earth salt hydrate in NMA should be preferentially solvated with NMA. Furthermore, the properties of the resulting mixed solvent should differ negligibly from those of pure NMA.

The limiting equivalent conductances of the strontium, calcium, barium and magnesium ions in NMA at 40° are 10.4, 10.2, 10.1 and 9.8 ohm^{-1} cm.^{2} equiv.$^{-1}$, respectively. These are based on the values of anionic conductances which were reported in a previous paper.[6] Insofar as the series of alkaline earth ions is concerned, the barium ion is generally the most conducting; however, in NMA its limiting equivalent conductance is intermediate in the series. This behavior is very much analogous to sodium salts having greater limiting equivalent conductances than corresponding potassium salts in N,N-dimethylacetamide[16] and N,N-dimethylpropionamide.[17] In comparison to aqueous solutions, obviously unusual relative ionic solvation effects are operative in the amides. This is further illustrated by the limiting equivalent conductance of each of the alkaline earth ions in NMA being 15–20% greater than that of the potassium ion which is the most conducting of the alkali metal ions which have been studied.

As indicated earlier in the discussion, the results presented in Table II are based on the Shedlovsky equation[14] which at low concentrations reduces to the limiting theoretical Onsager equation. Since this same method of analysis has been used for treating the data for alkaline earth salts in aqueous solutions,[18] convenient comparisons are facilitated. An analysis of the data by the new Fuoss method[19] is inapplicable since the method has been worked out only for the symmetrical valence type of electrolyte.

This research involving the use of NMA as a solvent represents by far the most comprehensive study of the conductances of alkaline earth salts in a non-aqueous medium. Additional work involving the behavior of NMA solutions of several other 2–1, 3–1, 2–2, 1–2 and 1–3 salts is in progress in this Laboratory.

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[16] G. R. Lester, T. A. Gover and P. G. Sears, *J. Phys. Chem.*, **60**, 1076 (1956).

[17] E. D. Wilhoit and P. G. Sears, *Trans. Ky. Acad. Sci.*, **17**, 123 (1956).

[18] T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1932).

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LEXINGTON, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND ELECTRICAL ENGINEERING RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Dielectric Dispersion in Symmetric Top Molecules[1]

BY JAMES E. BOGGS

RECEIVED MARCH 3, 1958

The dielectric constants of CH_3CN, CHF_3, $CHCl_3$ and CH_3CCl_3 have been measured at 9400 megacycles over a range of pressures and temperatures. For these gases, as well as CH_3Cl and CH_3Br reported earlier, the orientation polarization at 9400 megacycles is appreciably lower than the static value. The difference is shown to be due to dispersion associated with low-frequency inversion transitions. The dielectric constant measurements are correlated with published data on microwave absorption by the pressure-broadened inversion transitions. Moreover, the measured dielectric constants can be accurately predicted by application of the Van Vleck–Weisskopf theory of the intensity of spectral lines to an inversion transition occurring at zero frequency.

Most studies of the dielectric constants of gases have been made at relatively low frequency, generally of the order of 1 megacycle. In the range between 0 and 10 megacycles the dielectric constant has been found to be frequency-independent for all gases. At the other extreme of frequency, refractive index measurements of high accuracy are available in the optical region where the dielectric constant is found to be much lower. Between the frequency regions accessible by these two methods there is a wide range of frequency where measurements were not possible before the development of microwave techniques.

For gases at moderate or low pressure, it has been presumed generally that the dielectric constant would be independent of frequency until the measuring frequency approached the lowest resonance frequency of the molecule, normally for the $J = 0 \rightarrow J = 1$ rotational transition. Boggs, Crain and Whiteford,[2] however, have measured the dielectric constant of a number of gases at a frequency of 9400 megacycles and have found that while some gases show the static value of dielectric constant, others (CH_3Cl, $CHClF_2$, $CHCl_2F$, CH_3Br, and possibly $CClF_3$ and CCl_3F) have a distinctly lower dielectric constant at 9400 megacycles than at low frequency. This result cannot be attributed to dispersion involving a pure rotational transition, since, for CH_3Cl and CH_3Br at least, the measurement frequency is well below the frequency of the first rotational spectral line. More recently, Boggs, Thompson and Crain[3] have shown that no measurable variation in the dielectric constant occurs in the frequency region surrounding the first rotational line of cyanoacetylene or the third rotational line of *t*-butyl iodide. While such a variation would certainly be expected to be present, its magnitude must be below the ± 0.5% level which could be detected. These workers also have shown[3] that the dielectric constants of CH_3Cl and CH_3CCl_3, which are lower at 9400 megacycles than at low frequency, are still decreasing at 9400 megacycles.

