ments, therefore, bear out the picture developed above. We expect to make some further measurements at smaller pulse sizes.

One may also expect that the rise-time of the pulse will be slowed down if the capacity of the wire-system is increased. This was tested and found to be the case. Increasing the capacity also has the effect of decreasing the pulse size. Similar effects were noted by Ramsey[3] and are found in his curves.

DISCUSSION

In conclusion a few words may be said about high counting rates. In the Geiger region the normal recovery time is determined by the mobility of the positive ion sheath. This may be shortened by collecting the positives on the center wire, using the Simpson[4] circuit. The effective speed of operation of this circuit is limited by the spread-time of the sheath.[5] In the proportional region, the sheath does not spread the whole length of the wire,[1] and the recovery times can be made much more rapid.[6] The greater the gas amplification, however, the larger the number of positive ions that produce space charge which will limit counting speeds. At low amplifications, recovery times can be considerably shortened, but the recovery time still is the limiting factor. Only a small benefit can be achieved by operating the counter at a higher voltage. The field is increased, and hence the electron velocity is higher, but many more positives are formed at varying distances from the wire. The use of grids[7] is beneficial, since the positives have a smaller distance to travel. However, grids present added constructional difficulty and in the proportional region pose collection problems. A pulse sufficient in size to be easy to measure can be obtained in 10^{-7} sec., as we have shown. Therefore, an application of the Simpson circuit to a proportional counter will permit counting at rates up to several million per second. The matter is under study and further tests will be reported in due course.

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[4] J. A. Simpson, Phys. Rev. 66, 39 (1944).

[5] E. Wantuch, Phys. Rev. 71, 646 (1947).

[6] C. O. Muelhause and H. Friedman, Rev. Sci. Inst. 17 506 (1946).

[7] S. A. Korff, Phys. Rev. 68, 53 (1945).

The Absorption Spectrum of InCl

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A study of the band spectrum of InCl has been carried out in absorption with a determination of vibrational, rotational, and electronic energy levels associated with the band system in the region 2650 to 3000 angstrom units. The B_v' and B_v'' values were found to be of the order of 0.11 wave numbers, from which can be calculated a nuclear separation of the order of 2.3×10^{-8} centimeter. Predissociation in the band system provided a value for the energy of dissociation of the ground state between 4.64 and 4.66 electron volts.

INTRODUCTION

WHILE studying the absorption of a mixture of Hg and In vapor, Winans, Davis, and Leitzke[1] observed a band system appearing in the region 2650 to 2800 angstrom units. The present study is the outgrowth of an attempt to verify the earlier observations and to study the bands under greater dispersion. By duplicating the conditions previously found necessary to produce the bands, it was possible to photograph them with sufficient dispersion to make an accurate measurement of the isotope shift. These measurements showed that the bands were due to InCl and not HgIn, as first supposed.

A survey of the literature showed that this same band system had been observed previously a number of times. Grotrian[2] obtained the

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[1] J. G. Winans, Frances Davis, and Victor Leitzke, Phys. Rev. 57, 1079 (1940).

[2] W. Grotrian, Zeits. f. Physik 12, 229 (1923).

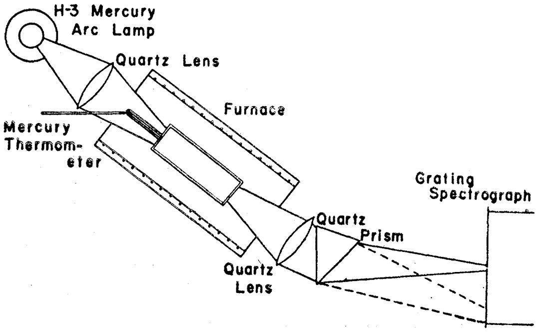

FIG. 1. Schematic diagram of apparatus.

stronger bands in a study of the absorption of In vapor. He interpreted the system as being due to a weakly bound In_2 molecule. Waring[3] obtained the same spectrum in the absorption of In and Cd vapor. He suggested that the spectrum was probably that of the InCd molecule. Barratt and Bonar[4] observed bands in absorption by Bi vapor whose wave-length agreed with those reported by Waring. They attributed these bands to the Bi_2 molecule. Miescher and Wehrli[5] were the first observers to obtain the bands under sufficient dispersion to positively identify the spectrum as due to InCl. They substantiated their assignment to InCl with measurements on the isotope shift due to Cl_{35} and Cl_{37}.

Since none of the previous investigators had studied the band system with sufficient dispersion to resolve the rotational structure or to make an accurate null-line vibrational analysis, it seemed desirable to make a rather detailed study of the band system.

The spectrum was photographed in the fourth order of a 21-foot grating spectrograph, which gave a dispersion of approximately 0.6 angstrom per millimeter and resolved lines as close as 0.03 angstrom unit. The grating was one ruled by R. W. Wood on an aluminum surface to give maximum intensity at 11,000 angstrom units in the first order.

EXPERIMENTAL PROCEDURE

After the band system was positively identified as due to the InCl molecule, a fused-quartz absorption cell, 10 centimeters in length and 2.5 centimeters in diameter, was prepared containing the sample. The quartz cell was evacuated by a two-stage mercury diffusion pump system equipped with a liquid air trap. As soon as a vacuum of the order of 10^{-4} millimeter of mercury was obtained, the absorption cell was baked at a temperature just below the softening point of the quartz until a "sticking vacuum" was obtained as indicated by a McLeod gauge. At this point the system was opened and a small pellet of high purity In was placed in a tube extending back from the absorption cell. On the other side of the absorption cell, toward the vacuum system proper, was placed at the same time a small amount of $InCl_3$. This was accomplished as rapidly as possible so that the quartz cell was open to the atmosphere only as long as absolutely necessary. After the system was sealed and a vacuum of the order of 10^{-6} millimeter of mercury was obtained, a furnace was placed over the cell in such a way that the tube with the In was at the hottest point in the furnace. In spite of the fact that the vapor pressure of In is extremely small even at 1000°C, it was possible,

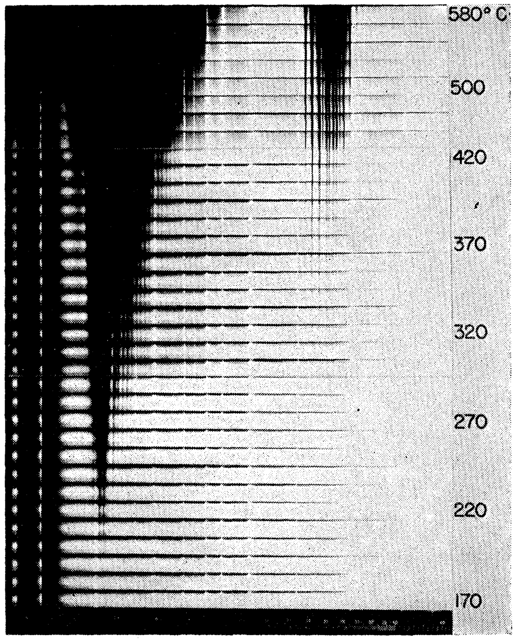

FIG. 2. The absorption of InCl vapor at pressures up to one atmosphere. Temperatures indicated were those measured at the coldest part of the cell.

