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Author
Shirley, D.A.

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34

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ESTIMATES OF CORRELATION TIMES OF DISSOLVED COMPLEXES FROM "ROTATIONAL TRACER" EXPERIMENTS*

D. A. Shirley

Department of Chemistry and
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

February 1970

Recent angular-correlation studies have demonstrated the efficacy of gamma-emitting "rotational tracers" in detecting the tumbling of labeled macromolecules in solution.[1,2] The purpose of this note is to point out that the perturbation factor[3] $G_{22}(t)$ in the time-dependent angular correlation function $W(\theta,t) = 1 + A_2 G_{22}(t) P_2 (\cos \theta)$ can provide a rough estimate of the rotational correlation time τ_c. In the theory of Abragam and Pound[4] (applicable for short τ_c) τ_c is defined as the characteristic decay time for the auto-correlation function of the random transition matrix elements governing spin relaxation in the intermediate nuclear state.

Experimentally $G_{22}(t)$ shows either "static" or "dynamic" behavior.[1,2] The static $G_{22}(t)$ curves (in which, however, $G_{22}(t)$ is itself time-dependent) are observed for samples in which the intermediate-state Hamiltonian is expected to be time-independent, e.g., very large molecules, solids, or frozen solutions. $G_{22}(t)^{(\text{static})}$ falls quickly to zero, then rises to a low maximum at time T and remains essentially constant. Under certain assumptions[5] an average quadrupole-coupling constant can be derived from T. For the ^{111}Cd spin-5/2 state the relation is $\overline{(e^2qQ)} = 20\ h/3T$.[6] For solutions of ^{111m}Cd-labeled N-benzyliminodiacetic acid (NBIDA) frozen and cooled to 77°K,[2] T = 36 nsec and $\overline{(e^2qQ)} = 1.23 \times 10^{-18}$ erg.

The "dynamic" $G_{22}(t)$ decays exponentially with decay constant λ_2, given by

$$\lambda_2 = \frac{63}{1000} \frac{\overline{\overline{(eqQ)^2}}}{\hbar^2} \tau_c \quad , \tag{1}$$

for the spin 5/2 case, using the Abragam-Pound theory.[7] Here $\overline{\overline{(eqQ)^2}}$ is the average square (time-dependent) quadrupole-coupling constant that relaxes the nuclear spin. This "dynamic" $G_{22}(t)$ was observed for several small molecules in solution[2]: derived λ_2 values are given in Table I.

For all cases studied, reorientation of the static e.f.g. tensor due to molecular rotation should be the chief contributor to $\overline{\overline{(e^2qQ)^2}}$. We may thus relate τ_c to λ_2 by assuming $\overline{\overline{(e^2qQ)^2}} \approx \overline{\overline{(e^2qQ)}}^2$. Values of τ_c were estimated for several complexes by combining $\overline{\overline{(e^2qQ)}}_{NBIDA}$ with Eq. (1). Figure 1 is a plot of the time-integral attenuation factor $\bar{G}_{22} = (1 + \lambda_2 \tau_N)^{-1}$ versus τ_c.[8] The actual values of τ_c are not very accurate because $\overline{\overline{(e^2qQ)^2}}$ is probably overestimated, but this plot illustrates the range of τ_c that has been studied.

It is a pleasure to acknowledge the collaboration of J. D. Baldeschwieler, T. K. Leipert, R. G. Bryant, and C. F. Meares in obtaining the experimental data used in Table I.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

1. T. K. Leipert, J. D. Baldeschwieler, and D. A. Shirley, Nature 220, 907 (1968).

2. C. F. Meares, R. G. Bryant, J. D. Baldeschwieler, and D. A. Shirley, Proc. Nat. Acad. Sci., to be published.

3. A good summary of angular-correlation theory is given by R. M. Steffen and H. Frauenfelder, in "Perturbed Angular Correlations," ed. by E. Karlsson, E. Matthias, and K. Siegbahn, (North-Holland Publishing Co., 1964).

4. A. Abragam and R. V. Pound, Phys. Rev. 92, 943 (1953).

5. E. Matthias, W. Schneider, and R. M. Steffen, Phys. Letters 4, 41 (1963).

6. Reference 3, pp. 19-24.

7. Reference 3, p. 46.

8. Here τ_N is the nuclear meanlife of 123 nsec. See Fig. 23, Ref. 3, and discussion. Our choice of $\overline{e^2qQ}$ translates the curve slightly.

