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The Optical Dispersion of HCl in the Infrared

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There is, at present, a discrepancy of 162×10^{-6} between the temperature invariant part of the dielectric constant of HCl and the square of the index of refraction extrapolated to infinite wave-length; a difference which is more than 10 times the estimated uncertainty of the measurements, and which is usually assumed to be due to the contribution of infrared vibration bands to the index. In order to test the validity of the above assumption and also to investigate a seldom used method of determining the effective charge of molecules, the optical dispersion of HCl has been measured between 1 and 10μ. These measurements yield a value of $(1.00\pm 0.05)\times 10^{-10}$ e.s.u. for the effective charge of the rotator-vibrator; which shows, in agreement with measurements of intensity of absorption, that the contribution of the rotator-vibrator to n_∞ is much too small to explain the above discrepancy. Since the uncertainty in n_∞^2 as obtained from the refraction measurements is not more than 3×10^{-6}, this indicates that the uncertainty in the dielectric constant measurements must be somewhat larger than is ordinarily assumed. During the course of the investigation, it was discovered that the contribution of the pure rotation to the index of refraction was large enough to be measured with a fair degree of accuracy. Since most of the rotators are in excited states, these data furnish a quantitative check of the negative terms in the Kramers dispersion formula. They also furnish a new means of determining the electric moment; and the fact that the moment which is obtained agrees with that obtained from dielectric constant measurements indicates that the low absorption intensities observed by Czerny and by Badger must be in error.

INTRODUCTION

According to ordinary dispersion theory, the temperature invariant part of the dielectric constant should be equal to the square of the index of refraction extrapolated to zero frequency. Van Vleck[1] has pointed out that for HCl there is a difference between the two which is far greater than the estimated uncertainty of the measurements. For example, the index of refraction measurements of Cuthbertson and Cuthbertson,[2] extrapolated from the visible, give for n_∞^2-1, $878\cdot 10^{-6}\pm 2\cdot 10^{-6}$; while, from dielectric constant measurements, Zahn[3] obtains $1040\cdot 10^{-6}\pm 10\cdot 10^{-6}$, a difference of $(162\pm 12)\cdot 10^{-6}$. The usual explanation for such discrepancies, that is, that they are due to the contribution of molecular vibration to the index, seemed in this case to be extremely improbable, since the absorption intensity measurements of Bourgin[4] indicate a contribution of the infrared vibration to n_∞ of only $1\cdot 10^{-6}$. However, accurate measurements of absolute intensity are extremely difficult to make, and the wide range of values reported by various observers[5] makes a determination by a different method highly desirable.

It was Professor Van Vleck's suggestion that

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[1] Van Vleck, *The Theory of Electric and Magnetic Susceptibilities.*

[2] C. and M. Cuthbertson, Phil. Trans. Roy. Soc. **A213**, 1 (1913).

[3] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

[4] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).

[5] For a review of intensity measurements up to 1926, see D. M. Dennison, Phil. Mag. **1**, 216 (1926).

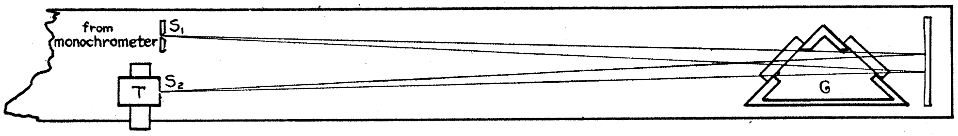

FIG. 1. The gas spectrometer. *T*, thermopile; *G*, gas prism. The distance from the gas prism to the slits is approximately 91 cm.

measurements of the index of refraction should be taken in the neighborhood of the rotation-vibration band. From these measurements it is possible to calculate the effective charge (for the vibration), that is, the rate of change of electric moment with internuclear distance; and consequently, from this, the contribution of the rotator-vibrator to n_∞. Since refraction measurements may be taken entirely outside the region of absorption, they are thus free from troublesome corrections due to nonhomogeneity of the light used. It was therefore believed that this type of measurement would provide a simpler and more accurate method of determining the effective charge than absolute intensity measurements, at least for molecules whose effective charge is fairly large.[6]

