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Dielectric Relaxation and Molecular Structure. V. Application of the Single Frequency Method to Systems with two Debye Dispersions

Keniti Higasi, Yoshinori Koga, and Masahiko Nakamura
School of Science and Engineering, Waseda University, Shinjuku, Tokyo

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There are four Debye equations for dilute solutions which can be used to determine the relaxation time of a polar solute molecule. This paper offers a critical examination of these equations, especially two representative formulas which are mutually independent. If the solute molecule has a non-rigid configuration and has two relaxation times, τ_1 and τ_2, for overall and internal rotations, respectively, average relaxation times will be obtained from these equations based on measurements at a single frequency. However, the analysis of this paper shows that under a certain condition (if a proper frequency for the measurement and a suitable equation for the calculation are employed) one may make a crude estimate regarding one of the two relaxation times. Further, the ratio of two relaxation times seems to afford a clue for investigating the mechanism of internal rotation. In addition, Cole-Cole dispersion and atomic polarization problems are also discussed.

The dielectric constant ε' and loss ε'' of the dilute solution are represented by the following equations

$$\left.\begin{aligned} &\varepsilon' = \varepsilon_1' + a'w_2 \\ &\varepsilon_0 = \varepsilon_{10} + a_0w_2, \quad \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \\ &\varepsilon'' = \varepsilon_1'' + a''w_2 \end{aligned}\right\} \tag{1}$$

in which subscript 1 refers to the pure solvent and 2 refers to the solute, while subscript 0 refers to the zero frequency measurement in the static field and ∞ to the infinite frequency measurement (at a very high frequency). The concentration w_2 in the present work is the weight fraction but any concentration units (*e.g.*, mole fraction) can be used instead.

The Debye equations for dilute solutions are[1)]

$$\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + \omega^2\tau^2} \tag{2}$$

and

$$\frac{a''}{a_0 - a_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{3}$$

where a', a_0, a_∞, and a'' are the so-called "slopes" defined by Eq. (1), ω is the angular frequency and τ the relaxation time. The relaxation time τ is obtained from Eq. (2)

$$\tau = \frac{1}{\omega}\sqrt{\frac{a_0 - a'}{a' - a_\infty}} \tag{4}$$

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1) K. Higasi, This Bulletin, **39**, 2157 (1966).

And from Eq. (3)

$$\tau = \frac{1}{\omega}[A \pm \sqrt{A^2 - 1}] \tag{5}$$

where

$$A = \frac{a_0 - a_\infty}{2a''}$$

Combination of Eqs. (2) and (3) gives two independent equations

$$\tau = \frac{1}{\omega}\frac{a''}{a' - a_\infty} \tag{6}$$

and

$$\tau = \frac{1}{\omega}\frac{a_0 - a'}{a''} \tag{7}$$

If the solute molecule is provided not with one relaxation time but with two relaxation times, τ_1 and τ_2, Eqs. (2) and (3) will lead to the following expressions:

$$\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1 - C_2}{1 + \omega^2\tau_1{}^2} + \frac{C_2}{1 + \omega^2\tau_2{}^2} \tag{8}$$

$$\frac{a''}{a_0 - a_\infty} = \frac{(1 - C_2)\omega\tau_1}{1 + \omega^2\tau_1{}^2} + \frac{C_2\omega\tau_2}{1 + \omega^2\tau_2{}^2} \tag{9}$$

The coefficients, $C_1 \equiv 1 - C_2$ and C_2 are the weight factors of the two Debye processes defined by τ_1 and τ_2 respectively. The purpose of this paper is to make a critical examination of the average τ values obtained from a_0, a', a'', and a_∞ by the use of Eqs. (6) and (7) when the dielectric system actually does follow Eqs. (8) and (9).