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[1] A portion of this work was supported by Air Force Contract AF 33(616)-2842.

[2] J. E. Boggs, C. M. Crain and J. E. Whiteford, *J. Phys. Chem.*, **61**, 482 (1957).

[3] J. E. Boggs, C. M. Thompson and C. M. Crain, *ibid.*, **61**, 1625 (1957).

In the relatively early days of microwave studies, several workers[4–6] observed appreciable absorption in gaseous alkyl halides, which they attributed to pressure broadening of low-frequency inversion transition lines. Birnbaum has recently made a much more thorough study[7,8] of this effect for symmetric top molecules. Application of the Van Vleck–Weisskopf equation for the shape of pressure-broadened lines to a transition at zero frequency gives an expression for absorption as a function of frequency identical with the Debye equation which describes dielectric relaxation in polar liquids. The absorption data obtained by Birnbaum are in fairly good agreement with the Debye equation but are better fitted by the Cole–Cole equation which makes allowance for a distribution of relaxation times.

The present study presents the results of dielectric constant measurements on certain symmetric top molecules at a frequency of 9400 megacycles and correlates the resulting information on dielectric dispersion with Birnbaum's data on microwave absorption. It also shows that the observed dielectric data can be predicted from fundamental theory, assuming that the dispersion is due to the possibility of low-frequency inversion transitions.

Experimental

The apparatus and general methods of measurement were similar to those used by Boggs, Crain and Whiteford.[2] Dielectric constant values were obtained for each gas using a Crain refractometer,[9,10] a series of measurements being made at varying gas pressures at each of four different temperatures between 30 and 90°. At the low pressures used (1.5 to 10 cm.), deviations from the ideal gas law were not observed. There was a considerable tendency for some of the gases to adsorb on the wall of the refractometer cavity, but after a short time the pressure and refractometer readings became stable. Since the electric field in the cavity is zero at the walls, the electrical effect of adsorbed gas should be minimal.

All of the liquids were purified by fractional distillation through an efficient column. Compounds which are gases at room temperature were purified by fractional distillation on a vacuum line. In some cases, tests for purity were made by gas phase chromatography.

Results

For all of the gases measured, the quantity ($\epsilon - 1$) was found to be a linear function of pressure over the rather limited pressure range used. In each case, a straight line was obtained when the molar polarization was plotted against the reciprocal temperature. The value of the molar polarization at 30° taken from this line together with the extrapolated distortion polarization and the low-frequency values of the same quantities taken from the literature are shown in Table I. The data for CH_3Cl and CH_3Br previously reported by Boggs, Crain and Whiteford[2] are included for comparison.

It will be noted from Table I that the distortion polarization measured at 9400 megacycles agrees within experimental error with the value obtained from low-frequency measurements. In every case, however, the total polarization is appreciably lower at the higher frequency, indicating a smaller value for the orientation polarization.

TABLE I

Gas	P_{30} (cc.) 9400 Mc.	P_{30} (cc.) "Static"	P_D (cc.) 9400 Mc.	P_D (cc.) "Static"
CH_3Cl	78.0	84.4[a]	14.2	14.1[a]
CH_3Br	76.2	80.3[b]	14.6	15.2[b]
CH_3CN	291	322[c]	15	11.1[c]
CHF_3	41.1	63.2[d]	8.0	8.8[e]
$CHCl_3$	37.0	45.9[f]	23.3	25.3[f]
CH_3CCl_3	66.5	91.4[f]	28.4	27.0[f]

[a] R. Sanger, O. Steiger and K. Gächter, *Helv. Phys. Acta*, **5**, 200 (1932). [b] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934). [c] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937). [d] J. N. Shoolery and A. H. Sharbaugh, *Phys. Rev.*, **82**, 95 (1951). [e] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, **A2**, 364 and 630 (1935). [f] A. A. Maryott, M. E. Hobbs and P. M. Cross, THIS JOURNAL, **63**, 659 (1941).

