

## The Absorption Spectrum of Iodine Monochloride in the Near Infrared

BY ORRELL DARBYSHIRE

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE

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Previous analyses of the absorption spectrum of ICl vapour were confined to the region  $\lambda 6940$  to  $\lambda 5736\text{\AA}$  where, at normal temperature, it consists chiefly of two  $v'$  progressions ( $v''=0$  and  $v''=1$ ). No bands of these progressions for which  $v' < 7$ ,  $v' < 6$ , respectively, were measured, so that the determination of  $\omega_0'$  involved a fairly long extrapolation which, in view of the non-linearity of the  $\omega_v', v'$  relationship, was somewhat untrustworthy. Only a few bands of the  $v''=2$  progression were measured and consequently the values of  $\omega_0''x''$  and  $\omega_0''$  required further examination. By raising the temperature of ICl vapour to  $400^\circ\text{C}$  and suitably adjusting the pressure the absorption spectrum between  $\lambda 6750$  and  $\lambda 8770\text{\AA}$  has been photographed. In this region the spectrum consists of portions of seven progressions for which  $v''=1$  to  $v''=7$ , the  $v''=0$  progression not being appreciably developed. Values of  $\omega_v'$  from  $v'=2$  to  $v'=9$ , and of  $\omega_v''$  from  $v''=1$  to  $v''=6$ , have been determined. Graphical extrapolation of two units of  $v'$  gave  $\omega_0'$  as  $209.7\text{ cm}^{-1}$  and assuming a linear  $\omega_v'', v''$  law,  $\omega_0''$  was found to be  $383.0\text{ cm}^{-1}$ . The values of  $\omega_0'$  and  $\omega_0''$  given by Patkowski and Curtis were  $223.7\text{ cm}^{-1}$  and  $382.0\text{ cm}^{-1}$  respectively. It appears that Wilson's value for the convergence limit of the  $v''=0$  progression is about  $90\text{ cm}^{-1}$  too high. The dissociation energy for the normal state as found by extrapolation from the lowest eight levels is some  $5700\text{ cm}^{-1}$  units greater than the energy required to dissociate the molecule by raising it to the higher state and increasing the energy in that state, so that there is a crossing of the potential energy curves. The possible significance of this with regard to the products of dissociation from the lower state is discussed. Bands of the  $v''=3, 4, 5$  progressions of the ICl<sub>g</sub> spectrum have been identified and for them the isotopic shifts are opposite in sign to that of the higher  $v'$  members of the  $v''=0$  progression previously recorded. Examination of the  $G', \omega_v'$  data showed that a third parabola, in addition to the two previously recorded by Curtis and Darbyshire, is now required to represent the observations. The revised values of vibrational and related constants for the ICl molecule are as follows (in  $\text{cm}^{-1}$  units):

$$\omega_0' = 209.7, \quad \omega_e' = 212.3, \quad \omega_0'' = 383.0, \quad \omega_e'' = 384.6,$$

$$v_{\text{head}}^{00} = 13655.3(1.686\text{ Volt}), \quad v_{\text{el}} = 13742(1.695V),$$

$$v_{\text{con.}}^{00} = 17343(2.139V), \quad D_0' = \int_0^{v_0} \omega_v dv = 3690(0.455V)$$

$$D_0'' (\text{extrap.}) = 23069(2.847V), \quad D_0'' - (D_0' + v^{00}) = 5724(0.706V).$$

### INTRODUCTION

IN RECENT years the absorption band spectrum of ICl has received considerable attention from experimental and theoretical physicists. In the visible region it has been photographed and analysed by Gibson and Ramsperger,<sup>1</sup> Wilson,<sup>2</sup> Patkowski and Curtis.<sup>3</sup> In this region the spectrum of

<sup>1</sup> G. E. Gibson and H. C. Ramsperger, Phys. Rev. **30**, 598 (1927).

<sup>2</sup> E. D. Wilson, Phys. Rev. **32**, 611 (1928).

<sup>3</sup> J. Patkowski and W. E. Curtis, Trans. Faraday Soc. **25**, 725 (1929).

the  $\text{ICl}_{35}$  molecule consists of portions of four progressions ( $v'' = \text{constant}$ ) the longest of which (progression I) proceeds, according to Wilson, to convergence near  $\lambda 5736\text{\AA}$ . Progressions II and III are displaced with reference to I about  $380$  and  $760\text{ cm}^{-1}$  to the red respectively. Under normal conditions progression IV is weak and though several members of this progression were identified by Patkowski and Curtis no measurements have yet been recorded. A portion of the spectrum of the  $\text{ICl}_{35}$  molecule in the visible has also been been measured by the same workers although Wilson did not recognize it as such.

From observations of the effect of temperature on the relative intensities of I and II and calculations based on the Maxwell-Boltzmann formula applied to the distribution of vibrational energy among the  $v'$  progressions, Gibson concluded that for progression I  $v'' = 1$ . The implication was that molecules in the lowest vibrational state are not, on excitation, raised to other quantised energy levels but are dissociated, so that instead of bands continuous absorption results. According to Kuhn<sup>4</sup> this was the case for chlorine. By methods based on the isotope effect Patkowski and Curtis<sup>3</sup> have established that Gibson and Ramsperger were in error and that for progression I  $v'' = 0$ . More recently, Birge<sup>5</sup> has shown that Kuhn's result for  $\text{Cl}_2$  is incorrect and that in this case also the first progression must be due to molecules in the lowest vibrational state ( $v'' = 0$ ).

