

## Rotational Structure of Some Electronic Bands of Chlorine Dioxide

Jesse B. Coon

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## Rotational Structure of Some Electronic Bands of Chlorine Dioxide

JESSE B. COON

*Department of Physics, A. and M. College of Texas, College Station, Texas*

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The rotational structure of several violet absorption bands of  $\text{ClO}_2$  has been studied. The bands considered correspond to the vibration transitions  $(v_1' 0 0) \leftarrow (0 0 0)$  where  $v_1' = 1, 2, 3, 4$ , and 5. The most prominent identifiable feature of the rotational structure is a doublet  $qQ$  branch resolved in the tail of each band. For  $v_1' = 1, 2$ , and 3, the rotational wave numbers of these branches are given by

$$\begin{aligned} \nu_{1,2} = & -\frac{1}{2}(0.0615 + 0.0042v_1')L(L+1) \\ & -\frac{1}{2}(1.188 + 0.008v_1')K^2 + 0.13L + 0.174(v_1' - 0.4)K \\ & \mp \frac{1}{2}[0.109(2K - L) - 0.045(v_1' - 1)]. \end{aligned}$$

This fits the spectrum in the observed range of quantum numbers,  $K = 11$  to 20 and  $L = K$  to  $K + 8$ . The first two terms are associated with that prolate symmetrical top which comes closest to the actual  $\text{ClO}_2$  molecule. Hence, neglecting the effect of asymmetry on the spectrum,

$$2\Delta\bar{B} = -(0.0615 + 0.0042v_1') \text{ cm}^{-1}$$

and

$$2(\Delta A - \Delta\bar{B}) = -(1.188 + 0.008v_1') \text{ cm}^{-1}.$$

The last term is associated with spin doubling. The coupling is shown to be close to Hund's "case b." The linear

terms in  $L$  and  $K$  may be a consequence of the doubling. The term in  $v_1'K$  describes an outstanding feature of the spectrum but is not interpreted. The bands are shown to be of the parallel type. A few  $qP$  and  $qR$  branches have also been identified and  $\Delta_1F$  values have been found. Assuming the spectrum to be that of a prolate symmetrical top, the resulting values of  $2\bar{B}$  for the vibrationless states are  $2\bar{B}'' = 0.612 \text{ cm}^{-1}$  and  $2\bar{B}' = 0.550 \text{ cm}^{-1}$ . The value of  $2\bar{B}''$  with the  $\text{Cl}-\text{O}$  distance  $s'' = 1.53 \text{ \AA}$  from electron diffraction is sufficient to determine the lower electronic state. The upper state is then determined from the values of  $2\Delta\bar{B}$  and  $2(\Delta A - \Delta\bar{B})$  for the vibrationless states. The resulting model of both states is designated as model (2). Error in this model, because of the fact that the effect of asymmetry was neglected, is found to be small. Asymmetry correction made on model (2) leads to the following model:

$$\begin{aligned} 2\theta'' &= 109^\circ \pm 3^\circ, & 2\theta' &= 92^\circ \pm 6^\circ, \\ s'' &= 1.53 \text{ \AA} \pm 0.02 \text{ \AA}, & s' &= 1.805 \text{ \AA} \pm 0.05 \text{ \AA}. \end{aligned}$$

The rotational isotope effect is observed and explained but gives no additional information about the molecular model.

## PART I

## 1. INTRODUCTION

PREVIOUS work<sup>1</sup> on the violet absorption spectrum of  $\text{ClO}_2$  has concerned the vibrational structure. Urey and Johnston, and Ku have attempted vibrational analyses which have been modified by the author.<sup>2</sup> Urey and Johnston give an estimate of the relative intensities of the bands of some of the strongest progressions. Ku's measurements of band heads which were made from spectrograms taken with a 21-ft. grating are probably the most accurate published and these spectrograms show evidence of resolvable rotational structure.

The rotational structures of the electronic spectra of only a few non-linear polyatomic molecules have been partially resolved and studied.<sup>3</sup> The violet absorption spectrum of

chlorine dioxide offers an opportunity for observing fine structure because an interval of about  $250 \text{ cm}^{-1}$  in several of the strongest bands is free from overlapping and because one of the moments of inertia differs considerably in the two electronic states. Photographs taken on the University of Chicago 30-foot grating spectrograph in the second order show interesting resolved fine structure in the tails of some bands. It is the purpose of this paper to describe and interpret as much of this rotational structure as seems possible.

## 2. THE ABSORPTION TUBE

The chlorine dioxide used in the absorption tube was prepared by the reaction of oxalic acid and potassium chlorate as described by Bray.<sup>4</sup> About eight parts of oxalic acid, two parts of potassium chlorate, and one part of water were mixed and sealed into a flask connected to an all

<sup>1</sup> H. C. Urey and H. Johnston, *Phys. Rev.* **38**, 2131 (1931). Z. W. Ku, *Phys. Rev.* **44**, 376 (1933).

<sup>2</sup> Jesse B. Coon, *Phys. Rev.* **58**, 926L (1940). The author plans to publish a detailed account of the vibrational analysis after taking more spectrograms in the vicinity of the origin.

<sup>3</sup> *Formaldehyde*, G. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.* **45**, 4 (1934). *Nitrogen dioxide*, Louis Harris and G. W. King, *J. Chem. Phys.* **8**, 775 (1940). *Ammonia*,

A. B. F. Duncan and G. R. Harrison, *Phys. Rev.* **49**, 211 (1936). *Benzene*, Anthony Turkevich and Mark Fred, *Rev. Mod. Phys.* **14**, 246 (1942). *Sulfur Dioxide*, N. C. Metropolis (cf. R. S. Mulliken), *Rev. Mod. Phys.* **14**, 204 (1942).

<sup>4</sup> W. Bray, *Zeits. f. physik. Chemie* **54**, 575 (1906).

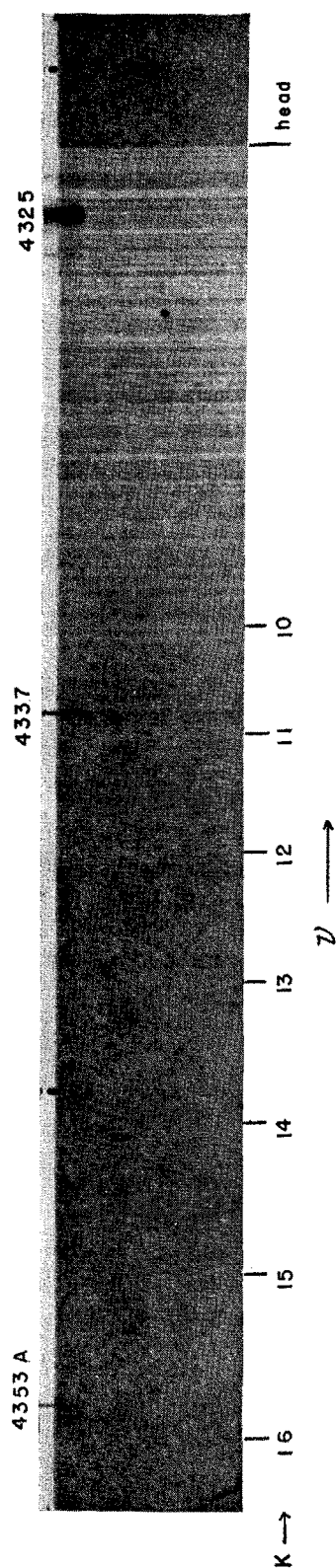


FIG. 1. Band 3. Leaders indicate first line of  $\nu_1$  series (persistent component of doublet Q branch) for seven sub-bands.

glass line consisting, in the following order, of a  $P_2O_5$  tube, dry ice trap, 50-cm absorption tube with fused-on Pyrex windows, capillary tube, liquid nitrogen trap, the only stopcock, and an oil pump. The mixture was heated to  $60^\circ C$  under atmospheric pressure and the resulting gaseous mixture ( $ClO_2$ ,  $CO_2$ ,  $H_2O$ ) displaced the air in the system. The  $ClO_2$  was deposited in the dry ice trap in the form of orange red crystals. When the reaction was complete the  $CO_2$  was pumped out, then the reaction flask and  $P_2O_5$  tube were sealed off.

The vapor pressure of  $ClO_2$  at dry ice temperature, less than one mm, was found sufficient to give many of the strong bands. The weaker bands were obtained by replacing the dry ice by a warmer mixture. The weakest band studied, referred to below as band 1, was obtained when the  $ClO_2$  pressure was about 1 cm. Because of the decomposition of  $ClO_2$  upon exposure to light, it was necessary to keep the gas flowing through the absorption tube during an exposure. The rate of flow was limited by the capillary tube at the exit end of the absorption tube. The oil pump was kept running during an exposure. After passing through the capillary, at least four of the constituents of the exposed gas were deposited in the liquid nitrogen trap. These substances were deposited in rings in the trap, the depth of the ring depending on the ease with which the substance condensed.  $Cl_2$  gas penetrated to the bottom of the trap giving a lemon colored condensation. A thin deposit of undecomposed  $ClO_2$  above this was orange in color. A red substance, probably  $Cl_2O$ , deposited above the  $ClO_2$ . When the liquid nitrogen was removed, the  $ClO_2$  evaporated more quickly than the  $Cl_2O$ . Above this was observed, at times, a reddish orange ring which was much slower to evaporate than the other substances when the liquid nitrogen was removed. It is probable that this was  $Cl_2O_6$ .<sup>5</sup> The decomposition rate was greatly reduced by using a "noviol A" filter which cut out most of the radiation below 4300A.

### 3. DESCRIPTION OF BANDS MEASURED

Part of the lines of five bands in the region 4000–4700A were measured. These bands corre-

<sup>5</sup> Charles F. Goodeve and Frederick D. Richardson, J. Chem. Soc. 294 (1937, part 1).



TABLE I. Wave numbers of lines of observed  $qQ$  doublet branches ( $\nu_1$  components, lower left;  $\nu_2$  components, upper right). The band number given is the value of  $\nu_1'$ .

| Band 1     |          |        |        |        |        |        |        |        |            |
|------------|----------|--------|--------|--------|--------|--------|--------|--------|------------|
| $K$        | 12       | 13     | 14     | 15     | 16     | 17     | 18     | 19     | $L(\nu_2)$ |
|            |          |        | 607.34 | 590.19 |        |        |        |        | 14         |
|            |          |        | 606.36 | 589.22 | 570.90 |        |        |        | 15         |
|            |          |        | 605.34 | 588.17 |        | 550.36 |        |        | 16         |
|            |          |        | 604.22 | 587.07 |        | 549.22 | 528.52 |        | 17         |
|            |          |        |        | 585.93 |        | 548.07 | 527.31 | 505.45 | 18         |
|            |          |        |        |        |        | 546.82 | 526.06 | 504.18 | 19         |
|            |          |        |        |        |        | 545.59 | 524.80 | 502.88 | 20         |
| $L(\nu_1)$ |          |        |        |        |        |        | 523.45 | 501.51 | 21         |
| 13         |          | 623.57 |        |        |        |        | 522.09 | 500.13 | 22         |
| 14         | 21637.72 | 622.86 | 606.73 |        |        |        |        |        | 23         |
| 15         | 21636.91 | 622.05 | 605.95 | 588.60 |        |        |        |        |            |
| 16         | 21636.02 | 621.21 | 605.07 | 587.72 | 569.15 |        |        |        |            |
| 17         | 21635.07 | 620.20 | 604.13 | 586.77 | 568.25 | 548.46 |        |        |            |
| 18         | 21634.09 |        | 603.12 | 585.78 | 567.24 | 547.50 | 526.56 |        |            |
| 19         |          |        |        | 584.72 | 566.14 | 546.44 | 525.49 | 503.35 |            |
| 20         |          |        |        | 583.55 | 565.06 | 545.30 | 524.40 | 502.23 |            |
| 21         |          |        |        | 582.40 | 563.84 | 544.12 | 523.20 | 501.04 |            |
| 22         |          |        |        | 581.10 | 562.60 | 542.85 | 521.92 | 499.78 |            |
| 23         |          |        |        | 579.79 | 561.27 | 541.52 | 520.60 | 498.49 |            |
| 24         |          |        |        |        | 559.87 | 540.14 | 519.17 | 497.07 |            |
| 25         |          |        |        |        | 558.43 | 538.68 |        | 495.60 |            |
| 26         |          |        |        |        | 556.93 | 537.19 | 516.22 | 494.10 |            |
| 27         |          |        |        |        |        | 535.59 | 514.65 |        |            |
| 28         |          |        |        |        |        |        |        | 490.88 |            |
| 29         |          |        |        |        |        |        |        | 489.17 |            |

