AUGUST 15, 1932 *PHYSICAL REVIEW* *VOLUME 41*

Isotope Separations in the Infrared Absorption Spectrum of HCl and the Possible Existence of a Chlorine Isotope of Mass 39

By J. D. HARDY* AND G. B. B. M. SUTHERLAND**
Physics Department, University of Michigan

(Received June 30, 1932)

The absorption band of HCl at 1.7μ has been reëxamined under high dispersion in an attempt to verify the work of Hettner and Böhme on the existence of a third chlorine isotope, Cl^{39}. No trace of the isotope was observed although a path length of three meters, some ten times the path used by Hettner and Böhme, was used. The isotope separations due to Cl^{35} and Cl^{37} have been measured very accurately and do not agree with the separations calculated by the simple theory. When the anharmonic terms in the energy are taken into account the agreement between the calculated and observed isotope separations is within the experimental error. The isotope separation for HCl^{39} molecule has been calculated and found to be slightly different from that observed by Hettner and Böhme. Our results indicate that the relative abundance of Cl^{39} to Cl^{39} cannot be greater than 1 to 500.

RECENTLY Becker[1] has predicted the existence of a chlorine isotope, Cl^{39}, from a consideration of the form of the infrared absorption curves of HCl. This prediction was made from the curves published by Meyer and Levin[2] and by Becker[1] himself. The absorption maxima in these curves which Becker attributes to HCl^{39} are so small as to be probably within the error of the experiment. In fact, Meyer and Levin state specifically that the unevenness of their base line was due to errors in galvanometer readings, and if one examines the original curves of Meyer and Levin it is seen that the maxima mentioned by Becker do not fall at equal distances from the maxima due to Cl^{35} and in many cases do not show up at all. However, the existence of Cl^{39} was later apparently confirmed by Hettner and Böhme[3] working on the R branch of the HCl harmonic. In this work the maxima due to HCl^{39} stand out in all clearness with the expected constant frequency difference between these maxima and those due to Cl^{35}. The present work was undertaken with two objects in view, to verify the work of Hettner and Böhme and to measure more accurately, under high dispersion, the separation of the maxima due to HCl^{35} and HCl^{37}. The interest in the third isotope arose naturally from the apparent disagreement of observers about its existence. Aston[4] at one time considered the possibility of a Cl^{39} isotope but finally decided against its existence. Ashley and Jenkins[5] studied the absorption of AgCl in a region

---

* National Research Fellow.

** Commonwealth Fund Fellow.

[1] H. Becker, Zeits. f. Physik **59**, 583 and 601 (1930).

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

[3] G. Hettner and J. Böhme, Zeits. f. Physik **72**, 95 (1931).

[4] F. W. Aston, Isotopes, p. 68, 2nd ed., 1924.

[5] M. Ashley and J. A. Jenkins, Phys. Rev. **37**, 1712 (1931).

favorable for showing the isotope but found no trace of an $AgCl^{39}$ molecule. E. K. Plyler (private communication) made an attempt to find the absorption lines due to the third isotope by a close examination of the fundamental band at 3.4μ. He used the same instrument that Meyer and Levin used in their work and his results were negative within the error of his observations. The interest in the isotope separation arose from a discrepancy in the observed values and those calculated on the simple theory.

With a new type spectrometer[6] whose resolution and sensitivity are greater than any of those yet applied to the problem, the work of Hettner and Böhme, Becker, and Meyer and Levin has been repeated. That is, the short wave-length side of the harmonic band at 1.7μ has been carefully examined. A description of the spectrometer has already appeared and it need only be mentioned here that by altering the dimensions of the thermocouple a 50 percent gain in sensitivity has been realized over previous arrangements.

