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MEASUREMENTS ON THE NEAR INFRA-RED ABSORPTION OF SOME DIATOMIC GASES

By ELMER S. IMES

The importance of the study of the near infra-red absorption bands of gases is being more clearly realized the farther this study is carried. This importance arises from two main considerations. The first is the information which the absorption in this region gives with regard to the structure and mechanics of the molecule. This includes, of course, the inferences as to atomic structure, which are not only possible, but become necessary if the molecular facts are to be explained. The second is that there is found here a new application and test for the quantum theory in that it is extended to the originally excluded region of the rotational energy of molecules.

SUMMARY OF THEORY AND PREVIOUS WORK

It was Drude[1] who first announced the theory that the infra-red absorption and emission bands of the majority of substances have their origin in the vibrations of electrically charged atoms and molecules, and not in the oscillations of the electrons within the atoms. The two widely separated absorption regions usually appearing in the infra-red spectra of gases were naturally assigned, the one in the far infra-red to molecular rotation and that in the near infra-red to atomic vibrations within the molecule. N. Bjerrum[2] pointed out, however, that in all probability the shorter-wave absorption was due to a combination of the two frequencies, that of rotation and that of vibration. This observation was based on Lord Rayleigh's[3] combination principle: viz., that an oscillator which emits and absorbs at a frequency ν_0 due to its oscillations alone would, when rotating about an axis perpendicular to its line of vibration with a frequency ν_r, emit and

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[1] *Annalen der Physik* (4), **14**, 677, 1904.

[2] *Nernst Festschrift*, p. 90, 1912.

[3] *Philosophical Magazine* (5), **24**, 410, 1892.

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absorb at the new frequencies $\nu_o+\nu_r$ and $\nu_o-\nu_r$. The assumption of a Maxwellian distribution of rotational velocities would require that the near infra-red band consist of two broad absorption areas having maxima at $\nu_o\pm\bar{\nu}_r$, where $\bar{\nu}_r$ is the most probable rotational frequency, and a sharp maximum for ν_o due to molecules whose rotation frequency was zero or in a plane perpendicular to the line of sight. W. Burmeister's[1] work in this region showed the two broad areas for most of the gases investigated, but gave no sign of the sharp line corresponding to ν_o, from which it was concluded that either the dispersion used was not great enough to show it, or, at least in the case of diatomic molecules, there might be no absorption for ν_o, i.e., no molecules having no rotation.

H. Rubens and H. von Wartenberg[2] had found in the far infra-red the bands for some of the gases investigated by Burmeister, and the values for $\bar{\nu}_r$ computed from Burmeister's doublet maxima agreed well with their directly obtained values.

A complication arose, however, in the discovery that these near infra-red absorption bands did not always present, even with the low dispersion available, continuous areas with a single maximum each for $\nu_o+\nu_r$ and $\nu_o-\nu_r$. Rubens'[3] work on the water-vapor band at 6 μ and even F. Paschen's[4] much earlier work on the same band showed many separate maxima in these areas. Finally Eva von Bahr[5] in her work on water-vapor and hydrochloric acid showed such marked discontinuity in these bands that an extension[6] of the theory of their origin, abandoning the assumption of a Maxwellian distribution of rotational velocities and introducing the quantum theory, was made necessary. As a matter of fact W. Nernst[7] had previous to this time arrived at the conclusion that the quantum theory must be applied to molecular rotation. This

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[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 589, 1913.

[2] *Ibid.*, **13**, 796, 1911.

[3] *Sitzungsberichte Preussische Akademie*, p. 513, 1913.

[4] *Wiedemanns Annalen*, **52**, 215, 1894.

[5] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 710, 731, 1150, 1913.

[6] N. Bjerrum, *loc. cit.;* E. von Bahr, *loc. cit.;* A. Eucken, *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1159, 1913.

[7] *Zeitschrift für Elektrochemie*, **17**, 265, 1911.

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conclusion was based on two observations: first, that molecular rotation causes radiation in the case of charged molecules; and, second, that even for infinitely thick layers of gas no shorter wavelengths are emitted. Work was done on the specific heat of gases at low temperatures with a view to finding this quantum effect, and various explanations of the results arrived at were attempted. Perhaps the best of these was that of P. Ehrenfest[1] who proposed the equation

$$\frac{1}{2}I(2\pi\nu_r)^2=n\frac{h\nu_r}{2},$$

(where I is the moment of inertia of the molecule, ν_r the rotation frequency, n a whole number, and h Planck's constant), as representing the energy of rotation of a diatomic molecule and as a starting-point in the desired explanation. This equation differs from that proposed by Bjerrum[2] by the factor 2 in the denominator of the second member of the equation, since Ehrenfest concluded that the rotation quantum of energy is $h\nu_r/2$ instead of $h\nu_r$ as assumed by Bjerrum. E. C. Kemble[3] gives a derivation, based on the classical statistical mechanics, which leads to the equation

$$I=\frac{RT}{4\pi^2\bar{\nu}_r^2N}$$

as giving the moment of inertia of a diatomic molecule in terms of the rotation frequency, $\bar{\nu}_r$, obtained from the Bjerrum doublet. He shows that this checks with Ehrenfest's assumption rather than with that of Bjerrum.

It is unfortunate that only the order of magnitude of numerical results computed from such formulae is possible of verification. This, however, in no sense minimizes the importance or the desirability of further and more exact work on the infra-red absorption of diatomic gases. There can be little hope of interpreting properly the results already obtained in the cases of water-vapor and CO_2, to say nothing of more complex molecules yet to be studied, until by

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[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 451, 1913.

[2] *Loc. cit.*

[3] *Physical Review* (2), **8**, 689, 1916.

systematic study of these simpler diatomic molecules the material for generalization is gathered.

In the hope of adding to the amount of such material available for theoretical work the writer undertook the study of the absorption of HCl in the near infra-red, with greater dispersion than had previously been available. Burmeister's[1] original curve for this gas showed only the doublet consisting of broad areas having maxima at 3.4 μ and 3.55 μ. Von Bahr[2] succeeded in resolving these into twelve separate maxima, of which five were on the long-wave side of the center, thus making only five pairs available for measurement. Finally J. B. Brinsmade and E. C. Kemble[3] have published, since this work was begun, a curve for HCl showing eight maxima on the long-wave side of the center of the band at 3.46 μ, as well as a partially resolved curve for the "harmonic" at 1.76 μ.

It has been possible in the present work to extend both of these, there being twelve pairs of maxima given for the band at 3.46 μ and the band at 1.76 μ being resolved over eight pairs of maxima. In addition to these curves for HCl the writer has also obtained curves for the HBr band at 3.91 μ and the HF band at 2.52 μ. For the former of these Burmeister has published a doublet having maxima at 3.84 μ and 4.01 μ. For the latter the writer has found no published work.

APPARATUS

The apparatus designed and used by W. W. Sleator[4] in his work on water-vapor was admirably adapted to this present work and was fortunately available.