Results

(I) $\tau(1)$ from Eq. (6). By dividing Eq. (9) by Eq. (8) we get

$$\frac{a''}{a_0' - a_\infty} = \frac{\dfrac{(1 - C_2)\omega\tau_1}{1 + \omega^2\tau_1{}^2} + \dfrac{C_2\omega\tau_2}{1 + \omega^2\tau_2{}^2}}{\dfrac{1 - C_2}{1 + \omega^2\tau_1{}^2} + \dfrac{C_2}{1 + \omega^2\tau_2{}^2}}$$

Consequently, the relaxation time τ defined by Eq. (6) will become

$$\tau(1) = \frac{1}{\omega}\frac{a''}{a' - a_\infty}$$
$$= \frac{(1 - C_2)\tau_1 + C_2\tau_2 + \omega^2\tau_1\tau_2[(1 - C_2)\tau_2 + C_2\tau_1]}{1 + [(1 - C_2)\tau_2{}^2 + C_2\tau_1{}^2]\omega^2} \tag{10}$$

Put

$$\tau_1 = m\tau_2 : \quad \omega\tau_2 = x \tag{11}$$

and we get

$$\tau(1) = A\tau_2 \tag{12}$$

where

$$A = \frac{[m - (m - 1)C_2] + mx^2[1 + (m - 1)C_2]}{1 + [1 + (m^2 - 1)C_2]x^2} \tag{13}$$

Eq. (13) contains a term m which was defined in Eq. (11) as the ratio of τ_1 to τ_2. The molecular relaxation time, τ_1, for overall rotation has been well investigated over the past twenty years. The relation between τ_1 and the molecular size and shape has been fairly well established so that one may be able to make a good guess for any polar molecule under given conditions,[2] although opinions may differ as to the accuracy of such an estimation.[3]

More recently extensive investigation have been made concerning the second relaxation time, τ_2, which arises from internal rotation of a polar group in the molecule.[2] The magnitude of τ_2 for a given polar group varies according to the investigator. For instance, German workers[4] find τ_2 in the range of 0.5—3 psec, mostly 1—2 psec, while American[2] and British[5] scientists give somewhat higher τ_2 values for the same group often in the range of 2—4 psec. Accuracy for the determination of τ_2 from the measurement is considered to be lower than that for τ_1. The value of τ_1,[2,3] the relaxation time for overall rotation is much larger and depends on the viscosity of the solvent. Perhaps τ_1 for a benzene derivative in benzene solution would be around 8—15 psec and those for molecules with two benzene rings in the same solvent would be 16—30 psec. According to the above estimates of τ_1 and τ_2 one may consider

$$1 < m \simeq 2 - 30$$

At the frequency of 100 GHz ($\omega = 0.6282 \times 10^{12}$), the condition $\omega\tau = 1$ gives $\tau = 1.59$ psec which corresponds to an average value of $\tau_2 \simeq 1$—2 psec estimated by Knobloch[4] and other German workers: $x = 1(\omega\tau_2 = 1)$. And $x = 2(\omega\tau_2 = 2)$ at 100 GHz will be in accordance with other estimate for τ_2.[2,5]

From Eq. (13) it follows:

Overall rotation only:

$$C_2 = 0: \ A = \frac{m + mx^2}{1 + x^2} = m \quad \tau(1) \to \tau_1$$

Internal rotation only:

$$C_2 = 1: \ A = \frac{1 + mx^2}{1 + mx^2} = 1 \quad \tau(1) \to \tau_2$$

$$\text{Further} \quad m \to \infty \quad A \to \frac{C_2x^2}{C_2x^2} = 1 \quad \tau(1) \to \tau_2$$

In Fig. 1 the relation of A *versus* C_2 is plotted for four cases, viz., $m = 10$ $x = 1$, $x = 0.3$; $m = 5$ $x = 1$, $x = 0.3$. It will be seen that with increase in m and x the curve becomes flat, A approaching to unity in the region of large C_2 values. For example, $1 < A \leq 1.2$ if $C_2 \geq 0.5$, $m \geq 10$ and $x \geq 1$. This will imply that the average relaxation time, $\tau(1)$, obtained at 100 GHz by use of the Eq. (6) would be larger by only 20% than the smaller relaxation time τ_2, if the absorption intensity due to the internal rotation is significant and two absorption peaks are fairly separated. However, at lower frequencies such as $x \to 0$, Eq. (13) gives $A \to (1/2)(m+1)$ at $C_2 = 1/2$, i.e.,

$$\tau(1) \to (1/2)(\tau_1 + \tau_2) \quad \text{at } C_2 = 0.5.$$

(II) $\tau(2)$ from Eq. (7). We may denote the relaxation time defined by Eq. (7) as $\tau(2)$ and will obtain

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[2] C. P. Smyth, *Ann. Rev. Phys. Chem.*, **17**, 433 (1966).

