The Absorption Spectrum of Isotopic Diatomic Antimony (^{123}Sb-^{123}Sb). Analysis of the D ← X System in the 2860—2920 Å Region

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A rotational analysis of several bands of the D ← X system of ^{123}Sb – ^{123}Sb is carried out. It is shown that the hitherto assumed vibrational classification of the D ← X system is certainly incorrect, as well as a previously given value for the rotational constant of the X state. $B(X\,^1\Sigma_g^+, v=0)$ is found equal to 0.044263 cm^{-1}. The perturbations appearing in the various vibrational levels are interpreted in terms of interactions with a new electronic state, labelled L.

Introduction

The first work on diatomic antimony, in the spectral range 2800 – 3350 Å, was carried out by Genard[1] and Siksna[2], who studied the fluorescence of this molecule and recorded several resonance series. Nakamura and Shidei[3] examined later the absorption bands lying in this same region, and classified them at low resolution in a single system. Moreover, they calculated the vibrational constants of the fundamental and excited states involved in the transition. On the other hand, this same absorption spectrum has been studied by Naudé[4, 5]. His classification and assignment of the quantum numbers v' and v'' differ from those suggested by earlier authors, and take into account the isotopic effect due to the presence of both antimony isotopes. His work proved that the system usually referred to as D ← X, in which the bands are degraded towards longer wavelengths, is considerably perturbed.

The natural antimony has two isotopes: ^{121}Sb (57%) and ^{123}Sb (43%). Therefore its diatomic structure consists of three molecular types: (^{121}Sb – ^{121}Sb), (^{121}Sb – ^{123}Sb), and (^{123}Sb – ^{123}Sb). The great complexity of the spectra combined with their considerable perturbations suggested us the construction of an absorption cell containing isotopic antimony with a ^{123}Sb proportion of 96%. Thus, it has been possible to record at very high resolution, in the spectral region 2800 – 3350 Å, the absorption spectrum of the corresponding diatomic molecule ^{123}Sb – ^{123}Sb. We analysed the rotational structure of seven bands of the D ← X system, corresponding to the 2860 – 2920 Å range. The perturbations observed in these bands have been also investigated. We finally determined the rotational constants of all the levels involved, together with the interaction parameters, and proved these perturbations to be due to an hitherto unknown electronic state.

Apparatus

The experimental set-up used, as well as the method of preparing the absorption tube, have been described in an earlier paper[6]. Antimony was placed in a double-walled fused silica cell, whose internal tube was connected to a side-arm. Both tubes were heated to a high temperature by means of two independent cylindrical furnaces; one of them surrounded the main cell, and the other the side-arm. The space between the two walls was evacuated by the spectrograph pumping system. The latter furnace allowed to alter the vapour pressure. Whereas modification of the temperature in the main furnace results in variation of the proportion of diatomic molecules formed by dissociation of antimony tetramers.

The background radiation was supplied by a 900-W Xenon high pressure lamp. Pictures were recorded by means of the 4-m vacuum spectrograph of the University College London[7]. Using Spectrum Analysis n° 1 films, exposure times of a few minutes were sufficient. The best spectra were obtained by heating the absorption tube to approximately 940 °C and the side-arm to about 650 °C. With a slit of 20 μm the resolution attained is better than 400 000 in the 20th order, the mean reciprocal dispersion being 0.16 Å/mm (Figure 1). An iron hollow-cathode lamp, filled with Neon, was used to calibrate the spectra. The maximum error on the measured wavenumbers is about 0.02cm^{-1}.