| Band 2     |          |        |        |        |        |        |        |        |        |
|------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| $K$        | 12       | 13     | 14     | 15     | 16     | 17     | 18     | 19     | 20     |
|            | 22341.03 |        |        |        |        |        |        |        |        |
|            | 22340.20 | 325.55 |        |        |        |        |        |        |        |
|            | 22339.26 | 324.64 | 308.75 |        |        |        |        |        |        |
|            |          | 323.66 | 307.79 | 290.66 |        |        |        |        |        |
|            |          |        | 306.68 | 289.61 | 271.31 |        |        |        |        |
|            |          |        | 305.65 | 288.52 | 270.20 | 250.74 |        |        |        |
|            |          |        |        | 287.36 | 269.03 | 249.55 | 228.87 |        |        |
| $L(\nu_1)$ |          |        |        |        | 267.82 | 248.31 | 227.67 | 205.75 |        |
| 12         | 22339.78 |        |        |        |        | 247.07 | 226.40 | 204.45 | 181.38 |
| 13         | 22339.05 | 324.18 |        |        |        | 245.68 | 225.09 | 203.09 | 179.98 |
| 14         | 22338.27 | 323.37 | 307.27 |        |        |        |        | 201.66 | 178.53 |
| 15         | 22337.36 | 322.51 | 306.42 | 289.09 |        |        |        |        | 177.06 |
| 16         | 22336.35 | 321.49 | 305.45 | 288.13 | 269.59 |        |        |        | 175.46 |
| 17         | 22335.34 | 320.36 | 304.44 | 287.15 | 268.63 | 248.91 |        |        |        |
| 18         | 22334.29 | 319.43 | 303.34 | 286.09 | 267.55 | 247.86 | 226.99 |        |        |
| 19         | 22333.14 |        | 302.21 | 284.88 | 266.41 | 246.73 | 225.89 | 203.74 |        |
| 20         | 22331.86 |        | 300.93 | 283.71 | 265.19 | 245.50 | 224.73 | 202.53 | 179.24 |
| 21         |          |        | 299.68 | 282.41 | 263.91 | 244.30 | 223.48 | 201.26 | 177.94 |
| 22         |          |        | 298.33 | 281.06 | 262.55 | 242.88 | 222.16 | 199.89 | 176.62 |
| 23         |          |        |        |        | 261.17 | 241.66 |        | 198.49 | 175.18 |
| 24         |          |        |        |        | 259.67 | 240.04 | 219.32 | 196.96 | 173.47 |
| 25         |          |        |        |        |        | 238.45 | 217.67 |        | 171.80 |
| 26         |          |        |        |        |        | 236.85 |        | 193.75 |        |
| 27         |          |        |        |        |        | 235.15 |        | 192.09 |        |
| 28         |          |        |        |        |        |        |        | 190.29 |        |
| 29         |          |        |        |        |        |        |        |        |        |

series by  $\nu_2$ . In all sub-bands, the doubling is large enough so that the first two lines of the  $\nu_2$  series come before the first line of the  $\nu_1$  series. However, the interval between successive lines is greater for the  $\nu_2$  components and after a few lines the  $(n+1)$ th  $\nu_2$  line blends with the  $n$ th  $\nu_1$  line. The last line of  $\nu_2$  before blending is in

most cases weaker or more diffuse than the corresponding line of  $\nu_1$ . Up to that point  $\nu_1$  and  $\nu_2$  have approximately equal intensity. In general about two lines of  $\nu_1$  are considerably reinforced by this blending. The resulting strong lines have the appearance that would be expected from superimposing a fairly sharp line

TABLE I.—Continued.

| Band 3     |          |        |        |        |        |        |        |        |        |        |
|------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| K          | 11       | 12     | 13     | 14     | 15     | 16     | 17     | 18     | 19     | 20     |
|            | 23048.98 |        |        |        |        |        |        |        |        |        |
|            |          | 034.80 |        |        |        |        |        |        |        |        |
|            |          | 033.78 | 019.28 |        |        |        |        |        |        |        |
|            |          |        | 018.25 | 002.49 |        |        |        |        |        |        |
|            |          |        |        | 001.39 | 984.34 |        |        |        |        |        |
|            |          |        |        | 000.26 | 983.20 | 964.93 |        |        |        |        |
|            |          |        |        |        | 982.01 | 963.72 | 944.23 |        |        |        |
|            |          |        |        |        |        | 962.51 | 942.99 | 922.31 |        |        |
| $L(\nu_1)$ |          |        |        |        |        |        | 941.64 | 920.98 | 899.09 |        |
| 11         | 23047.89 |        |        |        |        |        |        |        |        |        |
| 12         | 23046.86 | 033.60 |        |        |        | 959.77 |        | 919.56 | 897.69 | 874.62 |
| 13         | 23045.86 | 032.70 | 017.98 |        |        |        | 938.79 | 918.12 | 896.24 | 873.18 |
| 14         | 23044.74 | 031.67 | 017.06 | 001.07 |        |        |        | 916.56 | 894.70 | 871.62 |
| 15         | 23043.56 | 030.63 | 016.04 | 000.09 | 982.81 |        |        |        | 893.03 | 870.03 |
| 16         |          | 029.49 | 014.93 | 999.03 | 981.78 | 963.29 |        |        |        |        |
| 17         |          | 028.34 | 013.80 | 997.87 | 980.69 | 962.19 | 942.49 |        |        |        |
| 18         |          |        | 012.53 | 996.69 | 979.47 | 961.03 | 941.33 | 920.44 |        |        |
| 19         |          |        |        | 995.38 | 978.19 | 959.77 | 940.09 | 919.23 | 897.13 |        |
| 20         |          |        |        | 994.04 | 976.86 | 958.40 | 938.79 | 917.93 | 895.83 | 872.56 |
| 21         |          |        |        | 992.55 | 975.44 | 957.04 | 937.38 | 916.56 | 894.46 | 871.20 |
| 22         |          |        |        |        | 973.97 | 955.57 | 935.92 | 915.07 | 893.03 | 869.77 |
| 23         |          |        |        |        | 972.40 | 953.98 | 934.45 | 913.53 | 891.48 | 868.26 |
| 24         |          |        |        |        | 970.76 |        | 932.79 | 911.98 | 889.89 | 866.68 |
| 25         |          |        |        |        |        |        | 931.13 | 910.37 | 888.23 | 864.97 |
| 26         |          |        |        |        |        |        | 929.35 | 908.52 | 886.50 | 863.28 |
| 27         |          |        |        |        |        |        | 927.51 | 906.70 | 884.64 | 861.48 |
| 28         |          |        |        |        |        |        |        | 904.91 | 882.76 |        |
| 29         |          |        |        |        |        |        |        |        | 880.82 |        |
| 30         |          |        |        |        |        |        |        |        | 878.81 |        |
| 31         |          |        |        |        |        |        |        |        | 876.70 |        |

| Band 4     |          |        |        |        | Band 5 |   |          |        |        |
|------------|----------|--------|--------|--------|--------|---|----------|--------|--------|
| K          | 16       | 17     | 18     | 19     | 20     | K | 19       | 20     | 21     |
|            | 23652.14 |        |        |        |        |   | 24267.33 |        |        |
|            |          | 631.42 |        |        |        |   |          | 242.77 |        |
|            |          | 629.99 | 609.36 |        |        |   |          |        | 216.99 |
|            |          |        | 607.87 | 586.07 |        |   |          |        |        |
|            |          |        | 606.31 | 584.53 | 561.55 |   |          |        |        |
| $L(\nu_1)$ |          |        |        | 582.92 | 559.93 |   |          |        |        |
| 16         | 23650.53 |        |        |        | 558.29 |   |          |        |        |
| 17         | 23649.13 | 629.67 |        |        |        |   |          |        |        |
| 18         | 23647.70 | 628.31 | 607.52 |        |        |   |          |        |        |
| 19         | 23646.19 | 626.88 | 606.16 | 584.14 |        |   |          |        |        |
| 20         | 23644.65 | 625.37 | 604.70 | 582.70 | 559.52 |   |          |        |        |
| 21         |          | 623.81 | 603.17 | 581.21 | 558.03 |   |          |        |        |
| 22         |          | 622.13 | 601.54 | 579.65 | 556.50 |   |          |        |        |
| 23         |          | 620.40 | 599.85 | 577.95 | 554.84 |   |          |        |        |
| 24         |          | 618.59 | 598.06 | 576.22 | 553.12 |   |          |        |        |
| 25         |          |        | 596.22 | 574.39 | 551.34 |   |          |        |        |
| 26         |          |        | 594.26 | 572.49 | 549.43 |   |          |        |        |
| 27         |          |        |        | 570.50 | 547.47 |   |          |        |        |
| 28         |          |        |        | 568.37 | 545.51 |   |          |        |        |

and a more diffuse line. Farther along the intensity of the  $\nu_1$  lines return to normal, but the  $\nu_2$  lines do not reappear on the other side of the  $\nu_1$  lines unless perhaps in some cases as very diffuse lines.

The intervals between lines of the  $\nu_1$  (and  $\nu_2$ ) series in a sub-band increase with vibrational quantum number, while the doublet widths remain nearly constant. As a result the blending of the  $\nu_1$  and  $\nu_2$  lines takes place sooner for high

than for low vibrational quantum numbers. Nevertheless, the above description of the relationship between  $\nu_1$  and  $\nu_2$  is true for all bands. Hence, more  $\nu_2$  lines are observed in bands corresponding to low vibration. For example, Table I shows that only one  $\nu_2$  line is observed in each sub-band of band 5 while five  $\nu_2$  lines are observed in each sub-band of band 1. However, it is believed that the coincidence of overlapping with the disappearance of  $\nu_2$  may be accidental,

TABLE II. First and second differences of  $\nu_1$  series in  $\text{cm}^{-1}$ .  $\delta_L$ =best value for interval between first and second lines of a  $\nu_1$  series.  $\delta\delta_L$ =second difference in a  $\nu_1$  series.

|        | $K$ | $\delta_L$ | $\delta\delta_L$ | wt.           | Av. $\delta\delta_L$ |
|--------|-----|------------|------------------|---------------|----------------------|
| Band 1 | 15  | -0.874     | -0.0657          | 1             |                      |
|        | 16  | -0.931     | -0.0647          | 1             |                      |
|        | 17  | -0.985     | -0.0670          | 1             |                      |
|        | 18  | -1.064     | -0.0648          | 1             |                      |
|        | 19  | -1.125     | -0.0652          | 1             | --0.0655             |
| Band 2 | 14  | -0.878     | -0.0683          | 1             |                      |
|        | 15  | -0.941     | -0.0686          | 1             |                      |
|        | 16  | -0.990     | -0.0714          | 1             |                      |
|        | 17  | -1.049     | -0.0727          | $\frac{1}{2}$ |                      |
|        | 18  | -1.097     | -0.0731          | $\frac{1}{2}$ |                      |
|        | 19  | -1.212     | -0.0707          | 1             | -0.0704              |
| Band 3 | 11  | -0.998     | -0.057           | 0             |                      |
|        | 12  | -0.930     | -0.061           | 0             |                      |
|        | 13  | -0.937     | -0.0720          | 0             |                      |
|        | 14  | -0.988     | -0.0734          | $\frac{1}{2}$ |                      |
|        | 15  | -1.038     | -0.0753          | 1             |                      |
|        | 16  | -1.104     | -0.0731          | $\frac{1}{2}$ |                      |
|        | 17  | -1.158     | -0.0755          | 1             |                      |
|        | 18  | -1.238     | -0.0668          | 0             |                      |
|        | 19  | -1.303     | -0.0726          | 1             |                      |
|        | 20  | -1.364     | -0.0729          | 1             | -0.0739              |
| Band 4 | 16  | -1.395     | -0.050           | 0             |                      |
|        | 17  | -1.356     | -0.0757          | $\frac{1}{2}$ |                      |
|        | 18  | -1.372     | -0.0807          | 1             |                      |
|        | 19  | -1.424     | -0.0802          | 1             |                      |
|        | 20  | -1.476     | -0.0818          | 1             | -0.080               |
| Band 5 | 19  | -1.77      | -0.0537          |               |                      |
|        | 20  | -1.71      | -0.0754          |               |                      |
|        | 21  | -1.74      | -0.0749          |               |                      |

since predissociation seems to eliminate more and more lines from observation as the vibrational quantum number  $\nu_1'$  increases. This effect of predissociation also shows up in the fact that for bands 1 and 2 the branches are relatively hard to pick out from the numerous background lines associated with unidentified branches, while bands 4 and 5 appear quite simple, showing relatively few lines in addition to the branches measured.

#### 4. TABLE I

Table I shows the wave numbers of the strong doublet branch for each of thirty-five sub-bands. Most of the lines were measured only once from one plate. However, in the case of band 3, some of the lines were measured on each of two plates. The agreement obtained in that case as well as the agreement when lines of band 4 were measured a second time, indicates that the wave numbers of very few of the lines

have an error greater than  $0.02 \text{ cm}^{-1}$ . Some of the plates were measured by the Massachusetts Institute of Technology recording microphotometer. Because of the large amount of similar data available, it was thought unnecessary to repeat all measurements systematically. A source of error in determining the absolute values of the wave numbers arose from the fact that iron standards on the plates taken were relatively few, so that the correction curve often could not be drawn to a greater accuracy than  $\pm 0.02 \text{ cm}^{-1}$ .

Some uncertainty in the measured frequencies is introduced by the frequent blending of lines measured with background fluctuations caused by the great mass of unidentified weak lines. Additional small irregularities in intensities and in line positions apparently exist which may probably be attributed to genuine but minor quantum-mechanical perturbing effects.

It is of interest that the observed resolving power is of the order of 160,000 instead of the theoretical 300,000. This may be caused by broadening of lines because of predissociation.

The arrangement of Table I will now be considered. Two quantum numbers,  $K$  and  $L$ , are needed (see Eq. (6) below) to describe the rotational component of the wave numbers of the lines of a rigid, symmetrical top, to which the  $\text{ClO}_2$  molecule approximates (see below). Providing the spectral positions of the band lines are a good deal more sensitive to one of these quantum numbers than to the other, there occurs for a given value of the sensitive quantum number a more or less isolated group of lines corresponding to various values of the insensitive quantum number. Such a group of lines is referred to as a sub-band. Since no products between quantum numbers occur in the theoretical expression for the spectrum of a rigid, symmetrical top, every sub-band should contain the same wave number intervals except as explained by so-called missing lines. Hence, the lines in one sub-band "corresponding" to the lines in another may be found by comparing the intervals of one sub-band with those of the other.

