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The Absorption Spectrum of Chlorine Dioxide

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The spectrum of the visible and ultraviolet absorption bands of ClO_2 has been studied under various dispersions. The band heads were measured with high precision. The result of the vibrational analysis shows that the bands may be represented by

$$\begin{aligned}\nu = 20957.2 &+ 302.9(v_1'+\tfrac{1}{2}) - 2.3(v_1'+\tfrac{1}{2})^2 + 721.68(v_2'+\tfrac{1}{2})\\ &- 2.797(v_2'+\tfrac{1}{2})^2 + 271.2(v_3'+\tfrac{1}{2})\\ &- 4.42(v_1'+\tfrac{1}{2})(v_2'+\tfrac{1}{2}) - 3.9(v_1'+\tfrac{1}{2})(v_3'+\tfrac{1}{2})\\ &- 5.9(v_2'+\tfrac{1}{2})(v_3'+\tfrac{1}{2}) - 529.0(v_1''+\tfrac{1}{2})\\ &- 1104.8(v_2''+\tfrac{1}{2}) - 954.4(v_3''+\tfrac{1}{2}) + 4.8(v_3''+\tfrac{1}{2})^2,\end{aligned}$$

yielding three normal frequencies for each upper and lower electronic state. The essential difference between the present analysis and that of the previous investigators is discussed. Rotational lines are partially resolved on the plates taken in the second order with a 21-foot grating. Two fundamental and one combination bands in the region 4–11μ were located with a self-recording spectrometer, and these are compared with the recent observation of Bailey and Cassie. Molecular constants have been calculated from a characteristic determinant given by Yates. They are found to be consistent with the observed isotope effect of chlorine.

THE absorption spectrum of chlorine dioxide has lately been studied by a number of investigators,[1, 2, 3] but the work of Urey and Johnston has been the most extensive. They have measured the bands in the region 5042–3226A. Their analysis of the vibrational structure yields three normal frequencies in the lower, and two in the upper electronic state. The observed intensity distribution has been found to be consistent with an extension of the Franck-Condon principle to polyatomic molecules.

Some time ago, as a preliminary for our study of intensity distribution in a band system of a triatomic molecule, the writer also examined the absorption spectrum of ClO_2 under various dispersions. In general, our measurements check well with those of Finkelnburg and Schumacher who photographed the spectrum with a two-meter grating, but they are more complete and extend into a higher frequency region. The rotational lines are partially resolved on our grating plates and reveal some interesting features. With a self-recording spectrometer,[4] the fundamental and combination bands in the region 4 to 11μ were found. Our observation has been confirmed by the recent work of Bailey and Cassie.[5] It is the purpose of this paper to present our experimental results, to propose a new interpretation of the origin of the various progressions in the band system based on their relative intensities and the infrared data, and to deduce certain molecular constants from the results of the present analysis.

EXPERIMENTAL

As a source of illumination in the visible region, a Phillips lamp was employed with a glass or quartz spectrograph, and a 500-watt tungsten lamp with a grating spectrograph. In the ultraviolet region a water-cooled hydrogen discharge tube of the Bay and Steiner type,[6] was used. Chlorine dioxide was prepared by reduction of Baker-analyzed potassium chlorate with oxalic crystals in the presence of a small amount of water as recommended by Bray.[7] The gas was dried, fractionated, and frozen into crystals which could be kept for some time.

Two absorption cells of 20 cm and 1 meter length were made of Pyrex with fused quartz

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[1] Goodeve and Stein, Trans. Faraday Soc. **25**, 738 (1929).

[2] Finkelnburg and Schumacher, Zeits. f. physik. Chemie Bodenstein-Festband, 704 (1931).

[3] Urey and Johnston, Phys. Rev. **38**, 2131 (1931).

[4] Randall and Strong, Rev. Sci. Inst. **2**, 585 (1931).

[5] Bailey and Cassie, Nature **129**, 652 (1932). Proc. Roy. Soc. **A137**, 622 (1932).

[6] Bay and Steiner, Zeits. f. Physik **45**, 337 (1927); **59**, 48 (1929).