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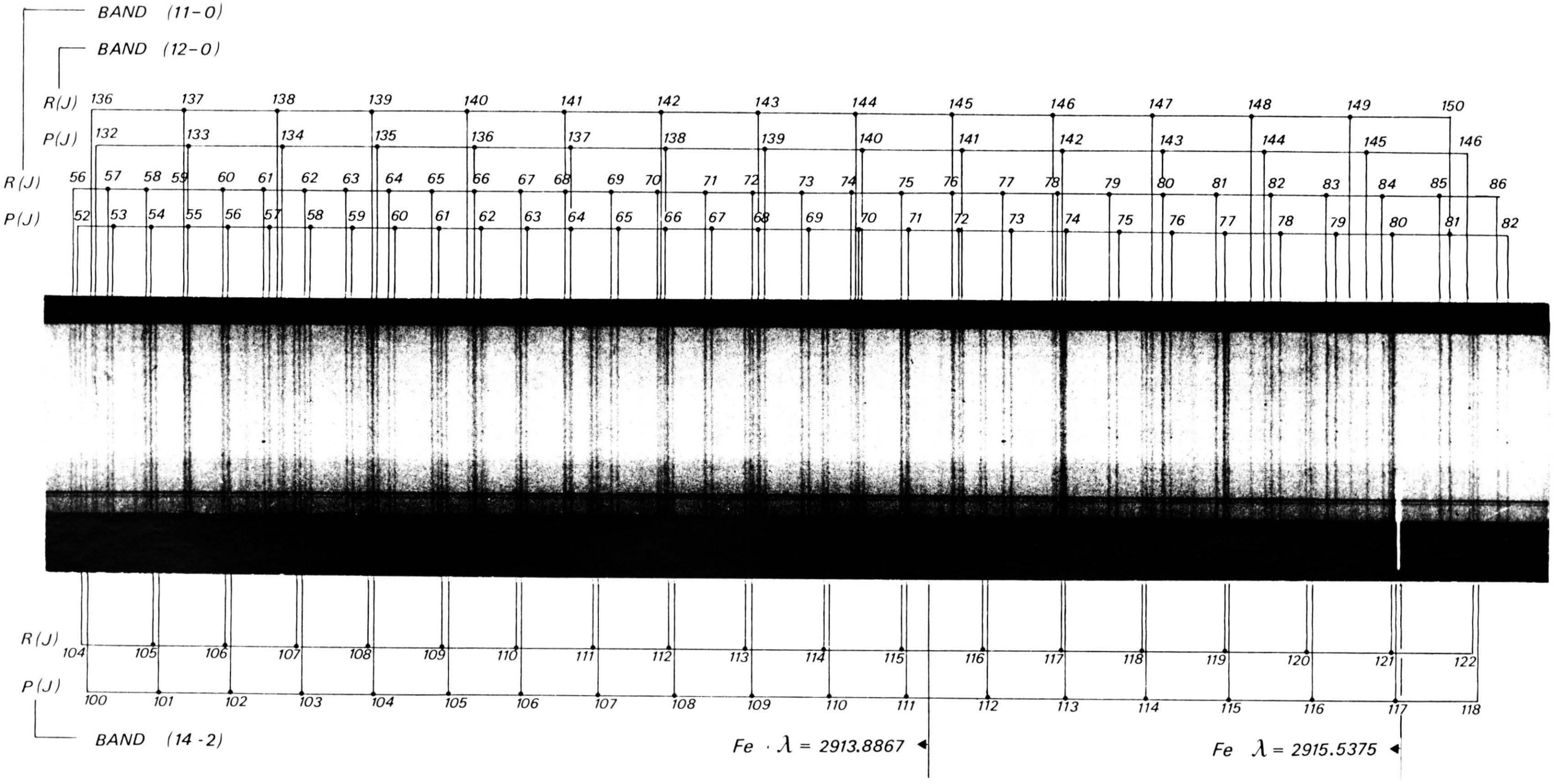

Fig. 1. High resolution absorption spectrum of $^{123}Sb-^{123}Sb$ near 2910 Å.

Rotational Analysis

The seven investigated bands possess only P and R branches with an intensity alternation in the successive lines. Four of these bands are related to the so-called $v''=2$ progression: (13,3) (14,2), (15,2) and (16,2), and the remaining three to the so-called $v''=0$ progression: (11,0), (12,0) and (13,0).

The only paper giving values for the rotational constants of the ground state refers to the (2,2) band of the $B \rightarrow X$ system[8]. This band was observed in emission, with a relatively low resolution, and its analysis had led to B and D values which now should be regarded as inaccurate, since we have been unable, in the present work, to assign a rotational quantum number J to each of the P and R lines well suited to these values. Therefore we carried out the true assignment of J taking into account the following two conditions:

1) The strong lines should correspond to odd values of J.
2) The rotational constant B'' of the ground state, determined from the analysis of a given band, must agree with the values calculated from other bands of same v''-progression.