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[3] R. K. Waring, Phys. Rev. **32**, 441 (1928).

[4] S. Barratt and A. R. Bonar, Phil. Mag. **9**, 1519 (1930).

[5] E. Miescher and M. Wehrli, Helv. Phys. Acta **7**, 298 (1934).

with sufficient time, to distill the In from the extended tube into the absorption cell. When this had been achieved the furnace was removed, and the portion of the tube containing the undistilled In was sealed off from the system under vacuum. Then with a hand torch a quantity of the $InCl_3$ was distilled from the other side into the absorption cell. After the cell was sealed off, it then contained pure In metal and a small amount of $InCl_3$ under a vacuum of the order of 10^{-7} millimeter of mercury. When this was heated in a furnace to just above the melting point of the In, the $InCl_3$ was converted to InCl. Care was taken to assure that there should be an excess of In so that the conversion would be complete. Otherwise one might encounter troublesome absorption either caused by $InCl_2$ or $InCl_3$. The above described method of preparing the sample proved to be very satisfactory and yet simpler than that used for example by Miescher and Wehrli.[5]

To provide the continuous background for the absorption, a H-3 high pressure mercury lamp was used as described previously by Winans.[1] Since the continuum of the mercury discharge in this type of lamp is comparatively intense from 5000 angstrom units to 2536 angstrom units, it was possible to obtain good spectrograms even in the fourth order of the grating spectrograph with a maximum exposure time of only a few hours, using Eastman 40 or Eastman II-0 plates.

A number of preliminary plates were taken with a Bausch and Lomb medium quartz spectrograph. This was done to determine the proper conditions to obtain a particular band of the system and to explore the extent of the system or any other systems due to this molecule.

To eliminate the overlapping of orders in the grating spectrograph, the arrangement shown schematically in Fig. 1 was used. With this set-up it was possible to eliminate almost completely the third order without appreciable loss of intensity in the fourth order. All of the spectrograms of the system from 2650 to 3000 angstrom units were taken with this arrangement.

Two other band systems of this molecule which overlap occur in the range from 3300 to 3700 angstrom units. They could be conveniently photographed in the third order. To eliminate the overlapping from the fourth order here, the light was taken from the high pressure mercury lamp through the glass envelope which absorbed the radiation below 3000 angstrom units. In all cases, the overlapping caused by the second order gave no difficulty, since the plate emulsions used were insensitive in that wave-length region.

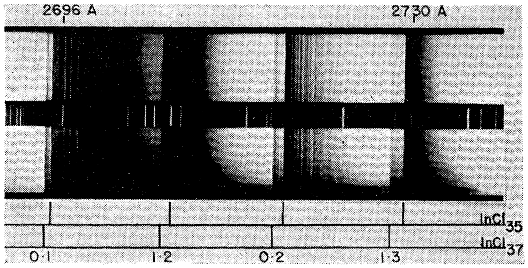

FIG. 3. Bands of the fundamental system taken in the fourth order of the 21 foot grating spectrograph.

DESCRIPTION OF THE SPECTRUM

Figure 2 is a photograph of the spectrum of the InCl molecule taken on the Bausch and Lomb medium quartz spectrograph. The exposures were taken at various pressures of the absorbing gas, which was controlled by varying the temperature of the furnace in which the absorption cell was placed. As indicated in the figure, the pressures were determined by the temperature as measured at the end of the protruding tube of the absorption cell where the excess liquid InCl collected. Temperatures were measured with a high temperature mercury thermometer.

From a spectrogram with the dispersion of Fig. 2 it is not possible to obtain more than a qualitative idea of the band system. At temperatures as low as 200°C a very intense absorption appears at about 2650 angstrom units. With increasing temperature and hence pressure of the absorbing vapor, this system broadens toward the red until at a temperature corresponding to about one atmosphere of the vapor it extends from 2650 to 3000 angstrom units. The individual bands of the system show a double head, and throughout the region all are shaded toward the red.

At about 300°C another system or systems in the region from 3300 to 3700 angstrom units appears. This group of bands broadens somewhat symmetrically with increasing pressure of the

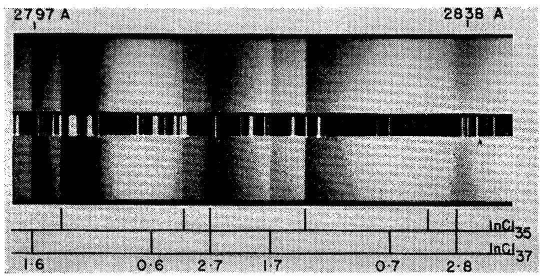

FIG. 4. Bands of the fundamental system taken in the fourth order of the 21 foot grating spectrograph. Two bands of the $(2,v'')$ progression can be detected superimposed on the (0,6) and (0,7) bands.

absorbing vapor. Although this group of bands has a much more complicated pattern than the 2650 angstrom group, it can be easily seen to consist of a series of overlapping bands with sharp heads, each band shaded toward the violet.

At the higher pressures two regions of continuous absorption also appear. One is at about 2610 angstrom units. With increasing pressure it broadens and merges into the absorption in the 2650 angstrom region. Another region of continuous absorption appears to set in at about 2100 angstrom units and broadens toward the red, finally joining with the absorption in the 2610 angstrom region.

Figures 3 and 4 are spectrograms of the fundamental system (the system in the region 2650–3000 angstrom units) taken in the fourth order of the 21 foot grating spectrograph. These spectrograms show that the system consists of a series of nearly equally spaced bands with alternate bands showing rotational structure and the others no rotational structure. All bands have sharp heads with the exception of some showing in Fig. 4. Superimposed on the (0,6) and (0,7) bands there is another series of bands overlapping the ones with rotational structure. For these bands not only is the rotational structure missing but also the heads are not sharp.

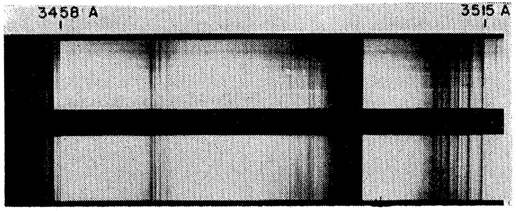

FIG. 5. Bands of the intercombination systems of InCl, taken in the third order of the 21 foot grating spectrograph.

