

EMISSION SPECTRUM OF BISMUTH MONOCHLORIDE

Part I. The Vibrational Analysis of the 6170-4220 Å System*

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ABSTRACT

Bismuth chloride has been excited in flowing condition with an uncondensed transformer discharge. About 390 bands are observed in the present experiments of which only 140 were recorded by earlier workers. The vibrational constants obtained are the same as those obtained by Morgan from absorption experiments except for the addition of a cubic term for the upper state. It appears quite likely that the upper state of the system dissociates into Bi ($^4S_{3/2}$) + Cl ($^2P_{1/2}$) while the lower state, which is probably the ground state, dissociates into Bi ($^4S_{3/2}$) + Cl ($^2P_{3/2}$). The rough values of the dissociation energies obtained by extrapolations are $D_0' = 3750 \text{ cm.}^{-1}$ and $D_0'' = 24614 \text{ cm.}^{-1}$

INTRODUCTION

VISIBLE bands in the region 4300–5400 Å attributed to bismuth monochloride are well known from a long time back. Saper¹ excited the vapour of bismuth trichloride in active nitrogen and analysed the bands in the region 4300–5400 Å as emitted by the diatomic bismuth monochloride molecule. His analysis was confirmed by the observed isotopic shifts which tallied fairly well with those calculated from the BiCl molecule. Ghosh,² however, rephotographed the bands lying in the region 4300–6600 Å by feeding carbon arc with metallic bismuth or bismuth trichloride and attributed them to the BiO molecule. Morgan³ studied bismuth halides extensively by taking absorption spectrum of all of them. Halogens were passed over molten mass of bismuth which was placed inside the furnace heated up to 900–1400° C. He obtained all the systems also by placing different bismuth halides inside the furnace. Two systems one in the region 5400–4300 Å and the other lying in the region 4000–3600 Å were obtained in the bismuth monochloride

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molecule. He observed the isotopic shifts of the right magnitude for the band heads of BiCl and BiBr molecules. The presence of the isotopic shifts as well as the presence of analogous systems in all the halides led him to conclude that these bands are due to bismuth halides.

Ray⁴ further studied the spectrum of bismuth monochloride in absorption and also in emission by feeding carbon arc with bismuth trichloride. He confirmed the formula proposed by Morgan³ for the less refrangible system and showed that the emitter of the system is BiCl molecule.

However, in the experiments of all the workers mentioned above, there was a possibility of the presence of different impurities as the experiments were conducted in the open atmosphere. Therefore, it was felt necessary to obtain these bands using a discharge tube avoiding the presence of atmospheric gases and thus to give a better experimental proof for them. As no rotational structure was observed and analysed so far for this molecule, it was expected that such a work will help us to determine the rotational constants and the electronic transitions involved. Further it was also expected that the transformer discharge might give larger number of new bands which might help us to extend and improve the vibrational analysis.

The experiments performed were found to be quite successful to develop the system 6170–4220 Å extensively and the present paper deals with the vibrational analysis of the bands so developed. The rotational analysis of some of these bands will be discussed in the next paper.

EXPERIMENTAL DETAILS

The discharge tube, having cylindrical nickel electrodes placed coaxially along its length, was 0.8 cm. in diameter and 40 cm. in length. It was continuously pumped out from one end through a stopcock whereas at the other end a side tube containing bismuth trichloride was attached. Since BiCl₃ is hygroscopic, it was dehydrated completely before starting the experiment.

The vapour was excited by an uncondensed transformer discharge applying 15 K.V. with a Hilger $\frac{1}{4}$ K.W. power transformer. The discharge tube near the electrodes as well as the side tubes containing the sample were heated continuously by a Bunsen burner so as to maintain a sufficient high pressure of the vapour. The samples obtained from two different sources, *i.e.*, B.D.H. and E. Merck were tried. The colour of the discharge was intense greenish-blue. Only one system lying in the region 6170–4220 Å was obtained. The other system, that was obtained by the earlier workers on the shorter wavelength side of this system, was not excited in the present experiments.

