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THE ABSORPTION SPECTRUM OF CHLORINE DIOXIDE*

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ABSTRACT

The wave-lengths of 134 absorption bands of ClO_2 have been measured with the Hilger E-1 and E-185 quartz instruments. The bands have been arranged in progressions and the energy levels deduced. Five vibrational levels of the normal electronic state have been found; the vibrational levels of the excited electronic state can be described with the use of two vibrational quantum numbers. Formulae for these bands and their isotope separations are given. The shapes of the molecule in the normal and excited electronic states have been calculated from Bjerrum's formulae for the vibrations assuming valency forces and all but one solution for each electronic state is excluded by the isotope effect or the intensity distribution of the bands. The central force formulae give no possible solutions. The normal modes of vibration for the molecule have been calculated. The intensity distribution is consistent with the extension of the Franck-Condon principle to polyatomic molecules. The predissociation limit agrees with a very approximate extrapolated value for the energy of dissociation through one mode of vibration of the excited electronic state into a ClO molecule and an O atom. Dissociation through a second mode of vibration of the excited electronic state gives only a very rough value. A discontinuity in the $\Delta E{:}v_2'$ curve noted by Goodeve and Stein appears at about the energy required for an oscillation of the molecule through a straight line position and it is proposed that this is the cause of the discontinuity.

OF THE various triatomic molecules whose electronic bands lie in the more accessible wave-length regions, chlorine dioxide seems to be one of the most promising molecules. It has an intense absorption spectrum lying between λλ 5225 to 2600A and because chlorine has two isotopes of comparable abundance, it is possible to study the isotope effect, giving another way of attacking the assignment of vibrational quantum numbers to its energy levels. This research was undertaken on this molecular spectrum in order to make use of this particular advantage.

The first attempt to classify the bands of ClO_2 was made by Käbitz.[2] Mayer[3] succeeded in arranging them into progressions. In both of these researches only about forty nine bands were considered. Goodeve and Stein[4] investigated the spectrum of ClO_2 and measured 138 bands, and found that many of the observed bands were isotopic bands. These bands were arranged

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[1] The material in this paper is taken from the dissertation submitted by Helen Johnston in partial fulfillment of the requirements of the degree of Doctor of Philosophy, Columbia University, 1931.

[2] B. Käbitz, Diss. Bonn, 1905.

[3] H. Mayer, Zeits. f. physik. Chem. **113**, 220 (1924).

[4] C. F. Goodeven and C. P. Stein, Trans. Faraday; Soc. **25**, 738 (1929).

into 4 principal and 5 sub-"series." They also observed the phenomenon of predissociation, which they located at λ3293A. Very recently Finkelnburg and Schumacher[5] have published a paper on ClO_2. These experimentors have photographed the band heads with a two meter grating, but have not arranged the bands into progressions. They have also determined the limit of predissociation λ3753.28A.

EXPERIMENTAL

The chlorine dioxide was prepared by the reaction of oxalic acid and potassium chlorate as described by Bray.[6] The gas evolved was collected in a trap cooled with dry ice. This trap was connected directly to the absorption cell.

Since chlorine dioxide is decomposed rather rapidly by light, it was necessary to keep a stream of the gas flowing through the absorption cell during the time of exposure. To do this we connected a glass needle valve to an outlet tube of the absorption cell to regulate the rate of flow of the ClO_2 and evacuated the system protecting the pump with a liquid air trap. When this procedure was used, the trap containing the chlorine dioxide was cooled in dry ice or dry ice-alcohol mixtures in order to regulate the pressure of ClO_2. In some cases a stream of nitrogen was passed through the chlorine dioxide trap and then through the absorption cell and thus the cell was kept filled with undecomposed chlorine dioxide. The dry ice-alcohol bath provided a range of temperatures from -76°C to 10°C. The bath was easily regulated to within $\pm 0.5°$ by the addition of dry ice about every 15 or 20 minutes.

Three absorption cells were used in these experiments. The first cell was made of Pyrex with plane Pyrex windows. There were three compartments in this cell, the two end ones ten cm long being evacuated and sealed off. The middle compartment was 30 cm long. This construction was used so that the middle compartment containing the ClO_2 gas could be cooled in dry ice in order to sharpen the band heads and simplify the general band structure. This could only be used for the stronger bands. The second cell consisted of a Pyrex tube 60 cm long with quartz windows sealed on which de Khotinsky cement. (ClO_2 is said to explode when brought in contact with organic matter, but we had no such difficulty.) The third cell was an all quartz one of the same general design as the first described above.

As sources of light in the visible and near ultraviolet we used a tungsten filament lamp or a point-o-lite lamp. A Pfund iron arc was used as a reference source. This was mounted directly in front of the slit with the lower electrode remaining in place during the exposure of the absorption spectrum to insure its correct alignment during the exposure of the reference spectrum.

The Hilger E-1 Quartz Spectrograph was used for nearly all our measurements, only a small number being made with the Hilger E-185 three meter instrument.

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[5] W. Finkelnburg and H. J. Schumacher, Zeits. f. physik. Chemie, Bodenstein-Festband, 704 (1931).

[6] W. Bray, Zeits. f. physik. Chemie **54,** 575 (1906).

EXPERIMENTAL RESULTS

We have measured 134 bands of ClO_2 between λλ5042 and 3226. The reproducibility of our measurements on different plates is about 0.7A or from 3 to 6 cm^{-1} depending on the wave-length range. Table I gives the wave numbers of all bands measured by us and the wave numbers given by Finkelnburg and Schumacher and by Goodeve and Stein. Goodeve and Stein say that their results could be duplicated to within a few wave numbers but that sometimes readings differed by as much as 10 cm^{-1}. In the far ultraviolet, they claimed not to be able to repeat within 15 cm^{-1}. Finkelnburg and Schumacher claim an accuracy of ± 0.05A in the visible and ± 0.5A in the far ultraviolet. We find that the measurements of the latter authors do not follow smooth formulae as well as ours and we do not feel certain that these band heads can be measured so precisely as they claim. The wave-lengths which we secured were reduced to vacuum by reducing the wave-lengths of the standard iron lines to vacuum and making the entire calculation with these standards. The wave-lengths were calculated by using the usual Hartmann formula.

CLASSIFICATION OF BANDS

Inspection of Goodeve and Stein's results immediately shows that it is impossible to derive a formula that will fit the isotope effect. A formula can be made to fit the isotope effect from the sixth member of their "sequence," but their classification up to this point must be incorrect or the isotope effect surprisingly irregular. Our arrangement of the bands into progressions differs in many details from that of Goodeve and Stein though the main features remain.

In discussing our arrangement, it is convenient to adopt the assignment of vibrational quantum numbers at this point and justify this selection later. We find it necessary to use three quantum numbers for the normal state, v_1'', v_2'' and v_3'', and two for the excited state, v_1' and v_2'. Transitions can be indicated by the symbol $(v_1', v_2') \leftarrow (v_1'', v_2'', v_3'')$, the arrow indicating the direction of the change in absorption.

