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# ABSORPTION BAND SPECTRUM OF IODINE MONOCHLORIDE

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## Abstract

**Wave-lengths and series relations in the visible absorption spectrum of ICl.**—The visible absorption spectrum of ICl has been photographed and measured. Eight new members have been located in the two series described by Gibson and Ramsperger as corresponding to $n''=1$ and $n''=2$. The limit of convergence of the former series is at $\nu=17430\pm 5$ cm$^{-1}$, which makes the heat of dissociation equal to $49650\pm 15$ calories per mol. Four members of a new series for which $n''=3$ have been found, so that it has been possible to compute the fundamental vibratory frequency of the molecule as 381.9 cm$^{-1}$. Still another series of five members is recorded, whose presence may be due to the existence of a close electronic doublet having a separation of about 36 cm$^{-1}$. The *ratio of the two specific heats* of gaseous ICl has been calculated to be 1.30 in agreement with empirical results. The *fine structure* of three consecutive bands has been measured, and the corresponding values of the parabolic parameter $C$ have been computed to be in agreement with the theory of change of moment of inertia, $I$, with $\omega$, the frequency of vibration of the molecule. By combining both sets of data for band heads and fine structure, the following approximate values for the *moment of inertia* have been computed: $I''=575\pm 100\times 10^{-40}$ g·cm$^2$; $I'=995\pm 200\times 10^{-40}$ g·cm$^2$.

## Introduction

SINCE the experimental researches of Wood on the fluorescence spectrum of iodine and the interpretation of his results by Lenz in terms of quantum theory, attention has been focused upon the band spectra of molecules from the halogen group of elements. Further investigations of the molecular spectra of $I_2$ and also of $Br_2$ and $Cl_2$, notably by Mecke and Kuhn, has led logically to new research upon the corresponding spectra of IBr and ICl. Because of its unsusually high state of dissociation at ordinary temperatures, the absorption spectrum of IBr vapor has not yet been measured; but the more favorable monochloride has yielded definite results, its spectrum—in common with those of all the other halogen molecules—being situated in the red-to-green part of the visible spectrum and possessing one series which obviously converges to a definite limit.

Aside from preliminary work by Roscoe and Thorpe,[1] iodine monochloride has been investigated recently by Gibson and Ramsperger[2] and independently by the writer. It is felt that the present interest in the band spectrum of ICl warrants the presentation of somewhat more accurate measurements, which in addition to extending the series recorded by Gibson and Ramsperger and adding two new series, also include measurements of fine structure not made heretofore. The writer's investigation is therefore briefly outlined in the following.

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[1] Roscoe and Thorpe, Phil. Trans. **167**, 207 (1876).

[2] Gibson and Ramsperger, Phys. Rev. **30**, 598 (1927).

TABLE I. *Absorption band heads of ICl*

| λ(I. A.) | ν(vac.) | λ(I. A.) | ν(vac.) | λ(I. A.) | ν(vac.) | λ(I. A.) | ν(vac.) |
|---|---|---|---|---|---|---|---|
| 5730.13 | 17446.9 | 5891.06 | 16970.2 | 6229.5 | 16048.2 | 6516.14 | 15342.3 |
| 69.4 | 328.0 | 5915.10 | 901.2 | 67.1 | 15951.9 | 44.36 | 276.1 |
| 73.23 | 316.6 | 41.31 | 826.9 | 68.8 | 947.6 | 88.00 | 174.9 |
| 78.7 | 300.1 | 70.62 | 744.0 | 82.78 | 912.1 | 6610.8 | 122.6 |
| 85.1 | 281.0 | 6002.97 | 16653.8 | 6315.0 | 830.9 | 63.96 | 002.0 |
| 92.90 | 257.7 | 38.7 | 555.3 | 24.92 | 806.1 | 82.3 | 14960.8 |
| 5801.8 | 232.7 | 78.12 | 447.9 | 38.83 | 771.4 | 6709.9 | 899.2 |
| 11.88 | 201.3 | 6120.63 | 333.7 | 6366.74 | 15702.3 | 57.6 | 794.1 |
| 23.72 | 166.5 | 34.9 | 295.7 | 85.06 | 657.3 | 81.3 | 742.4 |
| 37.5 | 125.9 | 66.33 | 212.6 | 6422.44 | 566.1 | 6836.80 | 622.7 |
| 53.04 | 080.4 | 80.66 | 175.0 | 48.57 | 503.0 | 56.35 | 581.0 |
| 70.82 | 028.7 | 6215.59 | 084.1 | 81.43 | 424.4 | 6920.8 | 445.2 |
|  |  | 22.25 | 066.9 |  |  | 35.8 | 414.0 |

