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ON THE ABSORPTION SPECTRUM OF HYDROGEN CHLORIDE

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ABSTRACT

The *fundamental band* and the *harmonic band* of hydrogen chloride have been measured with narrow slits. The lines of the *fundamental* as previously measured, have been resolved, each into two lines arising from the existence of the isotopes Cl_{35} and Cl_{37}. The relative intensities of the lines in the two series are in accord with the accepted ratio for the abundance of the isotopes. In the *harmonic*, a slight separation of the lines arising from the isotopes had been previously achieved by Randall and Imes. In the present work the degree of separation is greatly enchanced. Wave-number and intensity determinations for the two series of lines in each band are submitted. Figures are given representing the bands in the new form. The ratio of the intensities of the fundamental and harmonic bands, as experimentally determined, is found to be in good agreement with the computed value.

THE vibration-rotation spectrum of hydrogen chloride consists principally of a fundamental band at 3.46μ and a harmonic at 1.76μ. The work of Randall and Imes[1] demonstrated that the principal lines in the harmonic are accompanied by faint companions, which were interpreted by Loomis,[2] and Kratzer,[3] independently as arising from the existence of the isotope Cl_{37} in combination with hydrogen, the principal lines arising from the more abundant Cl_{35}. The suggested interpretation was supported by good agreement between observed and computed values of the separation of the principal lines and the companions. The companion lines were barely evident in the experimental curve, but their reality seemed established through the fact that a companion was indicated for nearly every principal line, and the success of the above mentioned hypothesis added further weight to the evidence.

In the fundamental band, companions were not observed, but there was no reason for believing that they did not exist. The failure to find them was presumably due to less favorable experimental conditions as determined by the spacing of the grating used, in relation to the expected separation. Subsequent investigators obtained in one case slight evidence,[4] and in another case indirect evidence[5] for the existence of the companions, but the companions were in no way separated from the principal lines.

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[1] Randall and Imes, Phys. Rev. **15,** 152 (1920); also Imes, Astrophys. J. **50,** 251 (1919).

[2] F. W. Loomis, Astrophys. J. **52,** 248 (1920).

[3] A. Kratzer, Zeits. f. Physik **3,** 460 (1920).

[4] W. F. Colby and C. F. Meyer, Astrophys. J. **53,** 300 (1921).

[5] E. C. Kemble and D. G. Bourgin, Nature **117,** 789 (1926); also D. G. Bourgin, Phys. Rev., 29, 794 (1927).

The performance of a new spectrometer, described elsewhere,[6] led to the belief that the separation in the fundamental might now be achieved. Preliminary trials at once demonstrated the existence of the companions, and by narrowing the slits to the extreme, the principal and companion lines were separated to a degree which exceeded the most optimistic expectations. The slits were narrowed to 0.25 mm, and as the focal length of the spectrometer is 1 m, the spectral range included by the slit is about one-fourth of that of the older work in which slits of 0.5 mm were usually employed with a focal length of 0.5 m.

In Fig. 1 are shown several of the curves which have been obtained. The abscissae represent settings of the grating circle. These were made at every fifteen seconds of arc, as indicated by the plotted points. The ordinates represent percent of absorption, correction being made for the diminution of energy by the rock-salt windows of the cell.

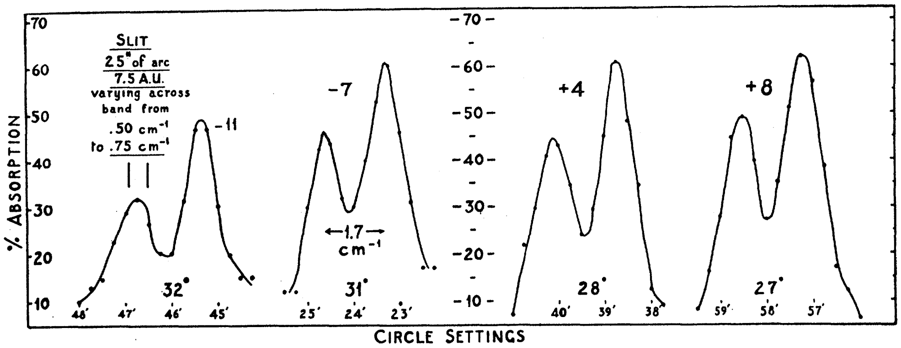

Fig. 1. Doublet structure of lines of the fundamental band. The right hand member of each doublet is due to HCl_{35}; the left hand member is due to HCl_{37}.

