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The Infrared Spectrum of H^2Cl

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The fundamental absorption band due to HCl molecules involving the heavier isotope of hydrogen has been observed, using a cell 700 cm long with gas at atmospheric pressure. It lies in the region of 4.8μ. Both ordinary HCl and samples enriched in H^2 were examined. Nineteen lines have been measured in the band of H^2Cl^{35}, and seventeen in the band of H^2Cl^{37}. The estimated abundance of H^2 relative to H^1 is 1 to 35,000.

A satisfactory equation has been developed for the positions of these lines on the basis of measurements by Meyer and Levin upon the bands of H^1Cl, assuming identical dimensions and force fields for both molecules. The parameter ρ of this equation, representing the ratio of the reduced masses for H^2Cl and H^1Cl, has been adjusted to give the best agreement with the observed frequencies, and is found to be $\rho = 0.514430 \pm 0.000004$. Sources of error other than those involved in the observations are discussed, and an attempt is made to evaluate them. When these are taken into account, the values indicated for the mass of H^2 (on the scale $H^1 = 1.00778$ for the mass defect are: mass $H^2 = 2.01367 \pm 0.00010$, mass defect $= 0.00189 \pm 0.00010$. These values are compared with the results obtained by Bainbridge with the mass spectrograph.

§1

THE existence of a heavier isotope of hydrogen, recently discovered by Urey, Brickwedde and Murphy[1] suggests the search for band spectra due to molecules containing hydrogen nuclei, since the very large relative difference in mass between H^1 and H^2 must result in isotope displacements of correspondingly large frequency. Naturally the first substance to be chosen for such a study is HCl, both because of the simple character and accessible position of its fundamental band, and because its spectrum has already been investigated so thoroughly. A comparison of the bands due to H^1Cl and H^2Cl should yield a very reliable estimate of the relative abundance of the two species of hydrogen, and also provide a precise determination of the ratio between their masses.

§2

From the first reports of relative abundance it appeared that there should be little difficulty in locating the H^2Cl fundamental band without essential changes in the apparatus already in use. However, a careful examination of the region in which the band was expected, showed no trace of absorption lines in radiation which had traversed 30 cm of gas at atmospheric pressure. According to the data of Meyer and Levin this is more than 3000 times the minimum path length necessary for measurements upon the H^1Cl band at

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[1] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. **40,** 1 (1932).

3.46μ. The path length in HCl was then increased to seven meters, which would ensure the detection of the band even if H^2Cl should be present only to the extent of one part in 10^5 of H^1Cl. This was the maximum length which could be conveniently fitted into the room, and proved to be quite adequate for the purpose.

A plan of the optical system is shown in Fig. 1. The cell was constructed of galvanized iron tubing eight inches in diameter, and coated heavily inside with paraffin. The windows were of heavy mica, firmly cemented and clamped so as to withstand variations of pressure up to 40 mm of mercury. This was necessary to allow for changes of atmospheric pressure outside, and of gas pressure within the cell. Since it was not feasible to move this long cell into and out of the beam, measurements have been made only by comparing curves obtained with the cell filled with dry air and then with HCl. This procedure gives satisfactory results whenever the background is fairly clear, and fortunately the atmospheric absorption between 4.6μ and 5.1μ consists only of scattered narrow lines due to H_2O and possibly CO_2. The HCl gas was at first obtained in the usual manner from sodium chloride and sulphuric acid, and allowed to flow directly from the generator into the cell, slowly displacing the air. In the samples thus prepared the first indications of a molecule of H^2Cl were found. However the impurities in the salt developed a trace of CO which has a very strong absorption band in this same region, so that many of the H^2Cl lines were completely hidden. This difficulty was eliminated by generating the HCl from distilled water which was dropped slowly upon pure phosphorus pentachloride. As the gas evolved it was frozen out in a large trap cooled in liquid air, and then slowly evaporated into the cell, a small residue being discarded so that moisture and other impurities were effectively avoided. The air displaced from the cell was passed through a second trap immersed in liquid air to prevent the escape of HCl. After some hours the contents of this trap were distilled back into the cell by transferring the liquid air to the first trap. A number of repetitions of this process made it possible to bring the concentration of HCl in the tube up to about 96 percent. The gas pressure inside the cell was kept about 10 mm above that of the atmosphere because HCl slowly disappears due to chlorinization of the paraffin. A test