[7] Bray, Zeits. f. physik. Chemie **54**, 574 (1905).

plates cemented on both ends. The system was arranged for evacuation and circulation of the sample under observation. The pressure of the gas ranged from a few mm in the short cell to 1 atmosphere in the long cell. The best development of individual bands was found to be quite critical as to pressure, so it was not feasible to take a series of plates at once when working with the grating spectrograph.

The vibrational structure in the visible region was studied with the Michigan large glass spectrograph giving a dispersion of 9.0A per mm at 5000A, and in the ultraviolet region with a Hilger E1 quartz spectrograph. The rotational structure was photographed in the visible region with a 21-foot Rowland concave grating in a Paschen mounting giving a dispersion of 1.1A per mm at 4600A in the second order. Cramer's contrast and spectrum plates were used, and the time of exposure varied from fifteen to thirty minutes with a glass or quartz spectrograph, and two to four hours with a grating spectrograph. All the plates were taken at room temperature.

The plates were measured on a precision comparator. The wave-lengths were determined by comparison with the standard iron arc lines taken on the same plate. It is hoped that the wave numbers are correct within 1 cm^{-1} for the band heads. The precision of measurements for the bands with wave-length shorter than 3330A was comparatively low because from there on the bands are no longer sharp and it was found difficult to make proper settings. The intensities were estimated by eye and checked with microphotometer records.

Description of Spectrum

Fig. 1 is an enlarged reproduction of the spectrograms taken with a Hilger E1 spectrograph, and Fig. 2 is reprinted from the grating plates. An examination of the spectrograms reveals four or five well developed progressions indicated by the relative positions of the band heads, their intensities, and the similarity in the appearance of the rotational structure. The isotope effect of chlorine is prominent in certain bands, but ob-

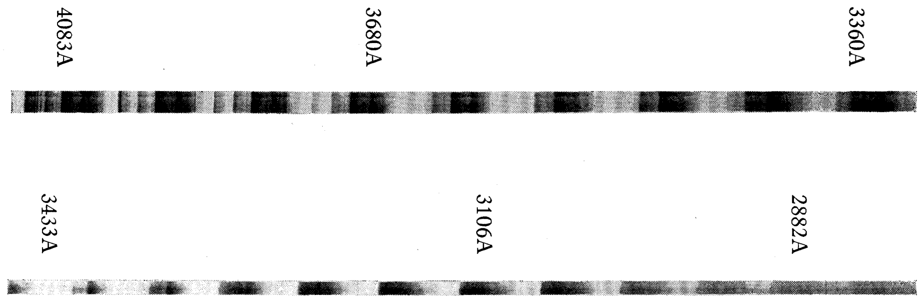

Fig. 1. Band system of ClO_2.

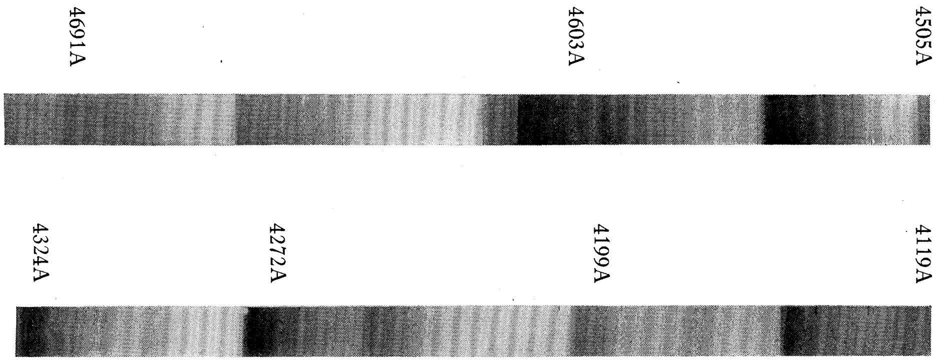

Fig. 2. Rotational structure of ClO_2 absorption bands.