When the lines are separated to the degree which is here represented they no longer have the appearance of a *principal* line and a *faint* companion, but rather that of a *major* and a *minor* component of a pair. The ratio of the abundance of the isotopes Cl_{35} to Cl_{37} is about 3:1 and it is surprising to find that the maxima of absorption attained by the two components, as measured, should differ by so little as they do. However, the relation existing between measured maximum of absorption and true intensity of a line is an involved one, and it is not to be concluded that an anomaly is in evidence. A direct experimental comparison of the intensities was made by determining the absorption curve for one line (+4) first with a cell 1 mm in length, and then with a cell 3 mm in length. In Fig. 2 the left hand curve represents the result in the first instance, and the right hand curve represents the result in the second instance. As is to be expected the maximum of absorption attained by the major component in the first case is approximately equal to the maximum attained by the minor component in the second case.[7] The

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[6] A. A. Levin and C. F. Meyer, J.O.S.A. & R.S.I. **16,** 137 (1928).

[7] See also note on relative intensities by D. M. Dennison in the last section of this article.

points near the maxima in question were determined with more than ordinary care. Each final, plotted, point represents the mean position of three or four original points obtained in measuring back and forth across the line. Each original point represents the percentage of absorption calculated from eight galvanometer deflections taken with the cell in the beam, and eight with the cell out of the beam.

The primary object of the present investigation was to furnish measurements of the positions of the lines when separated as above shown and a secondary object was to furnish measurements of the intensities. It is important for the development of the theory of the vibrating rotating dipole, that the laws of both spacing and intensity be determined as accurately as possible. The older measurements, which showed the lines as composite, could not reveal these laws as closely as might be desired. It is believed that the present work presents greatly improved data in regard to spacing. As for intensity, it is a necessary consequence of the use of narrower slits that the total available energy is reduced, and that the errors in absorption percentages are increased. Therefore the percentages will not be as accurately given as in some previous work.[5] Nevertheless, because of the very fact that the slit width is so much narrower, and because the lines are separated into their components, it is believed that the measurements of intensity will also have value.

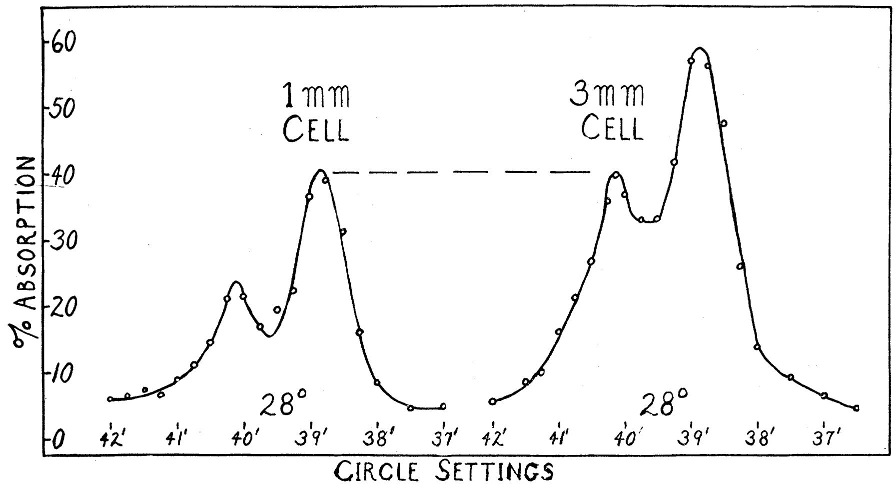

Fig. 2. Comparison of intensities of major and minor components.

CALIBRATION ETC.