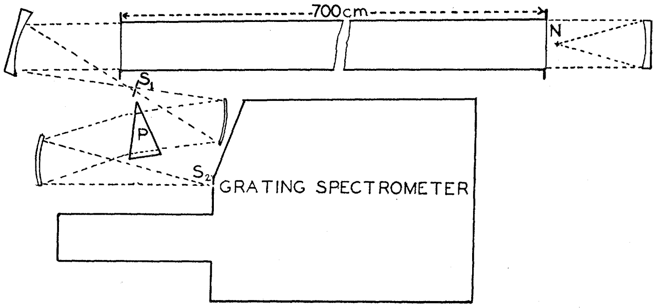

Fig. 1. Plan of spectrometer, fore prism and absorption cell.

for purity was made each day before taking observations. This consisted in the removal of a small amount of gas from the tube into a flask which had first been evacuated. The flask was then immersed in liquid air to freeze out the HCl, and the concentration determined from the resulting change in pressure.

Professor Urey suggested to us that a somewhat enriched source of the heavier hydrogen could be obtained from the electrolytic residue taken from cells in which commercial hydrogen is made. A sample of this residue was very kindly sent to us by Dr. Rohrer of the Ohio Chemical Company. It was distilled in order to eliminate the rather large amount of alkali contained in it, and then used to generate the gas with which most of our observations were made. The resulting increase in intensity of absorption made the measurements both easier and more precise.

The source of radiation for this experiment was a Nernst glower which was mounted directly in front of the cell window and exactly at the focal point of a concave mirror of 15 cm aperture and one meter radius. Placing the source in this position caused a minimum of distortion of the image and a minimum loss of energy due to divergence of the beam as it passed through the cell. At the spectrometer end of the tube the radiation fell upon a second concave mirror and was brought to a focus on the slit of the fore-prism spectrometer. From this slit it was collimated, sent through a large rocksalt prism, and finally brought to a focus upon the first slit of the grating instrument. The salt prism satisfactorily separated the first order of 4.8μ from the second order of 2.4μ. As a test of the separation, readings were made by adjusting the prism with the grating set at 4.8μ for maximum deflection and at 2.4μ for minimum deflection. These measurements showed the spectrum at 4.8μ to be contaminated with about 18 percent of second and third order impurity. The amount of impurity in the spectrum is of importance only in determining the intensities of the lines.

The grating spectrometer was built by one of us and has been described in previous papers. The grating had 4800 lines to the inch and a ruled surface of 4×5 inches, and was designed for concentration of the energy in the region around 5μ; its figure was found to be good and the lines it produced were very sharp. The calibration was carried out by means of the helium line at 10,830.32A, in the third, fourth and fifth orders. These lines were very strong and sharp and their positions could be determined to half a second of arc. The temperature of the room during the entire experiment was kept constant to within a degree centigrade and no correction was needed for change in grating constant due to temperature.

Slit widths varying from 0.15 mm to 0.25 mm were used, most of the measurements being made with 0.2 mm slits. The spectral range across the slit was then 9A or 0.4 cm^{-1}. The corresponding deflections were about 60 cm with the seven meter cell. The steadiness of the detecting system was such that readings could usually be repeated to within one percent. The detecting device consisted of a single junction thermocouple connected to a Leeds and Northrup H.S. galvanometer, which in turn actuated a Pfund amplifier, so

