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DIELECTRIC STUDIES—VI

A BRIDGE METHOD AT 4·3 mm WAVELENGTH FOR DILUTE SOLUTIONS

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Abstract—A bridge method has been developed for measuring the dielectric absorption of dilute solutions of a polar solute in a non-polar solvent at 4·3 mm wavelengths. The dielectric absorption of acetophenone and also benzophenone in cyclohexane has been measured at wavelengths of 0·43, 0·86, 1·25, 1·85 and 3·22 cm and the benzophenone also at 9·4 cm while the static dielectric constant has been determined at a frequency of 1 Mc/s. The satisfactory character of the measurements at 4·3 mm is shown by the fact that in each case the point for this wavelength lies on the Cole–Cole plot. Further, the ε_∞ value derived by extrapolation of this plot at the high frequency end leads to dipole moments in good agreement with literature values. In addition, the relaxation times for both acetophenone and benzophenone, which are again highly dependent on this extrapolation, appear reasonable. Other reasons for the desirability of 4·3 mm dielectric absorption measurements are also considered. Potentially, it is a most attractive region for studying certain intramolecular processes.

INTRODUCTION

FOR many organic molecules such as, for example, substituted ethanes, benzenes, diphenyls and naphthalenes the dielectric absorption due to re-orientation of the whole molecule and group re-orientation (e.g. —OR, OH, $N(CH_3)_2$, $—COCH_3$ or $—OCF_3$) overlaps in the mm and cm regions and mm data are invaluable in the analysis for the accurate determination of the relaxation times corresponding to these processes. From these two relaxation times the free energy of activation for overall and group re-orientation may be obtained. The latter which is better known as the energy of activation is of topical interest to organic chemists.[1] Potentially the dielectric method would seem one of the most versatile approaches since it is not limited to symmetric-top or molecules closely approaching these in symmetry (as is the case for microwave absorption of gases) nor does it have to assume a potential energy function as has the rotation-vibration spectral approach which again is largely restricted to similar types of molecules.

For molecules with two relaxation times, in which the energy barrier for group re-orientation is of the order 1 to 4 kcal/mole, the microwave dielectric absorption method would appear one of the most powerful especially since an error of $\pm 20\%$ in the relaxation time leads to an error of only about $\pm 0{\cdot}1$ kcal/mole in such an energy barrier. The NMR approach also studies a relaxation phenomenon but this is best suited to accurate determination of somewhat higher energy barriers.

The most accurate dielectric relaxation data are derived when measurements have been carried out at a number of different wave-lengths (e.g. at least three but preferably four) together with measurement of the static dielectric constant (ε_0 at, for example, 1 Mc/s). In addition, it is desirable to have a fairly even distribution of points in the Cole–Cole plot[2] and most of all to have a point at a low wavelength such as 4·3 mm

[1] E. L. Eliel, *Stereochemistry of Carbon Compounds*. McGraw-Hill, New York (1962).
[2] K. S. Cole and R. H. Cole, *J. Chem. Phys.* 9, 341 (1941).

(known as "O" band), since the length of extrapolation of the Cole–Cole[2] plot to obtain the dielectric constant at infinite frequency (ε_∞) is then considerably reduced. An accurate value of ε_∞ is imperative in the subsequent Bergmann[3] analysis of the dielectric data into two (or even three) relaxation times. Furthermore, additional reasons for requiring accurate ε_∞ values are:

(i) When ε_∞ is appreciably greater than the square of the refractive index, as determined by sodium-D light, then some additional—probably unsuspected—type of motion has to be considered such as libration of a particular group.[4]

(ii) Work by Poley[5] on the difference in value between ε_∞ and the square of the refractive index (extrapolated from measurements in the visible and IR regions) for a number of polar solutes in a non-polar solvent showed that in certain cases the difference increases with concentration. From such studies he concluded that for certain systems the explanation is to be sought in the strong local field exerted on a molecule by its neighbours.

(iii) From the value of $\varepsilon_0 - \varepsilon_\infty$ for dilute solutions of a polar solute in a non-polar solvent the electric dipole moment may be evaluated (see later). This procedure, unlike the Halverstadt-Kumler[6] or Guggenheim[7] approaches, does not involve any atomic polarization approximations.