The spectrum was first taken on a Zeiss three-prism glass spectrograph having a dispersion of 11.4 Å/mm. at 4800 Å and then on the first and second

TABLE I

*Wavelengths, wavenumbers and relative intensities of the band system
6170–4220 Å of BiCl*

λ_{air}	I	$\nu_{\text{vac.}}$	λ_{air}	I	$\nu_{\text{vac.}}$
6173.4	2	16194	43.3	2	17109
6093.6	2	16406	39.8	4	17119
88.4	2	16420	35.1	2	17133
79.2	2	16445	30.6	1	17146
69.2	1	16472	26.6	0	17158
65.9	1	16481	21.5	1	17173
57.8	1	16503	12.7	4	17199
51.6	0	16520	11.3	6	17203
45.7	1	16536	05.3	2	17221
10.5	0	16633	5799.8	2	17237
02.2	2	16656	95.5	1	17250
5997.5	1	16669	91.1	1	17263
94.3	3	16678	84.8	1	17282
89.2	1	16692	79.1	4	17299
73.5	2	16736	75.1	2	17311
69.6	2	16747	66.4	1	17337
67.4	2	16753	59.8	1	17357
63.2	3	16765	55.1	1	17371
58.9	1	16777	50.2	4	17386
55.3	1	16787	46.9	1	17396
49.3	1	16804	5736.6	2	17427
43.0	1	16822	32.0	1	17441
38.4	1	16835	23.8	1	17466
35.2	1	16844	19.5	5	17479
30.6	3	16857	08.5	1	17513
25.0	1	16873	02.6	1	17531
20.1	1	16887	5695.4	3	17553
15.9	1	16899	90.6	5	17568
5908.9	3	16919	89.0	3	17573
01.6	5	16940	69.3	2	17634
5893.2	1	16964	61.6†	5	17658
83.1	2	16993	48.8	1	17698
76.2	0	17013	37.6	?	17733
71.4	2	17027	33.2†	6	17747
69.3	4	17033	20.5	?	17787
64.5	2	17047	05.1†	6	17836
55.6	1	17073	5599.7	1	17856
46.0	2	17101	95.7	1	17866 _p

TABLE I (Contd.)

λ_{air}	I	$\nu_{\text{vac.}}$	λ_{air}	I	$\nu_{\text{vac.}}$
81.3	2	17912 _g	5346.8	0	18698 _g
79.1†	?	17919 _g	45.0†	3	18704 _g
76.0†	6	17929 _g	35.8	2	18736 _g
72.6	0	17940 _g	31.0*	4	18753 _g
64.5	2	17966 _g	26.5	1	18679
57.1	0	17990	12.6†	1	18818 _v
51.2	1	18009 _g	08.9	2	18831 _g
48.2†	5	18019 _g	07.2*	5	18837 _g
36.5	1	18057 _g	03.8†	2	18849 _g
32.5	1	18070	5298.8	1	18867 _g
27.6	1	18086 _g	89.3†	2	18901
21.5†	6	18106 _g	84.8*	4	18917 _g
12.1	2	18137 _g	76.4*	2	18947 _g
5509.4	0	18146 _g	66.4†	1	18983 _g
00.5	1	18175 _g	63.3*	2	18994 _g
5496.0†	4	18190 _g	51.5*	4	19037 _g
92.1†	2	18203 _g	46.0	0	19057 _g
87.9	0	18217	42.7	1	19069 _g
82.1	1	18236 _g	34.1	1	19100
71.3†	4	18272 _g	32.5	1	19106 _g
68.9	0	18280 _g	28.1*	5	19122 _g
67.7	0	18284 _g	14.7	?	19171 _g
65.1	2	18293 _g	12.3†	1	19180
64.2†	5	18296 _g	05.8*	3	19204 _g
52.8	1	18334 _g	01.7	3	19219 _g
49.0†	2	18347 _g	5198.0	2	19233
43.6	2	18365 _g	90.7*	2	19260
37.7†	6	18385 _g	86.7	2	19275 _g
27.1	1	18421 _g	83.9*	4	19285 _g
19.4	2	18447 _g	79.1	2	19303 _g
15.6	2	18460 _g	75.3*	3	19317 _g
12.7†	4	18470 _g	5169.2†	1	19340
09.5	2	18481 _g	64.1*	2	19359
06.8	1	18524 _g	59.9	2	19375
5397.0	?	18490 _g	50.8*	4	19409 _g
91.2	2	18544 _g	49.2	1	19415 _g
88.5*	3	18553 _g	47.6	0	19421 _g
82.4†	2	18574 _g	40.0	2	19450 _g
75.1	1	18599 _g	36.5†	0	19463 _g
71.8	1	18611 _g	28.4*	6	19494 _g
69.1	1	18620 _g	24.2	2	19510 _g
67.4	2	18626 _g	20.7†	0	19523
65.6†	2	18632	15.0*	4	19545 _g
61.6	0	18646 _g	09.2	1	19567 _g
56.1†	4	18665 _g	07.4*	8	19574 _g