TABLE II. *Fine structure of ICl bands at* λ6325, λ6385 and λ6449.

| *m** | λ(I. A.) | ν(vac.) | *m* | λ(I. A.) | ν(vac.) | *m* | λ(I. A.) | ν(vac.) |
|---|---|---|---|---|---|---|---|---|
| 0 | 6324.92 | 15806.1 | ? | 6371.17 | 15691.4 | 55 | 6435.10 | 15535.5 |
| 15 | 29.04 | 795.8 | 53 | 72.16 | 88.9 | ? | 40.39 | 22.7 |
| 16 | 29.58 | 94.5 | 54 | 73.94 | 84.6 | ? | 41.53 | 20.0 |
| 17 | 30.04 | 93.3 | 55 | 75.72 | 80.2 | 58 | 42.67 | 17.2 |
| 18 | 30.67 | 91.7 | 56 | 77.42 | 76.0 | 60 | 46.40 | 08.2 |
| 19 | 31.27 | 90.2 | 57 | 79.34 | 71.3 | ? | 49.04 | 01.9 |
| 20 | 31.88 | 88.7 | 0 | 85.06 | 57.2 | 0 | 48.57 | 03.0 |
| 21 | 32.64 | 86.8 | ? | 89.67 | 45.9 | 19 | 54.83 | 488.0 |
| 22 | 33.27 | 85.3 | ? | 90.40 | 44.1 | 20 | 55.48 | 86.4 |
| 23 | 34.08 | 83.2 | 23 | 93.93 | 35.5 | 21 | 56.13 | 84.9 |
| 24 | 34.91 | 81.2 | 24 | 94.70 | 33.6 | 22 | 56.78 | 83.3 |
| 25 | 35.61 | 79.4 | 25 | 95.52 | 31.6 | 23 | 57.55 | 81.4 |
| 26 | 36.42 | 77.4 | 26 | 96.34 | 29.6 | 24 | 58.28 | 79.7 |
| 27 | 37.43 | 74.9 | 27 | 97.17 | 27.6 | 25 | 59.12 | 77.7 |
| 28 | 38.19 | 73.0 | 28 | 98.13 | 25.3 | 26 | 59.89 | 75.8 |
| 29 | 39.23 | 70.4 | 29 | 98.99 | 23.1 | 27 | 60.85 | 73.6 |
| 30 | 40.18 | 68.1 | 30 | 99.93 | 20.9 | 28 | 61.68 | 71.6 |
| 31 | 41.24 | 65.4 | 31 | 6400.92 | 18.4 | 29 | 62.65 | 69.3 |
| 32 | 42.20 | 63.0 | 32 | 02.01 | 15.8 | 30 | 63.54 | 67.1 |
| 33 | 43.67 | 59.4 | 33 | 03.09 | 13.1 | 31 | 64.53 | 64.8 |
| 34 | 44.43 | 57.5 | 34 | 04.15 | 10.6 | 32 | 65.57 | 62.3 |
| 35 | 45.70 | 54.3 | 35 | 05.25 | 07.4 | 33 | 66.54 | 59.9 |
| 36 | 46.74 | 51.8 | 36 | 06.48 | 04.9 | 34 | 67.75 | 57.1 |
| 37 | 47.96 | 48.7 | 37 | 07.65 | 02.1 | 35 | 68.85 | 54.4 |
| 38 | 49.25 | 45.5 | 38 | 08.85 | 599.1 | 36 | 69.93 | 51.9 |
| 39 | 50.54 | 42.3 | 39 | 10.18 | 95.9 | 37 | 71.11 | 49.0 |
| 40 | 51.94 | 38.9 | 40 | 11.44 | 92.8 | 38 | 72.40 | 45.9 |
| ? | 52.75 | 36.9 | 41 | 12.92 | 89.2 | 39 | 73.56 | 43.2 |
| 41 | 53.43 | 35.2 | 42 | 14.14 | 86.2 | 40 | 74.96 | 39.8 |
| 42 | 54.57 | 32.3 | 43 | 15.62 | 82.7 | ? | 75.12 | 39.5 |
| 43 | 56.05 | 28.7 | 44 | 16.85 | 79.7 | 42 | 77.59 | 33.6 |
| 44 | 57.59 | 24.9 | 45 | 18.32 | 76.1 | 43 | 78.92 | 30.4 |
| ? | 58.79 | 21.9 | 46 | 19.88 | 72.3 | 44 | 80.36 | 27.0 |
| ? | 59.77 | 19.5 | 47 | 21.45 | 68.5 | 45 | 81.81 | 23.5 |
| ? | 60.52 | 17.6 | 48 | 22.89 | 65.0 | 46 | 83.29 | 20.0 |
| 47 | 62.14 | 13.6 | 49 | 24.81 | 60.4 | 47 | 84.73 | 16.7 |
| 48 | 63.49 | 10.3 | 50 | 26.31 | 56.7 | 48 | 86.38 | 12.7 |
| 49 | 65.19 | 06.1 | 51 | 27.97 | 52.7 | ? | 95.19 | 391.7 |
| 50 | 66.76 | 02.2 | 52 | 29.73 | 48.5 | ? | 98.14 | 84.8 |
| 51 | 68.43 | 698.1 | 53 | 31.48 | 44.2 |  |  |  |
| 52 | 70.13 | 93.9 | 54 | 33.38 | 39.6 |  |  |  |