TABLE I. *Wave numbers in vacuum.*

19,850.0	22,431.0	23,967.1	25,939.2	28,007.0	30,100	32,584
20,070.3	450.6	24,079.0	974.0	063.9	154	683
125.7	537.4	228.4	26,060.4	137.8	378	718
318.6	558.4	313.3	095.9	187.9	422	764
335.2	600.0	464.1	195.7	268.9	459	33,066
360.8	671.1	488.1	232.3	469.9	510	165
568.4	704.5	568.3	312.9	530.8	543	265
779.7	710.0	612.0	502.4	586.4	601	323
784.6	861.0	636.6	595.0	660.6	700	383
829.8	874.9	733.9	635.2	710.9	767	753
21,018.1	906.7	756.8	718.6	792.9	930	851
066.1	943.7	907.6	758.0	839.8	992	930
142.2	23,119.1	986.7	851.9	905.9	31,059	34,238
278.8	124.2	25,136.3	889.1	29,113.9	127	261
306.1	133.4	164.4	967.3	164.3	215	337
480.1	222.4	242.4	27,164.1	223.8	299	772
485.0	282.2	276.8	247.4	292.6	362	851
724.2	381.5	307.7	290.9	350.8	527	35,301
729.6	396.0	397.8	414.2	472.2	594	804
760.9	543.9	429.1	496.1	533.1	737	36,283
844.2	553.4	540.1	541.0	752.7	826	750
979.1	632.2	571.7	616.0	846.7	894	180
22,009.5	806.9	616.6	818.8	889.1	949	580
173.5	814.0	646.0	834.8	924.6	32,114	
177.7	900.0	836.0	893.6	980.6	183	
425.5	960.6	905.2	940.6	30,057.0	477	

scure in many others because of the high intensity near the band heads and the superposition of one band upon another. The relative intensity of various progressions and the isotope separation are seen in Fig. 3, which represents a part of the microphotometer records. The intensity of bands in each progression attains a maximum at about 3360A and decreases uniformly on either side of the maximum. All bands lying below 3000A fade away before their heads are reached. Several bands reported by the previous observers have not been confirmed, while additional ones have been found. In all we have measured 179 bands. The wave numbers in vacuum are given in Table I.

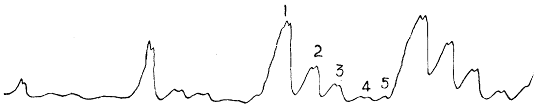

FIG. 3. 1. (0, 8, 0)←(0, 0, 0); 2. (0, 9, 0)←(1, 0, 0); 3. (1, 8, 0) ←(0, 0, 0); 4. (0, 10, 0)←(0, 0, 1); 5. (1, 8, 1)←(0, 0, 0).

The great complexity of the rotational structure is evident. Each band consists of a few hundred lines of which many are unresolved. In general, the intensity of the band lines is highest near the head, decreasing rapidly toward the red till the lines merge into the head of a neighboring band. It is interesting to notice that in nearly all the bands certain intense lines show up in groups at almost regular intervals on the wave-length scale. This feature is very prominent in the most intense progression and may be seen in Fig. 2. We have measured the lines in a few bands in the visible region, but have not been able to make an analysis. For further study of the rotational structure it will be necessary to examine the spectrum under higher dispersion.

Near infrared absorption bands were found to exist in three regions. There is a doublet with maxima at 10.78μ and 10.44μ respectively; a broad, intense absorption region extends between 9.26–8.88μ; and a weaker band appears at 4.94μ. Weak absorption was also observed at 14.96μ and 4.28μ, but these are probably due to the presence of carbon dioxide as impurity. Two independent runs covering the region 1–19μ were made, and both records gave the same results.* The results of Bailey and Cassie[5] are compared with these in Table II. The first half of each double column gives their measurements and the second ours.

ANALYSIS OF BAND STRUCTURE

The analysis of Urey and Johnston[3] assumes the existence of three fundamental frequencies

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* I should like to thank Professor W. W. Sleator for helping me to obtain these records.