The molecule under consideration is not quite rigid, symmetrical, or unperturbed; nevertheless, wave number intervals of one sub-band are here found to be almost equal to those of other sub-

bands in the same band. The lower the band number, the better this equality is found to be. Table I gives the wave numbers of the strong doublet branches arranged for each band as follows. Both components of a doublet branch lie in the same column, the  $\nu_1$  lines below and the  $\nu_2$  lines above. "Corresponding" lines of different sub-bands lie in the same horizontal row. It is to be noted that in passing from any sub-band to the next sub-band toward lower frequencies, one doublet disappears. The quantum number assignment indicated in Table I will be discussed below.

### 5. FIRST AND SECOND DIFFERENCES WITHIN SUB-BANDS

Table II shows the second difference  $\delta\delta_L$  for the  $\nu_1$  series of lines of each sub-band; also the best value for the interval  $\delta_L$  between the first two lines of the  $\nu_1$  series of each sub-band is given. In the table each sub-band is characterized by a particular value of  $K$ . The best values of  $\delta\delta_L$  and  $\delta_L$  were determined for each sub-band by applying the method of least squares to the series of numbers representing the intervals between the lines assuming a constant second difference. Thus  $\delta_L$  depends on the trend of these intervals.

Within any given sub-band no systematic variation in the second difference was observed. However, because of fluctuations in the second differences, a third difference as large as  $0.001 \text{ cm}^{-1}$  could easily exist without being detectable.

It may be noted from Table II that within experimental error the second difference  $\delta\delta_L$  is independent of  $K$ , that is, it is constant within a given band except for the first one or two sub-bands observed in bands 3, 4, and 5; these sub-bands have an abnormally low second difference. It is interesting that, in the case of these three bands, it is the first sub-bands having recognizable structure that have the low second difference. The irregularity of these first sub-bands must be caused by a perturbing effect which according to the data advances to higher rotational energies as the vibrational energy increases. It is also of interest that although the second difference is small for these irregular sub-bands, the first interval  $\delta_L$  is larger than would be expected from the trend of the more

regular  $\delta_L$  values. It should further be noted that for a given band the average difference between the first intervals  $\delta_L$  might be expected to equal, but are smaller than, the average of the second differences  $\delta\delta_L$ . This anomalous characteristic of the spectrum decreases with decreasing band number becoming fairly small for band 1. This is attributed to a small warping of the spectrum, because of the above-mentioned perturbing effect, which decreases with band number. These irregularities will be disregarded from here on, all considerations below being based on the more regular features of the spectrum.

A second difference has been determined for each band by averaging the values of the second differences obtained from the separate sub-bands. In so doing, the sub-bands were weighted roughly according to the number of observed lines and the smoothness of the observed second differences. From the average second differences for bands 1, 2, and 3, that for band 0 was determined by extrapolation:

$$\delta\delta_L = -0.0615 \text{ cm}^{-1} \quad (\text{band 0}).$$

There are not enough data to determine accurately the second difference for the  $\nu_2$  series of lines in each sub-band. However, the second differences of  $\nu_2$  are about the same or possibly smaller than those for  $\nu_1$ .

TABLE III.

| a. Intervals $\delta K$ between sub-bands in $\text{cm}^{-1}$ . |               |               |               |               |
|---|---------------|---------------|---------------|---------------|
| $K$   | <i>band 0</i> | <i>band 1</i> | <i>band 2</i> | <i>band 3</i> |
| 12  |               | -14.86*       | -14.87        | -14.60*       |
| 13  | (-16.16)      | -16.12        | -16.08        | -15.93*       |
| 14  | (-17.39)      | -17.35        | -17.30        | -17.23        |
| 15  | (-18.58)      | -18.54        | -18.52        | -18.45        |
| 16  | (-19.78)      | -19.74        | -19.69        | -19.68        |
| 17  | (-20.98)      | -20.94        | -20.79*       | -20.85        |
| 18  | (-22.18)      | -22.14        | -22.21*       | -22.09        |
| 19  | (-23.38)      |               | -23.30        | -23.25        |

| b. Second differences $\delta\delta K$ between sub-bands in $\text{cm}^{-1}$ . |               |               |               |               |               |
|--|---------------|---------------|---------------|---------------|---------------|
| $K$  | <i>band 1</i> | <i>band 2</i> | <i>band 3</i> | <i>band 4</i> | <i>band 5</i> |
| 12   | -1.260*       | -1.198        | -1.37*        |               |               |
| 13   | -1.240*       | -1.217        | -1.33*        |               |               |
| 14   | -1.185        | -1.229        | -1.263*       |               |               |
| 15   | -1.208        | -1.163        | -1.227        |               |               |
| 16   | -1.195        | -1.112        | -1.212        | -1.40*        |               |
| 17   | -1.196        | -1.421        | -1.229        | -1.32*        |               |
| 18   |               | -1.088        | -1.180        | -1.225        |               |
| 19   |               |               |               |               | -1.45*        |

|                  |                 |                 |                 |        |
|------------------|-----------------|-----------------|-----------------|--------|
| Av               |                 |                 |                 |        |
| $\delta\delta K$ | -1.196          | -1.204          | -1.212          | -1.225 |
|                  | ( $\pm 0.001$ ) | ( $\pm 0.003$ ) | ( $\pm 0.006$ ) |        |



TABLE IV. Values of the doublings  $\Delta\nu(K, L) = \nu_2(K, L) - \nu_1(K, L)$  observed for band 3, and their differences.

| <i>L</i> | 12   | 13   | 14   | 15   | 16   | 17   | 18   | 19   | 20   | 21   | 22   | 23   |      |      |      |      |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| <i>K</i> |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 12       | 1.20 | .12  | 1.08 |      |      |      |      |      |      |      |      |      |      |      |      |      |
|          |      | .22  |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 13       |      | 1.30 | .11  | 1.19 |      |      |      |      |      |      |      |      |      |      |      |      |
|          |      |      | .23  |      |      |      |      |      |      |      |      |      |      |      |      |      |
| 14       |      |      | 1.42 | .12  | 1.30 | .07  | 1.23 |      |      |      |      |      |      |      |      |      |
|          |      |      |      | .23  | .19  |      |      |      |      |      |      |      |      |      |      |      |
| 15       |      |      |      | 1.53 | .11  | 1.42 | .10  | 1.32 |      |      |      |      |      |      |      |      |
|          |      |      |      |      | .22  | .21  |      |      |      |      |      |      |      |      |      |      |
| 16       |      |      |      |      | 1.64 | .11  | 1.53 | .05  | 1.48 |      |      |      |      |      |      |      |
|          |      |      |      |      |      | .21  | .18  |      |      |      |      |      |      |      |      |      |
| 17       |      |      |      |      |      | 1.74 | .08  | 1.66 | .11  | 1.55 |      |      |      |      |      |      |
|          |      |      |      |      |      |      | .21  | .20  |      |      |      |      |      |      |      |      |
| 18       |      |      |      |      |      |      | 1.87 | .12  | 1.75 | .12  | 1.63 | .07  | 1.56 | .07  | 1.49 |      |
|          |      |      |      |      |      |      |      | .21  | .23  | .22  |      | .18  |      |      |      |      |
| 19       |      |      |      |      |      |      |      | 1.96 | .10  | 1.86 | .08  | 1.78 | .11  | 1.67 | .12  | 1.55 |
|          |      |      |      |      |      |      |      |      | .20  | .20  | .18  |      | .22  |      |      |      |
| 20       |      |      |      |      |      |      |      |      | 2.06 | .08  | 1.98 | .13  | 1.85 | .08  | 1.77 |      |

## 6. FIRST AND SECOND DIFFERENCES BETWEEN SUB-BANDS

Table IIIa shows the best values for the intervals  $\delta_K = \nu_1(K+1, L) - \nu_1(K, L)$  between sub-bands. Each number of the table is the average of the intervals between corresponding  $\nu_1$  lines of two neighboring sub-bands. The intervals marked by asterisks do not follow the general trend. Values of  $\delta_K$  for band 0 are determined by extrapolating from observed  $\delta_K$  values.

The second differences  $\delta\delta_K = \delta_{K+1} - \delta_K$  between sub-bands are shown in Table IIIb. Each number of the table is obtained from the three adjacent sub-bands characterized by  $K$ ,  $K+1$ , and  $K+2$  and is the average of the second difference between corresponding lines of these three bands. No systematic variation with  $L$  is observed. The high second differences marked with an asterisk in bands 3, 4, and 5 are apparently caused by the perturbing effect already mentioned. These particular second differences were not included in the determination of the average second difference for each band. From the average  $\delta\delta_K$  values for bands 1, 2, and 3, that for band 0 was determined by extrapolation:

$$\delta\delta_K = -1.188 \text{ cm}^{-1} \quad (\text{band 0}).$$

The  $\nu_2$  series furnish relatively few second differences, but the average for all bands is  $-1.20 \text{ cm}^{-1}$ .

It is interesting to note that as the band number increases the second differences  $\delta\delta_K$  increase while the first differences  $\delta_K$  decrease.

This will be described by a linear term in  $K$  which varies with vibration.

## 7. OBSERVED DOUBLING

Since  $\text{ClO}_2$  has an odd number of electrons, a spin doubling is expected. As was mentioned in Section 3, the strong branch in each sub-band is composed of doublets. Let the doublet widths  $\nu_2(K, L) - \nu_1(K, L)$  be designated by  $\Delta\nu(K, L)$ . It will be shown that the  $\Delta\nu(K, L)$  values may be represented reasonably well by

$$\Delta\nu(K, L) = \Delta\gamma(2K - L) - a(v' - 1), \quad (1)$$

with  $\Delta\gamma = 0.109 \text{ cm}^{-1}$  and  $a = 0.045 \text{ cm}^{-1}$ . Here the first term describes the major part of the doubling.

The  $\Delta\nu(K, L)$  values obtained from the data of band 3 are shown in Table IV. There are three types of differences that can be taken from this table of  $\Delta\nu(K, L)$  values: namely, horizontal ( $h$ ), vertical ( $v$ ), and diagonal ( $d$ ). There is no definite indication that any of these differences vary with  $L$  or with  $K$ . However, a significant variation could be hidden by the fluctuation of the data and the shortness of the series. According to Eq. (1), the horizontal and diagonal differences should be the same, and equal to  $\Delta\gamma$ , while the vertical differences should be twice this. When the experimental differences are determined, it is found that these simple relations are nearly but not quite true.

A value for the diagonal difference was obtained by applying the method of least squares

to each diagonal. The results for five bands are shown in Table Va. The numbers are underlined according to their weight. The weighted average of these numbers gives a diagonal difference of 0.109. The average of horizontal and vertical differences for the first three bands are shown in Table Vb. The fact that these differences indicate a slightly lower value for  $\Delta\gamma$  than the diagonal differences shows that Eq. (1) does not represent the data exactly.

It is observed that for given values of  $K$  and  $L$  the magnitudes  $\Delta\nu(K, L)$  of the doublet widths decrease slightly with increasing vibrational quantum number. To illustrate this variation, smoothed observed values for  $\Delta\nu(19, 19)$  and  $\Delta\nu(16, 16)$  were estimated to within 0.01 cm<sup>-1</sup> for each band and compared with values calculated from Eq. (1). The results are given in Table VI. The second term of Eq. (1) is required to describe this variation with band number which appears to be essentially independent of  $K$  and  $L$ .

#### 8. EVIDENCE FOR "CASE *b*" COUPLING

A theoretical expression<sup>6</sup> for the rotational term values of a rigid diatomic molecule including doubling due to a resultant electronic spin  $S = \frac{1}{2}$  is given by Hill and Van Vleck. In their notation the term values are

$$F_j = B \left\{ (j + \frac{1}{2})^2 - \sigma_k^2 \pm \frac{1}{2} [4(j + \frac{1}{2})^2 + \lambda(\lambda + 4)\sigma_k^2] \right\}.$$

Here  $j$  determines the total angular momentum of the molecule including spin, and  $\sigma_k$  the

TABLE V.

| a. Observed diagonal differences = $\Delta\gamma_d = \Delta\nu(K+1, L+1) - \Delta\nu(K, L)$ . |               |               |               |               |               |
|---|---------------|---------------|---------------|---------------|---------------|
|   | <i>band 1</i> | <i>band 2</i> | <i>band 3</i> | <i>band 4</i> | <i>band 5</i> |
| $L = K$   | 0.123         | 0.109         | 0.109         | 0.102         | 0.105         |
| $L = K+1$   | 0.111         | 0.109         | 0.1125        | 0.078         |               |
| $L = K+2$   | 0.104         | 0.111         | 0.105         |               |               |
| $L = K+3$   | 0.104         | 0.115         |               |               |               |
| $L = K+4$   | 0.109         |               |               |               |               |
| b. Observed horizontal differences, and vertical differences.                                 |               |               |               |               |               |
|   | <i>band 1</i> | <i>band 2</i> | <i>band 3</i> |               |               |
| $\Delta\gamma_h = \Delta\nu(K, L)$  |               |               |               |               |               |
| $-\Delta\nu(K, L+1)$  |               | 0.105         | 0.105         | 0.101         |               |
| $2\Delta\gamma_v = \Delta\nu(K+1, L)$   |               |               |               |               |               |
| $-\Delta\nu(K, L)$  | 2×0.107       | 2×0.108       | 2×0.104       |               |               |

<sup>6</sup> E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 261 (1928).