* Values of *m* assume $m=0$ at head and have no theoretical significance.

The wave-lengths of all observed band heads were measured from the plates by means of a low-power comparator. These measurements together with corresponding frequencies are recorded in Table I. The fine structure of three consecutive bands in the red was measured under much higher magnification. The resulting data are arranged in Table II.

## Arrangement of Band Series

No attempt is made here to assign independently quantum values of $n''$ to the Deslandres' series, but the plausible assignments by Gibson and Ramsperger are adopted. However, their arbitrary assignments of $n'$ are shifted one unit to admit a new member on the long wave-length end of the series $n''=2$. Table III shows specifically that six new members have been added to the converging series $n''=1$ and two new members to the weaker series $n''=2$. The series $n''=3$, consisting of four members is entirely new. Thus a value of 379.8 $cm^{-1}$ is obtained for the second frequency interval in the normal group of energy levels in addition to the value of 381.2 $cm^{-1}$ for the first interval.

## Experimental Procedure

Photographs were made in the first order on panchromatic plates with a 10-foot Rowland concave grating mounted in Eagle fashion. Continuous radiation, supplied by a 400-watt stereopticon bulb, was projected through ICl vapor contained in a tube of Pyrex glass, 60 cm long, with fused-on end plates of the same material. The vapor from pure ICl was admitted into the evacuated chamber at the center and was caused to progress slowly toward exhaust outlets near each end by proper adjustment of the pump. By this means the absorption spectrum of iodine as a dissociation product was reduced to a minimum. Exposures varied from 5 to 60 minutes. The iron arc was used for a comparison spectrum.