TABLE II. *Infrared absorption bands.*

Band center (μ)		Maxima (cm^{-1})		Intensity		Identification†	
	14.96		668		weak		CO_2
		932	928				
10.57	10.61	963	958	20	medium	ν_3	ν_3
		1095	1080				
9.017	9.07	1106		50	intense	ν_1	ν_2
		1123	1126				
		1870					
5.307		1884?		2		$2\nu_3$	
		1900					
4.916	4.94	2034	2024	4	weak	$\nu_1+\nu_3$	$\nu_2+\nu_3$
	4.28		2336		weak		CO_2

† It should be pointed out that the assignment of ν_1 and ν_2 is quite arbitrary and an interchange of the subscripts introduces no change in the molecular constants.

which are not found in the infrared absorption. On the other hand, we are now quite sure that two of them are 1103 cm^{-1} and 943 cm^{-1} approximately, and we would expect them to be observable in the ultraviolet absorption. For according to the Boltzmann distribution law, molecules of a gas at ordinary temperatures will be present in appreciable numbers in all those higher states the energy of which does not differ from that of the lowest state by an amount of a higher order of magnitude than kT, while the majority of the molecules will be in the zero vibrational state. With the notation $(v_1', v_2', v_3') \leftarrow (v_1'', v_2'', v_3'')$ to represent a transition in absorption, and by taking the most intense v_2' progression to be $(0, v_2', 0) \leftarrow (0, 0, 0)$, we may look for those progressions originating from $(0, v_2', 0) \leftarrow (0, 1, 0)$ and $(0, v_2', 0) \leftarrow (0, 0, 1)$. These are found to be present. Among the bands in the long wavelength region a few members representing $(0, v_2', 0) \leftarrow (0, 0, 2)$ are also found. The third most intense v_2' progression may be regarded as arising from $(1, v_2', 0) \leftarrow (0, 0, 0)$. The assignment of bands to $(1, v_2', 0) \leftarrow (0, 0, 1)$ and $(1, v_2', 0) \leftarrow (0, 0, 2)$ then readily follows. We further note that of the remaining progressions three may be best accounted for as originating from the lowest level of the normal state to $(0, v_2', 0)$, $(1, v_2', 1)$, and $(2, v_2', 1)$ levels of the excited state. There remains but one well developed intense progression which probably originates from a first vibrational level of the normal state with a vibrational energy 529 cm^{-1}. We shall, with the previous investigators, regard it as representing $(0, v_2', 0) \leftarrow (1, 0, 0)$.

If this assignment of the origin of these progressions be adopted, their relative quantum numbers are fixed. The bands are thus arranged in Table III. Up to $\nu = 30{,}378$ cm^{-1} all but a few bands are included.

It has been found that the measurements can be represented by the following expression:

$$\begin{aligned}\nu = {} & 20{,}957.2 + 302.9(v_1' + \tfrac{1}{2}) - 2.3(v_1' + \tfrac{1}{2})^2 \\ & + 721.68(v_2' + \tfrac{1}{2}) - 2.797(v_2' + \tfrac{1}{2})^2 \\ & + 271.2(v_3' + \tfrac{1}{2}) - 4.42(v_1' + \tfrac{1}{2})(v_2' + \tfrac{1}{2}) \\ & - 3.9(v_1' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) - 5.9(v_2' + \tfrac{1}{2})(v_3' + \tfrac{1}{2}) \\ & - 529.0(v_1'' + \tfrac{1}{2}) - 1104.8(v_2'' + \tfrac{1}{2}) \\ & - \left\{\begin{matrix} 954.4 \\ 940.6 \end{matrix}\right. (v_3'' + \tfrac{1}{2}) + 4.8(v_3'' + \tfrac{1}{2})^2.\end{aligned}$$

This formula applies only to bands with v_2' equal to or less than 15. The members in the $(0, v_2', 0) \leftarrow (0, 0, 1)$ progression follow $\omega_3'' = 954.5$ for $v_2' \leqq 7$ and $\omega_3'' = 940.6$ for $v_2' > 7$. The $\nu_{\text{obs.}} - \nu_{\text{calc.}}$ values are given in parentheses in Table III.