The region to be investigated, between 1.71μ and 1.75μ, is a particularly favorable one in which to work. It is practically free from water vapor absorption and in it lies the energy peak of the Nernst heater. Further, the impurity of the spectrum due to overlapping orders is very slight even without the use of any filtering device. The first order energy of 0.85μ is small and in the second order the energy will be only 10 percent of that in the first order. The difference between curves taken with a filter and without a filter is negligible. The filter used was opaque to visible light, transmitted 9 percent from 0.8μ to 0.9μ, and had 70 percent transmission at 1.73μ.

The grating used in this experiment was ruled by Wood with 15,000 lines to the inch and had a ruled surface of 6×3.5 inches. Previously the emission lines of helium had been examined with this grating and the definition was found to be good enough to resolve lines at 10829.1A and 10830.3A in the second order. The spectrometer was calibrated by means of the helium lines at 10830.3A and 20582.1A. The width of the slits for the most detailed examination was 0.075 mm and for the rougher curve 0.15 mm. The wave-length range across the slit in the first instance was 0.97A or $0.32\ cm^{-1}$, and in the rougher curve $0.64\ cm^{-1}$. Readings were taken one slit-width apart, and each point represents usually a single observation. The steadiness of the instrument was such that an observation could be repeated to within 2 percent in the detailed curves, where the deflections were about 30 cm between lines, and to within about 1 percent in the rougher curve where the deflections were about 60 cm. The deflections at places of maximum absorption were practically zero for the strong lines, the residual deflection probably being due to a slight impurity of the spectrum coming from overlapping orders. No radical departures from the base line were observed anywhere except in regions of the absorption lines of HCl^{35} and HCl^{37}.

The present work was done with two cell lengths. The first work, with very narrow slits, was done with a cell 31 cm long. This is the length of cell used by previous workers and it was found that the strong lines due to

---

[6] J. D. Hardy, Phys. Rev. **38**, 2162 (1931).

HCl^{35} gave nearly 100 percent absorption with this cell length. When this length of cell failed to show the lines due to HCl^{39} a cell of three meters length was used, and it was felt that had the isotope been present in the HCl gas which was examined; it would not have escaped detection, assuming that its relative abundance to Cl^{35} is about that shown by Hettner and Böhme's curves.

The 31 cm cell was a brass tube provided with strong windows of plate glass. The cell was evacuated and filled with HCl gas from a liquid air trap so as to ensure dryness of the gas. The HCl was prepared in the usual manner by allowing sulfuric acid to combine with pure NaCl in an evacuated Kipps apparatus. The HCl was frozen out by liquid air and then introduced into the evacuated cell to a pressure of 90 cm of mercury. The trap from which the HCl was evaporated was never allowed to come up to the temperature of 0°C during this process. The three meter cell was of galvanized iron thickly coated inside with paraffin. The cell was eight inches in diameter and provided with stout mica windows. The HCl was introduced into the cell from a liquid air trap and the air gradually displaced by continuous flowing of the gas for several hours. Tests at the end of the filling showed that the gas inside was about 92 percent HCl.