APPARATUS AND PROCEDURE

The apparatus was essentially the same as that used by Statescu[7] and by Wetterblad[8] for measurement of the index of refraction of CO_2. The method consists in measuring the change in deviation produced by a change in pressure in a hollow prism containing the gas being studied. Monochromatic light was obtained from a Wadsworth type rocksalt monochromator. A Nernst glower served as the source. Wavelengths were obtained from the calibration tables published by P. C. Cross.[9] Small errors in wavelength were not important in this work since the dispersion curve was nowhere very steep. The gas prism, a 90° hollow brass prism with holes 5 cm high by 6 cm wide, was provided with rocksalt windows 2 cm thick, the surfaces of which were sufficiently plane and parallel so that no troublesome corrections were necessary. These windows were pressed against rubber gaskets cemented to the brass by a mixture of beeswax and rosin. The joint between the salt and rubber was made vacuum tight by Lubriseal. Fig. 1 shows the arrangement and essential dimensions of the gas spectrometer.

The HCl generator and reservoir were all glass, except for the stopper in the generator flask which was rubber with a coat of wax on the bottom. The HCl was generated by dropping Merck's Reagent H_2SO_4 on Baker's Analyzed NaCl. The gas was condensed in a liquid-air trap. The whole system was kept evacuated by a Hyvac for some time before starting the reaction and during the generation. When an adequate supply of HCl had been condensed in the trap, it was shut off from the generator flask and the HCl was allowed to distill slowly into the gas prism and connections until a little more than the maximum pressure desired for the measurements had been reached. The stopcock between the prism and the first liquid-air trap was then closed, and the gas was condensed in a second trap which was connected through a stopcock to the gas prism so that the desired pressure could be developed in the prism and the stopcock then closed. After a run the gas was condensed in the trap.

An indication that reactions taking place in the gas prism were of little or no importance is furnished by the fact that, although the HCl was twice allowed to stand in the gas prism for about a month at a pressure of between one and two atmospheres, subsequent index determinations showed that there was no change greater than $0.5 \cdot 10^{-6}$ in the index. The slight apparent increase may have been error in measurement.

Gas pressures were read to one-tenth millimeter on an invar tape which was suspended between the two arms of a mercury manometer. The temperature of the gas prism was estimated to 1/100°C on a mercury thermometer which was checked at zero. Because of temperature

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[6] Concerning the importance of effective charge measurements in the study of molecular structure, see R. S. Mulliken, J. Chem. Phys. **2**, 400; **2**, 712 (1934).

[7] J. Statescu, Phil. Mag. **30**, 737 (1915).

[8] T. Wetterblad, *Dissertation* (Upsala, 1924).

[9] P. C. Cross, Rev. Sci. Inst. **4**, 197 (1933).

variations in the room as well as the unreliability of the mercury thermometer, the temperature readings may have been in error by as much as 0.15°C.

A two junction, bismuth-tellurium, vacuum thermopile, rigidly mounted on the carriage of a comparator, served as a detector for the radiation. Several of the first runs were made with a pile equipped with a charcoal trap immersed in liquid air to maintain the vacuum. With this arrangement the determinations of image position showed small irregularities which were apparently attributable to small displacements of the comparator carriage caused by a variation in buoyancy due to evaporation of the liquid air. When a thermopile without a trap was used, it had to be repumped about once a month.

Changes of deviation were measured for changes of pressure of one to two atmospheres. To determine the position of the image, galvanometer readings were taken at definite space intervals as the thermopile was moved across the image. When 0.2 mm slits were used the reading was recorded every 0.050 mm, with 0.5 mm slits every 0.100 mm, and with 1 mm slits, every 0.200 mm. These readings were plotted, deflection against position, and the center of gravity of the resulting curve determined. This was averaged with the intersection of tangents drawn on opposite sides of the maximum. For some of the readings the direction of motion of the comparator was reversed. A comparison of the direct and reverse readings for the 0.2 mm slits indicates that the determinations of the image position are dependable to within 0.002 mm with large energies, and to about 0.005 mm with the smallest energy used. With 0.5 mm slits the uncertainty is about 0.004 mm and with 1 mm slits about 0.020 mm. The change of deviation for a change of two atmospheres in the HCl pressure was about 2.9 mm.