A grating of 7200 lines per inch (2835 per cm), ruled by E. F. Barker, was used for work on the fundamental. One of 15,000 lines per inch (5900 per cm), by J. A. Anderson, was used for the harmonic. Both were calibrated by means of the 1.014μ mercury line for which the exact wave-length was taken as 10,139.8A. in air at the temperature and pressure of the experiment, about 23°C and 74 cm. The wave-numbers for the HCl lines have been reduced to vacuum by taking $n-1$ equal to $25.\times 10^{-5}$ in the region of the fundamental, and equal to $26.\times 10^{-5}$ in the region of the harmonic, n being the index of refraction for air.[8]

Much attention has been given in the present investigation to reducing error, and it is believed that the wave-number determinations are more accurate than previous ones in infra-red absorption measurements. The greater sharpness of the lines when measured with narrow slits, and the comparative freedom from overlapping should also contribute materaially toward achieving this result. In the past, independent sets of determinations made by different observers, working with different apparatus, have usually shown minor discrepancies which indicated systematic error. It is hoped that such error has been decidedly reduced, but positive claims to this effect cannot be made and the authors do not wish to insist on high *absolute* accuracy for the measurements. The *relative* accuracy of the wave-number determinations should however be distinctly greater than that of previous determinations, and moreover the *law of spacing* should appear with much improvement because the series of lines arising from the two isotopes are now determined separately.

THE FUNDAMENTAL BAND

In the work on the fundamental it was not feasible to follow the usual procedure of measuring the entire band with a fixed cell length and gas content. It was desired to measure twelve lines in each branch of the band. The variation in intensity among these is so great that no one amount of gas will do for all. In the more intense lines the major and minor components will overlap considerably while the fainter lines will show insufficient absorption for proper measurement. Consequently, a set of position measurements was first made, with varying amounts of hydrogen chloride in the beam, the quantity being adjusted until the line or lines which were shortly to be measured exerted a proper amount of absorption. Air remained in

TABLE I. *Fundamental band, observed wave-numbers, cm^{-1}, vacuum.*

Line No.	Major Comp.	Minor Comp.	Diff.	Line No.	Major Comp.	Minor Comp.	Diff.
−12	2599.00	2597.43	1.57	1	2906.25	2904.16	2.09
−11	2625.74	2624.03	1.71	2	25.78	23.69	2.09
−10	51.97	50.36	1.61	3	44.81	42.71	2.10
−9	77.73	75.90	1.83	4	63.24	61.08	2.16
−8	2703.06	2701.29	1.77	5	80.90	78.68	2.22
−7	27.75	26.01	1.74	6	97.78	95.66	2.12
−6	52.03	50.31	1.72	7	3014.29	3012.16	2.13
−5	75.79	73.77	2.02	8	29.96	27.69	2.27
−4	98.78	96.88	1.90	9	44.88	42.62	2.26
−3	2821.49	2819.51	1.98	10	59.07	56.84	2.23
−2	43.56	41.59	1.97	11	72.76	70.51	2.25
−1	65.09	62.99	2.10	12	85.62	83.28	2.34

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[8] F. Paschen, Ann. d. Phys. **27**, 537 (1908); **29**, 625 (1909); **38**, 717 (1910).

the cell admixed with the hydrogen chloride, the pressure of the mixture being atmospheric. The separation of the components in this set of measurements was throughout about as complete as shown for the lines of Fig. 1. Had the separation been less complete, it would have been necessary to make a correction for the position of each component due to the influence of its neighbor. As it was, such a correction was deemed unnecessary. The wave-numbers for the above mentioned series of measurements are given in Table I as are likewise the separations between the major and minor components.

Subsequently the first six lines in each branch of the band were measured with a cell of fixed length of 3 mm, filled with hydrogen choloride at atmospheric pressure. The curves obtained are given in Fig. 3. They are submitted because of such interest as they may have in regard to intensity of absorption. In plotting them, correction was of course made for the diminution of energy due to the windows of the cell. At the base of the curve for each pair of lines, short horizontal marks indicate the height of the absorption curve in the intervening regions between the pairs of lines. These intervening regions were explored throughout, but with large intervals between successive settings of the grating. The curve rises and falls irregularly in the region between the lines due to the observational error of individual determinations of percentage of absorption. The range of variation is usually two or