While several of these progressions extend far into the high frequency region no satisfactory formula has been obtained to represent this part of the spectrum. This is chiefly due to the irregularity in the $\omega_v : v$[*] relation. We shall return to this point later.

Knowing the three normal frequencies of vibration, we may proceed to calculate the force constants and the half-angle α at the apex of the triangular model XY_2. On the assumption that the forces are central about each atom, Dennison has obtained a characteristic equation[8] which enables us to express the force constants and the half-angle in terms of the frequencies of mechanical vibration of infinitesimal amplitudes. We find that with these two particular sets of observed frequencies his equation yields no consistent solutions. Yates,[9] on the other hand, as-

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[*] Mulliken (Rev. Mod. Phys. **2**, 506 (1930)) defines $\Delta G(v+\frac{1}{2}) = G(v+1) - G(v)$. It follows that $\omega_v = \frac{1}{2}[\Delta G(v+\frac{1}{2}) + \Delta G(v-\frac{1}{2})]$.

[8] Dennison, Phil. Mag. **1**, 195 (1926).

[9] Yates, Phys. Rev. **36**, 555 (1930).

TABLE III. *Classification of bands. Values of* $\nu_{obs.} - \nu_{calc.}$ *are in parenthesis.*

v_2'	$(0, v_2', 0) \leftarrow (0, 0, v_3'')$			$(1, v_2', 0) \leftarrow (0, 0, v_3'')$		
	$v_3''=0$	1	2	$v_3''=0$	1	2
0	20318.6?(11.2)					
1	21018.1 (−0.2)	20070.3 (−3.2)	19134.1*(−4.2)	21306.1 (−1.9)	20360.8 (−2.4)	19424.4*(−3.6)
2	21724.2 (0.5)	20779.7 (0.8)	19841.7*(−2.0)	22009.5 (0.6)	21066.1 (2.0)	20125.7 (−3.2)
3	22425.5 (2.1)	21480.1 (1.5)	20542.3*(−1.1)	22704.5 (0.3)	21760.9 (1.5)	20829.8 (5.6)
4	23119.1 (1.6)	22173.5 (0.8)		23396.0 (2.1)	22450.6 (1.5)	
5	23806.9 (0.8)	22861.0 (−0.3)		24079.0 (0.9)	23133.4 (0.1)	
6	24488.1 (−0.9)	23543.9 (−0.3)		24756.8 (0.2)		
7	25164.4 (−2.0)	24228.4‡(6.8)		25429.1 (−0.5)		
8	25836.0 (−2.2)	24907.6 (−0.6)		26095.9 (−1.0)		
9	26502.4 (−1.9)	25571.7 (−2.6)		26758.0 (−0.6)		
10	27164.1 (−0.8)	26232.3 (−2.6)		27414.2 (−0.6)		
11	27818.8 (−1.1)	26889.1 (−0.8)		28063.9 (−1.5)		
12	28469.9 (0.6)	27541.0 (1.7)		28710.9 (0.5)		
13	29113.9 (0.8)	28187.9 (4.8)		29350.8 (1.1)		
14	29752.7 (1.4)			29980.6 (−2.9)		
15	30377.6 (−6.3)			30601.2		