TABLE VI.

| Band | Obs.<br>$\Delta\nu(19, 19)$ | Calc.<br>$\Delta\nu(19, 19)$ | Obs.<br>$\Delta\nu(16, 16)$ | Calc.<br>$\Delta\nu(16, 16)$ |
|------|-----------------------------|------------------------------|-----------------------------|------------------------------|
| 1    | 2.07                        | 2.07                         | 1.73                        | 1.74                         |
| 2    | 2.02                        | 2.03                         | 1.68                        | 1.70                         |
| 3    | 1.97                        | 1.98                         | 1.65                        | 1.65                         |
| 4    | 1.93                        | 1.94                         | 1.61                        | 1.61                         |

component of the latter along the line joining the atoms. The quantity  $\lambda B$  is the coupling constant between  $\sigma_k$  and spin. Interaction between spin and rotation about an axis perpendicular to the symmetry axis is neglected by Hill and Van Vleck. The minus sign corresponds in Hund's "case *b*" to terms arising from parallel coupling ( $j = j_k + \frac{1}{2}$ ) and the plus sign to anti-parallel coupling ( $j = j_k - \frac{1}{2}$ ), where  $j_k$  is the total angular momentum excluding spin.

Apparently this formula should also apply to any rigid symmetrical top molecule with  $S = \frac{1}{2}$  if a term  $AK^2$  is added to include the rotational energy about the symmetry axis of the molecule. If the notation is changed to that of the present paper<sup>7</sup> ( $j \rightarrow J$ ,  $j_k \rightarrow L$ ,  $\sigma_k \rightarrow K$ ,  $\lambda \rightarrow \gamma/\bar{B}$ ) and if the formula is expressed in terms of  $L$  instead of  $J$ , it may be written in the form

$$F_1 = AK^2 + \bar{B} \{ (L+1)^2 - K^2 - \frac{1}{2} [4(L+1)^2 + \lambda(\lambda-4)K^2] \}^{\frac{1}{2}},$$

$$F_2 = AK^2 + \bar{B} \{ (L)^2 - K^2 + \frac{1}{2} [4L^2 + \lambda(\lambda-4)K^2] \}^{\frac{1}{2}}. \quad (2)$$

For Hund's "case *b*" a term having given values of  $K$  and  $L$  is split into two components  $F_1$  and  $F_2$  given by the above formulas.  $F_1$  and  $F_2$  correspond, respectively, to  $J_1 = L + \frac{1}{2}$  and  $J_2 = L - \frac{1}{2}$ . It is not known whether  $\nu_1$  and  $\nu_2$ , defined empirically in Section 3, correspond to  $F_1$  and  $F_2$ , respectively, or *vice versa*.

If it is assumed that the spin coupling in ClO<sub>2</sub> is close to "case *b*" type ( $\lambda$  small) and if it is noted that  $L$  is approximately equal to  $K$  for the doublets observed, the  $F$ 's may be expanded in terms of  $\gamma$  and the following approximate expression for the observed doublet widths

<sup>7</sup> Throughout this paper,  $L$  is used as the quantum number of the total angular momentum of molecular rotation excluding electron spin, while  $J$  is used for the quantum number of the total angular momentum including the electron spin.

$\Delta\nu = (F_1' - F_1'') - (F_2' - F_2'')$  may be obtained:

$$\Delta\nu = \Delta\gamma K^2/L + \frac{1}{2}. \quad (3)$$

It is found that the doubling is approximately symmetrical.

This theoretical expression does not fit the data as well as the empirical relation given by Eq. (1), but a certain qualitative agreement between (1) and (3) indicates that the coupling type is close to "case *b*." For the large  $K$  values of the observed doublets, Eq. (3) does not differ greatly from the empirical expression  $\Delta\gamma(2K-L)$  which composes the large part of the observed  $\Delta\nu$ . According to Eq. (3) the diagonal differences should be quite close to  $\Delta\gamma$ , and the horizontal differences should average about  $0.8\Delta\gamma$ . This disagreement between diagonal and horizontal differences has the same sign as is observed, but has about four times the observed magnitude. This departure from "case *b*" appears to be a likely explanation for the observed linear terms in  $L$  and  $K$ . (See Sections 12 and 13.)

## PART II

### 9. ENERGY LEVELS OF AN ASYMMETRICAL TOP<sup>8</sup>

Let  $I_A < I_B < I_C$  be the three moments of inertia of a molecule and let  $A, B, C$  be the corresponding "reciprocals of inertia" where  $A = h^2/8\pi^2 CI_A$ , etc. Formulas for calculating the exact energy levels of a rigid asymmetrical top are known<sup>9</sup> for values of the rotational angular momentum<sup>7</sup> up to  $L=11$ . However, the range of quantum numbers associated with the spectral lines here observed lies above  $L=11$ , being essentially  $L=K$  to  $K+8$  with  $K=11$  to 20.

For these large values of  $L$  an approximate formula given by Witmer<sup>10</sup> is useful. This formula may be written in two forms. One form is

$$F_p = \bar{B}_p L(L+1) + (A - \bar{B}_p) K_p^2 + \frac{1}{32} \frac{(B-C)^2}{(A - \bar{B}_p)} \left[ \frac{L^2(L+1)^2}{K_p^2 - 1} + 2L(L+1) - 3K_p^2 \right], \quad (4)$$

<sup>8</sup> A theoretical discussion of rotational energy levels of non-linear triatomic molecules is given by R. S. Mulliken, *Phys. Rev.* **59**, 873 (1941).

<sup>9</sup> H. H. Nielsen, *Phys. Rev.* **38**, 1432 (1931). For corrections and extension to  $L=11$ , see H. M. Randall, D. M. Dennison, N. Ginsberg, and L. R. Weber, *Phys. Rev.* **52**, 160 (1937). See also G. W. King, R. M. Hainer, and P. C. Cross, *J. Chem. Phys.* **11**, 27 (1943).

<sup>10</sup> E. E. Witmer, *Proc. Nat. Acad.* **13**, 60 (1927).

where  $2\bar{B}_p = B + C$ , and  $F_p$  is the rotational term value in  $\text{cm}^{-1}$ . The first two terms will be referred to as the "prolate symmetrical top approximation." The last term is the first correction term for asymmetry. Witmer's formula may also be written in the form

$$F_o = \bar{B}_o L(L+1) + (C - \bar{B}_o) K_o^2 + \frac{1}{32} \frac{(A-B)^2}{(C - \bar{B}_o)} \left[ \frac{L^2(L+1)^2}{K_o^2 - 1} + 2L(L+1) - 3K_o^2 \right], \quad (5)$$

where  $2\bar{B}_o = A + B$ . Here the first two terms will be referred to as the "oblate symmetrical top approximation."  $K_p$  and  $K_o$  are approximate quantum numbers.

The range of quantum numbers for which formulas (4) and (5) may be applied will now be considered. The energy levels of a rigid asymmetrical top model may be calculated for say  $L=8$  using the exact formulas of Nielsen. The levels obtained are doublets. If the average be taken for each doublet, a set of levels are obtained which may be compared to the two sets of levels obtained by using Eqs. (4) and (5) and if this comparison is made for several models of different asymmetry, the following relationships may be noted. For a given value of  $L$ , the high energy levels (average of doublets) may be approximately calculated using Eq. (4) ( $K_p = L$  giving the highest level) while the low energy levels may be calculated using Eq. (5) ( $K_o = L$  giving the lowest level). Only a few intermediate levels cannot be approximated in this way. Hence, the approximate quantum number  $K_p$  may be associated with the high doublet levels and  $K_o$  may be associated with the low doublet levels. The doublet separation for a given  $L$  is small when  $K=L$  and increases as  $(L-K)$  increases, remaining small compared to the asymmetry correction except for the few intermediate levels. If the top is more nearly prolate than oblate, Eq. (4) holds through a greater range than Eq. (5); and *vice versa*. If the top is only slightly asymmetric being nearly prolate for example, Eq. (4) holds except for the lowest values of  $K$ .

In the next section it will be shown, on the basis of what is already known about  $\text{ClO}_2$ , that it is closer to a prolate symmetrical top than to an oblate top. Hence, in the following sections the prolate symmetrical top approximation is

assumed. The energy levels will be designated by the quantum numbers of the corresponding prolate symmetrical top. In a closing section it will be shown that the asymmetry correction is of the order of experimental error.

#### 10. TENTATIVE MODEL OF $\text{ClO}_2$ MOLECULE AND IDENTIFICATION OF $K$ AND $L$ STRUCTURES

Tentative moments of inertia were calculated for the lower electronic state using the  $\text{Cl}-\text{O}$  distance of 1.53 Å found from electron diffraction experiments<sup>11</sup> and the approximate  $\text{O}-\text{Cl}-\text{O}$  angle of  $122^\circ 50'$  determined from the three vibrational frequencies established for the lower state.<sup>2</sup> It is recognized that the angle determined on the basis of the valence force approximation may have a considerable error. However, that the angle is fairly large in the ground state is supported by the electron diffraction result for this angle,  $137^\circ \pm 15^\circ$ . Thus, tentatively,

$$\begin{aligned} I_A'' &= 14.77 \times 10^{-40} \text{ g-cm}^2, \\ I_B'' &= 95.2 \times 10^{-40} \text{ g-cm}^2, \\ I_C'' &= 110.0 \times 10^{-40} \text{ g-cm}^2. \end{aligned}$$

Since  $I_B$  and  $I_C$  are roughly equal, the molecule in the normal state approximates a prolate symmetrical top with the symmetry axis ( $A$  axis) parallel to the line joining the oxygen atoms. The same is assumed to be true for the excited state since, according to vibrational analysis, the angle diminishes only about 11 degrees in this state.

In order to make some preliminary calculations, it will be assumed that the rotational energy levels of  $\text{ClO}_2$  are given by the "prolate top approximation" formula

$$F(K, L) = \bar{B}L(L+1) + (A - \bar{B})K^2. \quad (6)$$

Here  $K$  must not be too small. This approximation neglects the asymmetry term which is quite small for the above-mentioned model. Even for a  $109^\circ$  model the coefficient of the asymmetry term of Eq. (4) is less than 0.0002 while  $\bar{B}$  is of the order of 0.3. The effect of asymmetry will be discussed in detail in a later section. This expression also neglects terms such as might arise from rotational stretching, interactions between rotation and vibration, and perturbations.

<sup>11</sup> L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).

The wave number  $\nu$  of a line of an electronic band is usually expressed as the sum of three terms, namely, electronic, vibrational, and rotational. That is,

$$\nu = \nu^e + \nu^v + \nu^r.$$

For a symmetrical top molecule the rotational part is given by

$$\nu^r(K'', L'') = F'(K', L') - F''(K'', L''). \quad (7)$$

According to customary symmetrical top notation,  $\Delta K \equiv K' - K'' = -1, 0, +1$  correspond, respectively, to  $p, q$ , and  $r$  branches, while  $\Delta L \equiv L' - L'' = -1, 0, +1$  correspond, respectively, to  $P, Q$ , and  $R$  branches.

Whether we are dealing with perpendicular-type bands ( $\Delta K = \pm 1$ ) or with parallel-type bands ( $\Delta K = 0$ ), and regardless of what branches in these bands we are dealing with, the second differences in the  $L$  structure ( $K'$  and  $K''$  constant) and in the  $K$  structure ( $L'$  and  $L''$  constant) should, on the basis of Eqs. (6) and (7), be equal to  $2\Delta\bar{B}$  and  $2(\Delta A - \Delta\bar{B})$ , respectively, where

$$\left. \begin{aligned} \Delta\bar{B} &= \frac{h}{8\pi^2c} \left( \frac{1}{I_{B'}} - \frac{1}{I_{B''}} \right) \\ \Delta A &= \frac{h}{8\pi^2c} \left( \frac{1}{I_{A'}} - \frac{1}{I_{A''}} \right) \end{aligned} \right\} \quad (8)$$

and

in which

$$\frac{1}{I_{\bar{B}}} = \frac{1}{2} \left( \frac{1}{I_B} + \frac{1}{I_C} \right).$$

It is necessary to determine which of the second differences called  $\delta\delta_L$  and  $\delta\delta_K$  in Sections 5 and 6 is to be identified as essentially  $2\Delta\bar{B}$  and which as  $2(\Delta A - \Delta\bar{B})$ . Both the intervals between the sub-bands and the intervals between the lines of a sub-band increase toward the red end of the spectrum. Hence, both of the observed second differences are negative; therefore, both  $\Delta\bar{B}$  and  $(\Delta A - \Delta\bar{B})$  are negative. It then follows from (8) that both  $I_{\bar{B}}$  and  $I_A$  become larger in the excited state. The observed second differences divided by two are approximately  $-0.03$  and  $-0.6$ . Considering the value of  $I_{B''} \approx I_{C''}$  calculated above, it is impossible to identify  $-0.6$

with  $\Delta\bar{B}$  since  $h/8\pi^2cI_B''$  is considerably less than 0.6. Therefore,  $-0.03$  is identified with  $\Delta\bar{B}$  and  $-0.6$  with  $(\Delta A - \Delta\bar{B})$ . Hence,

$$\delta\delta_L \approx 2\Delta\bar{B}, \quad \delta\delta_K \approx 2(\Delta A - \Delta\bar{B}). \quad (9)$$

These relations are not necessarily exact because Eq. (6) is not the exact expression for the actual term values. Equation (9) means that  $K$  quantum numbers are associated with the sub-bands and  $L$  quantum numbers are associated with the lines of the sub-bands and explains the notation already used for the observed differences. Whether this or the reverse assignment is correct may also be determined on the basis of the rule  $L \geq K$ .

