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Absorbing and Reflecting Powers of Electrolytes in the Far Infrared

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The absorbing and reflecting powers and the dispersion of different concentrations of HCl, LiCl, NaCl, KCl, KBr, LiI, KI, ZnI₂, MgSO₄, KOH and H₂SO₄ were measured in the spectral region of 50μ to 150μ. The results are discussed in terms of, (1) Maxwell's equations in which the inertia of the ions is included, (2) the influence of ions on the absorbing power of water molecules, (3) the electrical conductivity for high frequency electromagnetic fields, (4) the radius of ions, (5) the hydration of ions and (6) the validity of Stokes' law for the microscopic process involved.

INTRODUCTION

THE interaction between radiation and matter can be interpreted in terms of the displacements of electric charges. Although spectroscopy has been mainly concerned with the motion of bound charges and the application of quantum theory, there are important problems to be solved which deal with the translational motion of charges in an electromagnetic field. Probably the reason why spectroscopy has not turned to more of these problems is due to the experimental difficulties; namely, the necessity to measure absolute intensities rather than just the positions of eigenfrequencies, which often suffice for quantum theory problems. The experimental work on the translation of charges has been almost entirely limited to the movement of free electrons in metals under the action of infrared radiation and the movement of electrolytic ions due to static fields and short radio waves. In the present investigation, we have studied the motion of several ions under the influence of infrared radiation from 50μ to 150μ by determining the reflecting and absorbing powers and hence the dispersion of electrolytes. We will be concerned mainly with the following problems: (1) Under what conditions does the inertia of an ion become dominant in hindering its movement in an alternating electric field as the frequency is varied? (2) Are the ions bound in a quasicrystalline structure so that a characteristic frequency of oscillation exists which corresponds to the reststrahlen frequency of an ionic crystal? (3) What is the effective mass and radius of an ion in an electrolyte; or, how many

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water molecules are bound to an ion? (4) Do the anomalously high electrical conductivities of H⁺ and OH⁻ ions and especially small electrical conductivities of Li⁺ and Mg⁺⁺ ions, as observed with a static field or radio waves, also occur under the influence of infrared radiation?

One difficulty in applying any theory to the motion of ions in an electrolyte is the value to be assigned to the intensity of the electric field; that is, the validity of the formula, $E = (n^2 + 2)F/3$, for determining the microscopic field about an ion from the macroscopic field that is measured. In this respect, measurements of conductivity with infrared radiation seem particularly favorable because the dielectric constant, $\epsilon = n^2$, is considerably smaller in the infrared than for radio waves or a static field and hence a smaller error should be introduced in calculating the effective field acting on an ion.

SIMPLE THEORY

We will assume that the motion of an ion in an electromagnetic field satisfies the equation:

$$mdv/dt + pv = eEe^{i\omega t}, \qquad (1)$$

where m is the mass of the ion of charge e, $Ee^{i\omega t}$ the intensity of the alternating field and p is the frictional force for unit velocity. The frictional force, p, partly takes account of forces existing between the ions and surrounding water molecules, but we will neglect any resonance phenomenon. The current, I, which is produced by the electric field is:

$$I = Zev = Ze^2Ee^{i\omega t}/p = \Lambda Ee^{i\omega t}, \qquad (2)$$

where Z is the number of ions per unit volume and Λ is the specific conductivity of the electro-

lyte. Solving Eq. (1) under these conditions gives:

$$\Lambda = Ze^2/(p+i\omega m),\qquad(3)$$

which shows that when

$$\nu_0 = c/\lambda_0 = \omega_0/2\pi = p/2\pi m,\qquad(4)$$

the frictional force and the inertia of an ion are equally effective in hindering its motion in an alternating electric field of frequency ν_0 or wave-length λ_0. For longer wave-lengths, the inertia becomes less important. Using Stokes' law for the frictional force,

$$p = 6\pi\eta r,\qquad(5)$$

where η is the viscosity of the electrolyte and r is the radius of the ion, Eq. (4) becomes

$$\lambda_0 = mc/3\eta r.\qquad(6)$$

Assuming no water molecules to be tightly bound to the ions, inserting the usual values for m and r in Eq. (6) shows the order of magnitude of λ_0's to be $\lambda_{Cl^-}=30\mu$, $\lambda_{K^+}=50\mu$, $\lambda_{Br^-}=70\mu$ and $\lambda_{I^-}=100\mu$.

The electrical conductivity of the ions is determined from the absolute intensity of absorption; that is the proportion of the electromagnetic radiation that is converted into heat by the ions. Writing Maxwell's equation as

$$\left(\frac{i\omega\epsilon}{c}+\frac{4\pi\Lambda}{c}\right)Ee^{i\omega t}=\frac{i\omega}{c}\left(\epsilon-\frac{-i4\pi\Lambda}{\omega}\right)Ee^{i\omega t}$$
$$=\mathrm{Curl}\,He^{i\omega t},\qquad(7)$$

and using complex values for the dielectric constant, ϵ, and the index of refraction, n,

$$\bar{\epsilon}=\epsilon-i4\pi\Lambda/\omega=\bar{\eta}^2=n^2(1-ia)^2=n^2-i4\pi\Lambda/\omega.\qquad(8)$$

Equating imaginary terms in expression (8) using Eqs. (3) and (4) for Λ and ν_0 give:

$$n4\pi na\nu = (2Ze^2/m)[\nu_0/(\nu^2+\nu_0^2)],\qquad(9)$$
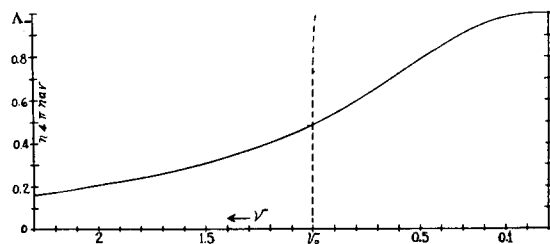

FIG. 1. Theoretical absorption of an ion as a function of wave-length.