v_2'	$(0, v_2', 1)$ $(0, 0, 0)$	$(0, v_2', 1)$ $(0, 0, 1)$	$(1, v_2', 1)$ $(0, 0, 0)$	$(2, v_2', 1)$ $(0, 0, 0)$	$(0, v_2', 0)$ $(1, 0, 0)$	$(0, v_2', 0)$ $(0, 1, 0)$
0	20568.4 (−5.3)	19625.4*(−3.5)		21142.2?(−7.3)		
1	21278.8 (0.1)	20335.2 (1.3)		21844.2 (−1.5)		
2	21979.1 (0.9)			22537.4 (1.1)		
3	22671.1 (−0.9)		22943.7?(−5.2)	23222.4 (1.1)		
4			23632.2 (−0.5)	23900.0 (−0.6)	22590.9 (2.4)	22009.5†(−3.2)
5			24313.3 (2.3)	24568.3 (−6.2)	23282.2 (5.1)	22704.5†(3.2)
6			24986.7 (3.1)	25242.4 (−0.3)	23960.6 (0.6)	23381.5 (−2.7)
7			25646.0 (−4.7)	25905.2 (−0.1)	24636.6 (−0.8)	24058.6*(−3.0)
8			26312.9 (0.8)	26549.5	25307.7 (−1.5)	24733.9 (0.5)
9			26967.3 (−0.6)		25974.0 (−1.3)	25397.8 (−1.7)
10			27616.0 (−2.2)		26635.2 (−0.7)	26060.4 (0.3)
11			28268.9 (6.0)		27290.9 (0.0)	26718.6 (3.5)
12			28905.9 (3.9)		27940.6 (0.3)	27368.6*(4.1)
13			29533.1 (−2.3)		28586.4 (2.3)	28007.0 (−1.3)
14			30154.2 (−9.1)		29223.8 (1.5)	
15					29846.7	

? Measured on one plate only.
* Measured by the previous observers.
† Coincidence with another band.
‡ Probably representing (1, 6, 0)←(1, 0, 0).

sumes that the force tending to restore a particle after a displacement is the sum of two types, the first acting along the line XY and obeying Hooke's law, the second, an angular restoring force acting at right angles to the first and proportional to the arc displacement of the Y's. His expression is

$$\lambda - K'[1/m + 2\sin^2\alpha/M] = 0,$$

$$\lambda^2 - [(K'+2k)/m + 2(K'\cos^2\alpha + 2K\sin^2\alpha)/M]\lambda + 2K'K(2/M+1/m)/m = 0, \quad (1)$$

where K' and K are the force constants, m and M, the masses of the Y and X atoms respectively; α is the half-angle between the bonds and $\nu_i = \lambda_i^{\frac{1}{2}}/2\pi$, λ_i being the roots of Eqs. (1).

We have obtained two sets of solution for each electronic state. They are given in Table IV.

TABLE IV. $\omega(\text{cm}^{-1})$, $K(10^5$ dynes per cm).

	Normal state		Excited state	
I	$\omega_1''=529$,	$K'=6.74$	$\omega_1'=271.2$,	$K'=0.56$
	$\omega_2''=1105$,	$K=1.16$	$\omega_2'=721.7$,	$K=1.56$
	$\omega_3''=954$,	$\alpha=32°30'$	$\omega_3'=302.9$,	$\alpha=49°27'$
II	$\omega_1''=954$,	$K'=6.74$	$\omega_1'=302.9$,	$K'=0.56$
	$\omega_2''=1105$,	$K=0.87$	$\omega_2'=721.7$,	$K=1.56$
	$\omega_3''=529$,	$\alpha=60°40'$	$\omega_3'=271.2$,	$\alpha=29°53'$

For the normal state, Bailey and Cassie[5] applying Hund's idea of chemical binding[10] and Dennison's investigation of an asymmetrical top molecule[11] consider the probable model to be an equilateral triangle, the length of the sides being approximately 1.2A. According to them the first

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[10] Hund, Zeits. f. Physik **73**, 1, 565 (1932).

[11] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

set of constants should be chosen. In obtaining this set of constants, we have assumed that the fundamental band 954 cm^{-1} corresponds to the unsymmetrical vibration ν_3 in which the electric moment oscillates along the axis of middle moment of inertia B, and hence there should be no zero branch. We assumed further that the fundamental band 1105 cm^{-1} is to be associated with a symmetrical vibration in which the electric moment oscillates along the axis of least moment of inertia A—in the present case, along the bisector of the angle between the bonds—and, therefore, a zero branch would be expected ($A/B \cong 0.8$). Now the envelopes of these bands appear to be in good accord with these characteristics. Thus we are led to the conclusion that the second set of constants is very improbable.

Now the doublet separation 30 cm^{-1} corresponds to a moment of inertia 52×10^{-40} g cm^2. This value may be associated with either the least or the largest moment of inertia. In the first case, we obtain 1.84×10^{-8} cm for the distance between O–Cl; in the second case, 1.22×10^{-8} cm. The model chosen ($\alpha=32°30'$) is definitely in favor of the lower value.

