

## The Pure Rotational Spectrum of ICl

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Frequencies and intensities of a number of lines of the  $J=3\rightarrow 4$  rotational transition of ICl were measured and the spectrum analyzed. Constants obtained for ICl<sup>35</sup> are (in megacycles)

$B_e = 3422.300$ ,  $\alpha_e = 16.060$ ,  $eq_1Q_1 = -2930.0$ ,  $eq_{Cl}Q_{Cl} = -82.5$ . The mass ratio  $\frac{Cl^{35}}{Cl^{37}}$  obtained

from this spectrum is 0.9459801, which appears inconsistent with the most recent mass spectroscopic determination. The molecular dipole moment is approximately  $0.65 \times 10^{-18}$  e.s.u. from intensity measurements.

THE molecule ICl is the first diatomic molecule whose pure rotational spectrum has been investigated by microwave spectroscopy. The value of the molecular constants  $B_e$  and  $\alpha_e$  are fairly accurately known from measurements in higher frequency regions.<sup>1,2</sup> When the pure rotation spectrum is examined under the high resolution afforded by microwave spectroscopy, it is not as simple as might at first be expected, but is split into a large number of lines by nuclear quadrupole effects. Weidner<sup>3</sup> has detected the  $J=0\rightarrow 1$  transition of ICl at a wavelength near 4.5 cm, but encountered some difficulties in interpretation because of the quadrupole splitting. Spectrum of the transition  $J=3\rightarrow 4$  is investigated here and all molecular constants which are involved are evaluated. Both the iodine and chlorine nuclei show electric quadrupole moments, which break up the single transition  $J=3\rightarrow 4$  for the ground state of a single isotopic species into about 150 lines. Fortunately, most of the intensity is concentrated in a smaller number of these, of which about twenty-five have been measured.

### I. EXPERIMENTAL CONSIDERATIONS

Detection of the ICl lines was accomplished by the usual sweeping technique,<sup>4,5</sup> the rectified microwave signal which had traversed an absorp-

tion cell of ICl being amplified and arranged to produce pips on an oscilloscope representing a plot of absorption *versus* frequency. The sweep was repeated at the slow rate of about once per second to allow the use of a narrow band (15 cycles/sec.) amplifier to aid in noise elimination. About 5 milliwatts of microwave power was obtained from a 2K50 microwave oscillator which had been accidentally electrically overloaded so that its normal frequency of oscillation was changed to the region of interest near 27,000 mc. Using a 16-ft. absorption cell, the minimum detectable absorption lines had absorption coefficients of about  $4 \times 10^{-7}$  cm<sup>-1</sup> or  $2 \times 10^{-7}$  nepers/cm.

Because of the reactivity of ICl, the usual silver wave guide could not be used, but was replaced by a 16-ft. stainless steel guide made to standard K-band dimensions by the Superior Tube Company of Norristown, Pennsylvania. This guide had an attenuation of about 10 db at the frequencies used, which proved no great handicap.

The ICl had to be kept from contacting mercury, but greased stopcocks could be used in the gas system because the grease was attacked sufficiently slowly. After opening the absorption cell to the air, there was apparently enough absorption and change in surface conditions to produce reactions with the first few fillings of ICl gas, which reacted and produced very weak lines after standing in the guide a few minutes. Subsequently ICl admitted to the cell appeared to show only very slow reaction.

Since it was desired to measure frequency differences, in particular the isotopic shift, rather

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<sup>1</sup> W. G. Brown and G. E. Gibson, *Phys. Rev.* **40**, 529 (1932).

<sup>2</sup> W. E. Curtis and J. Patkowski, *Phil. Trans. Roy. Soc.* **232**, 395 (1934).

<sup>3</sup> R. T. Weidner, *Phys. Rev.* **72**, 1268 (1947); *Phys. Rev.* **73**, 254 (1948).

<sup>4</sup> C. H. Townes, *Phys. Rev.* **70**, 665 (1946).