The values of  $\Delta\bar{B}$  and  $(\Delta A - \Delta\bar{B})$  from the observed second differences determine the changes in the moments of inertia at excitation. Using the tentative moments of inertia calculated above for the lower state, and the second differences  $-0.0739 \approx 2\Delta\bar{B}$  and  $-1.212 \approx 2(\Delta A - \Delta\bar{B})$  that were found from band 3, tentative moments of inertia for the excited state may be calculated. These are

$$I_A' = 22.50 \times 10^{-40} \text{ g-cm}^2, \\ I_B' = 118.2 \times 10^{-40} \text{ g-cm}^2.$$

These moments of inertia correspond to a Cl—O distance of 1.69 Å and an angle of  $115^\circ$ . This angle is qualitatively consistent with the result of  $112^\circ$  determined from the three vibrational frequencies established for the upper state.<sup>2</sup> The above considerations give tentative models for both states.

#### 11. PROOF THAT THE OBSERVED BANDS ARE PARALLEL BANDS

Evidence will now be given to show that the electric moment associated with the electronic transition is parallel to the quasi-symmetry axis ( $A$  axis). On the basis of the above-mentioned tentative model, diagrams of sub-bands for both parallel- and perpendicular-type bands were constructed,<sup>12</sup> showing the distribution of the separate lines as well as their relative intensities. The relative intensities of the lines are given by the Hönl-London formulae.<sup>13</sup> It was found that,

<sup>12</sup> Some examples of such a construction for  $\text{SO}_2$  are discussed by N. Metropolis, Phys. Rev. **60**, 283 (1941).

<sup>13</sup> G. Herzberg, *Infra-Red and Raman Spectra* (D. Van Nostrand Company, New York, 1945), pp. 421 and 426.

for sub-bands with  $K$  values greater than 10, there are certain similarities between perpendicular-type sub-bands with  $\Delta K = -1$  and parallel-type sub-bands. Figure 4 shows an example of each type of sub-band. In both types each sub-band has a strong branch consisting of a group of lines in which the spacing increases and the intensity decreases toward the red, and a weaker branch which starts on the violet side of the first line of the strong branch and extends into the strong branch. In the case of the perpendicular-type sub-band the two branches mentioned are  $P$  (strong) and  $Q$  (weak), while in the case of the parallel-type sub-band the two branches are  $Q$  (strong) and  $R$  (weak). The third branch which is weak in both types of sub-bands will be mentioned below.

In the spectrum under consideration, it is observed that there is one strong branch (doublet) in each sub-band. A weak branch which follows the above description is also found in eight of the sub-bands (see Fig. 3). It is observed that at a given point in the spectrum the interval between two lines of the strong branch is smaller than the interval between two lines of the weak branch. This means that the strong branch must be a  $Q$  branch and, hence, that the weak branch is an  $R$  branch. *Therefore, the observed bands must be of the parallel type.*

Further evidence supporting this conclusion is the fact that a weak third branch ( $P$ ) has been observed in two sub-bands. These  $P$  branches are qualitatively in the same position as in the constructed diagram of a parallel sub-band. The reality of the above-mentioned  $P$  branches was proven by obtaining the same  $\Delta_1 F'$  and  $\Delta_1 F''$  values (see Eq. (18) below) from these  $P$  and the  $Q$  branches as are obtained from the  $R$  and  $Q$  branches.

Additional evidence that the bands are of the parallel type is given by the fact that the  $r$  branch of sub-bands ( $\Delta K = +1$ ) expected for perpendicular-type bands does not appear. Using the observed second differences in the  $K$  structure one can compute that, if the bands were perpendicular, the  $r$  branch of sub-bands would come to a head very quickly and degrade to the red only about three sub-bands behind the  $p$  branch of sub-bands ( $\Delta K = -1$ ).

A qualitative consideration of the observed

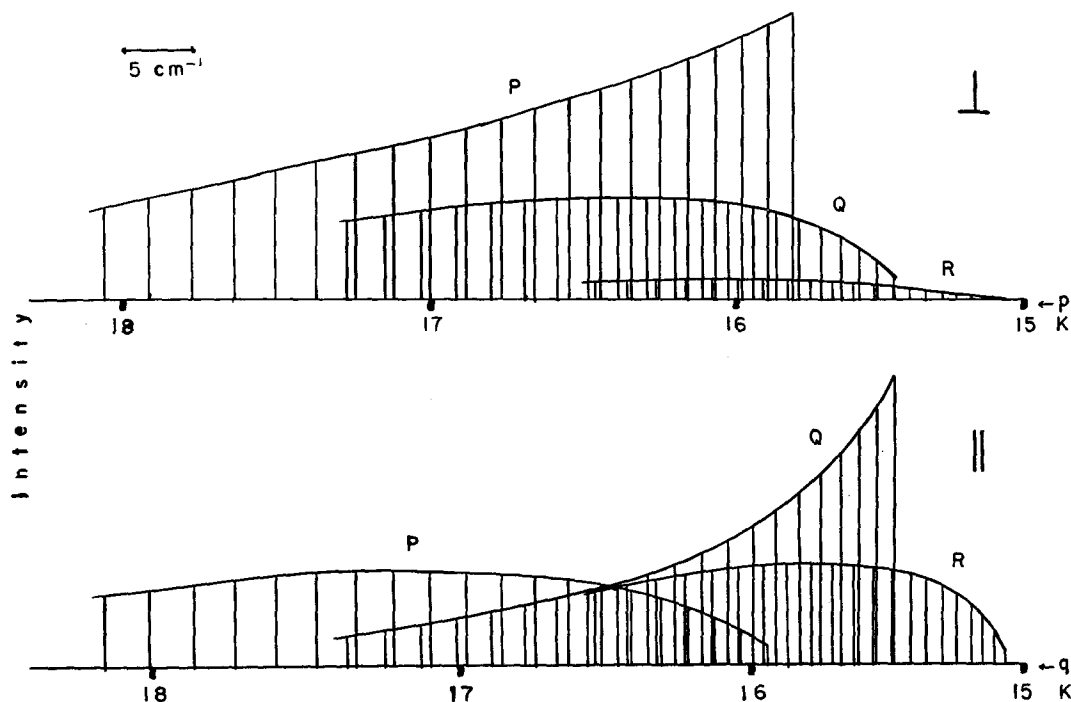


FIG. 4. Computed sub-band  $K''=15$  constructed for both perpendicular and parallel type bands on the basis of the symmetrical top approximation and the tentative model. (See Section 10 for the moments of inertia of this model.) The heavy leaders show the relative positions of the origins of other sub-bands,  $p$  branch of origins above and  $q$  branch below. Wave numbers increase toward the right.

distribution of intensity within the sub-bands also indicates parallel type bands. The  $Q$  branch of a sub-band of a parallel type band diminishes in intensity faster than the  $P$  branch of a sub-band of a perpendicular type band. The author noticed this indication of parallel bands before any of the above arguments were considered.

## 12. ASSIGNMENT OF THE QUANTUM NUMBERING AND DESCRIPTION OF THE $K$ STRUCTURE

The large second difference in the  $K$  structure must, of course, be attributed primarily to the coefficient of the  $K^2$  term in the prolate symmetrical top approximation, see Eq. (6). Because of the large magnitude of this second difference, which is attributed to the fact that  $I_A$  approximately doubles in the excited state, it is considered probable that terms such as might arise from stretching, asymmetry, perturbations, and interactions would be small in comparison to the  $K^2$  term. Therefore, the quantum numbering determined in this section on the basis of the  $K$  structure is considered more reliable than that determined from any other feature of the spec-

trum. For the first line of a  $Q$  branch of a given sub-band  $L=K$ . Hence, if the  $K$  numbering is determined, the  $L$  numbering is known.

On the basis of the prolate symmetrical top approximation to the energy levels, the  $qQ$  branch ( $\Delta L = \Delta K = 0$ ) for a given band should be given by

$$\nu_{1,2}^r = (\Delta\bar{B})L(L+1) + (\Delta A - \Delta\bar{B})K^2 \mp \frac{1}{2}[\Delta\gamma(2K-L) - a(v'-1)], \quad (10)$$

where the quantity in square brackets is added to describe the doubling attributed to spin. Since  $\nu_1$  has been chosen to designate the doubling component toward the red, it corresponds to the minus sign in the doubling term. It is not known whether  $\nu_1^r$ , defined here empirically, corresponds to  $F_1' - F_1''$  or to  $F_2' - F_2''$ , see Eq. (2).

On the basis of (9) and (10) it might be expected that the  $K$  structure would be fairly well described by

$$\nu_{1,2}^r = f(L, v') + \frac{1}{2}\delta\delta_K K^2 \mp \frac{1}{2}\Delta\gamma(2K). \quad (11)$$

Substituting Eq. (11) into the expression  $\delta_K = \nu_1^r(K+1, L) - \nu_1^r(K, L)$  giving the first difference

TABLE VII. Values of  $K$  calculated from the  $K$  structure.

|                              |       |       |       |       |       |       |       |       |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>Band 1</i>                | 11.83 | 12.89 | 13.91 | 14.91 | 15.91 | 16.92 | 17.92 |       |
| <i>Band 2</i>                | 11.76 | 12.76 | 13.78 | 14.79 | 15.76 | 16.68 | 17.88 | 18.76 |
| <i>Band 3</i>                | 11.46 | 12.55 | 13.63 | 14.63 | 15.65 | 16.61 | 17.64 | 18.59 |
| <i>K numbering indicated</i> | 12    | 13    | 14    | 15    | 16    | 17    | 18    | 19    |

in the  $K$  structure, one may obtain

$$\delta_K = \frac{1}{2}\delta\delta_K(2K+1) - \Delta\gamma. \quad (12)$$

Using the experimental values of  $\delta_K$  and  $\delta\delta_K$  from Section 6 and the value of  $\Delta\gamma = 0.11 \text{ cm}^{-1}$  from Section 7, a value of  $K$  was calculated for each sub-band interval. The results are given in Table VII. The  $K$  numbering indicated here is adopted as correct and is the same as that used throughout the paper. Since this integral  $K$  numbering is assumed correct, a term must be added to the right member of Eq. (12) in order to make it describe accurately the observed values of  $\delta_K$  given in Section 6. This term is empirically found to be  $\Delta b(v'-d)$  where  $\Delta b = 0.174 \text{ cm}^{-1}$  and  $d = 0.41$ . The addition of this term to the right member of Eq. (12) requires that the term  $\Delta b(v'-d)K$  be added to the right member of Eqs. (10) and (11). Hence, the  $K$  structure of the  $qQ$  branch is accurately described by

$$\nu_{1,2} = f(L, v') + \frac{1}{2}\delta\delta_K K^2 + \Delta b(v'-d)K \mp \frac{1}{2}\Delta\gamma(2K). \quad (13)$$

Because of the experimental error in  $\delta\delta_K$ , the values of  $\Delta b$  and  $d$  may be in considerable error. For example, the variation in  $\delta\delta_K$  with band number could be adjusted within experimental error so as to reduce  $d$  to zero. On the other hand, it is certain that the term  $\Delta b v' K$  describes a real characteristic of the observed  $K$  structure.

### 13. QUANTUM NUMBERING INDICATED BY $L$ STRUCTURE AND DESCRIPTION OF THE $L$ STRUCTURE

The quantum number assignment may be determined on the basis of the  $L$  structure in a manner analogous to the determination on the basis of the  $K$  structure. On the basis of Eq. (10), it might be expected that the  $L$  structure would be fairly well described by

$$\nu_{1,2} = F(K, v') + \frac{1}{2}\delta\delta_L L(L+1) \pm \frac{1}{2}\Delta\gamma L. \quad (14)$$

Now the first interval of the  $\nu_1$  series for a given

sub-band is  $\delta_L = \nu_1'(L+1, K) - \nu_1'(L, K)$  in which  $L = K$ . Hence by using (14),

$$\delta_L = \delta\delta_L(L+1) + \frac{1}{2}\Delta\gamma, \quad (L=K). \quad (15)$$

Using experimental values of  $\delta_L$  and  $\delta\delta_L$  given in Table II and using the value of  $\Delta\gamma = 0.11 \text{ cm}^{-1}$  from Section 7,  $K$  was calculated for each sub-band. The results are given in Table VIII.

As shown in the table, the numbering indicated by the  $L$  structure is two less than that indicated by the  $K$  structure. The  $L$  structure determination is, however, considered less reliable because the second differences  $\delta\delta_L$  are relatively small and any terms that have been neglected would be likely to produce a significant effect.

Substituting the adopted quantum numbering and the observed constants into Eq. (15), it is found that a term must be added to the right member in order to describe the experimental values of  $\delta_L$ . This term is constant ( $\Delta c = 0.13 \text{ cm}^{-1}$ ) within a band, especially for band 1. There may be some increase of this constant with  $v'$ , but this increase is of the order of experimental error. The addition of a constant  $\Delta c$  to the right member of Eq. (15) requires the addition of a term  $\Delta c L$  to the right member of Eq. (14). Hence, the  $L$  structure of the  $qQ$  branch is accurately described by

$$\nu_{1,2} = F(K, v') + \frac{1}{2}\delta\delta_L L(L+1) + \Delta c L \pm \frac{1}{2}\Delta\gamma L. \quad (16)$$

### 14. FINAL DESCRIPTION OF $qQ$ BRANCHES AND POSITION OF BAND HEADS

It has been shown that the  $qQ$  branches of bands 1, 2, and 3 can be described by

$$\nu_{1,2} = \frac{1}{2}\delta\delta_L L(L+1) + \frac{1}{2}\delta\delta_K K^2 + \Delta c L + \Delta b(v'-d)K \mp \frac{1}{2}[\Delta\gamma(2K-L) - a(v'-1)]. \quad (17)$$

It should be emphasized that this formula does not necessarily hold outside of the range of observations,  $K = 11$  to 20 and  $L = K$  to  $K+8$ .