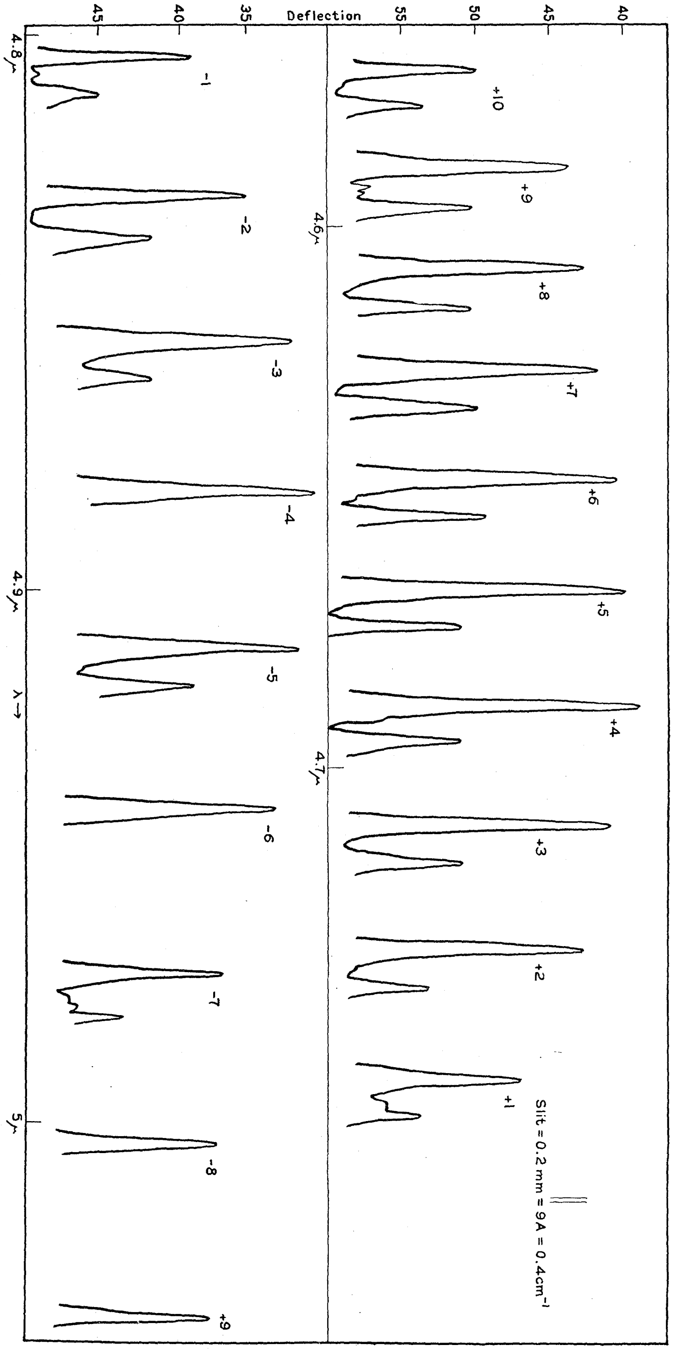

Fig. 2. The H^2Cl fundamental band. Positive branch above, negative branch below.

that the final deflections were about seven hundred times as large as would have been observed upon the first galvanometer at one meter.

In order to estimate the effectiveness of the instrument with the long cell, the lines of the band due to H^1Cl were observed as far out as possible on the negative branch. The faintest line that could be measured was the weaker component of -16. The ratio between its intensity and that of the strongest line $(+3)$ is approximately 1:270,000. The positions of the major components of lines -14 and -15 were determined carefully, and found to be 2544.10 cm^{-1} and 2516.07 cm^{-1} respectively, while the corresponding values, computed by extrapolating the series of Meyer and Levin, are 2544.11 and 2516.03. This agreement is particularly gratifying since their observations were made upon a different instrument, with a different grating, and calibrated in terms of the Hg line $\lambda 1.014$.