<sup>5</sup> W. E. Good, *Phys. Rev.* **70**, 213 (1946).

accurately, arrangement was made for accurately comparing the signal oscillator frequency with side bands produced by mixing outputs of a stabilized microwave oscillator and a quartz crystal oscillator. Thus the quartz crystal oscillator became the standard for measuring frequency differences. Absolute frequencies were measured only by comparing in the same way some of the ICl lines with a known NH<sub>3</sub> line. Additional details of this technique will be described in a subsequent paper.

## II. ANALYSIS OF THE SPECTRUM

Table I lists the ICl<sup>35</sup> lines due to the  $J=3 \rightarrow 4$  transition which were measured, as well as their identification and frequencies calculated from the molecular constants assumed. The quantity  $F_1$  is the angular momentum in units of  $h/2\pi$  resulting from the vector addition of  $\mathbf{J}$  and the angular momentum of the iodine nucleus  $I_1$ .  $F$  is the total angular momentum in units of  $h/2\pi$ , which results from the vector addition of  $\mathbf{J}$  and the spins of both nuclei. Since the quadrupole coupling of the iodine nucleus is much stronger than that of the chlorine nucleus,  $F_1$  is, in most cases, a sufficiently good quantum number for identification of the lines. However, in the particular cases  $J=3$ ,  $F_1=7/2$  and  $J=3$ ,  $F_1=9/2$ , the iodine quadrupole energies are almost identical, and this accidental degeneracy is removed by the energies connected with the Cl quadrupole. Under these conditions,  $F_1$  is a poor means of identifying the levels, and it has been given the combination of values  $7/2$ ,  $9/2$ .

The frequency difference between each line and the center of gravity of the  $F_1=11/2 \rightarrow 13/2$  group of the ground state of ICl<sup>35</sup> was measured by the technique described above. Absolute frequencies were then obtained by measuring the interval between the center of this group and the NH<sub>3</sub> 7,7 line,<sup>6,7</sup> which was found to be  $1621.89 \pm 0.15$  mc. Incidental to these measurements, the NH<sub>3</sub> 8,8 line was found and the interval between it and the NH<sub>3</sub> 7,7 line measured as  $803.54 \pm 0.15$  mc.

Table II lists the values of molecular constants required to give the theoretical frequencies listed

<sup>6</sup> D. K. Coles and W. E. Good, Phys. Rev. **71**, 383 (1947).  
<sup>7</sup> M. W. P. Strandberg, R. Kyhl, T. Wentink, and R. W. Hillger, Phys. Rev. **71**, 326 (1947).

TABLE I. ICl<sup>35</sup> lines of the transition  $J=3 \rightarrow 4$ .

Designation of line	Measured frequency in megacycles	Theoretical frequency in megacycles	Frequency difference	Theoretical relative intensity	
ICl <sup>35</sup> ground vibrational state					
$F_1$					
$3/2 \rightarrow 5/2$	2-3	27194.75	27195.04	-0.30	.13
$3/2 \rightarrow 5/2$	1-2	27202.64	27202.56	0.08	.07
$3/2 \rightarrow 5/2$	3-4	27204.99	27204.84	0.15	.21
$3/2 \rightarrow 5/2$	0-1	—	27211.74	—	.03
$3/2 \rightarrow 7/2$	3-4	27217.51	27217.36	0.15	.21
$5/2 \rightarrow 7/2$	2-3	27221.02	27221.45	-0.43	.15
$5/2 \rightarrow 7/2$	4-5	27225.32	27225.38	-0.06	.29
$5/2 \rightarrow 7/2$	1-2	27228.34	27228.44	-0.10	.10
$1/2 \rightarrow 3/2$	1-2	27242.59	27242.74	-0.15	.06
$1/2 \rightarrow 3/2$	2-3	27254.90	27255.00	-0.10	.16
$7/2$ , $9/2 \rightarrow 9/2$		27283.66			
$7/2$ , $9/2 \rightarrow 9/2$		27286.25			
$7/2$ , $9/2 \rightarrow 9/2$		27292.63			
$7/2$ , $9/2 \rightarrow 9/2$		27295.05			
$7/2$ , $9/2 \rightarrow 11/2$	5-6	27333.85			
$11/2 \rightarrow 13/2$	6-7	27336.68	27336.51	0.17	.99
	5-6				
$11/2 \rightarrow 13/2$	7-8	27337.38	27337.53	-0.15	1.00
	4-5				
$7/2$ , $9/2 \rightarrow 11/2$	3-4	27346.31			
$7/2$ , $9/2 \rightarrow 11/2$	4-5	27354.71			
$7/2$ , $9/2 \rightarrow 11/2$	6-7	27356.58	27356.41	0.17	
$7/2$ , $9/2 \rightarrow 11/2$	5-6	27357.73			
ICl <sup>35</sup> excited vibrational state ( $v=1$ )					
$11/2 \rightarrow 13/2$		27208.54			.31