TABLE VIII. Values of  $K$  calculated from  $L$  structure.

|                                 |      |      |      |      |      |      |      |
|---------------------------------|------|------|------|------|------|------|------|
| <i>Band 1</i>                   |      | 13.2 | 14.0 | 14.9 | 16.1 | 17.0 |      |
| <i>Band 2</i>                   | 12.2 | 13.1 | 13.8 | 14.7 | 15.4 | 17.0 | 18.3 |
| <i>Band 3</i>                   |      |      |      | 15.4 | 16.5 | 17.4 | 18.2 |
| <i>Band 4</i>                   |      |      |      |      |      | 17.5 | 18.1 |
| Numbering indicated here        | 12   | 13   | 14   | 15   | 16   | 17   | 18   |
| Numbering used throughout paper | 14   | 15   | 16   | 17   | 18   | 19   | 20   |

It is also to be noted that all the constants except  $\Delta\gamma$  and  $a$  were obtained from the  $\nu_1$  series, which corresponds to the minus sign in the doubling term. The first two terms are identified with the prolate symmetrical top approximation. The constants of these terms, given in Tables II and IIIb, vary with band number  $\nu'$ . In Section 18 it will be shown that asymmetry may contribute as much as 30 percent to  $\delta\delta_L$ . However, up to that Section it is considered that, except for the linear terms, the spectrum is that of a symmetrical top. The doubling term is attributed to spin. The constants of this term are given in Section 7. The third and fourth terms, see Sections 12 and 13, are empirical terms which, except for  $\Delta bK\nu'$ , may possibly be associated with the spin doubling. This term in  $K\nu'$  is not interpreted. There is no empirical evidence of the existence of fourth power terms in  $L$  and  $K$ .

The observed interval between a line  $K=L=19$  and the head of the corresponding band may be determined from the wave number of the line given in Table I and the wave number of the band head given in Section 3. This interval for five bands is given in the right hand column of Table IX. It is interesting to compare this interval with the value of  $\nu_1^r$  calculated for bands 1, 2, and 3 from Eq. (17). The results of this calculation are given in the left-hand column. It is to be noted that Eq. (17) was obtained without reference to the band heads. The position of the band origin with respect to the observed lines  $K=L$  is, of course, not appreciably affected by asymmetry if, as is the case, the energy levels for high  $K=L$  values are not appreciably affected by asymmetry.

In order to compare  $\nu_1^r$  with  $\nu_1 - \nu_{\text{head}}$ , the interval between the band origin and the band head, which should be caused by the  $R$  branch of the first sub-band, must be added to the magnitude of  $\nu_1^r$ . If the effect of asymmetry is taken into account, the calculated interval is about  $1.3 \text{ cm}^{-1}$ . Hence, for band 1 the disagreement between calculated and observed  $\nu_1 - \nu_{\text{head}}$  is about  $5.4 \text{ cm}^{-1}$ . It seems possible that this disagreement is caused by the observed perturbation. For example, for band 3, see Table III, the first few intervals  $\delta_K$  between sub-bands are smaller than would be expected on the basis

TABLE IX.

|               | $\nu_1^r(19, 19) \text{ calc.}$ | $\nu_1(19, 19) - \nu_{\text{head}}$ |
|---------------|---------------------------------|-------------------------------------|
| <i>Band 1</i> | $-224.9 \text{ cm}^{-1}$        | $-220.8 \text{ cm}^{-1}$            |
| <i>Band 2</i> | $-224.0$                        | $-221.8$                            |
| <i>Band 3</i> | $-222.8$                        | $-222.0$                            |
| <i>Band 4</i> |                                 | $-222.8$                            |
| <i>Band 5</i> |                                 | $-222.6$                            |

of a constant second difference of about 1.20. If it be supposed that the intervals between several of the unobserved sub-bands in all bands are smaller than would be expected on the basis of a constant second difference, the actual distance to the head would be less than the theoretical distance, as is found to be the case.

### PART III

#### 15. $\Delta_1 F$ VALUES

It has been pointed out that each sub-band contains a strong doublet  $Q$  branch which was easily identified. However, it was also necessary to locate the weaker  $P$  and  $R$  branches (see Fig. 4) in order to determine the moments of inertia for the upper and lower states without having to assume for the lower state a model based partly on vibration analysis as is done in Section 10. Since both components of the doublets are observed for only the first few members of each  $Q$  branch, it is not to be expected that the doubling would be observed in the  $P$  and  $R$  branches, where the first few members are so weak that they are not observed at all. Since in the  $Q$  branches the  $\nu_1$  series is more persistent, it is assumed that the  $P$  and  $R$  lines observed are all  $\nu_1$  lines. Hence these branches will be designated by  $P_1$  and  $R_1$ , and the corresponding term values by  $F_1$ . This  $F_1$  is not to be necessarily identified with  $F_1$  of Eq. (2). With the aid of the constructed band diagram given in Fig. 4 and after considerable searching, the branches given in Table X were picked out. Figure 3 shows some of the  $R$  branches. The wave numbers were determined by interpolation between lines of  $Q$  branches which had previously been measured. The  $L$  assignments were obtained as described below.

If it be assumed that any  $K$  doubling, caused by asymmetry or by interactions analogous to those which give rise to  $\Lambda$ -doubling for diatomic



TABLE X. Observed  $P_1$  and  $R_1$  branches.

| $K$ | Band 2         |                | Band 3         |                |                |                |                |                | Band 4         |                |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|     | 15<br>$R_1(L)$ | 17<br>$R_1(L)$ | 15<br>$R_1(L)$ | 16<br>$R_1(L)$ | 17<br>$R_1(L)$ | 18<br>$R_1(L)$ | 19<br>$R_1(L)$ | 19<br>$P_1(L)$ | 18<br>$P_1(L)$ | 19<br>$R_1(L)$ |
| $L$ |                |                |                |                |                |                |                |                |                |                |
| 19  | 22295.32       |                |                |                |                |                |                |                |                |                |
| 20  | 294.62         |                |                |                |                |                |                |                |                |                |
| 21  | 293.91         |                | 22986.82       |                |                |                |                |                |                |                |
| 22  | 293.06         | 22254.86       | 985.86         | 22967.50       |                |                |                |                |                |                |
| 23  | 292.22         | 254.04         | 984.83         | 966.52         |                |                |                | 22879.57       |                | 23590.30       |
| 24  | 291.21         | 253.08         | 983.77         | 965.38         | 22945.80       |                |                | 877.41         | 23585.76       | 589.14         |
| 25  |                | 252.06         |                | 964.23         | 944.64         | 22923.66       |                | 875.24         | 583.44         | 587.82         |
| 26  |                | 251.06         |                | 963.02         | 943.35         | 922.56         | 22900.53       | 872.91         | 580.93         | 586.42         |
| 27  |                | 249.91         |                |                | 942.12         | 921.31         | 899.32         | 870.63         | 578.39         | 584.89         |
| 28  |                | 248.68         |                |                | 940.74         | 920.04         | 897.97         |                | 575.79         | 583.44         |
| 29  |                | 247.42         |                |                |                | 918.59         | 896.54         |                | 573.06         | 581.88         |
| 30  |                | 246.10         |                |                |                |                | 895.00         |                |                | 580.19         |
| 31  |                | 244.64         |                |                |                |                |                |                |                |                |

molecules, is of negligible magnitude, a simple energy level diagram may be used to verify the following combination relations:

$$\begin{aligned}\Delta_1 F'(L) &\equiv F'(L+1) - F'(L) = Q(L+1) \\ &\quad - P(L+1) = R(L) - Q(L), \\ \Delta_1 F''(L) &\equiv F''(L+1) - F''(L) = Q(L) \\ &\quad - P(L+1) = R(L) - Q(L+1); \quad (18)\end{aligned}$$

$K$  is constant for a given relation.

To find the  $\Delta_1 F_1'$  values for a given band the wave numbers of the lines of a  $P$  branch were subtracted from those of the  $Q$  branch of the same sub-band, shifting one branch with respect to the other until the numbers obtained agreed with those obtained from another sub-band by similarly subtracting the lines of the  $Q$  branch from those of the  $R$  branch. That the above  $Q-P$  combination does not belong to the same sub-band as the  $R-Q$  combination is permissible since the  $\Delta_1 F$  values are found to be independent of  $K$  within experimental error. In accordance with Eq. (18), when the same  $\Delta_1 F_1'$  value is obtained from a  $Q-P$  combination and an  $R-Q$  combination, the  $L$  number of the  $Q$  line of the first combination must be one greater than the  $L$  number of the  $Q$  line of the second combination. This limitation was an aid in finding the desired agreement. Having found an agreement and having numbered the lines of the  $P$  and  $R$  branches on the basis of the known numbering of the  $Q$  branches, a check was obtained by finding agreement between the  $\Delta_1 F_1''$  values obtained from both pairs of branches. The results are shown in Table XI. The subscript  $e$  means that

the value was obtained using a  $Q$  branch line whose wave number was obtained by extrapolating beyond observed lines. The fact that the same  $\Delta_1 F_1''$  values are obtained from three different bands is further proof that the  $\Delta_1 F_1$  values are correct since the three bands are known to have a common lower vibrational state. It is to be noted that no systematic variation of the  $\Delta_1 F_1$  values with  $K$  is evident.

Although the  $\Delta_1 F_1'$  values are different for different bands as would be expected, they are the same for different sub-bands within a given band except in band 4. In this band it seems that the perturbation effect, which is greater the higher the band number, causes the  $\Delta_1 F_1'$  values to vary from sub-band to sub-band.

Within each band a weighted mean value of  $\Delta_1 F_1'$  for each value of  $L$  was chosen and recorded in Table XII. Also a weighted mean value of  $\Delta_1 F_1''$  for each value of  $L$  was determined using data from all bands. The first differences between the  $\Delta_1 F_1$  values are constant within experimental error except for a possible slight alternation in magnitude. This can be attributed to a very small  $K$  doubling with one component of each doublet missing because of the zero spin of oxygen nuclei.  $\Delta F$  values with a subscript  $e$  were obtained essentially from  $\Delta F$  values in Table XI having a subscript  $e$ .

#### 16. DETERMINATION OF CONSTANTS FROM $\Delta F$ VALUES

On the basis of Eq. (9) and the empirical expression for the  $qQ$  branches given by Eq.

(16), the rotational term values are assumed to have the form

$$F_{1,2} = f(K, v') + \bar{B}L(L+1) + cL \pm \frac{1}{2}\gamma L, \quad (19)$$

where the plus sign corresponds to the subscript one. Accordingly,

$$\Delta_1 F_1(L) = F_1(L+1) - F_1(L) = 2\bar{B}(L+1) + c + \frac{1}{2}\gamma, \quad (20)$$

and the first differences between these  $\Delta_1 F_1$  values should be given by

$$\delta(\Delta_1 F_1) = 2\bar{B}. \quad (21)$$

The value of  $\delta(\Delta_1 F_1)$  was determined for each column in Table XII by the method of least squares. Numbers in this table having a subscript  $e$  were not used. The results are given in Table XIII. The last column of this table gives the values of  $2\bar{B}'$  as calculated from  $2\bar{B}'' = 0.612 \text{ cm}^{-1}$  and the second differences  $2\Delta\bar{B} = \delta\delta_L$  given in

Table II. The values for  $2\bar{B}'$  in the last column are considered the more accurate. Extrapolation gives the value of  $2\bar{B}'$  for band 0 as  $0.550 \text{ cm}^{-1}$ . Since theoretically,  $\delta\delta_L = \delta(\Delta F') - \delta(\Delta F'')$  regardless of the interpretation of these constants and regardless of the choice of the quantum numbering, the experimental agreement between the two members of this equation is considered as support for the identification of the  $\Delta F$  values.

The constant  $(c + \frac{1}{2}\gamma)$  may now be determined from Eq. (20). A value for this constant was determined from each  $\Delta_1 F_1'$  value of band 2 in Table XII, as well as from each  $\Delta_1 F_1''$  in this table. The value of  $(c + \frac{1}{2}\gamma)$  was found to be constant with respect to  $L$ . Averaging for all values of  $L$

$$(c + \frac{1}{2}\gamma)' = -0.45, \quad (c + \frac{1}{2}\gamma)'' = -0.62.$$

Hence,

$$\Delta(c + \frac{1}{2}\gamma) = 0.17.$$

TABLE XI.