Smyth *et al.*[8] developed an interferometric method for the measurement of dielectric constants and losses of liquids at 4·3 mm wavelengths using an harmonic from an 8·7 mm klystron source. Although conventional waveguide techniques are used for the production and detection of the microwave power, the waveguide power is converted to a plane wave in free space by a horn. This power is then reflected from the cell containing the liquid and picked up by a similar horn. The viewpoint which appears to have fairly common acceptance is that a free space method such as this is essential for studying the dielectric absorption of liquids and solutions at these low wavelengths. Thus, it was stated by Illinger[9] that "Although waveguide standing wave techniques have been employed in the mm region, they become increasingly inaccurate with decreasing wavelength and free space techniques appear to be more promising". A summary of such approaches is given in this most valuable article.

Unfortunately, the accuracy of the dielectric constant by free space methods decreases as the loss decreases. Consequently, the method is not suitable for dielectric constant measurements of dilute solutions. Our aim was to develop a method of sufficient accuracy to be of use for dipole moment determination and formulation of a Cole–Cole plot (for dilute solutions) which was capable of subsequent Bergmann analysis into two or even three relaxation times.

BASIC THEORY

A bridge method is employed and the attenuation and phase shift are measured for various path lengths of solution.

[3] K. Bergmann, Doctoral Dissertations, Freiburg/Bresgau, W. Germany (1957).
[4] E. Forest and C. P. Smyth, *J. Amer. Chem. Soc.* **86**, 3474 (1964).
[5] J. P. Poley, *J. Appl. Sci. Res.* **B4**, 337 (1955).
[6] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).
[7] E. A. Guggenheim, *Trans. Far Soc.* **45**, 714 (1949).
[8] W. E. Vaughan, J. Bergmann and C. P. Smyth, *J. Phys. Chem.* **65**, 94 (1961).
[9] K. H. Illinger, *Progress in Dielectrics* **4**, 37 (1962).

The attenuation reading in nepers is plotted against the length of solution added in cms and the slope is α_1. The length of solution is known from the volume added and the cross section of the waveguide.

The phase shift in radians is plotted against the length of added solution and the slope is β_{meas}. The value of β_{meas} is not that of the solution however since:

$$\beta_{\text{soln}} = \beta_{\text{meas}} + \beta_{\text{air}} \tag{1}$$

and

$$\beta_{\text{air}} = \frac{2\pi}{\lambda g} \tag{2}$$

where λg is the wavelength in the guide.

The equations for the determination of the loss factor (ε'') and dielectric constant (ε') are:

$$\varepsilon'' = \frac{\lambda_0^2}{4\pi^2} 2\alpha_1\beta \tag{3}$$

$$\varepsilon' = (\beta^2 - \alpha_1^2)\frac{\lambda_0^2}{4\pi^2} + \left(\frac{\lambda_0}{2a}\right)^2 \tag{4}$$

where λ_0 is the wavelength in cm of the radiation in vacuum as deduced from the frequency meter reading and "a" is the inner broad side width of the cross section of the waveguide. ε' may be related to the usual picture of dielectric constant whereas ε'' measures the ability of the medium to dissipate energy.

Since α_1, β, λ_0 are measured and "a" is known, the ε'' and ε' values for a particular wavelength may be determined. This procedure for evaluation of ε' and ε'' was employed for all the bridge method results.

ε' and ε'' are related to the relaxation time (τ) and the angular frequency ω by the equations:

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{5}$$

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + \omega^2\tau^2} \tag{6}$$

where ε_0 is the static dielectric constant (e.g. the value measured at 1 Mc/s frequency) and ε_∞ is the dielectric constant at very high frequency.

On elimination of $\omega\tau$ from Eqs (5) and (6) the equation of a circle is obtained:

$$\left[\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right]^2 + \varepsilon''^2 = \left[\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2 \tag{7}$$

from which a plot of ε'' (ordinate axis) against ε' in the complex plane gives what is known as the Cole–Cole plot. If the diameter of the semicircle lies along the abscissa, the dielectric data may be explained in terms of one relaxation time. If, however, this diameter has been displaced by an angle of $\alpha\pi/2$ in a clockwise direction, then this suggests the presence of more than one relaxation time.