in Table I. The constants  $B_e$  and  $\alpha_e$  are in agreement with the values  $0.11414 \text{ cm}^{-1}$  and  $0.00050 \text{ cm}^{-1}$ , respectively, given by measurements of Curtis and Patkowski<sup>2</sup> in the visible region. The excited state line at  $27,208.49$  mc from which  $\alpha_e$  was determined was the only line found in the region of lines produced by ICl<sup>35</sup> which could not be fitted to a line of the ground vibrational state. It was of the correct intensity with respect to the corresponding group of lines of the ground vibrational state, and appeared to have the width to be expected from the fact that it is a group of four lines rather than a single line as are its neighbors. The next most intense group of lines ( $F_1=7/2$ ,  $9/2 \rightarrow 11/2$ ) due to ICl<sup>35</sup> in the excited vibrational state is rather widely split by the chlorine quadrupole and hence weak. Its main intensity should fall at about  $27,227$  mc, where it would be confused with lines of the ground state.

TABLE II. Molecular constants for ICl<sup>35</sup> expressed in megacycles.

$B_e$	$3422.300 \pm 0.02$
$\alpha_e$	$16.060 \pm 0.02$
$eq_I Q_I \equiv eQ_I \frac{\partial^2 V_I}{\partial z^2}$	$-2930.0 \pm 4$
$eq_{Cl} Q_{Cl} \equiv eQ_{Cl} \frac{\partial^2 V_{Cl}}{\partial z^2}$	$-82.5 \pm 1$

In addition, this identification of the line at 27208.49 mc gives a value of  $\alpha_e$  which agrees well with that obtained by Curtis and Patkowski. The fact that the iodine quadrupole constant is unusually large and the chlorine constant about the same as in ClCN appears to be consistent with the atomic wave function model.<sup>8</sup> This will be discussed in more detail in a later paper.

The method of Bardeen and Townes<sup>9</sup> was used to analyze the splitting produced by quadrupole moments of iodine and chlorine. The iodine quadrupole coupling is so large, however, that effects of the order  $(eq_I Q_I)^2/B_e$  must be taken into account to obtain a satisfactory fit of the experimental data. Thus  $J$  is not actually fixed, but in the lower state labeled  $J=3$ , values  $J=1$  and  $J=5$  are of some importance, and similarly for the upper state. Expressions for the matrix elements necessary for calculating the shift in energy values produced by these second-order effects are given elsewhere.<sup>10</sup> The magnitude of their contributions to the line positions in this case is of the order of one megacycle.