| a. $\Delta_1 F_1'$ values.  |                           |                           |                           |                           |                           |                           |                           |                             |                             |                           |
|-----------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-----------------------------|-----------------------------|---------------------------|
| K                           | Band 2                    |                           | Band 3                    |                           |                           |                           |                           |                             | Band 4                      |                           |
|                             | 15<br>$R(L)$<br>$-Q(L)$   | 17<br>$R(L)$<br>$-Q(L)$   | 15<br>$R(L)$<br>$-Q(L)$   | 16<br>$R(L)$<br>$-Q(L)$   | 17<br>$R(L)$<br>$-Q(L)$   | 18<br>$R(L)$<br>$-Q(L)$   | 19<br>$R(L)$<br>$-Q(L)$   | 19<br>$Q(L+1)$<br>$-P(L+1)$ | 18<br>$Q(L+1)$<br>$-P(L+1)$ | 19<br>$R(L)$<br>$-Q(L)$   |
| L                           |                           |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 19                          | 10.44                     |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 20                          | 10.91                     |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 21                          | 11.50                     |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 22                          | 12.00                     | 11.98                     | 11.38                     | 11.89                     | 11.93                     |                           |                           | 11.91                       |                             |                           |
| 23                          | 12.59 <sub>e</sub>        | 12.38                     | 12.43                     | 12.50                     |                           |                           |                           | 12.48                       | 12.30                       | 12.35                     |
| 24                          | 13.08 <sub>e</sub>        | 13.04                     | 13.01                     | 12.99 <sub>e</sub>        | 13.01                     |                           |                           | 12.99                       | 12.78                       | 12.92                     |
| 25                          |                           | 13.61                     |                           | 13.54 <sub>e</sub>        | 13.51                     | 13.29                     |                           | 13.59                       | 13.33                       | 13.43                     |
| 26                          |                           | 14.21                     |                           | 14.11 <sub>e</sub>        | 14.00                     | 14.04                     | 14.03                     | 14.01                       | 13.85 <sub>e</sub>          | 13.93                     |
| 27                          |                           | 14.76                     |                           |                           | 14.61                     | 14.61                     | 14.68                     |                             | 14.35 <sub>e</sub>          | 14.39                     |
| 28                          |                           | 15.30 <sub>e</sub>        |                           |                           | 15.14 <sub>e</sub>        | 15.23                     | 15.21                     |                             | 14.90 <sub>e</sub>          | 15.07                     |
| 29                          |                           | 15.88 <sub>e</sub>        |                           |                           |                           | 15.75 <sub>e</sub>        | 15.72                     |                             |                             | 15.60 <sub>e</sub>        |
| 30                          |                           | 16.46 <sub>e</sub>        |                           |                           |                           |                           | 16.19                     |                             |                             | 16.14 <sub>e</sub>        |
| b. $\Delta_1 F_1''$ values. |                           |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| K                           | Band 2                    |                           | Band 3                    |                           |                           |                           |                           |                             | Band 4                      |                           |
|                             | 15<br>$R(L)$<br>$-Q(L+1)$ | 17<br>$R(L)$<br>$-Q(L+1)$ | 15<br>$R(L)$<br>$-Q(L+1)$ | 16<br>$R(L)$<br>$-Q(L+1)$ | 17<br>$R(L)$<br>$-Q(L+1)$ | 18<br>$R(L)$<br>$-Q(L+1)$ | 19<br>$R(L)$<br>$-Q(L+1)$ | 19<br>$Q(L)$<br>$-P(L+1)$   | 18<br>$Q(L)$<br>$-P(L+1)$   | 19<br>$R(L)$<br>$-Q(L+1)$ |
| L                           |                           |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 19                          | 11.61                     |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 20                          | 12.21                     |                           |                           |                           |                           |                           |                           |                             |                             |                           |
| 21                          | 12.85                     |                           | 12.85                     |                           |                           |                           |                           |                             |                             |                           |
| 22                          | 13.43 <sub>e</sub>        | 13.20                     | 13.46                     | 13.48                     |                           |                           |                           | 13.46                       |                             |                           |
| 23                          | 14.09 <sub>e</sub>        | 14.00                     | 14.07                     | 14.13 <sub>e</sub>        |                           |                           |                           | 14.07                       | 14.09                       | 14.08                     |
| 24                          | 14.65 <sub>e</sub>        | 14.63                     | 14.73 <sub>e</sub>        | 14.69 <sub>e</sub>        | 14.67                     |                           |                           | 14.65                       | 14.62                       | 14.75                     |
| 25                          |                           | 15.21                     |                           | 15.32 <sub>e</sub>        | 15.29                     | 15.14                     |                           | 15.32                       | 15.29                       | 15.33                     |
| 26                          |                           | 15.91                     |                           |                           | 15.84                     | 15.86                     | 15.89                     | 15.87                       | 15.87                       | 15.92                     |
| 27                          |                           | 16.53 <sub>e</sub>        |                           |                           | 16.52 <sub>e</sub>        | 16.50                     | 16.56                     |                             | 16.45 <sub>e</sub>          | 16.52                     |
| 28                          |                           | 17.14 <sub>e</sub>        |                           |                           | 17.13 <sub>e</sub>        | 17.20 <sub>e</sub>        | 17.15                     |                             | 17.08 <sub>e</sub>          | 17.16 <sub>e</sub>        |
| 29                          |                           | 17.78 <sub>e</sub>        |                           |                           |                           |                           | 17.73                     |                             |                             | 17.83 <sub>e</sub>        |
| 30                          |                           |                           |                           |                           |                           |                           |                           |                             |                             | 18.45 <sub>e</sub>        |

TABLE XII.

| <i>L</i> | $\Delta_1 F_1'$    |        |                    | $\Delta_1 F_1''$<br>all bands |
|----------|--------------------|--------|--------------------|-------------------------------|
|          | band 2             | band 3 | band 4             |                               |
| 19       | 10.44              |        |                    | 11.61                         |
| 20       | 10.91              |        |                    | 12.21                         |
| 21       | 11.50              | 11.38  |                    | 12.85                         |
| 22       | 11.99              | 11.91  |                    | 13.46                         |
| 23       | 12.59              | 12.47  | 12.33              | 14.09                         |
| 24       | 13.06              | 13.00  | 12.85              | 14.67                         |
| 25       | 13.61              | 13.54  | 13.38              | 15.30                         |
| 26       | 14.21              | 14.02  | 13.89              | 15.88                         |
| 27       | 14.76              | 14.63  | 14.37              | 16.52                         |
| 28       | 15.30 <sub>e</sub> | 15.20  | 14.99              | 17.15 <sub>e</sub>            |
| 29       | 15.88 <sub>e</sub> | 15.73  | 15.55 <sub>e</sub> | 17.78 <sub>e</sub>            |
| 30       | 16.46 <sub>e</sub> | 16.19  | 16.09 <sub>e</sub> |                               |

From the values of  $\Delta\gamma=0.11$  (Section 7) and  $\Delta c=0.13$  (Section 13)

$$\Delta(c+\frac{1}{2}\gamma)=0.185,$$

which agrees with 0.17.

It may be instructive, in connection with the constant  $(c+\frac{1}{2}\gamma)$ , to note the identity  $\delta_L \equiv \Delta_1 F_1' - \Delta_1 F_1''$  which holds regardless of the interpretation of the constants of the identity. In Section 13 it was shown that a constant  $(\Delta c + \frac{1}{2}\Delta\gamma)$  was needed to describe the observed  $\delta_L$  values of the  $\nu_1$  series. According to the above identity, this requires a constant  $(c + \frac{1}{2}\gamma)$  in the expression for  $\Delta_1 F_1$  as has already been shown (see Eq. (20)). These constants depend on the choice of the quantum numbering.

If any numbering is indicated by the  $\Delta F$  values, it is that given by  $\Delta F/\delta(\Delta F) \approx L+1$  which may be obtained from Eqs. (20) and (21). This expression would be sufficiently accurate to determine the numbering if  $(c + \frac{1}{2}\gamma)$  were fairly small compared to  $\delta(\Delta F)$ , as is entirely possible. The numbering calculated on the basis of this expression is nearly integral and almost the same, whether using  $\Delta F'$  or  $\Delta F''$  values. The indicated quantum numbering, which is one less than that used throughout the paper, is therefore considered plausible. However, the fact that the unknown constant  $(c + \frac{1}{2}\gamma)$  is present in the expression for  $\Delta F$  makes this numbering uncertain. In any case, the quantum numbering does not affect the  $\bar{B}$  values.

## 17. MOLECULAR MODEL

The following is a list of constants available for calculating a molecular model for both elec-

tronic states. These constants correspond to the vibrational transition  $(0\ 0\ 0) \leftarrow (0\ 0\ 0)$ .  $s$  designates the Cl-O distance and  $2\theta$ , the O-Cl-O angle.

$$s'' = 1.53 \pm 0.02 \text{ \AA}$$

from electron diffraction.<sup>11</sup>

$$\left. \begin{aligned} 2\theta'' &= 122^\circ 50' \\ 2\theta' &= 112^\circ 10' \end{aligned} \right\}$$

from vibrational frequencies<sup>2</sup> using valence force approximation.

$$2\Delta\bar{B} = -0.0615 \pm 0.001 \text{ cm}^{-1}$$

from second differences in  $L$  structure, Section 5; and Eq. (9).

$$2(\Delta A - \Delta\bar{B}) = -1.188 \pm 0.005 \text{ cm}^{-1}$$

from second differences in  $K$  structure, Section 6; and Eq. (9).

$$2\bar{B}'' = 0.612 \pm 0.003 \text{ cm}^{-1}$$

from  $\Delta_1 F_1''$  values, Section 16.

$$2\bar{B}' = 0.550 \pm 0.003 \text{ cm}^{-1}$$

from  $2\bar{B}''$  and  $2\Delta\bar{B}$ ; also from  $\Delta_1 F_1'$  values, Section 16.

The last four constants are obtained in the present paper and are based on the prolate symmetrical top approximation. They, therefore, contain small errors because of the asymmetry of the actual molecule. The effect of asymmetry is neglected for the present but will be discussed in the next section.

For a bent triatomic molecule only two constants are required to determine the geometrical configuration of a given electronic state, while three constants  $s''$ ,  $2\theta''$ ,  $2\bar{B}''$  are here available for calculating a model for the lower state. That these constants are definitely inconsistent is illustrated in Table XIVa, where, for a given model, the constant in parenthesis is calculated from the other two. Physical constants used in the calculation are:

$$\begin{aligned} \text{physical mass unit} &= 1.6599 \times 10^{-24} \text{ g,} \\ \text{mass of O}^{16} &= 16.00 \text{ mass units,} \\ \text{mass of Cl}^{35} &= 34.98 \text{ mass units,} \\ h/8\pi^2 c &= 27.98 \times 10^{-40} \text{ g cm.} \end{aligned}$$

For a given lower state model, the upper state constants may be determined using the sec-

TABLE XIII.  $\bar{B}'$  and  $\bar{B}''$  from  $\Delta F$  values.

| Band | $2\bar{B}'' = \delta(\Delta_1 F_1'')$ | $2\bar{B}' = \delta(\Delta_1 F_1')$ | $2\bar{B}' = \delta(\Delta_1 F_1'') + \delta\delta_L$ |
|------|---------------------------------------|-------------------------------------|---|
| 0    |                                       |                                     | (0.550)   |
| 1    |                                       |                                     | 0.546   |
| 2    | } 0.612                               | 0.543                               | 0.542   |
| 3    |                                       | 0.536                               | 0.538   |
| 4    |                                       | 0.525                               | 0.532   |

TABLE XIV.

| Model | a       |                   |                            | b      |                 |                         |
|-------|---------|-------------------|----------------------------|--------|-----------------|-------------------------|
|       | $s''$   | $2\theta''$       | $2\bar{B}''$               | $s'$   | $2\theta'$      | $2\bar{B}'$             |
| (1)   | 1.53A   | $122^\circ 50'$   | $(0.5445) \text{ cm}^{-1}$ | 1.671A | $115^\circ 10'$ | $0.483 \text{ cm}^{-1}$ |
| (2)   | 1.53    | $(108^\circ 10')$ | 0.612                      | 1.785  | $89^\circ 40'$  | 0.550                   |
| (3)   | (1.443) | $122^\circ 50'$   | 0.612                      | 1.559  | $116^\circ 20'$ | 0.550                   |

ond differences  $2\Delta\bar{B} = -0.0615$  and  $2(\Delta A - \Delta\bar{B}) = -1.188$ . A model for the upper electronic state was calculated for each lower state model and the results are given in Table XIVb. Fairly accurate intermediate models may be determined from Table XIV by interpolation.

According to experience with other molecules, it is entirely possible that  $2\theta'' = 122^\circ 50'$  calculated from the vibrational analysis on the basis of the valence force approximation is considerably in error. For this reason the author considers that *model (2) is probably the most nearly correct*. The greatest source of error is considered to be the uncertainty in the electron diffraction value of  $s''$ . From Table XIV it may be seen that an experimental error of 0.02A in  $s''$  corresponds to an error of  $3^\circ$  in  $2\theta''$  and to errors of 0.05A and  $6^\circ$  in  $s'$  and  $2\theta'$ , respectively.

Figure 5 shows both states of model (2) corrected for asymmetry, see Section 18. It is interesting to note that as the molecule goes into the upper state, the distance between the oxygen atoms changes only very slightly. It is also of interest that the vibrational structure of the absorption spectrum shows that only the breathing vibration is appreciably excited in the upper state and that this mode of vibration is excited considerably. On the basis of these facts the Franck-Condon principle requires that the motion of the oxygen atoms in this mode in the upper state is roughly perpendicular to the line joining the oxygen atoms. In such a case the valence force approximation would not be expected to give very good values for the angles.

A more complete vibrational analysis<sup>2</sup> of this electronic band system which would include isotope frequencies would allow a fairly accurate calculation of the angles for both states giving an interesting check on the correctness of this model. Also a quantitative application of the Franck-Condon principle would give a check on the change of the Cl—O distance at excitation.

## 18. CONSIDERATION OF ASYMMETRY

Model (2) was determined using constants of the spectrum which were interpreted as if the spectrum were that of a symmetrical top. Hence, model (2) differs from the actual molecule because the effect of asymmetry on the constants of the spectrum has not been allowed for. It will be seen that this difference, because of asymmetry, between model (2) and the actual molecule is small. Hence, the contribution of the asymmetry term of Eq. (4) to the constants of the spectrum is about the same for molecule and model and may be approximately computed using model (2). If these contributions are subtracted from the observed constants of the spectrum, an approximate value of the constants corrected for the effect of asymmetry may be obtained. A corrected model may then be calculated from the corrected constants.