where na is the absorption coefficient of an electrolyte due to the presence of ions and n is the index of refraction of the electrolyte for radiation of frequency ν. When $\nu\ll\nu_0$, $(\nu_0=p/2\pi m)$,

$$n4\pi na\nu = 2Ze^2/m\nu_0 = 4\pi Ze^2/p = 2Ze^2/3\eta r,\qquad(10)$$
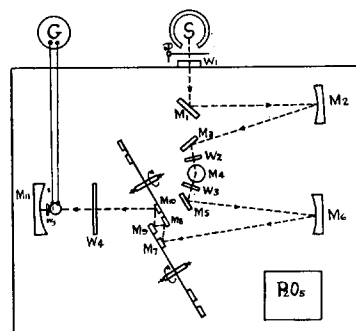
where in the last expression, Stokes' law of

FIG. 2. Reststrahlen apparatus.

friction $(p=6\pi\eta r)$ is assumed. For a frequency $\nu=\nu_0$ the value of $n4\pi na\nu$ should be just half as great as given by Eq. (10).

From Maxwell's equations it follows that the electrical conductivity is related to the absorption coefficient by the relation:

$$\Lambda = nna\nu.\qquad(11)$$

In Fig. 1 is shown the electrical conductivity, obtained from Eqs. (9) and (11), due to a single kind of ion as a function of frequency. Naturally we must always deal with the simultaneous action of two kinds of ions for which the λ_0's are in general different and therefore the observed conductivity should be the sum of two curves as shown in Fig. 1.

APPARATUS AND EXPERIMENTAL CONDITIONS

Figure 2 shows schematically a top view of the reststrahlen apparatus used for obtaining monochromatic radiations of 52μ, 63μ, 83μ, 100μ, 117μ and 152μ. A small Auer gas mantle protected by a water-cooled envelope served as a source of radiation. The radiation was periodically interrupted by a shutter of NaCl which was only opaque to wave-lengths longer than 20μ. The radiation then entered an hermetically sealed box, in which the air was dried with P_2O_5, through a paraffin window, W_1, of 2 mm thickness and was reflected from mirror M_1 of

roughened aluminum. After being reflected from the spherical mirror M_2, the radiation was reflected downward at an angle of less than 10° to the vertical by a plane mirror M_3 and passed through a window of paraffin, W_2, of 1 mm thickness. The radiation was brought to a focus at M_4 where it was again reflected. It then proceeded by a symmetrical path through the paraffin window W_3 and was reflected by mirrors M_5 and M_6 to fall on the reststrahlen crystals M_7, M_8, M_9 and M_{10}. The radiation was finally condensed by mirror M_{11} on one receiver of a compensated thermocouple after it passed through a thin paraffin filter, W_4, and a window of crystalline quartz, W_5.

For reflection measurements, the liquids to be studied and a mirror of evaporated tin were mounted on a horizontal disk that could be rotated externally to bring a liquid surface or the tin mirror to position M_4. The reflection at M_4 occurred in a separate compartment that was sealed by the paraffin windows W_2 and W_3.

For transmission measurements, windows W_2 and W_3 were removed and the electrolyte contained between two plates of crystalline quartz, each 2 mm thick, was mounted between M_4 and M_5. By an external mechanism, the absorption cell could be replaced by a comparison plate of crystalline quartz 4 mm thick.

The reststrahlen crystals were all mounted on two large disks that could be turned externally so as to change the wave-length of the radiation. The vacuum thermocouple was constructed with bismuth alloy wires with two active junctions and two compensating junctions. Two types of receiving surfaces were tried with about equal success. For one pe, typowdered glass was put on the front of a thin gold receiver. For the other, thin glass with a back surface of evaporated gold was used. The main feature of the thermocouple was a very careful compensation for eliminating zero-drift. Besides constructing the active and compensating junctions and the receivers as nearly alike as possible, an added compensation was obtained by using a resistance across the more sensitive pair of junctions. Actually the drift was reduced by a factor of 1000 by the use of the compensating junctions instead of only the active ones and the size of the deflections were reduced only 40 percent.

The galvanometer was of special construction with the moving system very carefully balanced. It had a period of 10 seconds and was mounted on a vibrationless support having internal damping. The galvanometer deflections were read by a parallel-plate optical amplifier which was constructed so that first-order drifts were automatically eliminated.

The essential features of our reststrahlen apparatus were the precautions taken to avoid impurities in the desired spectrum due to short wave-length radiation, the protection of the liquids studied from direct radiation from the source, the mechanical facilities for changing the liquids being measured for reflection and transmission, the mechanical means for changing the reststrahlen crystals in a dry atmosphere and the stability of the galvanometer readings. By measuring the transmission of NaCl when two metal mirrors replaced two reststrahlen crystals, it was estimated that less than 0.01 percent of the desired radiation was due to short wave radiation. The inaccuracy of the measurements was of the order of 1 percent for transmission and 0.1 percent for reflection. The best precision was obtained for 100μ for which the galvanometer deflection was about 130 mm for reflection from the tin mirror and about 65 mm for the transmission of the empty absorption cell. These values correspond to a scale at 5 m distance from the galvanometer; the average Brownian motion fluctuations amounted to about 0.1 mm for the galvanometer we used.