We have thus been able to classify all the rotational lines of the bands analyzed, and derive values for the constants ν_0, B', B'', D' and D''. Perturbations have been observed and the interaction parameters calculated as well.

(11,0) band

The structure of this band was measurable from $P(11)$ and $R(15)$; the P and R branches are superimposed in such a way that $P(J)=R(J+4)$ up to $J=25$. Application of the combination rules shows that the $B'_{v'=11}$ value is constant and equal to $0.02981\ \mathrm{cm}^{-1}$ for $J<70$, but increases slowly beyond, which indicates the occurrence of a perturbation (Figure 2).

(12,0) band

This band was resolved almost down to the head, and the structure is developed up to $J=155$. It is observed that the B_v-curve of the upper level exhibits a sudden variation from $J=140$ on (Fig. 2), which reveals an interaction with a level whose rotational constant has a higher value.

(13,0) band

The structure appears from $J=41$ and is well developed up to $J=123$. A strong perturbation is observed, as it can be seen from the $B'_{v'=13}$ curve on Figure 2. But in this case we were able to display extra lines arising from the interacting level, which has not been possible for the (11,0) and (12,0) transitions. These extra lines have been classified into P and R branches of a band labelled $(l, 0)$, with $30<J<71$, and the corresponding B_v-curve is drawn on Figure 2. The mutual interaction of this l level and the upper level of the (13,0) band is beyond doubt.

(13,2) band

P and R branches are superimposed in such a way that $P(J)=R(J+4)$, up to $J=29$. No anomalous variation of the B_v-value of the upper level was discovered (Fig. 3), so that the behaviour of this level is quite different from that observed for the (13,0) band. Accordingly the so-called (13,0) and (13,2) transitions cannot have the same upper state, and the vibrational assignments must be reinvestigated.

(14,2) band

The structure is measurable from $P(39)$ and $R(38)$, and is developed up to $P(137)$ and $R(141)$. The B_v-curve of the upper state (Fig. 3) shows a characteristic perturbation feature, the maximum of which must occur for $J<30$. But no structure related to the perturbing level was in evidence.

(15,2) band

P and R branches are superimposed [with $P(J)=R(J+4)$] up to $J=71$. The B_v-value of the upper state shows an increasing from $J=80$ to 119 (Figure 3). Extra lines have been discovered and attributed to a $(l', 2)$ band, whose l' level interacts with the upper level of the (15,2) band.

(16,2) band

The structure of this band is resolved almost down to the head, and can be followed up to $P(76)$ and $R(76)$. In the range of observed values of J, the B_v-curve of the upper state is a horizontal line, corresponding to $0.02935\ \mathrm{cm}^{-1}$.

Tables I and II give the wavenumbers of P and R lines for the seven investigated bands.