TABLE I (Contd.)

λ_{air}	I	$\nu_{vac.}$	λ_{air}	I	$\nu_{vac.}$
5098.2†	1	19609	66.5*	8	20543 _s
94.6†	2	19623	63.4	1	20556 _s
91.3	2	19636	60.1*	2	20570 _s
87.1*	4	19652	59.4	2	20573 _s
74.7*	1	19700	58.7*	2	20576 _s
68.8	1	19723	56.3	1	20586
53.7*	3	19782	52.5†	1	20602
48.8*	2	19801	43.1	1	20642
41.5†	1	19830	37.3*	3	20667 _s
36.9	0	19848	34.5	1	20679 _s
32.3*	7	19866	33.3	0	20684 _s
27.7	1	19884	31.2†	1	20693
24.7*	2	19896	29.1	0	20702
21.2*	3	19910 _s	27.0	1	20711
15.2	1	19934 _s	17.9	2	20750
11.6*	5	19948 _s	15.6†	1	20760
5008.4	1	19961	12.8	1	20772
01.1*	3	19990 _s	10.7†	1	20781
4991.9	1	20027	07.0	1	20797
81.9	2	20067	03.3	1	20813
79.7†	1	20076	4796.2*	10	20844 _s
76.7*	2	20088	92.8	2	20859 _s
70.8	0	20112	91.1*	3	20866 _s
69.0†	1	20119 _s	89.8	1	20872 _s
66.6†	1	20129	86.4	2	20887 _s
58.2*	4	20163 _s	84.5†	0	20895 _s
55.0	1	20176	79.0	0	20919
51.3*	2	20191 _s	77.0	1	20928
49.4†	1	20199 _s	71.0	0	20954
46.4	0	20211	4767.4*	4	20970 _s
42.5	1	20227 _s	63.8	2	20986 _s
38.1*	10	20245 _s	59.9†	2	21003 _s
30.8	1	20275 _s	55.8	2	21021 _s
29.6*	3	20280 _s	49.7	1	21048
28.1*	1	20286	47.5*	3	21058
21.1	1	20315 _s	43.2*	2	21077 _s
11.7	0	20354	36.9	1	21105 _s
07.1†	1	20373	33.1	2	21122
01.1	1	20398	30.6	1	21133
4899.4†	0	20405	27.5*	5	21147 _s
94.1	0	20427	25.9	?	21154 _s
91.5	0	20438	24.1*	2	21162 _s
86.9†	4	20457 _s	21.7	1	12173 _s
81.2†	1	20481	16.1	1	21198 _s
4872.9†	0	20516	14.1	1	21207

TABLE I (Contd.)

