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MEASUREMENTS ON THE NEAR INFRA-RED ABSORPTION of SOME DIATOMIC GASES.

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

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Measurements on the Near Infra-red Absorption of Some Diatomic Gases.

The importance of the study of the near infra-red absorption bands of gases is being more clearly realized the further 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 charges atoms and molecules, and not in the oscillations of the electrons within the atoms. The two widely separated

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1. P. Drude, Ann. d. Phys. (4), 14, p.677, 1904.

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. 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_o due to its oscillations alone would, when rotating about an axis perpendicular to its line of vibration with a frequency ν_r, emit and absorb at the new frequencies $\nu_o \pm \nu_r$. 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. Burmeister's[4] 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

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2. N. Bjerrum, Nernst Festschrift, p.90, 1912.
3. Lord Rayleigh, Phil. Mag.(5), 24, p.410, 1892.
4. W. Burmeister, Verh.d.D.phys.Ges.,15, p.589,1913.

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.

Rubens and v.Wartenberg[5] 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 continuous areas with a single maximum each for $\nu_o + \nu_r$ and $\nu_o - \nu_r$. Rubens'[6] work on the water vapor band at 6μ and even Paschen's[7] much earlier work on the same band showed many separate maxima in these areas. Finally von Bahr[8] in her work on water vapor and hydrochloric acid showed such marked discontinuity in these bands that an extension[9] 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 Nernst[10] had previous to

5. H.Rubens and H.v.Wartenberg,Verh.d.D.phys.Ges.,13,p.796,1911
6. H.Rubens, Sitzber.preuss.Akad.,1913,p.513.
7. F.Paschen, Wied.Ann.,52, p.215,1894.
8. E.v.Bahr,Verh.d.D.phys.Ges.,15,pp.710,731,1150- 1913.
9. N.Bjerrum, l.c.
   E.v.Bahr, l.c.
   A.Eucken, Verh.d.D.phys.Ges.,15, p.1159, 1913.
10. W.Nernst, Zeitschr.f.Electroch.,17,p.265,1911.

this time arrived at the conclusion that the quantum theory must be applied to molecular rotation. This conclusion was based upon 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 wave lengths are emitted. Work was done on the specific heat of gases at low temperatures with a view of finding this quantum effect, and various explanations of the results arrived at were attempted. Perhaps the best of these was that of Ehrenfest[11] who proposed the equation,

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

(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 explanation. This equation differs from that proposed by Bjerrum[12] by the factor 2 in the denominator of the second member of the equation, since Ehrenfest concluded that the rotation quantum of energy is $h\nu/2$ instead of $h\nu$ as assumed by Bjerrum. Kemble[13] gives a derivation, based on the classical statistical mechanics, which leads to the equation,

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

as giving the moment of inertia of a diatomic molecule

11. P.Ehrenfest, Verh.d.D.phys.Ges.,15, p.451, 1913.
12. N.Bjerrum, l.c.
13. E.C.Kemble, Phys.Rev.,(2), 8,p.689, 1916.

in terms of the rotation frequency, ν_r, obtained from the Bjerrum doublet. He shows that this checks with Ehrenfest's assumption rather than 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 case of water vapor and CO_2, to say nothing of more complex molecules yet to be studied, until by 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[14] original curve for this gas gave only the doublet consisting of broad areas having maxima at 3.4μ and 3.55μ. Von Bahr[15] 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 Brinsmade and Kemble[16] have published since this work

14. W.Burmeister, l.c.
15. E.v.Bahr, Phil.Mag.(6),28,p.71,1914.
Verh.d.D.phys.Ges.,15,p.1150,1913.
16. J.B.Brinsmade and E.C.Kemble, Proc.Nat.Acad.Sci.,3,p.420, 1917.

was begun, a curve for HCl giving eight maxima on the long-wave side of the center of the band at 3.46μ, as well as a partially resolved curve for the "harmonic" at 1.76μ.

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

Apparatus.

The apparatus designed and used by Sleator[17] in his work on water vapor was admirably adapted to this present work and was fortunately available. A very few minor changes and additions dictated for the most part solely by the comfort and convenience of the observer were all that were made. Since a detailed description of this apparatus can be found in Dr. Sleator's paper only a brief description need be given here.

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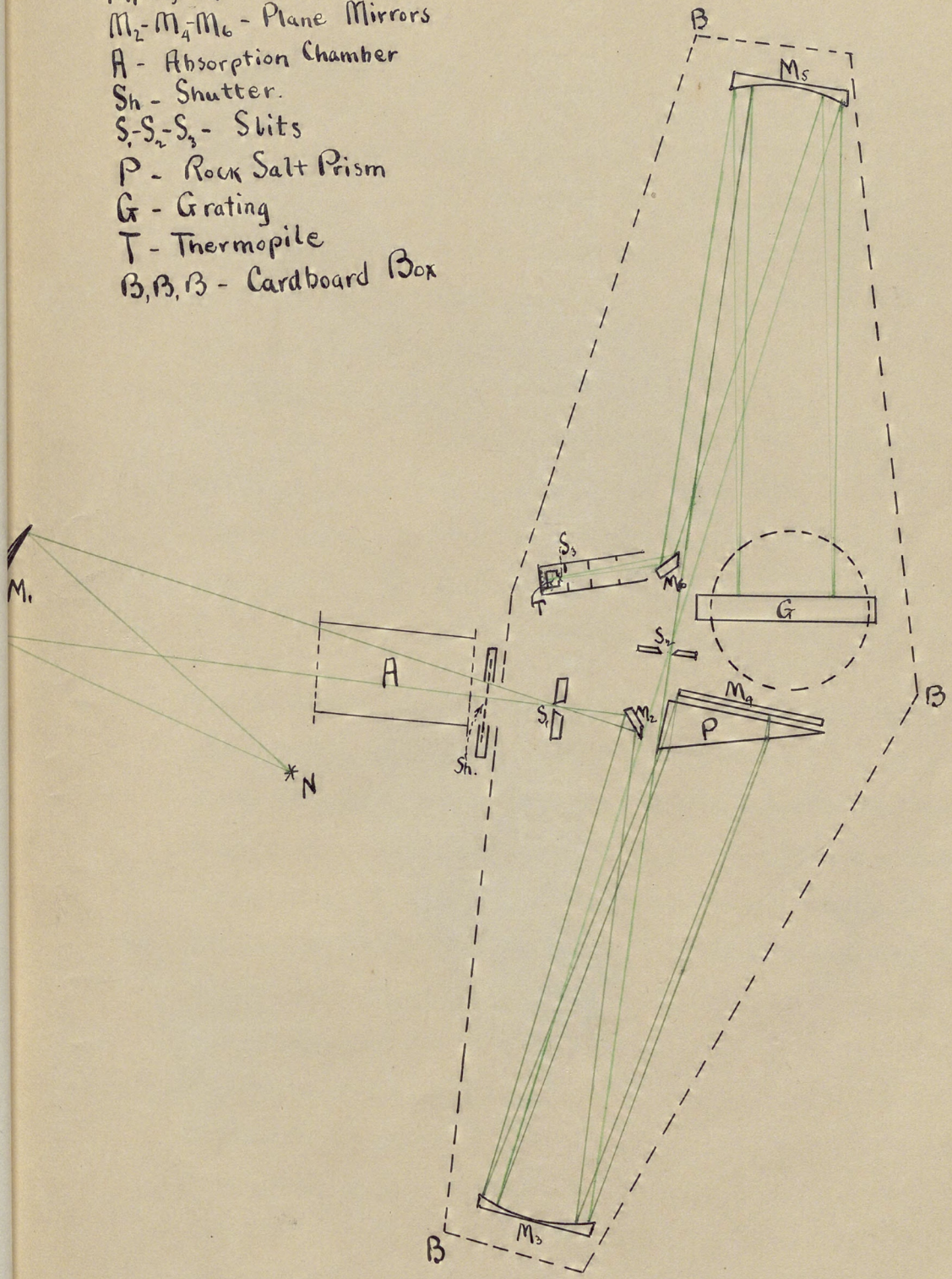
17. W.W.Sleator,"The Absorption of Near Infra-red Radiation by Water Vapor"- to be published in the Astrophysical Journal.