Anticipating the final assignment of quantum numbers, the progression with the most intense bands is $(0, v_2') \leftarrow (0, 0, 0)$, $v_2' = 0$ to 30, the third most intense band system $(1, v_2') \leftarrow (0, 0, 0)$, $v_2' = 1$ to 17, the second $(0, v_2') \leftarrow (0, 0, 1)$, $v_2' = 4$ to 15, and the fourth $(1, v_2') \leftarrow (0, 0, 1)$, $v_2' = 0$ to 13. If the progression difference between progressions $(0, v_2') \leftarrow (0\ 0\ 0)$ and $(0, v_2') \leftarrow (0, 0, 1)$ and between progressions $(1, v_2') \leftarrow (0, 0, 0)$ and $(1, v_2') \leftarrow (0, 0, 1)$ are taken it will be found that this difference is 528.8 cm^{-1}. It would thus appear that the first and third most intense progressions originate from the same unexcited level and go to different excited levels and the second and fourth in intensity come from a level with 528.8 cm^{-1} more energy and terminate on the same two sets of excited levels. If the differences between the bands having the same value of v_2' of the progressions $(0, v_2') \leftarrow (0, 0, 0)$ and $(1, v_2') \leftarrow (0, 0, 0)$ and of progressions $(0, v_2') \leftarrow (0, 0, 1)$ and $(1, v_2') \leftarrow (0.\ 0, 1)$ and of progressions $(1, v_2') \leftarrow (0, 0, 1)$ and $(2, v_2') \leftarrow (0, 0, 1)$ are taken it is found to be about 300

TABLE I.

U. & J. $\tilde{\nu}$ in cm^{-1} in vacuo	F. & S. $\tilde{\nu}$ in cm^{-1} in vacuo	G. & S. $\tilde{\nu}$ in cm^{-1} in air
	19134.1	19140
	19424.4	19423
†	19625.4	19635
19831.9	19841.7	19848
†		19900
20070.2		20079
*20080.2	20081.5	
20125.8	20130.4	20130
†20185.3		
20332.7		20341
20359.8		20368
*20368.4	20369.9	
20542.3		20548
20569.4		20574
*20574.2	20572.7	
20782.1	20778.8	20786
*20785.9		
20825.1		20835
21014.2	21016.4	21023
21064.6	21064.1	21070
21275.8	21276.2	21283
21307.7	21305.4	21310
21479.8	21480.4	21483
*21716.8		
21724.8	21724.3	21733
21760.6	21761.2	21769
21842.2		21849
21979.1		21980
22009.7	22010.3	22016
22172.3	22173.7	22178
†22369.4		
22426.4	22425.4	22437
22449.2	22450.2	22457
22536.2	22537.0	22542
22590.9	22598.7	22580
		22675
*22703.2		22703
22706.4	22706.3	22711
*22860.6	22860.7	22856
22873.2	22875.0	22869
†23029.2		
*23107.6		23116
23120.5	23119.2	23124
23140.5		
23221.7		23225
23280.5	23281.7	23277
*23382.2		23391
23395.7	23395.8	23402
23548.6	23553.0	23556
*23789.7		23796
23806.3	23813.8	23812
23902.0		23904
*23938.2		23944
23959.1		23967
*24058.6		24062
24078.2	24079.3	24084
†‡24169.6		
24227.7	24228.3	24232
†	24241.0	
*24463.9		24471
24488.1	24488.4	24495
*24610.9		
24635.8	24636.8	24641
24709.7		
*24732.2		24738
24757.2	24757.1	24763
24899.1	24907.4	24904
		24986
25116.3		
*25132.8		25141
25163.9	25164.2	25170
25238.7		
*25274.6		25284
25307.0	25307.5	25313
*25397.8		25397
25428.0	25428.0	25436
*25536.9		25544
25569.2	25571.4	25575
		25656
25769.9		
*25799.7		25810
25834.2	25835.4	25843
25903.4		
†25916.5		
*25936.2		25948
25972.1	25973.6	25979
26029.9		
*26059.5		26065
26094.4	26095.4	26107
†‡26151.9		
26195.5		26208
26230.7	26232.2	26242
26303.4	26310.6	26306
*26459.4		
26500.4	26504.9	26503
26549.5		
*26591.4		
26633.5	26635.8	26648
26664.0		
26686.5		
*26715.5		
26756.0	26757.4	26764
*26843.5		26860
†26875.8		

* Isotopic bands.

† Unclassified bands.

‡ These are the two bands that agree approximately with the calculated values for transitions (2, 6)←(1, 0, 0) and (2, 9)←(1, 0, 0).

The Editors of the Physical Review suggest that the accuracy of our measurements probably does not justify the use of six significant figures. We fully agree with them but we retain the sixth significant figure because all of our tables and calculation would have to be revised if this figure were dropped. Also the precision of the isotopic separations probably warrants the retension of the fractional values.

TABLE I.—(*Continued*)

U. & J. $\tilde{\nu}$ in cm^{-1} in vacuo	F. & S. $\tilde{\nu}$ in cm^{-1} in vacuo	G. & S. $\tilde{\nu}$ in cm^{-1} in air	U. & J. $\tilde{\nu}$ in cm^{-1} in vacuo	F. & S. $\tilde{\nu}$ in cm^{-1} in vacuo	G. & S. $\tilde{\nu}$ in cm^{-1} in air
26887.0	26888.6	26900	†		29900
26963.8	26967.2	26971	*		29936
*27117.4			29980.9	29982.2	29996
27162.3		27163		30153	
*27240.2			*		30307
27288.6	27293.2	27302	30375.3	30380	30377
*27368.6		27377	*		30400
27412.9	27414.9	27424	30435.6		30477
*		27507	†		30529
†27525.0			†30570.9		
27536.6	27540.4	27550			30613
27625.2	27618.5	27623	*		30976
*27761.5		27772	30989.3	30996	31014
27815.7		27821	†		31142
†27829.7					31218
*27883.1			*		31539
27939.0	27946.7	27956		31601	31619
*		28021	†		31749
†28037.3					31847
28063.0	28065.1	28079		32190	32202
*		28148		32768	32779
28172.8	28186.0	28194		33330	33336
*28415.0		28424	*		33761
28470.7		28475		33848	33877
*28523.5			*		34238
28583.7	28590.2	28603		34346	34341
28704.5	28713.8	28724	*		34746
†28762.8				34841	34855
†28843.9		28840		35288	
29112.4		29114			35370
†29170.1				35805	35840
29223.8	29229.3	29236			36260
*		29304		36321	
29346.0	29351.8	29365			36700
*29685.1		29686			37106
29748.7		29745			37509
29843.0	29850.5	29858			37922

cm^{-1} if v_2' is small and that this difference decreases with increasing v_2'. With this procedure it was found necessary to postulate three upper sets of energy levels and two unexcited energy levels. This is essentially the scheme used by Goodeve and Stein.

The search for further vibration levels of the normal electronic state was then made by first plotting all bands not included in these progressions and then moving a scale having the differences of the $(0, v_2')$, $(1, v_2')$ and $(2, v_2')$ levels along this until agreement with the positions of the unclassified bands was secured. In this way evidence for five vibrational levels of the normal state was secured.

We have not been able to find convincing evidence for the third fundamental vibration frequency of the excited state. Those agreements we have found could be explained as due to chance coincidences.

The final arrangement of bands and combination differences are given in Tables II, III, and IV. The wave number differences are indicated by numbers placed between the columns and rows. The differences indicated by the

Δ's at the top of the columns are the differences between the column of wave numbers following a particular Δ and the first column of the table in each case. In this way the Δ's represent the wave number differences between the lowest lying level and the four higher vibrational levels of the normal state.

TABLE II.