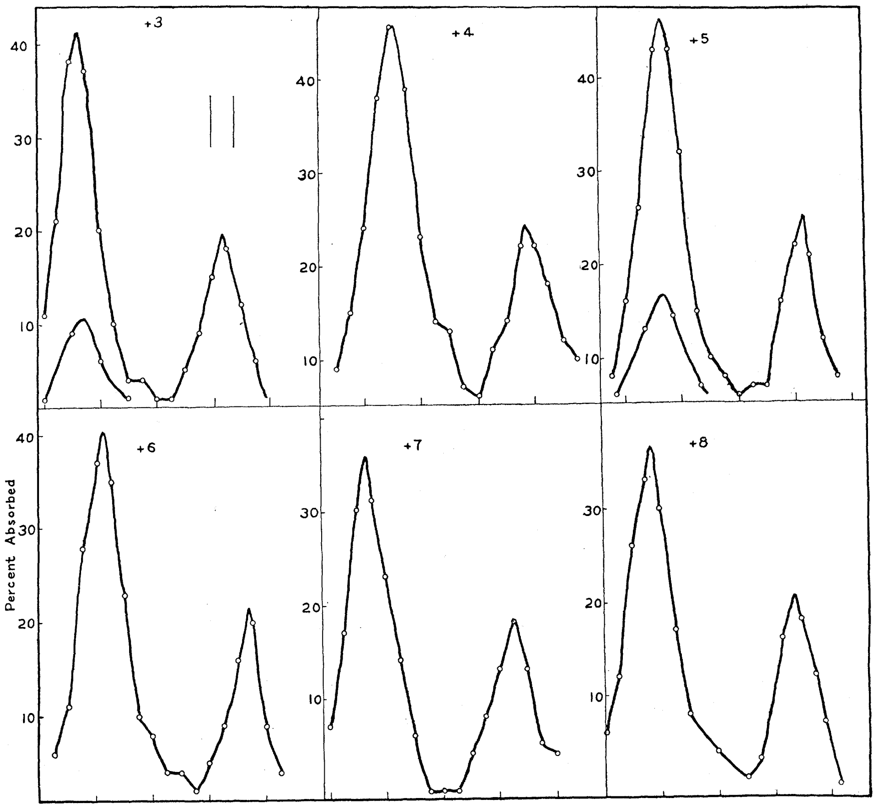

Fig. 3. Six lines of the positive branch in detail. Divisions on the horizontal scale are minutes, and correspond approximately to wave numbers.

A survey of the background was made with dry air in the cell, to determine the positions and intensities of the atmospheric absorption lines, and this was followed by a similar set of observations upon HCl, other conditions being kept as nearly the same as possible. The absorption lines due to H^2Cl^{35} were unmistakable. Nineteen lines of easily measurable intensity were found in which no serious distortion due to background appeared. In most cases the weaker component due to H^2Cl^{37} could also be observed. Fig. 2 is a plot of the entire band as measured with the seven meter cell filled with gas from the electrolytic residue. Galvanometer deflections are plotted against wavelengths, and atmospheric absorption lines have been omitted. A few of the weaker component lines on the negative side are absent because they were hidden or so badly distorted that their positions could not be determined satisfactorily.

After these lines had been located each one was remeasured with care, its contour being determined by at least five or six points taken at fifteen-second intervals on the circle. A few of the lines were measured several times as a test of consistency and it was found that their positions could be reproduced to within about two seconds of arc, which corresponds to ± 0.02 cm^{-1}. It seems safe to assume an experimental accuracy of about ± 0.05 cm^{-1} across the whole band. In Fig. 3 are shown several lines of the positive branch plotted in detail. To arrive at an estimate of the percent absorption the undisturbed background was assumed to be completely transparent, and all the other readings on a line reduced to the same scale. Corrections were made for spectrum impurities due to slight overlapping of higher orders.