λ_{air}	I	$\nu_{\text{vac.}}$	λ_{air}	I	$\nu_{\text{vac.}}$
11.0	1	21221 _g	81.4	0	21821
09.0	1	21230	79.6	2	21830
07.0	1	21239	75.6	0	21849
03.2	0	21256	4574.1	0	21856
00.1†	3	21270 _g	72.4	2	21864
4697.9†	1	21280	69.7*	6	21877 _g
96.0	1	21289	68.3	2	21884
93.7	0	21299	58.1	1	21933 _g
85.8	0	21335 _g	55.4	2	21946 _g
83.8	1	21344 _g	49.8*	5	21973 _g
79.9*	7	21362 _g	48.9	2	21977 _g
77.7*	2	21372	46.0	1	21991
75.5	1	21382	44.1	2	22000
73.3	1	21392 _g	42.3	0	22009
70.1	1	21407	40.0	1	22020
67.9	0	21417 _g	38.2	1	22029 _g
4666.1	1	21425 _g	34.5	2	22047
64.2	0	21434 _g	32.9†	3	22055
60.5*	4	21451 _g	30.6	0	22066
59.0*	2	21458	28.3*	0	22077
57.0	2	21467	27.5*	1	22081
55.1*	3	21476 _g	21.6	1	22110
53.3	1	21484	19.1	1	22122
51.2	1	21494	16.5	1	22135
47.7	1	21510	14.0	1	22147
43.2	0	21531	12.4	1	22155
40.6	1	21543	10.8	2	22163
37.8	1	21556 _g	08.7*	3	22173
35.4	2	21567	06.9*	6	22182
34.3*	3	21572 _g	4496.8	1	22232
32.6*	1	21580	94.5†	2	22243
31.6	2	21585	90.2	2	22265
29.8	0	21593	87.5†	1	22278
25.3	2	21614 _g	85.9	1	22286
20.0	0	21639	84.1	1	22295
14.2*	6	21666 _g	80.4	0	22313
13.0*	2	21672	72.8	0	22351
08.9	0	21691 _g	71.2†	1	22359
06.6	1	21702 _g	68.2*	2	22374
02.8	0	21720	65.6*	6	22387
4597.0	1	21747 _g	60.8	1	22411
94.9*	2	21757 _g	59.0†	2	22420
92.4	1	21769	56.5	1	22433
90.7†	2	21777	53.1	0	22450
82.3	1	21817 _g	51.5	0	22458

TABLE I (Contd.)

λ_{air}	I	$\nu_{\text{vac.}}$	λ_{air}	I	$\nu_{\text{vac.}}$
47.7*	3	22477	67.5*	1	22890
36.5	1	22534	64.2*	1	22907
34.7	2	22543	58.5	2	22937
32.4†	1	22555	56.6*	1	22947
29.0*	2	22572	52.2*	2	22970
27.9	1	22578	46.0*	0	23003
25.9*	5	22588	40.8*	1	23031
23.9†	1	22598	38.1	0	23045
23.0	2	22603	36.8	1	23052
21.0	1	22613	34.2	0	23066
14.6†	0	22646	32.1†	0	23077
12.4	1	22657	20.5	0	23139
11.0*	2	22664	17.3*	0	23156
03.5*	0	22703	15.1	0	23168
01.3	0	22714	10.6	0	23192
4399.6*	2	22723	08.0†	2	23206
96.7	0	22738	4285.3	0	23329
94.0	0	22752	80.5	2	23355
92.6*	2	22759	79.3	0	23362
88.0*	2	22783	57.8	0	23480
4380.5	1	22822	51.8‡	2	23513
78.6*	0	22833	23.9	2	23668
75.3*	2	22849			

Note.—The bands marked with a suffix *g* are obtained from the plates taken in the first order of the 21-foot grating spectrograph. Others are obtained from the plates taken on the three-prism spectrograph.

The bands marked † are obtained also earlier by Ray and those marked by an asterisk mark are obtained by Ray as well as by Morgan. The band marked ‡ has also been recorded earlier by Morgan.

orders of a 21-foot grating spectrograph with a dispersion of 2.5 Å/mm. and 1.25 Å/mm. respectively. One to two hours' exposures were needed to record the spectrum on the three-prism glass spectrograph, whereas six hours were needed in the case of the 21-foot grating spectrograph. Measurements of the plates taken were carried out with a Zeiss Abbe Comparator.