Discussion

According to the Debye equations, the real part of the complex dielectric constant

$$\epsilon^* = \epsilon' + i\epsilon''$$

is given by

$$\epsilon' = \epsilon_\infty' + \frac{\epsilon_0' - \epsilon_\infty'}{1 + (\lambda_M/\lambda)^2} \tag{1}$$

and the imaginary part, or loss factor, is given by

$$\epsilon'' = \frac{(\epsilon_0' - \epsilon_\infty')\,\lambda_M/\lambda}{1 + (\lambda_M/\lambda)^2} \tag{2}$$

where λ is the wave length of the measuring radiation, λ_M is the critical wave length for which the loss factor is a maximum, ϵ_0' is the value of the dielectric constant at zero frequency and ϵ_∞' is the value the dielectric constant approaches at frequencies well above those at which absorption occurs. As has been pointed out by Birnbaum,[7,8] the Van Vleck–Weisskopf equation for the shape of spectral lines broadened by molecular collisions reduces to this same form when written for the special case of a line at zero frequency.

Rearranging equation 1 gives

$$\epsilon' - 1 = \frac{(\epsilon_0' - \epsilon_\infty')}{1 + (\lambda_M/\lambda)^2} + (\epsilon_\infty' - 1)$$

Since ($\epsilon_0' - \epsilon_\infty'$) and ($\epsilon_\infty' - 1$) are each proportional to pressure and λ_M decreases with increasing pressure, this leads in general to a rather complex dependence on pressure. However, if λ_M/λ is large, ($\epsilon' - 1$) becomes essentially equal to ($\epsilon_\infty' - 1$), and consequently is directly proportional to pressure. Since this is the pressure dependence we have observed experimentally, it must be that λ_M is well above the wave length of 3.2 cm. used in our measurements and we are observing the value of the dielectric constant after all of the dispersion connected with the low-frequency absorption has had its effect. If our measurements had been extended to higher pressure, which was impossible experimentally, the value of λ_M would have decreased, and we would presumably no longer have found a linear relation between ($\epsilon' - 1$) and pressure.

Of the gases we have studied, Birnbaum[7,8] has measured the loss factor for CH_3Cl, CH_3Br, CH_3CN

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(4) W. D. Hershberger, *J. Appl. Phys.*, **17**, 495 (1946).

(5) J. E. Walter and W. D. Hershberger, *ibid.*, **17**, 814 (1946).

(6) B. Bleaney and J. H. N. Loubser, *Proc. Phys. Soc.* (*London*), **A63**, 483 (1950).

(7) G. Birnbaum, *J. Chem. Phys.*, **27**, 360 (1957).

(8) G. Birnbaum, Ph.D. dissertation, George Washington University, 1956.

(9) C. M. Crain, *Rev. Sci. Instr.*, **21**, 456 (1950).

(10) C. M. Crain and C. E. Williams, *Electronics*, **29**, 150 (1956).

and CHF_3 over a range of frequencies and pressures. From his measurements and the Debye relations he derives values for $(\tan \delta/p)_M$, the maximum value of the ratio of the loss tangent to pressure (which is independent of frequency), and for $\Delta\nu/p$, the variation of line width with pressure. The maximum absorption is obtained when $\nu = \Delta\nu$, so $\lambda_M = 1/\Delta\nu$. From equation 2, $\epsilon_M'' = {}^1/_2\,(\epsilon_0' - \epsilon_\infty')$, so $(\epsilon_0' - \epsilon_\infty')$ at any pressure will be given by $2\,(\tan \delta/p)_M$. Table II shows the values of the critical wave length and $(\epsilon_0' - \epsilon_\infty')$ calculated from Birnbaum's absorption data and the value of $(\epsilon_0' - \epsilon')$ measured by us, all calculated at the temperature of 26° used by Birnbaum and at a pressure of 100 mm., which is the highest pressure we have used. It must be emphasized that the ϵ_∞' involved in this calculation is not the value of the dielectric constant at infinite frequency but the value to which the dielectric constant would be reduced at high frequency by the Debye absorption alone. At still higher frequency, dispersion connected with rotational transitions would appear, and the dielectric constant associated with molecular distortion alone might be considerably lower.