Table III. *Series in band system of ICl*

| | $n''=1$ | | $\Delta\nu'$ | | $n''=2$ | | $\Delta\nu'$ | | $n''=3$ | $\Delta\nu'$ | $\Delta\nu''(1,2)$ | | $\Delta\nu''(2,3)$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n'$ | Writer | G&R | Writer | G&R | Writer | G&R | Writer | G&R | Writer | Writer | Writer | G&R | Writer | $n'$ |
| 0 | (14825.4) | | | | 14445.2 | | 177.5 | | | | | | | 0 |
| 1 | 15002.0 | | 172.9 | | 622.7 | 627 | 171.4 | 171 | | | 379.3 | | | 1 |
| 2 | 174.9 | | 167.4 | | 794.1 | 798 | 166.7 | 167 | 14414.0 | 167.0 | 380.8 | | 380.1 | 2 |
| 3 | 342.3 | 347 | 160.7 | 162 | 960.8 | 965 | 161.8 | 160 | 581.0 | 161.4 | 381.5 | 382 | 379.8 | 3 |
| 4 | 503.0 | 509 | 154.3 | 152 | 15122.6 | 125 | 153.5 | 155 | 742.4 | 156.8 | 380.4 | 384 | 380.2 | 4 |
| 5 | 657.3 | 661 | 148.8 | 149 | 276.1 | 280 | 148.3 | 150 | 899.2 | | 381.2 | 381 | 376.9 | 5 |
| 6 | 806.1 | 810 | 141.5 | 143 | 424.4 | 430 | 141.7 | 140 | | | 381.7 | 380 | —— | 6 |
| 7 | 947.6 | 953 | 135.7 | 135 | 566.1 | 570 | 136.2 | 136 | | | 381.5 | 383 | 379.8 | 7 |
| 8 | 16084.1 | 088 | 128.5 | 127 | 702.3 | 706 | 128.6 | 128 | | | 381.8 | 382 | Weighted | 8 |
| 9 | 212.6 | 215 | 121.1 | 123 | 830.9 | 834 | 121.0 | 119 | | | 381.7 | 380 | mean | 9 |
| 10 | 333.7 | 338 | 114.2 | 113 | 951.9 | 953 | 115.0 | 120 | | | 381.8 | 385 | | 10 |
| 11 | 447.9 | 451 | 107.4 | 106 | 16066.9 | 073 | 108.1 | 106 | | | 381.0 | 378 | | 11 |
| 12 | 555.3 | 557 | 98.5 | 100 | 175.0 | 179 | 96.5 | | | | 380.3 | 378 | | 12 |
| 13 | 653.8 | 657 | 90.2 | 90 | 271.5 | | | | | | 382.3 | | | 13 |
| 14 | 744.0 | 747 | 82.9 | 84 | | | | | | | —— | —— | | |
| 15 | 826.9 | 831 | 74.3 | 74 | | | | | | | 381.2 | 382 : mean | | |
| 16 | 901.2 | 905 | 69.0 | 67 | | | | | | | | | | |
| 17 | 970.2 | 972 | 58.5 | 60 | | | | | | | | | | |
| 18 | 17028.7 | 032 | 51.7 | 52 | | | | | | | | | | |
| 19 | 080.4 | 084 | 45.5 | 45 | | | | | | | | | | |
| 20 | 125.9 | 129 | 40.6 | 41 | | | | | | | | | | |
| 21 | 166.5 | 170 | 34.8 | 35 | | | | | | | | | | |
| 22 | 209.3 | 205 | 31.4 | 32 | | | | | | | | | | |
| 23 | 232.7 | 237 | 25.0 | 24 | | | | | | | | | | |
| 24 | 257.7 | 261 | 23.3 | | | | | | | | | | | |
| 25 | 287.0 | | 19.3 | | | | | | | | | | | |
| 26 | 300.1 | | 16.5 | | | | | | | | | | | |
| 27 | 316.6 | | 11.4 | | | | | | | | | | | |
| 28 | 328.0 | | | | | | | | | | | | | |
| 29 | | | | | | | | | | | | | | |
| 30 | | | | | | | | | | | | | | |
| 31 | | | | | | | | | | | | | | |
| 32 | 17430± 5 | | 17410± 30 : limit of convergence | | | | | | | | | | | |

Fig. 1 is an energy level diagram including the new levels and showing the disposition of one of the new series.