TABLE I. *Index of refraction of HCl.* Column V gives the method of observation. (1) One vacuum reading and one HCl reading, (2) vacuum readings before and after the HCl readings, (3) direct and reversed readings in each case with vacuum readings before and after the HCl readings.

WAVE-LENGTH (microns)	$(n_0-1)\times 10^6$	p (mm)	SLIT WIDTH (mm)	METHOD OF OBS.
0.915	442.7	1495	0.5	1
1.06	442.6	1495	0.5	2
1.29	441.3	920	0.2	3
1.925	440.0	920	0.2	3
2.21	439.6	920	0.2	3
2.32	438.2	743	0.2	1
2.40	438.4	1506	0.2	1
2.48	438.4	743	0.2	1
2.53	438.3	920	0.2	3
2.56	437.4	1509	0.2	2
2.56	437.6	1506	0.2	2
2.645	436.5	743	0.2	1
2.73	437.2	1506	0.2	1
2.815	436.5	743	0.2	1
2.90	435.6	1509	0.2	1
2.90	435.7	1506	0.2	1
2.985	435.0	743	0.2	1
3.07	433.6	1506	0.2	1
3.15	433.0	743	0.2	1
3.23	426.3	1506	0.2	1
3.315	422.6	743	0.2	1
3.705	446.9	1506	0.2	1
3.705	444.3	1495	0.5	3
3.78	446.1	1509	0.2	1
3.855	442.4	1506	0.2	1
3.855	442.6	1495	0.5	1
3.855	443.4	1418	0.5	3
3.925	443.0	1509	0.2	1
3.995	441.4	1506	0.2	1
3.995	441.1	1495	0.5	3
4.06	439.8	1509	0.2	1
4.135	441.5	1506	0.5	1
4.135	440.3	1495	0.5	1
4.135	442.2	1418	0.5	3
4.40	439.2	1506	0.5	1
4.40	439.4	1495	0.5	2
4.59	438.5	1506	0.5	1
4.59	439.4	1495	0.5	2
4.59	439.7	1418	0.5	3
4.955	438.6	1506	0.5	1
4.955	437.8	1418	0.5	3
5.185	436.3	1495	0.5	2
5.755	437.7	1506	0.5	1
5.755	435.1	1495	0.5	2
6.055	435.6	1418	0.5	3
6.96	432.1	1307	1.0	3
8.00	431.1	1307	1.0	3
8.95	429.6	1307	1.0	3
10.20	428.1	1307	1.0	3*

* Poor data.

RESULTS

The relationship between change of deviation and index of refraction is given by the expression[8]

$$n-1-\Delta N=K(L-L_0)[1-K(L-L_0)/2].$$

In this equation ΔN takes care of the changes of index of the air surrounding the prism due to changes in temperature and barometric pressure occurring between the times the vacuum and high pressure readings were taken. L and L_0 are the positions of the slit image when the gas prism is full and evacuated, respectively. The constant K, which depends on the geometry of construction of the gas spectrometer, was determined by calibration with dry air. As standards the following values given by Wetterblad were used:

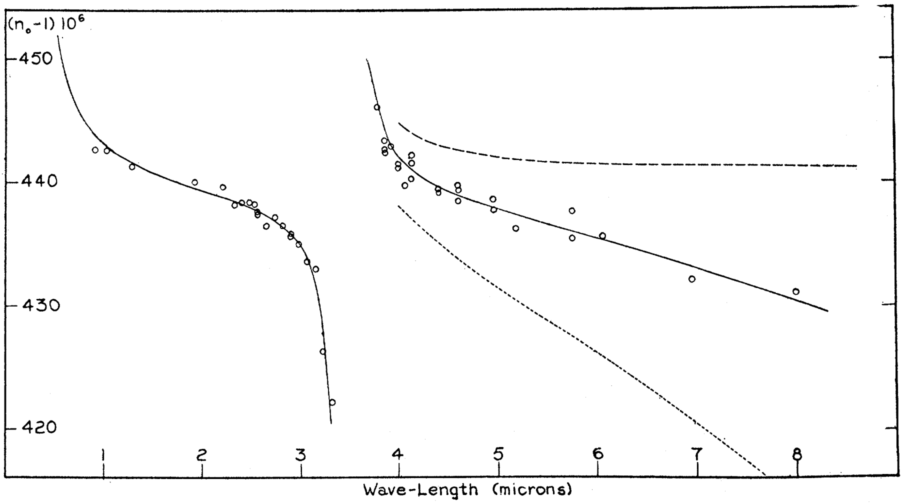

FIG. 2. Index of refraction of HCl as a function of wave-length. The continuous curve is the result of substituting $\epsilon=1.00\times10^{-10}$ e.s.u. and $\mu=1.18\times10^{-18}$ e.s.u. in the Kramers dispersion formula. The dotted curve represents the computed curve when the negative terms are omitted from the dispersion formula. The dashed curve indicates the course the curve would take if the pure rotation contributed nothing to the index of refraction.

$(n_0-1)10^6=288.78$ at 1.27μ; 288.12 at 2.32μ; 287.90 at 4.59μ; at 760 mm 0°C. In reducing from experimental to standard conditions and *vice versa*, the following relation was used:[8]

$$n_0-1=\frac{(n-1)(1+\alpha t)760}{p[1+\beta(p-760)]},$$

where α is the temperature coefficient of expansion and β is a factor introduced to allow for the fact that the index of refraction is not exactly proportional to the pressure. For air β is equal to $8\cdot10^{-7}$ (Wetterblad), and for HCl it is $1.6\cdot10^{-5}$. For HCl, since there were no tabulated values of β, this reduction was made by means of extrapolated pv data[10] and the Clausius-Masotti equation.

The values of n_0-1 are given in Table I and plotted in Fig. 2. In each case, all readings for one wave-length taken in one run are averaged. Column V indicates the method of observation: (1) One vacuum reading and one HCl reading, (2) vacuum readings before and after the HCl readings, (3) direct and reversed readings in each case with vacuum readings before and after the HCl readings. A smooth curve—not shown—was drawn to fit these points and the values of the index for particular wave-lengths were read from this curve. This curve was redrawn several times and the average values used in the following analysis.

CALCULATION OF ϵ AND μ

In the interpretation of the above data, contributions from three sources must be considered, the electrons, the vibrator-rotator, and the rigid rotator. The electronic contribution was obtained by extrapolation from the data of Cuthbertson and Cuthbertson reduced to standard conditions. In order to get best agreement with theory on both sides of the rotation-vibration band it was necessary to add $0.9\cdot10^{-6}$ to their values. This shift is reasonable since the values of the index of air used for calibration by Cuthbertson and by Wetterblad differed by approximately this amount. A constant shift such as was used means that the Cuthbertson data were actually used only to determine the rate of change of the electronic contribution with frequency.

In computing the contribution of the vibrator-rotator it was found that the use of a single frequency was unsatisfactory near the band. In order to consider the effect of the several frequencies in the band, the values of the ampli-

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[10] R. W. Gray and F. P. Burt, J. Chem. Soc. **95**, 1633 (1909).

tudes as given by Oppenheimer[11] were substituted in the Kramers dispersion formula[12]

$$n^2-1=\frac{8\pi N}{\sum_{l} e^{-W_l^0/kT}}\sum_{l,\,l'}\frac{\nu(l';l)\,|P_E{}^0(l;l')|^2}{h[\nu(l';l)^2-\nu_0{}^2]}e^{-W_l^0/kT}. \tag{1}$$

The final result obtained for the contribution of the vibrator-rotator was

$$\Delta_{VR}(n^2-1)=\frac{N\epsilon^2}{3\pi m_{\text{eff}}\sum_0^\infty(2m+1)e^{-W_m/kT}}\sum_{m=1}^{\infty}\frac{mFe^{-W_m/kT}}{\nu(0,m;1,m-1)^2-\nu^2}+\frac{mF'e^{-W_{m-1}/kT}}{\nu(0,m-1;1,m)^2-\nu^2},$$

where ϵ = effective charge, ν = the frequency of the incident light, I = the moment of inertia of the unexcited molecule, ν_0 = the normal frequency of vibration,

$$F=[\nu(0,m;1,m-1)/\nu_0][1+4rm(1+\tfrac{5}{8}rm-\tfrac{3}{8}r)],$$
$$F'=[\nu(0,m-1;1,m)/\nu_0][1-4rm(1-\tfrac{5}{8}rm-\tfrac{3}{8}r)] \quad r=h/4\pi^2I\nu_0.$$