TABLE II

Gas	Birnbaum λ_M (cm.)	Birnbaum $(\epsilon_0' - \epsilon_\infty') \times 10^5$	Observed $(\epsilon_0' - \epsilon') \times 10^5$
CH_3Cl	66	10.0	10.2
CH_3Br	78	7.6	6.6
CH_3CN	22	32	49
CHF_3	147	33	36

It will be noted from Table II that there is good agreement between the values of $(\epsilon_0' - \epsilon_\infty')$ calculated from Birnbaum's adsorption data and the measured values of $(\epsilon_0' - \epsilon')$ for CH_3Cl, CH_3Br and CHF_3. This confirms the conclusion reached from the pressure dependence of the dielectric constant that at the pressures we have used all of the dispersion connected with the low-frequency absorption has had its effect below the measuring frequency of 9400 megacycles so that ϵ' is equal to ϵ_∞'. The discrepancy between the measured and calculated values of CH_3CN is considerably larger than the estimated error in our measurements of ϵ'. The sample we used was Eastman spectroscopic grade and showed only completely negligible traces of impurities in a vapor phase chromatograph. The average deviation of the points on our plot of molar polarization *vs.* reciprocal temperature was 0.4%. It must be remembered, however, that $(\epsilon_0' - \epsilon')$ represents a small difference between two relatively large numbers, especially in the case of CH_3CN where the orientation polarization is down by only about 9% at 9400 megacycles compared with the static value. If the low-frequency measurements, made in 1937, were in error by as much as 3%, our value of 49×10^{-5} would be reduced to 32×10^{-5} in agreement with Birnbaum. An error of 2% of the low-frequency dielectric constant would put our measurement in agreement with the theoretical value to be discussed below.

The loss measurements made by Birnbaum deviate somewhat from the values predicted by the Debye equations. The deviation is of the sort that would be expected if there was a distribution of relaxation times or line widths rather than the single value on which the Debye theory is based. Such a situation is treated by the empirical relations of Cole and Cole,[11] which may be written in the form

$$\epsilon' = \epsilon_\infty' + \frac{(\epsilon_0' - \epsilon_\infty')\,[1 + (\lambda_M/\lambda)^{1-\alpha} \sin (\alpha\pi/2)\,]}{1 + 2(\lambda_M/\lambda)^{1-\alpha} \sin (\alpha\pi/2) + (\lambda_M/\lambda)^{2(1-\alpha)}} \qquad (3)$$

and

$$\epsilon'' = \frac{(\epsilon_0' - \epsilon_\infty')(\lambda_M/\lambda)^{1-\alpha} \cos (\alpha\pi/2)}{1 + 2(\lambda_M/\lambda)^{1-\alpha} \sin (\alpha\pi/2) + (\lambda_M/\lambda)^{2(1-\alpha)}} \qquad (4)$$

where α is a constant with values between 0 and 1. For $\alpha = 0$ the Cole–Cole equations reduce to the Debye expressions.

From his absorption measurements, Birnbaum[7,8] has derived a value of $\alpha = 0.051$ for CH_3Cl. Using Birnbaum's measurements of the loss factor at 1193 and 2216 megacycles, equation 4 can be solved for λ_M and for $(\epsilon_0' - \epsilon_\infty')$, giving values of 81 cm. and 13×10^{-5}, respectively, for CH_3Cl. The distribution of relaxation times results in the dispersion curve being spread out over a somewhat wider frequency range. If the Cole–Cole equation is valid, it would appear that our dielectric constant measurement at 9400 megacycles might not be quite down to the ϵ_∞' value. This calculation and those used in preparing Table II, however, are made for a pressure of 100 mm., which is the upper limit of the pressures we have used in measuring the dielectric constant. At lower pressures the value of λ_M will be greater and the variation in the dielectric constant will occur at a lower frequency.