[3] K. Chitoku and K. Higasi, This Bulletin, **36**, 1064 (1963); O. Kiyohara and K. Higasi, *Bull. Res. Inst. Appl. Elec.*, **18**, 123, 138 (1966).

[4] For instance, P. Knobloch, *Z. Naturforsch.*, **20a**, 580 (1965).

[5] S. W. Tucker and S. Walker, *Can. J. Chem.*, **47**, 681 (1969).

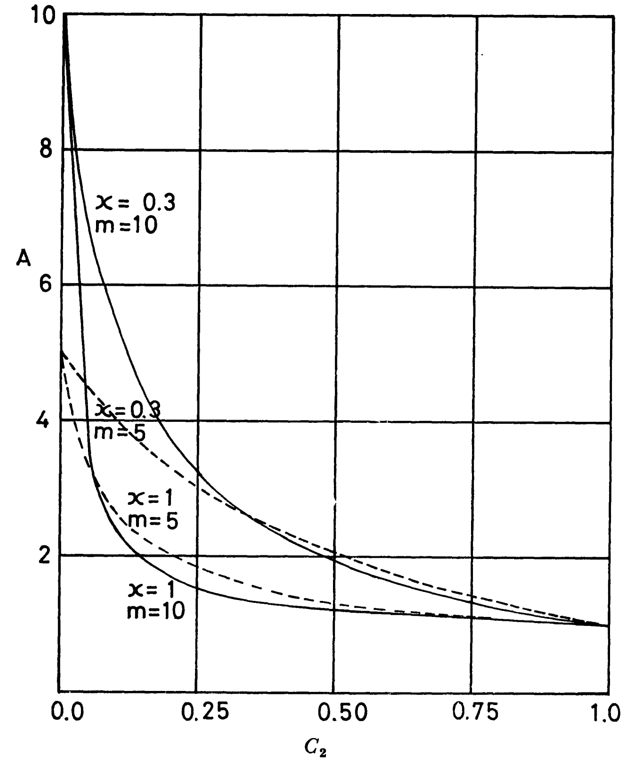

Fig. 1. Graphs relating ratio $\tau(1)/\tau_2 \equiv \boldsymbol{A}$ to the weight factor for internal rotation C_2, when $\tau_1/\tau_2 \equiv m=5$, 10 and $\omega\tau_2 \equiv x=0.3$, 1. The plots are based on Eq. (13).

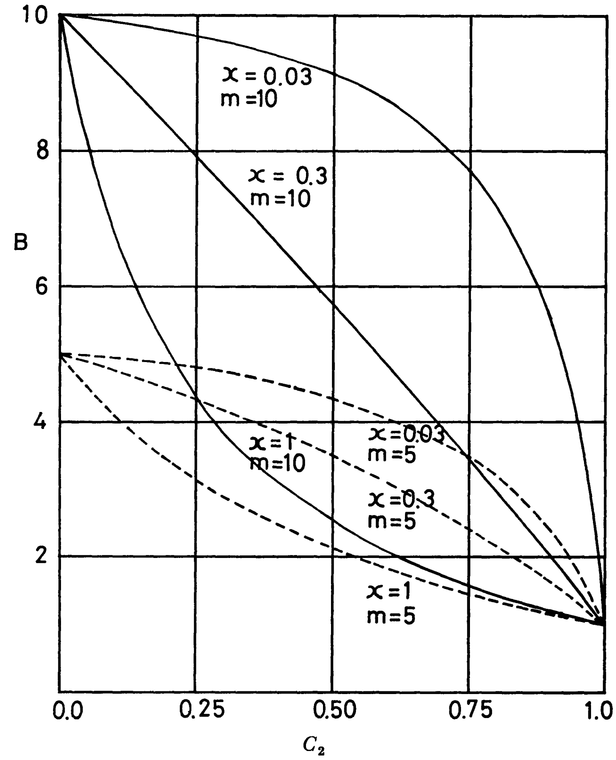

Fig. 2. Graphs relating ratio $\tau(2)/\tau_2 \equiv \boldsymbol{B}$ to the weight factor for internal rotation C_2, when $\tau_1/\tau_2 \equiv m=5$, 10 and $x=\omega\tau_2=0.03$, 0.3, 1. Plots are based on Eq. (15).