N - Nernst Glower.
M_1-M_3-M_5 - Concave Mirrors
M_2-M_4-M_6 - Plane Mirrors
A - Absorption Chamber
Sh - Shutter.
S_1-S_2-S_3 - Slits
P - Rock Salt Prism
G - Grating
T - Thermopile
B,B,B - Cardboard Box



The Spectrometer.
Fig. 1.

The Galvanometer.

The galvanometer is of the Paschen type, a modification of the Thomson four-coil astatic instrument, built in our shops. As used with the scale 200 cm. distant and with a period of about 6 seconds the figure of merit of this galvanometer is approximately 2.2×10^{-10} amp. per mm. deflection.

The Spectrometer.

Figure 1 gives the arrangement of the spectrometer, which consists really of two spectrometers, both of the mirror type. The first is a prism spectrometer, $S_1M_2M_3PM_4M_3$, which presents a portion of its spectrum to the slit S_2 of the grating spectrometer, $S_2M_5GM_5M_6T$.

The prism is of rock salt and has a refracting angle of about 18°. The face of the prism is about 12 x 14 cm. Three gratings were used. The first, a brass grating by Hilger, has a ruled surface 4.2 x 5 cm. It has a constant of about 211476 A.U. and was useful mainly for exploration. The entire band at 3.46μ was included in an interval of not much more than one degree, and although the resolution was good no measurements were made from the curve obtained by it save as a rough check upon the better curve given by the 7500-line grating. This 7500-line grating, by Anderson of JohnsHopkins, is ruled on speculum metal. Its ruled surface is 9.2 x 12.2 cm. It was calibrated by means of the green mercury line (λ=5460.7μ) from a Heraeus lamp. Two calibrations extending to the

fourth order spectra made over six months apart gave respectively 67693.1 and 67692.9 as the constant. Accordingly the value 67693. A.U. was used in all wave length determinations, and is considered quite as accurate as may be hoped for. The third grating, also ruled on speculum metal by Anderson, has 20,000 lines to the inch. Its ruled surface is 5.2 x 8 cm. and its constant 25374.5 A.U.

The advantage of the double spectrometer method in this work has been carefully ststed by Sleator. It is sufficient to say here that it has proved a highly successful method of bringing the desired high dispersion of the grating to bear on this 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 we wish to interpret the results. This is especially true where, as in the present work, photographs are impossible. There is some hope of detecting overlapping on the photographic plate, but none whatever in the throw of a galvanometer. In the double spectrometer method a very limited portion of the prism spectrum is presented to 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

$$\frac{d\lambda}{\lambda} = \frac{1}{Nn},$$

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

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

$$d\lambda = \frac{3.46}{22500 \times 1} = .00016\mu = 1.6 \text{ A.U.}$$

But this is based on the assumption of infinitely narrow slits which is not at all the case in this work, both grating spectrometer slits being .5 mm. wide. A better idea of the resolution obtained may be gained from the following consideration. - The width of the thermopile slit (S_3) 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

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

In other words the thermopile slit includes 29. A.U. of the spectrum formed by this grating at 3.46μ. Against this 29 A.U. Kemble worked with approximately 70 A.U.

and von Bahr with 100 A.U. in their best results.

The Thermopile.

The "eye piece" of the spectrometer consists of a thermopile and the galvanometer. The thermopile is a linear bismuth-silver group made by Coblentz. It has about ten junctions in its center line and a resistance of about 2 ohms. It is mounted behind a .5 mm. slit at the focus of the mirror M_5, this focus being reflected by the plane mirror M_6 at about 90°, so that the thermopile will not obstruct the beam from the slit, S_2, to M_5. 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, but owing to age and use the heating c coils and finally all available ballast coils gave out, and it was difficult, if not impossible, to obtain a new supply. Fortunately a few of the filaments remained on hand and in its final form the "lamp" consisted of an adjustable wire rheostat, a tungsten lamp rheostat for ballast, and a filament mounted in an alundum cement mould that shielded it to some extent from convection currents. Previously the lamp had been driven by D.C. from a storage battery for steadiness, but the polarization was annoying and hard on the limited supply of filaments. A.C. was accordingly used during the latter part of the work. As all the observations were taken

between 1 a.m. and 5 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. In addition, 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. It was provided with two stop cocks through which gas could be driven into and out of it. 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 carried in a small clamp so as to be in the beam when the chamber was out. The whole was mounted so that it could be swung into the "in" and "out" positions by means of a wire and a system of pulleys operated from the observer's seat on the opposite side of the spectrometer. The thickness of the mica plates was of the order of .03 mm. For work in the region of 2.5μ 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 percent 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 2.6μ - it was thought best to provide a compensating chamber similar in dimensions to the absorption chamber and carefully filled with dried air that had been freed also from CO_2 by passing through KOH solution.