It was found sufficient to sum up to $m=12$. The frequencies and energy levels were obtained from the values given by Colby, Meyer, and Bronk.[13]

The contribution of the pure rotation was calculated by means of the Kramers dispersion formula in the form given by Debye (polar molecules). The same result may of course be obtained by substituting in Eq. (1) the matrix components of the electric moment of the rigid rotator. Since, in the region investigated, the rotational frequencies are always small compared with the frequency of the radiation used, ν_r could be neglected in the denominator. The contribution of the rotator may then be written

$$\Delta_R(n^2-1)=\frac{2N\mu^2}{3\pi I\nu^2\sum_0^\infty(2m+1)e^{-W_m/kT}}\sum_1^\infty(m^2e^{-W_{m-1}/kT}-m^2e^{-W_m/kT}),$$

where μ is the electric moment.

Considering all the contributions to the index of refraction, we then have $n_0{}^2-1=(n_0{}^2-1)_{\text{C\&C}}+f(\lambda)\epsilon^2+g(\lambda)\mu^2$. We thus have two disposable constants, ϵ and μ which are to be evaluated by comparison with the experimental results. These may be evaluated by successive approximations. We therefore assume a value of ϵ^2 and calculate μ^2 by comparison with the experimental curve, use this value of μ^2 and correct ϵ^2, continuing this process until the values obtained for ϵ^2 and μ^2 remain constant throughout the range of wavelengths available. In this calculation, the extrapolated values from Cuthbertson and Cuthbertson are shifted a small amount as indicated previously. The average values of ϵ^2 and μ^2 are obtained by weighting each value of ϵ^2 or μ^2 in proportion to the contribution to the index at that point, excluding the values at 9 and 10μ where the probable error in the experimental values of n_0-1 is large. The final results for ϵ and μ are

$$\epsilon=1.00\times10^{-10}\text{ e.s.u.};\ \mu=1.18\times10^{-18}\text{ e.s.u.}$$

These values of ϵ and μ were used in calculating the values of n_0-1 shown in Table II. This table also shows the agreement between the computed values and the experimental values used in the analysis. The smooth curve in Fig. 2 is plotted from the computed values to show the agreement with the experimental points.

DISCUSSION

Although precise estimates of probable error are difficult to make for measurements such as these, it is possible, without any long rigorous analysis, to set rather definite limits to the uncertainty in the values of the effective charge and electric moment which have been calculated

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[11] J. R. Oppenheimer, Camb. Phil. Soc. Proc. **23**, 327 (1926). See also, D. M. Dennison, Phys. Rev. **31**, 501 (1928). *Note added in proof:* The theory of the dispersion of a polar gas has recently been treated by C. Manneback, *Zeeman, Verhandelingen*, pp. 293–301.

[12] Reference 1, p. 361.

[13] Colby, Meyer and Bronk, Astrophys. J. **57**, 7 (1923).