The main procedure employed to assess the "O" band ε'' and ε' values has been to examine whether it lay on the Cole–Cole plot expressed in the form of a'' (ordinate axis) against a' (abscissa) in which a'' is the slope of the plot of $\varepsilon'' v\, w_2$ (weight fraction

of solute) and a' the slope of $\varepsilon' v\ w_2$ where the slopes are determined by the method of least squares. The relevant equations for the parameters in this form of the Cole–Cole plot are:

$$\begin{aligned}\varepsilon'' &= a'' w_2 \\ \varepsilon' &= \varepsilon_1 + a' w_2 \\ \varepsilon_0 &= \varepsilon_1 + a_0 w_2 \\ \varepsilon_\infty &= \varepsilon_1 + a_\infty w_2\end{aligned}$$

where ε_1 is the dielectric constant of the solvent. These equations apply to dilute solutions of a polar solute in a non-polar solvent.[10]

In order to check whether the Cole–Cole plot itself is satisfactory, the electric dipole moment was evaluated from the following equation:

$$\mu = \left\{\frac{27kT}{4\pi}\frac{M_2}{N}\frac{1}{d_1}\frac{(a_0 - a_\infty)}{(\varepsilon_1 + 2)^2}\right\}^{\frac{1}{2}} \tag{8}$$

where k is the Boltzmann constant, N the Avogadro number, T the absolute temperature and M_2 the mol. wt. of solute, ε_1 and d_1 are the dielectric constant and density respectively of the solvent. Since the a_∞ value is obtained by extrapolation of the Cole–Cole plot to infinite frequency, the dipole moment value provides a reasonable test of a satisfactory plot—especially since a_0 can be determined with greater accuracy. The two solutes, acetophenone and benzophenone, chosen to test the "O" band data have both moments of about 3D and for such a large value (in the absence of exceptionally high P_A values) the approximation $P_A + P_E = R_D$ is negligible. Hence, it is feasible to compare the dipole moments evaluated by the Halverstadt-Kumler method with the ensuing microwave values.

EXPERIMENTAL

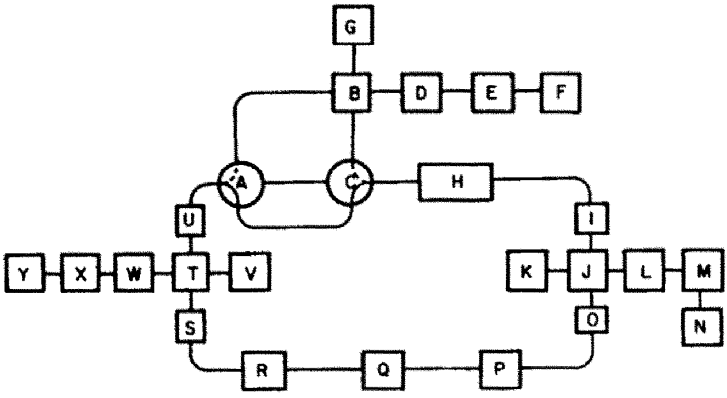

FIG. 1. Block diagram of 4·3 mm bridge circuit.

The cross section of the waveguide required for the propagation of 4·3 mm radiation is only 0·122 × 0·061 sq ins which necessitates minimizing reflections. Hence, it is vital to be able to assess reflections. Unfortunately, the use of a standing wave indicator at these wavelengths is open to objection for the most accurate measurements. This has governed our choice of an impedance meter (G—see Fig. 1) from which the standing wave ratio (ρ) may be assessed from:

$$\rho = \frac{1 + |M|}{1 - |M|} \tag{9}$$

[10] C. P. Smyth, *Dielectric Behaviour and Structure* McGraw-Hill, New York and London (1955).

in which M is the modulus reading on the impedance meter. The aim is to achieve a low value of ρ (e.g. less than 1·15). The items A, B, C, D, E, F and G are employed in the assessment of ρ. B is a hybrid-T and when the impedance in the arm BG and BC is equal then the vector sum output in arm BDE is zero; this is detected by the crystal E which is connected to a high gain low noise amplifier and voltmeter (F). D is a slide screw tuner which is employed to match E to the magic-T. A and C are waveguide switches and the dotted lines indicate the path of a wave when the standing ratio is being measured in front of the cell H. This is carried out for each length of solution for which the attenuation and phase shift are determined, since for certain lengths of solution the reflections can be appreciable. As the waveguide itself is significantly attenuating, the value of ρ immediately in front of the cell window is not determined. In fact, it is the changes of ρ which are followed and any attenuation or phase shift readings corresponding to appreciably higher values of ρ are rejected.