Miescher and Wehrli[5] have identified the band at 2672.3 angstrom units as the $v'=0$, $v''=0$ band and have shown that all of these bands fit as members of the $(0,v'')$, $(1,v'')$, and $(2,v'')$ progressions. Bands in the $(0,v'')$ progression have rotational structure. Bands in the $(1,v'')$ progression have sharp heads but no rotational structure. Bands in the $(2,v'')$ progression not only have no rotational structure but also have diffuse heads. This spectrum is a striking example of predissociation in the upper electronic state. That this is actually the phenomenon of predissociation is verified by the fact that in emission only the $(0,v'')$ progression is obtained.

The absorption in the region 3300 to 3700 angstrom units, which hereafter will be referred to as the intercombination systems, is shown in Fig. 5. Under the larger dispersion, it is found from a study of the isotope shift that actually in this region there are two separate band systems which almost completely overlap each other.[5] Miescher and Wehrli showed that the lower vibrational levels for these bands are the same as those for the fundamental system. As can be seen from the plate, all of these bands have rotational structure. Since the intercombination systems and the fundamental system have the same lower electronic state, this is further evidence that the breaking off of fine structure in the fundamental system is actually a predissociation in the upper state.

ANALYSIS OF THE FUNDAMENTAL SYSTEM

a. Vibrational Analysis

A vibrational analysis of this spectrum and an assignment of quantum numbers has been made by Miescher and Wehrli[5] from spectrograms taken under low dispersion. Only the band heads were measured and these somewhat inaccurately. Since the bands arise from a $^1\Pi\leftrightarrow\Sigma_0^+$ transition (see later section), they consist of a P, Q, and R branch. Even with the high dispersion available in the present experiment in the fourth order of the grating spectrograph, the rotational lines in the neighborhood of the null line are not resolved. Nevertheless, the Q branch head is for practical purposes located at the null line. On the spectrograms taken in this experiment, the Q branch head could be measured in the $(0,v'')$ and $(1,v'')$ progressions. The Q branch heads can be detected for some bands in these progressions in Figs. 3 and 4. For the $(2,v'')$ progression, since the R heads are not even sharp, an attempt was made to locate the maximum of absorption in each band. The observed bands are arranged in Table I according to the Deslandres' scheme.[6] Since each band is double because the two Cl isotopes, both components are entered in the table. The upper numbers refer to the Cl_{35} component, and the lower numbers refer to the Cl_{37} component. Also listed are the wave numbers calculated from the formula

$$\nu_{\mathrm{cm}^{-1}}=37483.6+\genfrac{}{}{0pt}{}{177.3}{173.6}(v'+\tfrac{1}{2})-\genfrac{}{}{0pt}{}{12.6}{12.1}(v'+\tfrac{1}{2})^2$$

$$-\genfrac{}{}{0pt}{}{317.4}{310.8}(v''+\tfrac{1}{2})+\genfrac{}{}{0pt}{}{1.01}{0.97}(v''+\tfrac{1}{2})^2.$$

It can be seen that in all cases the agreement between the observed and calculated values is less than one wave number.

By considering the coefficients in the formula for $InCl_{35}$ and $InCl_{37}$, it is verified that the two components are due to these isotopes. When ρ is calculated, using Cl_{35} and Cl_{37} and In_{115}, one obtains

$$\rho=0.9790.$$

The average value from the coefficients of the empirical equation gives

$$\rho=0.9796.$$

b. Rotational Analysis

As mentioned previously, each band of the fundamental system consists of a single P, Q, and R branch. Since the bands are shaded toward the red, it is the R branch that forms the head.[6] At a distance from the band head, where the rotational lines are resolved, the intensity of the R branch has practically dropped to zero. Thus, in the resolved region of a band, there remain only the P and Q branches which intersect each other, producing a kind of modulation noticeable in Fig. 3. Alternately, they are in phase, so to speak, and are not resolved, and then out of phase and then resolved. In the regions where the two series of lines are neither in phase or out of phase, a measurement gives a wave-length or wave number which does not truly represent either a Q line or a P line. Because of this inherent difficulty it was not possible to apply the combination relations[6] directly to a set of measurements on a band to determine the numbering in the two branches. In the $(0,v'')$ progression all bands have a common upper state, so that if the combination relations could be worked out, the relative numbering of the P and Q lines could be determined and then the absolute numbering. However, because of the above mentioned difficulty, the combination differences were too erratic to show when the correct relative numbering had been obtained, if these differences were computed from the values measured directly.

TABLE I. Deslandres table (scheme of origins) of the fundamental system of InCl.

v''	$v'=0$		$v'=1$		$v'=2$	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0	37410.6	37410.6	37562.9	37562.7	37690	37689.6
	37412.2	37412.2		37561.6		37686.8
1	37095.0	37095.2	37247.3	37247.3		
	37103.2	37104.3	37252.8	37253.7		
2	36781.6	36781.8	36934.0	36933.9		
	36796.2	36796.5	36946.2	36945.9		
3	36470.5	36470.5	36622.5	36622.6		
	36491.5	36491.5	36641.2	36640.9		
4	36161.2	36161.2	36313.2	36313.3		
	36188.6	36188.5	36338.2	36337.9		
5	35854.2	35853.9	36006.0	36006.0		
	35887.6	35887.5	36036.8	36036.9		
6	35549.2	35548.6	35700.9	35700.7	35828	35827.6
	35588.9	35588.3	35738.2	35737.7		35862.9
7			35397.4	35397.4	35524	35524.3
			35440.8	35440.5		35565.7
8			35095.9	35096.1	35223	35223.0
			35145.3	35145.3		35270.5
9			34796.8	34796.9	34924	34923.8
			34852.1	34852.0		34977.2
10			34499.7	34499.7	34627	34626.6
				34560.6		34685.8
11			34204.5	34204.5	34331	34331.4
				34271.2		34396.4
12					34038	34038.2
						34108.9

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[6] Gerhard Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall Inc., New York, 1939). All theory necessary for the interpretation can be found there.