The reststrahlen crystals were of NaCl (52μ), KCl (63μ), KBr (83μ), TlCl (100μ), TlBr (117μ) and TlI (152μ). The average wave-length of the radiation obtained by the method of reststrahlen depends somewhat on the particular apparatus; since the actual radiation obtained depends on the energy distribution of the source, the absorption of the atmosphere, the roughness of the reflecting surfaces, and the absorption of the windows and filters. We determined the average wave-lengths obtained from our apparatus by measuring the transmission of crystalline quartz. In Fig. 3 is shown a curve for the absorbing power of crystalline quartz obtained with a grating spectrometer;[1] the short horizontal lines give the values obtained with the reststrahlen

[1] C. H. Cartwright, Zeits. f. Physik 90, 480 (1934).

apparatus. Taking into account that when the absorbing power of a medium is changing as a function of wave-length, any lack of strict monochromacy produces an apparently smaller absorbing power, the values for the wave-lengths obtained agree well with the maxima reflecting powers of the salts. The reststrahlen radiation obtained from TlCl is usually taken as 92μ but in our case 100μ corresponds better to the absorption of crystalline quartz. This difference is not surprising when we consider that the reflecting powers of thallium salts are not nearly so well defined as for NaCl, KCl and KBr; this is illustrated by the dotted curves in Fig. 3.[2] The precautions we took to purify the spectrum of short wave-length radiation shifted the average wave-length from 92μ to 100μ after four reflections. The effectiveness of thallium salts for reststrahlen is however much greater than appears from the curve in Fig. 3 because the intensity of the radiation diminishes very rapidly with wave-length.

From the transmission measurements, the absorption coefficient, na, of an electrolyte was calculated for each wave-length by the usual formula:

$$I = I_0 e^{-4\pi n a d/\lambda}, \tag{12}$$

where I is the intensity of the radiation transmitted by the quartz cell containing a thickness d of an electrolyte and I_0 is the intensity transmitted by the comparison quartz plate. To account for the loss by reflection from the two surfaces quartz-liquid and liquid-quartz, I in Eq. (12) should be multiplied by a factor

$$\left\{ 1 - \left(\frac{n_q - n}{n_q + n} \right)^2 \right\}^2, \tag{13}$$

where n_q is the index of refraction for quartz and n that of the liquid. In Table I are given

TABLE I.

λ in μ	52	63	83	100	117	152
ν in cm^{-1}	192	159	120	100	85	66
n_q	2.26	2.22	2.19	2.18	2.17	2.16

the values of n_q for crystalline quartz as measured by Rubens.[3] As will be seen from the data

[2] H. Rubens and H. V. Wartenberg, Berlin Ber. 69 (1914).
[3] H. Rubens, Berlin Ber. 556 (1917).

to follow, the differences between n and n_q are sufficiently small for the electrolytes we studied to justify neglecting the factor (13). The reflections air-quartz and quartz-air as well as the
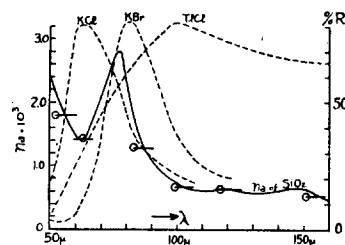

FIG. 3. Reststrahlen reflections and quartz absorption.

absorption by the quartz were taken into account in Eq. (12) by using the comparison quartz plate. Any multiple interference between the two surfaces of the electrolyte can be neglected because of the small reflection of liquid-quartz and the large absorption of the electrolyte. Multiple reflections between the outer quartz surfaces of the comparison cell can also be neglected due to the thickness of the quartz plates compared with the resolving power.[4]

The index of refraction of an electrolyte was determined from the reflecting power, R, and the absorption coefficient, na, by the usual formula,

$$R = \frac{(n-1)^2 + n^2 a^2}{(n+1)^2 + n^2 a^2}, \tag{14}$$

which can be rewritten to facilitate calculation as:

$$n = \frac{R+1}{R-1} = \left\{ \left(\frac{R+1}{R-1} \right)^2 - n^2 a^2 - 1 \right\}^{\frac{1}{2}}. \tag{15}$$

A technical difficulty occurred in measuring the absorption of electrolytes between 50μ and 100μ due to the strong absorption of water. Rather than rely on the thickness of about 20μ spacers between the quartz plates comprising the absorption cell or to measure the thickness of the electrolyte each time by interference methods, we determined the absorption coefficients of the electrolytes for a thickness of $d = 34.6\mu$ at $\lambda = 117\mu$ where the absorption coeffi-

[4] C. H. Cartwright and M. Czerny, Zeits. f. Physik 85, 269 (1933).

TABLE II.

H₂O

	52	63	83	100	117	152
λ in μ	52	63	83	100	117	152
ν in cm⁻¹	192	159	120	100	85	66
% R (Average)	9.30	10.74	11.75	12.28	12.80	13.40
na (Average)	0.48	0.51	0.47	0.370	0.337	0.388
$4\pi na\nu$ in cm⁻¹	1160	1020	710	464	362	320
n (Average)	1.68	1.77	1.89	2.01	2.04	2.09

6 Normal HCl

	52	63	83	100	117	152
% R	13.71	15.71	17.15	18.45	19.50	20.05
% Trans. (d=34.6μ)					14.2	
% Trans. (d=18.2μ)	7.5	8.0	20.5	28.5	35.7	40.0
na	0.59	0.70	0.58	0.545	0.526	0.607
n	1.94	2.01	2.17	2.35	2.45	2.44

3 Normal HCl

	52	63	83	100	117	152
% R	11.37	—	—	15.70	17.12	17.90
% Trans. (d=34.6μ)	—	—	—	—	19.1	—
na	—	—	—	—	0.446	—
n	—	—	—	—	2.31	—

6 Normal LiCl

	52	63	83	100	117	152
% R	11.20	12.73	13.28	13.39	13.40	14.40
% Trans. (d=38.2μ)					26.6	
% Trans. (d=10.5μ)	33.7	37.0	52.0	63.4	69.3	73.7
na	0.43	0.48	0.41	0.345	0.324	0.353
n	1.87	1.96	2.04	2.08	2.09	2.15

3 Normal LiCl

	52	63	83	100	117	152
% Trans. (d=38.2μ)					26.0	
na					0.329	

5 Normal NaCl

	52	63	83	100	117	152
% R	11.04	13.30	14.20	15.45	16.68	17.40
% Trans. (d=38.2μ)					15.9	
% Trans. (d=10.5μ)	23.5	26.9	40.1	51.4	60.0	64.8
% Trans. (d=19.1μ)	6.5	10.0	19.4	29.3	39.7	45.9
na (Average)	0.58	0.61	0.57	0.510	0.450	0.496
n	1.73	1.89	2.01	2.14	2.27	2.30