The basic bridge circuit is the path of the radiation from the klystron (Y) to the detector (M) when the waveguide switches are set in the full-time position. The monochromatic 4·3 mm radiation is generated by the klystron (to which square wave reflector modulation of 1000 c/s is applied and to which the detector is set) and propagated along the rectangular waveguide. An isolator (X) prevents "pulling of the klystron". The frequency is read directly on the frequency meter (W). At T the power is split into two equal halves by the hybrid-T, one half passing through the cell (H) containing the solution and the other half along the other side of the bridge through the calibrated rotary-vane attenuator (R) and two 180° phase shifters (Q and P).* The polar solution shifts the phase and attenuates the wave; hence, the procedure in principle is to alter the phase and attenuation in the other side of the bridge so that the waves cancel at the output hybrid-T (J) and the signal detector system indicates a null point. By this procedure the variability and calibration of the crystal are overcome. It is essential to match the components and to minimise reflections; to this end the slide screw tuners (D and L) and isolators (U, S, I, O) are employed. K and V are matched loads which terminate the remaining arms of the hybrid-T's.

The cell is jacketted and is about 10 cm long with mica windows at each end of the waveguide, the angle of inclination of these tapered windows being ~15° to the main length of the waveguide. Additions of solution to the cell are made from an Agla micrometer syringe through a very small hole through the centre of the waveguide at the upper end of the cell. Based on preliminary experiments sufficient solution is added to give a phase shift of precisely 360°, as this avoids introducing unwanted attenuation from the phase shifter. About twelve such additions of solution are made and the attenuation measured at each addition. The attenuation is read directly in decibels, then converted to nepers.

A few practical points which may be noted are:

(i) the solution creeps up the side of the cell and to reduce this an inclination of ~40° was employed on the bench supporting the apparatus.
(ii) the cell is normally half filled with solution before the readings are recorded.
(iii) the Agla needle must be sufficiently long to project about 1″ into the cell.
(iv) the mica window thickness should not be greater than about 0·001 cm.

RESULTS

The dielectric absorption of acetophenone in cyclohexane was measured at 25° at wavelengths of 0·43, 0·86, 1·25, 1·85, 3·22 and 9·4 cm, known respectively as O, Q, K, P, X and S bands, by the bridge methods and the results are given in Fig. 2 in the $a'' - a'$ form of a Cole–Cole plot. Eight solutions were employed in each of these determinations of a', a'' and a_0.

Benzophenone in cyclohexane was also examined (at 20°). This is a particularly difficult case for analysis since the dielectric absorption of the intramolecular process is not readily separated from the overall rotation of the molecule, and, in fact, several workers have interpreted the dielectric data solely in terms of the overall relaxation of the molecule and not detected the intramolecular rotation.[11] For the

* In theory these could be dispensed with since the solution itself is employed as the phase shifter. However, it is convenient to use these in balancing the bridge.

[11] J. Schneider, *J. Chem. Phys.* **32**, 665 (1960).

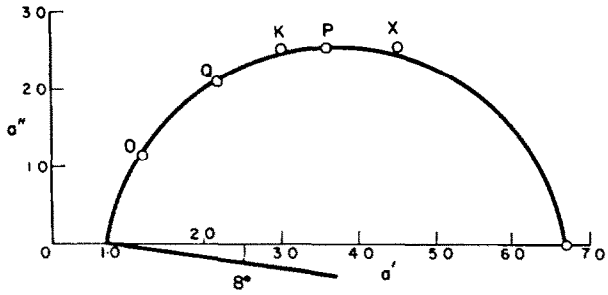

FIG. 2. Cole–Cole plot for acetophenone in cyclohexane at 25°.

analysis of this solute an accurate a_∞ is essential and, thus, a small extrapolation of the Cole–Cole plot desirable. With this system we have made a stringent test of the dielectric procedure by measuring the O, Q and K band points by the bridge techniques, K (labelled K′ in Fig. 3), P and X bands by an impedance method[12] and the S band by a coaxial cavity. The a_0 value was obtained at 1 Mc/s. The resulting $a'' - a'$ plot is given in Fig. 3.