(v_1', v_2')	(v_1'', v_2'', v_3'')(0, 0, 0)	Δ_1	(0, 0, 1)	Δ_2	(0, 1, 0)	Δ_3	(1, 0, 0)
0, 0	20332.7						
	681.5						
0, 1	21014.2						
	710.6						
0, 2	21724.8						
	701.6						
0, 3	22426.4						
	694.1						
0, 4	23120.5	529.6	22590.9				
	685.8		689.6				
0, 5	23806.3	525.8	23280.5				
	681.8		678.6				
0, 6	24488.1	529.0	23959.1				
	675.8		676.7				
0, 7	25163.9	528.1	24635.8				
	670.3		671.2				
0, 8	25834.2	527.2	25307.0	717.9	25116.3	855.2	24979.0*
	666.2		665.1		653.6		669.8
0, 9	26500.4	528.3	25972.1	730.5	25769.9	851.6	25648.8*
	661.9		661.4				654.6
0, 10	27162.3	528.8	26633.5			858.9	26303.4
	653.4		655.1				660.4
0, 11	27815.7	527.1	27288.6			841.9	26963.8
	655.0		650.4				661.4
0, 12	28470.7	531.7	27939.0			845.5	27625.2
	642.0		644.7				
0, 13	29112.7	529.0	28583.7				
	636.0		640.1				
0, 14	29748.7	524.9	29223.8				
	626.6		619.2				
0, 15	30375.3	532.3	29843.0				
	614.0						
0, 16	30989.3						
Ave.		528.5		724.2		850.6	

Some variation in these differences is present but no evidence of trends in values. The wave numbers marked with an asterisk are those of Goodeve and Stein corrected to vacuum.

The energy levels of the normal electronic state are spaced as follows above the lowest level:

(0, 0, 0)	0 cm^{-1}
(0, 0, 1)	528.8 "
(0, 1, 0)	727.0 "
(1, 0, 0)	857.7 "
(0, 2, 0)	1471.3 "

The last level is classified as the first harmonic of the 727.0 cm^{-1} level. It is greater than twice the value of the fundamental but this is quite common among polyatomic molecular levels. These values do not represent average value of all the differences of Table II, III, and IV but only average values of our own measurements.

All but 21 bands have been assigned to progressions, of this number six were reported by Goodeve and Stein and one by Finkelnburg and Schumacher and have not been confirmed by the authors of this paper and fourteen were first reported by us. Two of the latter fourteen agree very approximately with the calculated values using the formulae below for the transitions (2, 6)←(1, 0, 0) and (2, 9)←(1, 0, 0). These unclassified bands are denoted by a dagger in Table I.

TABLE III.

(v_1'', v_2'', v_3'') (v_1', v_2')	(0,0,0)	Δ_1	(0,0,1)	Δ_2	(0,1,0)	Δ_3	(1,0,0)	Δ_4	(0,2,0)
1,0			20070.2						19134.7*
			711.9						697.2
1,1	21307.7	525.6	20782.1	738.3	20569.4			1475.8	19831.9
	702.0		697.7		706.4				710.4
1,2	22009.7	529.9	21479.8	733.9	21275.8			1467.4	20542.9
	696.7		692.5		703.3				
1,3	22706.4	534.1	22172.3	727.3	21979.1	864.2	21842.2		
	689.3		700.9		689.8		694.0		
1,4	23395.7	522.5	22873.2	727.0	22688.7*	859.5	22536.2		
	682.5		675.4				685.5		
1,5	24078.2	529.6	23548.6			856.5	23221.7		
	679.0		679.1				680.3		
1,6	24757.2	529.5	24227.7			855.2	23902.0		
	670.8		671.4						
1,7	25428.0	528.9	24899.1	718.3	24709.7				
	666.4		670.1						
1,8	26094.4	525.2	25569.2			855.7	25238.7		
	661.6		661.5				664.7		
1,9	26756.0	525.3	26230.7	726.1	26029.9	852.6	25903.4		
	656.9		656.3		656.5		646.1		
1,10	27412.9	525.9	26887.0	726.4	26686.5	863.4	26549.5		
	650.1		649.6						
1,11	28063.0	526.4	27536.6						
	641.5		636.2						
1,12	28704.5	531.7	28172.8						
	638.5								
1,13	29343.0								
	637.9								
1,14	29980.9								
	Ave.	527.9		728.2		858.2		1471.6	

TABLE IV.

(v_1'', v_2'', v_3'') (v_1', v_2')	(0, 0, 1)	$\Delta_4-\Delta_1$	(0, 2, 0)
2,0	20359.8	942.2	19417.6*
	704.8		708.2
2,1	21064.6	938.8	20125.8
	696.0		699.3
2,2	21760.6	935.5	20825.1
	688.6		
2,3	22449.2		
	691.3		
2,4	23140.5		
Ave.		938.8	

TABLE V.

$(v_1'', v_2'', v_3'')\rightarrow$ v_2'	(0, 0, 0) $v_1'=0$	(0, 0, 1) $v_1'=0$	(0, 0, 0,) $v_1'=1$	(0, 0, 1) $v_1'=1$	(0, 0, 1) $v_1'=2$	(0, 1, 0) $v_1'=1$	(0, 1, 0) $v_1'=0$	(1, 0, 0) $v_1'=0$	(1, 0, 0) $v_1'=1$	(1, 0, 0) $v_1'=2$	(0, 2, 0) $v_1'=1$	(0, 2, 0) $v_1'=2$
0	+27.8			−3.3	+6.1						+3.7*	−5.8*
1	−2.0		−1.0	+2.4	−2.8	−12.3					−5.9	+0.9
2	+3.0		+0.3	−0.8	−1.7	−6.6					+3.6	+4.3
3	+4.6		+1.9	−3.4	−4.3	+1.6			−4.6			
4	+4.3	+3.4	+1.7	+8.0	+2.5	+1.7*			−0.1			
5	+1.4	+4.4	+0.4	−0.4					+1.6			
6	+0.1	−0.1	+1.2	+0.5					+3.7	+8.2		
7	−1.5	−0.6	−0.6	−0.7		+8.1						
8	−3.0	−1.4	−1.1	+2.5			+6.1	−0.6*	+0.9			
9	−3.0	−2.5	−0.8	+2.7		+0.1	−6.5	+3.1*	+4.3	+4.4		
10	−1.7	−1.7	+0.4	+3.3		+1.0		−2.9	−5.7			
11	−3.2	−1.5	+0.5	+2.9				+2.6				
12	+3.3	−0.4	−1.4	−5.3				+14.7				
13	+0.9	−5.3	−2.6									
14	−1.6	+2.3	+1.7									
15	−7.3	−10.1										
16	−20.1											

TABLE VI.

v_2'	$v_1''=0, v_2''=0, v_3''=0$ $v_1'=0$		$v_1''=0, v_2''=0, v_3''=1$ $v_1'=0$		$v_1''=0, v_2''=0, v_3''=0$ $v_1'=1$		$v_1''=0, v_2''=0, v_3''=1$ $v_1'=1$		$v_1''=0, v_2''=0, v_3''=1$ $v_1'=2$		$v_1''=0, v_2, =1, v_3, =0.$ $v_1'=1$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0		8.1		11.3		8.3	10.0	10.5	8.6	9.7		
1		2.7		6.0		2.9	5.0	5.2		4.4	4.8	6.5
2	−4.5	−2.7		0.6		−2.5		−0.2				0.1
3		−8.0		−4.8		−7.8		−5.6				
4	−12.9	−13.4		−10.2	−13.5	−13.2	−12.6	−11.0				
5	−16.6	−18.8		−15.2	−19.6	−18.6		−16.3				
6	−24.2	−24.2	−20.9	−20.9	−25.0	−24.0		−21.7				
7	−31.1	−29.5	−24.9	−26.3	−30.2	−29.3		−27.1				
8	−34.5	−34.9	−32.4	−31.6	−34.9	−34.7	−32.3	−32.4				
9	−41.0	−40.3	−35.9	−37.0	−40.5	−40.1	−35.2	−37.8				
10	−44.9	−45.6	−42.1	−42.4	−44.3	−45.4	−43.5	−43.2				
11	−54.2	−51.0	−48.4	−47.8		−50.8	−53.7	−48.6				
12	−55.7	−56.4	−55.9	−53.1				−53.9				
13		−61.7	−60.2	−58.4								
14	−63.6	−67.1		−63.8								
15												
16												