The lines which involve the degenerate levels ( $J=3$ ,  $F_1=7/2$ ,  $9/2$ ) have not been calculated exactly. A calculation taking into account energies associated with first-order quadrupole interactions for iodine and chlorine and second-order energies  $(eq_I Q_I)^2/B_e$  for iodine was made which gave lines agreeing within about two megacycles with those found experimentally. This probably allows a correct identification of the lines in those cases where values of  $F$  are given in Table I. Second-order energies of the type  $e^2 q_{Cl} Q_{Cl} q_I Q_I/B_e$  and  $(eq_{Cl} Q_{Cl})^2/B_e$  have not yet been taken into account because their calculation is somewhat involved. Although these energies are not large, final energy values for the degenerate levels are very sensitive to small effects, and perhaps inclusion of these remaining second-order effects will give agreement with the measured frequencies. All lines which do not involve degenerate levels were fitted well by the theory and indicate that fairly accurate values of quadrupole coupling constants for iodine and chlorine are obtained.

<sup>8</sup> C. H. Townes, Phys. Rev. **71**, 909 (1947).

<sup>9</sup> J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

<sup>10</sup> J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

No interactions of the form  $cI \cdot J$  are in evidence, although small interactions of approximately the magnitude found by Nierenberg and Ramsey<sup>11</sup> in the alkali halides may be present. The upper limit which may be put on  $|c|$  from the present measurements is 0.05 mc.

### III. THE ISOTOPIC SHIFT

Evaluation of  $\alpha_e$  and analysis of the quadrupole coupling energies should allow an accurate prediction of the isotopic shift from the known isotopic mass ratios. The position of the center of the strongest group of lines ( $F_1=11/2 \rightarrow 13/2$ ) of  $ICl^{35}$  is given theoretically by

$$\nu_{35} = 8B_e - 4\alpha_e - 0.0075757eq_I Q_I + 0.00029 \times [(eq_I Q_I)^2/B_e] + 0.0007eq_{Cl} Q_{Cl}$$

For  $ICl^{37}$ , the value of  $\nu$  should be obtainable from the known  $ICl^{35}$  frequency since  $B_e$  is inversely proportional to the reduced mass  $\mu$  of the molecule and  $\alpha_e$  is inversely proportional to  $\mu^{\frac{1}{2}}$ . The effect of the chlorine quadrupole is very small, and its change can be calculated from the known ratio of quadrupole moments<sup>12,13</sup> of the chlorine isotopes. Taking the isotopic masses from Mattauch<sup>14</sup> and using the numerical values of  $B_e$ ,  $\alpha_e$ ,  $q_I Q_I$ , and  $q_{Cl} Q_{Cl}$  obtained here, the isotopic shift should be

$$\begin{aligned} \nu_{35} - \nu_{37} &= 8B_e \left( 1 - \frac{\mu_{35}}{\mu_{37}} \right) - 4\alpha_e \left[ 1 - \left( \frac{\mu_{35}}{\mu_{37}} \right)^{\frac{1}{2}} \right] \\ &\quad \times 0.0029 \frac{(eq_I Q_I)^2}{B_e} \left( 1 - \frac{\mu_{37}}{\mu_{35}} \right) \\ &\quad + 0.0015eq_{Cl} Q_{Cl} \left( 1 - \frac{Q_{Cl}^{37}}{Q_{Cl}^{35}} \right) \\ &= 1160.259 - 4.040 - 0.031 - 0.012 \\ &= 1156.176 \text{ megacycles.} \end{aligned}$$

The measured frequency difference between the center of the group of lines  $11/2 \rightarrow 13/2$  for  $ICl^{35}$  and  $ICl^{37}$  was  $1155.40 \pm 0.10$  megacycles. This measurement thus appears to give a difference

<sup>11</sup> W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

<sup>12</sup> C. H. Townes, A. N. Holden, J. Bardeen, and F. R. Merritt, Phys. Rev. **71**, 644 (1947).

<sup>13</sup> W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **72**, 344 (1947).