Curtis and Darbyshire<sup>6</sup> have pointed out the difficulty of deciding the  $v''$  numeration by measuring the relative intensities of a band at two temperatures. Using a method which depended on the recognition of equal intensities at two temperatures and which was free from other possible sources of error common to Gibson and Ramsperger's and Kuhn's methods they attempted to determine the cause of the inconsistency between the results obtained by the temperature variation and isotope methods. It was found that superposed on the band absorption was a continuous absorption which increased with temperature. Allowing for this by measurements made by means of a self-recording microphotometer there was strong evidence to support the conclusion previously reached by Patkowski and Curtis, namely that it was progression II and not progression I which was to be identified with  $v'' = 1$ , and that the first and longest progression originates in the lowest vibrational state,  $v'' = 0$ .

For the determination of the absolute numeration of the upper levels the temperature method is not available but in favorable cases it may be deduced by analysis of the fluorescent spectrum or from measurements of separations of isotopic band heads. The latter method was applied to ICl by Gibson<sup>7</sup> and by Patkowski and Curtis,<sup>3</sup> substantially the same conclusion being arrived at by both pairs of workers. In this paper the  $v''$  and  $v'$  numeration used is that found by Patkowski and Curtis.

<sup>4</sup> H. Kuhn, *Zeits. f. Physik* **39**, 77 (1926).

<sup>5</sup> Private communication to Professor Curtis.

<sup>6</sup> W. E. Curtis and O. Darbyshire, *Trans. Faraday Soc.* **117**, 78 (1931).

<sup>7</sup> G. E. Gibson, *Zeits. f. Physik* **50**, 692 (1928).

Under normal conditions of temperature and pressure bands of progression I for which  $v' < 7$  and bands of progression II for which  $v' < 6$  are too weak to be measured. Calculation based on the Maxwell-Boltzmann formula gives the result that when the pressure is maintained constant and the temperature raised from 15°C to 200°C I should decrease in intensity, II should remain unchanged whilst III and higher progressions should be strengthened (reference 6, Table I and Fig. 2). This was verified experimentally. It is to be expected therefore that by raising the temperature of the ICl considerably and increasing the pressure the lower  $v'$  members of the higher progressions might be developed. It was thought possible in this way (1) to confirm directly the accepted  $v'$  numeration, (2) to extend the known  $\omega_{v'}$  values to  $v' = 0$ , so making more complete the  $\omega_{v'}, v'$  curve, of importance for the calculation of dissociation energy,<sup>8</sup> (3) to determine  $\omega_0', \omega_0''$  directly so that the vibrational constants of the ICl molecule might be determined more accurately than those previously obtained by extrapolation, (4) if several higher  $v'$  progressions are developed, to examine the variation of the  $\omega_{v''}$  values with  $v''$  (5) to determine whether for values of  $v' < 9$  the  $G', \omega_{v'}$  parabola is identical with that found from  $v' = 9$  to  $v' = 18$ , that is, whether the corresponding law of force holds right down to the lowest levels in the excited state.

#### EXPERIMENTAL PROCEDURE

The tube containing the ICl vapor was the one previously used by Curtis and Darbyshire.<sup>6</sup> It was of Pyrex, 240 cm long, 2.5 cm in diameter, and had a side tube about 20 cm long and 5 mm internal diameter bent twice at right angles and containing ICl. Previous experience had proved that much of the trouble due to dissociation was a consequence of insufficient drying and that it was advisable to leave a little  $P_2O_5$  in the apparatus permanently between the main tube and the reservoir. According to Gibson  $I_2$  bands are strongly in evidence above 200°C but with the above apparatus it was found that a temperature of 400°C could be maintained indefinitely without any trace of dissociation. Immediately in contact with the tube was wound uniformly a length of fine copper wire of resistance 7.97 ohms at 18°C. Around this was a layer of asbestos, then a heating coil of nichrome wire evenly spaced except near the ends where the windings were closer and wound over metal tubes provided with glass windows to prevent condensation on the tube windows. Over the heating coil was additional asbestos lagging. Measurement of the resistance of the copper wire made it possible to estimate fairly accurately the temperature of the ICl. The vapor pressure could be varied by means of a subsidiary heating coil wound on an insulated metal sheath enclosing the side tube the temperature of which was indicated by a thermometer in contact with it.

The source of light was a Neron pointolite of 100 c.p. run at 1.8 amp. A lens of focal length 5 cm directed a fairly parallel beam along the axis of the

<sup>8</sup> The notation used in this paper is that recommended by Mulliken (Reviews of Modern Physics 2, pp. 60 and 115. (1930)) who defines  $\Delta G(v)$  as  $G(v + \frac{1}{2}) - G(v - \frac{1}{2})$ .  $\omega_v$ , the classical frequency of vibration as used here is the mean of  $\Delta G(v)$  and  $\Delta G(v+1)$  and refers to the molecule in half-integral quantum, and therefore possible, vibrational states.

tube. The spectrograph used throughout was a large Littrow two-prism instrument having a dispersion of about 8A in the red. Kodak Extreme Red and Kodak Infrared plates were used being hypersensitized before exposure by immersion for 45 seconds in a bath containing 3.5 cc of 0.880 ammonia in 100 cc of water and then dried rapidly in a current of hot air from an electric fan.

Exposures ranged from 30 minutes to 3 hours according to slit width and density of the ICl vapor. The temperatures of the side tube and main tube were kept practically constant during each exposure but for different exposures were within the ranges 80°C to 100°C and 200°C and 400°C respectively. Measurements were made on ten different plates by a Hilger L 13 comparator.

#### RESULTS

In Table I are set out measured wave-numbers in vacuo ranging from progression II to progression VIII. The values given are in most cases the means of four independent determinations. Deviations from the mean were satisfactorily small. (W) indicates values obtained by Wilson. Except for III9 and III8 agreement is good. The III8 head is unusually diffuse and apparently an accurate setting is difficult: though one may obtain a consistent result by setting on the same grain aggregation the corresponding value may be several units in error. The mean of Wilson's and my value is given in square brackets as are also the corresponding differences. On account of the uncertainty attaching to this value these differences are not taken into account in calculating  $\omega_8'$ ,  $\omega_9'$  and  $\omega_1''$ ,  $\omega_2''$ .