VIBRATIONAL ANALYSIS

The wavelengths, wavenumbers and their visually estimated relative intensities of the band heads are given in Table I. The wavelengths of the intense bands are from plates taken on the I order of the 21-foot grating spectrograph while the others are obtained from the plates taken on the three-prism glass spectrograph. All the bands are clearly degraded to longer

wavelengths. The errors involved in the band heads may vary from $\pm 1 \text{ cm.}^{-1}$ for the bands recorded on the grating spectrograph to $\pm 3 \text{ cm.}^{-1}$ for the others. The agreement, between the measurements of all the bands observed in absorption and emission by the previous workers and those measured in the present experiment, shows clearly that the present system is the same as that observed by Morgan in absorption. The Deslandres scheme for the band system in the region 6170–4220 Å corresponding to the more abundant molecule BiCl^{35} is given in Table II. All the bands could be fairly well represented within $\pm 4 \text{ cm.}^{-1}$ by the formula

$$\nu = 21757 + (217.8 v' - 2.5 v'^2 - 0.02 v'^3) - (307.4 v'' - 0.96 v''^2)$$

in which the same constants are being used as reported by Morgan and Ray except that a negative cubic term has been added for the upper state.

ISOTOPIC SHIFTS

As the natural abundance ratio of Cl^{37} and Cl^{35} is 1:3, we expect two isotopic band heads of BiCl molecule namely, of BiCl^{35} and BiCl^{37} which will be having the intensity ratio of 3:1 respectively. The band heads which can be represented as isotopic components are listed in Table III, where the corresponding observed and calculated isotopic shifts are also included for comparison. Some of the bands which have been listed in Table III as belonging to BiCl^{37} can also be represented as belonging to BiCl^{35} with different v' , v'' values and are, therefore, also shown as such in Tables II and III.

The agreement between the observed and calculated isotopic shifts from the present experiments as well as that observed in absorption by Morgan and Ray indicate clearly that this band system can, most probably, be attributed to the BiCl molecule.

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The present band system occurs in absorption as well as in emission. The very fact that the system has been observed in absorption shows that the lower state of the system is, most probably, the ground state of the BiCl molecule dissociating into $\text{Bi} (^4S_{3/2}) + \text{Cl} (^2P_{3/2})$ atoms which are the ground states of bismuth and chlorine atoms respectively. The dissociation energies of the upper and the lower states of the system cannot be determined accurately as the convergence limit of the system is not known. However, the linear extrapolation gives a value of $D_0 = 24614 \text{ cm.}^{-1}$ for the lower state of the system which, as mentioned above, is probably the ground state

TABLE III

The probable isotopic shifts for the 6170-4220 Å system of BiCl

v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}	v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}
9, 24	16787	1	109	1, 13	18217	0	80
	16678	3	(111)		18137	2	(81)
11, 25	16844	1	108	7, 17	18284	0	81
	16736	2	(112)		18203	2	(80)
8, 23	16873	1	108	2, 13	18421	1	74
	16765	3	(109)		18347	2	(76)
7, 22	16964	1	107	5, 15	18460	2	75
	16857	3	(107)		18385	6	(76)
9, 23	17047	2	107	10, 18	18524	1	77
	16940	5	(106)		18447	2	(77)
2, 18	17073	1	105	4, 14	18544	2	74
	16964	1	(105)		18470	4	(74)
8, 22	17133	2	106	3, 13	18620	1	67
	17027	2	(104)		18553	3	(72)
15, 26	17158	0	111	6, 15	18646	0	72
	17047	2	(112)		18574	2	(72)
7, 21	17221	2	102	17, 21	18698	0	87
	17119	4	(102)		18611	1	(86)
12, 24	17250	1	104	5, 14	18736	2	71
	17146	1	(105)		18665	4	(70)
2, 17	17337	1	100	1, 11	18769	1	65
	17237	2	(99)		18704	3	(69)
8, 21	17396	1	97	4, 13	18818	1	65
	17299	4	(99)		18753	4	(68)
6, 19	17573	3	94	3, 12	18901	2	64
	17479	5	(94)		18837	5	(66)
1, 14	17940	0	84	2, 11	18983	1	66
	17856	1	(87)		18917	4	(64)
11, 20	18146	0	89	1, 10	19057	0	63
	18057	1	(86)		18994	2	(63)

TABLE III (Contd.)