The analysis as it was finally obtained was made in essentially two independent ways. First an empirical formula of the type

$$\nu = \nu_0 + am(m+1) + bm^2(m+1)^2$$

was obtained to represent the Q branch in the (0,0) and (0,2) bands. From quantum theory analysis the Q branch should be represented by[6]

$$\nu = \nu_0 + (B_v' - B_v'')m(m+1) - (D_v' - D_v'')m^2(m+1)^2.$$

Thus when the empirical equation for the Q branch is known for any band, one has the value of $(B_v' - B_v'')$. Also since the R branch is represented theoretically by

$$\nu = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2,$$

which is valid for small m, the quantity $(B_v' + B_v'')$ can be obtained from measurements on ν_0 and ν at the band head. The procedure is as follows:

$$d\nu/dm = (B_v' + \mathrm{A}_v'') + 2m(\mathrm{A}_v' - B_v''),$$

and

$$d\nu/dm\,|_{\mathrm{Head}} = 0$$

so

$$m_{\mathrm{Head}} = \frac{-(B_v' + B_v'')}{2(B_v' - B_v'')}.$$

Then

$$\nu_{\mathrm{Head}} = \nu_0 - \frac{(B_v' + B_v'')^2}{2(B_v' - B_v'')} + \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')}.$$

This gives

$$(B_v' + B_v'')^2 = -4(B_v' - B_v'')(\nu_{\mathrm{Head}} - \nu_0).$$

If the Q branch has been analyzed, $(B_v' - B_v'')$ is known and thus $(B_v' + B_v'')$ can be determined. Two simultaneous equations are then available to determine B_v' and B_v''.

The above method of analysis was carried out for the (0,0) and (0,2) bands. The difficulties are in measuring accurately the null line, ν_0, and determining the m value of Q branch lines. Since the lines are not resolved down to the null line, it is impossible to obtain the m value directly. To find it the following procedure was used. The wave number of two Q lines which could be measured accurately was selected. One of the lines was as close to the null line as possible and the other as far from the null line as possible. Even though the absolute m number for either line was not known, the difference Δm was known by merely counting the intervening lines. Then with the measured value of ν_0 and an assumed value for the m of the first of these lines, the a and b values in the empirical equation were computed. Since Δm was known, the m value of the second line was determined by the assumed value plus Δm. Using this scheme, the assumed m for the first line was systematically varied, each time obtaining different values of the constants a and b. From the table of a and b values thus obtained, the pair was chosen which gave an equation which not only passed through ν_0 and the two lines chosen, but also represented the intervening lines the best. With this method it was possible to obtain the absolute numbering to within possible ± 2. By this method the molecular constants

$$B_0' = 0.1037\ \mathrm{cm}^{-1}, \quad B_0'' = 0.1107\ \mathrm{cm}^{-1},$$

$$B_2'' = 0.1093\ \mathrm{cm}^{-1}$$

were determined.[7] The empirical formulas arrived at for the Q branches of these bands were

$$(0,0);\quad \nu = 37410.60 - 0.00696m(m+1) - 1.39\times 10^{-7}m^2(m+1)^2$$

$$(0,2);\quad \nu = 36781.84 - 0.00609m(m+1) - 1.40\times 10^{-7}m^2(m+1)^2.$$

Since the values of the molecular constants obtained by the above method are subject to the errors in determining the true numbering in the band and the exact position of the null line, some method of using the combination relations seemed desirable.

As is evident from Fig. 3, the P and Q branches intersect each other several times throughout a band. There are regions where both branches are completely resolved and regions where both branches coincide. Thus, in these regions the true position of the lines of both branches could be determined. The procedure was as follows. An empirical formula was used to compute the wave numbers in a Q branch. Then the difference between the observed wave numbers and the calculated wave numbers was formed for both the P and Q branches. When these differences are plotted against a running number, the re-

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[7] J. G. Winans and H. M. Foslie, Phys. Rev. **71**, 137 (1947).

sulting curve should be a smooth one. If the empirical formula was the true one, for example, for the Q branch, these differences should average zero. If the empirical formula was off either in the m number or the value of ν_0, at least the trend should be a continuous one. The plot of the differences between the observed lines in the (0,0) band and values calculated from

$$\nu = 37410.6 - 0.007m(m+1) - 1.35\times10^{-7}m^2(m+1)^2$$

is shown in Fig. 6. The solid circles are the values of the differences in the regions where the branches were completely resolved or completely on top of each other, as indicated by sharp spectral lines. These points were used to determine the course of the smooth curve which was drawn. The distribution of the points shows very strikingly the measurement errors when the two branches are not resolved and yet not coincident. With the use of the curve the correct differences between wave numbers of an actual line and those calculated from the equation were obtained and combined with the calculated wave numbers to give the true line-wave number. This gives the wave number which would have been obtained if the P and Q lines could have been resolved. With these corrected wave numbers for lines in the P and Q branches, it was possible to apply the combination relations

$$Q(J+1) - P(J+1) = \Delta_1 F'(J),$$

where $\Delta_1 F'(J)$ is the separation of successive rotational levels in the upper electronic state, and J is the number of any particular line referred to the rotational quantum number of the lower electronic state. This method of correcting the measurements was carried out for the (0,0), (0,1), and (0,2) bands of the fundamental system. Since all of these bands have a common upper state, the $\Delta_1 F'(J)$ should agree within the experimental error when the correct relative numbering of the P and Q branches has been found. The wave numbers of the bands, after correction by the above method, are listed in Table II as well as the $\Delta_1 F'(J)$ and the $\Delta_1 F''(J)$.

To obtain the molecular constants from the values of the combination relations, the following graphical method was used. According to the theory we have[6]

$$\Delta_1 F(J)/(J+1) = 2B - 4D(J+1)^2,$$

so that $\Delta_1 F(J)/(J+1)$ plotted against $(J+1)^2$ should give a straight line with an intercept of $2B$ and a slope of $-4D$. The plots of the $\Delta_1 F(J)/(J+1)$ values given in Table II *versus* $(J+1)^2$ are shown in Fig. 7, and the values of the

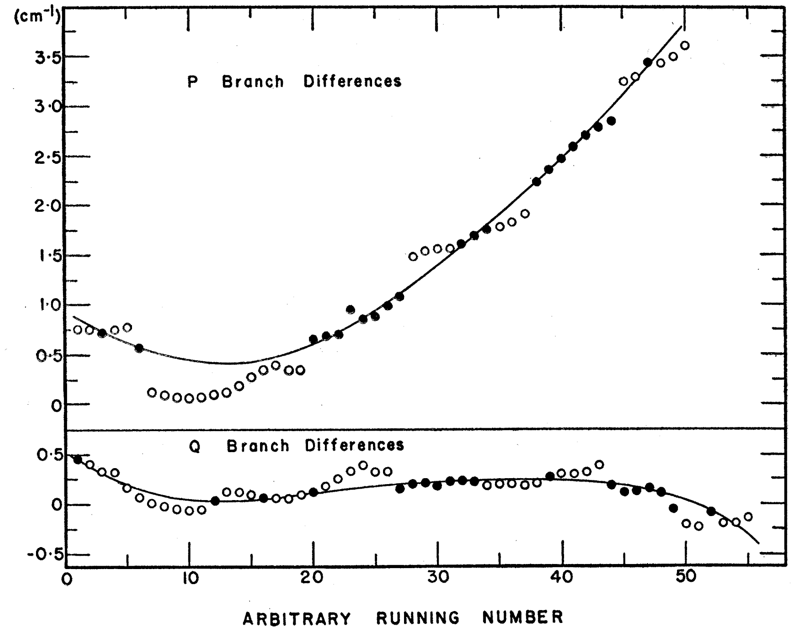

FIG. 6. Differences between wave numbers of an actual line in the P and Q branches of the (0,0) band and those calculated from an empirical equation.