<sup>14</sup> J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers, Inc., New York, 1946).

between the two chlorine masses which is about one part in 1500 less than that assumed in making the calculation of isotopic shift. The  $F_1=7/2, 9/2 \rightarrow 11/2$  group of lines of ICl<sup>37</sup> was also found, but was not measured because its width and the weakness of single components did not allow accurate measurement of the isotopic shift. The mass ratio calculated from the measured isotopic shift is  $0.9459801 \pm 0.0000050$ , as compared with the value  $0.9459441 \pm 0.0000065$  obtained from Mattauch, which is based primarily on the mass spectroscopic measurements of Okuda, Ogata, Aoki, and Sugawara.<sup>15</sup> The ratio obtained here does agree well with the value  $0.9459806 \pm 0.0000300$  obtained from Aston's work,<sup>16</sup> but his quoted errors are rather large. Since microwave spectroscopy should be able to give a number of mass ratios in the future, and possibly with an accuracy ten times that obtained here assuming the theory is complete, it is of considerable interest to know whether the present disagreement with the results of Okuda *et al.* is experimental, or due to some unrecognized source of frequency shift between the two ICl isotopic species.

#### IV. INTENSITY

The intensity and half-widths of the ICl<sup>35</sup> group of lines  $11/2 \rightarrow 13/2$  was measured at a pressure high enough that the separation of individual lines was considerably smaller than their width. The half-width, or total width at half maximum intensity, was found to be 13.3 mc. for gas in equilibrium with a trap of temperature  $-15^\circ\text{C}$ . The pressure measured for this temperature by Cornog and Bauer<sup>17</sup> is 1.2 mm

Hg, so that the half-width at a pressure of 1 mm. of mercury would be  $11 \pm 2$  mc. This is comparable with the half-width of the 24,326 mc line of OCS, which has approximately the same dipole moment, but almost twice as large as the value found by Weidner<sup>3</sup> for the ICl  $0 \rightarrow 1$  transition. The peak intensity of the  $11/2 \rightarrow 13/2$  lines at pressures high enough to make their peak intensities additive was found to be  $1.36 \pm 0.14 \times 10^{-5} \text{ cm}^{-1}$  or  $6.8 \pm 0.7 \times 10^{-6}$  nepers/cm in free space. Using the half-width quoted above, and assuming a dipole moment of  $0.5 \times 10^{-18}$  e.s.u.,<sup>18</sup> this peak intensity may be calculated to be  $0.94 \pm 0.18 \times 10^{-5} \text{ cm}^{-1}$ , considerably less than the measured value. Examination of the intensity and half-width measurements of Weidner<sup>3</sup> shows a similar discrepancy. Interpreting his measured ICl<sup>35</sup> line as the sum of all quadrupole splitting components, he obtained agreement with the calculated intensity. However, because of quadrupole splitting this line includes only 4/9 the intensity of the entire  $J=0 \rightarrow 1$  transition, so that it is more intense by approximately the factor 9/4 factor than his theoretical expectations. More exactly, he obtained an intensity for the  $J=0 \rightarrow 1, F_1=5/2 \rightarrow 7/2$  line of  $1.1 \times 10^{-6} \text{ cm}^{-1}$  and a half width  $0.168 \text{ cm}^{-1}$  at atmospheric pressure or 6.6 mc. at one mm. Hg. pressure.<sup>\*\*\*</sup> Although experimental inaccuracies in intensity and half-width measurements do not allow a determination of the ICl dipole moment to an accuracy better than about 10 percent, they do indicate that the value 0.5 Debye units given by Luft<sup>18</sup> is definitely too small. A value of 0.65 Debye units would better fit the mean of Weidner's and our own experimental results.

<sup>15</sup> T. Okuda, K. Ogata, K. Aoki, and Y. Sugawara, *Phys. Rev.* **58**, 578 (1940).

<sup>16</sup> F. W. Aston, *Proc. Roy. Soc.* **163**, 391 (1937).

<sup>17</sup> J. Cornog and E. E. Bauer, *J. Am. Chem. Soc.* **64**, 2620 (1942).

<sup>18</sup> K. F. Luft, *Zeits. f. Physik* **84**, 767 (1933).

<sup>\*\*\*</sup> The authors are indebted to Dr. Weidner for a discussion of intensities and for supplying the exact values of his experimental results.