The absorption curves for the unenriched sample provide a means of determining the relative abundance of H^2 and H^1. Since the absorption percentages are not very large, and the resolution is high, there is no considerable error in assuming that the area under any line is proportional to the integral of the absorption coefficient over the line. Thus the relative path lengths necessary for equal intensities of absorption may be determined for any pair of lines. The differences in transition probabilities must be taken into account, and also the differences in population of the various rotation states, since both the amplitude of vibration and the Boltzmann factor depend upon the reduced mass. Computations upon this basis indicate that H^2Cl is present in the ordinary gas in a concentration of about one part in 35,000 of H^1Cl and that the enriched sample has a concentration about ten times as great.

In determining the frequencies of the various lines it is necessary to correct for the index of refraction of air, the values of which were obtained from the work of M. Rusch.[2] His data indicate that $n-1=28.9\times 10^{-5}$ is probably a satisfactory value for both the 3.5μ and 5μ regions. This correction is slightly different from the one used by Meyer and Levin, but the difference has been taken into account in comparing our results with theirs. Table I shows the observed frequencies reduced to vacuum for the nineteen lines in the H^2Cl^{35} band. These are compared with a set of computed values, and the differences, column 4, lie for the most part within the limit of observational error. Instead of listing the frequencies of the minor components due to absorption by H^2Cl^{37}, the table indicates in column 5 their displacements from the corresponding major components. These displacements have also been calculated, and the differences are shown in column 7. The formulae by which the calculated values were derived is discussed in §3. A few of the

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[2] M. Rusch, Ann. d. Physik **70,** 373 (1923).

TABLE I.

	Frequencies		Dif.	Isotope separations		Dif.
Line	Obs.	Calc.		Obs.	Calc.	
−9	1986.07	1986.11	+0.04	2.76	2.68	−0.08
−8	1998.53	1998.56	+0.03			
−7	2010.76	2010.82	+0.06	3.04	2.76	−0.28
−6	2022.85	2022.87	+0.02	2.91	2.79	−0.12
−5	2034.73	2034.72	−0.01	2.88	2.83	−0.05
−4	2046.38	2046.36	−0.02			
−3	2057.79	2057.78	−0.01	2.93	2.91	−0.02
−2	2068.95	2069.00	+0.05	3.13	2.94	−0.07
−1	2079.98	2080.00	+0.02	3.04	2.97	−0.07
+1	2101.28	2101.33	+0.05	3.04	3.03	−0.01
+2	2111.69	2111.65	−0.04	3.06	3.06	0.00
+3	2121.81	2121.75	−0.06	3.10	3.09	−0.01
+4	2131.62	2131.62	0.00	3.12	3.11	−0.01
+5	2141.29	2141.24	−0.05	3.15	3.15	0.00
+6	2150.64	2150.63	−0.01	3.19	3.17	−0.02
+7	2159.81	2159.78	−0.03	3.22	3.20	−0.02
+8	2168.66	2168.67	+0.01	3.29	3.22	−0.07
+9	2177.34	2177.32	−0.02	3.19	3.24	+0.05
+10	2185.74	2185.72	−0.02	3.24	3.26	+0.02

residuals in column 8 are larger than the error in observation, and these, as well as the larger ones in column 4, are probably due to displacements resulting from blends with weak atmospheric lines. The measurements on the minor components are probably also somewhat less accurate.

§3

The first step in comparing the infrared bands of H^1Cl and H^2Cl, and eventually in obtaining the ratio of the masses of H^1 and H^2, is to assume that the force fields and dimensions of the two molecules are identical. This assumption appears to be fully justified both on theoretical and experimental grounds. From the theoretical side, the principal difference which might occur would be caused by a difference in the spins of the two hydrogen nuclei. The normal electronic state of HCl is a Σ state and consequently the nuclear spin of the hydrogen would be coupled with the nuclear spin of the chlorine and with the field produced by the rotation of the molecule. In either case the coupling energy is so extremely minute that the change in the energy states or in the force field would be quite too small to be measurable by spectroscopic means. From the experimental side the assumption is justified by the fact that all the band spectrum measurements on molecules containing isotope nuclei may be consistently correlated when the force fields in the molecules are taken to be identical.