The lower state of model (2) was determined using  $s''$  from electron diffraction experiments, and the value of  $\delta(\Delta_1 F'')$  which is interpreted as  $2\bar{B}''$ . In the range of observation the average contribution of the asymmetry term of Eq. (4) to the value of  $\delta(\Delta_1 F'')$  is positive and about 0.8 percent. Hence, the value of  $2\bar{B}''$  given in Section 17 is 0.8 percent too large. Therefore,

$$2\bar{B}'' = 0.607 \text{ cm}^{-1} \text{ (corrected).}$$

The upper state was determined from the experimental constants  $\delta(\Delta_1 F')$  and  $\delta\delta_K$  which were interpreted as  $2\bar{B}'$  and  $2(\Delta A - \Delta\bar{B})$ , respectively. In the range of observation the average contribution of the asymmetry term of Eq. (4) to  $\delta(\Delta_1 F')$  is a positive and about 5 percent. Hence, the correct value of  $2\bar{B}'$  is about 5 percent smaller than the value given in Section 17, so that

$$2\bar{B}' = 0.522 \text{ cm}^{-1} \text{ (corrected).}$$

The effect of the asymmetry term is to reduce the magnitude of  $\delta\delta_K$  by about 0.7 percent.

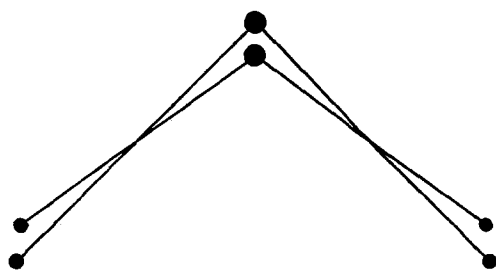


FIG. 5. Probable model for both states. The model with the larger angle represents the normal state, O-Cl-O angle =  $109^\circ$ , Cl-O distance =  $1.53\text{\AA}$ . The model with the smaller angle represents the excited state, O-Cl-O angle =  $92^\circ$ , Cl-O distance =  $1.805\text{\AA}$ . The models are drawn so that their centers of gravity coincide.

Hence, the correct magnitude of  $2(\Delta A - \Delta \bar{B})$  is about 0.7 percent greater than the value given in Section 17,

$$2(\Delta A - \Delta \bar{B}) = -1.196 \text{ cm}^{-1} \text{ (corrected).}$$

The above three corrected constants with the electron diffraction value of  $s''$  determine model (2) corrected for the effect of asymmetry. The resulting model is

$$\begin{array}{ll} 2\theta'' = 109^\circ & 2\theta' = 92^\circ \\ s'' = 1.53\text{\AA} & s' = 1.805\text{\AA} \end{array}$$

*This is considered as the probable model for both states.* It is of interest that for the range of quantum numbers observed the error caused by neglecting the effect of asymmetry (see model (2), Table XIV) is small even though the upper state model has an angle of  $92^\circ$ .

A formula for the magnitude of the splitting of the rotational levels due to asymmetry is given by Wang.<sup>14</sup> For levels which are expressed in terms of prolate symmetrical top quantum numbers (see Eq. (4)), this formula, written in the notation of this paper, is

$$\Delta\nu = \left[ \frac{C-B}{2(A-\bar{B})} \right]^K \frac{8(A-\bar{B})}{2^{3K}} \frac{(L+K)!}{(L-K)!(K-1)!^2} \quad (22)$$

where  $\Delta\nu$  is in  $\text{cm}^{-1}$ . This formula is obtained on the basis of the assumption that the asymmetry factor  $b$  in square brackets is limited by  $|b| \ll 1$ . For the  $92^\circ$  model  $b$  is about 0.1. This splitting is much too small to be observed for the range of quantum numbers involved in this paper, being, for example,  $3 \times 10^{-7} \text{ cm}^{-1}$  for the level

<sup>14</sup> S. C. Wang, Phys. Rev. **34**, 249 (1929).

$K=15$ ,  $L=25$  of the  $92^\circ$  model. For a given  $K$ , the splitting decreases as  $L$  decreases.

The quantum numbering was determined on the basis of the  $K$  structure using the constants  $\delta_K$  and  $\delta\delta_K$ , see Eq. (12). The effect of asymmetry is to reduce the magnitude of both of these constants by a little less than 1 percent. Hence, the  $K$  value calculated essentially from their ratio is affected very little by asymmetry.

The effect of asymmetry on the observed  $L$  structure is fairly large for model (2). Calculation shows that the effect of asymmetry is to reduce the first interval in the  $L$  structure by about 10 percent, while the magnitudes of the second difference in the  $L$  structure would be reduced by 30 percent on the average. This would cause the value of the  $K$  numbering, calculated from the ratio of the first interval to the second difference in the  $L$  structure, to be too large by about 3. But Table VII shows that the  $K$  numbering calculated by this method is too small by about 2. Hence, if model (2) is correct, there is apparently some term which more than balances this effect of asymmetry on the  $L$  structure.

## 19. ISOTOPE EFFECT

Absorption lines arising from molecules containing the less plentiful of the two isotopes of chlorine,  $\text{Cl}^{37}$ , are to be expected, and some of the stronger lines of the  $qQ$  doublet branches of  $\text{Cl}^{37}\text{O}_2$  are observed in bands 3 and 4 (see Table XV). Though the isotope lines of band 4 were easily found, those of band 3 were located with considerable difficulty because of the jumble of background lines.

In general, no systematic variation of the total isotope shift  $\nu_{37} - \nu_{35} = P(v, K)$  was observed within a sub-band. A weighted average value for this shift for each sub-band is given in Table XVI. These values are probably correct to within  $0.02 \text{ cm}^{-1}$ . Although the total isotope shift is quite different for bands 3 and 4, the differences  $P(v, K+1) - P(v, K)$ , also shown in Table XVI, are essentially the same for both bands.

The approximate theoretical magnitude of the rotational isotope shift will now be determined. The rotational component  $P_r$  of the isotope

TABLE XV.

| K          | Isotope lines of $qQ$ doublet branch of band 3 |          |          |          |          |          | $L(\nu_2)$ |
|------------|--|----------|----------|----------|----------|----------|------------|
|            | 15   | 16       | 17       | 18       | 19       | 20       |            |
|            | 22975.30                                       |          |          |          |          |          | 15         |
|            | 974.10   | 22956.34 |          |          |          |          | 16         |
| $L(\nu_1)$ |  | 955.15   | 22936.24 |          |          |          | 17         |
| 15         | 973.79   |          | 934.92   | 22914.78 |          |          | 18         |
| 16         | 972.77   | 954.72   |          | 913.42   | 22892.04 |          | 19         |
| 17         | 971.63   | 953.68   | 934.53   |          | 890.76   | 22868.28 | 20         |
| 18         | 970.41   | 952.50   | 933.35   | 912.96   |          | 866.98   | 21         |
| 19         |  | 951.19   | 932.13   | 911.70   | 890.21   |          |            |
| 20         |  | 949.95   | 930.72   | 910.42   | 888.90   | 866.22   |            |
| 21         |  |          | 929.35   | 909.00   | 887.58   | 864.92   |            |
| 22         |  |          |          | 907.56   | 886.10   | 863.48   |            |

| K          | Isotope lines of $qQ$ doublet branch of band 4 |          |          |          | $L(\nu_2)$ |
|------------|--|----------|----------|----------|------------|
|            | 16   | 17       | 18       | 19       |            |
|            | 23636.97                                       |          |          |          | 16         |
| $L(\nu_1)$ |  | 23617.74 |          |          | 17         |
| 16         | 636.43   |          | 23596.22 |          | 18         |
| 17         | 634.93   | 616.06   |          | 23573.53 | 19         |
| 18         |  | 614.68   | 594.50   |          |            |
| 19         |  | 613.20   | 593.10   | 571.67   |            |
| 20         |  | 611.64   | 591.60   | 570.22   |            |
| 21         |  |          | 590.05   | 568.71   |            |
| 22         |  |          |          | 567.18   |            |
|            |  |          |          | 565.48   |            |

shift is given by

$$P_r = \nu_{37} - \nu_{35} = (F_{37}' - F_{37}'') - (F_{35}' - F_{35}''). \quad (23)$$

The prolate symmetrical top approximation to the energy levels is

$$F = \frac{h}{8\pi^2c} \frac{1}{I_B} [L(L+1) - K^2] + \frac{h}{8\pi^2c} \frac{K^2}{I_A}. \quad (24)$$

Since the chlorine atom contributes relatively little to  $I_B$  and since  $I_B$  is nearly the same in both electronic states, the coefficient of the  $[L(L+1) - K^2]$  term in  $P_r$  is expected to be small. Calculation shows that for model (2) this coefficient is about 1 percent of the coefficient  $K^2$ . The fact that  $L$  does not differ greatly from  $K$  gives further reason for neglecting this term. Hence,

$$P_r = (\Delta A_{37} - \Delta A_{35}) K^2. \quad (25)$$

Now  $\Delta A = (\Delta A - \Delta \bar{B}) + \Delta \bar{B}$ , so that for band 3  $\Delta A_{35} = (-1.212/2) - (0.0739/2) = -0.643 \text{ cm}^{-1}$ . It may be shown that

$$\Delta A_{37} = [(35 \times 69)/(37 \times 67)] \Delta A_{35}.$$

Hence,

$$P_r = 0.0166 K^2 \text{ (theoretical).}$$

Correcting  $\Delta A$  for asymmetry increases the coefficient of  $K^2$  to about  $0.0170 \text{ cm}^{-1}$ .

The coefficient of  $K^2$  may also be determined empirically from the observed isotope shift. The total isotope shift of the Cl<sup>37</sup>O<sub>2</sub> spectrum with respect to the Cl<sup>35</sup>O<sub>2</sub> spectrum is described by

$$\nu_{37} - \nu_{35} = P(v, K) = P_v(v) + P_r(K), \quad (26)$$

where  $P_v$  is the vibrational component and  $P_r = \alpha K^2$  is the rotational component of the isotope shift. Both  $P_v$  and  $P$  are observed to be negative, that is, both the band heads and the lines observed in the tail of the bands have an isotope shift toward the red. However, the fact that the magnitude of the total shift decreases as  $K$  increases shows that the rotational component  $P_r$  is positive. For a given band  $P_v$  is

TABLE XVI. Observed isotope effect  $P(v, K)$  and differences.

| K  | band 3 | band 4 |
|----|--------|--------|
| 15 | -9.04  |        |
|    | 0.47   |        |
| 16 | -8.57  | -14.10 |
|    | 0.50   | 0.49   |
| 17 | -8.07? | -13.61 |
|    | 0.55   | 0.55   |
| 18 | -7.52  | -13.06 |
|    | 0.59   | 0.58   |
| 19 | -6.93  | -12.48 |
|    | 0.62   |        |
| 20 | -6.31  |        |

constant so that

$$P(v, K+1) - P(v, K) = P_r(K+1) - P_r(K) = \alpha(2K+1).$$

Hence,

$$\alpha = \frac{P(v, K+1) - P(v, K)}{2K+1}. \quad (27)$$

By use of the data of Table XVI for band 3, this formula gives an average value of  $\alpha = 0.0156 \pm 0.0003$ . Hence,

$$P_r = 0.0156K^2 \text{ (empirical).}$$

It may be significant that if the numbering were reduced by one, as is suggested by the  $\Delta F$  values, this empirical coefficient of  $K^2$  becomes 0.0165 which is in better agreement with the theoretical coefficient of  $K^2$ . However, the linear term in  $K$ , which varies with  $v'$ , may contribute to the isotope effect.

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### Erratum: "Note on the Conditions of Equilibrium for Systems of Many Constituents"

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STUART R. BRINKLEY, JR.

Research and Development Division, Department of the Interior, Bureau of Mines, Pittsburgh, Pennsylvania

THE paragraphs given below should be inserted following the paragraph containing Eq. (8) in the second column of page 564. The author did not receive proof and was, therefore, unable to supply this correction before publication of the article.

The derivation by means of the method employed by Gibbs,<sup>4</sup> subject to the constraints of Eqs. (8), of the conditions for equilibrium is straight forward, and it is unnecessary to reproduce it here. The usual conditions for thermal and mechanical equilibrium are obtained, and the conditions for chemical equilibrium take the form,

$$\mu_j^{(k)} = \lambda_j, \quad (9)$$

$$\mu_j^{(k)} = \sum_{i=1}^c \nu_{ij} \lambda_j, \quad (10)$$

$$k = 1, 2, \dots, p; j = 1, 2, \dots, c; i = c+1, c+2, \dots, s,$$

where  $\mu_i^{(k)}$  and  $\mu_j^{(k)}$  are the chemical potentials in the  $k$ th phase of the  $i$ th and  $j$ th substances, respectively, the  $\lambda_j$  are constants which may be eliminated from Eqs. (9), and where it has been assumed for simplicity that each substance of the system is included in every phase.<sup>8</sup>

<sup>8</sup> If a particular component, say the  $j'$ th, is a possible but not an actual constituent of a particular phase, say the  $k'$ th, then the determination of the conditions for equilibrium is subject to the additional constraint,  $\delta n_{j'}^{(k')} \geq 0$ , and the corresponding number of Eqs. (7) becomes  $\mu_{j'}^{(k')} \geq \lambda_{j'}$ . A similar additional constraint must be applied if a particular dependent constituent, say the  $i'$ th, is a possible but not an actual constituent of the  $k'$ th phase, the corresponding member of Eqs. (9) becoming

$$\mu_{i'}^{(k')} \geq \sum_{j=1}^c \nu_{i'j} \lambda_j. \text{ If the } j'\text{th component is excluded } a \text{ priori}$$

from the  $k'$ th phase, the corresponding member of Eqs. (9) disappears as being without meaning, and similar considerations obtain if the  $i'$ th dependent constituent is excluded *a priori* from the  $k'$ th phase. The number of relations in Eqs. (9) and (10) is reduced by the number of such additional constraints, and the number of variables upon which the chemical potentials depend is reduced by the same number, thereby producing no effect upon the phase rule, Eq. (11). See Gibbs, reference 3, pp. 66, 67.