It is seen that the higher the  $v'$  progression (greater  $v''$ ) the smaller is the extent of its development and the more does the maximum of intensity within a progression approach the origin ( $v' = 0$ ). Both experimental facts are readily explained by reference to the Franck-Condon potential energy curves (Fig. 2). In the case of no progression was the  $v' = 0$  head measurable although a contrasty enlargement revealed faint indications of its existence in VI and VII.

Owing to the limited extent to which the progressions are developed and the steepness of the intensity gradients in each of the higher progressions the presence or absence of  $v' = 0$  could not be taken as conclusive evidence of the correctness of the accepted numeration.

The  $\omega_v''$  values from  $v'' = 1$  to  $v'' = 5$  are such as to give constant differences between themselves successively within the limits of experimental error as is required by theory, but the  $\omega_5''$ ,  $\omega_6''$  difference is considerably less than it should be for a linear increase of  $\omega_v''$  with  $v''$ . It is unfortunate that further values of  $\omega_v''$  for higher  $v''$  numbers are not measurable to decide whether there is here a definite discontinuity.

#### THE VIBRATIONAL CONSTANTS OF THE ICl MOLECULE

The fundamental vibration frequencies of the ICl molecule have been estimated by Patkowski and Curtis<sup>3</sup> by extrapolation of the experimental  $\omega_u$  values determined at that time and assuming a linear variation of  $\omega_u$  with  $u$ . In the formula  $\omega_u' = \omega_0' - \alpha'u'$  they substituted  $\alpha' = 6.594$  giving  $\omega_0' = 223.7$

TABLE I.

$v'$	$\Delta G''(1)$	1 (II)	$\Delta G''(2)$	2 (III)	$\Delta G''(3)$	3 (IV)	$\Delta G''(4)$	4 (V)	$\Delta G''(5)$	5 (VI)	$\Delta G''(6)$	6 (VII)	$\Delta G''(7)$	7 (VIII)	Mean $\Delta G''(\bar{v})$	$\omega_v'$
9		14060.8 (V)	378.1	14582.7 14581.0(W) 14580.8	375.4	14207.3									163.7 = $\omega_9$	
8		14794.6 171.9	[378.7]	[14415.9] 14414.0(W) 14414.0	[374.9]	14041.0									166.3 169.1 = $\omega_8$	
7		14622.7	378.7	14244.0	374.7	13869.3									171.8 174.7 = $\omega_7$	
6		14445.2	378.8	14066.4	374.8	13691.6									177.6 179.9 = $\omega_6$	
5		14262.7	378.2	13884.5	374.7	13509.8	373.0	13136.8							182.1 185.2 = $\omega_5$	
4		14074.7				13320.7	371.7	12949.0	368.2	12580.8					188.3 190.6 = $\omega_4$	
3		13882.9				193.2	371.1	12756.4	369.4	193.8	365.5	12021.5			192.9 195.3 = $\omega_3$	
2						196.9	372.5	12558.1	368.8	197.7	365.6	11823.7	363.5	11460.2	197.7 200.1 = $\omega_2$	
1						12930.6				202.5	365.5	202.4			202.5 = $\omega_1$	
Mean $\Delta G''(\bar{v})$			378.45		374.90		372.08		368.80		365.53		363.5			
$\omega_v'$		379.82 = $\omega_1$		376.68 = $\omega_2$		373.49 = $\omega_3$		370.44 = $\omega_4$		367.15 = $\omega_5$		364.5 = $\omega_6$				
Diffs.			3.14		3.19		3.05		3.29		2.65					

$\text{cm}^{-1}$  as the fundamental frequency i.e., in the lowest attainable vibrational level ( $u' = \frac{1}{2}$ ) of the excited state. For the normal state for which from Wilson's  $\omega_1''$ ,  $\omega_2''$  values  $\alpha'' = 1.4$ , they gave  $\omega_0'' = 382.0 \text{ cm}^{-1}$ . Actually the  $\omega_v'$ ,  $v'$  curve for the excited state is known not to be linear<sup>6</sup> and indeed, the results here given indicate that the departure is greater than was first supposed (see later). By a graphical extrapolation of one unit of  $v'$  the value of  $\omega_0'$  according to the present measurements is given as  $209.7 \text{ cm}^{-1}$ . Assuming the linearity of the  $\omega_v''$ ,  $v''$  law, as appears justifiable from measured values from  $\omega_1''$  to  $\omega_4''$ ,  $\omega_0'' = 383.0 \text{ cm}^{-1}$ . Taking the binding force as proportional to the square of the vibration frequency the decrease in this force due to excitation would be 3.38:1 as against the previous value 2.9:1 (Patkowski and Curtis). For  $\text{Cl}_2$  and  $\text{I}_2$  the ratios are 3.2:1 and 2.8:1 respectively so far as is at present ascertainable. Analysis of the rotation structure according to Patkowski and Curtis<sup>9</sup> shows that as expected, the increase in the moment of inertia of the ICl molecule on excitation is considerable being in the ratio 1.31:1.