It is of interest to examine the slope of the curve of dielectric constant *vs.* frequency in the region of our measurements. Converting wave length to frequency and taking the derivative, one obtains from equation 1

$$\frac{d\epsilon'}{d\nu} = -\frac{2(\epsilon_0' - \epsilon_\infty')(\nu/\nu_M)}{\nu_M\,[1 + (\nu/\nu_M)^2]^2}$$

Substituting the values for CH_3Cl at 100 mm. pressure and $\nu = 9400$ megacycles, gives $d\epsilon'/d\nu = -5.0 \times 10^{-17}$ per cycle. If one assumes the Cole–Cole equation rather than the Debye equation, the slope is given by the derivative of equation 3, which is

$$\frac{d\epsilon'}{d\nu} = -\frac{2(\epsilon_0' - \epsilon_\infty')(1 - \alpha)(\nu/\nu_M)^{1-\alpha}}{\nu_M\,[1 + 2(\nu/\nu_M)^{1-\alpha} \sin (\alpha\pi/2) + (\nu/\nu_M)^{2(1-\alpha)}]^2}$$

Inserting the appropriate values for CH_3Cl at 100 mm., 26°, and a frequency of 9400 megacycles gives $d\epsilon'/d\nu = -6.6 \times 10^{-17}$ per cycle. Boggs, Thompson and Crain[3] have measured the frequency dependence of the dielectric constant of CH_3Cl at 42° and 9400 megacycles and have reported a value equivalent to $d\epsilon'/d\nu = -(2.0 \pm 0.4) \times 10^{-14}$ per cycle at a pressure of 100 mm. It is clear that the frequency variation of the dielectric constant which they observed, if real, cannot be explained in terms of the low-frequency Debye absorption alone.

The extent of lowering of the dielectric constant of a gas due to low-frequency inversion transitions also can be approached in a more fundamental way by making use of the Van Vleck–

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[11] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

Weisskopf evaluation of the intensity of a pressure-broadened spectral line applied to the special case of a transition at zero frequency and using the dipole moment matrix element for an inversion transition. The dipole moment of a rotating molecule may be resolved into two components, one perpendicular to the direction of total angular momentum which gives rise to the ordinary rotational spectrum, and one parallel to this direction which can interact with an electromagnetic field only if the molecule undergoes inversion. It is the latter component with which we are concerned.

The Van Vleck–Weisskopf equation specialized as described above becomes

$$\epsilon'' = \frac{4\pi N}{3kT} \Sigma f_{\mathrm{JK}} |\mu_{\mathrm{JK}}|^2 \frac{\nu \Delta\nu}{\nu^2 + \Delta\nu^2}$$

where N is the number of molecules per cc., f_{JK} is the fractional number of molecules occupying the JK rotational energy level, and $|\mu_{\mathrm{JK}}|$ is the dipole moment matrix element for an inversion transition Birnbaum[7,8] gives a closed expression for evaluating the sum

$$<\mu^2_{\mathrm{JK}}> = \Sigma f_{\mathrm{JK}} |\mu_{\mathrm{JK}}|^2$$

in terms of the permanent dipole moment, μ, and the molecular rotation constants, A_0 and B_0. At a given pressure, the maximum loss occurs when $\nu = \Delta\nu$, and at this pressure $\epsilon_0' - \epsilon_\infty' = 2\,\epsilon_{\mathrm{M}}''$.