Methods and Results.

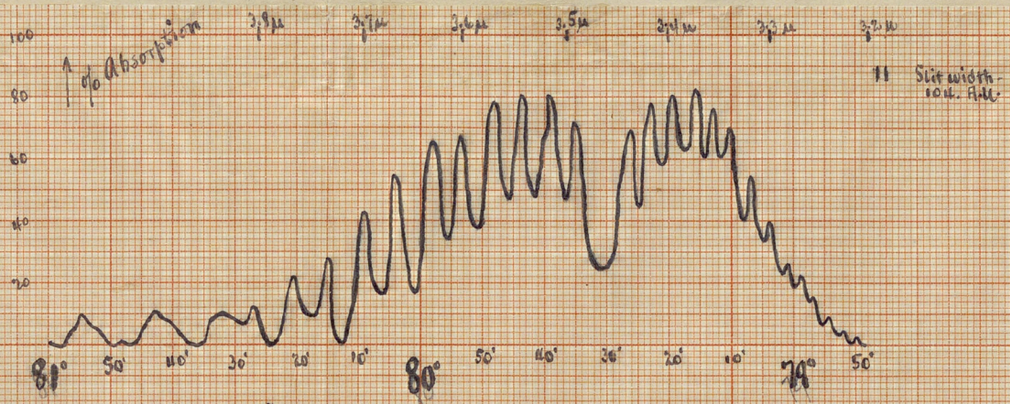
Hydrochloric acid.

The first work was done with HCl in the region of 3.5μ. The HCl was generated by dropping H_2SO_4 on $CaCl_2$ and dried by being passed through concentrated H_2SO_4. Both chemicals were chemically pure - 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 galvanpmeter deflection

were taken through the absorbing gas and a like number through only the compensating plates, the deflections being obtained by opening or closing a 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 percent transmission, and the difference between this and 100 percent being the percent 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.4).

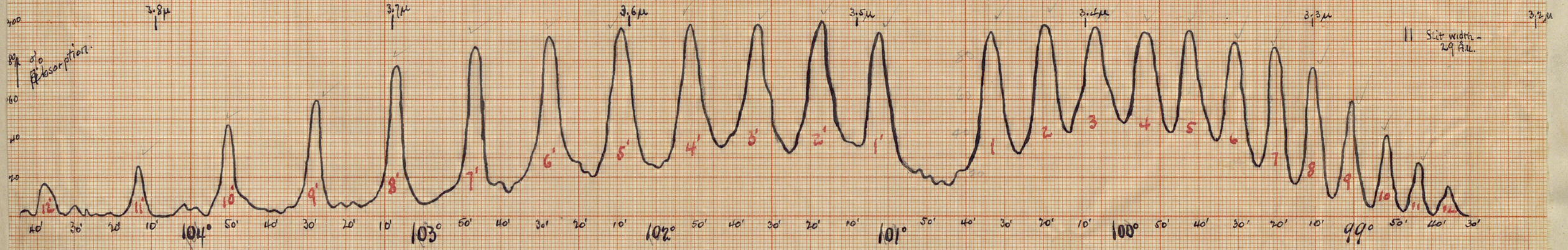
The extreme sensitivity of the galvanometer used in this work to the slightest mechanical or magnetic disturbance is a source of regret. Many times it was not possible to obtain consistent deflections even during the favorable hours between midnight and dawn chosen for observation. No claim for extreme accuracy is made for the percentages obtained, but it is not likely that there



← Grating Setting.
Zero Setting - 70°5'10"

HCl at atmospheric pressure - "Fundamental" Band.
- with Brass Grating - K = 2.11476. A.U.

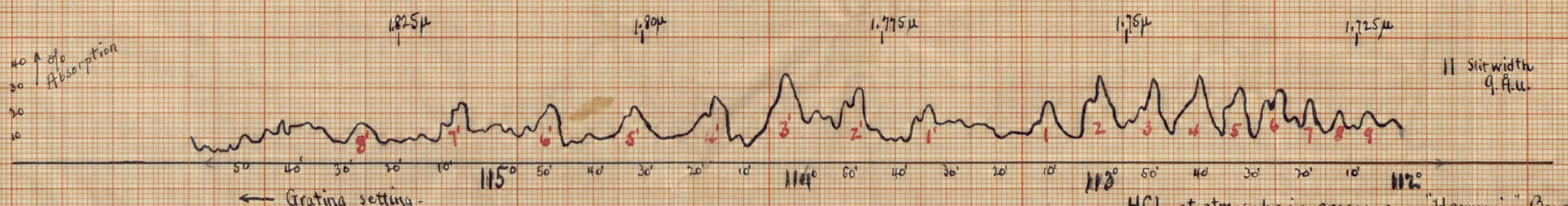
Fig. 2.



← Grating setting
- Zero setting 70°0'0" to 70°1'0".

HCl at atmospheric pressure - "Fundamental" Band.
- with 7500-line Grating - K = 67693. A.U.

Fig. 3.



← Grating setting -
Zero setting varies between 69°18'20" and 69°19'30".

HCl at atmospheric pressure - "Harmonic" Band.
- with 29000-line Grating - K = 25374.5 A.U.

Fig. 4.

TABLE I.