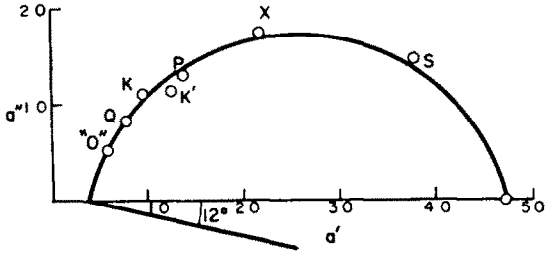

FIG. 3. Cole–Cole plot for benzophenone in cyclohexane at 20°.

In Table 1 the dipole moment values of the two relaxation times τ_1 and τ_2 are given for acetophenone and also benzophenone in cyclohexane.

TABLE 1. DIPOLE MOMENT AND RELAXATION TIME DATA FOR ACETOPHENONE AND BENZOPHENONE IN CYCLOHEXANE

Solute	Temp	w_s range	$\tau_1 \times 10^{12}$	$\tau_2 \times 10^{12}$	μ (in D)
Acetophenone	25°	0·01 to 0·03	17	6·0	2·92
Benzophenone	20°	0·01 to 0·04	27	3·5	2·99

Some appreciation of the deviations in the a' and a'' results for different wavebands may be gained from Table 2. The a' and a'' are the experimental values and a'_{calc} and a''_{calc} the values calculated from the modified Eqs (5) and (6) as applied to a system with two relaxation times.

$$\frac{a''}{a_0 - a_\infty} = C_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + C_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \tag{10}$$

$$\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{C_1}{1 + \omega^2\tau_1^2} + \frac{C_2}{1 + \omega^2\tau_2^2} \tag{11}$$

assuming the values determined for benzophenone in cyclohexane at 20° (i.e. $\tau_1 = 27 \times 10^{-12}$ sec, $\tau_2 = 3{\cdot}5 \times 10^{-12}$ sec and $C_1 = 0{\cdot}87$), the values of a'_{calc} and a''_{calc} could

[12] W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *J. Amer. Chem. Soc.* **72**, 3443 (1950).

be found from the above equations. The actual procedure, though, in determining the τ_1, τ_2 and C_1 values was first to obtain an initial estimate by the Bergmann method[3] and then to feed these values into a computer programmed to solve Eq. 10.

TABLE 2. COMPARISON OF SLOPES OF MEASURED AND CALCULATED DIELECTRIC CONSTANTS AND LOSSES FOR BENZOPHENONE IN CYCLOHEXANE AT 20°C. Δa SIGNIFIES THE % VARIATION $100(a_{calc} - a_{obs})/a_{obs}$ WHERE THE DASH SUPERSCRIPT REFERS TO DIELECTRIC CONSTANT DATA AND THE DOUBLE DASH TO LOSS

Band	a'	a'_{calc}	a''	a''_{calc}	$\Delta a'$	$\Delta a''$
O	0·57	0·61	0·59	0·57	+7·0	−3·0
Q	0·79	0·88	0·85	0·89	+10·5	+5·6
K	0·98	1·07	1·15	1·11	+9·6	−3·7
P	1·42	1·36	1·34	1·39	−3·8	+4·3
X	2·18	2·05	1·77	1·81	−6·1	+2·7
S	3·73	3·90	1·49	1·60	+4·5	+7·7

The results obtained compare well with those of Fong and Smyth[13] who examined 2-naphthol and 2-naphthalenethiol, their $\Delta a''$ were up to 6% on K and X bands and up to 20% on S band. For $\Delta a'$ they experienced errors of up to 4% but a 4 mm point was not examined.