TABLE II. Fine structure of the bands of the fundamental system of InCl.

Wave numbers of the lines of the (0,0), (0,1), and (0,2) bands and the combination differences for these bands.

J	$Q(J)$	$P(J)$	$\Delta_1F'(J)$	$\Delta_1F''(J)$	$\frac{\Delta_1F'(J)}{(J+1)}$	$\frac{\Delta_1F''(J)}{(J+1)}$
		(0,0) band				
43			9.69		0.2202	
44	37397.97	37388.28	9.89	10.61	0.2198	0.2358
45	397.25	387.36	10.06	10.81	0.2187	0.2350
46	396.50	386.44	10.25	10.99	0.2181	0.2338
47	395.76	385.51	10.46	11.20	0.2179	0.2333
48	395.02	384.56	10.67	11.43	0.2178	0.2333
49	394.26	383.59	10.87	11.64	0.2174	0.2328
50	393.49	382.62	11.09	11.87	0.2175	0.2327
51	392.71	381.62	11.31	12.10	0.2175	0.2327
52	391.92	380.61	11.55	12.34	0.2179	0.2328
53	391.13	379.58	11.75	12.56	0.2176	0.2325
54	390.32	378.57	11.97	12.79	0.2176	0.2325
55	389.50	377.53	12.18	13.03	0.2175	0.2327
56	388.65	376.47	12.40	13.25	0.2175	0.2325
57	387.80	375.40	12.62	13.48	0.2176	0.2324
58	386.92	374.32	12.86	13.72	0.2180	0.2325
59	386.03	373.20	13.05	13.96	0.2175	0.2327
60	385.12	372.07	13.25	14.18	0.2172	0.2325
61	384.19	370.94	13.46	14.40	0.2171	0.2323
62	383.25	369.79	13.70	14.65	0.2175	0.2325
63	382.30	368.60	13.90	14.88	0.2172	0.2325
64	381.32	367.42	14.12	15.11	0.2172	0.2325
65	380.33	366.21	14.33	15.36	0.2171	0.2327
66	379.30	364.97	14.55	15.58	0.2172	0.2325
67	378.27	363.72	14.74	15.82	0.2168	0.2326
68	377.19	362.45	14.95	16.04	0.2167	0.2325
69	376.10	361.15	15.16	16.27	0.2166	0.2324
70	374.99	359.83	15.35	16.49	0.2162	0.2323
71	373.85	358.50	15.56	16.71	0.2161	0.2321
72	372.70	357.14	15.77	16.96	0.2160	0.2323
73	371.51	355.74	15.97	17.17	0.2158	0.2320
74	370.31	354.34	16.18	17.41	0.2175	0.2321
75	369.08	352.90	16.37	17.63	0.2154	0.2320
76	367.82	351.45	16.59	17.86	0.2155	0.2319
77	366.55	349.96	16.80	18.09	0.2154	0.2319
78	365.26	348.46	17.00	18.33	0.2152	0.2320
79	363.93	346.93	17.20	18.55	0.2150	0.2319
80	362.58	345.38	17.40	18.77	0.2148	0.2317
81	361.21	343.81	17.60	19.00	0.2146	0.2317
82	359.81	342.21	17.79	19.23	0.2143	0.2317
83	358.37	340.58	17.99	19.43	0.2142	0.2313
84	356.93	338.94	18.19	19.67	0.2140	0.2314
85	355.45	337.26	18.37	19.89	0.2136	0.2313
86	353.93	335.56	18.58	20.11	0.2136	0.2311
87	352.40	333.82				
		(0,1) band				
40	...	...	8.97	...	0.2188	...
41	37084.78	37075.81	9.17	9.77	0.2183	0.2326
42	084.18	075.01	9.38	9.99	0.2181	0.2323
43	083.57	074.19	9.58	10.19	0.2177	0.2316
44	082.96	073.38	9.78	10.41	0.2173	0.2313
45	082.33	072.55	10.01	10.63	0.2176	0.2311
46	081.71	071.70	10.21	10.86	0.2172	0.2311
47	081.06	070.85	10.45	11.09	0.2177	0.2310
48	080.42	069.97	10.66	11.32	0.2175	0.2310
49	079.76	069.10	10.87	11.55	0.2174	0.2310
50	079.08	068.21	11.06	11.77	0.2169	0.2308
51	078.37	067.31	11.29	11.98	0.2171	0.2304
52	077.68	066.39	11.51	12.22	0.2172	0.2306
53	076.97	065.46	11.72	12.46	0.2170	0.2307
54	076.23	064.51	11.94	12.69	0.2171	0.2307
55	075.48	063.54	12.15	12.93	0.2170	0.2309
56	074.70	062.55	12.37	13.15	0.2170	0.2307
57	073.92	061.55	12.58	13.38	0.2169	0.2307
58	073.12	060.54	12.80	13.63	0.2169	0.2310
		(0,1) band (*continued*)				
59	072.29	059.49	13.03	13.86	0.2172	0.2310
60	071.46	058.43	13.23	14.10	0.2169	0.2312
61	070.59	057.36	13.44	14.31	0.2168	0.2308
62	069.72	056.28	13.67	14.56	0.2170	0.2311
63	068.83	055.16	13.87	14.79	0.2167	0.2311
64	067.91	054.04	14.09	15.02	0.2168	0.2311
65	066.98	052.89	14.31	15.26	0.2168	0.2312
66	066.03	051.72	14.51	15.49	0.2165	0.2312
67	065.05	050.54	14.73	15.71	0.2166	0.2310
68	064.07	049.34	14.92	15.94	0.2162	0.2310
69	063.05	048.13	15.13	16.17	0.2161	0.2310
70	062.01	046.88	15.34	16.39	0.2160	0.2308
71	060.96	045.62	15.56	16.64	0.2161	0.2311
72	059.88	044.42	15.76	16.86	0.2159	0.2309
73	058.78	043.02	15.97	17.09	0.2158	0.2309
74	057.66	041.69	16.17	17.31	0.2156	0.2308
75	056.52	040.35	16.36	17.53	0.2152	0.2307
76	055.35	038.99	16.58	17.77	0.2153	0.2308
77	054.16	037.58	16.80	18.02	0.2153	0.2310
78	052.94	036.14	17.01	18.26	0.2153	0.2311
79	051.69	034.68	17.21	18.48	0.2151	0.2310
80	050.42	033.21	17.43	18.72	0.2152	0.2311
81	049.13	031.70	17.63	18.95	0.2150	0.2311
82	047.81	030.18				
		(0,2) band				
66	...	...	14.43	...	0.2154	...
67	36754.02	36739.59	14.67	15.60	0.2157	0.2294
68	753.09	738.42	14.89	15.84	0.2158	0.2296
69	752.14	737.25	15.10	16.08	0.2157	0.2297
70	751.16	736.06	15.32	16.31	0.2158	0.2297
71	750.17	734.85	15.53	16.55	0.2157	0.2299
72	749.15	733.62	15.74	16.77	0.2156	0.2297
73	748.12	732.38	15.94	16.99	0.2154	0.2296
74	747.07	731.13	16.13	17.21	0.2151	0.2295
75	745.99	729.86	16.34	17.44	0.2150	0.2295
76	744.89	728.55	16.54	17.66	0.2148	0.2294
77	743.77	727.23	16.73	17.88	0.2145	0.2292
78	742.62	725.89	16.95	18.11	0.2146	0.2292
79	741.46	724.51	17.12	18.32	0.2140	0.2290
80	740.26	723.14	17.34	18.55	0.2141	0.2290
81	739.05	721.71	17.62	18.75	0.2148	0.2287
82	737.92	720.30	17.76	19.13	0.2140	0.2305
83	736.55	718.79	17.97	19.26	0.2139	0.2292
84	735.26	717.29	18.16	19.48	0.2136	0.2292
85	733.94	715.78	18.37	19.71	0.2136	0.2292
86	732.60	714.23	18.60	19.95	0.2138	0.2293
87	731.25	712.65	18.82	20.21	0.2139	0.2297
88	729.86	711.04	19.03	20.46	0.2138	0.2299
89	728.43	709.40	19.25	20.69	0.2139	0.2299
90	726.99	707.74	19.45	20.94	0.2137	0.2301
91	725.50	706.05	19.69	21.18	0.2140	0.2302
92	724.01	704.32	19.90	21.44	0.2139	0.2305
93	722.47	702.57	20.11	21.68	0.2139	0.2306
94	720.90	700.79	20.32	21.92	0.2139	0.2307
95	719.30	698.98	20.50	22.15	0.2135	0.2307
96	717.65	697.15	20.71	22.39	0.2135	0.2308
97	715.97	695.26	20.88	22.61	0.2131	0.2307
98	714.24	693.36	21.05	22.81	0.2126	0.2304
99	712.48	691.43	21.22	23.03	0.2122	0.2303
100	710.67	689.45	21.37	23.21	0.2116	0.2298
101	708.83	687.46	21.53	23.41	0.2111	0.2295
102	706.95	685.42	21.65	23.58	0.2102	0.2289
103	705.02	683.37	21.77	23.75	0.2093	0.2284
104	703.04	681.27	22.21	23.91	0.2115	0.2277
105	701.34	679.13				