TABLE II. *Experimental and computed values of* n_0-1 *for HCl.*

λ	A $\times 10^{-6}$	B $\times 10^{-6}$	C $\times 10^{-6}$	D n_0-1 (COMP.) $\times 10^{-6}$	E n_0-1 (EXP. CURVE) $\times 10^{-6}$	D−E $\times 10^{-6}$
1.0	443.41	−0.11	−0.17	443.13	442.7	+0.4
1.5	441.33	−.27	−.38	440.68	440.6	+.1
2.0	440.61	−.59	−.67	439.35	439.6	−.2
2.5	440.27	−1.28	−1.05	437.94	438.1	−.2
2.6	440.22	−1.50	−1.14	437.58	437.7	−.1
2.7	440.18	−1.81	−1.23	437.14	437.2	−.1
2.8	440.15	−2.22	−1.33	436.60	436.5	+.1
2.9	440.12	−2.78	−1.41	435.93	435.8	+.1
3.0	440.09	−3.63	−1.52	434.94	434.8	+.1
3.1	440.06	−5.04	−1.62	433.40	433.4	.0
3.2	440.04	−8.06	−1.73	430.25	430.5	−.2
3.3	440.02	−17.16*	−1.84	(421.02)	421.8	−.8
3.7	439.95	+12.05*	−2.31	(449.69)	446.4	+3.3
3.8	439.94	+8.45	−2.44	445.95	443.0	+3.0
3.9	439.92	+5.99	−2.58	443.33	443.0	+.3
4.0	439.91	+4.87	−2.70	442.08	442.2	−.1
4.1	439.90	+4.18	−2.84	441.24	441.4	−.2
4.2	439.89	+3.71	−2.98	440.62	440.8	−.2
4.3	439.88	+3.36	−3.12	440.12	440.3	−.2
4.4	439.87	+3.09	−3.27	439.69	439.8	−.1
4.5	439.86	+2.87	−3.41	439.32	439.4	−.1
5.0	439.83	+2.23	−4.21	437.85	437.8	+.1
5.5	439.80	+1.92	−5.11	436.61	436.4	+.2
6.0	439.78	+1.73	−6.08	435.43	435.1	+.3
6.5	439.77	+1.65	−7.11	434.31	434.0	+.3
7.0	439.75	+1.57	−8.28	433.04	432.9	+.1
7.5	439.74	+1.51	−9.51	431.74	431.9	−.2
8.0	439.74	+1.46	−10.80	430.40	431.0	−.6
9.0	439.72	+1.39	−13.67	427.44	429.4	−2.0
10.0	439.72	+1.34	−16.88	424.18	427.9	−3.7

A, $(n-1)$ by extrapolating data of Cuthbertson and Cuthbertson and adding 0.90×10^{-6}.
B, contribution of vibrator-rotator to index (computed).
C, contribution of rotator to index (computed).
* Too close to the absorption band to be reliable.

above. The average deviation of the experimental points from the computed curve is 0.34×10^{-6} on the short wave-length side of the vibration band and 0.47×10^{-6} on the long wave-length side. Considering the number of experimental points, a generous estimate of the probable uncertainty is then 0.1×10^{-6} on the short wave-length side and 0.2×10^{-6} on the long wave-length side. Inspection of Table II shows that if the readings are weighted as before, according to the size of the contribution, this corresponds roughly to an error of about 0.05×10^{-20} in the square of the effective charge or 0.025×10^{-10} in the effective charge. While this may be a little optimistic, we feel confident that this value of the effective charge cannot be in error by more than $\pm 0.05\times 10^{-10}$ e.s.u. As corroborative evidence there are the data obtained with the old thermopile, data which were not used in the final computations for the reason mentioned above. Three complete dispersion curves obtained with this pile gave a value for the effective charge of 0.95×10^{-10} on rough computation by ignoring the contribution of the pure rotation, and by using mainly the short wave-length side of the band. Taking account of the effect of the rotator would of course raise the result.

The value of the effective charge [$(1.00\pm 0.05)\times 10^{-10}$ e.s.u.] which we have obtained from measurements of the index of refraction, agrees with that obtained by Bourgin[14] from measurements of intensity of absorption. Other intensity measurements,[5] both earlier and more recent, giving values for the effective charge varying between 0.2 and $0.5\cdot 10^{-10}$ cannot be reconciled with the refraction measurements. For example, the value of 0.48×10^{-10} reported comparatively recently by Bartholomé[15] would require a contribution to the index of refraction only one-fourth as large as is observed.[16] The results indicate, therefore, that for molecules with effective charges as large as that of HCl or larger, the refraction measurements probably afford a more accurate determination of the effective charge than do measurements of intensity of absorption. The prism method used in this work is, of course, unsatisfactory for the case of molecules (or modes of vibration) of much smaller effective charge, but interference refractometry is not limited in this way and should furnish sufficiently accurate results in such cases.

As has already been pointed out, the fact that the effective charge is as small as 1.00×10^{-10}, means that the contribution of the rotator-vibrator to n_∞^2 is about 2×10^{-6}, a contribution far too small to be of any help in removing the discrepancy of 162×10^{-6} between the value obtained by extrapolating optical index of refraction data and that obtained from dielectric constant measurements. The authors have had the benefit of numerous discussions with Dr. Zahn concerning the possible causes of this discrepancy. Dr. Zahn has made several suggestions concerning refinements in the interpretation of the dielectric constant measurements, but

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[14] From Bourgin's data, Dennison computes $\epsilon=0.94\times 10^{-10}$ while Bourgin obtains 0.86×10^{-10} e.s.u.