$$\tau(2) = \frac{1}{\omega}\frac{a_0 - a'}{a''} = \boldsymbol{B}\tau_2 \tag{14}$$

where

$$\boldsymbol{B} = \frac{m^2 - (m^2-1)C_2 + m^2x^2}{m - (m-1)C_2 + mx^2[1 + (m-1)C_2]} \tag{15}$$

Overall rotation only:

$$C_2 = 0: \ \boldsymbol{B} = \frac{m^2 + m^2x^2}{m + mx^2} = m, \quad \tau(2) \to \tau_1$$

Internal rotation only:

$$C_2 = 1: \ \boldsymbol{B} = \frac{1 + m^2x^2}{1 + m^2x^2} = 1, \quad \tau(2) \to \tau_2$$

Further at lower frequencies ($x \to 0$)

$$\boldsymbol{B} \to m, \quad \tau(2) \to \tau_1$$

In Fig. 2 the relation of $\boldsymbol{B}$ to C_2 is plotted for six cases, $m=10$, 5 and $x=1$, 0.3, 0.03. It will be seen $\tau(2)$ gives a larger relaxation time than $\tau(1)$ for the dielectric system consisting in two Debye dispersions.

Gopala Krishna's equation[6] is based essentially on the same principle[1] with Eq. (7); recently, Vij and Srivastava[7] made a critical analysis of these equations. The relaxation times of non-rigid molecules[7,8] calculated by Gopala Krishna's procedure as well as by Eq. (7) would correspond to $\tau(2)$ for a given frequency.

(III) $\boldsymbol{B/A}$ *and* C_2. We have $\tau(1)=\boldsymbol{A}\tau_2$ and $\tau(2)=\boldsymbol{B}\tau_2$. The ratio $\boldsymbol{B/A}$ is unity at $C_2=0$ and $C_2=1$ and varies with m, x and C_2. In Fig. 3 are shown curves of $\boldsymbol{B/A}$ *vs.* C_2 for $m=5$ and 10 and $x=1$ and 3. The maximum of $\boldsymbol{B/A}$ becomes larger with increase in m.

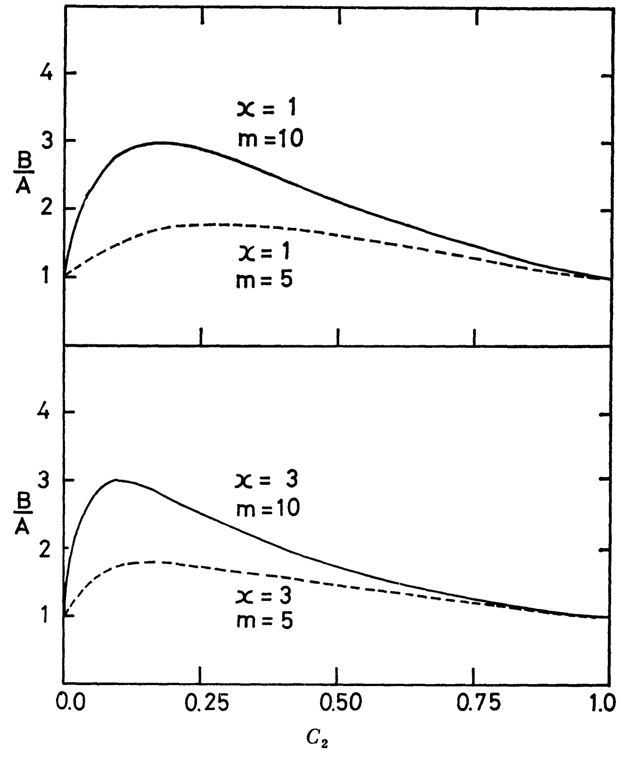

Fig. 3. Graphs relating ratio $\tau(2)/\tau(1) \equiv \boldsymbol{B/A}$ to the weight factor C_2, when $\tau_1/\tau_2 \equiv m=5$, 10, $\omega\tau_2 \equiv x=3$, 1.

