DIAS-STP-88-18

Further Theoretical Investigations on Nuclear Magnetic Spin-Rotational Relaxation

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The rotational Brownian motion of an asymmetric top was studied by Ford, Lewis and McConnell[1] about ten years ago by employing a generalization of the Langevin equation and a stochastic rotation operator $R(t)$, which describes the rotation of the top from its orientation at time zero to its orientation at time t. The results of these studies were applied successfully to the discussion of complex polarizability[2] and of nuclear magnetic relaxation by intramolecular dipolar interactions, anisotropic chemical shift and quadrupole interaction[3]. When the relaxation mechanism was spin-rotational, serious difficulties were encountered.

The spin-rotational interaction $\hbar G(t)$ is expressed by

$$\hbar G(t) = \hbar \sum_{\mu\nu=1}^{3} S_\mu C_{\mu\nu} J_\nu$$

in the inertial frame of reference of the molecule that contains the interacting nucleus. S_μ is a cartesian component of the spin operator of the nucleus, $\hbar J_\nu$ is a component of the angular momentum operator of the molecule and $C_{\mu\nu}$ is a component of the real spin-rotation tensor. We replace $\hbar J_\nu$ by its classical value $I_\nu \omega_\nu(t)$, write

$$b_{o\nu} = C_{3\nu} \quad , \quad b_{\pm 1,\nu} = \mp \frac{C_{1\nu} \mp i C_{2\nu}}{2^{\frac{1}{2}}} \tag{1}$$

and define $c(s)$ and $j(\omega)$ by

$$c(s) = \frac{1}{3\hbar^2} \sum_{\mu,\nu=1}^{3} \sum_{m,n=-1}^{1} (-)^m b_{n\mu} b_{m\nu} \mathrm{I}_\mu \mathrm{I}_\nu \times \left(\int_o^\infty e^{-st} < R(t)\omega_\mu(t)\omega_\nu(o) > dt \right)_{n,-m} \tag{2}$$

$$j(\omega) = \frac{1}{2}\left[c(i\omega) + c(-i\omega)\right]. \tag{3}$$

Then the relaxation times are given by

$$\frac{1}{T_1} = 2j(\omega_o) \quad , \quad \frac{1}{T_2} = j(o) + j(\omega_o), \tag{4}$$

where ω_o is the Larmor angular frequency.

An expression for the definite integral in (2) has been derived[3]. The first term in the expression is

$$\delta_{\mu\nu}\mathrm{I}\frac{kT}{\mathrm{I}_\mu}(-G + [B_\mu + s]\mathrm{I})^{-1}, \tag{5}$$

where

$$G = -\sum_{\ell=1}^{3}(D_\ell^{(1)} + D_\ell^{(2)})J_\ell^2 \quad , \quad D_\ell^{(1)} = \frac{kT}{\mathrm{I}_\ell B_\ell}, \tag{6}$$

$I_\ell B_\ell$ is a coefficient of rotational friction and $D_\ell^{(2)}$ is smaller than $D_\ell^{(1)}$ by a small dimensionless factor of order κ_ℓ defined by $\kappa_\ell = kT/(\mathrm{I}_\ell B_\ell^2)$. With one exception all the terms other than (5) in the expression of the integral are smaller than (5) by a factor of order κ_ℓ. The exception is the term

$$\frac{-(kT)^2}{\mathrm{I}_\mu \mathrm{I}_\nu}\frac{J_\mu J_\nu}{B_\mu B_\nu}(-G + s\mathrm{I})^{-1}. \tag{7}$$

Now in the extreme narrowing approximation ω_o in (4) is replaced by zero and hence $s = 0$ in (2). On putting $s = 0$ in (7) and noting from (6) that $(-G)^{-1}$ is of order $\mathrm{I}_\ell B_\ell/(kT)$ we see that (7) becomes of the same order as (5), so that to derive a first order correction to (5) we would have to extend the calculations of ref. 1 to the next higher order of approximation in κ_ℓ. While the method

of ref. 1 shows how this could be done in principle, the calculation would in practice be wellnigh impossible.

We have therefore examined what are the necessary and sufficient mathematical conditions to be imposed on the spin-rotation tensor so that no contribution comes from (7). These conditions are just

$$C_{\mu\nu} = 0 \quad (\mu \neq \nu); \tag{8}$$

in other words, the spin-rotation tensor must be diagonal in our molecular frame of reference.

Admitting the relation (8) we have calculated the relaxation times from (1) – (4). Since the expressions for the times are very lengthy when calculated in the inertial theory, we limit ourselves to giving the rotational diffusion theory results:

$$\frac{1}{T_1} = \frac{2kT}{3\hbar^2}\left\{\frac{\mathrm{I}_1 C_{11}^2}{B_1[1+(\omega_o/B_1)^2]} + \frac{\mathrm{I}_2 C_{22}^2}{B_2[1+(\omega_o/B_2)^2]} + \frac{\mathrm{I}_3 C_{33}^2}{B_3[1+(\omega_o/B_3)^2]}\right\}$$

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{2kT}{3\hbar^2}\left\{\frac{\mathrm{I}_1 C_{11}^2}{B_1} + \frac{\mathrm{I}_2 C_{22}^2}{B_2} + \frac{\mathrm{I}_3 C_{33}^2}{B_3}\right\}.$$

References

1) G.W. Ford, J.T. Lewis and J. McConnell, Rotational Brownian motion of an asymmetric top, Phys. Rev. A 19, 907-919 (1979).

2) J. McConnell, Rotational Brownian Motion and Dielectric Theory (Academic Press, London, 1980).

3) J. McConnell, The Theory of Nuclear Magnetic Relaxation in Liquids (Cambridge Univ. Press, 1987).