

# EMISSION SPECTRUM OF BISMUTH MONOCHLORIDE

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

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Received May 29, 1959

### 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. Saper<sup>1</sup> 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,<sup>2</sup> 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. Morgan<sup>3</sup> 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

\* This forms part of the Ph.D. thesis submitted by B. N. K. to M.U., Aligarh.

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.

Ray<sup>4</sup> 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 Morgan<sup>3</sup> 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 BiCl<sub>3</sub> 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*

$\lambda_{\text{air}}$	I	$\nu_{\text{vac.}}$	$\lambda_{\text{air}}$	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,

TABLE I (Contd.)

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

TABLE I (Contd.)

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

TABLE I (Contd.)

$\lambda_{\text{air}}$	I	$\nu_{\text{vac.}}$	$\lambda_{\text{air}}$	I	$\nu_{\text{vac.}}$
11.0	1	21221 <sub>g</sub>	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 <sub>g</sub>	72.4	2	21864
4697.9†	1	21280	69.7*	6	21877 <sub>g</sub>
96.0	1	21289	68.3	2	21884
93.7	0	21299	58.1	1	21933 <sub>g</sub>
85.8	0	21335 <sub>g</sub>	55.4	2	21946 <sub>g</sub>
83.8	1	21344 <sub>g</sub>	49.8*	5	21973 <sub>g</sub>
79.9*	7	21362 <sub>g</sub>	48.9	2	21977 <sub>g</sub>
77.7*	2	21372	46.0	1	21991
75.5	1	21382	44.1	2	22000
73.3	1	21392 <sub>g</sub>	42.3	0	22009
70.1	1	21407	40.0	1	22020
67.9	0	21417 <sub>g</sub>	38.2	1	22029 <sub>g</sub>
4666.1	1	21425 <sub>g</sub>	34.5	2	22047
64.2	0	21434 <sub>g</sub>	32.9†	3	22055
60.5*	4	21451 <sub>g</sub>	30.6	0	22066
59.0*	2	21458	28.3*	0	22077
57.0	2	21467	27.5*	1	22081
55.1*	3	21476 <sub>g</sub>	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 <sub>g</sub>	08.7*	3	22173
35.4	2	21567	06.9*	6	22182
34.3*	3	21572 <sub>g</sub>	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 <sub>g</sub>	85.9	1	22286
20.0	0	21639	84.1	1	22295
14.2*	6	21666 <sub>g</sub>	80.4	0	22313
13.0*	2	21672	72.8	0	22351
08.9	0	21691 <sub>g</sub>	71.2†	1	22359
06.6	1	21702 <sub>g</sub>	68.2*	2	22374
02.8	0	21720	65.6*	6	22387
4597.0	1	21747 <sub>g</sub>	60.8	1	22411
94.9*	2	21757 <sub>g</sub>	59.0†	2	22420
92.4	1	21769	56.5	1	22433
90.7†	2	21777	53.1	0	22450
82.3	1	21817 <sub>g</sub>	51.5	0	22458

TABLE I (Contd.)

$\lambda_{\text{air}}$	I	$\nu_{\text{vac.}}$	$\lambda_{\text{air}}$	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  $\text{BiCl}^{35}$  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  $\text{Cl}^{37}$  and  $\text{Cl}^{35}$  is 1:3, we expect two isotopic band heads of  $\text{BiCl}$  molecule namely, of  $\text{BiCl}^{35}$  and  $\text{BiCl}^{37}$  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  $\text{BiCl}^{37}$  can also be represented as belonging to  $\text{BiCl}^{35}$  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  $\text{BiCl}$  molecule.

#### THE DISSOCIATION PRODUCTS AND THE DISSOCIATION ENERGIES OF THE STATES INVOLVED

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  $\text{BiCl}$  molecule dissociating into  $\text{Bi} (^4\text{S}_{3/2}) + \text{Cl} (^2\text{P}_{3/2})$  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*

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

TABLE III (Contd.)

$\nu', \nu''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}$	$\nu', \nu''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}^{-1}$
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.)

$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}^{-1}$	$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}^{-1}$
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.)

$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}^{-1}$	$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu$ in $\text{cm.}^{-1}$
14, 9	21593	0	21	3, 0	22374	2	13
	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  $25507 \text{ cm.}^{-1}$ . 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  $25507 \text{ cm.}^{-1}$  and  $24614 \text{ cm.}^{-1}$  comes out to be  $893 \text{ cm.}^{-1}$  which is quite close to the normal doublet separation of  $881 \text{ cm.}^{-1}$  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  $35910 \text{ cm.}^{-1}$  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  $24855 \text{ cm.}^{-1}$  which has  $\Delta G \simeq 104.8 \text{ cm.}^{-1}$  whereas the dissociation limit by linear extrapolation for the lower state is at  $24614 \text{ cm.}^{-1}$ . 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  $24614 \text{ cm.}^{-1}$  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  $24614 \text{ cm.}^{-1}$ .

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to the Council of Scientific and Industrial Research for the sanction of a research scheme.

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