The wave numbers of these classified bands can be calculated by an equation of the type,

$$\tilde{\nu} = \tilde{\nu}_e + a(v_2' + \tfrac{1}{2}) - b(v_2' + \tfrac{1}{2})^2 + c(v_1' + \tfrac{1}{2}) - d(v_1' + \tfrac{1}{2})^2 - e(v_1' + \tfrac{1}{2})(v_2' + \tfrac{1}{2}) - \tilde{\nu}''$$

where $\tilde{\nu}_e$ is the wave number for the electronic transition and $\tilde{\nu}''$ is the wave number of the normal vibrational level and a, b, c, d, and e are constants. With the numerical values of the constants which we have secured this becomes,

$$\tilde{\nu} = 19795.38 + 719.34(v_2' + \tfrac{1}{2}) - 2.817(v_2' + \tfrac{1}{2})^2 + 304.82(v_1' + \tfrac{1}{2}) - 2.488(v_1' + \tfrac{1}{2})^2 - 4.892(v_1' + \tfrac{1}{2})(v_2' + \tfrac{1}{2}) - \tilde{\nu}''. \quad (1)$$

This formula applies to bands for which v_2' is equal to or less than 14. The precision with which the measurements in the far ultraviolet can be made is so low that it is impossible to derive a satisfactory formula for this region. In Table V we have given the results of the observed minus the calculated values for the band heads. In most cases there is very close agreement, and the agreement in the case of nearly all the bands is satisfactory and probably within the limits of error of the measurements.

Fig. 1 is the energy level diagram consisting of the levels required by our assignment of quantum numbers. The black circles indicate the observed bands.

THE ISOTOPE EFFECT

The isotope effect is very prominent in these bands. We have indicated the isotopic bands in Table I with an asterisk. This selection was made partly by inspection and partly by means of the formulae derived in this section. The $Cl^{37}O_2$ bands lie on the high frequency side of $Cl^{35}O_2$ bands in the case of bands involving transitions to the lowest excited vibrational levels, but otherwise on the low frequency side.

We have found it possible to fit the experimental differences, $(Cl^{37}O_2) - (Cl^{35}O_2)$, to the formula

$$\Delta\tilde{\nu} = -5.37(v_2' + \tfrac{1}{2}) - 0.80(v_1' + \tfrac{1}{2}) - \Delta\tilde{\nu}'', \quad (2)$$

where $\Delta\tilde{\nu}''$ is -11.16 cm^{-1}, -14.42 cm^{-1} and -15.75 cm^{-1} for the (0, 0, 0), (0, 0, 1) and (0, 1, 0) normal vibrational levels, respectively. The agreement between this formula and the observed values is shown in Table VI, which also shows which isotope bands have been observed. The isotopic bands in many cases could not be observed because of fine structure, superposition of the weaker $Cl^{37}O_2$ band on the strong $Cl^{35}O_2$ band, diffuseness of band heads in the predissociation region, and the general weakness of many of the bands, both $Cl^{35}O_2$ and $Cl^{37}O_2$.

The separations of the vibrational levels in either the excited or normal electronic state should follow a formula of the form,

$$\frac{\Delta E}{hc} = a(v_1 + \tfrac{1}{2}) + b(v_2 + \tfrac{1}{2}) + c(v_3 + \tfrac{1}{2})$$

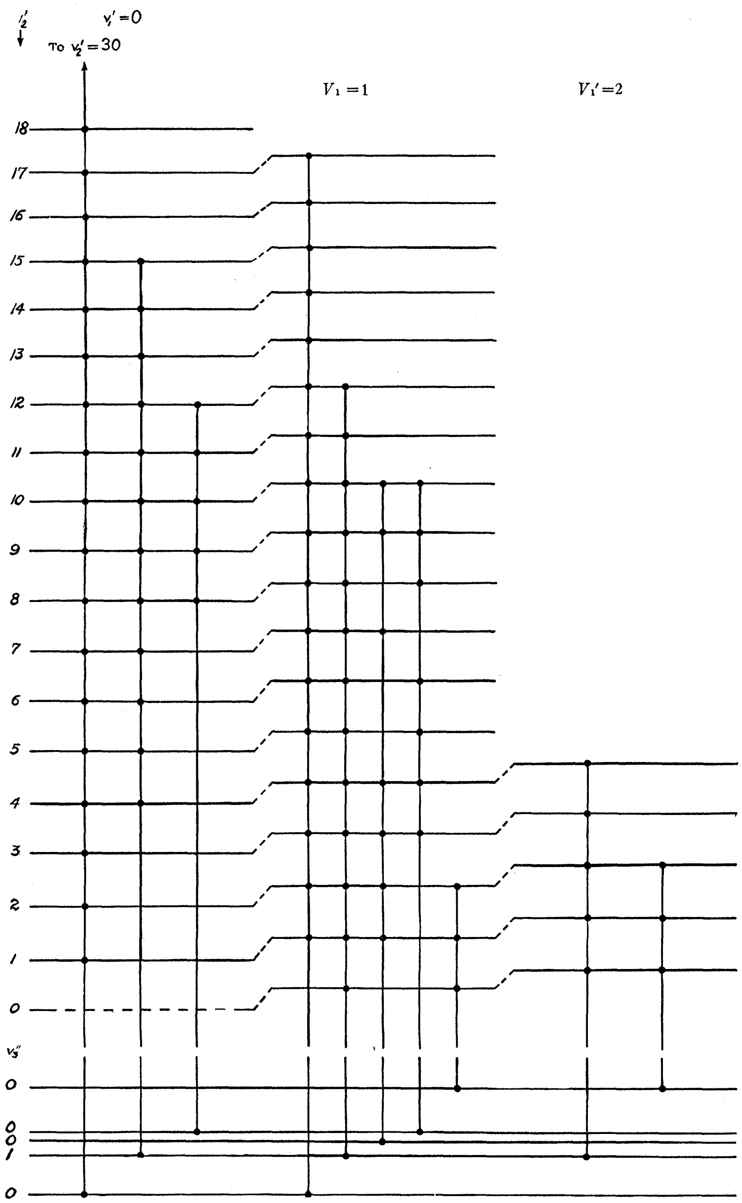

Fig. 1. Energy level diagram of the ClO$_2$ molecule. Bands that agree approximately with the calculated values for the transitions. (0, 8)←(0, 1, 0); (0, 9)←(0, 1, 0); (2, 6)←(1, 0, 0) and (2, 9) − (1, 0, 0) are omitted. These transitions are discussed in the text.

where the a, b, and c will be negative if ΔE is the energy of the $Cl^{37}O_2$ molecule minus that of the $Cl^{35}O_2$ molecule and higher power terms in the v's are neglected. If we assume that $v_3' = 0$ for all levels which we have observed the isotope separation is then,

$$\tilde{\nu}_{37} - \tilde{\nu}_{35} = \Delta\tilde{\nu} = a'(v_1' + \tfrac{1}{2}) + b'(v_2' + \tfrac{1}{2}) + c'/2$$
$$- a''(v_1'' + \tfrac{1}{2}) - b''(v_2'' + \tfrac{1}{2}) - c''(v_3'' + \tfrac{1}{2}). \quad (3)$$

With our assignment of quantum numbers we see from Eqs. (2) and (3) and the values of $\Delta\tilde{\nu}''$, that

$$\begin{array}{ll} a' = -0.80 & \dfrac{c'}{2} - \dfrac{a''}{2} - \dfrac{b''}{2} - \dfrac{c''}{2} = -\Delta\tilde{\nu}'' \\ b' = -5.37 & b'' = -15.76 + 11.16 = -4.60 \\ & c'' = -14.42 + 11.16 = -3.26 \end{array}$$

and thus

$$\frac{c'}{2} - \frac{a''}{2} = 7.23. \quad (4)$$

Our calculated value (see below) for this difference is 3.19 cm^{-1}. This difference would be diminished, if the 11.16, 14.42, and 15.76 cm^{-1} differences in our formula (2) were decreased. This would mean that our calculated differences for the bands having $v_2' = 0$ should be less than those given in Table VI by about 4 cm^{-1}. Examination of that table shows that a change of a few wave numbers in these values may be possible. We shall discuss this further after the theoretical formulae have been presented.

