x + D_y)/4d \tag{22e}$$

where

$$d = D_x D_y + D_y D_z + D_z D_x \tag{22f}$$

In the diffusion limit the correlation times τ_{xy}, τ_{xx}, τ_{yy}, and τ_{zz} (or τ_{xx-yy} as desired) are not linearly independent, but are determined by the three diffusion constants D_x, D_y, and D_z. The remaining piece of experimental information can then be used to determine the XAX' angle, θ. Thus, when the diffusion equation is applicable, three correlation times (e.g., τ_{xx}, τ_{yy}, and τ_{zz}) are sufficient to specify the motional features important to spin relaxation. Under these conditions, the additional correlation times can be derived from the other three, namely,

$$\tau_{xx-yy} = \tfrac{2}{3}(\tau_{xx} + \tau_{yy}) - \tfrac{1}{3}\tau_{zz} \tag{23a}$$

and

$$\tau_{xy} = \Lambda / 3\tau_{zz} \tag{23b}$$

$$\Lambda = 2\tau_{xx}\tau_{yy} + 2\tau_{xx}\tau_{zz} + 2\tau_{yy}\tau_{zz} - \tau_{xx} - \tau_{yy} - \tau_{zz} \tag{23c}$$

In the spherical top limit,

$$D_x = D_y = D_z = D \tag{24}$$

and the orientational correlation times are all equal to

$$\tau = 1/(6D) \tag{25}$$

For a symmetric top molecule with $D_\perp = D_x = D_y$, and $D_\parallel = D_z$, the correlation times are

$$\tau_{zz} = 1/(6D_\perp) \tag{26a}$$

$$\tau_{xx} = \tau_{yy} = \frac{1 + \epsilon}{4D_\parallel + 2D_\perp} = \frac{(5D_\perp + D_\parallel)}{12D_\perp(D_\perp + 2D_\parallel)} \tag{26b}$$

$$\tau_{xy} = \tau_{xx-yy} = \frac{1}{4D_\parallel + 2D_\perp} \tag{26c}$$

with $\epsilon = (D_\parallel - D_\perp)/6D_\perp$. In the symmetric top case only two τ's are required to characterize rotational motion as it is possible to express τ_{xy} in terms of τ_{xx} and τ_{zz},

$$\tau_{xy} = (4\tau_{xx} - \tau_{zz})/3 \tag{26d}$$

Once again the additional relaxation data can be used to determine the XAX' angle, θ.

Consider the relations for the symmetric top derived in eq 26. If $D_\parallel > D_\perp$, then the correlation times satisfy the inequality

$$\tau_{zz} > \tau_{xx} = \tau_{yy} > \tau_{xy} = \tau_{xx-yy} \tag{27}$$

The times τ_{xy} and τ_{xx-yy} are equal since both measure the rotational dephasing of a common basis oriented in the plane perpendicular to the z symmetry axis. τ_{xy} is less than τ_{xx} and τ_{yy} because any rotation about the x, y, or z axes will decorrelate the $\tilde{T}_{xy}$ tensor. In contrast, the tensor functions $\tilde{T}_{xx}$ and $\tilde{T}_{yy}$ are invariant with respect to rotations about the x and y axes, respectively. Stated simply, τ_{xy} "senses" rotations about all axes, whereas τ_q (for $q = xx, yy, zz$) "senses" only reorientation about the two axes orthogonal to the q axis.

Discussion

The two autocorrelated dipolar power densities (J_{AX} and $J_{XX'}$) and the two cross-correlated dipolar terms ($J_{AX,AX'}$ and $J_{AX,XX'}$)

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have been expressed in terms of four autocorrelated reduced Cartesian power densities. The Cartesian form of the spectral densities leads to expressions for the correlation times, and the correlation times have a simple physical interpretation.

The Cartesian correlation functions describe the reorientation of geometrical constructs having the shape of d orbitals. Thus, τ_{xx}, τ_{yy}, and τ_{zz} are the correlation times for the motion of a d_0 structure fixed along the x, y, and z axes, respectively, while τ_{xy} and τ_{xx-yy} are the correlation times of a clover leaf structure of the d_{xy} and d_{xx-yy} form.[20] As with d orbitals, τ_{xx-yy} is linearly dependent upon τ_{xx}, τ_{yy}, and τ_{zz} and so a degree of arbitrariness in our final choice of basis must be recognized. Under axial symmetry about the z axis, τ_{xy} and τ_{xx-yy} are equal as are τ_{xx} and τ_{yy}. Rotational correlation functions exist for xz and yz constructs, but for the AX_2 spin system discussed in this paper it is not possible to determine these specific power densities experimentally from the spin-relaxation data because of the symmetry and orientation of the spin system.