The galvanometer.—The galvanometer is of the Paschen type, a modification of the Thomson four-coil astatic instrument, and was built in the department's shop. The resistance of this galvanometer as used in the present work is approximately 2 ohms and

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[1] *Loc. cit.*

[2] *Philosophical Magazine* (6), **28**, 71, 1914; *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1150, 1913.

[3] *Proceedings of National Academy of Sciences*, **3**, 420, 1917.

[4] *Astrophysical Journal*, **48**, 125, 1918.

with the scale 200 cm distant and the period adjusted to 6 seconds the sensitivity is about 2.2×10^{-10} amp. per mm deflection.

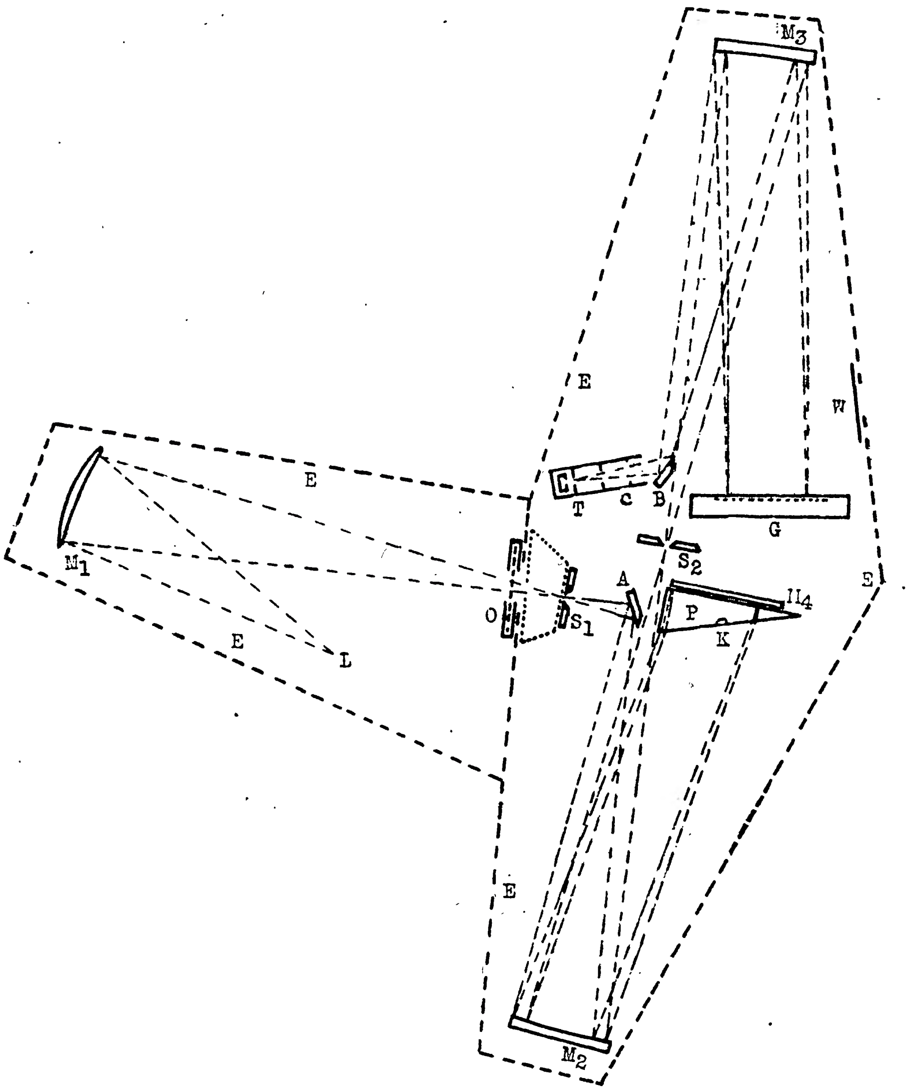

FIG. 1.—The spectrometer

L, Nernst glower; S_1, S_2, slits; M_1, 10 cm mirror, f = 20 cm; *P*, salt prism; M_2; M_3, 10 cm mirrors, f = 50 cm; M_4, *A*, *B*, plane mirrors; *G*, grating; *C*, case for *T*, the thermopile; *W*, window in box *E*; *O*, shutter. The path of the light is $LM_1S_1AM_2PM_4PM_2S_2M_3GM_3BT$. A spectrum appears at S_2. *P* and M_4 rotate together about *K*, so that any region of the spectrum may be isolated for the grating, and the overlapping of spectra is avoided. (From paper by W. W. Sleator, *Astrophysical Journal*, **48**, 127, 1918.)

The spectrometer.—Figure 1 shows the arrangement of the spectrometer, which consists really of two spectrometers, both of the mirror type. The first is a prism spectrometer, $S_1AM_2PM_4M_2$, which presents a portion of its spectrum to the slit, S_2, of the grating spectrometer, $S_2M_3GM_3BT$. The prism is of rock salt and has a refracting angle of about 18°. Its face is about 12×14 cm. Three gratings were used in the course of the work—a brass grating by Hilger, a 7500-line grating, and a 20,000-line grating, both on speculum metal by Anderson, of Johns Hopkins University. With the brass grating the spectrometer constant is 211,476 A, while with the 7500-line grating it is 67,693 A and with the 20,000-line grating it is 25,375 A.

The double-spectrometer method has proved highly successful in bringing the desired high dispersion of the grating to bear on the infra-red problem. Obviously the grating must not be called upon to analyze a spectral range containing wave-lengths which are integral multiples of each other, if the results are to be interpreted. This is especially true where, as in the present case, photographs are impossible. In the double-spectrometer method a very limited portion of the prism spectrum is thrown upon the slit of the grating spectrometer. If this slit is narrow enough to allow no multiple wave-lengths to pass, the problem of overlapping is solved.

The theoretical value of the resolving power of the grating spectrometer is given in the equation

$$d\lambda/\lambda = 1/Nn$$

(where $d\lambda$ is the wave-length separation of two lines which may just be seen as separate lines, N the number of grating lines used, and n the order of the spectrum observed).

For the 7500-line grating at the center of the HCl band at $3.46\ \mu$, the beam covering 7.5 cm of grating surface and the observations being taken in the first-order spectrum, this equation gives

$$d\lambda = \frac{3.46}{22500 \times 1} = 0.00016\ \mu = 1.6\ \text{A}.$$

But this is based upon the assumption of infinitely narrow slits, which is not at all the case in this work, both slits of the grating spectrometer being 0.5 mm wide. A better idea of the resolution obtained may be gained from the following consideration. The width of the thermopile slit corresponds to 1.7 minutes' angular displacement of the grating. This is $d\theta$ in the equation

$$d\lambda = k \cos \theta d\theta$$

derived from the spectrometer equation $\lambda = k \sin \theta$. Substituting this value of $d\theta$ and that of $\cos \theta$ for $\lambda = 3.46\ \mu$, it is found that

$$d\lambda = 29.1\ \text{A}.$$

In other words the thermopile slit includes 29 A of the spectrum formed by this grating at 3.46 μ. Kemble worked with approximately 70 A and von Bahr with 100 A for their best results.