THE NORMAL MODES OF VIBRATION OF THE ClO_2 MOLECULE

Bjerrum[7] has considered the problem of the vibrations of molecules of this kind assuming two types of binding; (1) the potential energy is a function of the linear distances between the nuclei, that is the forces are central; (2) the restoring forces consist of harmonic forces along the chemical bond and perpendicular to this direction, that is, the forces are valency forces as he called them. The three frequencies of vibration in each case are functions of three constants, two force constants and the half angle at the apex of the isosceles triangle. All solutions for this angle using the formulae based on assumption (1) gave imaginary angles.

The equation for θ the half angle at the apex by using the formulae based on assumption (2) is a cubic in $\cos^2\theta$ and there are three possible ways of assigning the observed frequencies to the theoretical formulae for the frequencies. This gives nine possible solutions. The possible values of $\cos^2\theta$ must be real and lie between 0 and 1. We find that there are three possible values for θ in the normal electronic state and thus three possibilities for the two force constants k_1, and k_2 as well. In the case of the ClO_2 normal state, our experimental data give us the isotope effect constants as well and it must

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[7] N. Bjerrum, Verh. d. D. phys. Ges. **16,** 737 (1914).

TABLE VII.

Assumed assignment of frequencies			Normal electronic state									
$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	$k_1 \times 10^4$	$k_2 \times 10^4$	θ	2θ	$\Delta\tilde{\nu}_1$ Calc.	$\Delta\tilde{\nu}_1$ Obs.	$\Delta\tilde{\nu}_2$ Calc.	$\Delta\tilde{\nu}_2$ Obs.	$\Delta\tilde{\nu}_3$ Calc.	$\Delta\tilde{\nu}_3$ Obs.
528.8	857.7	727.0	26.06	34.17	1°19′	2°38′	−0.0073	−3.20		—		−4.60
727.0	857.7	528.8	38.71	11.61	31°55′	63°55′	−4.17	−4.60	−10.90	—	−0.39	−3.26
857.7	727.0	528.8	38.59	8.41	65°10′	130°20′	−10.32	—	−5.88	−4.60	−2.80	−3.26
			Excited electronic state									
661.1*	719.34	304.8	36.65	3.015	55°19′	110°38′			(−5.37)	−5.37	−1.88	−0.80
226.1*	719.34	304.8	6.03	18.33	34°39′	69°18′			(−5.32)	−5.37	−1.90	−0.80
I 719.34	779.6*	304.8	35.86	3.62	38°28′	76°56′	(−5.37)	−5.37	−8.53	—	−0.83	−0.80
II 304.82	719.34	382.1*	7.96	21.81	18°47′	37°34′	(−0.80)	−0.80	−6.06	−5.37	−3.93	—

* These are calculated frequencies.

be possible to calculate these from the formulae by using the same set of values of k_1, k_2 and θ.

In the case of the excited electronic state we have observed two fundamental frequencies and the isotope effects for each of these. With three of these quantities we can solve for the constants k_1, k_2 and θ again and the fourth quantity must also agree with the calculated value. We find four possible values of θ of which two give sets of values for k_1, k_2 and θ from which the second isotope effect can be calculated. The formulae for ν_1, ν_2 and ν_3 and for the isotope effects for each of these are given below. Table VII gives the results of the calculations for the normal and excited states. Columns 1, 2, 3 give the possible assignments of the observed frequencies to the three theoretical formulae, columns 4, 5, 6, 7 the calculated constants, and columns 8, 9, 10 the calculated and observed isotope effects.

$$\nu_1 = \frac{1}{2\pi} k_1^{1/2}\left(\frac{1}{m} + \frac{2\sin^2\theta}{M}\right)^{1/2} \tag{5}$$

$$\nu_{2,3} = \frac{1}{2\pi}\left\{\frac{k_1+2k_2}{2m} + \frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M} \pm \left[\left(\frac{k_1+2k_2}{2m} + \frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M}\right)^2 - 2k_1k_2\frac{2m+M}{m^2M}\right]^{1/2}\right\}^{1/2} \tag{6}$$

$$\Delta\nu_1 = \frac{\partial\nu_1}{\partial M}\Delta M = -\frac{\Delta M k_1 \sin^2\theta}{4\pi^2\nu M^2} \tag{7}$$

$$\Delta\nu_{2,3} = \frac{\partial\nu_{2,3}}{\partial M}\Delta M = \frac{\Delta M}{8\pi^2\nu_{2,3}M}\left\{-\frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M} \pm \frac{1}{2\left[\left(\frac{k_1+2k_2}{2m} + \frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M}\right)^2 - 2k_1k_2\frac{2m+M}{m^2M}\right]^{1/2}} \cdot\left[-\left(\frac{k_1+2k_2}{m}\right)\left(\frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M}\right) - 2\left(\frac{k_1\cos^2\theta + 2k_2\sin^2\theta}{M}\right)^2 + \frac{4k_1k_2}{mM}\right]\right\} \tag{8}$$

We have calculated the one possible set of normal coordinates for the normal state and the two possible sets of coordinates for the excited state. The results are shown in Fig. 2.[8] Since the calculations for the excited state make

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[8] The normal coordinates for these modes of vibration in terms of Cartesian coordinates with origin at the center of mass and x-axis parallel to the line joining the like atoms in the equilibrium position, are

$$q_1 = 2(x_1 + x_2) + y_1 - y_2$$
$$q_2 = B(x_1 - x_2) - 2(y_1 + y_2)$$
$$q_3 = A(x_1 - x_2) + 2(y_1 + y_2)$$

use of the small and inaccurate isotope effects, the shape, normal coordinates and force constants for this state are very approximate. These quantities in the case of the normal state should be much more reliable. Of course, the assumption of valency forces may be only approximate.

INTENSITIES AND THE APPLICATION OF THE FRANCK-CONDON PRINCIPLE

Intensities have not been given in the tables for we have been unable to get consistent relative intensities for the bands by comparing spectra with different times of exposure and different pressures of ClO_2 gas in the absorption cell. We can see no evidence of irregularities in intensities of the bands in any progression and therefore we have constructed curves giving the approximate intensity distributions for the four most intense progressions as shown in Fig. 3 in the following way. The strongest bands are found to be suitable for measurement when the partial pressure of ClO_2 in the cell is about 0.2 mm. This was secured by cooling the trap containing the ClO_2 in

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where x_1, x_2, y_1 and y_2 are the displacements of the like atoms from the equilibrium position and A and B are constants. The conservation of momentum and angular momentum (both taken equal to zero) give the relations

$$y_2 = y_1 + \cot\theta(x_1 + x_2),\quad x_3 = -\frac{m}{M}(x_1 + x_2) \text{ and } y_3 = -\frac{m}{M}(y_1 + y_2),$$

x_3 and y_3 being the displacements of the unlike atom from the equilibrium position. From these equations it is a simple matter to secure the values of the Cartesian coordinates of each atom for each mode of vibration.