Mecke<sup>10</sup> and Morse<sup>11</sup> have pointed out independently that in the case of many molecules an empirical relation exists of the form  $\omega_0 r_0^p = a$  constant,  $K$ , where  $r_0$  is the nuclear separation in the equilibrium position. If  $\omega_0$  is in  $\text{cm}^{-1}$  and  $r_0$  in  $\text{Å}$  then according to Mecke  $p = 2$  and  $K$ , though the same for any one molecule in its lower and upper states, is different for different molecules. Morse, from examination of 56 molecules, favors  $p = 3$  and  $K = 3000$  for all molecules. Mecke's law is not well obeyed by  $\text{I}_2$ ,  $\text{Cl}_2$  or ICl, for solution of the equation  $\omega_0' r_0'^p = \omega_0'' r_0''^p$  leads to the values  $p = 4.2$  for  $\text{I}_2$ , 4.3 for  $\text{Cl}_2$  and 4.4 for ICl, the corresponding values of  $K$  being about 13000, 10500, and 15000, respectively.  $\text{I}_2$  and  $\text{Cl}_2$  conform to Morse's law rather better than does ICl, the deviation in every case being greater for the lower than for the higher state. The values of  $K'$  and  $K''$  in  $\omega_0' r_0'^3 = K'$ ,  $\omega_0'' r_0''^3 = K''$  are as follows:  $\text{I}_2$ ,  $K' = 3486$ ,  $K'' = 4036$ ;  $\text{Cl}_2$ ,  $K' = 3316$ ,  $K'' = 4328$ ; ICl,  $K' = 3872$ ,  $K'' = 4695$ . Morse found that his formula was least satisfactorily obeyed by the least symmetrical molecules, so that the greater deviation here found in the case of ICl as compared with  $\text{I}_2$  and  $\text{Cl}_2$  is evidently attributable to its relative nonsymmetry.

The frequency of the  $v'' = 0$ ,  $v' = 0$  band-head,  $\nu_{\text{head}}^{00}$ , is found to be  $13655.3 \text{ cm}^{-1}$  by extrapolation of one unit of  $v'$ . The separation of this head from the origin of the band, calculated by means of the rotational data,<sup>9</sup> is  $0.37 \text{ cm}^{-1}$ . The electronic frequency,  $\nu^{el}$ , associated with the system is given by  $\nu_{\text{head}}^{00} = \nu^{el} + \omega_0' u' - \omega_0 x' u'^2 - \omega_0'' u'' + \omega_0'' x'' u''^2$  in which  $u' = \frac{1}{2}$ ,  $u'' = \frac{1}{2}$ ,  $\omega_0' x' = 2.6$  (determined from observed  $\nu$ 's from  $v' = 1$  to  $v' = 10$ ) and  $\omega_0'' x'' = 1.58$ , as  $13742 \text{ cm}^{-1}$ .

The convergence limit of progression I was given by Wilson as  $17430 \text{ cm}^{-1}$ . Extrapolation of his  $\nu$  values set out on reference 2, page 613 gives its value as  $17341 \text{ cm}^{-1}$ . Following the method of Birge and Sponer<sup>12</sup> an inte-

<sup>9</sup> J. Patkowski and W. E. Curtis, *Nature*, May 9, 1931.

<sup>10</sup> R. Mecke, *Zeits. f. Physik* **32**, 823 (1925).

<sup>11</sup> P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

<sup>12</sup> R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 259 (1926).

graph evaluation of the area under the  $v'$ ,  $\omega_v'$  curve (Fig. 1) between the limits  $v'=0$  and the value of  $v'$  for which  $\omega_v'$  vanishes ( $D_0' = 3690 \text{ cm}^{-1} = 0.455 \text{ V}$ ) leads to the value  $17345 \text{ cm}^{-1}$ , or 2.139 volts, for the limit.<sup>13</sup>

#### THE POTENTIAL ENERGY CURVES OF ICI

Within the limits of experimental error the  $\omega_v''$  values decrease linearly as  $v''$  increases from 1 to 6. Assuming the same law to hold to the limit of convergence in the lower state, the energy of dissociation in this state reckoned from the equilibrium position (zero vibrational energy) is  $23260 \text{ cm}^{-1}$  ( $D_e'' = 2.870 \text{ V}$ ). Reckoned from the  $v''=0$  level it is  $23069 \text{ cm}^{-1}$  ( $D_0'' = 2.847 \text{ V}$ ),

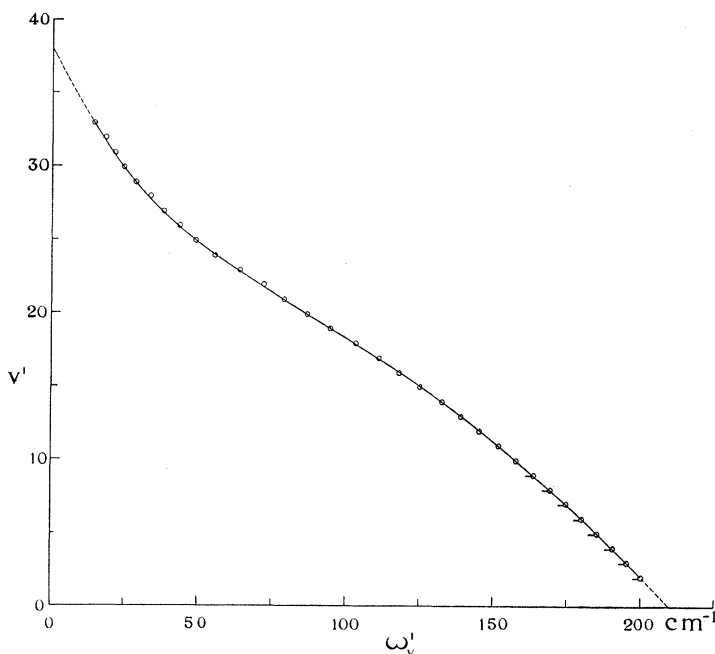


Fig. 1.  $v'$ ,  $\omega_v'$  curve. Circles, Wilson's observations; circles with dashes, present observations; dotted line, extrapolation to  $\omega_0'$  and to  $\omega_v'=0$ .

that is,  $5724 \text{ cm}^{-1}$  or  $0.706 \text{ V}$  greater than the energy required to dissociate the molecule by raising it from the same level to the higher state and increasing its vibrational energy in that state.