HCl Band at 3.46μ — From curve of Fig.3

n	λ (in μ)	$\nu_n \times 3\cdot10^{-10}$	$\Delta\nu_n \times 3\cdot10^{-10}$	$\nu_{on} \times 3\cdot10^{-10}$	$\nu_{on} \times 3\cdot10^{-10}$ computed	$\nu_{rn} \times 3\cdot10^{-10}$	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		2886.97	2886.73	20.79	20.79
			21.75				
2'	3.51565	2844.42		2886.22	2885.83	41.36	20.68
			22.48				
3'	3.54366	2821.94		2884.15	2884.33	62.21	20.73
			22.49				
4'	3.57214	2799.45		2882.21	2882.23	82.76	20.69
			23.04				
5'	3.60178	2776.41		2879.38	2879.52	102.97	20.59
			23.85				
6'	3.63298	2752.56		2876.27	2876.22	123.71	20.62
			23.67				
7'	3.66450	2728.89		2872.58	2872.32	143.69	20.53
			25.30				
8'	3.69878	2703.59		2867.89	2867.81	163.80	20.48
			25.03				
9'	3.73335	2678.56		2862.83	2862.71	184.26	20.47
			25.91				
10'	3.76982	2652.65		2857.11	2857.03	204.45	20.45
			26.15				
11'	3.80735	2626.50		2850.69	2850.67	224.16	20.38
			26.62				
12'	3.84633	2599.88		2843.78	2843.78	243.90	20.33

TABLE II.

HCl Band at 1.76μ — From curve of Fig.4

n	λ (in μ)	$\nu_n \times 3\cdot10^{-10}$	$\Delta\nu_n \times 3\cdot10^{-10}$	$\nu_{on} \times 3\cdot10^{-10}$	$\nu_{on} \times 3\cdot10^{-10}$ Computed	$\nu_{rn} \times 3\cdot10^{-10}$	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

is any undue uncertainty about the location of the maxima, which have all been repeated - some as many as four and five times. 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 3.46μ with two different gratings. Table I. gives the measurements and computations made from the better curve. Figure 4 gives the curve obtained for the so-called "harmonic" of HCl at 1.76μ with the 20000-line grating and Table II. gives the measurements and computations from this curve.

Hydrobromic acid.

The production of pure HBr was more of a task than that of HCl. It was finally 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 carefully dried. Chemically pure bromine was washed in a KOH solution in a separating funnel 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 traces of water vapor. Burmeister[18] speaks of drying HBr by passing it through

18. W.Burmeister, Verh. d. D. phys. Ges., 15, p. 596, 1913.

P_2O_5. This process would give rise to volatile compounds of phosphorous and bromine, and would no doubt account for some of the difficulty he had in obtaining satisfactorily pure HBr.

Because of the rather elaborate nature of the apparatus required for the generation of HBr no attempt was made to keep a stream passing through the absorption chamber. It was thought sufficient to start each new series of observations with a freshly generated absorption chamber full of the gas, 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 of the air was displaced. In addition, it was aimed to generate the gas 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 remarked previously, since the interest has been only in the location of these maxima, and variations in pressure do not displace them laterally.

The 7500-line grating was used and the long-wave limit was determined by the strong atmospheric absorption

beyond 4.2μ, which cut down the galvanometer deflections to so small a figure as unduly to magnify 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.5, and the table of values read and computed appears as TableIII.

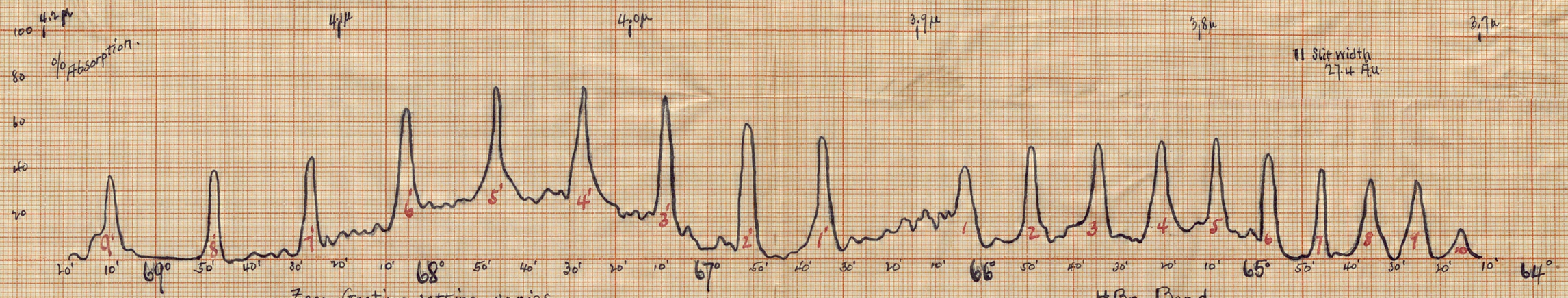
A search was made for the "harmonic" of HBr at 2μ found by Brinsmade and Kemble[19]. Nothing was found by any one of the three gratings, the conclusion being that the length of the column of absorbing gas was not great enough to give strong absorption in this region nor was it possible with the time available to do the remodeling that a sensibly longer chamber would require.

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 rubber tubing it was absolutely necessary to use. The gas was generated in a small iron retort by the action of concentrated

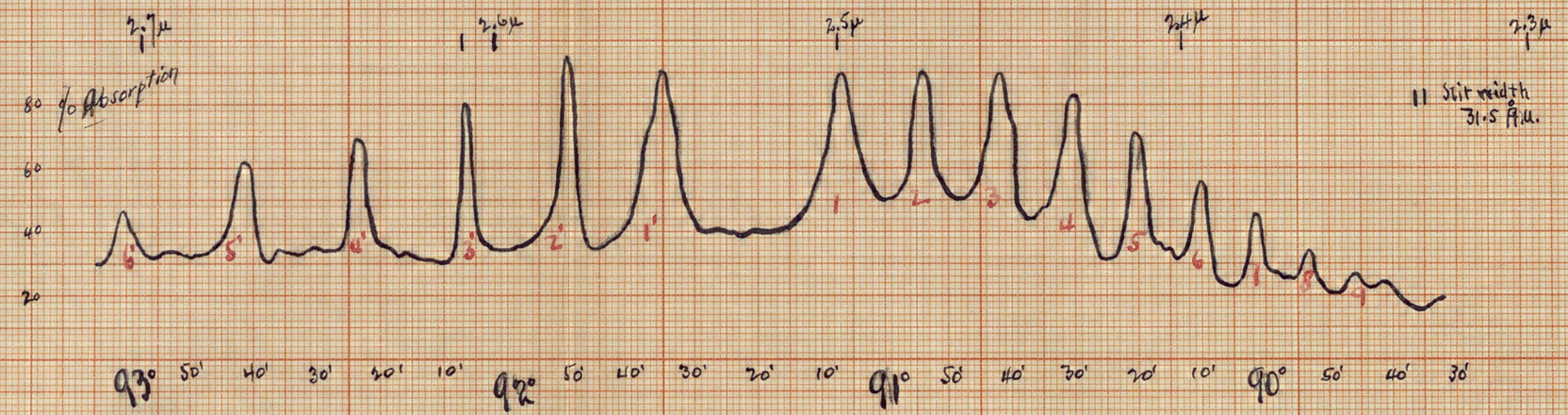
19. Brinsmade and Kemble, Proc.Nat.Acad.Sci.,3,p.420,1917.



