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Nuclear Magnetic Relaxation by Intramolecular Dipolar Coupling

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Abragam derived expressions for relaxation times T_1, T_2 arising from dipolar coupling in spherical molecules[1]. He employed a rotational Brownian motion theory with the Debye approximation that inertial effects are neglected. We have now developed an inertial theory for spherical, linear, symmetric and asymmetric molecular models.

Considering for simplicity the interaction of two like nuclei with spin I and gyromagnetic ratio γ at a distance r apart we have

$$\frac{1}{T_1} = I(I+1)\{\frac{4}{3}j(\omega_0) + \frac{16}{3}j(2\omega_0)\}$$
$$\frac{1}{T_2} = I(I+1)\{2j(o) + \frac{10}{3}j(o) + \frac{4}{3}j(2\omega_0)\}, \qquad (1)$$

where ω_0 is the Larmor angular frequency,

$$j(\omega) = \frac{3\pi\gamma^4\hbar^2}{5r^6}\int_{-\infty}^{\infty}\langle Y_{20}(\theta(o),\phi(o))\, Y_{20}(\theta(t),\phi(t))\rangle e^{-i\omega t}dt \qquad (2)$$

and $\theta(t),\phi(t)$ are the polar angles at time t in the laboratory frame of one nucleus with respect to the other. We transcribe (2) to [2]

$$j(\omega) = \frac{3\pi\gamma^4\hbar^2}{25r^6}\sum_{m,m'=-2}^{2} Y'_{2m}\, Y'^{*}_{2m'}\, \langle R^{+}(t)\rangle^{2}_{mm'} e^{-i\omega t}dt, \qquad (3)$$

where R(t) is the rotation operator which takes the body frame at time zero to its orientation at time t, and the spherical harmonics refer to the fixed direction in the body frame from one nucleus to the other.

When (3) is applied to the sphere, or linear rotator, or symmetric rotator and the line joining the nuclei is parallel to the rotator axis, it is found that in Debye approximation

$$j(\omega) = \frac{3\gamma^4\hbar^2\tau_2}{10r^6}\,\frac{1}{1+\omega^2\tau_2^2}, \qquad (4)$$

where τ_2 is the correlation time. For the sphere (1) combined with (4) is equivalent to Abragam's results. We have therefore shown that in Debye approximation Abragam's results are also applicable to the linear and symmetric rotator models. This is no longer true in the inertial theory.

1. A, Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961, p. 289.
2. G.W. Ford, J.T. Lewis and J. McConnell, Phys. Rev. A 19, 907 (1979), Appendix.