molecular constants obtained by this method are listed in Table III.

The accuracy obtained in the present experiment is not sufficient to detect a definite trend in the D_v'' values. Actually the D_1'' and D_2'' are less than the D_0''. It is not believed that this is significant, so that the D' and D'' values listed in Table III are the average values obtained from the three bands analyzed.

The above rotational analysis appears completely satisfactory with possibly one exception. In the bands observed, the R branch was not resolved and measurable, and hence the $P-R$ combination relations could not be used. Using only the $Q-P$ combination relations does not give an opportunity to ascertain whether "Λ doubling" in the ${}^1\Pi_1$ state is appreciable. Should it be significant, the rotational constants obtained would not be the true rotational constants for the states. However, the AlCl molecule does not appear to show an appreciable "Λ doubling."[8] Since InCl is even heavier, one would expect the doubling to be even less for InCl than for the AlCl molecule.

The values of the molecular constants, as obtained by the two essentially independent methods, differ by as much as six percent. Although it is difficult to estimate the percentage error for the two methods, one would expect the values obtained from the combination relations to be more reliable.

TABLE III. Molecular constants for the fundamental system of InCl.

B_0'(cm^{-1})	B_0''(cm^{-1})	B_1''(cm^{-1})	B_2''(cm^{-1})	D'(cm^{-1})	D''(cm^{-1})
0.1091	0.1166	0.1155	0.1149	1.2×10^{-7}	2×10^{-8}
r_0'(cm)	r_0''(cm)	α_e''			
2.39×10^{-8}	2.32×10^{-8}	0.0009			

ELECTRONIC CONFIGURATION FOR InCl AND DISSOCIATION ENERGY

The Cl atom has 5 p-electrons and the In atom has 1p-electron in their outer electron shells. Hence in the ground state of the molecule there is formed a closed shell of the type $\sigma^2\pi^4$. Thus the ground state is probably a ${}^1\Sigma_0{}^+$ state similar to the situation for atoms where a closed shell gives a ${}^1S$ state. According to the theory $\mathrm{In}({}^2P_{\frac{1}{2}})\mathrm{Cl}({}^2P_{\frac{3}{2}})$ should result in the following electronic states: ${}^3\Pi_{2,1,0}$; ${}^1\Pi_1$; ${}^1\Sigma_0{}^+$; ${}^1\Sigma_0{}^-$. Since the fundamental system is much more intense in absorption, it is reasonable to suppose that it is due to ${}^1\Pi_1 \leftrightarrow {}^1\Sigma_0{}^+$ transition. The intercombination system then must result from a transition from the ${}^1\Sigma_0{}^+$ ground state to the ${}^3\Pi$ terms and is thus less intense, because the transition probability between single and triplet terms is much less than the transition probability between two singlet terms. The fact that the intercombination system consists of two band systems further supports this. The selection rules forbid a transition from ${}^3\Pi_2$ to ${}^1\Sigma_0{}^+$. Also because of "Λ-type doubling," the ${}^3\Pi_0$ term splits into two