The thermopile.—The "eyepiece" of the spectrometer consists of a thermopile and the galvanometer. The thermopile is a linear bismuth-silver group made by Coblentz. It has ten junctions in its center line and a resistance of about 2 ohms. It is mounted behind a 0.5 mm slit at the focus of the mirror M_3, the beam from M_3 being reflected by the plane mirror B at about 90°, so that the thermopile will not obstruct the beam from the slit S_2 to M_3. The mounting is so designed as to keep the thermal junctions at the same temperature, except when radiation is absorbed by the row exposed to the slit.

The source.—A Nernst glower was used as the source of energy. The work was started with the Nernst lamp in practically its original form and driven by D.C. from a storage battery for the sake of steadiness. Toward the end of the work, however, the original mounting of the filament had given out and it was impossible to obtain new parts for its repair. Accordingly the expedient of simply mounting the filament in a suitable alundum cement mold and using a bank of tungsten lamps as ballast was resorted to. In order to avoid a troublesome amount of polarization of the filaments A.C. was used at this stage. As all of the observations were taken between 1:00 A.M. and 5:00 A.M., when the mechanical and magnetic disturbances to which the galvanometer responds so decidedly were at a minimum, the fluctuations of voltage on the A.C. lines were practically negligible. Furthermore, current was drawn almost directly from a transformer on the 2300-volt lines, having no other load, and the glower circuit was so arranged that the fall of potential across the filament was only a fraction of the total fall in the circuit, thus making steadiness quite assured.

The absorption chamber.—The absorption chamber was of brass, 15 cm long and about 8 cm in diameter. For the greater part of the work thin mica plates were used as windows. They were cemented over the ends of the chamber, and another pair of plates, cut from the same sheets, was so mounted as to be in the beam when the chamber was out. The thickness of these plates was of the order of 0.03 mm. For work in the region of 2.5 μ and at shorter wave-lengths certain specimens of glass plates were available as windows.

Although the total length of the air path of the beam of light is more than 5 meters, the greater part of it is inside the box that contains the spectrometer, and is dried by vessels of calcium chloride, while the length of the absorption chamber is quite 20 per cent of that of the undried air path outside the box. Accordingly, for the part of the work done in regions of strong water-vapor absorption—notably at 2.6 μ—it was thought best to provide a compensating chamber similar in dimensions to the absorption chamber and carefully filled with dried air that had also been freed from CO_2 by passing through KOH solution.

METHODS AND RESULTS

Hydrochloric acid.—The first work was done with HCl in the region of 3.5 μ. The gas was generated by dropping H_2SO_4 on $CaCl_2$ and dried by being passed through concentrated H_2SO_4. Both chemicals were the "analyzed" product of the Baker and Adamson Company. A slow stream of the gas was kept passing through the absorption chamber and disposed of by absorption in water. Gum rubber tubing was used, since the ordinary vulcanized tubing was attacked by the HCl giving rise to enough H_2S to be distinctly perceptible by its odor. The unequivocal nature of the curves obtained is taken as sufficient evidence of the purity of the HCl thus generated, so far as the presence of any substances having overlapping absorption is concerned.

For each point of the curve—one minute of arc apart—six to eight readings of the galvanometer deflection were taken through the absorbing gas and a like number through only the compensating plates, the deflections being obtained by opening or closing the shutter in front of the slit S_1. These readings were not taken consecutively, but alternately in pairs—two with the chamber "in," then two with it "out," and so on. The percentage of absorption was computed from the two averages, the direct ratio between the "in" and "out" averages being translated into a per cent transmission, and the difference between this and 100 per cent being the per cent absorption plotted against the grating setting for that point of the curve. This method has obvious advantages over a method used by some observers who have gone over the entire band first with no absorbing medium (sometimes vacuum) in the chamber, and then with the chamber filled with the substance under observation. Any failure to reproduce a spectrometer setting must result in a corresponding error in the value so obtained. This error would be especially large in the case of a substance having, for example, the very sharp absorption maxima shown by HBr (Fig. 6).

The extreme sensitivity of the galvanometer used in this work to the slightest mechanical or magnetic disturbance is a source of regret. Many times it was not possible to obtain consistent deflections even during the favorable hours, between midnight and dawn, chosen for observation. No claim for extreme accuracy is made for the percentages obtained, but it is not likely that there is any uncertainty with regard to the location of the maxima, which have all been repeated—some as many as four or five times and never with a greater disagreement than two or three angstroms. The location of these maxima, and not their magnitude, has been the problem.

Figures 2 and 3 give the curves obtained for the HCl band at $3.46\ \mu$ with two different gratings. Table II gives the measurements and computations made from the better curve. Figure 5 gives the curve obtained for the so-called harmonic of HCl at

1.76 μ with the 20,000-line grating and Table III gives the measurements and computations from this curve.

These curves as well as those for HBr and HF (Figs. 6 and 7) have been idealized to the extent of omitting small irregularities and averaging all the percentages obtained for each point. Table I gives specimen data and Fig. 4 shows the actual curve plotted from this data for a small portion of the HCl band at 3.46 μ.

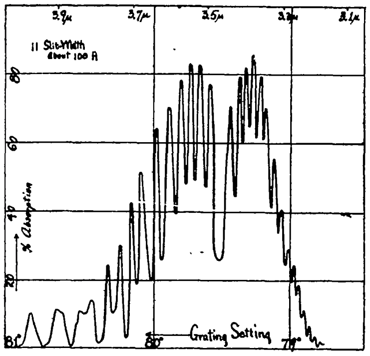

FIG. 2.—The HCl band at 3.46 μ, mapped with brass grating.

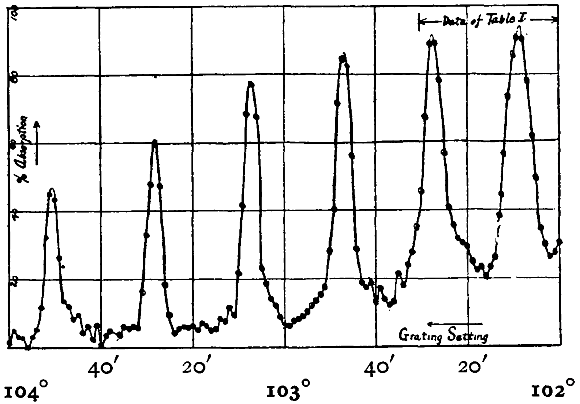

FIG. 4.—A portion of the HCl band at 3.46 μ, plotted from a single set of data.

The curves given in Figs. 2, 3, 5, 6, and 7 are plotted from averages of such sets of data and have omitted the slight irregularities appearing in the minima above, since they are not significant.