In making a choice between the two sets of constants for the excited state, we shall turn to the theory of the isotope effect. Referring to Eqs. (1), we find that the calculated values of the isotope shift are somewhat too large compared with the observed values if the first set of constants (see Table IV) be used. On the other hand, from the second set we obtain a general agreement.

To a first approximation, the isotope shift is given by

$$\nu_2-\nu_1=\sum[(\rho_i'-1)\omega_i'(v_i'+\tfrac{1}{2}) -(\rho_i''-1)\omega_i''(v_i''+\tfrac{1}{2})],$$

where the subscripts 1 and 2 refer to the more and less abundant isotopes respectively, and ρ stands for the square root of the equivalent reduced masses, or $\rho=(\mu_1/\mu_2)^{\frac{1}{2}}$.

Using the second set of constants we obtain the following expressions for the isotope displacement:

$$(0, v_2', 0)\leftarrow(0, 0, 0),\quad \nu_2-\nu_1= 5.4-4.3v_2';$$

$$(1, v_2', 0)\leftarrow(0, 0, 0),\quad \nu_2-\nu_1= 3.1-4.3v_2';$$

$$(0, v_2', 0)\leftarrow(1, 0, 0),\quad \nu_2-\nu_1= 6.1-4.3v_2';$$

$$(0, v_2', 0)\leftarrow(0, 0, 1),\quad \nu_2-\nu_1=10.6-4.3v_2'.$$

For the reasons already mentioned the isotope bands could be measured only with difficulty. In many cases the displacements turn out to be quite irregular; in others, our measurements do not check with those of previous observers. The observed and calculated values are compared in Table V. Perhaps without a knowledge of the band centers and the rotational structure a closer agreement can hardly be expected.

TABLE V. *Isotope bands.*

	$(0, v_2', 0)\leftarrow(0, 0, 0)$		$(1, v_2', 0)\leftarrow(0, 0, 0)$		$(0, v_2', 0)\leftarrow(1, 0, 0)$		$(0, v_2', 0)\leftarrow(0, 0, 1)$	
v_2'	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
4	−11.5*	−11.7	−14.5	−14.0				
5	−17.2*	−16.0	−20.4*	−18.3				
6	−24.0	−20.3	−22.9	−22.6	−22.4*	−19.6		
7	−28.1	−24.6	−31.3	−26.9	−24.6	−23.9		
8			−35.5	−31.2	−30.9	−28.2		
9			−38.3	−35.5	−34.8	−32.5	−31.6	−28.0
10				−39.8	−40.2	−36.8	−36.6	−32.3
11				−44.1	−43.5	−41.1	−37.2	−36.6
12			−50.3	−48.4	−47.0	−45.4	−44.9	−40.9
13				−52.7				
14			−56.0	−57.0				

* Measured by the previous observers.

Goodeve and Stein[1] have pointed out that there is a discontinuity in the curve when ω_v is plotted against v. The break in the curve occurs between $v_2'=14$ and $v_2'=15$, and has been accounted for as an indication of predissociation. From our measurements of the $(0, v_2', 0)\leftarrow(0,0,0)$ progression we have plotted this curve and is shown in Fig. 4. The curve is evidently nonlinear throughout its extent.

As has been pointed out by Birge[12] this feature is quite common with diatomic molecules, so

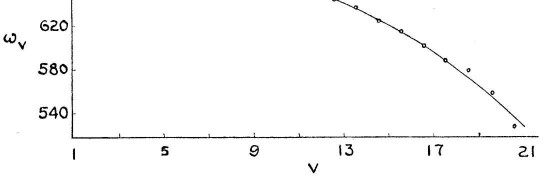

FIG. 4.

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[12] Birge, Trans. Faraday Soc. **25**, 707 (1931).

presumably it must also exist with more complicated ones. Unfortunately, we have not been able to trace the curve beyond $v=20$ with certainty, although we have measured 30 members in this progression and there is every indication that it extends far beyond the limit of observation. In view of this nonlinear relationship between ω_v and v, and the limited extent of our observation, any extrapolation to determine the heat of dissociation will be untrustworthy.