Zero Grating setting varies between 31° 3' 0" and 31° 4' 0"

HBr Band
with 7500-line Grating - K = 67693. A.U.

Fig. 5.



Zero Grating setting - 69° 2' 0"

HF Band -
with 7500-line Grating - K = 67693. A.U.

Fig. 6.

TABLE III.

HBr Band — From curve of Fig.5

n	λ (in μ)	$\nu_n \times 3\cdot10^{10}$	$\Delta\nu_n \times 3\cdot10^{10}$	$\nu_{on} \times 3\cdot10^{10}$	$\nu_{on} \times 3\cdot10^{10}$ computed	$\nu_{rn} \times 3\cdot10^{10}$	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		2558.89	2558.93	16.79	16.79
			16.65				
2'	3.95969	2525.45		2558.39	2558.23	32.94	16.47
			18.05				
3'	3.98819	2507.40		2557.05	2557.08	49.65	16.55
			18.00				
4'	4.01704	2489.40		2555.63	2555.46	66.23	16.56
			18.49				
5'	4.04709	2470.91		2553.12	2553.38	82.21	16.44
			18.69				
6'	4.07793	2452.22		2550.76	2550.84	98.54	16.42
			19.33				
7'	4.11034	2432.89		2547.82	2547.74	114.93	16.42
			19.40				
8'	4.14338	2413.49		2544.60	2544.37	131.11	16.39
			20.19				
9'	4.17833	2393.30		2540.41	2540.44	147.11	16.35

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 2.6μ 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 was built, so constructed 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 will be immediately 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.

The long-wave limit of this work was determined by the strong atmospheric (water vapor) absorption beyond 2.6μ, 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.6, the measurements appearing in Table IV.

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

TABLE IV.

HF Band — From curve of Fig.6

n	λ (in μ)	$\nu_n \times 3\cdot10^{10}$	$\Delta\nu_n \times 3\cdot10^{10}$	$\nu_{on} \times 3\cdot10^{10}$	$\nu_{on} \times 3\cdot10^{10}$ computed	$\nu_{rn} \times 3\cdot10^{10}$	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 (p.4) to the variance between the Bjerrum and Ehrenfest assumptions with regard to the size of the energy quantum. From the newer point of view which regards the quantum of action and not the energy quantum as fundamental, the Ehrenfest[20] equation may be justified. To do this use is made of Sommerfeld's[21] extension of the Planck phase-integral in which he splits up the general integral for f-degrees of freedom;

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

(the q's are position coordinates and the p's the corresponding momentum coordinates);

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

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20. Proposed also by Eucken. (See A.Eucken, Verh.d.D.phys.Ges., 15,p.1159,1913.)
21. A.Sommerfeld, Ann.d.Phys.(4),51,p.1,1916.

quite simply into

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

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

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

From this equation there is obtained directly

$$\nu_r = n\frac{h}{4\pi^2 I} \qquad (1)$$

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 - as before - ν_o is 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

$$\left.\begin{aligned} \nu_u &= \nu_0 + \nu_{rn} \\ \nu_{u'} &= \nu_0 - \nu_{rn} \end{aligned}\right\} \quad - - - - - - - - - - - - \quad (2)$$

whence

$$\nu_{rn} = \frac{\nu_u - \nu_{u'}}{2} \quad - - - - - - - - - - - \quad (3)$$

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

$$I = n \frac{h}{4\pi^2 \nu_{rn}} \quad - - - - - - - - - \quad (4)$$

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

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

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

Table V.

Molecule	I x10^{-40}	lx10^{-8}	I x 10^{-40} (Kinetic Theory)
HF	1.37	.94	--
HCl	2.64	1.28	2.45
HBr	3½27	1.42	3.35

Von Bahr[22] gives values of I and λ for HCl computed from her experimental data and the Bjerrum hypothesis differing from these by the factor 2 in the case of I and $\sqrt{2}$ in the case of λ, within very close agreement.

Some check is desirable on any such values. In this 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 of page 4 -

$$I = \frac{RT}{4\pi^2 \bar{\nu}_r^2 N} , \qquad (6)$$

and using the values obtained by Burmeister for the doublet maxima, as corresponding to the most probable frequency through the equations $\nu_m = \nu_0 \pm \bar{\nu}_r$, values for I may be obtained for HCl and HBr. (The present work, it is to be observed, gives no means of determining this most probable frequency.) Taking $R = 8.26 \times 10^7$, $N = 6.12 \times 10^{23}$, $T = 292^\circ$ - equation (6) gives:

for HCl, $I = 2.45 \times 10^{-40}$

for HBr, $I = 3.35 \times 10^{-40}$.

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

If one turns to the curves of Fig.3 and the accompanying table (Table I.) it is at once apparent that the expected symmetry of the maxima, i.e. the arithmetic progression expected in the frequencies

22. E.v.Bahr, Phil.Mag. (6), 28, p.82, 1914.

of the maxima, does not exist. Instead, there is a gradual increase in frequency difference between two adjacent maxima as one goes further into the infra-red.