The values of A and B were secured by making the transformation of coordinates from the $x, y, \cdots$ etc. to q_1, q_2, q_3 and expressing the potential and kinetic energies in these coordinates. The determinental equation for the frequencies is diagonal then, if,

$$AB = \frac{4M}{M + 2m} \equiv \frac{4}{\mu}$$

and

$$A - B = -\frac{M}{M + 2m}\,\frac{2k_1\tan\theta + 4k_2\cot\theta}{k_1 - 2k_2} + \frac{2k_1\cot\theta + 4k_2\tan\theta}{k_1 - 2k_2}.$$

Setting the quantity on the right equal to X and solving for A and B,

$$A = \frac{X}{2} + \left[\frac{X^2}{4} + \frac{4}{\mu}\right]^{1/2}$$

$$B = -\frac{X}{2} + \left[\frac{X^2}{4} + \frac{4}{\mu}\right]^{1/2}.$$

(Other values for A and B are secured by using the minus sign before the radical, but this gives nothing new for q_2 only becomes q_3 and q_3 becomes q_2.) The frequencies associated with the coordinates q_2 and q_3 are then,

$$\nu_2 = \frac{1}{2\pi}\left[\frac{\frac{1}{2}k_1(\sin\theta - \frac{1}{2}\cos\theta\mu B)^2 + k_2(\cos\theta + \frac{1}{2}\sin\theta\mu B)^2}{\frac{1}{2}m + \frac{1}{8}B^2m/\mu}\right]^{1/2}$$

and

$$\nu_3 = \frac{1}{2\pi}\left[\frac{\frac{1}{2}k_1(\sin\theta + \frac{1}{2}\cos\theta\mu A)^2 + k_2(\cos\theta - \frac{1}{2}\sin\theta\mu A)^2}{\frac{1}{2}m + \frac{1}{8}B^2m/\mu}\right]^{1/2}$$

These expressions are equivalent to those given above except that either ν_2 or ν_3 may be the greater of the two depending on the values of the constants k_1, k_2 and θ.

dry ice so that the vapor pressure of ClO_2 was about 2 mm[9] and passing 1/10 of a stream of air through the trap and cell and the remainder past the trap and through the cell, the gas stream being divided by using capillary tubes of different lengths. The weakest bands were photographed with the trap containing the ClO_2 at about 5°C at which temperature the vapor pressure of ClO_2 is about 600 mm. Thus the ratio of most intense to least intense bands is considerably more than 3000 probably, for the strongest bands were yet easily measureable and the weakest difficult to observe. From our plates we can determine the most intense bands of each progression and also the bands at which two progressions have the same intensity. We have determined the bands of greatest intensity from plates taken with a hydrogen discharge tube as source since it gives a more uniform intensity in this region. No correction has been attempted for the changing dispersion of the instrument, which, of course, changes the blackening on the plate at different wave-lengths even if the intensity of the source were uniform.

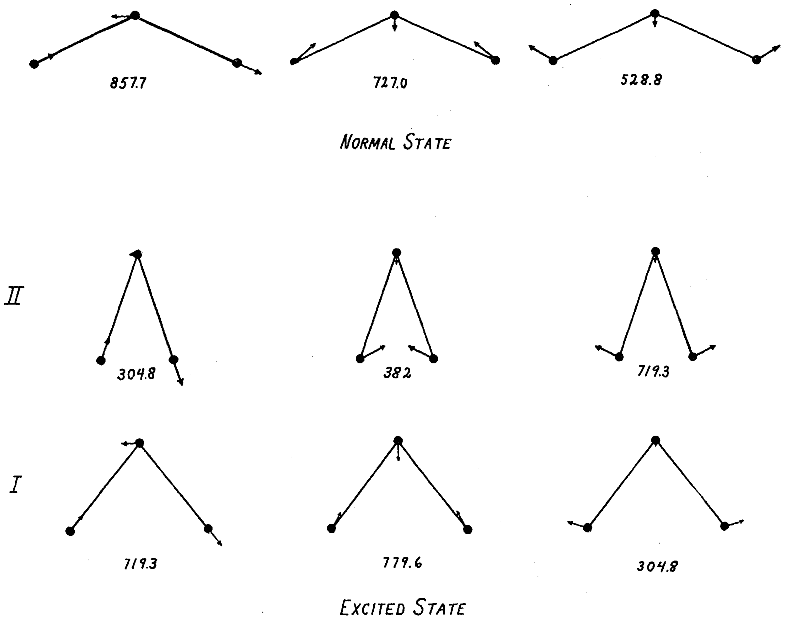

Fig. 2. Normal coordinates of the ClO_2 molecule. The acute angles between the direction of vibration of the oxygen atoms and a horizontal line are:
Normal state: $\tilde{\nu}_1=857.7$, $\alpha=24°50'$; $\nu_2=727.0$, $\alpha=41°39'$; $\nu_3=528.8$, $\alpha=30°25'$;
Excited state: Configuration I; $\tilde{\nu}_1=719.3$, $\alpha=51°32'$; $\tilde{\nu}_2=779.6$, $\alpha=60°23'$; $\tilde{\ }_3=304.8$, $\alpha=16°33'$.
Configuration II; $\tilde{\nu}_1=304.8$, $\alpha=71°13'$; $\tilde{\nu}_2=719.3$, $\alpha=22°30'$; $\tilde{\nu}_3=382$, $\alpha=51°34'$.

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[9] This was determined by passing a slow stream of N_2 gas through the trap, catching the ClO_2 with liquid air, measuring the volume of gas passed through and determining the amount of ClO_2 vaporized by the method described by Bray (W. Bray, Zeits. f. physik. Chemie **54**, 569 (1906)).

The most intense band of the system is in the progression $(0, v_2') \leftarrow (0, 0, 0)$ and has been assigned the intensity 3000, while the first observed band of each progression has been given the intensity 1. The most intense band of the $(0, v_2') \leftarrow (0, 0, 1)$ progression has been assigned an intensity of 300. This appears to be about right and would be the intensity, if the Boltzmann factor, $e^{-h\nu/kT}$, giving the relative abundance of molecules in the two normal levels were the only factor determining the relative intensities. The maximum intensity of the strongest band of the $(1, v_2') \leftarrow (0, 0, 0)$ comes at $v_2' = 11$ which has the same intensity as the $v_2' = 6$ band of the $(0, v_2') \leftarrow (0, 0, 0)$ progression. The maximum of the $(1, v_2') \leftarrow (0, 0, 1)$ progression is taken as 1/10 that of the $(1, v_2') \leftarrow (0, 0, 0)$ progression agreeing again with the Boltzmann factor