When a rigid molecule rotates in accord with the small step diffusion model, the Cartesian correlation functions (either in the form of $\mathcal{J}$'s or τ's) may be directly related to the rotational diffusion tensor. The only case treated here is that where the principal axes of the molecular diffusion tensor are coincident with the symmetry axes of the AX_2 spin system. Other spatial relationships could be derived as needed. In Cartesian form the power densities are

free of molecular structural parameters and relate directly to the rotational diffusion tensor. If the molecule is rigid and conforms to the diffusion equation, the four otherwise linearly independent correlation times can be expressed in only three terms (τ_{xx}, τ_{yy}, and τ_{zz} are a convenient subset), leaving the fourth dipolar power density available for setting one of the structural parameters (e.g., the XAX' angle). Symmetric top and spherical top conditions reduce the number of correlation functions to two and one, respectively.

A direct relationship between τ's and the D's is not known in cases where the rotational dynamics are not diffusional. For molecules undergoing extended free precession or large angle jumps, or for flexible molecules, there is no simple relationship between a correlation time a diffusion coefficient. Likewise, more than three correlation times are necessary to define the dynamics completely as has been shown by Lynden-Bell.[21] Nonetheless, because the Cartesian correlation times or power densities are model independent, they continue to be an appropriate parameter set to characterize the motions important in spin relaxation. The four experimental correlation times provide a stiff test of alternative theoretical models of molecular motion. When the molecular motion has important frequency components in the relevant NMR frequency range, no more powerful spectroscopic method exists for characterizing the anisotropy of motion affecting the coupled spins.

(20) Please note that a d_0 construct arises from the zeroth projection of the second-order Legendre polynomial, $\langle P_2(e_i(0)\cdot e_i(t))\rangle$, where e_i in the dot product is the unit vector pointing along the $i(x,y,z)$ axis. The d_{xy} construct, while not a zeroth projection of P_2 is no less important in a complete description of the molecular motion and may also be expressed as a dot product of unit vectors, i.e., $2J_{xy} = \int_0^\infty dt\,[\langle P_1(e_x\cdot e_y(t))P_1(e_y\cdot e_x(t))\rangle + \langle P_1(e_y\cdot e_y(t))P_1(e_x\cdot e_x(t))\rangle]$. At time zero the first term is zero and likely never grows very large. The second term, however, starts at unity, but will rapidly, compared with a P_2 function, drop to zero because if the motion does not dephase the dot product $e_x e_x(t)$ it must of necessity dephase the dot product in y and vice versa.

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Rotational Dynamics of Flexible Alkanes. An NMR Coupled Relaxation and a Brownian Dynamics Study[1]

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Abstract: The selectively labeled nonanes $C_4D_9{}^{13}CH_2C_4D_9$ and $C_7D_{15}{}^{13}CH_2CD_3$ and the heneicosane $C_{10}D_{21}{}^{13}CH_2C_{10}D_{21}$ have been synthesized and the spin–lattice relaxations of the isolated $^{13}CH_2$ groups studied by carbon-13 NMR coupled relaxation methods. Selective and nonselective π pulses were applied to the carbon and proton transitions of these AX_2 spin systems and partially relaxed carbon-13 spectra were obtained for various evolution periods after the pulse. Experiments were performed on the nonanes at 233, 273, 313, and 353 K, and on the heneicosane at 313, 353, and 393 K. The data are fitted using the Redfield formalism for NMR dipolar relaxation in terms of four dipolar spectral densities J_{CH}, J_{HCH}, J_{CHH}, and J_{HH}. These four spectral densities are transformed to a reduced Cartesian basis as described in the previous paper by Fuson et al. to give model independent reorientational correlation times τ_{xx}, τ_{yy}, τ_{zz}, and τ_{xy}. The correlation times are compared with results calculated from computer simulations utilizing a Brownian dynamics algorithm. Generally, the results indicate that the motion at each segment of the chain has local prolate symmetric top character and that the correlation times indicate greater motional anisotropy at the middle of a chain than the ends. There is good agreement between the experimental and theoretical correlation times, both in terms of absolute values and in degree of anisotropy.

I. Introduction

Nuclear magnetic resonance (NMR) relaxation experiments are widely used to investigate the rotational dynamics and structure

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of molecules in solution. The most commonly performed experiments (e.g., inversion recovery, NOE) are generally interpreted in terms of the longitudinal (or spin–lattice) relaxation time T_1 and the transverse (or spin–spin) relaxation time T_2. These time constants are used in the Bloch equations[2-4] to describe the relaxation of an isolated spin $^1/_2$ nucleus. In more complicated spin