As was noted by Smyth *et al.*[14] that for dilute solutions, because of the smallness of the differences, $\varepsilon_0 - \varepsilon_1$ and $\varepsilon' - \varepsilon_1$, the average deviations of the slopes a_0 and a' are magnified to about $\pm 5\%$. The average deviations in the values of a'' will also be about $\pm 5\%$. In relation to this the data in Table 2 seem reasonable—especially since the a'_{calc} and a''_{calc} values are highly sensitive to the a_∞ value which is extrapolated from the experimental data in the Cole–Cole plot.

CONCLUSIONS

The dipole moment value of 2·99D for benzophenone in cyclohexane compares well with the majority of literature values[15] for this solute in benzene of 2·98D as determined by Halverstandt-Kumler approach. The difference of 0·01D may be due to a solvent effect but as this is the quoted experimental error for the latter method the two values may be looked upon as coincident. The majority of literature[15] values for acetophenone in benzene lie between 2·91 and 2·96D and compare well with our value of 2·92D.

It must be stressed, though, that this work does not establish the reality of the relaxation times or the nature of the intramolecular motion. Many workers have studied benzophenone[16] and molecules of the type $(C_6H_5)_2X$, and four different types of intramolecular relaxation have been advanced. Often a detailed study of a considerable number of molecules is necessary to identify a particular type of intramolecular re-orientation. So far, re-orientation of the —O—H group in phenols has

[13] F. S. Fong and C. P. Smyth, *J. Phys. Chem.* **67**, 226 (1963).
[14] A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *J. Amer. Chem. Soc.* **72**, 3447 (1950).
[15] A. L. McClellan, *Tables of Experimental Dipole Moments*. W. Freeman, San Francisco and London (1963).
[16] D. A. Pitt and C. P. Smyth, *J. Phys. Chem.* **63**, 582 (1959).

been established while the re-orientation of —O—CH_3 in anisole and its derivatives seems probable as does that of the acetyl group in aromatic molecules such as acetophenone. Our τ_2 value of 6×10^{-12} sec for acetophenone is of the same order as that obtained by Smyth for a number of aromatic compounds containing the acetyl grouping which have yielded τ_2 values within the range 7×10^{-12} sec $\pm 20\%$. In addition as would be expected for group re-orientation the τ_2 values have been reasonably insensitive to the macroscopic viscosity of the solvent.[17]

Since the 4·3 mm ε'' and ε' values for both acetophenone and benzophenone fall on Cole–Cole plots established by measurement at several wavelengths, then this is convincing proof of the success of the method. This is particularly so in the benzophenone case since the loss is so low and such measurements are necessarily the least accurate. We have also applied this 4·3 mm procedure to several other systems as, for example, tetrahydrofuran, tetrahydrothiophen, cyclopentanone and pyrrolidine, the solvent in each case being cyclohexane.* For all these solutes the absorption at 4·3 mm is near the maximum on the Cole–Cole plot and the point was invaluable in formulating the plot.

It is not to be supposed that the 4·3 mm bridge method is as accurate and repeatable as the other type of bridge procedure employed at higher wavelengths.[18] For the latter approach it is possible to make good Cole–Cole $\varepsilon'' - \varepsilon'$ plots from measurements at one concentration and to establish a sufficient degree of accuracy to obtain two relaxation times from the analysis. This is not to be recommended for the 4·3 mm ε'' and ε' data. It is desirable to measure these for about eight solutions and employ the $a'' - a'$ plots. If it is wished to incorporate the 4·3 mm data in an $\varepsilon'' - \varepsilon'$ graph, it is best to make $\varepsilon'' v\ w_2$ and $\varepsilon' v\ w_2$ plots (inserting the best straight line by the method of least mean squares) and interpolate the required 4·3 mm data at the appropriate weight fraction. Furthermore, the results fall away in accuracy at loss factors less than about 0·02 and much greater awareness, skill and time are required in measurement. However, in spite of such drawbacks this largely unexplored region is potentially most attractive.

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* To be published.

[17] W. P. Purcell and C. P. Smyth, *J. Amer. Chem. Soc.* **83**, 1063 (1961).

[18] W. F. Hassell, M. D. Magee, Miss S. Tucker and S. Walker, *Tetrahedron* **20**, 2137 (1964).