[15] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).

[16] See, however, a discussion of Bartholomé's method by Kemble in J. Chem. Phys. **3**, 316 (1935).

rough estimates indicate that the contribution to n_∞^2 is invariably very small compared to the existing difference of 162×10^{-6}. The fact that von Braunmühl's[17] result for n_∞^2 differs from that of Zahn by 562×10^{-6} indicates that perhaps some source of error has been overlooked. It must also be kept in mind that, for the case of HCl, n_∞^2 is small compared with the total dielectric constant, so that a fairly small change in the dielectric constant data would be sufficient to bring about complete agreement.[1]

So far as the electric moment is concerned, a rough computation, such as that already made for the effective charge, indicates an uncertainty of about 0.09×10^{-36} in μ^2 or about 0.045×10^{-18} in μ. Eight percent would, therefore, be a generous estimate of the uncertainty in μ. The values of μ which seem to be most generally quoted in the literature are those of Zahn[3] and von Braunmühl[17] who obtained 1.034×10^{-18} and 1.18×10^{-18} e.s.u., respectively, using temperature variation of the dielectric constant. However, for the temperature invariant part of the dielectric constant, Zahn obtains 1040×10^{-6} and von Braunmühl obtains 478×10^{-6} while $n_\infty^2-1=880\times10^{-6}$. Consideration of the above measurements of the index of refraction together with the data of Cuthbertson and Cuthbertson shows definitely that the value $880\cdot10^{-6}$ for n_∞^2-1 cannot be in error by more than 3×10^{-6}, indicating that the uncertainties in the dielectric constant measurements must be somewhat larger than is generally assumed. If we use the value of n_∞^2-1 obtained from the refraction measurements and Zahn's dielectric constant we obtain 1.07×10^{-18} e.s.u. for μ, and, using von Braunmühl's dielectric constant, 1.12×10^{-18} e.s.u. If correction is made for the fact that the Langevin-Debye formula is not strictly applicable to HCl at room temperature,[18] these values are raised about 0.016×10^{-18}. The agreement between these values for μ and the one which we obtain from our dispersion measurements, $1.18\times10^{-18}\pm10\times10^{-18}$ e.s.u., must be considered satisfactory since the uncertainty of the different values is larger than the difference between them. The present knowledge of the magnitude of the electric moment of HCl is probably best expressed by $\mu=(1.11\pm0.05)\times10^{-18}$ e.s.u. Further index of refraction measurements, especially at longer wave-lengths, should reduce the uncertainty in μ to well below 5 percent.

The importance of the negative terms in the dispersion formula is shown in Fig. 2. The dotted line in the long wave-length region is obtained by considering only the positive terms in the rotational part of the Kramers dispersion formula, those corresponding to absorption, and neglecting the negative terms corresponding to induced emission. The dashed line indicates the course the curve would take if there were no contribution from the rotator. It will be noted that the contribution which would be obtained by using only the positive terms is about $2\frac{1}{2}$ times that by using the complete formula. The necessity for negative terms in the dispersion formula has, of course, already been demonstrated by the careful and extensive work of Ladenburg[19] and his associates on the dispersion of electrically excited gases. In their experiments, however, it was extremely difficult to determine the concentration of atoms in excited states, and furthermore, only a small fraction of the atoms could be maintained in these excited states. The conditions in the present work on HCl were more favorable for a quantitative check since most of the molecules were in excited rotational states, and since the distribution among the excited states was definitely determined by the temperature of the gas.

The fact that a reasonable value of μ is obtained from the contribution of the pure rotation to the index of refraction suggests that the anomalously low absorption intensities measured by Czerny[20] and by Badger[21] are to be explained by the fact that measurements of absolute intensity are extremely difficult to make, especially in the far infrared.[22]

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[19] R. Ladenburg, Rev. Mod. Phys. **5**, 243 (1933).

[20] Czerny, Zeits. f. Physik **34**, 227 (1926).

[21] Badger, Proc. Nat. Acad. Sci. **13**, 408 (1926).

[22] Professor Herzfeld has informed us that he has recently been able to show that the absorption intensities should be much smaller than has been calculated by older theories, but not enough smaller to remove the discrepancy.