Discussion of Results

It should be pointed out that the members forming the $(0, v_2', 0) \leftarrow (0, 0, 1)$ progression lie in regions where the $(1, v_2', 0) \leftarrow (1, 0, 0)$ progression should appear, and that the members representing the $(0, v_2', 0) \leftarrow (0, 1, 0)$ progression occupy the places where the isotope bands of the $(1, v_2', 0) \leftarrow (0, 0, 0)$ would be expected. This superposition effect very probably makes the intensity of these progressions higher than that estimated from the Boltzmann temperature factor $e^{-W/KT}$.

The present analysis yields three normal frequencies. There seems to be no obvious reason why no more bands forming a v_1' or v_3' progression could be found. As has been pointed out in an early paragraph, the intensity in the most intense v_2' progression increases rapidly at first with the vibrational quantum number, reaches a maximum at about $v_2'=15$, and then decreases gradually. This most favored transition is connected with the change in the molecular configuration due to the electronic transition and is discussed in the following paper.

It is seen that the constants calculated from the electronic band spectrum data are in good agreement with the values deduced by Bailey and Cassie[5] from the infrared band spectrum. This seems to support the results of the present analysis. However, in evaluating the molecular constants for the normal state we have assumed the existence of a fundamental band $\nu_1=529$ cm^{-1} which has not been observed in the infrared absorption. This band, if it really exists, should lie approximately at 19μ which was the limit of our observation.

I wish to thank Professor D. M. Dennison for the guidance of this work, Professor W. F. Colby for helpful suggestions and discussions, and Professor R. A. Sawyer for kind help and advice during the course of experimentation.

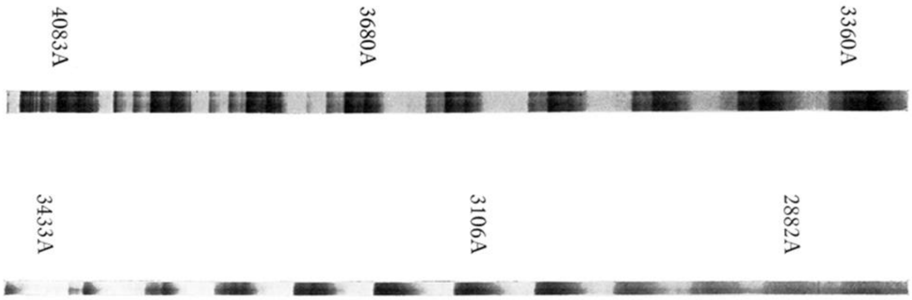

FIG. 1. Band system of ClO_2.

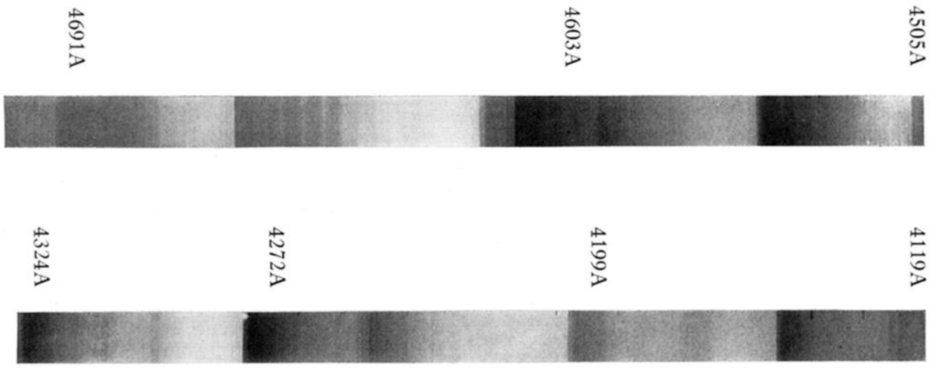

FIG. 2. Rotational structure of ClO_2 absorption bands.