The second step in the analysis is to show how the bands of H^1Cl and H^2Cl are to be related. To do this we use the equation developed by Fues[3]

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[3] E. Fues, Ann. d. Physik **80,** 367 (1926).

for the energy levels of a rotating dipole. The frequencies of the lines of the fundamental band are given by the expression,

$$\begin{aligned}\nu = (\nu_0 - hC/4\pi^2I - \nu_0B/4)\\ + (h/4\pi^2I - 2\nu_0B - hk^2/8\pi^2I)J\\ - \nu_0BJ^2 - hk^2J^3/2\pi^2I.\end{aligned} \tag{1}$$

The constant ν_0 varies as $\mu^{-1/2}$, I as μ^1, k^2 as μ^{-1} and ν_0B as $\mu^{-3/2}$ where μ is the reduced mass of the system. The constant C is independent of μ.

These constants which determine the positions of the infrared lines have been very accurately deduced by Colby[4] from the measurements by Meyer and Levin.[5] Their values, slightly modified on account of the difference in the factor used for reduction of the wave-lengths to vacuum are as follows: $\nu_0 = 2989.24$ cm^{-1}; $\nu_0B = 0.3030$; $h/4\pi^2I = 21.1678$, $hk^2/4\pi^2I = 0.00106$; $hC/4\pi^2I = 103.40$.

If the ratio of the reduced mass of H^1Cl to the reduced mass of H^2Cl is is called ρ, the equation for the lines of the fundamental band of H^2Cl may be written,

$$\begin{aligned}\nu = (2989.24\rho^{1/2} - 103.40\rho - 0.076\rho^{3/2})\\ + (21.1678\rho - 0.6060\rho^{3/2} - 0.0005\rho^2)J\\ - 0.3030\rho^{3/2}J^2 - 0.0020\rho^2J^3.\end{aligned} \tag{2}$$

One of two courses may now be followed. The observed lines of H^2Cl may be expressed by means of an equation of the above type using a least squares solution, and the coefficients of J^0, J, J^2 and J^3 equated to their corresponding theoretical values. Four independent values for ρ would thus be obtained, which should of course be consistent. However, the value determined from the constant term would be about ten times more accurate than that found from the coefficient of J, and the values obtained from the J^2 and J^3 terms would be still far less reliable.

A second procedure, and the one which was actually followed, is to choose a value of ρ and compute the corresponding positions of the lines. The positions so determined may then be compared with the frequencies of the nineteen observed lines. The differences between the observed and theoretical frequencies serve to fix a first order correction to ρ. Thus after a few approximations a value of ρ is obtained for which the sum of the residuals is zero. If all the residuals are within the experimental error and furthermore show no systematic trend, it is certain that a consistent method has been found for comparing the two bands.

The final equation (theoretical) which we obtain for the lines of the H^2Cl band is,

$$\nu = 2090.78 + 10.666J - 0.1118J^2 - 0.00056J^3. \tag{3}$$

This corresponds to a value of $\rho = 0.514430$.

The agreement between the observed and computed frequencies is shown in Table I and is very good indeed. The residuals are all very small,

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[4] W. F. Colby, Phys. Rev. **34,** 53 (1929).

[5] C. F. Meyer and A. A. Levin, Phys. Rev. **34,** 44 (1929).

of the order of the experimental error and show no appreciable trend. The average value of these residuals divided by the square root of the number of observations is a measure of the probable error in fitting the theoretical equation. This again may be used to obtain the probable error in ρ. We find that $\rho = 0.514430 \pm 0.000004$.