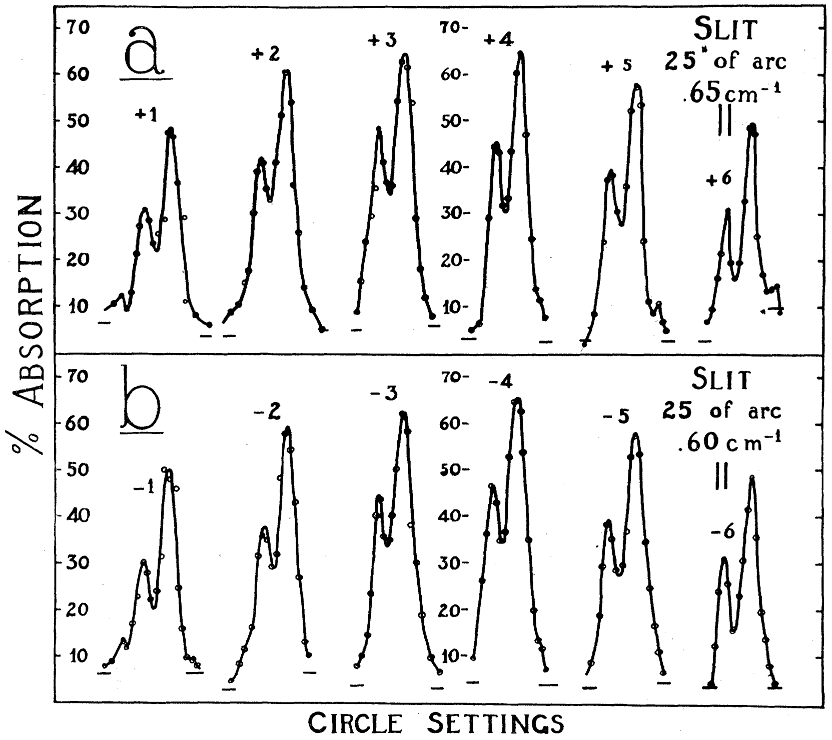

Fig. 3. Individual lines of the fundamental band.

three and sometimes as high as five percent. The separation between the major and minor components is not so complete in the curves of Fig. 3 as in those of which examples are given in Fig. 1. The difference is attributed to some slight change in the condition of the spectrometer which is not under control, perhaps a slight distortion in the large mirror or the grating which impaired the definition, or perhaps a refusal on the part of the slit to assume always the same width for the same setting of the micrometer head. Several months intervened between the two sets of observations.

It was deemed desirable to depict the *entire* band in its new form with the lines due to the isotopes separated. When the drawing of the figure was undertaken it became evident that the representation could not be made in the usual manner of an absorption *curve*, but would have to be shown as a "silhouette" of the absorption *area*. This is necessitated by the extreme narrowness of the lines in relation to the width of the region which must be depicted. The band is represented in Fig. 4. The first six lines in each branch are shown in accordance with the intensity measurements made with the 3 mm cell, and the intensities of the remaining six lines in each branch are estimated. The regions intervening between the pairs of lines have been smoothed out. If they had not been, the figure would have presented a confused appearance, as was demonstrated by a preliminary drawing.

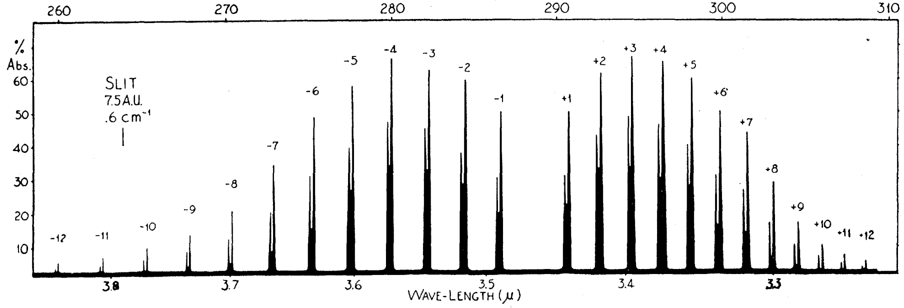

Fig. 4. The fundamental band.