2.5 Normal NaCl

	52	63	83	100	117	152
% R	10.10	12.20	13.10	13.98	15.56	15.78
% Trans. (d=38.2μ)					20.7	
% Trans. (d=13.7μ)	19.4	21.4	35.2	47.9	56.8	62.0
% Trans. (d=20.5μ)	10.1	11.8	22.2	32.9	43.0	48.4
na (Average)	0.48	0.55	0.50	0.430	0.385	0.426
n	1.74	1.86	1.98	2.00	2.22	2.22

3 Normal KCl

	52	63	83	100	117	152
% R	9.30	10.91	12.42	13.55	14.32	14.83
% Trans. (d=38.2μ)					15.8	
% Trans. (d=9.1μ)	30.8	33.1	45.5	54.5	64.6	69.2
na	0.54	0.61	0.57	0.532	0.451	0.491
n	1.62	1.67	1.85	1.98	2.09	2.11

1.5 Normal KCl

	52	63	83	100	117	152
% R	9.26	11.32	12.17	13.20	14.43	14.60
% Trans. (d=38.2μ)					19.8	
% Trans. (d=9.2μ)	33.4	35.2	50.0	62.5	67.7	70.6
na	0.49	0.57	0.50	0.406	0.395	0.457
n	1.66	1.76	1.90	2.03	2.13	2.11

4 Normal KBr

	52	63	83	100	117	152
% R	8.28	10.82	11.90	13.78	15.00	16.05
% Trans. (d=38.2μ)					15.6	
% Trans. (d=8.9μ)	34.9	36.6	48.8	59.0	64.8	66.7
na	0.49	0.57	0.53	0.474	0.454	0.552
n	1.53	1.72	1.84	2.04	2.14	2.16

2 Normal KBr

	52	63	83	100	117	152
% R	8.64	10.80	11.60	12.91	13.70	14.25
% Trans. (d=38.2μ)					19.0	
% Trans. (d=9.3μ)	34.1	37.0	49.2	61.5	66.5	70.0
na	0.48	0.54	0.50	0.418	0.406	0.465
n	1.62	1.75	1.85	2.01	2.07	2.08

6 Normal LiI

	52	63	83	100	117	152
% R	9.95	10.72	12.08	13.39	14.86	16.01
% Trans. (d=38.2μ)	4.4	4.6	6.1	13.4	19.4	21.9
% Trans. (d=18.4μ)	20.2	22.0	27.5	38.6	45.3	49.2
na (Average)	0.36	0.41	0.47	0.416	0.401	0.475
n	1.82	1.85	1.92	2.05	2.16	2.22

3 Normal LiI

	52	63	83	100	117	152
% Trans. (d=38.2μ)					23.0	
na					0.359	

4 Normal KI

	52	63	83	100	117	152
% R	8.40	8.53	9.97	11.78	13.48	15.41
% Trans. (d=38.2μ)					16.4	
% Trans. (d=12.8μ)	28.6	30.3	39.1	47.0	54.5	58.0
na	0.40	0.47	0.49	0.470	0.442	0.509
n	1.67	1.62	1.75	1.89	2.04	2.14

2 Normal KI

	52	63	83	100	117	152
% Trans. (d=38.2μ)					19.9	
na					0.394	

14.8 Normal ZnI₂

	52	63	83	100	117	152
% Trans. (d=38.2μ)					21.1	
na					0.380	

7.4 Normal ZnI₂

	52	63	83	100	117	152
% R	10.82	12.14	12.70	13.49	14.68	15.31
% Trans. (d=38.2μ)					24.5	
% Trans. (d=20.9μ)	11.0	13.6	25.4	41.3	46.2	50.0
na	0.44	0.48	0.43	0.337	0.344	0.401
n	1.84	1.91	1.98	2.09	2.18	2.20

4 Normal MgSO₄

	52	63	83	100	117	152
% R	12.00	13.25	13.48	13.94	14.20	14.60
% Trans. (d=38.2μ)					29.8	
% Trans. (d=19.5μ)	10.8	13.1	25.8	42.8	53.9	58.1
na	0.47	0.52	0.46	0.346	0.296	0.338
n	1.91	1.97	2.03	2.08	2.12	2.13

2 Normal MgSO₄

	52	63	83	100	117	152
% Trans. (d=38.2μ)					26.6	
na					0.324	

6 Normal KOH

	52	63	83	100	117	152
% R	11.70	13.50	13.80	15.00	15.95	16.80
% Trans. (d=34.6μ)					20.3	
% Trans. (d=20.5μ)	7.2	9.2	20.0	31.1	38.8	42.5
na	0.53	0.58	0.52	0.455	0.430	0.507
n	1.83	1.93	2.01	2.14	2.23	2.25

3 Normal KOH

	52	63	83	100	117	152
% R	10.73	—	—	13.60	14.51	15.45
% Trans. (d=34.6μ)					25.2	
na					0.372	
n					2.15	

TABLE II (*Continued*).

2 Normal H₂SO₄

	10.7	11.8	12.8	13.8	15.1	15.8
% R					20.7	
% Trans. ($d=34.6\mu$)						
% Trans. ($d=21.0\mu$)	7.0	8.5	15.5	29.2	38.5	44.0
na	0.53	0.59	0.59	0.47	0.42	0.47
n	1.75	1.78	1.87	2.07	2.17	2.19

6 Normal H₂SO₄

	13.1	14.7	16.2	17.0	18.5	19.7
% R					15.2	
% Trans. ($d=34.6\mu$)						
% Trans. ($d=21.4\mu$)	3.7	4.7	13.0	23.5	31.2	35.2
na	0.64	0.72	0.63	0.54	0.51	0.59
n	1.85	1.88	2.11	2.27	2.38	2.42

12 Normal H₂SO₄

	16.8	18.7	19.6	21.0	22.5	23.6
% R					11.5	
% Trans. ($d=34.6\mu$)						
% Trans. ($d=21.0\mu$)	2.0	3.2	10.3	18.8	26.9	29.9
na	0.77	0.82	0.71	0.63	0.58	0.70
n	2.02	2.13	2.33	2.53	2.66	2.69

cients change rather slowly with wave-length and the absorption coefficients are considerably less than for shorter wave-lengths where the broad water band occurs. Then a thinner spacer of platinum was used and its thickness was calculated by formula (12) by again measuring the transmission at $\lambda = 117\mu$.