Starting again with equations (2), the expression

$$\nu_o = \frac{\nu_n + \nu_{n'}}{2} \qquad (7)$$

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 assymetry of the band is the consequence of the shifting of these centers 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_{on} is computed, and plotting ν_{on} against n, the curve of Fig.7 is obtained. This curve appears at once to be a parabola. 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 I. is found. The equation of this curve is

$$\nu_{on} \times 3 \cdot 10^{-10} = 2887.03 - .30n^2.$$

For ν_{oo}, the extrapolated center of the band, the value is, of course, A of the equation, and the corresponding

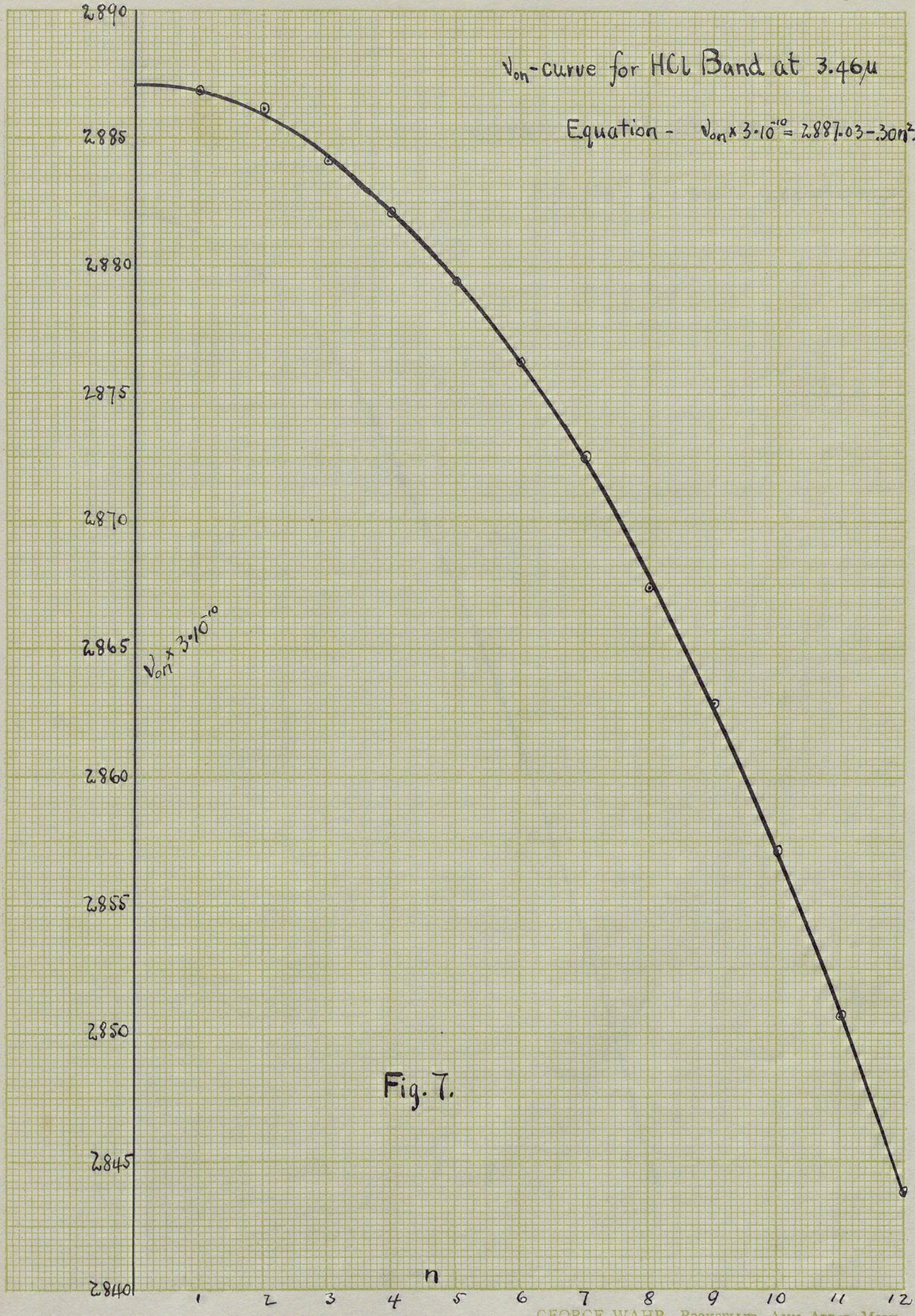

Fig. 7.

GEORGE WAHR—Bookseller, Ann Arbor, Mich.

ν_{on} - curve for HCl Band at 1.76 μ

Equation - $\nu_{on} \times 3 \cdot 10^{-10} = 5666.97 - .59n^2$.