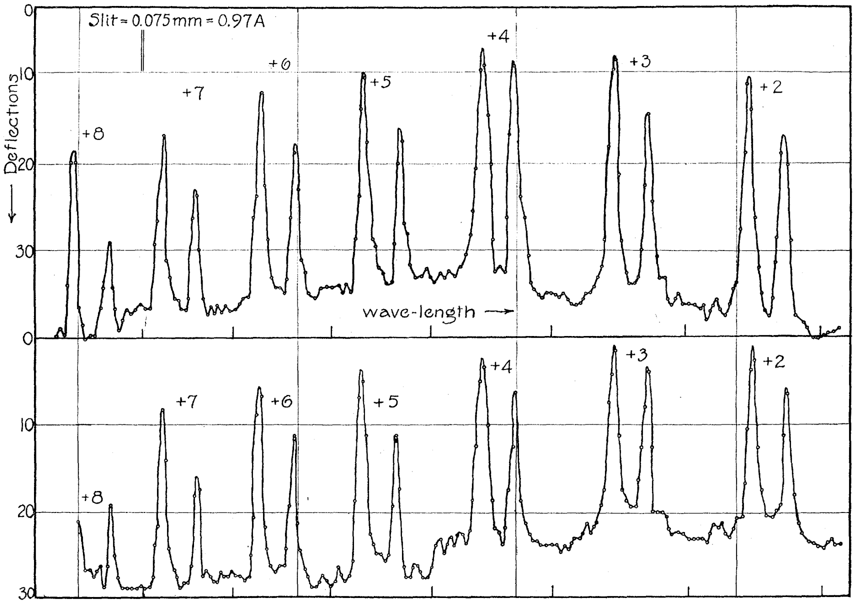

Fig. 1. Two sets of observations: *R* branch of HCl harmonic with 30 cm cell.

Readings were made by taking a complete curve with the empty cell and then a run with the cell full. The background with the empty cell was found to be very smooth and since lines and line positions were desired, percentage absorption was plotted for only one curve, and deflections with the cell full for the detailed curves.

The results of observations with the 31 cm cell are shown in Fig. 1. Lines are drawn to indicate the places where the third isotope might be expected from theory, account being taken of the anharmonic terms in the energy. In Table I are given the wave-lengths and frequency separations measured in this experiment as compared with the values obtained by Meyer and Levin.

TABLE I. *Wave-length and frequency separations in absorption spectrum of HCl.*

Line	Wave-length (A) Hardy and Sutherland	Wave-length (A) Meyer and Levin	Isotope separation Hardy and Sutherland (A)	Isotope separation Hardy and Sutherland (cm^{-1})
2	17519.8	17520.2	12.3	4.04 ± 0.08
3	17467.7	17467.9	12.2	4.03
4	17418.3	17419.2	12.2	4.03
5	17373.8	17374.9	12.7	4.21
6	17334.6	17334.0	12.7	4.21
7	17298.3	17298.1	12.4	4.14
8	17266.3	17265.2	12.7	4.24
9	17238.1		12.6	4.23 ± 0.09
10	17213.3		13.0	4.34
11	17193.2		12.8	4.29
12	17176.4			
13	17163.4			

The lines 9, 10, 11, 12, and 13 were observed with the three meter cell. The isotope separation for the last two lines is not given since the convergence of the band is so strong that the HCl^{37} component of one line overlaps the HCl^{35} component of its neighbor. In Fig. 2 are shown the results obtained with the three meter cell. Again no trace of the third isotope is visible. The strong lines toward the center of the band are very wide because of the very intense absorption in this region.

Hettner and Böhme state that the theoretical separation between the lines due to HCl^{35} and HCl^{37} is $\Delta\lambda = 13.54$A, whereas the value found by Meyer and Levin is $\Delta\lambda = 12.0 \pm 1$A. Hettner and Böhme attribute the discrepancy to the lack of good separation in the curves of Meyer and Levin, and thus to a resulting "attraction" of the stronger line for the weaker. In the present experiment the lines are well resolved, not overlapping at all, and the resulting separation is in good agreement with the value found by Meyer and Levin. Upon closer examination it is found that the separation expressed in wave numbers is not constant but steadily decreases as one goes toward longer wave-lengths. This variation in isotope separation from line to line illustrates the well-known rotational isotope effect. The agreement between the accurate theory and the most precise measurements is worth examining in some detail.