In Fig. 2 are shown the potential energy, nuclear separation curves for the ICI molecule in the lower and higher states calculated from the formula given by Morse<sup>11</sup> written in the form

$$U(r) = A + D_e[e^{-a(r-r_0)} - 1]^2$$

<sup>13</sup> Following the publication of a brief summary of the results of the present work (Letter to Phys. Rev. **39**, 162 (1932) I have received a communication from W. G. Brown in which he states that he has redetermined the convergence frequency of the  $v''=0$  progression from his own recent measurements and obtained a result  $2.142 \pm .003$  volts, which supports the correction here suggested.

where, for the lower state,  $A'' = 0$ ,  $D_e'' = 23260 \text{ cm}^{-1}$ ,  $r_0'' = 2.306 \text{ \AA}$ ,  $a'' = 1.657$ . In the calculation of the curve for the higher state the observed value of  $D_e'$ ,  $3794 \text{ cm}^{-1}$ , is used.  $a' = 2.264 \text{ \AA}$ ,  $A' = 13742 \text{ cm}^{-1}$ . The values of  $r_0'$  and  $r_0''$  are those derived by Patkowski and Curtis from their analysis of the rotational structure.

The crossing of the potential energy curves and the large excess of  $D_0''$  over  $\nu^{00} + D_0'$  by some  $5700 \text{ cm}^{-1}$  are features of interest in connection with the question of the products of dissociation of ICl. It is now generally ac-

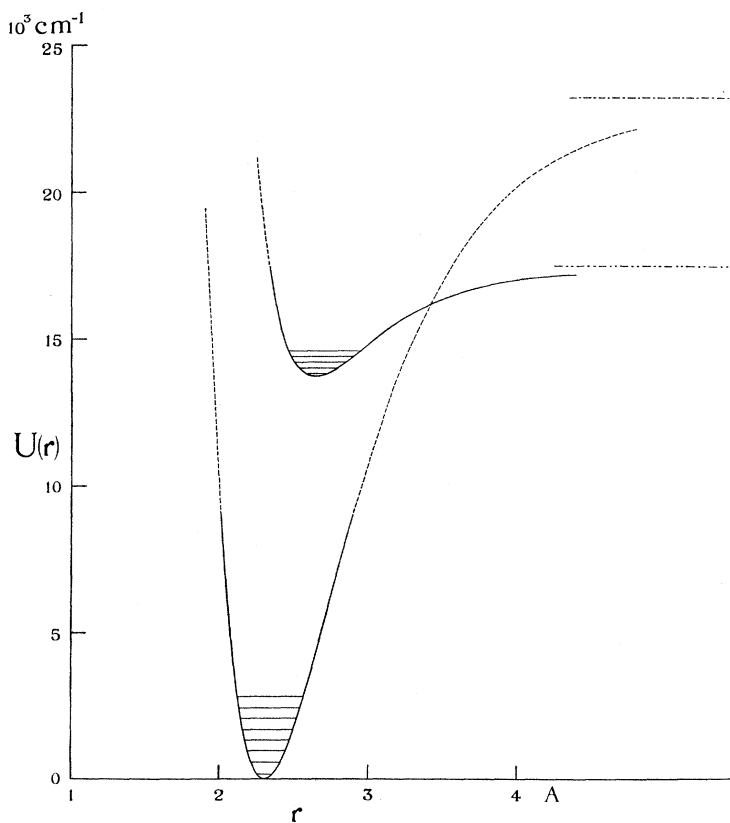


Fig. 2. Potential energy, nuclear separation curves. Horizontal lines represent vibrational levels; only a few of the observed upper state levels are represented.

cepted that the products of dissociation of the upper state of  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  are, in each case, a normal  $^2P_{3/2}$  atom and an excited  $^2P_{1/2}$  atom, the lower state yielding two normal atoms on dissociation. The experimental evidence for this is strongest in the case of  $\text{I}_2$  for which the value of  $D_0' + \nu^{00} - D_0''$  can almost certainly be identified with the separation of the deepest  $^2P$  levels. The determination of  $D_0''$  spectroscopically involves invariably a long extrapolation of the levels in the lower state to convergence which gives, in general, and excessive value for  $D_0''$ . Iodine provides one of the most favorable cases for such extrapolation, for, by resonance methods the lowest 26 levels have been



observed. The extrapolation is from  $v'' = 27$  to  $v'' = 112$ , corresponding to 65 percent of  $D_0''$ . The value of  $D_0''$  obtained in this way is 1.67 volts which agrees fairly well with the thermochemical value 1.50 volts. Since  $D_0' + \nu^{00} = 2.47$  volts, the calculated excitation energy is  $2.47 - 1.50 = 0.97$  volt, which is sufficiently near the value, 0.94 volt, given by Turner for  ${}^2P_{3/2} - {}^2P_{1/2}$  to justify the belief that the dissociation of the upper state leads to a normal  ${}^2P_{3/2}$  atom and an excited  ${}^2P_{1/2}$  atom. If, now, we subtract 0.94 from 2.47 we obtain indirectly the value 1.53 volts for  $D_0''$ . It is to be noted that this value depends entirely on spectroscopic data.