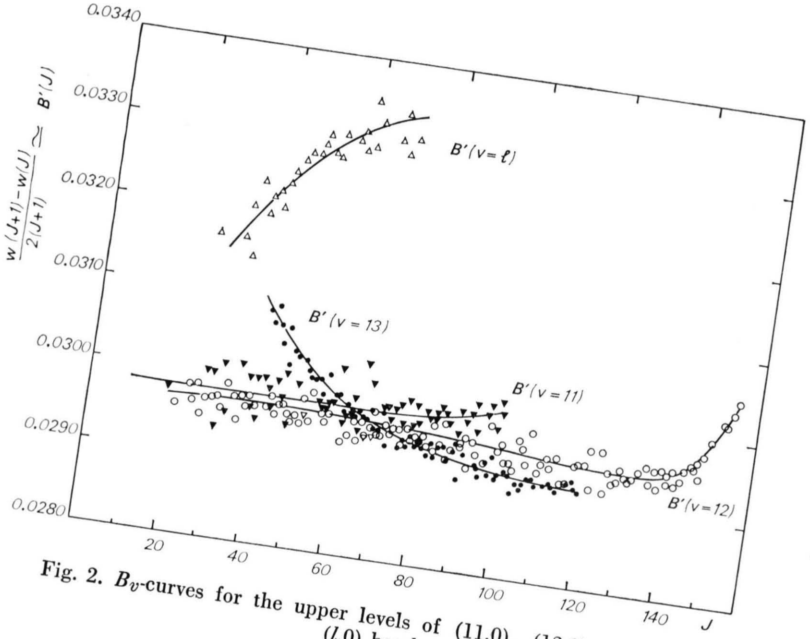

Fig. 2. B_v-curves for the upper levels of (11,0), (12,0), (13,0), and (l,0) bands.

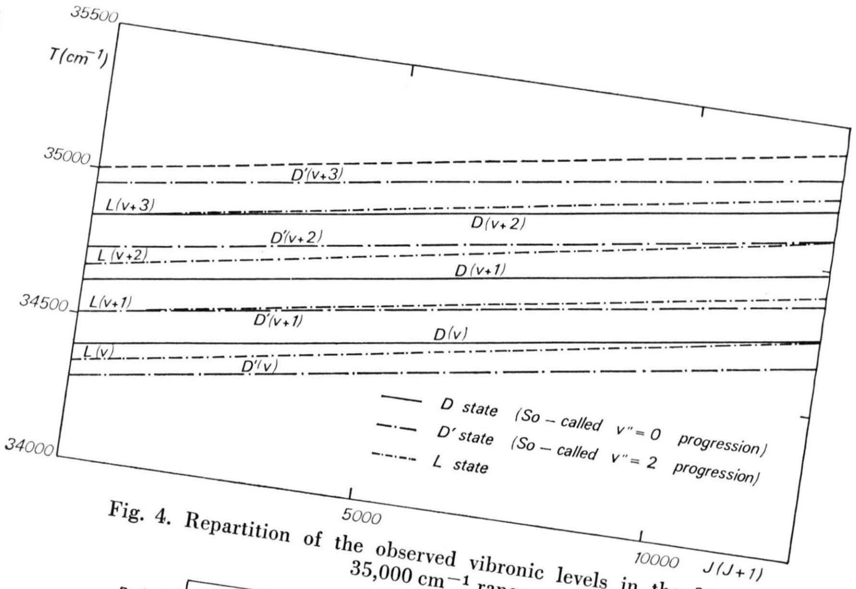

Fig. 4. Repartition of the observed vibronic levels in the 34,200 to 35,000 cm⁻¹ range.

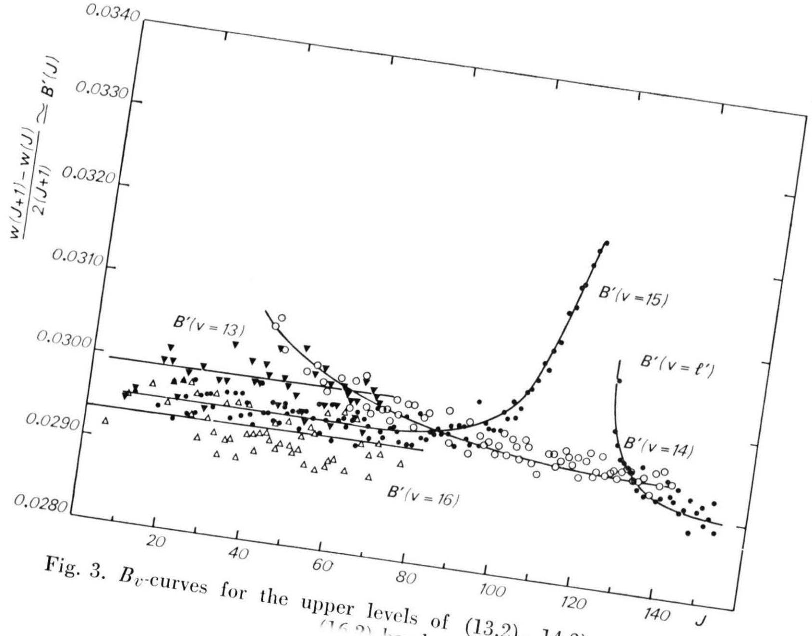

Fig. 3. B_v-curves for the upper levels of (13,2), 14,2), (15,2), and (16,2) bands.