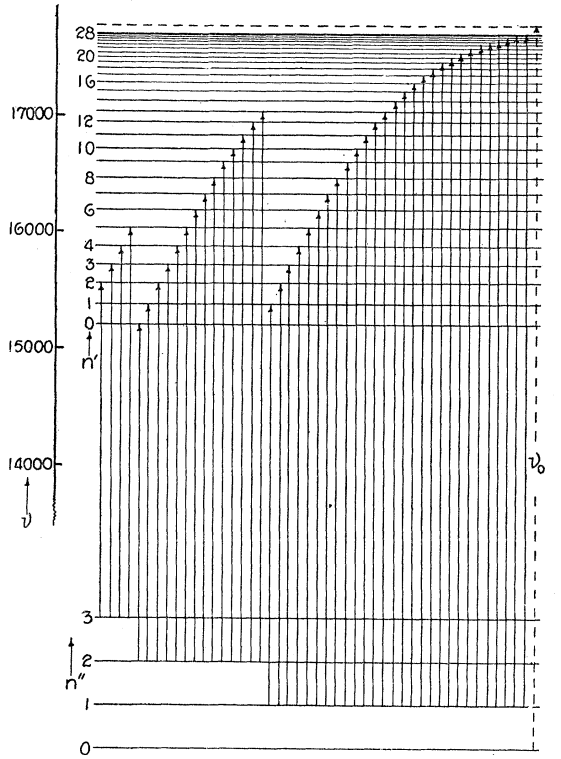

Fig. 1. Energy level diagram for the visible absorption spectrum of ICl.

Besides the heads classified in Table III, there remain out of Table I four additional ones which may be tabulated as follows:

| $\nu$ | $\Delta\nu'$ | $\nu(n''=1)$ | $\Delta\nu'$ | $\Delta\nu''$ |
|---|---|---|---|---|
| 15771.4 | 140.7 | 15806.1 | 141.5 | 34.7 |
| 15912.1 | 136.1 | 15947.6 | 135.7 | 35.5 |
| 16048.2 | 126.8 | 16084.1 | 128.5 | 35.9 |
| 16175.0 | 120.7 | 16212.6 | 121.1 | 37.6 |
| 16295.7 | | 16333.7 | | 38.0 |

wherein is included a member of the series $n''=2$. By comparison of $\Delta\nu''$s it is seen that there is a rather good agreement between these and a similar group in Table III. There seems to be a real increase in the values of $\Delta\nu''$ together with the increase in $\nu$. This would suggest an isotope effect, but the calculated displacement for this effect corresponding to $\nu=15806$ is 332 $\text{cm}^{-1}$, which is about ten times larger than the above values of $\Delta\nu''$.

This extra series may be due to the existence of an electronic doublet with a separation of about 36.3 $\text{cm}^{-1}$.

## HEAT OF DISSOCIATION OF ICl

According to a method developed by Birge and Sponer,[3] the frequency

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[3] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

at the limit of a convergent series for a non-polar molecule is given by

$$\nu_D = \nu_{n'} + \int_{n'}^{n_0'} \omega^{n'} dn',$$

where $\omega^{n'}$ is the frequency interval between $\nu_{n'}$ and $\nu_{n'-1}$, and $n'_0$ is the value of $n'$ for which $\omega$ becomes zero. If $\omega^{n'}$ is plotted against corresponding values of $n'$ (in which process $\omega^{n'}$ is to be considered as corresponding to $n'$ rather than to $n'-1$ or the average of the two), the area under the curve is a numerical measure of the integral. Fig. 2 is such a curve plotted from Table III. The computed area is 2604.6 units when $n'$ begins at zero. The extrapolated value of $\nu$ corresponding to $n'=0$ is 14825.4. Hence,