The Harmonic Band

In the work on the harmonic a cell 30 cm in length was employed which was fitted with plate glass windows. The cell was as long as the arrangement of the apparatus permitted. It contained hydrogen chloride at a pressure of about 60 cm, and with this was admixed air to atmospheric pressure. The amount of gas which was present was such that the more intense lines of the band exerted about the maximum of absorption which was consistent with having good separation between the components. As many lines were measured in each branch of the band as could be measured with this amount of gas, namely, eight in the P branch and nine in the R branch. The wave-numbers and separations for these are given in Table II, and the absorption curves for the individual lines are shown in Fig. 5. Short horizontal marks again indicate the height of the curve in the regions intervening between the lines. These regions were explored throughout. To the right of line −8 is shown a section of the curve which intervenes between lines −8 and −7. The irregularities here are typical, and this section is shown by way of example. Repetition of the measurements in some of the intervening regions indicated that the irregularities arose purely from accidental errors, due of course to the accidental disturbances of the galvanometer.

TABLE II. *Harmonic band, observed wave-numbers, cm^{-1}, vacuum.*

Line No.	Major Comp.	Minor Comp.	Diff.	Line No.	Major Comp.	Minor Comp.	Diff.
−8	5468.55	5464.67	3.88	1	5687.81	5683.91	3.90
−7	96.97	93.12	3.85	2	5706.21	5702.01	4.20
−6	5525.04	5521.23	3.81	3	23.29	19.42	3.87
−5	51.68	47.74	3.94	4	39.29	35.26	4.03
−4	77.25	73.40	3.85	5	53.88	49.69	4.19
−3	5602.05	97.98	4.07	6	67.50	63.28	4.22
−2	24.81	5620.92	3.89	7	79.54	75.40	4.14
−1	47.03	43.10	3.93	8	90.54	86.28	4.26
				9	99.94	96.04	3.90

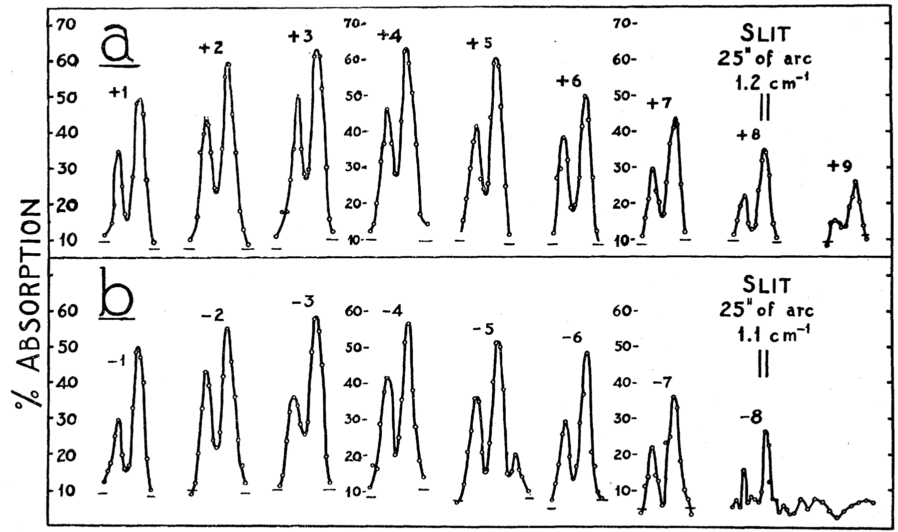

Fig. 5. Individual lines of the harmonic band.

It will be noted that the degree of separation of the major and minor components of the harmonic, as shown in Fig. 5 is about the same as that for the first series of measurements on the fundamental, Fig. 1. In point of time the observations on the harmonic succeeded those of the first series on the fundamental. Those of the second series on the fundamental were made later, and those in connection with Fig. 2 were made last and these show the greatest impairment of definition.

In Fig. 6 the harmonic is shown in “silhouetted.” form. The representation is according to measurement in regard to all of the lines. The intervening regions between the lines are smoothed out.

The separation between neighboring pairs of lines in the harmonic, when expressed in wave-numbers, is the same as the separation between corresponding neighbors in the fundamental. But the separation between the major and minor component of one pair in the harmonic is twice as great as the separation between the components of the corresponding pair in the fundamental. Consequently the harmonic presents a more crowded or fuller appearance than does the fundamental. Comparison of Figs. 4 and 6 elucidates the effect.