EXPERIMENTAL RESULTS

In Table II are recorded for the different reststrahlen frequencies, the reflecting power, R, the transmission of an electrolyte of thickness d, the absorption coefficient of the electrolyte, na, and the index of refraction, n.

DISCUSSION

1. Absorption of water

In order to apply Maxwell's equations to the movement of the ions in an electrolyte, it is necessary to subtract the effect of water from the observed quantities. As a first approximation, we shall make the *assumption* (*A*) that the absorbing power per molecule of water is the same in an electrolyte as in pure water; that is, we shall first calculate the absorption due to ions by the formula:

$$(na)_{\text{ions}} = (na)_{\text{mes.}} - (Cna)_{\text{H}_2\text{O}}, \qquad (16)$$

where the concentration, C, will be taken as the volume of water per volume of solution. This concentration as well as the results of other ways

of calculating concentration is tabulated in Table III along with the viscosity and electrical conductivity measured in a static field.

In Fig. 4A are shown the values of $n4\pi na\nu$ (ν is expressed in cm⁻¹) for the ions only as calculated according to the assumption underlying Eq. (16).

To correct more accurately for the water absorption which unfortunately plays a great rôle, it is necessary to understand the causes for the absorption due to the water. In Fig. 5 is shown the absorption coefficient for liquid water and we can distinguish between two types of absorption: one type due to a broad absorption band and one type causing a regular increase in the absorption coefficient. The broad absorption band, as shown by other investigations,[5] can be attributed to intermolecular origin and we shall at first assume that this absorption is not altered by the presence of ions. The more general type of absorption is well accounted for by the Debye theory of dipole orientation for which

$$4\pi na\nu\eta = \text{constant}. \qquad (17)$$

We shall assume that at $\lambda = 152\mu$ the water absorption is entirely due to the orientation of dipoles and this gives the constant (17) a value of 3.20 (ν is expressed in cm⁻¹ and η for water is 0.01). In Fig. 4B are shown the values of the absorption due only to ions as calculated by the formula

$$(na)_{\text{ions}} = (na)_{\text{mes.}}$$
$$- C[(na)_{\text{H}_2\text{O}} - (320/4\pi\nu)(1 - 1/\eta)], \qquad (18)$$

where for η we will take the viscosity of the electrolyte. In this formula we make the additional *assumption* (*B*), that the presence of ions does not alter the intensity of the broad absorption band in water but the absorption by the water molecules due to dipole orientation depends on the viscosity of the electrolyte. For electrolytes of high viscosity, the values in Fig. 4B differ considerably from those in Fig. 4A and the absorption as a function of wave-length, even allowing for inaccuracies, is in general much different from the addition of two curves of the type shown in Fig. 1. Most of the curves in Fig. 4A and 4B indicate that the presence of

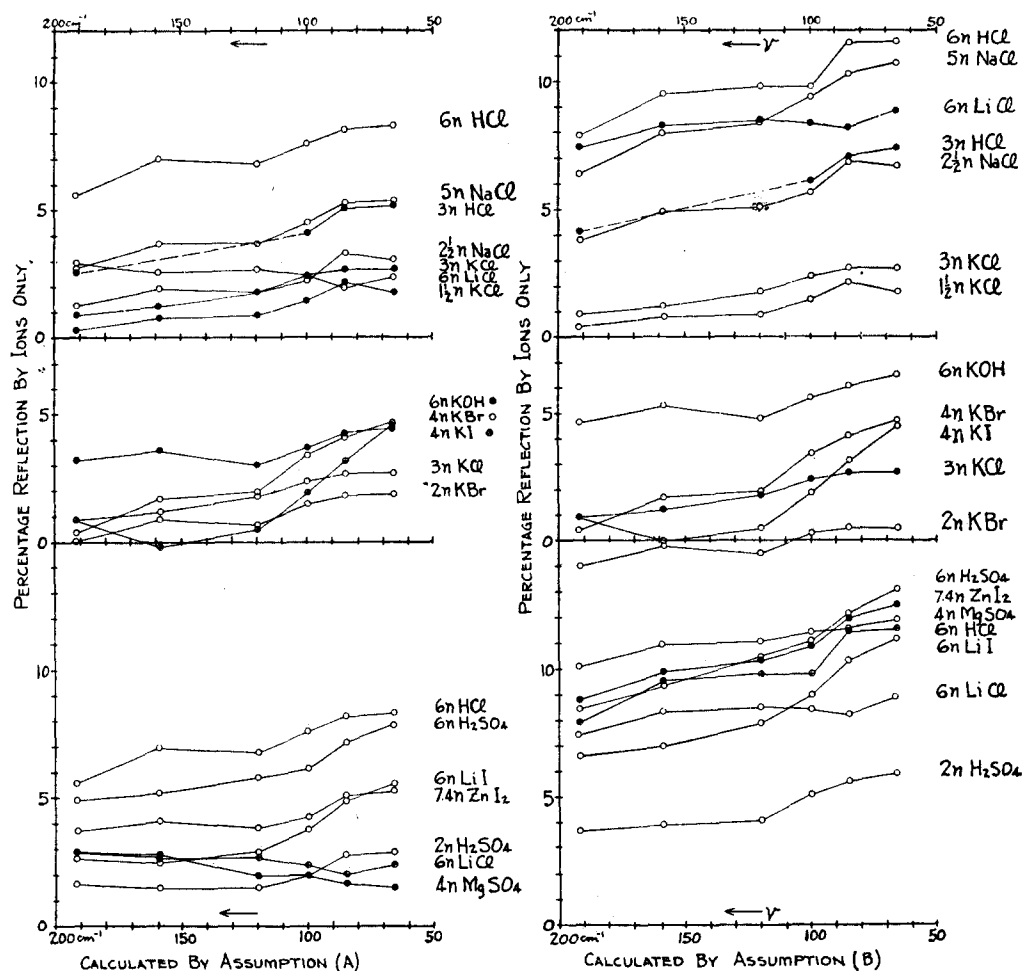[5] C. H. Cartwright, Nature **136**, 181 (1935).