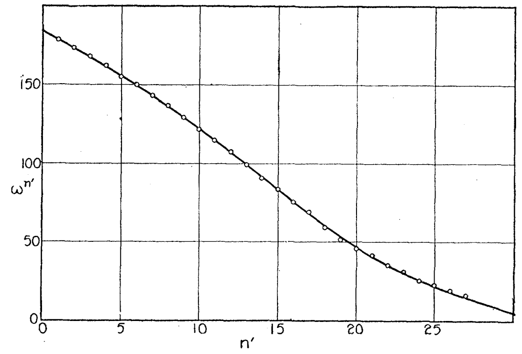

Fig. 2. Curve showing variation of $\omega^{n'}$ with $n'$.

$$\nu_D = 14825.4 + 2604.6 = 17430.0.$$

The estimated error is about ± 5 units.
The heat of dissociation becomes

$$D = 2.152 \pm 0.001 \text{ volt} = 49650 \pm 15 \text{ calories per mol.}$$

The new frequency interval furnished by the series for $n''=3$ gives a means of computing $\omega_0''$, the fundamental frequency of the molecule in the normal state. For by fundamental theory,

$$\omega_0''(1-x'') = 381.2;\ 2\omega_0''(1-2x'') = 381.2 + 379.8 = 761.0.$$

Hence, solving $\omega_0''=381.9$ and $x''=0.0018$. Finally also, $\omega_0''x''=0.69$. Assuming that this law of convergence holds to the limit, it is easy to compute that the normal series of levels would converge at about the 278th level or about 82100 $\text{cm}^{-1}$ from the zero state.

## RATIO OF SPECIFIC HEATS

It has been shown by Planck[4] that if $\nu$ is the fundamental frequency of vibration of a diatomic molecule, the specific heat at constant volume is given by the equation

$$\frac{C_v}{R} = \frac{5}{2} + \frac{x^2 e^x}{(e^x-1)^2},$$

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[4] Planck, La Theorie du Rayonnement et les Quanta, p. 112 (1911).

in which $x$ has been used as an abbreviation for $h\nu/RT$. For a temperature of 100°C, $x=1.466$.
Hence, $C_v/R=3.33$, and $C_p/R=1+C_v/R=4.33$. Therefore, $C_p/C_v=\gamma=1.30$. This value is in close agreement with the mean value 1.31 determined experimentally by Strecker[5] for $\gamma$ at the same temperature.

## Discussion of Fine Structure

Even a casual glance at Table II reveals that the fine structure must be of a simple nature. Aside from an occasional extra line, the measurements consist of three parabolic series corresponding to the three bands heading respectively at 6325, 6385 and 6449A. Fig. 3 is a curve plotted from the data for the latter band. The curve has been extended to tangency at the head according to a parabolic law. The data for the other two bands yield exactly similar curves. Unfortunately there is no definite indication of the presence of the null lines, and hence it is impossible to evaluate the frequency interval at the origin, which is necessary to a computation of moment of inertia. However, certain quantitative results may be definitely secured.

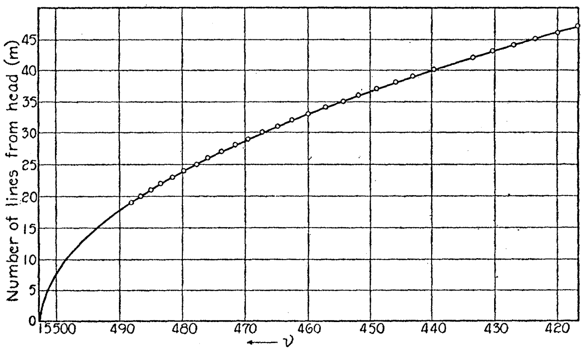

Fig. 3. Typical parabolic curve for fine structure.