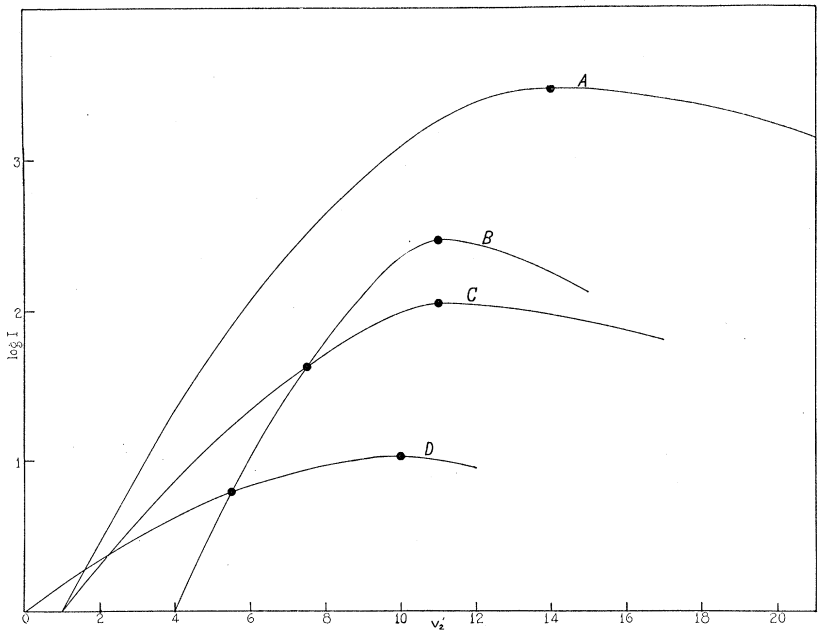

Fig. 3. Log I plotted against v_2'. A. Progression $(0, v_2') \leftarrow (0, 0, 0)$; B. Progression $(0, v_2') \leftarrow (0, 0, 1)$; C. Progression $(1, v_2') \leftarrow (0, 0, 0)$; D. Progression $(1, v_2') \leftarrow (0, 0, 1)$.

as mentioned above. The intersections marked by the dots have been determined by comparing the intensities of the bands of the two progressions. The The curves are terminated at the last observed band. The intensities are probably not small in this region but observation of the bands is difficult because of the diffuseness due to predissociation. The figure is somewhat more than a qualitative representation of the intensities, and does represent the general trend of intensities in the bands.

Large changes in the vibrational quantum number associated with the 719.34 cm^{-1} vibration have been observed and only small changes in that associated with the 304.8 cm^{-1} vibration while the third frequency has not been observed. The most intense bands of the $(0, v_2') \leftarrow (0, 0, 0)$ and $(1, v_2') \leftarrow (0, 0, 0)$ progressions are those to the levels with $v_2' = 14$ and 11. (This is using the final assignment of quantum numbers which has been done throughout this paper.) The Franck-Condon[10] principle should be applicable to polyatomic molecular spectra and enables us to make a choice between the two possible assignment of frequencies to the normal modes of vibrations of the excited state.

We consider the configuration I of Table VIII and Fig. 2 first. In the electronic transition from the normal state to the excited state, we assume with Condon that the dimensions of the molecule do not change. (The velocities are small in the normal state and thus need not be considered.) Superimposing the normal molecule (Fig. 2) on the excited molecule assuming configuration I, we see that the molecule should vibrate strongly with frequency 304.8 cm^{-1} thus leading us to expect large changes in the associated vibrational quantum number, in contradiction to observation. A large change in the equilibrium distance between Cl and O should cause large changes in the quantum number associated with the calculated 779.6 cm^{-1} frequency. Failure to observe this would be consistent with no change in this distance. The large change in the angle at the apex should not cause a large amplitude of oscillation of the 719.34 cm^{-1} frequency and thus small changes in the quantum number associated with this frequency should be observed again in contradiction to observation. Thus configuration I for the excited state appears to be impossible.

The configuration II for the excited state is consistent with the intensity distribution. Superposition of the normal molecule on this configuration II, shows that the frequency 719.34 should be strongly excited in agreement with observation. The frequency 382.1 (calc.) should be strongly excited if the equilibrium distance Cl-O changed markedly. That it is not observed indicates that this distance is not changed. The asymmetric vibration 304.8^{-1} should not be strongly excited again in agreement with observation. This qualitative agreement enables us to decide between configurations I and II and is, we believe, the first application of the Franck-Condon principle to polyatomic molecular spectra.

THE ASSIGNMENT OF QUANTUM NUMBERS

Thus far we have anticipated our final assignment of quantum numbers and we shall justify it at this point. The calculated structure of ClO_2 in the normal state requires that $\tilde{\nu}_1 = 857.7\ \text{cm}^{-1}$, $\tilde{\nu}_2 = 727.0\ \text{cm}^{-1}$ and $\tilde{\nu} = 528.8^{-1}$. From these calculations the assignment of quantum numbers in the normal state is $v_1'' = 1$ for the 857.7 cm^{-1} level, $v_2'' = 1$ for the 727.0 cm^{-1} level and $v_3'' = 1$ for the 528.8 cm^{-1} level. Since the 1471.3 cm^{-1} level is assumed to be a harmonic of the 727.0 cm^{-1} level it is designated by $v_2'' = 2$. Thus the assignment of quantum numbers in the normal state becomes

Level	v_1'', v_2'', v_3''
0. cm^{-1}	0, 0, 0
528.8 cm^{-1}	0, 0, 1

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[10] J. Franck, Trans. Faraday Soc. **21**, Part 3 (1925); E. U. Condon, Phys. Rev. **28**, 1182 (1926).

727.0 cm^{-1}	0,	1, 0
857.7 cm^{-1}	1,	0, 0
1471.3 cm^{-1}	0,	2, 0.

For the reasons given above v_1' is the quantum number associated with the 304.8 cm^{-1} frequency, v_2' with the 719.3 cm^{-1} frequency and v_3' with the calculated 382.1 cm^{-1} frequency. No transitions have been observed in which the 382.1 cm^{-1} frequency is involved and therefore we assume that v_3' is zero for all observed bands. We believe that the most intense progression has for its higher levels a set with $v_1'=0$ because we have been unable to find any evidence for levels with a smaller value of v_1', though we have found levels with v_1' one and two units larger.

In Eq. (4) we give the relation between the constants c' and a'' required by our experimental data. Our calculated values of c' and a'' taken from Table VII are -3.93 and -10.32 which make $c/2'-a/2''=+3.19$ instead of 7.23 required by our data, a difference of about 4 cm^{-1}. This may be partially accounted for on the assumption that the $\Delta\tilde{\nu}''$ of Eq. (2) may be too large as pointed out above. The isotope effects of the $\tilde{\nu}_1'$ and $\tilde{\nu}_2'$ frequencies have been estimated from the energy levels having large values of v_2'. Thus, we have calculated the configuration and frequencies of vibration and their isotope effects by using two frequencies for infinitesimal amplitudes of vibration and two isotope effects for large amplitudes of vibration. Thus even if the model were exact, some discrepancy between calculated and observed might be expected.

The difference between the calculated and observed values of $c/2'-a/2''$ could be eliminated by assuming that all bands having $v_2'=0$, as we have assigned the quantum numbers, do not belong to this band system and that the bands having $v_2'=1$ (our numbering) should be numbered as $v_2'=0$. However, we see no experimental reason for doing this and believe that the reason for the discrepancy lies in the approximate character of our calculations.

THE DISSOCIATION OF THE MOLECULE AND PREDISSOCIATION

From our assignment of frequencies to the normal modes of vibration, it is evident that the unsymmetric vibration of the excited state with $\tilde{\nu}_1'=304.8$ cm^{-1}, if the amplitude is large, will lead to dissociation into the ClO molecule and the O atom, either or both with energy of excitation. The formula (1) permits an extrapolation to dissociation though the value for the dissociation energy will probably be very approximate. This extrapolation gives 28968 cm^{-1} above the normal level of the molecule for this energy.