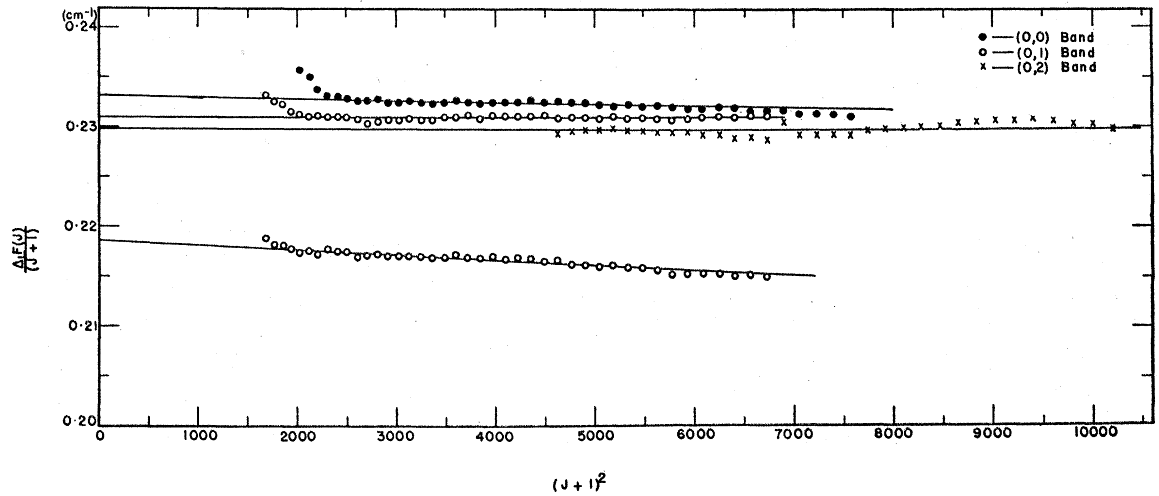

FIG. 7. Graphical determination of the molecular constants from the data given in Table II.

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[8] W. Holst, Zeits. f. Physik 93, 55 (1935).

components, namely, $^3\Pi_0{}^-$ and $^3\Pi_0{}^+$. Of these two only the transition $^3\Pi_0{}^+ \leftrightarrow {}^1\Sigma_0{}^+$ is permitted because of the selection rule that + combines only with +. There remain only the two possible transitions, $^3\Pi_1 \leftrightarrow {}^1\Sigma_0{}^+$ and $^3\Pi_0{}^+ \leftrightarrow {}^1\Sigma_0{}^+$. Further considerations show that one of these systems should contain a P, Q, and R branch, and the other system only a P and R branch.[5] Close examination of the bands bears this out.

The predissociation that takes place in the fundamental system makes it possible to determine the dissociation energy of the ground state within rather small limits. The upper state is a $^1\Pi$ state and, according to Kronig's selection rules for predissociation ($\Delta J=0$, $\Delta S=0$, $\Delta\Omega=0, \pm 1$, $+\nleftrightarrow-$), the perturbing state must be a $^1\Pi$ or a $^1\Delta$ state. A $^1\Sigma$ state is ruled out, since if it were the perturbing state only one Λ component of the $^1\Pi$ state would be predissociated, because the selection rules

$$\Delta J=0 \quad \text{and} \quad +\nleftrightarrow-$$

cannot be satisfied simultaneously for both Λ components. This type of predissociation would result in only the P and R branch or the Q

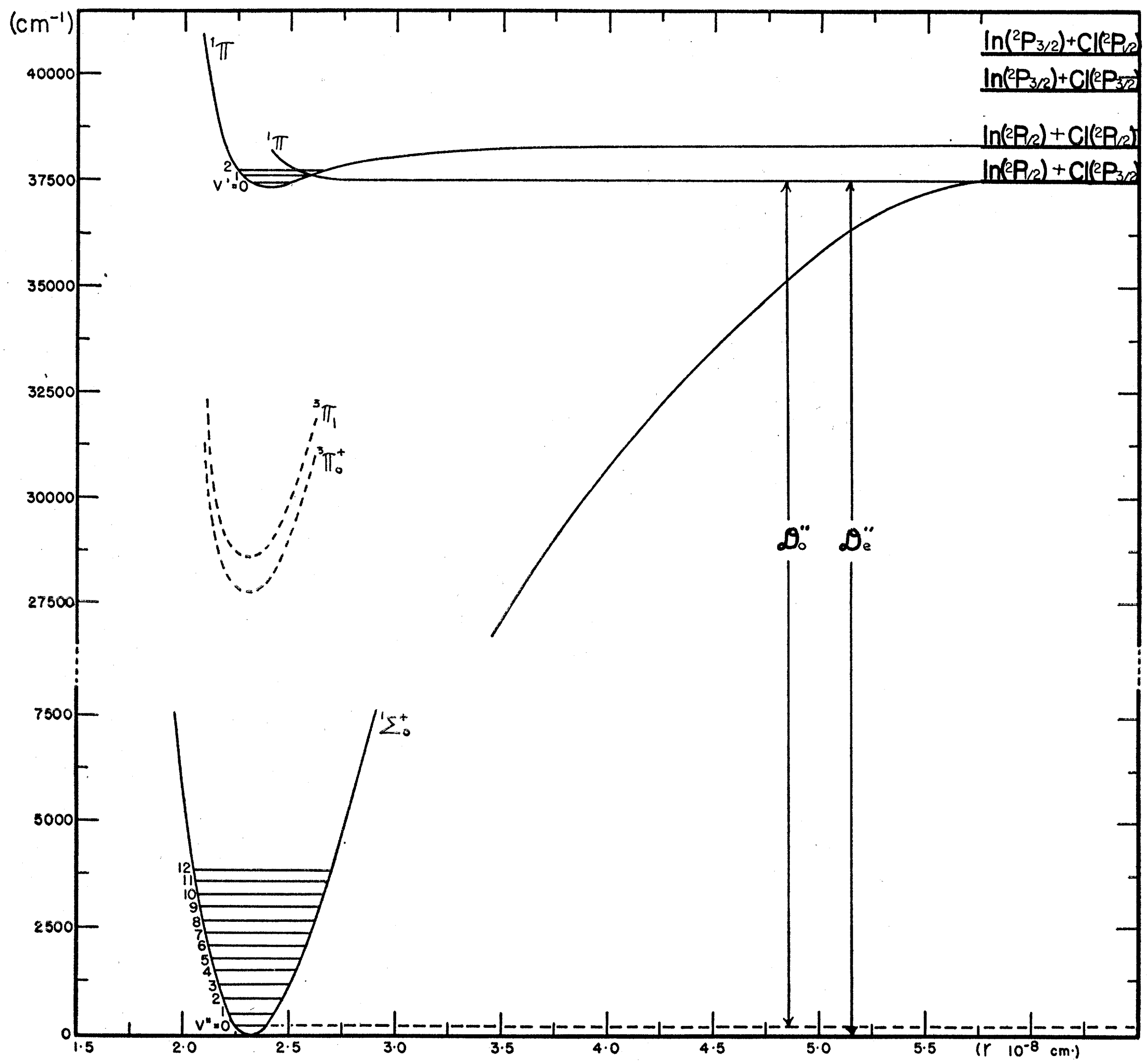

FIG. 8. Possible arrangement of the electronic states from which the fundamental and intercombination band systems of InCl arise. The perturbing state which causes predissociation in the fundamental system is also shown.

branch being predissociated. The observed bands show all branches predissociated.