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[6] K. V. Gopala Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).

[7] J. K. Vij and K. K. Srivastava, *ibid.*, **66**, 1087 (1970).

[8] K. K. Srivastava and J. K. Vij, This Bulletin, **43**, 2307, 2313 (1970).

The literature[2,4] gives values of τ_2 to be 1—4 psec and almost independent of solvent. This would imply $x \to 1$—3 for $\omega \simeq 0.6 \times 10^{12}$ (100 GHz). Regarding τ_1 for overall rotation we might make a good guess[2,9] for a molecule with known molecular size and shape if the solvent and temperature are known. For given m and x the weight factor C_2 will be found to be associated with $\boldsymbol{B}/\boldsymbol{A}$.

(IV) $\tau(3)$ and $\tau(4)$ from Eqs. (4) and (5). We may call the relaxation time from Eq. (4) as $\tau(3)$.

$$\tau(3) = \frac{1}{\omega}\sqrt{\frac{a_0 - a'}{a' - a_\infty}} = \frac{1}{\omega}\sqrt{\frac{a''}{a' - a_\infty}\cdot\frac{a_0 - a'}{a''}}$$

from Eqs. (6) and (7)

$$\tau(3) = \sqrt{\tau(1)\cdot\tau(2)} \tag{16}$$

Thus, $\tau(3)$ is a geometric mean of $\tau(1)$ and $\tau(2)$.

$\tau(4)$ is the relaxation time which follows from Eq. (5) and is not independent of $\tau(1)$ and $\tau(2)$. Since Debye introduced a variation of Eq. (3) first in estimating the relaxation time of a polar molecule by the dilute solution method, Eq. (3) as well as its variations have been employed by many workers.[10,11] Figure 4 provides $\tau(4)$ *vs.* C_2 curves for systems with two Debye dispersions.

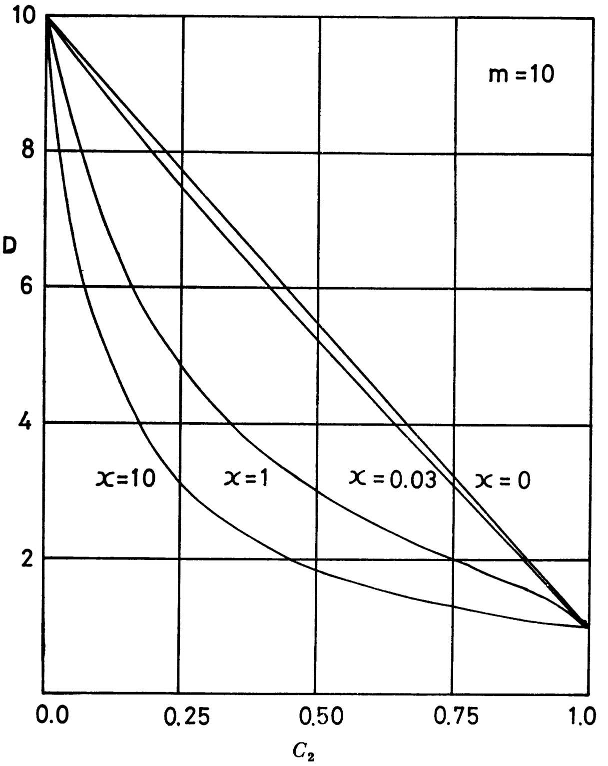

Fig. 4. Graphs relating ratio $\tau(4)/\tau_2 \equiv \boldsymbol{D}$ to the weight factor C_2 when $\tau_1/\tau_2 \equiv m = 10$ and $\omega\tau_2 \equiv x = 0$, 0.03, 1 and 10.