The method of deriving the mass of the H^2 nucleus from ρ requires an additional assumption concerning the nature of the vibratory motion of the HCl molecule. (The validity of this assumption will be discussed in §4.) The reduced mass μ is in first approximation equal to $mM/(M+m)$ where m and M are the masses of the two nuclei. In higher order of approximation the motion of the electrons during the vibration must also be accounted for. μ might still be set equal to $mM/M+m$ where m and M now represent effective masses of the nuclei. The magnitude of the permanent electric moment of HCl shows that the electrons may be thought of as having a distribution such that the electronic charge about the H nucleus is on the average $\frac{4}{5}$ of an electron and that about the Cl nucleus is $17+\frac{1}{5}$ electrons. The intensity of the fundamental band shows that the effective moving charge to be associated with the vibrating dipole is that of $\frac{1}{5}$ electron.[6]

From these two data it seems natural to assume that the effective masses m and M should be set equal to the mass of a hydrogen atom minus one-fifth of an electron and the mass of a chlorine atom plus one-fifth of an electron.

Let m_1 and m_2 be the effective moving masses of H^1 and H^2 respectively, and let M be the effective mass of Cl. Then

$$\rho = \mu_1/\mu_2 = [m_1M(m_2 + M)]/[(m_1 + M)m_2M]$$

or

$$m_2 = m_1/[\rho - (m_1/M)(1 - \rho)].$$

In mass units the mass of an H^1 atom is 1.00778 and that of an electron is 0.00055. Thus

$$m_1 = 1.00778 - 0.00011 = 1.00767$$

$$M = 34.983 + 0.00011 = 34.983.$$

On substituting these values, together with the observed value of ρ we obtain, $m_2 = 2.01356 \pm 0.00002$.

The mass of an H^2 atom referred to H^1 is therefore $m_2 + \frac{1}{5}$ electron or, $H^2 = 2.01367 \pm 0.00002$.

The mass of an H^2 nucleus is, $H^{2+} = 2.01312 \pm 0.00002$, and the mass defect is $H^{2+} - (H^1 + H^{1+}) = -0.00189 \pm 0.00002$.

Before proceeding to a discussion of the errors involved in our determination of the mass of the H^2 atom, it will be remarked that the satellite lines shown in Figs. 2 and 3 may be attributed to the molecule H^2Cl^{37}. The spacing of these satellites from the parent lines may be derived theoretically in a manner entirely similar to that used in finding the positions of the H^2Cl^{35} lines themselves. This difference may be expressed as a function of the line number J and has the following form (the contribution of the term cubic in J is here negligible), $(H^2Cl^{35}) - (H^2Cl^{37}) = 3.00 + 0.0311J - 0.00049J^2$.

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[6] D. M. Dennison, Phys. Rev. **31**, 503 (1928).

Table I contains a comparison of the measured and observed values of these displacements, and it is seen that the agreement is very satisfactory indeed. The residuals are somewhat larger than those of the lines of H^2Cl^{35} which is not surprising since the lines of H^2Cl^{37} are weaker and their positions are not as accurately determined.

§4

A probable error has been appended to the values for the mass of H^2 but this error represents merely the exactness of the agreement between the observed lines and positions computed from our formula. There are however other possible sources of error (systematic errors, errors in assumptions) which we will now discuss.

Our measurements are related to the constants derived by Colby from the data of Meyer and Levin. These observations were made on a different spectrometer using a different grating and the question of their accuracy becomes of great importance. Aside from the fact of the self-consistancy of Meyer and Levin's data (i.e., the small residuals between the observed positions of the lines and the positions predicted by Colby's formula) we have one independent test of their accuracy. As mentioned earlier, two of the outer lines, -14 and -15, of the fundamental band of H^1Cl^{35} were measured on our spectrometer. These positions agree with the positions derived from Colby's equation to within the experimental error. This check insures that the calibration of both instruments was alike and furnishes a strong verification of the correctness of Colby's constants. The error which might be introduced from this source is therefore about equal to the probable error which we have given above.