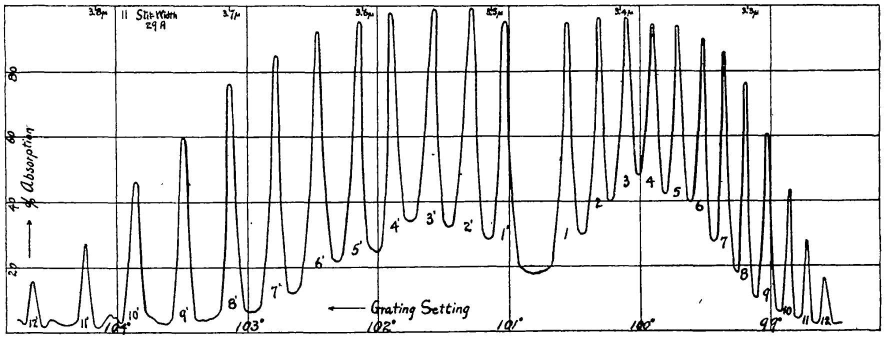

FIG. 3.—The HCl band at 3.46 μ, mapped with 7500-line grating. HCl at atmospheric pressure.

Hydrobromic acid.—HBr was obtained in a satisfactorily pure state by the direct union of hydrogen and bromine. The hydrogen was obtained by the electrolysis of NaOH solution and was carefully dried. Chemically pure bromine was washed in a KOH solution and twice distilled at as low a temperature as possible. The hydrogen was then bubbled through the bromine and the mixture passed through a combustion tube in which there was a platinum coil heated to a bright red by an electric current. The product was delivered through a long vertical glass tube surrounded by a mixture of snow and calcium chloride to condense any uncombined bromine as well as any remaining traces of water-vapor. Burmeister[1] speaks of drying HBr by passing it over P_2O_5. This process would give rise to volatile compounds of phosphorus and bromine, and would no doubt account for some of the difficulty he had in obtaining satisfactorily pure HBr.

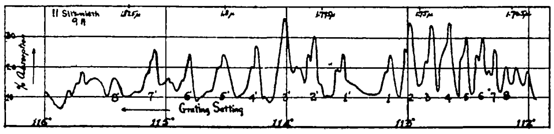

FIG. 5.—The HCl band at 1.76 μ, mapped with 20,000-line grating. HCl at atmospheric pressure.

Because of the rather elaborate nature of the apparatus required for the generation of HBr no attempt was made to keep a stream of the gas passing through the absorption chamber. It was thought sufficient to start each new series of observations with a freshly generated supply, the chamber having been washed out by drawing dry air through it by means of an aspirator for half an hour before it was filled with the gas. It was difficult to determine when the pressure of the gas in the chamber was that of the atmosphere; i.e., when all the air was displaced. Furthermore, it was aimed to generate the HBr so that an excess of hydrogen would be present and no simple means of determining constancy in the amount of this excess was at hand. The result is that the relative intensities of the various absorption maxima in the curve obtained for HBr cannot be taken as significant unless they were obtained in the same series of observations. This is not important, as

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[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 596, 1913.

TABLE I

Typical Data

HCl Band, 7500-line grating, June 18, 1917, 12:45 A.M.
Glower current = 0.75 amp.
Galvanometer period = 7 sec.
Grating temperature = 20°.5 C. Grating zero = 70°0′0″

Circle	In	Average	Out	Average	Percentage Trans.	Percentage Abs.
102°0′..........	7.5–7.4–7.8–7.7–7.6–7.5	7.6	11.5–11–10.5–10.8–10.9–11	10.95	69.4	30.6
1′..........	7.4–7.8–7.7–8.0–8.0–7.6	7.75	10.5–10.7–10.8–10.7–10.9–10.7	10.7	72.3	27.7
2′..........	8.0–7.8–8.0–7.9–8.0–7.8	7.9	10.5–10.7–11–10.5–10.8–10.7	10.7	73.7	26.3
3′..........	7.0–7.4–7.6–7.5–7.4–7.4	7.4	10.6–10.4–11–10.6–10.5–10.6	10.6	69.8	30.2
4′..........	7.0–6.5–6.9–6.9–7.0–7.0	6.9	10.5–10.8–10.5–10.6–10.4–10.5	10.55	65.4	34.6
5′..........	5.0–5.5–5.0–5.5–5.3–5.5	5.3	10.3–10.2–10.5–10.6–10.3–10.5	10.4	50.9	49.1
6′..........	4.0–4.0–4.2–4.0–4.1–4.0	4.05	10.5–11–10.2–10.9–10.6–10.9	10.65	38.0	62.0
7′..........	2.5–2.4–2.0–2.4–2.3–2.3	2.3	10.4–10.5–10.4–10.4–10.5–10.5	10.45	22.1	77.9
8′..........	About 1.0	1.0(?)	10.6–10.5–10.7–10.7–10.6–10.5	10.6	9.4	90.6(?)
9′..........	About 1.0	1.0(?)	10.3–10.3–10.8–10.2–10.3–10.5	10.4	9.6	90.4(?)
10′..........	1.5–1.5–1.4–1.4–1.5–1.4	1.45	10–11–9.6–10.5–10.2–10.1	10.2	14.2	85.8
11′..........	2.8–2.5–2.8–2.7–3.0–2.7	2.75	10.3–10.7–10.4–10.5–10.6–10.4	10.5	26.2	73.8
12′..........	4.8–4.5–4.7–4.6–4.6–4.7	4.65	10.8–11.2–10.2–10.8–10.7–10.8	10.75	43.2	56.8
13′..........	7.0–6.5–6.0–6.5–6.0–7.0	6.5	10.5–10.5–11–10.5–10.7–10.5	10.6	61.3	38.7
14′..........	7.0–7.5–7.0–7.5–7.0–7.5	7.25	10.0–11–10.5–10.4–10.5–10.5	10.5	69.0	31.0
15′..........	7.8–7.9–7.5–8.5–8.0–8.0	7.95	10.2–10.8–10–10.7–10.3–10.5	10.4	76.4	23.6
16′*..........	11.5–11.2–11.7–11.4–11.5–11.4	11.45	14.2–15–15–14–14.5–14.6	14.55	79.2	20.8
17′..........	11–11–11–10.7–11–10.8	10.9	14–14.5–14–14.2–14.1–14.3	14.2	76.7	23.3
18′..........	11–10.5–11.5–11–11	11.0	14–14.2–14–14.7–14–14.3	14.2	77.5	22.5
19′..........	11–10.5–11–11–11–10.9	10.9	14.7–14–15–14.2–14–15	14.5	75.2	24.8
20′..........	10.5–10.5–10.5–10.2–10.3–10.5	10.4	14.6–14.8–14.7–14.9–14.7–14.8	14.75	70.5	29.5
21′..........	10–10–10–10.5–10–10	10.1	14.5–14.5–14.6–14.6–14.5–14.6	14.55	69.4	30.6
22′..........	10–10–10.2–10–9.8–10	10.0	14–14.9–14.6–15–14.5–14.7	14.6	68.4	31.6
23′..........	9.5–9.5–9–9.5–9.5–9.5	9.4	14.9–14.2–15–14.3–14.4–14.8	14.6	64.3	35.7
24′..........	8.5–8.0–9.0–8.5–8.0–9.0	8.5	14–15–14.5–14–14.2–14.7	14.4	59.0	41.0
25′..........	7.0–5.0–6.0–6.0–5.5–6.5	6.0	13.8–14–14–14.2–14.1–13.9	14.0	42.8	57.2
26′..........	3.0–3.0–2.8–3.0–2.9–3.0	2.95	13.8–13.8–13.7–14–13.7–13.8	13.8	21.4	78.6
27′..........	1.5–1.5–1.5–1.5–1.5–1.5	1.5	14–14.5–14.3–14–14.5–14.5	14.3	10.5	89.5
28′..........	1.5–1.3–1.5–1.7–1.5–1.5	1.5	14–14–14.5–13.5–14–14	14.0	10.7	89.3
29′..........	4.5–4.8–4.5–4.8–4.6–4.7	4.65	14–14.5–14.5–14–14.5–14	14.25	32.6	67.4
30′..........	7.5–8.0–7.5–7.0–7.5–7.5	7.5	13.5–13.8–14–13.2–13.7–13.8	13.75	54.4	45.6