In the case of ICl there are not yet any resonance or thermochemical data to make a similar method of determination of  $D_0''$  possible. It may be that the long extrapolation from  $v'' = 6$  to  $v'' = 121$ , corresponding to 90 percent of  $D_0''$  leads to a value of  $D_0''$  much too high and that there is actually no crossing of the potential energy curves. Recently there has been some discussion as to whether dissociation of the upper state of ICl yields two normal atoms or a normal I atom and an excited Cl atom. That the former alternative was the more probable was suggested by Gibson and Ramsperger<sup>1</sup> on the basis of a correlation of spectroscopic and thermochemical data and also in view of their interpretation of two other systems beyond convergence of the main system, the convergence limit of one corresponding to dissociation into an excited Cl atom and a normal I atom, and that of the other to dissociation into an excited I atom and a normal Cl atom. Chemical experiments by Rollefson and Lindquist<sup>14</sup> have given evidence to support this suggestion and Mulliken<sup>15</sup> holds that it is in harmony with theory. It is supposed that, as in the case of  $I_2$ , the lower state leads to normal atoms on dissociation. Accepting Gibson and Ramsperger's suggestion regarding the upper state and remembering that ICl is comparatively polar it is evident that we cannot rely on a close analogy between the two molecules. If, indeed,  $D_0''$  for ICl is greater than  $D_0' + \nu^{00}$  by an amount which can be identified with the separation of the deepest  ${}^2P$  levels of I or Cl then it may be that the ICl molecule exhibits the same binding characteristics as  $N_2^+$ ,<sup>16</sup> namely, dissociation into normal atoms from the upper state and into an excited atom and an unexcited atom from the lower one. The excess found by extrapolation is 0.71 volt whilst the excitation energy of the I atom is 0.94 volt and that of the Cl atom is 0.11 volt, so that, if we regard the present value of  $D_0''$  merely as an upper limit the possibility of an excited I atom resulting from dissociation is ruled out and there remain the two alternatives, excited Cl and normal I, or two normal atoms.

#### THE ISOTOPE EFFECT

Band heads of the weaker  $ICl_{37}$  system hitherto measured<sup>3,5</sup> are  $v' = 12$  to  $v' = 26$  of progression I and  $v' = 8$  to  $v' = 13$  of progression II. The  $ICl_{37}$  progression I heads are from 31 to 37  $cm^{-1}$ , and progression II heads from 17 to

<sup>14</sup> G. K. Rollefson and F. F. Lindquist, J. Am. Chem. Soc. **52**, 2793 (1930); **53**, 1184 (1931).

<sup>15</sup> R. S. Mulliken, Phys. Rev. **37**, 1412 (1931).

<sup>16</sup> G. Herzberg, Ann. d. Physik **86**, 189 (1928). W. Heitler and G. Herzberg, Zeits. f. Physik **53**, 52 (1929).

29 cm<sup>-1</sup>, to the less refrangible side of the ICl<sub>35</sub> heads. Patkowski and Curtis showed that in the case of ICl the Mulliken theory of isotopic separation leads to the result that the separation must have a maximum value in the neighborhood of  $v' = 17$  for all progressions, that for a given  $v'$  the separation is less the higher the progression i.e., the greater  $v''$ , and that in the case of any one progression the separation diminishes parabolically from the vertex at  $v' = 17$  for  $v''$ 's greater and less than 17. In every progression therefore, there are two critical  $v''$ 's for which the separations are about zero and for  $v''$ 's less than the lower critical  $v'$  and greater than the higher critical  $v'$  the ICl<sub>37</sub> heads will be on the *more* refrangible side of the corresponding ICl<sub>35</sub> heads. The lower critical  $v'$  is greater the higher the progression. These observations are clearly illustrated in reference 3, Fig. 2, where it appears that in the region of the present measurements the isotopic separations in progressions IV, V, VI and VII should be opposite in sign to those previously observed in I and II and large enough to make fairly accurate measurements possible especially as the ICl<sub>37</sub> heads will be clear of the rotation structure of ICl<sub>35</sub> bands.

Actually on the plates there appear six or seven heads which cannot be attributed to ICl<sub>35</sub>. Six are strong and sharp enough to give reliable measurements and they are on the violet side of the corresponding ICl<sub>35</sub> heads as expected. Calculations of the separations as predicted by the Mulliken formula in which the present values of  $\omega_0''$ ,  $\omega_0'$ ,  $\omega_0''x''$ ,  $\omega_0'x'$  are used made it possible to identify the heads with certainty. Table II shows that in all cases agreement between observed and calculated values is good.

TABLE II.

$v''$	$v'$	ICl <sub>35</sub> (Obsvd.)	ICl <sub>37</sub> (Obsvd.)	ICl <sub>37</sub> (Calcd.)	Separation (Obsvd.)	Separation (Calcd.)
3	4	13320.7	13329.5	13330.7	8.8	10.0
3	5	13509.8	13515.5	13516.5	5.7	6.7
4	4	12949.0	12966.2	12966.7	17.2	17.7
4	5	13136.8	13151.1	13151.2	14.3	14.4
5	3	12387.0	12415.3	12415.6	28.3	28.6
5	4	12580.8	12605.1	12605.9	24.3	25.1

THE RELATIONS BETWEEN G,  $\omega_v$  AND  $v$

It is customary to express the available vibrational energy of the diatomic molecule, to a first approximation, in the form

$$G = \omega_0 v - \omega_0 x v^2 \tag{1}$$

the energy being expressed in cm<sup>-1</sup> units and  $\omega_0$  and  $x$  constants for the same molecular state.

The classical frequency of vibration, in cm<sup>-1</sup> units, is given by the derivative of  $G$  with respect to  $v$  so that

$$\omega_v \equiv \frac{dG}{dv} = \omega_0 - 2\omega_0 x v. \tag{2}$$

To a first approximation (1) and (2) are found to hold for many diatomic molecules.