Table III shows the values of $<\mu^2_{\mathrm{JK}}>/\mu^2$ calculated from Birnbaum's expression, values of B_0 as tabulated by Gordy, Smith and Trambarulo[12] and values of A_0 calculated from molecular structural parameters for the gases we have studied. It will be noted that this quantity represents the fraction of the total orientation polarization that is due to the inversion effect. The remaining fraction will disappear as the measuring frequency is increased through the region of rotational absorption for the molecule. Table III also shows the values of $(\epsilon_0' - \epsilon_\infty')$ at a pressure of 100 mm. calculated on the basis of this model and the observed values of $(\epsilon_0' - \epsilon')$. With the exception of the results for CH_3CN, as discussed above, the agreement is quite satisfactory. This lends strong support to the explanation we are proposing for the observed variation of dielectric constant with frequency.

TABLE III

Gas	$<(\mu^2_{\mathrm{JK}})>/\mu^2$	$\mu \times 10^{18}$	Theoretical $(\epsilon_0' - \epsilon_\infty')$ $\times 10^5$	Observed $(\epsilon_0' - \epsilon')$ $\times 10^5$
CH_3Cl	0.100	1.87	10.8	10.2
CH_3Br	.073	1.80	8.2	6.6
CH_3CN	.075	3.94	38	49
CHF_3	.415	1.64	37	36
$CHCl_3$	.425	1.01	14	14
CH_3CCl_3	.373	1.79	39	40

Contrary to previous expectations, dielectric dispersion in a gas is not restricted to the region of rotational absorption. A considerable portion of the orientation polarization, depending on the shape of the molecule, disappears at relatively low frequencies due to dispersion associated with low-frequency inversion transitions. Measurements of dielectric constants in the microwave region can be correlated with absorption measurements on the pressure-broadened inversion spectral lines, or the dielectric constant in the microwave region can be calculated accurately from molecular structural parameters.

AUSTIN 12, TEXAS

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[12] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, New York, N. Y., 1953.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Dielectric Properties of Hemoglobin. II. Anomalous Dispersion during Oxygenation

BY SHIRO TAKASHIMA AND RUFUS LUMRY

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The dielectric properties of horse and bovine hemoglobin were determined in the frequency range from 50 kc. to 6 mc. as a function of oxygen pressure. The anomalous dispersion which appears in this frequency region is well fitted by the equation of Cole and Cole so that the data can be analyzed in terms of the real component of the dielectric constant ϵ', the mean dielectric relaxation time τ_0 and the distribution parameter for these times α. The dipole moment μ, and τ_0 for unoxygenated horse hemoglobin were 380 debye and 14.5×10^{-8} sec.: for oxygenated horse hemoglobin 430 debye and 10^{-7} sec. and 270 and 12.7×10^{-8} sec. for bovine oxyhemoglobin. In confirmation of previous studies, the difference, $\epsilon_0 - \epsilon_\infty$, in dielectric constant at frequencies below and above the dispersion region, was found to pass through a series of maxima and minima. The maxima occur at about 25 and 75% oxygenation, the central minimum at 50%. Supplementing these findings both τ_0 and α were found to follow the same pattern with the extrema at the same oxygen pressures. α of horse hemoglobin was large at all oxygen pressures, indicating a wide distribution of relaxing species, but that of bovine hemoglobin was much smaller and its change as a function of oxygen was also less pronounced than horse hemoglobin. Aggregation or dissociation of the protein and protein–protein interactions are excluded as sources of phenomena and the possibilities that change in protein shape or charge distribution may be controlled by oxygen pressure are discussed.

In a search for means by which to connect the structure of proteins with their function, hemoglobin quickly presents itself as an interesting subject for experimental attack. Physical and chemical differences between hemoglobin with and without oxygen have been reported.[1] Of most interest among these is the marked difference between the X-ray diffraction patterns and the optical dichroism of the two forms.[2] Indeed the X-ray patterns are so different as to suggest that the internal structure of the molecule becomes drastically altered on oxygen uptake. The significance of this intriguing fact and its possible relationship to the

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[1] R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc., New York, N. Y., 1949, Chap. 6.

[2] J. Boyes-Watson, E. Davidson and M. F. Perutz, *Proc. Roy. Soc.* (*London*), **A191**, 83 (1947); M. F. Perutz, *ibid.*, **A195**, 474 (1949).