Since the upper state potential curve and the perturbing potential curve intersect very close to the minimum of the upper state potential curve, it is reasonable that the upper state cannot have the same dissociation products as the perturbing state or the ground state. The next higher energy possibility for the dissociation products of the upper state is normal In($^2P_{\frac{1}{2}}$) plus excited Cl($^2P_{\frac{1}{2}}$). Now the dissociation energy of the upper state for the fundamental system must be small, as shown by the large $\omega_e'x_e'$ in the formula for the vibrational states. Calculating the dissociation energy D_e' from the formula

$$D_e' = \omega_e'^2/4\omega_e'x_e'$$

given by the theory, one obtains $D_e' = 600$ cm^{-1}. If the dissociation products for the upper electronic state for the fundamental system are as suggested above, then the potential curves must be of the type shown in Fig. 8. The perturbing state and the ground state for the fundamental system have the same dissociation products as indicated. That the $v' = 0$ state lies below the asymptote for the perturbing state is indicated by the fact that the rotational lines in the $(0,v'')$ progression are sharp. If it actually was above the asymptote, one would expect the "barrier penetration" to make the lines in this progression somewhat diffuse. That the upper electronic state and the perturbing state intersect just above $v' = 1$ is indicated by the fact that, even though the bands in the $(1,v'')$ progression show no rotational structure in the region where one would expect it to be resolved, the band heads are still sharp. Since both the Q and R heads in this progression appear as sharp as in the $(0,v'')$ progression, it seems that, for small values of the rotational quantum number, J, in the $v' = 1$ state, there exists rotational quantitization, but for higher J values predissociation sets in, causing the lines to be diffuse in the region where they could be resolved. Therefore, for $J \cong 0$, the potential curves intersect just above $v' = 1$. For higher J values the change in the potential curves are due to rotation, which causes them to intersect just below $v' = 1$. The result is that any band in the $(1,v'')$ progression appears completely diffuse although actually, in the region of the null line, the lines must be sharp in order to produce the sharp band heads.

With the above observations, the electronic states for the fundamental system would appear to be determined to within the limits of one vibrational quantum of the upper state. It cannot be determined just where the asymptote for the perturbing state intersects between $v' = 0$ and $v' = 1$. The dissociation energy of the lower state must lie between

$$D_e'' = 37568 \text{ cm}^{-1} = 4.66 \text{ volts}$$

and

$$D_e'' = 37720 \text{ cm}^{-1} = 4.68 \text{ volts.}$$

Although this appears to be the most reasonable arrangement of the electronic states, the possibility of the upper state having In($^2P_{\frac{3}{2}}$)Cl($^2P_{\frac{1}{2}}$) as its dissociation products cannot be completely ruled out. However, this possibility would seem to be unlikely because any electronic state resulting from this combination would almost certainly be completely predissociated by the large number of electronic states arising from the less energetic combinations. Nevertheless, admitting this possibility places the dissociation energy between

$$D_e'' = 37720 \text{ cm}^{-1} = 4.68 \text{ volts}$$

and

$$D_e'' = 35520 \text{ cm}^{-1} = 4.40 \text{ volts.}$$

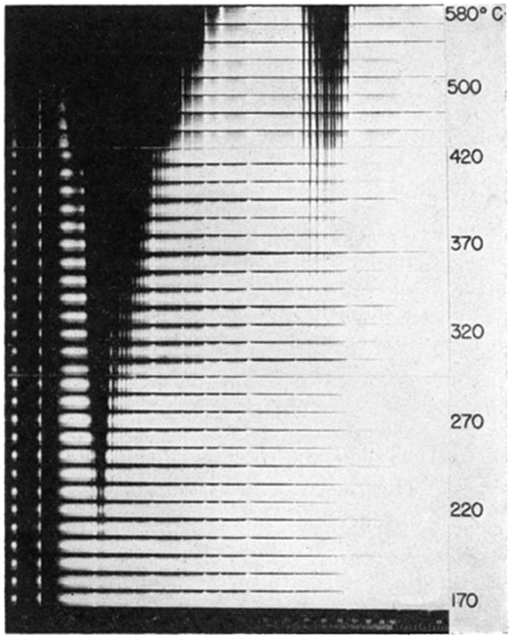

FIG. 2. The absorption of InCl vapor at pressures up to one atmosphere. Temperatures indicated were those measured at the coldest part of the cell.

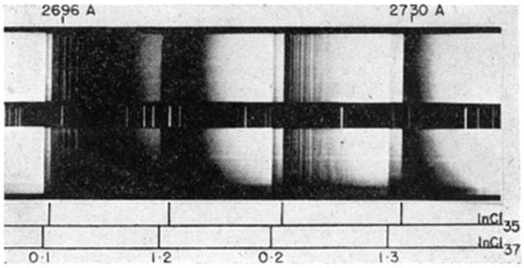

FIG. 3. Bands of the fundamental system taken in the fourth order of the 21 foot grating spectrograph.

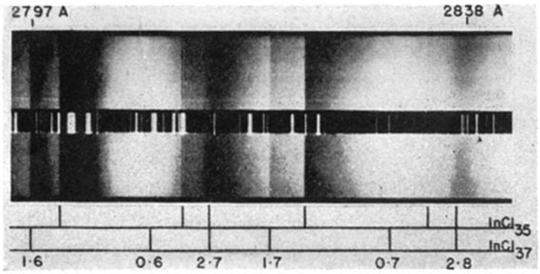

FIG. 4. Bands of the fundamental system taken in the fourth order of the 21 foot grating spectrograph. Two bands of the $(2,v'')$ progression can be detected superimposed on the (0,6) and (0,7) bands.

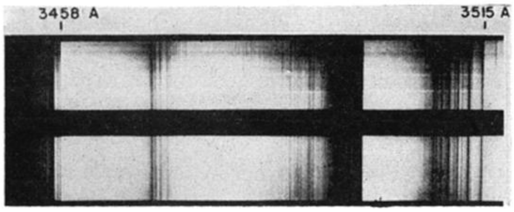

FIG. 5. Bands of the intercombination systems of InCl, taken in the third order of the 21 foot grating spectrograph.