We start from the Fues[7] expression for the energy of a rotating vibrating dipole.

$$E = A + h\nu_0(n+\tfrac{1}{2})[1 + B(j+\tfrac{1}{2})^2] + (h^2/8\pi^2J)(j+\tfrac{1}{2})^2[1 - K^2(j+\tfrac{1}{2})^2] - (h^2/8\pi^2J)(n+\tfrac{1}{2})^2C. \quad (1)$$

---

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

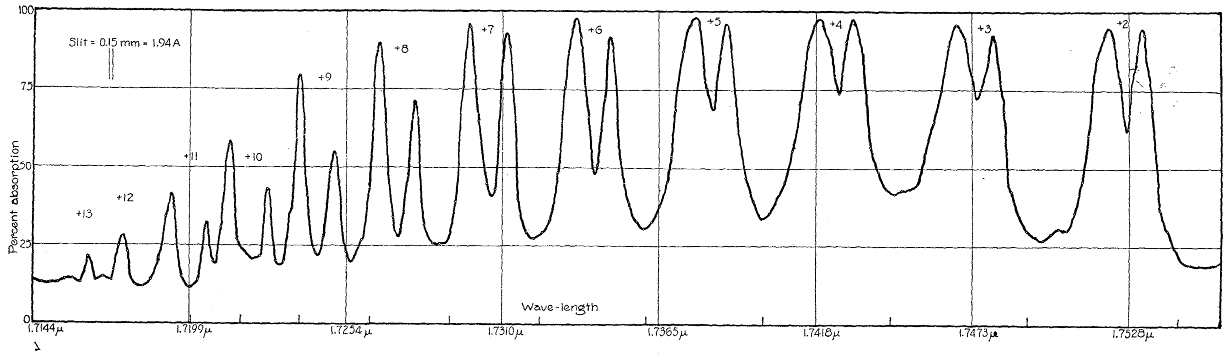

Fig. 2. Observations with three meter cell on *R* branch of HCl harmonic showing expected positions for HCl^{39}.

Where n is the vibrational quantum number; j is the rotational quantum number;

$$K = h/4\pi^2\nu_0 J;\ B = (3/2)K^2(1 + 2C_3);\ C = 3 + 15C_3 + (15/2)C_3^2 + 3C_4$$

and C_3 and C_4 are constants in the potential energy expression which measure the degree of anharmonicity of the motion. From this we can immediately write down the expression for the frequencies in a vibration-rotation band corresponding to the jump of n from 0 to Δn.

$$\begin{aligned}\nu = \nu_0\Delta n &- \tfrac{1}{4}\nu_0 B\Delta n - (h/8\pi^2 J)C(\Delta n^2 + \Delta n)\\ &+ j(-\nu_0 B - \nu_0 B\Delta n + h/4\pi^2 J - hK^2/8\pi^2 J)\\ &- j^2\nu_0 B\Delta n - j^3(h/8\pi^2 J)4K^2.\end{aligned} \tag{2}$$

Here we have arranged that j is the number of the line from the center of the band, positive for the positive branch, and negative for the negative branch. Colby[8] has shown that this formula is in excellent agreement with the experimental work of Meyer and Levin on the fundamental and overtone bands of HCl.

As usual let us take ρ as the ratio of the square roots of the reduced masses of the two molecules, then

$$\begin{aligned}\nu_1 - \nu_2 = {}&\nu_0\Delta n(1-\rho) - \tfrac{1}{4}\nu_0 B\Delta n(1-\rho^3) - (h/8\pi^2 J)C(\Delta n^2 + \Delta n)(1-\rho^2)\\ &+ j\{-\nu_0 B(1+\Delta n)(1-\rho^3) + h/4\pi^2 J(1-\rho^2) - (h/8\pi^2 J)K^2(1-\rho^4)\}\\ &- j^2\nu_0 B\Delta n(1-\rho^3) - j^3(h/2\pi^2 J)K^2(1-\rho^4)\end{aligned} \tag{3}$$

Where ν_1 corresponds to the HCl^{35} molecule, ν_2 corresponds to the HCl^{37} molecule,

$$\rho = [\mu(HCl^{35})/\mu(HCl^{37})]^{1/2}$$

and the dependence of the various factors on ρ can easily be verified. The values of the constants taken from Colby's analysis of the bands show that the terms with the coefficient $hk^2/\pi^2 J$ are quite negligible.