ν', ν''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.	ν', ν''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}
4, 12	19100 19037	1 4	63 (62)	1, 7	19910 19866	3 7	44 (44)
9, 15	19171 19106	? 1	65 (63)	4, 9	19934 19896	1 2	38 (43)
3, 11	19180 19122	1 5	58 (60)	0, 6	19990 19948	3 5	42 (42)
2, 10	19260 19204	2 3	56 (58)	3, 8	20027 19990	1 3	37 (41)
8, 14	19275 19219	2 3	56 (60)	2, 7	20112 20076	0 1	36 (39)
1, 9	19340 19285	1 4	55 (56)	2, 9	20129 20088	1 2	41 (40)
4, 11	19375 19317	2 3	58 (56)	1, 6	20199 20163	1 4	36 (37)
0, 8	19415 19359	1 2	56 (55)	7, 10	20211 20176	0 1	35 (39)
3, 10	19463 19409	0 4	54 (54)	4, 8	20227 20191	1 2	36 (37)
2, 9	19545 19494	4 6	51 (52)	0, 5	20280 20245	3 10	35 (35)
5, 11	19567 19510	1 2	57 (52)	3, 7	20315 20280	1 3	35 (35)
1, 8	19623 19574	2 8	49 (50)	2, 6	20405 20373	0 1	32 (33)
0, 7	19700 19652	1 4	48 (49)	10, 11	20438 20398	0 1	40 (37)
2, 8	19830 19782	1 3	48 (45)	4, 7	20516 20481	0 1	35 (31)
5, 10	19848 19801	0 2	47 (46)	0, 4	20573 20543	2 8	30 (29)

TABLE III (Contd.)

v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}	v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}
11, 11	20586	1	30	0, 2	21162	2	15
	20556	1	(35)		21147	5	(15)
6, 8	20602	1	32	18, 12	21230	1	32
	20570	2	(30)		21198	1	(36)
2, 5	20693	1	26	8, 7	21239	1	18
	20667	3	(26)		21221	1	(17)
5, 7	20702	0	23	2, 3	21280	1	10
	20679	1	(27)		21270	3	(12)
7, 8	20772	1	22	5, 5	21280	1	10
	20750	2	(26)		21270	3	(14)
1, 4	20781	1	21	19, 12	21335	0	36
	20760	1	(24)		21299	0	(37)
4, 6	20797	1	25	1, 2	21372	2	10
	20772	1	(24)		21362	7	(10)
0, 3	20866	3	22	4, 4	21382	1	10
	20844	10	(22)		21372	2	(11)
6, 7	20887	2	21	9, 7	21407	1	15
	20866	3	(23)		21392	1	(14)
3, 5	20895	0	23	0, 1	21458	2	7
	20872	1	(22)		21451	4	(8)
8, 8	20954	0	26	6, 5	21467	2	9
	20928	1	(23)		21458	2	(10)
2, 4	20986	2	16	3, 3	21484	1	8
	20970	4	(19)		21476	3	(6)
5, 6	20986	2	16	18, 11	21510	1	26
	20970	4	(20)		21484	1	(26)
1, 3	21077	2	19	21, 21	21531	0	37
	21058	3	(17)		21494	1	(39)
11, 9	21154	?	21	2, 2	21580	1	8
	21133	1	(22)		21572	3	(6)

TABLE III (Contd.)