FIG. 4. Absorption due to ions only in various electrolytes as calculated by subtracting the absorption due to water molecules from the observed absorption of the electrolytes.

ions in general increases the intensity of the broad absorption band in water.

2. The reflection due to ions

Figure 5 also shows the reflecting power of water and it is to be observed that the broad absorption band does not influence the reflecting power very much; rather the reflecting power can be almost entirely attributed to an orientation of the permanent dipoles. Thus a study of the reflecting power of the electrolytes should aid in distinguishing the absorption due to ions from the absorption due to the water.

In Fig. 6A is shown the percentage of reflection due to the ions only as obtained by the formula

$$R_{ions} = R_{mes.} - (CR)_{H_2O}, \qquad (19)$$

which corresponds to the *assumption* (A) underlying the data in Fig. 4A.

In Fig. 6B is shown the percentage of reflection due to the ions only as obtained by the formula

$$R_{ions} = R_{mes.} - (CR)_{H_2O}/\eta_{solution}, \qquad (20)$$

assumption (B), which takes into account the findings of Rubens that the reflecting power depends on viscosity. Fig. 6B therefore corresponds to Fig. 4B.

Figures 6A and 6B show that the reflecting power due to ions is much more in harmony with the assumptions underlying the theoretical curve in Fig. 1 than was in general obtained from absorption measurements. This we interpret as additional evidence that in general the
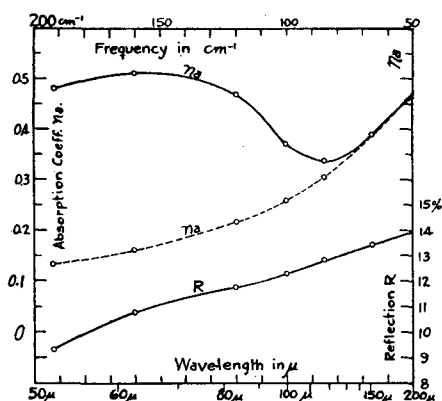
FIG. 5. Reflecting and absorbing power of water.

presence of ions increases the intensity of the broad absorption band in water.

3. Electrical conductivity and ionic radius

In Table IV are given the values for the equivalent electrical conductance as calculated

from formula (11). The calculations were made for $\lambda = 117\mu$ and 152μ so as to avoid as much as possible the influence of the water absorption band. A comparison with the conductivities observed for static field in Table III shows our values to be in general too small, especially when we consider that formula (11) assumes $\nu \ll \nu_0$; for $\nu = \nu_0$ the electrical conductivity should be twice as great. This can also be expressed by saying the ionic radii measured by infrared absorption are smaller than the accepted values. In Table IV is shown the average radius of the two types of ions in each electrolyte as calculated from formula (10); taking into account the effect of the inertia of the ions would make the ion radii in Table IV even smaller.

4. Resonance frequency of ions in an electrolyte

It is conceivable that the ions in an electrolyte are bound in a potential field so that an excessive absorption occurs for electromagnetic waves near
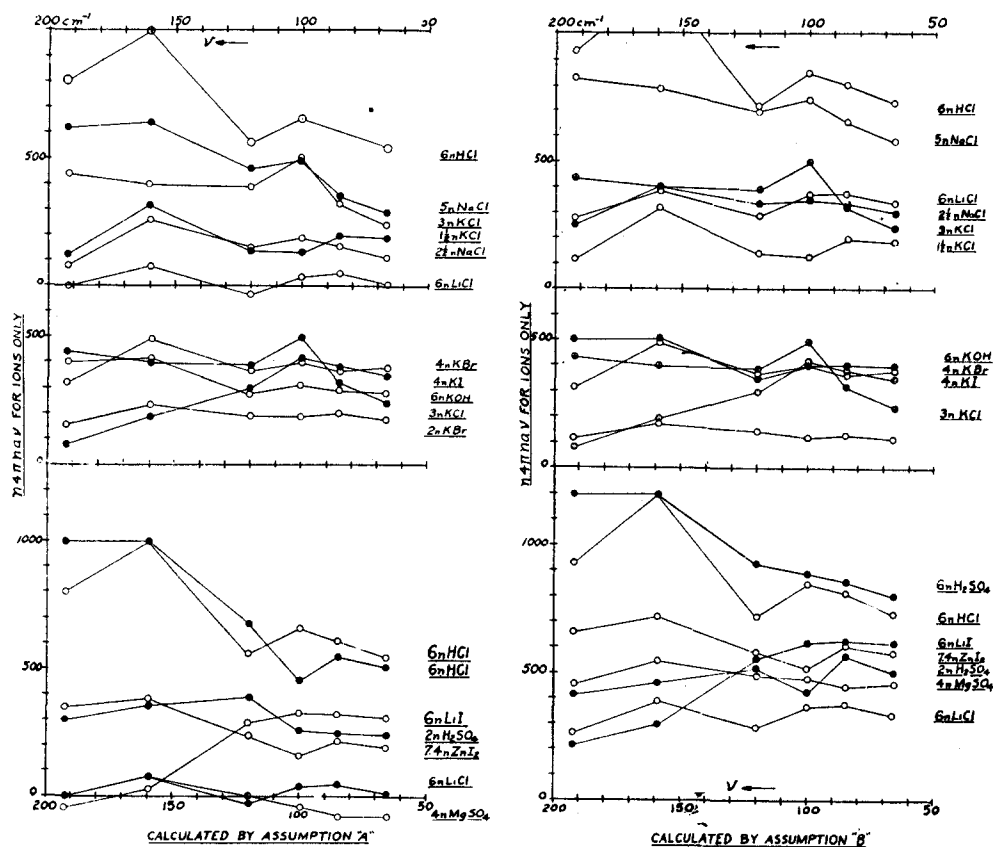

FIG. 6. Reflecting power of ions only as a function of wave-length. Calculated by subtracting the reflecting power of water from the measured reflecting power of various electrolytes.

the resonance frequency. A resonance phenomenon was not taken into consideration in the simple theory we gave and this might explain the rather high values obtained for the electrical conductivity and the apparently small ion radii. The difficulty in accounting for the influence of the water molecules weakens the evidence that our data on conductivity and ion radius show an effect of resonance; but other data strengthens the hypothesis that resonance might occur and occurs in the spectral region we investigated.