* At this point the prism was reset so as to give a greater amount of energy of the particular wave-length under study.

TABLE II

HCl Band at 3.4 μ (from curve of Fig. 3)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
12......	3.23868	3087.68	12.85				
11......	3.25224	3074.83	13.27				
10......	3.26631	3061.56	14.47				
9......	3.28182	3047.09	15.89				
8......	3.29903	3031.20	14.92				
7......	3.31534	3016.28	16.30				
6......	3.33336	2999.98	17.62				
5......	3.35305	2982.36	17.38				
4......	3.37270	2964.98	18.62				
3......	3.39402	2946.36	18.35				
2......	3.41529	2928.01	20.24				
1......	3.43907	2907.77	41.60				
1′......	3.48897	2866.17	21.75	2886.97	2886.73	20.80	20.80
2′......	3.51565	2844.42	22.48	2886.22	2885.83	41.79	20.89
3′......	3.54366	2821.94	22.49	2884.15	2884.33	62.21	20.73
4′......	3.57214	2799.45	23.04	2882.21	2882.23	82.76	20.69
5′......	3.60178	2776.41	23.85	2879.38	2879.52	102.97	20.59
6′......	3.63298	2752.56	23.67	2876.27	2876.22	123.71	20.62
7′......	3.66450	2728.89	25.30	2872.58	2872.32	143.69	20.53
8′......	3.69878	2703.59	25.03	2867.39	2867.81	163.80	20.48
9′......	3.73335	2678.56	25.91	2862.83	2862.71	184.26	20.47
10′......	3.76982	2652.65	26.15	2857.11	2857.03	204.45	20.45
11′......	3.80735	2626.50	26.62	2850.69	2850.67	224.16	20.38
12′......	3.84633	2599.88		2843.78	2843.78	243.90	20.33

NOTE.—In this and succeeding tables and figures n refers to the number of the absorption maximum counting from the center of the band. The subscripts o and r refer to vibration and rotation, as in the "Discussion of Results." Wave-numbers are given throughout instead of actual frequencies. ν_n stands for $\nu_n/3\times10^{10}$.

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remarked previously, since the interest has been only in the location of these maxima, and variations in pressure do not displace them laterally.

TABLE III

HCl Band at 1.76 μ (from curve of Fig. 5)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
8.......	1.72711	5790.00					
			10.85				
7.......	1.73036	5779.15					
			12.58				
6.......	1.73413	5766.57					
			14.28				
5.......	1.73844	5752.29					
			14.18				
4.......	1.74274	5738.11					
			15.55				
3.......	1.74747	5722.56					
			16.58				
2.......	1.75255	5705.98					
			17.58				
1.......	1.75797	5688.40					
			42.03				
1′.......	1.77015	5646.37		5667.38	5666.38	21.01	21.01
			23.17				
2′.......	1.77835	5623.20		5664.59	5664.61	41.39	20.70
			23.16				
3′.......	1.78570	5600.04		5661.30	5661.67	61.26	20.42
			23.70				
4′.......	1.79329	5576.34		5657.22	5657.55	80.88	20.22
			25.80				
5′.......	1.80163	5550.54		5651.41	5652.25	100.87	20.17
			25.58				
6′.......	1.80997	5524.96		5645.77	5645.78	120.80	20.13
			26.64				
7′.......	1.81874	5498.32		5638.74	5638.12	140.42	20.06
			29.71				
8′.......	1.82862	5468.61		5629.31	5629.29	160.70	20.09

The 7500-line grating was used and the long-wave limit was determined by the strong atmospheric absorption beyond 4.2 μ, which cut down the galvanometer deflections to so small a figure as to magnify unduly any observational errors in computing the differential effect sought. It was possible, however, to obtain nine good maxima on the long-wave side of the center of the band. The curve is given in Fig. 6, and the table of values read and computed appears as Table IV.

A search was made for the "harmonic" of HBr at 2 μ found by Brinsmade and Kemble.[1] Nothing was found by any one of the three gratings, the conclusion being that the length of the column of absorbing gas was not great enough to give strong absorption in this region, nor was it possible in the time available to do the remodeling of the apparatus that a sensibly longer chamber would require.

TABLE IV

HBr Band at 3.9 μ (from curve of Fig. 6)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
9	3.72089	2687.53	11.82				
8	3.73133	2675.71	12.96				
7	3.75550	2662.75	13.46				
6	3.77460	2649.29	13.96				
5	3.79460	2635.33	13.46				
4	3.81407	2621.87	15.17				
3	3.83628	2606.70	15.37				
2	3.85902	2591.33	15.64				
1	3.88245	2575.69	33.59				
1'	3.93376	2542.10	16.65	2558.89	2558.93	16.79	16.79
2'	3.95969	2525.45	18.05	2558.39	2558.23	32.94	16.47
3'	3.98819	2507.40	18.00	2557.05	2557.08	49.65	16.55
4'	4.01704	2489.40	18.49	2555.63	2555.46	66.23	16.56
5'	4.04709	2470.91	18.69	2553.12	2553.38	82.21	16.44
6'	4.07793	2452.22	19.33	2550.76	2550.84	98.54	16.42
7'	4.11034	2432.89	19.40	2547.82	2547.74	114.93	16.42
8'	4.14338	2413.49	20.19	2544.60	2544.37	131.11	16.39
9'	4.17833	2393.30		2540.41	2540.44	147.11	16.35

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[1] *Loc. cit.*

Hydrofluoric acid.—For the purposes of this study it was thought best to investigate a third gas of the halogen acid group. Of the two remaining, HF was thought the more likely to prove of theoretical value, and, aside from the difficulty of handling, easier to obtain in a pure state.