v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}	v', v''	ν in cm.^{-1}	I	$\Delta\nu$ in cm.^{-1}
	21572	3	(18)		22387	6	(13)
19, 11	21614	2	29	4, 0	22572	2	16
	21585	2	(31)		22588	5	(17)
8, 5	21821	0	4	9, 3	22572	2	16
	21817	1	(4)		22588	5	(13)
16, 9	21849	0	19	13, 5	22598	1	5
	21830	2	(17)		22603	2	(7)
12, 7	21884	2	7	6, 1	22646	0	18
	21877	6	(8)		22664	2	(17)
15, 8	22009	0	9	8, 2	22703	0	20
	22000	2	(11)		22723	2	(17)
13, 7	22029	1	9	10, 3	22738	0	14
	22020	1	(7)		22752	0	(15)
6, 3	22047	2	8	5, 0	22759	2	24
	22055	3	(8)		22783	2	(21)
3, 1	22077	0	4	7, 1	22822	1	27
	22081	1	(6)		22849	2	(21)
16, 8	22135	1	13	6, 0	22947	1	23
	22122	1	(11)		22970	2	(24)
2, 0	22173	3	9	10, 2	23031	1	21
	22182	6	(8)		23052	1	(22)
7, 3	22232	1	11	9, 1	23168	0	24
	22243	2	(7)		23192	0	(26)
15, 7	22286	1	9	10, 1	23329	0	26
	22295	1	(5)		23355	2	(29)
6, 2	22351	0	8	11, 1	23480	0	33
	22359	1	(10)		23513	2	(31)

Note.—In the last column of the table under the heading $\Delta\nu$, the values given in brackets represent the calculated $\Delta\nu$ values and the others the observed $\Delta\nu$ values.

of the molecule. The present analysis of the band system gives a cubic term for the upper state which involves observed levels up to about $v' = 20$. The extrapolation involving the cubic term leads to a dissociation energy of $D_0' = 3750 \text{ cm.}^{-1}$ for the upper state which will then dissociate at 25507 cm.^{-1} . One cannot attach much accuracy to these dissociation limits of the upper and lower states as these were obtained after fairly large extrapolations. However, it is to be noted that the difference between the two extrapolated dissociation limits 25507 cm.^{-1} and 24614 cm.^{-1} comes out to be 893 cm.^{-1} which is quite close to the normal doublet separation of 881 cm.^{-1} for the chlorine atom. Therefore, it appears quite likely that the dissociation limit of the upper state is not the same as that of the ground state but probably the next higher one with $\text{Bi } ({}^4\text{S}_{3/2}) + \text{Cl } ({}^2\text{P}_{1/2})$ atoms as the dissociation products. The next higher dissociation limit corresponding to $\text{Bi } ({}^2\text{D}_{3/2}) + \text{Cl } ({}^2\text{P}_{3/2})$ is expected to be at about 35910 cm.^{-1} which is too high for the present upper state to dissociate into.

The reasons for taking $\text{Bi } ({}^4\text{S}_{3/2}) + \text{Cl } ({}^2\text{P}_{1/2})$ as the dissociation products for the upper state are the following:

The present analysis shows the position of the level with $v' = 18$ at 24855 cm.^{-1} which has $\Delta G \simeq 104.8 \text{ cm.}^{-1}$ whereas the dissociation limit by linear extrapolation for the lower state is at 24614 cm.^{-1} . This value probably represents the maximum limit for D_0'' as the linear extrapolation for a non-ionic state is supposed to give a D_0 value higher than the actual one. If, however, the upper state is to dissociate at 24614 cm.^{-1} a cubic term with a coefficient of about 0.07 has to be introduced whereas the analysis does not warrant such a high coefficient. Further it will be difficult to explain the observed isotopic shifts if another alternative analysis is chosen such that the upper state dissociates at 24614 cm.^{-1} .

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REFERENCES

1. Saper .. *Phys. Rev.*, 1931, **37**, 1710.
2. Ghosh .. *Zeits. f. physik*, 1933, **86**, 241.
3. Morgan .. *Phys. Rev.*, 1936, **49**, 41.
4. Ray, S. K. .. *Ind. Jour. Phys.*, 1942, **16**, 35-48.