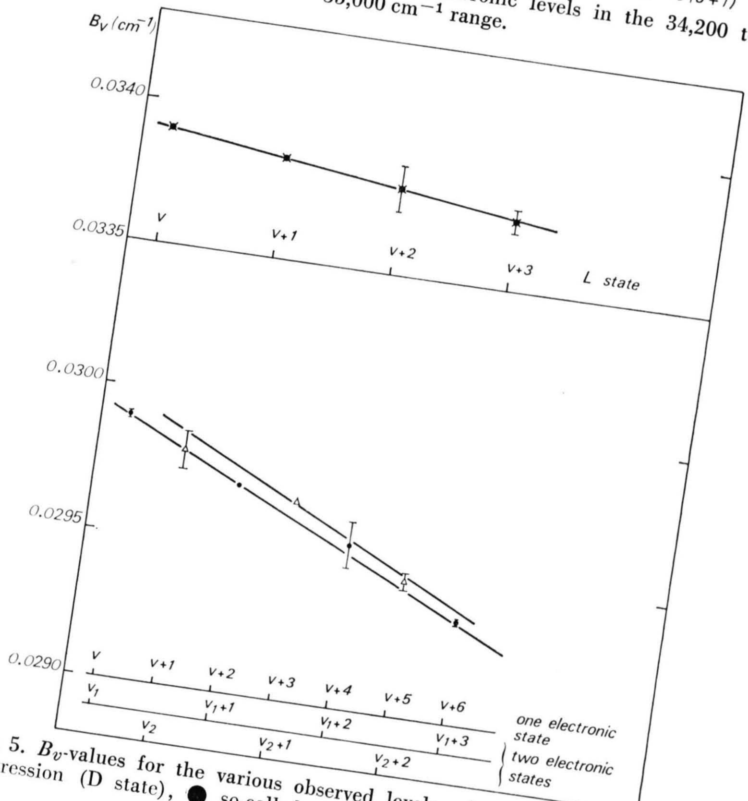

Fig. 5. B_v-values for the various observed levels: △ so-called $v''=0$ progression (D state), ● so-called $v''=2$ progression (D′ state) ✹ L state

Table I. Rotational assignments for the (11−0), (12−0), (13−0) and (l−0) bands (wavenumbers in cm^{-1}).