The inside of the absorption chamber was flowed with ceresin, as also was that of what tubing it was absolutely necessary to use. The gas was generated in a small iron retort by the action of concentrated H_2SO_4 on NaF. No attempt was made to dry it, but the absorption chamber was washed out with dry air before being filled with the HF, and the absence of any fuming as the gas entered the chamber was taken as evidence of the absence of sensible amounts of moisture. Because of the gradual destruction of the surface of the plates used on the ends of the absorption chamber the percentages of apparent absorption ran gradually up until, usually at the end of from thirty minutes to an hour, it was necessary to change the plates. The expedient of spreading a thin layer of oil, grease, or even wax on the inner surfaces of the plates was tried, but greatly cut down their transparency in the region under study. This was doubly undesirable because on the long-wave side of the center of the band there is the very strong water-vapor band at 2.6 μ, which also cuts down the energy in spots so as to make the observational errors unduly large. It was here that a compensating chamber filled with dried air was thought of great importance. Also a new absorption chamber

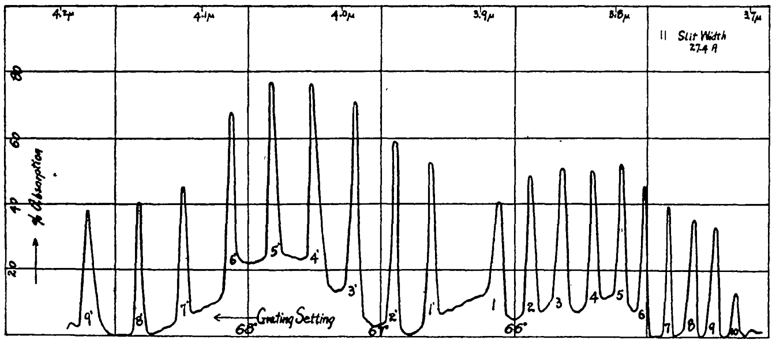

FIG. 6.—The HBr band at 3.9 μ, mapped with 7500-line grating

was built, so designed that the plates could be clamped in place rather than cemented, thus saving much time in the necessarily frequent changes. Both mica and glass plates were used, those of mica proving the more satisfactory.

It is to be noted that the product of the action of HF on silica, present in both glass and mica, is a gas, SiF_4. In order to make certain that the absorption observed was not due to this second gas, observations were made at the beginning of each run with fresh plates, on one or more of the maxima previously obtained. If these had been absent or very much lowered the conclusion would have been that they were due to SiF_4 which was then present in very small quantity. No such absence or lowering was observed.

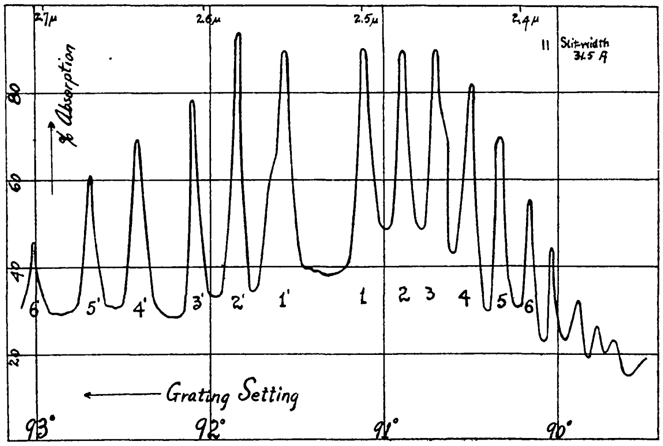

FIG. 7.—The HF band at 2.52 μ, mapped with 7500-line grating

The long-wave limit of this work was determined by the strong atmospheric (water-vapor) absorption beyond 2.6 μ, but it is to be noted that the number of maxima on the short-wave side of the center showing strong absorption is small as compared with that observed in the case of HCl.

The 7500-line grating was used in this work, except for the preliminary exploration done with the brass grating. The curve obtained for HF is given in Fig. 7, the measurements appearing in Table V.

A preliminary search was made for the possible "harmonic," to be expected in the region of 1.25 μ, but if it exists it was effectively masked by the rising general absorption due to the action of the gas on the windows of the absorption chamber.

TABLE V

HF Band 2.5 μ (from curve of Fig. 7)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
7.......	2.37911	4203.25					
			28.56				
6.......	2.39539	4174.69					
			31.84				
5.......	2.41380	4142.85					
			32.35				
4.......	2.43280	4110.50					
			34.36				
3.......	2.45330	4076.14					
			36.24				
2.......	2.47531	4039.90					
			37.88				
1.......	2.49874	4002.02					
			80.17				
1′.......	2.54982	3921.85		3961.93	3961.71	40.09	40.09
			42.75				
2′.......	2.57791	3879.10		3959.50	3959.43	80.40	40.20
			44.41				
3′.......	2.60778	3834.69		3955.41	3955.63	120.72	40.24
			44.63				
4′.......	2.63848	3790.06		3950.28	3950.33	160.22	40.05
			46.06				
5′.......	2.67094	3744.00		3943.43	3943.49	199.42	39.88
			47.93				
6′.......	2.70557	3696.07		3935.38	3935.13	239.31	39.88

DISCUSSION OF RESULTS

Reference has been made to the variance between the assumptions of Bjerrum and of Ehrenfest with regard to the size of the quantum of rotational energy. From the newer point of view, which states more generally and precisely the postulate of stationary states, the Ehrenfest[1] equation may be justified. To do this use is made of A. Sommerfeld's[2] extension of the Planck phase-integral

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[1] Proposed also by A. Eucken. See *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1159, 1913.

[2] *Annalen der Physik* (4), **51**, 1, 1916.

in which Sommerfeld splits up the general integral for f-degrees of freedom,

$$\int_{i=1}^{i=f} \Pi(dq_i dp_i) = h^f$$

(the q's are the position co-ordinates and the p's the corresponding momentum co-ordinates), into f separate integrals,

$$\int dq_i dp_i = h,$$

one equation for each degree of freedom. For a rotating diatomic molecule this quantum equation becomes

$$\int_0^{2\pi} I\omega_n d\theta = nh,$$

which must be regarded as a fundamental assumption.

In the case under consideration—that of rotation with constant angular velocity—this integral evaluates quite simply into

$$2\pi I\omega_n = nh,$$

which, written in terms of kinetic energy and rotation frequency, becomes the Ehrenfest equation,

$$\tfrac{1}{2}I(2\pi\bar{\nu}_r)^2 = n\frac{h\nu_r}{2}.$$

From this equation there is obtained directly

$$\nu_r = n\frac{h}{4\pi^2 I}, \tag{1}$$

giving rotation frequency in terms of the moment of inertia. This equation states that when the moment of inertia is constant, ν_r must have fixed values which are integral multiples of $h/4\pi^2 I$.