It is easily shown that if, as assumed by Birge,<sup>17</sup>

$$G = a + b\omega_v + c\omega_v^2 \quad (3)$$

then, for cases in which Eqs. (1) and (2) are strictly true so that  $\omega_v = f(v)$  is linear,  $b=0$  and a plot of  $dG/d\omega_v$  against  $\omega_v$  gives a straight line through the origin of coordinates. Often, however,  $b$  is not zero and may be negative or positive. The corresponding  $v$ ,  $\omega_v$  graphs are said to have negative or positive curvature respectively. The  $G$ ,  $\omega_v$  parabolas have vertices on ordinates through the points of intersection of the  $dG/d\omega_v$ ,  $\omega_v$  straight lines with the  $\omega_v$  axis so that if  $b$  is negative  $G_{\text{max}}$  occurs at a negative value of  $\omega_v$ , and if  $b$  is positive  $G_{\text{max}}$  occurs at a positive value of  $\omega_v$ .<sup>18</sup>

Birge<sup>17</sup> has pointed out that the  $v'$ ,  $\omega_v'$  graphs for  $O_2$ ,  $I_2$ ,  $Br_2$ ,  $Cl_2$ , and  $ICl$  are not linear, and that in each case there is a point of inflection between portions of positive and negative curvature (Fig. 1). Curtis and Darbyshire<sup>6</sup> showed that in the case of  $ICl$  the  $G'$ ,  $\omega_v'$  curve was indeed composite: for its complete representation two parabolas, one corresponding to positive, the other to negative, curvature were required.

If to  $G'$  (Eq. 3) be added the electronic energy the constants  $a$ ,  $b$  and  $c$  for these parabolas were given by them as follows:

$$(I\ 19—I\ 28) \quad a = 17291.2, \quad b = -1.5471, \quad c = -0.05499. \quad (A)$$

$$(I\ 9—I\ 18) \quad a = 16734.2, \quad b = -9.6975, \quad c = -0.11095. \quad (B)$$

These two parabolas will henceforth be referred to as parabolas  $A$  and  $B$  respectively.

The slopes of the  $dG'/d\omega_v'$ ,  $\omega_v'$  curves were thus  $-0.110$  and  $-0.222$  respectively, intersecting at  $\omega_v' = 100$ .

The physical interpretation of this double parabola representation is that at the  $G'$ ,  $\omega_v'$  values corresponding to the point of contact of the parabolas there is an abrupt change in the law of force and in neither case, since  $b \neq 0$ , can Eq. (1) be strictly true.

Similar discontinuities have been examined by Birge ( $O_2$ ,  $I_2$ ),<sup>17</sup> Elliott ( $Cl_2$ ),<sup>19</sup> and Brown ( $Br_2$ ).<sup>20</sup>

With a view to determining whether the present I 1—I 9 measurements were represented by the same parabola as I 9—I 18 the known  $G'$ ,  $\omega_v'$  values for  $ICl$  were plotted and a careful plot of the  $dG'/d\omega_v'$ ,  $\omega_v'$  curve made. Points in this latter plot lay remarkably well on two straight lines between points corresponding to I 23 and I 9 the point of intersection being at  $\omega_v' = 107$  i.e., between  $v' = 17$  and 18. Below I 9, however, there was a sudden upward deviation of the  $dG'/d\omega_v'$ ,  $\omega_v'$  line (plotted with coordinates as in Fig. 3) the new

<sup>17</sup> R. T. Birge, *Trans. Faraday Soc.* **25**, 707 (1929).

<sup>18</sup> This is not in accord with Birge's statement that when  $b$  is negative  $\omega_v$  for the corresponding parabola vertex is positive. On pp. 709, 711 reference 17 there are inconsistencies in nomenclature, due, presumably, to attributing the wrong sign to  $\Delta E_u$ .

<sup>19</sup> A. Elliott, *Proc. Roy. Soc.* **A127**, 638 (1930).

<sup>20</sup> W. G. Brown, *Phys. Rev.* **38**, 1179 (1931).

TABLE III. Values of  $\nu$  from  $v'=1$   $v'=9$  are from present measurements. The remainder are values given by Wilson except those for  $v'=28$  and  $v'=31$  which have been altered to make his  $\nu$  and  $d\nu$  values consistent.

$v'$	$\nu$	$\Delta G'(v)$	$\omega_{v'}$	Diffs.
1	13862.8			
2	14065.3	202.5	200.1	
3	263.0	197.7	195.3	4.8
4	455.9	192.9	190.6	4.7
5	644.2	188.3	185.2	5.4
6	826.3	182.1	179.9	5.3
7	15003.9	177.6	174.7	5.2
8	175.7	171.8	169.1	5.6
9	342.0	166.3	163.7	5.4
10	503.0	161.0	157.7	6.0
11	657.3	154.3	151.6	6.1
12	806.1	148.8	145.2	6.4
13	947.6	141.5	139.0	6.2
14	16084.1	136.5	132.5	6.5
15	212.6	128.5	124.8	7.7
16	333.7	121.1	117.7	7.1
17	447.9	114.2	110.8	6.9
18	555.3	107.4	103.0	6.8
19	653.8	98.5	94.4	8.6
20	744.0	90.2	86.6	7.8
21	826.9	82.9	78.6	8.0
22	901.2	74.3	71.7	6.9
23	970.2	69.0	63.8	7.9
24	17028.7	58.5	55.1	8.7
25	080.4	51.7	48.6	6.5
26	125.9	45.5	43.1	5.5
27	166.5	40.6	37.7	5.4
28	201.3	34.8	33.1	4.6
29	232.7	31.4	28.2	4.9
30	257.7	25.0	24.2	4.0
31	281.0	23.3	21.2	3.0
32	300.1	19.1	17.8	3.4
33	316.6	16.5	14.0	3.8
34	328.0	11.4		

slope being between 0.37 and 0.42 whereas the slope for I 9-18 was 0.26. Further, examination of successive differences (Table III) showed discontinuities near corresponding  $\omega_v''$ 's. It was therefore decided to apply the method of least squares to the observations.