There are several independent types of analysis that indicate the molecules in a liquid are bound in a quasicrystalline structure due to intermolecular fields. In the case of water, the two broad bands around 20μ and 60μ can be attributed to an oscillation of the hydrogen atoms[6] (this is in addition to the three fundamental frequencies of the water molecule found in the near infrared). The fact that salts dissolve in water also indicates that the ions in an electrolyte are subjected to strong electric fields. Assuming the field to be the same on an electrolytic ion as on the atoms in water this would give a resonance frequency for

$$\lambda_{\text{in }\mu} = 20M^{\frac{1}{3}}, \tag{21}$$

[6] C. H. Cartwright, Phys. Rev. **49**, 470 (1936).

where M is the atomic weight of the ion considered. This formula therefore predicts an excessive absorption for many ions in the spectral region we investigated; especially considering that in an electrolyte, any effect due to resonance if it occurs would probably cover a considerably broader spectral region than is observed for ions in crystals. Let us recall too that the ions we studied when in the crystal state have their resonance frequencies in or near the spectral region investigated here. To really answer the question of resonance it is of course necessary to consider analytically a model and take into account that the type (such as neon or argon type) and the radius of an ion would influence the field; however, as a first approximation, it can be assumed that the resonance frequency for heavy ions would in general lie at longer wave-lengths than for light ions. Our data support this assumption, especially for iodine ions.

5. Spectral properties of H+ and OH−

Special considerations deserve attention for ions of H+ and OH− (and possibly SO_4^{--}) because of permanent dipoles. It has been rather conclusively established that H+ does not exist alone in an electrolyte but forms an ion of H_3O^+.[7]

[7] M. Kolthoff, Rec. Chem. des Pays-Bas **49**, 401 (1930)

TABLE III. *Electrolytes.*

ELECTROLYTE	EQUIV. NORMALITY	CC H₂O PER 100 CC SOLUTION	VOL. CONC.	WEIGHT CONC.	MOLAR CONC.	VISCOSITY	SPEC. ELEC. COND.	EQUIV. ELEC. COND.	EQUIV. ELEC. COND. FOR INFINITE DIL.
			%	%	%				
HCl	6	87.9	14	19.8	10.9	0.014	0.77	128	379
"	3	94.1	7	10.4	5.4	0.012	0.64	215	
LiCl	6	89.5	12.1	22.0	10.8	0.022	0.17	28	99
"	3	94.0	6.1	11.7	5.4	0.018	0.13	45	
NaCl	5	89.3	13.1	24.6	9.2	0.018	0.21	43	109
"	2.5	95.0	6.6	13.2	4.5	0.014	0.15	60	
KCl	3	90.7	11.1	19.8	5.6	0.010	0.27	88	130
"	1.5	95.5	5.5	10.5	2.8	0.010	0.14	93	
KBr	4	84.9	17.2	35.9	7.8	0.010	0.34	85	132
"	2	92.6	8.7	20.4	3.8	0.009	0.19	95	
LiI	6	78.0	20.3	50.6	12.2	0.022	0.22	37	96
"	3	89.0	10.0	31.0	5.7	0.016	0.16	52	
KI	4	80.3	21.2	45.0	8.3	0.010	0.35	88	131
"	2	90.4	10.6	26.9	3.8	0.009	0.20	100	
ZnI₂	14.7	49.0	50	83	35	——	0.06	4	——
"	7.4	75.0	25	61	15	0.036	0.05	7	
MgSO₄	4	97.6	8.4	19.8	6.9	0.048	0.05	12	110
"	2	99.2	4.3	10.8	3.5	0.020	0.04	21	
KOH	6	92.0	15.1	26.8	10.5	0.012	0.56	90	236
"	3	96.9	7.8	14.7	5.3	0.011	0.43	142	
H₂SO₄	2	96.4	5.3	9.3	1.8	0.013	0.36	183	
"	6	88.4	15.4	25.0	6.7	0.018	0.72	120	383
"	12	75.0	30.0	44.0	12.6	0.03	0.63	52	

Hueckel and Fowler have given two interpretations for the anomalously large electrical conductivity of H^+ and OH^- but both agree on proton jumps accompanying the migration of these ions. Recently Wannier[8] has given a quantum-mechanical interpretation for the proton jumps which is based essentially on the Hueckel theory which takes into account a Debye dipole orientation of these ions.

It is questionable that proton jumps would influence the infrared properties of electrolytes but the dipole orientation of an ion should produce a general absorption such that

$$4\pi na\nu = \text{a constant depending on the} \quad \text{dipole moment,} \quad (22)$$

in excess to the absorption of a simple ion.

Our data on KOH indicate a general absorption in agreement with formula (22) but show no particularly large absorption; however, our data on ions of H^+ show evidence of an excess absorption and reflection. Following the theory of dipole absorption for ions of H^+ or more accurately H_3O^+, the effect of dipoles of H_2O and H_3O^+ should be treated separately. Since the formation of H_3O^+ ions results in a diminution in the number of H_2O molecules, an excess absorption over that of simple ions would mean that the electric moment of H_3O^+ is greater than of H_2O.