	(11−0)		(12−0)		(13−0)		(l−0)	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
6								
7				34616.54				
8				16.25				
9				15.93				
10				15.58				
11		34394.76	34616.54	15.25				
12		94.33	16.25	14.82				
13		93.94	15.93	14.38				
14		93.45	15.58	13.90				
15	34394.76	92.97	15.25	13.38				
16	94.33	92.36	14.82	12.85				
17	93.94	91.92	14.38	12.31				
18	93.45	91.41	13.90	11.72				
19	92.97	90.71	13.38	11.13				
20	92.36	90.15	12.85	10.48				
21	91.92	89.47	12.31	09.81				
22	91.41	88.77	11.72	09.12				
23	90.71	88.00	11.13	08.38				
24	90.16	87.24	10.48	07.57				
25	89.47	86.42	09.81	06.81				
26	88.77	85.64	09.12	06.01				
27	88.00	84.75	08.38	05.15				
28	87.24	83.97	07.57	04.28				
29	86.48	82.97	06.81	03.36				
30	85.66	82.09	06.01	02.47			34832.71	34828.82
31	84.92	81.14	05.15	01.48			31.99	27.97
32	83.98	80.26	04.28	00.50			31.24	27.11
33	83.12	79.10	03.36	34599.49			30.49	26.22
34	82.23	78.18	02.47	98.42			29.70	25.31
35	81.23	77.05	01.48	97.36			28.91	24.40
36	80.27	75.99	00.50	96.24			28.07	23.40
37	79.22	74.78	34599.49	95.14			27.26	22.47
38	78.18	73.64	98.42	93.95			26.40	21.47
39	77.11	72.44	97.36	92.75			25.55	20.46
40	76.04	71.25	96.24	91.54			24.63	19.43
41	74.90	69.99	95.14	90.28	34812.19		23.72	18.38
42	73.77	68.71	93.95	88.99	11.13	34805.91	22.80	17.29
43	72.59	67.38	92.75	87.71	10.07	04.72	21.83	16.21
44	71.34	66.07	91.54	86.33	08.94	03.46	20.87	15.11
45	70.17	64.72	90.28	84.96	07.76	02.17	19.89	13.97
46	68.87	63.36	88.99	83.56	06.56	00.86	18.86	12.84
47	67.60	61.91	87.71	82.15	05.29	34799.50	17.83	11.66
48	66.26	60.48	86.33	80.68	04.01	98.14	16.77	10.48
49	64.88	59.05	84.96	79.18	02.72	96.73	15.75	09.27
50	63.52	57.49	83.56	77.70	01.37	95.29	14.64	08.04
51	62.09	55.96	82.15	76.11	00.00	93.79	13.58	06.82
52	60.64	54.42	80.68	74.54	34798.61	92.30	12.44	05.59
53	59.21	52.84	79.18	72.93	97.19	90.74	11.31	04.28
54	57.66	51.21	77.70	71.30	95.71	89.16	10.07	03.00
55	56.17	49.89	76.11	69.63	94.21	87.53	08.94	01.69
56	54.63	47.97	74.55	67.96	92.67	85.91	07.76	00.35
57	53.05	46.22	72.95	66.22	91.13	84.23	06.56	34798.97
58	51.42	44.47	71.31	64.42	89.52	82.51	05.29	97.61
59	49.78	42.69	69.63	62.65	87.89	80.79	04.07	96.22
60	48.18	40.94	67.96	60.86	86.22	79.01	02.87	94.82
61	46.45	39.12	66.22	58.98	84.53	77.21	01.54	93.43
62	44.68	37.32	64.51	57.15	82.80	75.39	00.35	91.96
63	42.93	35.42	62.71	55.21	81.05	73.50	34798.97	90.53
64	41.17	33.54	60.89	53.35	79.26	71.61	97.61	89.05
65	39.35	31.58	59.06	51.36	77.45	69.68	96.22	87.53
66	37.57	29.61	57.22	49.40	75.60	67.69	94.82	
67	35.67	27.57	55.31	47.34	73.71	65.70	93.43	
68	33.79	25.65	53.35	45.29	71.80	63.67	91.96	

Table I (continued)