If, now, there is not the Maxwellian distribution of rotational velocities, but this series of frequencies differing by $h/4\pi^2 I$, it is evident that, still applying the combination principle, there would be expected in the near infra-red a series of pairs of absorption maxima corresponding to the frequencies $\nu_o \pm \nu_{rn}$ grouped symmetrically about ν_o, where ν_o is, as before, the frequency of vibration of the atoms within the molecule and ν_{rn} the rotation frequency corresponding to a given integral value of n.

Denoting the frequencies corresponding to a given pair of maxima by ν_n and $\nu_{n'}$ (the prime subscript referring to the long-wave side of the center of the band), ν_{rn} may be computed from the equations

$$\nu_n = \nu_o + \nu_{rn},$$

$$\nu_{n'} = \nu_o - \nu_{rn}, \tag{2}$$

whence

$$\nu_{rn} = \frac{\nu_n - \nu_{n'}}{2}. \tag{3}$$

The moment of inertia of the molecule will be, from equation (1),

$$I = n \frac{h}{4\pi^2 \nu_{rn}}. \tag{4}$$

From the moment of inertia thus determined it is possible to compute the length of the molecule. Assuming the masses, m_1 and m_2, of the atoms concentrated at their nuclei which are a distance l apart,

$$I = \frac{m_1 m_2}{m_1 + m_2} l^2,$$

whence

$$l = \left(I \frac{m_1 + m_2}{m_1 m_2} \right)^{\frac{1}{2}}. \tag{5}$$

For $n = 1$, i.e., for molecules having one quantum of rotational energy, the following experimental values are obtained by means of equations (4) and (5):

TABLE VI

Molecule	$I \times 10^{40}$	$l \times 10^{8}$	$I \times 10^{40}$ (Kinetic Theory)
HF.	1.37	.94	. . . .
HCl.	2.64	1.28	2.45
HBr.	3.27	1.42	3.35

Von Bahr[1] gives values of I and l for the HCl molecule computed from her experimental data and the Bjerrum hypothesis, differing from the values in the foregoing table by the factor 2 in the case of I and $\sqrt{2}$ in the case of l within very close agreement.

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[1] *Philosophical Magazine* (6), **28**, 82, 1914.

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Some check is desirable on any such values as these. In the present case the only one available is that furnished by the kinetic theory for the moment of inertia of a diatomic molecule in terms of its most probable rotational frequency. Accepting the equation previously given,

$$I=\frac{RT}{4\pi^2\nu_r^2N}, \tag{6}$$

and using the values obtained by Burmeister for the doublet maxima as corresponding to the most probable frequency through the equations $\nu_m=\nu_o\pm\bar{\nu}_r$, values may be obtained for the moments of inertia of HCl and HBr. (The present work, it is to be observed, furnishes no data for the determination of the most probable frequency.) Taking $R=8.26\times10^7$, $N=6.12\times10^{23}$, and $T=292°$, equation (6) gives:

for HCl, $I=2.45\times10^{-40}$,
for HBr, $I=3.35\times10^{-40}$.

It may, indeed, be questioned whether this is a real check, but at any rate the agreement is significant.

If one turns to the curve of Fig. 3 and the accompanying table, Table II, it is at once apparent that the predicted symmetry of the maxima, i.e., the arithmetic progression expected in the frequencies of the maxima, does not exist. Instead, there is a gradual increase in frequency difference between two adjacent maxima as one goes farther into the infra-red.

Starting again with equations (2), the expression

$$\nu_o=\frac{\nu_n+\nu_{n'}}{2} \tag{7}$$

is obtained as giving the frequency of vibration of the molecule. A value of ν_o computed from each pair of maxima appears in column 5 of the table. There are as many centers, then, as pairs of maxima, and the asymmetry of the band is the consequence of the shifting of these centers farther into the infra-red as the rotation velocity increases. In other words, it appears that the vibration frequency of the atoms in the molecule is dependent on the rotation frequency of the molecule.

Denoting the series of vibration frequencies by ν_{on}, where n in the subscript refers to the number of the pair of maxima from which the value of ν_o is computed, and plotting ν_{on} against n, the curve of Fig. 8 is obtained. Fitting it to the equation $\nu_{on}=A-Bn^2$ by the method of least squares, the agreement between observed and computed values shown in columns 5 and 6 of Table II is found. The equation of this curve is

$$\nu_{on}/3\times 10^{10}=2887.03-0.30n^2.$$

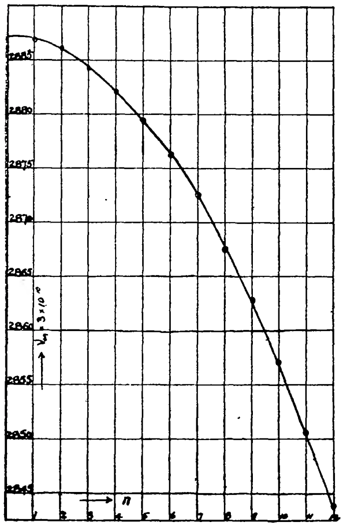

FIG. 8

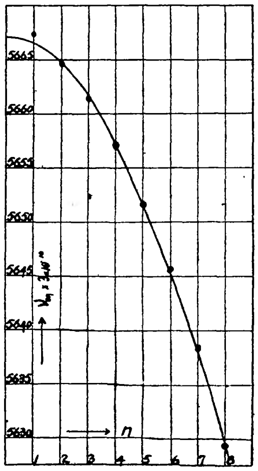

FIG. 9

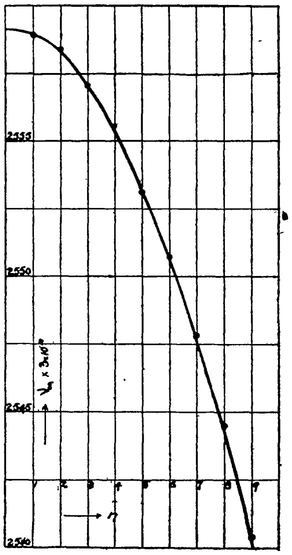

FIG. 10

FIG. 8. $\nu_{on}-n$ curve for the HCl band at 3.46 μ

FIG. 9. $\nu_{on}-n$ curve for the HCl band at 1.76 μ

FIG. 10. $\nu_{on}-n$ curve for the HBr band at 3.9 μ

For ν_{oo}, the extrapolated center of the band, the value is of course A of the equation above, and the corresponding wave-length is 3.4637 μ, as against 3.475 μ obtained from the doublet maxima.[1]

Figures 9, 10, and 11 give respectively the parabolas of centers of the HCl band at 1.76 μ, the HBr band at 3.91 μ, and the HF band at 2.52 μ. From these curves Table VII is obtained:

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[1] See Brinsmade and Kemble, *loc. cit.*

The last column of each of Tables II to V gives the experimental values obtained for ν_{rn}/n and confirms a previous observation of von Bahr that this value is not constant but decreases with increasing values of the rotation frequency. The variation is small, but as it appears in each of the four curves it cannot be regarded as accidental. Eucken suggests that this divergence from the constancy predicted by the Bjerrum formula is not due to a falsity of the formula but to an increase of the moment of inertia with the velocity of rotation. That such an increase does take place may be seen from the following values of the moment of inertia of the HCl molecule computed from the values of ν_{rn} given in Table II.