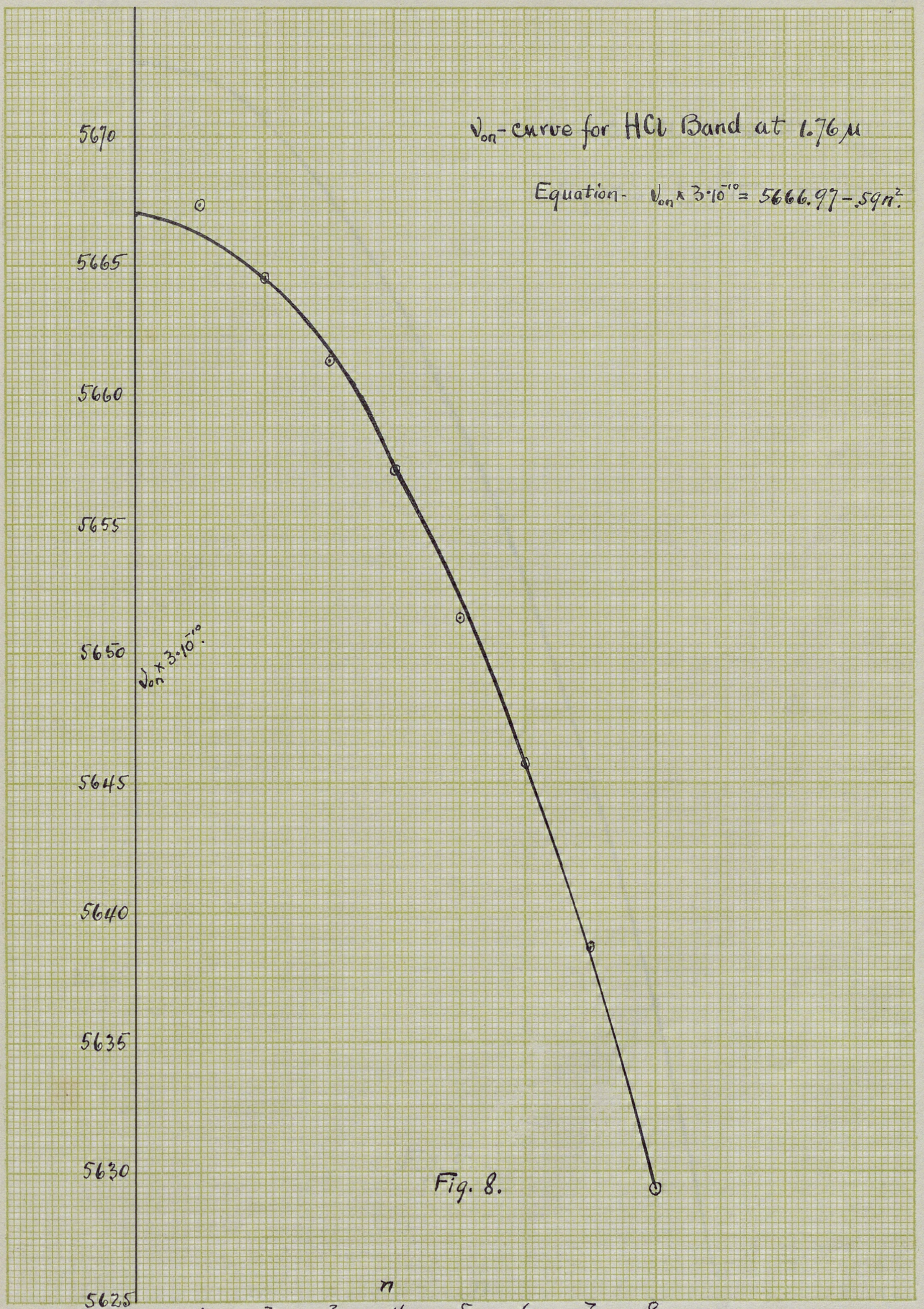

Fig. 8.

GEORGE WAHR—Bookseller, Ann Arbor, Mich.

ν_{on}-Curve for HBr Band at 3.91μ.

Equation $\nu_{on} \times 3 \cdot 10^{-10} = 2559.16 - .23n^2$.

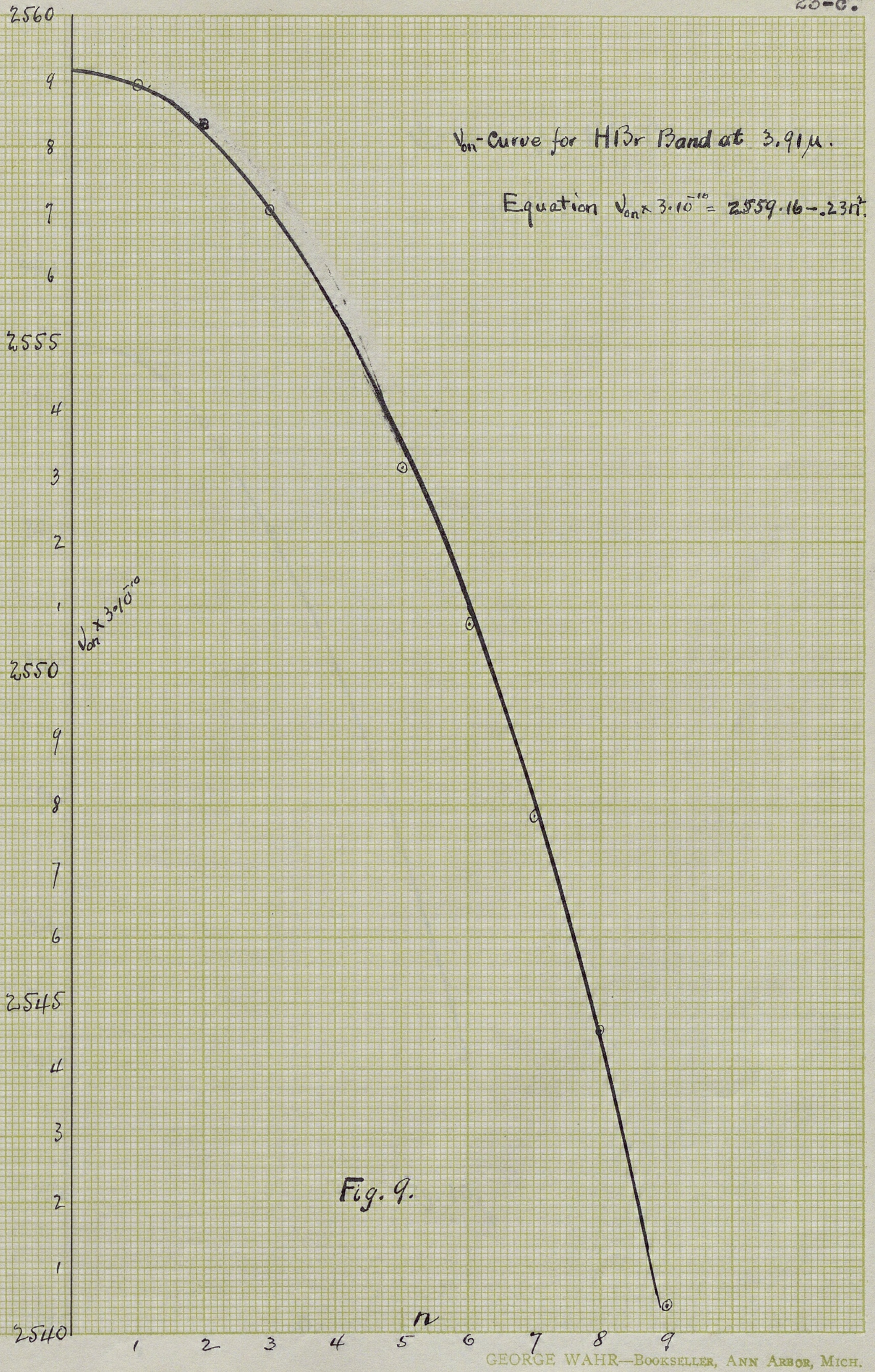

Fig. 9.

GEORGE WAHR—Bookseller, Ann Arbor, Mich.