One will find from the upper curve in Fig. 4 that if $x = \omega\tau_2 \to 0$

$$\tau(4) = \tau_2[m - (m-1)C_2] = (1 - C_2)\tau_1 + C_2\tau_2 \tag{17}$$

This is an equation for internal rotation often utilized in the measurements at lower frequencies.[12]

$$\tau_{\text{eff}} = \left(\frac{\mu_1}{\mu}\right)^2\tau_1 + \left(\frac{\mu_2}{\mu}\right)^2\tau_2 \tag{18}$$

in which μ_1 and μ_2 are the two components of the molecular dipole μ.

(V) Problem of a_∞ and α. Equations for evaluating the relaxation time, Eqs. (4), (5), and (6) have a common weakness; they have uncertainty as to the choice of a_∞. Studies on chlorobenzene and other polar molecules by Smyth and his co-workers[13] seems to suggest $a_\infty \simeq a_D$—certainly this approximation, if true, would be very convenient. In most cases, however, $a_\infty \gtrsim a_D$ would be more likely. The values $\tau(1)$ estimated based on $a_\infty \simeq a_D$ will be too small if actually a_∞ is larger than a_D.

If the dielectric system of dilute solution of a polar substance in non-polar solvent happens to obey the Cole-Cole empirical rule,[14] the following expression[1] will become valid.

$$\frac{a' - ja'' - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + (j\omega\tau_0)^{1-\alpha}} \tag{19}$$

τ_0 is the most probable relaxation time, and α is the distribution parameter. From Eq. (19) $\tau(1)$ and $\tau(2)$ become

$$\tau(1) = \frac{1}{\omega}\frac{(\omega\tau_0)^{1-\alpha}\cos(\pi\alpha/2)}{1 + (\omega\tau_0)^{1-\alpha}\sin(\pi\alpha/2)} \tag{20}$$

$$\tau(2) = \frac{1}{\omega}\frac{(\omega\tau_0)^{1-\alpha} + \sin(\pi\alpha/2)}{\cos(\pi\alpha/2)} \tag{21}$$

Both $\tau(1)$ and $\tau(2)$ have smaller values than τ_0 for $\alpha \neq 0$. For example, at 100 GHz $\tau(1) = 4.3$ psec, $\tau(2) = 7.9$ psec for $\alpha = 0.1$ and $\tau_0 = 9$ psec; $\tau(1) = 3.1$ psec, $\tau(2) = 7.4$ psec for $\alpha = 0.17$ and $\tau_0 = 9$ psec.

Concluding Remarks

1. For the study of dielectric behavior of polar molecules it would be most desirable to obtain the complete spectrum of dielectric constants and losses in the whole frequency range where the dispersion takes place. However, this is an almost impossible task, unless the dispersion occurs only in the lower frequencies, say, below 7 GHz. Unfortunately the dipole dispersions due to group rotation in non-rigid molecules appear in much higher frequency range than this. In fact the single frequency method has been employed[6,7] in spite of all its theoretical defects for studies in the microwave frequencies.

2. If one uses Gopala Krishna's method[6] for determining the relaxation time of a non-rigid molecule, it should be noted that this equation provides a *mean* values. Its value, *i.e.* $\tau(2)$ is given by Eqs. (14) and (15) if the system is a superposition of two Debye dispersions.

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[9] K. Higasi, *Kagaku*, **37**, 261 (1967); *Kagaku-no-Ryoiki*, (Supplement) **82**, 3 (1968).

[10] N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour," Van Nostrand, Reinhnld, London (1969); p. 289, Eq. (5.5).

[11] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1955) p. 64.

[12] E. Fischer, *Z. Naturforsch.*, **4a**, 707 (1949); *Z. Phys.*, **127**, 49 (1949); A. Aihara and M. Davies, *J. Colloid Sci.*, **11**, 671 (1956).

[13] S. K. Garg, H. Kilp, and C. P. Smyth, *J. Chem. Phys.*, **43**, 2341 (1965).

[14] K. S. Cole and R. H. Cole, *ibid.*, **9**, 341 (1941).

3. The analysis of $\tau(1)$ shows that the relaxation time for internal rotation τ_2 may be estimated from high frequency measurements if we could have a true a_∞ value. In fact, τ_2 is closely associated with a_∞. Both quantities are of extreme importance in molecular science. They might be estimated with some accuracy but at present we do not have any absolutely reliable method to determine them.

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