6. Hydration of ions

For static fields, as shown in Table III, the electrical conductivities of Mg^{++} and Li^+ ions are relatively small and this can be interpreted as evidence that these ions are hydrated or if we assume that all ions are hydrated then more hydrated than is usual for an ion. The fact that electrolytes containing Mg and Li ions are abnormally viscous is also most easily explained by assuming there are strong binding forces between these ions and surrounding water molecules.

The theory we have given does not take into account any direct interaction between the water molecules and ions such as might be the case if hydration occurs. Let us recall that the distinction between assumptions (A) and (B) is that the latter assumes a change in viscosity

[8] G. Wannier, Ann. d. Physik **24**, 545 and 569 (1935).

TABLE IV.

ELECTRO-LYTE	EQUIV-ALENT NOR-MAL-ITY	EQUIVALENT ELECTRICAL CONDUCTANCE, A 0.001 NOR.		EQUIVALENT REFLECTING POWER, R 0.001 NOR.		AVERAGE ION RADIUS ×10⁸ CM	
		(A)	(B)	(A)	(B)	(A)	(B)
HCl {6	6	250	330	130	190	0.4	0.3
{3	3	270	400	180	250	0.5	0.3
LiCl	6	15	170	40	140	4	0.6
NaCl {5	5	160	300	110	210	0.5	0.3
{2.5	2.5	120	320	120	260	0.7	0.3
KCl {3	3	230	230	90	90	0.4	0.4
{1.5	1.5	120	320	120	110	0.5	0.5
KBr {4	4	250	250	120	110	0.7	0.7
{2	2	250	150	100	20	0.7	1.0
LiI	6	130	270	90	180	0.5	0.3
KI	4	250	250	110	150	0.6	0.6
ZnI₂	7.4	70	200	70	170	0.6	0.2
MgSO₄	4	−50	300	40	300	large	0.1
KOH {6	6	130	180	70	110	1.0	0.8
{3	3	100	170	80	120	1.5	1.0
H₂SO₄ {2	2	300	650	150	300	0.4	0.2
{6	6	220	420	130	220	0.4	0.2

due to the presence of ions changes the degree to which the water dipoles are oriented by an electromagnetic field. If the properties of the ions and the water molecules are to a first approximation additive, then we might expect hydrated ions to reflect and absorb less than simple ions and have relatively large ionic radii. Our data in Table IV as calculated according to assumption (A) rather indicate that these ions are hydrated but when calculated according to assumption (B) they do not.

We shall leave the question of hydration for with it arises again the question of ionic resonance as well as the influence on the absorption by the water molecules. Without an analytical model it is difficult to estimate the influence hydration would have on the infrared spectral properties of electrolytes for it depends on the potential functions. The effect might not be very great in the spectral region we investigated. Previous observations on effects attributed to hydration, it should be considered, are for relatively slow motions. Thus liquid water displays spectroscopically two distinct aspects, one pertaining to its crystalline properties in the region of $\lambda = 20\mu$ and $\lambda = 60\mu$ and one pertaining to its dense-gaseous properties which are especially pronounced in the spectral region around $\lambda = 1$ cm.

It seems a criterion for deciding between assumptions (A) and (B) and whether it is permissible to neglect hydration or other interactions between the ions and water molecules

would be to consider the effect of ionic concentration. Unfortunately the data in Table IV do not give a unique answer; but, considering the difficulties in making absolute measurements in this region of the spectrum and the possibility of accumulative errors in calculating, the data in general justify the assumption that the properties of the ions and water molecules are additive.

7. The validity of Stokes' law of friction

Calculating the motion of ions in the electrolytes due to the intensity of radiation of the infrared frequencies we used shows that the displacement of the ions is small compared with 10^{-8} cm. Therefore it is not altogether justified to apply Stokes' law of friction, which was derived for macroscopic processes, to the microscopic phenomenon we investigated.

We introduced Stokes' law as a means of determining the ion radii and possibly it is not surprising that our values are somewhat too small. However, it is to be observed that Stokes' law at least gives the right order of magnitude for the ion radii; or stated otherwise, the calculated frictional forces acting on the ions are in fair agreement with Stokes' law.

The electrical conductivity of ions we obtained without taking account of their radii was greater than is observed for static fields. This might indicate that Stokes' law can be applied to both static and very high frequency fields for calculating ion radii but the effective radii depend on frequency. In view of the difficulties already mentioned in assigning a value to the absorption due only to the ions, it seems possible that we have overestimated their absorption and hence obtained in general too high values for the electrical conductivities. However, if such were the case it would mean that Stokes' law of friction can be used very well for even microscopic movements of ions in electrolytes.

The Absorption Spectrum of Diacetylene in the Near Ultraviolet. II

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The absorption spectrum of diacetylene has been reinvestigated with an instrument of higher dispersion. The bands in the region $\lambda\lambda2970-2650A$ are sharp and narrow, and very closely spaced. Two progressions with a frequency difference ~690 cm^{-1} have been found. Those below $\lambda2650A$ are very diffuse, but with a comparatively simpler gross structure. Ten progressions all with a frequency difference ~2100 cm^{-1} have been found. Through a brief and qualitative discussion of the normal vibrations and symmetry properties of the molecule, the frequency differences ~2100 cm^{-1} and ~1900 cm^{-1} are respectively ascribed as the totally symmetrical $\nu'_{c\equiv c}(s)$ and unsymmetrical $\nu'_{c\equiv c}(a)$ longitudinal frequencies in the excited state. The frequency ~635 cm^{-1} is assigned as one of the fundamental frequencies in the normal state, since bands with this frequency difference were relatively intensified at higher temperatures.

I N a recent communication[1] (which will hereafter be designated as I), the results of our

previous investigation of the absorption spectrum of diacetylene were reported. The spectrum was then taken with a small Hilger quartz spectrograph. The gross structure of the spectrum

[1] Sho-Chow Woo and T. C. Chu, J. Chem. Phys. **3**, 541 (1935).