A second possible source of error which must be investigated involves the range of validity of the Fues equation giving the energy of a rotating vibrator. An examination of this equation shows that the only term which might introduce an appreciable error is the constant term. The quantity ν_0 represents the zeroth order contribution to the frequency. The anharmonic part of the force function produces no effect in first approximation but in second approximation gives rise to the term $-hC/4\pi^2I$. It is to be expected that a fourth order perturbation would introduce a term, say $3D$, of which no account is taken in the Fues equation. Thus the energy of vibration could be written as a function of the vibrational quantum number v as follows;

$$W_v/h = A + \nu_0 v - hCv^2/8\pi^2I + Dv^3.$$

This new term would be important in the present investigation since, while ν_0 transforms as $\rho^{1/2}$ and $hC/8\pi^2I$ as ρ, D would transform as $\rho^{3/2}$. Since ν_0 is of the order 3000, and $hC/8\pi^2I$ of the order 50 we might expect D to be perhaps as large as 1. If this were the case the error in our determination of the mass of H^2 would be about 20 times as large as the probable error indicated. There are very good grounds for believing that this is not the case, however, and that D is much smaller than 1. In the first place the residuals shown in Table I are of the order of the experimental error and show no appreciable trend. This latter feature, the absence of trend, shows that the constant and linear terms of Eq. (3) are consistent, or in other words that the constant and linear terms transform in the manner indicated in Eq. (2). Thus the general consistency of our results shows that D must be considerably smaller than 1.

It would be possible to determine the value of D if a sufficient number of the overtone bands of HCl were known experimentally. This is unfortunately not the case but such series are known for many diatomic molecules and it is found that D is always extremely small and in most cases may be set equal to zero. The success of the Morse[7] potential function is largely due to this fact. In conclusion we estimate that the error introduced into the mass of H^2 from this cause cannot be of a larger order of magnitude than the probable error we have given.

Finally the assumption as to the magnitude of the effective moving masses m and M which enter the expression for μ must be considered. The effective inertia of the system depends not only upon the nuclear masses but also upon the masses of the electrons. The intensity of the fundamental band of HCl is consistent with the supposition that on the average $\frac{4}{5}$ of an electron moves with the H nucleus and $17\frac{1}{5}$ electrons move with the Cl nucleus. It seems reasonable therefore to assume that the effective moving mass m is equal to the mass of a hydrogen atom minus $\frac{1}{5}$ electron. In higher approximation this would be somewhat altered, perhaps by an amount of the order of $\frac{1}{5}$ the correction already introduced. This would mean that the error introduced would be about 0.00002 mass units, i.e., the same order as the probable error.

It has been shown that in addition to the probable error derived from the residuals of Table I, there are three independent sources of possible error, all of this same order of magnitude. These possible errors cannot be evaluated in detail but we estimate that their combined effect would be very liberally covered by a factor of ± 0.00010.

Our final values for the mass of an H^2 atom and of the mass defect in mass units $(0=16)$ are therefore,

$$H^2 = 2.01367 \pm 0.00010$$

$$\text{Mass defect} = 0.00189 \pm 0.00010.$$

These values agree quite satisfactorily with the results obtained by Bainbridge[8] using the mass spectrograph. He gives $H^2 = 2.01353 \pm 0.00006$ and mass defect $= 0.00203 \pm 0.00006$.

Note added in proof, September 26, 1932: It should perhaps be remarked that we have expressed our results relative to the mass of $H^1 = 1.00778$. If this value is in error by an amount ϵ, our value for H^2 would be in error by 2ϵ. However, in first order the mass defect is independent of any small error in the mass of H^1. In a similar manner the result obtained by Bainbridge for the mass of H^2 is given relative to the mass of H^1. Dr. Bainbridge has informed us that his probable error of 0.00006 must be increased to 0.00018 if his value of H^2 is referred to $0 = 16$ rather than to $H^1 = 1.00778$.

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[7] P. Morse, Phys. Rev. **34**, 57 (1929).

[8] K. T. Bainbridge, Phys. Rev. **41**, 115 (1932); **42**, 1 (1932).