ν_{on} curve for HF Band at 2.52 μ

Equation - $\nu_{on} \times 3 \cdot 10^{-10} = 3962.47 - .76n^2$

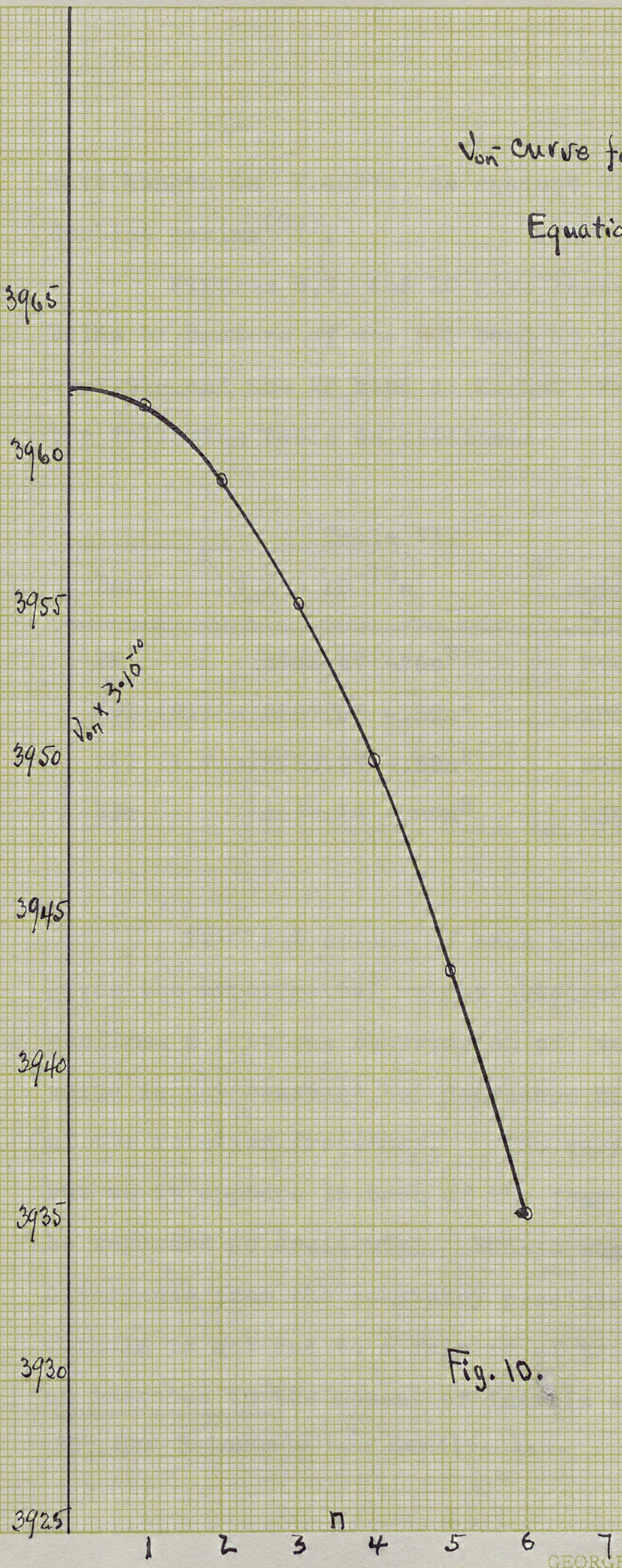

Fig. 10.

GEORGE WAHR—Bookseller, Ann Arbor, Mich.

wave length is 3.4637μ, as against 3.475μ given by the doublet maxima[23].

Figures 8, 9, and 10 give respectively the parabolas of centers of the HCl band at 1.76μ, the HBr band at 3.91μ and the HF band at 2.52μ. From these curves the following table is obtained:

Table VI.

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

The last column of each of tables I.-IV. gives the experimental values obtained for ν_m/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 in the moment of inertia with the velocity of

23. See Brinsmade and Kemble, l.c.

rotation. That such an increase does take place may be seem from the following values of the moment of inertia of the HCl molecule computed from the values of ν_{rn} given in Table I.:

Table VII.

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

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

$$I_n = (2.63 + .0055n + .000007n^2) \times 10^{-40}.$$

The computed values from this equation (neglecting the term in $\underline{n}^2$) are given parallel with the observed values above.

The "Harmonic".

Kemble[24] has advanced the theory that if the vibrational energy of the molecule also varies only by quanta 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-quarter of that of the maxima of the fundamental doublet (in wave length). A band approximately answering to these specifications had been observed by Burmeister in the case of CO and this was resolved into a doublet by Brinsmade and Kemble(l.c.). 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 further in the infra-red than demanded by the theory.

Fig. 4 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 $5666.97 \times 3 \cdot 10^{-10}$ while that of the center of the fundamental is $2887.03 \times 3 \cdot 10^{-10}$, 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 .033μ further in the infra-red than the predicted position. This displacement is greater than

24. E.C.Kemble, Phys.Rev.(2),8, p.701, 1916.

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

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 columns 4 of Tables I. and II. 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 the present curves to be composite.

Accuracy.

The question of the accuracy obtained in such a problem as this is of necessity involved. The constancy of the source of energy, the equality of the grating circle divisions, the accuracy of reading this circle, the constancy of the ratio of thermopile voltages to incident energy, the strictness of proportionality between galvanometer current and deflections, the correctness of the readings of these deflections, and the accuracy of the calibration of the grating, are all factors in the final accuracy of results. 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 Table I. Column 5 gives the frequency of the centers of the various pairs of maxima of the curve of Fig.3, while column 6 gives the values for the same centers computed by the method of least squares. The greatest variation of the observed values from the computed values is in the case for n = 8 where $d\nu = .42 \times 3 \cdot 10^{-10}$. This corresponds to a value of $d\lambda$ given by the equation

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

Substituting the values, $\nu = 2872.6 \times 3 \cdot 10^{10}$ and $d\nu = .42 \times 3 \cdot 10^{10}$, it is found that

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

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

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 has 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 have been obtained showing in greater detail the HCl bands at 1.76μ and 3.46μ 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 have been 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 here the writer's indebtedness to Professor Randall, who suggested the problem, for his continued interest and encouragement, - as also to Professor Colby whose lively interest in the theoretical considerations involved has been a stimulus throughout the investigation. In a very definite sense the ready availability of Dr. Sleator's experience in radiometry has contributed to whatever of success has been attained in the present work. From other members of the department and from Professor Willard of the Chemistry Depertment valuable suggestions and assistance have been received at various stages of the problem.

Physical Laboratory
April 30, 1918.

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