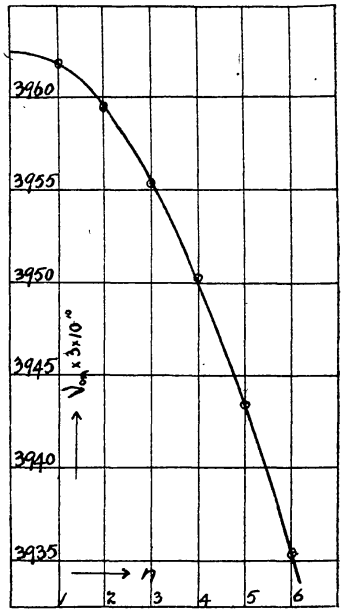

FIG. 11. $\nu_{on}-n$ curve for the HF band at 2.52 μ.

The relation between I_n and n is practically linear as shown by the equation obtained from the observed values above by the method of least squares,

$$I_n=(2.63+0.0055n+0.000007n^2)\times 10^{-40}.$$

The values computed from this equation (neglecting the term in n^2) are given parallel with the observed values in Table VIII.

The "harmonic."—Kemble[1] has advanced the theory that if the amplitude of vibration of the molecule be that required by even a single quantum the infra-red absorption bands discussed so far might be expected to be accompanied by faint harmonics. The center of the first harmonic according to this theory should be at one-half the wave-length of the center of the fundamental and the spacing of the doublet maxima should be one-fourth of that of the maxima of the fundamental doublet (in wave-length). A band approximately answering to these requirements had been observed by Burmeister in the case of carbon monoxide, and this

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[1] *Physical Review* (2), **8**, 701, 1916.

was resolved into a doublet by Brinsmade and Kemble. They also obtained doublets for HCl and HBr approximately agreeing with the prediction. The disagreement was in the location of the centers, which were all farther in the infra-red than demanded by the theory.

Figure 5 gives the curve obtained for the HCl harmonic in the present work. The extrapolated value of the frequency of the center of this band is $5666.97 \times 3 \times 10^{10}$, while that of the center of the fundamental is $2887.03 \times 3 \times 10^{10}$, the ratio being 1.963:1 instead of the expected 2:1. Or, to compare the bands as Brinsmade and Kemble compare them, the center of the harmonic is found 0.033 μ farther in the infra-red than the predicted position. This displacement is greater than the width of all eight maxima on the short-wave side of the band and greater than that observed by Brinsmade and Kemble. It disposes at once of their explanation that the disagreement observed in their work might be due to a slight error in the dispersion curve on which

TABLE VII

Band	$\nu_{on}/3\times10^{10}$	Extrapolated Center	
		$\nu_{oo}/3\times10^{10}$	λ_{oo} (in μ)
HF	$3962.47-.76n^2$	3962.47	2.5237
HCl (3.46 μ)	$2887.03-.30n^2$	2887.03	3.4637
HCl (1.76 μ)	$5666.97-.59n^2$	5666.97	1.7646
HBr	$2559.16-.23n^2$	2559.16	3.9075

TABLE VIII

I_n	Observed	Computed
I_1	2.64×10^{-40}	2.636×10^{-40}
I_2	2.67×10^{-40}	2.641×10^{-40}
I_3	2.65×10^{-40}	2.647×10^{-40}
I_4	2.65×10^{-40}	2.652×10^{-40}
I_5	2.66×10^{-40}	2.658×10^{-40}
I_6	2.66×10^{-40}	2.663×10^{-40}
I_7	2.67×10^{-40}	2.668×10^{-40}
I_8	2.68×10^{-40}	2.674×10^{-40}
I_9	2.68×10^{-40}	2.680×10^{-40}
I_{10}	2.68×10^{-40}	2.685×10^{-40}
I_{11}	2.69×10^{-40}	2.690×10^{-40}
I_{12}	2.70×10^{-40}	2.696×10^{-40}

their wave-length measurements were based, since there is no uncertainty as to dispersion in the present observations, made with a grating.

It is interesting to note that the frequency differences between adjacent maxima at the centers of the two bands (fundamental and harmonic) are sensibly the same, as shown in column 4 of Tables II and III. Also the moment of inertia of the molecule computed by means of equation (4) is the same for fundamental and harmonic.

It is to be regretted that only this one harmonic was obtained, and it is to be hoped that others may be carefully measured in the near future. The apparent tendency of some of the maxima to resolve into doublets in the case of the HCl harmonic may be due to errors of observation, but it seems significant that the small secondary maxima are all on the long-wave side of the principal maxima which they accompany. It is, of course, possible that still higher dispersion applied to the problem may show even the present curves to be composite.

Accuracy.—The question of the accuracy attained in such a problem as this is of necessity quite involved. An adequate estimate, however, of the accuracy of the determinations of the positions of the absorption maxima may be obtained by reference to columns 5 and 6 of Tables II to V inclusive. Column 5 of each table gives the frequency of the centers of the various pairs of maxima of the accompanying curves from wave-length readings on the curves. Column 6 of each table gives the values for the same centers computed by the method of least squares. In the case of Table II, the greatest variation of the observed value from the computed value is in the case for $n=8$, where $d\nu=0.42\times 3\times 10^{10}$. This corresponds to a value of $d\nu$ given by the equation

$$d\lambda=\frac{c}{\nu^2}d\nu.$$

Substituting the values $\nu=2872.6\times 3\times 10^{10}$ and $d\nu=0.42\times 3\times 10^{10}$, it is found that

$$d\lambda=5\times 10^{-8}\text{ cm}=5\text{ A}.$$

This is the extreme case. The average agreement is within ± 1.9 A.

SUMMARY

The object of the present work has been to obtain more extended and more accurate data with regard to the near infra-red absorption bands of certain diatomic gases than have been hitherto available. To this end the closely related HF, HCl, and HBr bands have been mapped, using greater dispersion than has been used before in this particular problem.

Curves are presented showing in greater detail the HCl bands at $1.76\,\mu$ and $3.46\,\mu$ and giving for HBr, instead of the simple doublet hitherto known, a curve resolved into its quantum lines. In addition, a similar curve is presented for HF which has not been studied before.

Several peculiarities in these curves are pointed out for the first time and one or two uncertainties in previous work are settled by material presented here.

From experimental results the lengths and moments of inertia of these three molecules have been computed.

It is hoped that in the material presented there will be found some of real value in the work which is yet to be done in reconciling theory and fact in the extremely interesting field of molecular mechanics. It is a very real pleasure to acknowledge the writer's indebtedness to Professor Randall, who suggested the problem, for his continued interest and encouragement during the progress of the work.

Physical Laboratory
University of Michigan
April 30, 1918