Taking out $(1-\rho)$ as a factor this may be written

$$\begin{aligned}\nu_1 - \nu_2 = {}&(1-\rho)\{\nu_0\Delta n - \tfrac{1}{4}\nu_0 B\Delta n(1+\rho+\rho^2) - (h/8\pi^2 J)C(\Delta n^2 + \Delta n)(1+\rho)\\ &+ j[-\nu_0 B(1+\Delta n)(1+\rho+\rho^2) + (h/4\pi^2 J)(1+\rho)]\\ &- j^2\nu_0 B\Delta n(1+\rho+\rho^2)\}.\end{aligned} \tag{4}$$

We may simplify this further by putting $\rho = 1$ everywhere except in the first factor. So the frequency separation for the general band when n changes from 0 to Δn is

$$\begin{aligned}\nu_1 - \nu_2 = (1-\rho)\{\nu_c &- (h/8\pi^2 J)C(\Delta n^2 + \Delta n) - \tfrac{1}{2}\nu_0 B\Delta n\\ &+ j[h/2\pi^2 J - 3B\nu_0(1+\Delta n)] - 3j^2 B\nu_0\Delta n\}.\end{aligned} \tag{5}$$

---

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

Where $\nu_c=\nu_0\Delta n-\frac{1}{4}\nu_0 B\Delta n-(h/8\pi^2 J)\ C(\Delta n^2+\Delta n)$ denotes the center of the band. The values of the constants deduced in Colby's[8] paper for the fundamental band of HCl^{35} are $C=4.885$, $B\nu_0=0.303$, $h/4\pi^2 J=K\nu_0=21.17$. Substituting those we obtain for the separations:

Fundamental

$$\nu_1-\nu_2=0.000751\{2885.88-103.3+40.5j-0.91j^2\}. \tag{6}$$

Harmonic

$$\nu_1-\nu_2=0.000751\{5667.96-309.9+39.6j-1.82j^2\}. \tag{7}$$

Tables II and III show the agreement between the values of the separations as determined experimentally and as calculated from these expressions.

TABLE II. *Isotope separations in the fundamental band in* cm^{-1}.

j	Positive branch Calculated value	 Meyer and Levin's value	Negative branch Calculated value	 Meyer and Levin's value
1	2.12	2.09	2.06	2.10
2	2.14	2.09	2.03	1.97
3	2.17	2.10	1.99	1.98
4	2.20	2.16	1.96	1.90
5	2.23	2.22	1.92	2.02
6	2.25	2.12	1.88	1.72
7	2.27	2.13	1.84	1.74
8	2.29	2.27	1.80	1.77
9	2.31	2.26	1.76	1.83
10	2.33	2.23	1.72	1.61
11	2.34	2.25	1.67	1.71
12	2.36	2.34	1.63	1.57

TABLE III. *Isotope separations in the harmonic band—positive branch.*

	Calculated		Observed				
			Hardy and Sutherland		Hettner and Böhme		Meyer and Levin
j	(cm^{-1})	(A)	(cm^{-1})	(A)	(A)	(A)	(cm^{-1})
2	4.08	12.5	4.04	12.3	12.5	12.5	4.20
3	4.10	12.5	4.03	12.2	12.0	12.5	3.87
4	4.12	12.5	4.03	12.2	12.5	12.5	4.03
5	4.14	12.5	4.21	12.7	12.0	12.0	4.19
6	4.15	12.5	4.21	12.7	12.0		4.22
7	4.16	12.45	4.14	12.4	12.0		4.14
8	4.17	12.4	4.24	12.7			4.26
Mean	4.13	12.5	4.12	12.5	12.3		4.13

The discrepancies between individual line separations as computed and as observed lie in each case within the experimental error. The agreement of the various values for the mean separation in the harmonic band is very satisfactory. The variation in the separation from one end of the fundamental band to the other illustrates particularly well the rotational isotope effect. The result of considering the anharmonic terms is to reduce the value of the separation from that calculated on the simple theory which would be given by Eq. (5) with $B=C=0$. The anharmonic term involving C is the most effective in reducing the separation. The interaction terms involving B begin to contribute appreciably only when j is very large.