In evaluating the constant $C$ of the general band formula, it is immaterial whether the measured lines belong to a $P$, $Q$, or $R$ branch, for $C$ is nearly identical for all three types.

For sake of definiteness, let us set for the frequency of any line of the branch in a band $\nu_1=A-2Bm_1-Cm_1^2$. Any other line in the same branch will be given approximately by $\nu_2=A-2Bm_2-Cm_2^2$. Subtracting, $\nu_1-\nu_2=(m_2-m_1)\ [2B+C(m_2+m_1)]$. Let $m_2-m_1=10$. Then, $\nu_1-\nu_2=20[B+C(m_1+5)]$. Similarly, if we set $m_3-m_1=20$, $\nu_1-\nu_3=40[B+C(m_1+10)]$. Both $B$ and $m_1$ may be readily eliminated so that one obtains $100C=\nu_2-(\nu_1+\nu_3)/2$ where $\nu_1$, $\nu_2$ and $\nu_3$ are the frequencies of lines ten intervals apart in order. This is a very convenient equation for determination of $C$, and shows that analytically $C$ is a measure of the difference between any frequency and the average value of two frequencies symmetrically situated on either

[5] Strecker, Wied. Ann. **17**, 93 (1882).

side. Applying this equation to all possible sets of lines in the three bands, the mean values of $C$ obtained for each band were:

| Band Head | 15503.0 | 15657.2 | 15806.1 |
|---|---|---|---|
| $C$ | 0.0388 | 0.0398 | 0.0412 |

The physical significance of $C$ as taken here is given by the identity

$$C \equiv \frac{h}{8\pi^2 c}\left[\frac{1}{I''}-\frac{1}{I'}\right],$$

where $I'$ is the moment of inertia in the excited state, and $I''$ that in the normal state. Comparing values of $C$ for the different bands, it can be readily observed that the value of $I'$ increases as one proceeds toward the limit of the series. This is in agreement with the established correlation between $I$ and $\omega$ (the vibrational frequency) which are consistently found to be roughly in inverse proportion. By approximate extrapolation, $C$ becomes 0.035 for $n'=0$ as assigned.

## Moment of Inertia

An approximation to the value of the moment of inertia of ICl can be obtained if it is assumed that the assignments of $n'$ are nearly correct. For Mecke[6] has pointed out that the product of the mean value of $\omega$ by the mean value of the moment of inertia is nearly equal to the product $\omega'' I''$. Or, $(178+382)\,(I'+I'')/2=382\, I''$; whence, $I'=1.73\, I''$. Also

$$C=\frac{h}{8\pi^2 c}\left[\frac{1}{I''}-\frac{1}{I'}\right]=0.035.$$

Solving these two equations simultaneously,

$$I''=(575\pm 100)10^{-40}\ \text{g}\cdot\text{cm}^2\ ;$$

$$I'=(995\pm 200)10^{-40}\ \text{g}\cdot\text{cm}^2.$$

As indicated, these results may be in error by as much as twenty percent.[7]

In conclusion, the writer wishes to express his thanks to Professor Alpheus W. Smith who originally suggested the problem and whose personal interest has been a strong incentive throughout the investigation.

Mendenhall Physical Laboratory,
Ohio State University.
May, 1928.

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[6] Mecke, Zeits. f. Physik **32,** 823 (1925).

[7] If we assume momentarily that the extra series tabulated below Table III might be the heads of $Q$ branches belonging to the nearest strong band, a position for the null line of the band at $\nu=15806$ would be determined. Under this assumption, the value of the constant $B$ turns out to be 1.195; whence, $I'=23.1\cdot 10^{-40}$ g·cm$^2$. This result is only two or three percent. of the approximate value obtained above by another method, and hence we dismiss the possibility of the extra series, being accounted for by $Q$ branches.