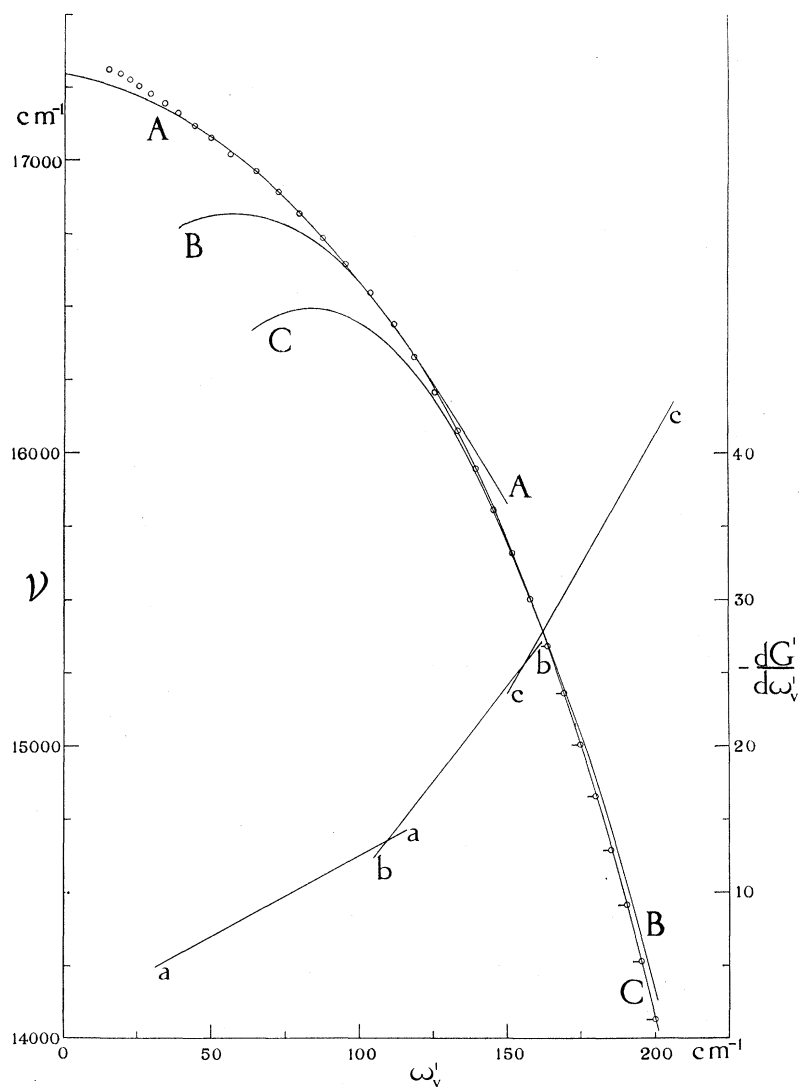


Fig. 3. *AA*, *BB*, *CC*, calculated  $G'$ ,  $\omega_v'$  parabolas. Circles, Wilson's observations; circles with dashes, present observations; *aa*, *bb*, *cc*,  $dG'/d\omega_v'$ ,  $\omega_v'$  lines. ( $dG'/d\omega_v' = d\nu/d\omega_v'$ )

Starting from I 10 for which Wilson and Patkowski and Curtis found independently that  $\nu = 15503.0 \text{ cm}^{-1}$  progression I was extended to I 1 using the observed  $\omega_v'$  values.<sup>21</sup> First the constants for parabola *B* were recal-

<sup>21</sup> Calculation of band-head, band-origin separations for the bands concerned showed that

lated to correct for errors in  $\omega_{\nu}'$  values used previously. The corrected constants were:

$$a = 16397.8, \quad b = 14.7880, \quad c = -0.129854$$

The calculated slope 0.260 agreed with the directly plotted slope. The extrapolation of this parabola to I 1 showed consistently bad agreement with experimental observations whilst an attempt to represent I 1—I 18 by a single parabola led to systematic 0–C errors indicative of a discontinuity about I 9. A least squares determination of the parabolic representation of the I 1 to I 9 gave the constants

$$a = 15296.4, \quad b = 28.9862, \quad c = -0.175502. \quad (\text{Parabola } C).$$

The change of slope of the  $dG'/d\omega_{\nu}'$ ,  $\omega_{\nu}'$  line in the neighborhood of I 9 is thus from 0.260 to 0.351 the change occurring at  $\omega_{\nu}' = 155.5$  i.e. near  $\nu' = 10$ . The change of slope for parabolas *A* and *B* is from 0.110 to 0.260 at  $\omega_{\nu}' = 109.1$  i.e. at  $\nu' = 17$ . It is worthy of remark that the discontinuity between *A* and *B* is in the neighborhood of I 16, the band whose abnormal appearance was mentioned by Curtis and Darbyshire and is unexplained so far. It is possible that examination of the rotation structure of this band now being undertaken may produce an explanation.

In Fig. 3 the three calculated parabolas and the corresponding slope-lines are drawn. It is seen that the six observed points nearest the convergence limit do not lie on parabola *A*. In view of the difficulty of obtaining accurate measurements in this neighborhood and the discrepancies in Wilson's tabulated  $\nu$ 's and  $d\nu$ 's previously referred to, the calculated parabola for these points is not recorded. It is almost certain, however, that the slope-line has very nearly the same inclination as that for parabola *A* and does not exhibit the pronounced downward curvature towards the origin found in the case of iodine by Brown.<sup>22</sup>

In conclusion I wish to acknowledge my indebtedness to Professor W. E. Curtis for much encouragement and helpful discussion. My thanks are also extended to Mr. J. L. Scott of the Naval Architecture Department of this College for an integrator determination of the area under the curve in Fig. 1 and for assistance in the preparation of the figures.

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the error in this procedure arising from differences between the separations for bands of the same  $\nu'$  but different  $\nu''$  was less than  $0.1 \text{ cm}^{-1}$  and therefore within the limits of experimental error.

<sup>22</sup> W. G. Brown, Phys. Rev. **38**, 709 (1931).