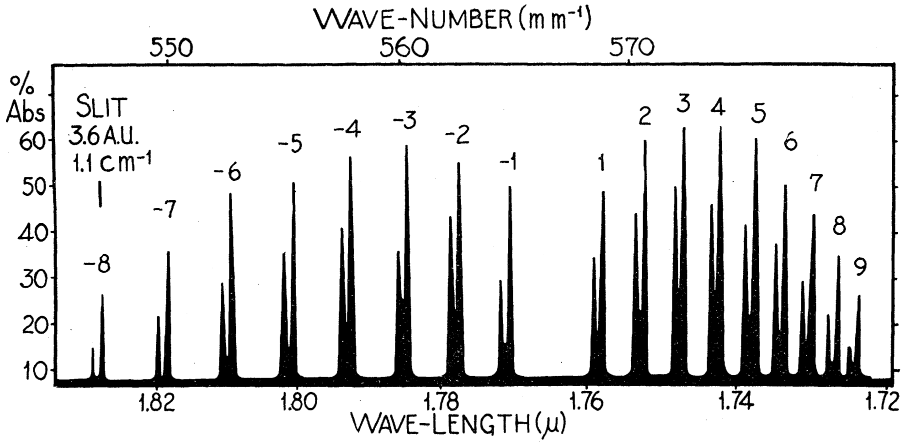

Fig. 6. The harmonic band.

In this investigation the problem of separating the components due to the isotopes was found to be much the same in the two bands. The grating which was used in the harmonic was of about twice the finensss of the one which was used in the fundamental. The separation of the components in seconds of arc on the grating circle was practically the same in the two cases. The slit width used for both bands was 0.25 mm. The available energy was greater in the region of the fundamental, perhaps because of more favorable concentration by the grating. Observations were easier in the fundamental, though they had been considered more difficult.

THE LINE INTENSITIES

The authors wish to acknowledge their indebtedness to Professor D. M. Dennison for the following numerical computations and remarks.

The intensities of the HCl lines as shown in the foregoing curves were examined in three ways: (*a*) the relative intensity of a line and its isotope companion; (*b*) the intensities of the stronger components in a band

(i. e. lines +1, +2, +3, etc); and (*c*) the relative intensity of corresponding lines in the fundamental and harmonic bands.

Under (*a*) the computation was carried out for several lines in the fundamental band of which the line −6 may be taken as representative. The observed ratio of the areas under the absorption curves of the major and minor components has the value $\rho = 2.2$. This ratio may be computed theoretically[9] by substituting the known constants of the HCl molecule and the slit width of the spectrometer and assuming that Cl_{35} is 3.3 times as abundant as Cl_{37}. The ratio thus obtained between the areas is $\rho = 2.1$ in good agreement with the observed ratio.

(*b*) The comparison of the stronger components in a band was carried out sufficiently to show that the observed intensities agree within the experimental error with the theoretical formula for band line intensities. The work by Kemble and Bourgin[5], which was performed with the express purpose of determining these line intensities, leads to results which are certainly more accurate than those which could be obtained from the present data.

(*c*) We may, however, compare the intensities of corresponding lines of the fundamental and first harmonic with greater precision then has been attained heretofore. Examination of several representative lines shows that the ratio of the intensities of the two bands I_2^0/I_1^0 lies between 0.017 and 0.025, the experimental error being rather large. This value of I_2^0/I_1^0 may also be given through the use of the wave mechanical solution of the perturbed oscillator in terms of the derivatives of the force function.

$$I_2^0/I_1^0 = (\phi'''/6\phi'')^2(h/2\pi^2\mu\nu_0).$$

Substituting the appropriate values of the constants (see the paper following by W. F. Colby), we obtain as a theoretical value $I_2^0/I_1^0 = 0.0197$. It is interesting to notice that the ratio as given by the older quantum theory and the correspondence principle[10] was twice as great, namely, .039, and lies distinctly outside the range of the experimental values.

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[9] D. M. Dennison, Phys. Rev. **31,** 503 (1928), see Eq. (13).

[10] D. M. Dennison, Phil. Mag. **1,** 195 (1926).