Table I.

Complex[a]	T, °K	λ_2 (MHz)[b]
NBIDA	77	(static)
NBIDA	273	71
NBIDA	295	37
NBIDA	328	12
NBIDA	358	8
EDTA	295	0.7
ATP	295	3.6
IDA	295	1.5
APO-CA	295	(static)
BSA	295	(static)

[a]All were labeled with ^{111m}Cd (Ref. 2). NBIDA = N-benzyliminodiacetic acid, EDTA = ethylenediame tetraacetic acid, ATP = adenosine triphosphate, IDA = iminodiacetic acid, APO-CA = apo-carbonic anhydrase, BSA = bovine serum albumin.

[b]Accuracy is about ±10%.

FIGURE CAPTION

Fig. 1. Variation of $\overline{G_{22}}$ with τ_c. The points are constrained to lie on the curves by our assumptions: both parameters are derived from λ_2. Dashed region is theoretically uncertain, as discussed in Ref. 3. The error in $\overline{G_{22}}$, where not shown, is ±0.05.

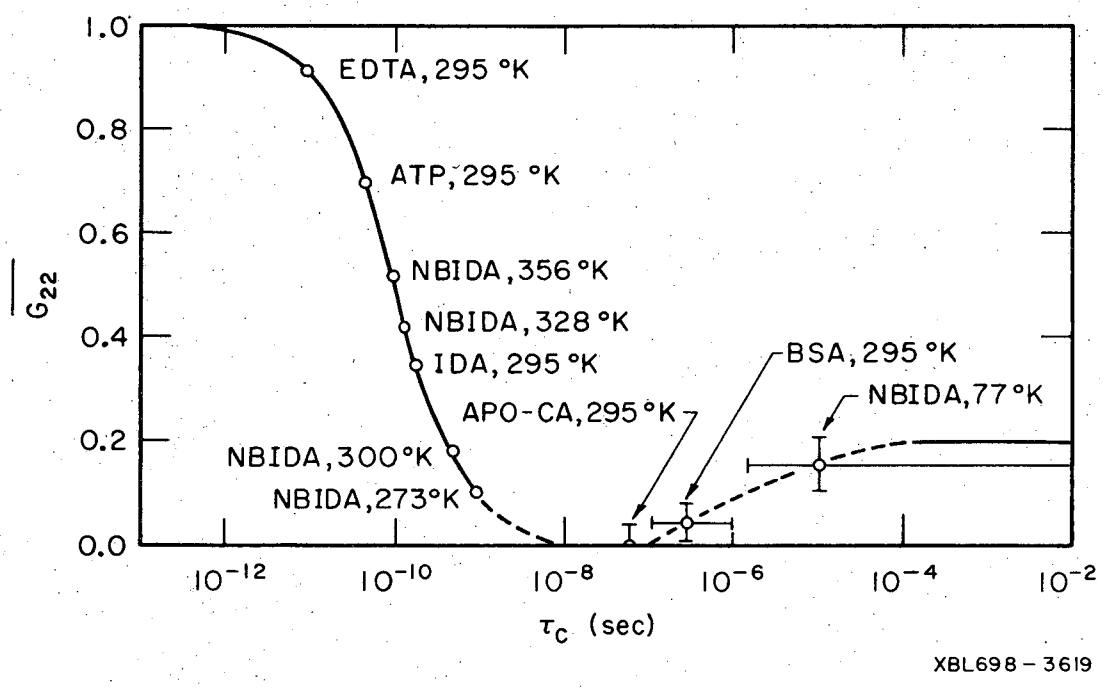
1.0
0.8
0.6
0.4
0.2
0.0
$|G_{22}|$
EDTA, 295 °K
ATP, 295 °K
NBIDA, 356 °K
NBIDA, 328 °K
IDA, 295 °K
APO-CA, 295 °K
NBIDA, 300 °K
NBIDA, 273 °K
BSA, 295 °K
NBIDA, 77 °K
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
τ_c (sec)
XBL698-3619

Fig. 1

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