If now we use the above formulae (with an appropriate value of ρ) to compute the isotope separations for an HCl^{39} molecule we obtain a set of values which disagree slightly with those found experimentally by Hettner and Böhme. The comparison is shown in Table IV.

TABLE IV. *Isotope separations in the harmonic band of* HCl^{39}.

j	Calculated value (A)	Hettner and Böhme's value (A)	
2	23.8	24.5	24.5
3	23.8	24.5	25.5
4	23.8	24.5	24.5
5	23.8	23.5	23.5
6	23.8		25.5
7	23.7		23.5
Mean	23.8	24.5	

The difference is small but the close agreement of calculated and observed separations in the case of the Cl^{37} isotope make it doubtful whether these lines are due to HCl^{39}.

To obtain an estimate of the smallest relative abundance of HCl^{39} to HCl^{35} which we could detect, we may compare the absorption coefficient of the weakest line of HCl^{35} which we could detect with that of the strongest, *viz.*, line 3. This can be done theoretically with formulae due to Dunham.[9] Now when α is the absorption coefficient so computed for a certain line it is well known that[10]

$$\alpha = KN$$

where N is the number of molecules in the initial energy level and K is an abbreviation for a number of factors which would not change appreciably for an HCl^{35} or an HCl^{39} molecule. If then we know the least ratio of α's which we can detect, we know the least ratio of N's which we can detect. We employ an equation of Dunham's, modified for use in the positive branch.

$$\frac{\alpha_3}{\alpha_m} = \frac{\bar{p}_3}{\bar{p}_m}\,\frac{\nu_3}{\nu_m}\left\{1 + 2a(\nu_m - \nu_3)\right\} e^{(E_{m-1}-E_2)/kT}$$

where m denotes the number of the line in the positive branch; $\bar{p}$ is the mean of the statistical weights of the initial and final states of the molecule; $2a$ is a small correction factor which we can calculate from Dunham's paper to be very close to 0.0154; E denotes the energy of the molecule in the mth rotational level of the zero vibrational level. When we apply this equation to calculate α_3/α_{13} using energy and frequency values from Colby's paper[8] we ob-

---

[9] J. L. Dunham, Phys. Rev. **34**, 438 (1929).

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

tain a ratio of 460 to 1. The calculated ratio of α_3/α_{14} was 1600 to 1. Using the three meter cell we could easily detect line 13 and there is an indication on the curve of what may be line 14. The latter is, however, uncertain, but we can safely state that had the Cl^{39} isotope been present in a ratio to Cl^{35} of 1 to 500 we could not have failed to detect it.[11]

There is still another viewpoint from which our inability to substantiate the work of Hettner and Böhme seems remarkable. The instrument we used was of considerably higher resolving power than that employed by them. Our lines are consequently deeper and have higher maxima than theirs and so our instrument is better adapted for the detection of faint companion lines. When we remember that the path length used in the present work was ten times that employed by Hettner and Böhme our failure to detect any sensible change in absorption at the expected places is quite irreconcilable with their conclusions.

It is a pleasure to express our thanks to Professor D. M. Dennison for the suggestion that the anharmonic terms might be important in the calculation of isotope separations and for his interest in the problem.

---

[11] *Note added in proof:* Since the above article was written the experiment has been repeated using an absorption cell seven meters long. There were still no indications of lines which might be interpreted as coming from an HCl^{39} molecule. Line 14 of the positive branch was easily detected giving quite a distinct absorption peak on the curve. This enables us to place the abundance ratio of Cl^{39} to Cl^{39} lower than 1 to 1600.