Goodeve and Stein observed predissociation from λ3293A, toward the ultraviolet. Our own plates indicate that the limit is about λ3595A, while Finkelnburg and Schumacher using highest dispersion have observed this limit as λ3753A. We believe their observation to be most reliable because of their higher resolving power.[11] Interpreting this in terms of our energy level

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[11] Dr. G. M. Murphy working in our laboratories has attempted to observe the resonance radiation of ClO_2 excited by the λ3660 lines of mercury with negative results as would be expected on the basis of Finkelnburg and Schumacher's value for the predissociation limit but not on the basis of either of the other values.

diagram we place the predissociation at 27162 cm^{-1} above the lowest level, which is as close to our value of 28968 cm^{-1} for dissociation as can be expected considering the likely errors in this extrapolation. The agreement shows that the predissociation limit *does* correspond to dissociation into ClO and O as has been assumed by the previous observers.

Goodeve and Stein[4] showed that there is a distinct break in the curve when the first differences of the progression $(0, v_2') \leftarrow (0, 0, 0)$ are plotted as ordinates against v_2' as abscissa. This is shown in Fig. 4 where we have plotted

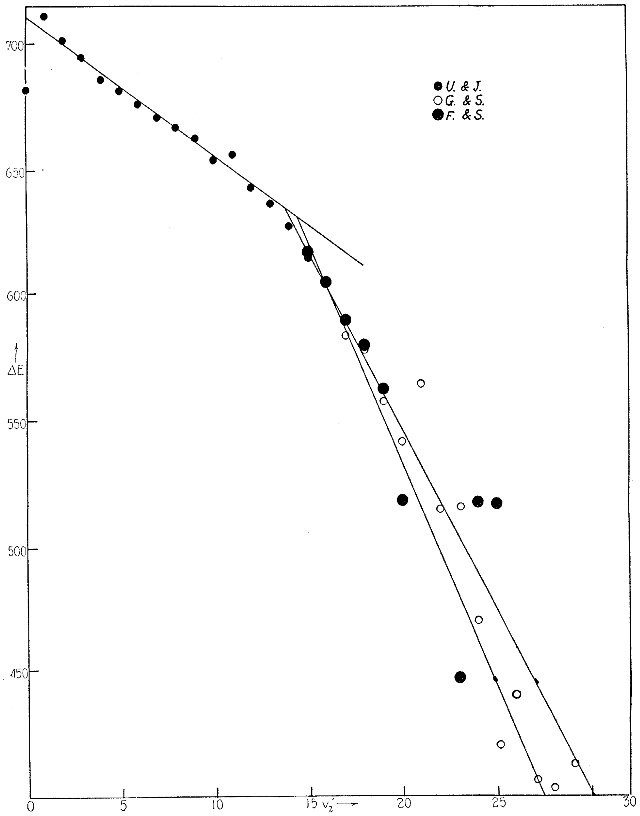

Fig. 4. Values of $E(v_2'+1)-E(v_2')$ plotted against v_2'.

our values up to $(v_2'=15)-(v_2'=14)$ difference and both Goodeve and Stein's and Finkelnburg and Schumacher's from that point on. The discontinuities in these differences is evident and the scattered character of the points from $v_2' = 15$ on shows that any formula fitting this part of the energy level diagram would be very doubtful and that any extrapolation to $\Delta E = 0$ would be doubtful using either set of data in this region of large values of v_2'. The extrapolated value of v_2' at dissociation might lie anywhere between about $v_2' = 59.11$ and $v_2' = 67.98$ and the energy of dissociation, assuming a straight line for the $\Delta E : v_2'$ curve from $v_2' = 15$ on and these two values of v_2', should lie between 48268.3 cm^{-1} and 51300.7 cm^{-1}. These wave numbers correspond to 137.1 and 145.7 cal. per mol., respectively. The scattered nature of the points, see Fig. 4, and the very doubtful extrapolation makes us feel that any energy of dissociation derived from such data and calculations is very doubtful except between very wide limits, perhaps even wider than those assumed in the above calculations.

Fig. 5 shows a plot of $\Delta E:v_2'$ in the region of small values of v_2' on a larger scale and including the points of all three sets of data. The straight line drawn through the data is that required by Eq. (1). It will be seen that our values follow a smoother curve than either of the other sets of data. Finkelnburg and Schumacher claim a higher precision for their work than we do and thus the greater irregularities which their data show may be real. Our values indicate that this curve is not a straight line but the precision of the data does not warrant a definite conclusion.

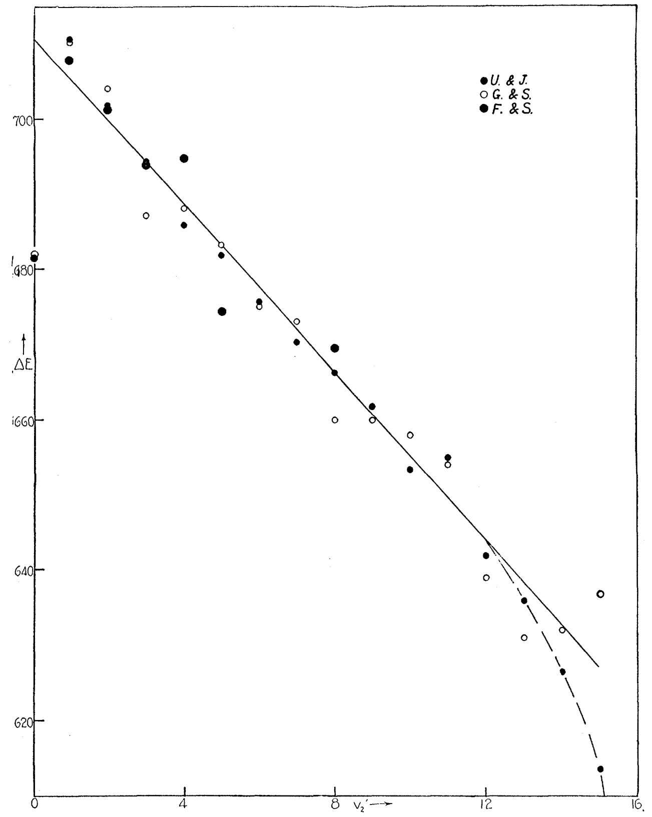

Fig. 5. Values of $E(v_2'+1)-E(v_2')$ plotted against v_2'.

The broken curve at the lower end of the figure shows the marked way in which the break in the curve occurs. The break in the curve at the left is very similar to the discontinuities in the SO$_2$, $\Delta E:v'$ curve as observed by Watson and Parker.[12] The curve with positive slope in the case of SO_2 extended over 3 or 4 differences whereas in ClO_2 it is apparent for only one difference, and therefore the discontinuity in this case may not be real.

THE CHARACTER OF THE HIGH AMPLITUDE VIBRATIONS

The half angle at the apex of the isoceles triangle in the excited state is nearly a normal coordinate of the molecule as can be seen from Fig. 2. The application of the Franck-Condon principle for the intensity distribution indicates that the oscillation using the classical model for the most intense band of any progression having the v_2' levels as higher levels, is between $\theta = 65°$, its value for the normal state, and something less than 18.5°. This most intense band appears to be that with $v_2' = 12$ approximately. It should not require much more energy in this mode of vibration to make the molecule oscillate between $\theta = 90°$ and some small angle. Such an oscillation would be an oscillation through the straight line position and would be similar to that of a straight line molecule.

The discontinuity in the plot ΔE against v_2 discovered by Goodeve and Stein and discussed above appears at $v_2' = 15$, just a few levels above the value of v_2' for the most intense band. Therefore it seems that the discontinuity in the $\Delta E{:}v_2'$ curve at $v_2' = 15$ may occur when the molecule first acquires sufficient energy to vibrate through the straight line position.

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[12] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).