	(11−0)		(12−0)		(13−0)		(*l*−0)	
J	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)	*P*(*J*)
69	34331.83	34323.55	34551.44	34543.20	34769.84	34761.61	34790.53	
70	29.84	21.56	49.44	41.11	67.87	59.55	89.14	
71	27.86	19.40	47.41	38.98	65.86	57.40	87.55	
72	25.87	17.23	45.39	36.83	63.79	55.24		
73	23.81	15.09	43.30	34.62	61.73	53.09		
74	21.76	12.89	41.19	32.41	59.64	50.86		
75	19.66	10.67	39.07	30.17	57.47	48.61		
76	17.53	08.43	36.88	27.91	55.31	46.33		
77	15.40	06.21	34.71	25.59	53.09	44.02		
78	13.24	03.88	32.48	23.24	50.86	41.66		
79	11.01	01.59	30.23	20.87	48.61	39.28		
80	08.76	34299.17	27.96	18.46	46.33	36.88		
81	06.52	96.84	25.65	16.05	44.02	34.42		
82	04.24	94.43	23.30	13.58	41.66	31.95		
83	01.92	91.98	20.93	11.09	39.28	29.45		
84	34299.59	89.51	18.55	08.57	36.85	26.90		
85	97.22	87.01	16.10	06.07	34.42	24.35		
86	94.83	84.49	13.69	03.45	31.95	21.75		
87	92.40	81.98	11.16	00.86	29.45	19.13		
88	89.96	79.40	08.64	34498.26	26.90	16.52		
89	87.46	76.78	06.11	95.58	24.32	13.78		
90	85.00	74.24	03.55	92.86	21.69	11.10		
91	82.46	71.54	00.95	90.16	19.13	08.44		
92	79.90	68.83	34498.30	87.42	16.50	05.61		
93	77.34	66.11	95.66	84.63	13.74	02.77		
94	74.70	63.41	92.94	81.80	11.01	00.01		
95	72.17	60.67	90.23	78.98	08.23	34697.06		
96	69.49	57.85	87.46	76.10	05.44	94.18		
97	66.84	55.10	84.70	73.23	02.60	91.23		
98	64.08	52.28	81.90	70.27	34699.81	88.28		
99	61.51	49.43	79.05	67.41	96.92	85.29		
100			76.19	64.42	94.01	82.28		
101			73.31	61.37	91.05	79.21		
102			70.36	58.34	88.11	76.11		
103				55.29	85.11	73.02		
104			64.42	52.14	82.05	69.96		
105			61.42	49.03	79.00	66.71		
106			58.38	45.79	75.90	63.48		
107			55.33	42.66	72.78	60.26		
108			52.21	39.50	69.66	56.97		
109			49.08	36.21	66.46	53.67		
110			45.90	32.88	63.22	50.35		
111			42.71	29.65	59.99	46.99		
112			39.51	26.29	56.73	43.61		
113			36.21	22.92	53.39	40.17		
114			33.01	19.54	49.94	36.74		
115			29.71	16.15	46.68	33.23		
116			26.34	12.68	43.30	29.71		
117			22.92	09.22	39.88	16.16		
118			19.54	05.66	36.45	22.59		
119			16.15	02.10	32.89	19.03		
120			12.68	34398.56	29.35			
121			09.22	94.96	25.85			
122			05.73	91.28	22.33			
123			02.14	87.66	18.64			
124			34398.61	83.97				
125			94.95	80.14				
126			91.38	76.51				
127			87.65	72.69				
128			83.95	68.87				
129			80.28	65.08				
130			76.57	61.22				
131			72.79	57.35				

Table I (continued)

J	(11−0) $R(J)$	(11−0) $P(J)$	(12−0) $R(J)$	(12−0) $P(J)$	(13−0) $R(J)$	(13−0) $P(J)$	(l−0) $R(J)$	(l−0) $P(J)$
132			34368.98	34353.40				
133			65.19	49.46				
134			61.26	45.49				
135			57.45	41.54				
136			53.52	37.44				
137			49.65	33.41				
138			45.67	29.34				
139			41.74	25.25				
140			37.72	21.09				
141			33.66	16.94				
142			29.61	12.76				
143			25.52	08.63				
144			21.43	04.36				
145			17.40	00.10				
146			13.23	34295.87				
147			09.08	91.57				
148			04.93	87.33				
149			00.81	82.94				
150			34296.71	78.66				
151			92.54	74.33				
152			88.49	70.02				
153			84.36	65.72				
154			80.23	61.40				
155			76.14	57.07				

Table II. Rotational assignments for the (13−2), (14−2), (15−2), (16−2) and (l'−2) bands (wavenumbers in cm^{-1}).

J	(13−2) $R(J)$	(13−2) $P(J)$	(14−2) $R(J)$	(14−2) $P(J)$	(15−2) $R(J)$	(15−2) $P(J)$	(16−2) $R(J)$	(16−2) $P(J)$
3								34947.93
4								47.75
5								47.54
6								47.31
7							34947.93	47.04
8		34284.74					47.75	46.71
9		84.49					47.54	46.42
10		84.16					47.31	45.98
11		83.78				34726.33	47.04	45.68
12	34284.74	83.33				25.90	46.71	45.26
13	84.49	82.88				25.47	46.40	44.82
14	84.16	82.46				25.00	45.98	44.32
15	83.78	81.98			34726.33	24.50	45.63	43.83
16	83.33	81.54			25.90	23.99	45.26	43.29
17	82.88	80.91			25.47	23.41	44.76	42.70
18	82.46	80.29			25.00	22.84	44.32	42.11
19	81.98	79.71			24.50	22.22	43.81	41.45
20	81.54	79.08			23.99	21.61	43.29	40.84
21	80.99	78.42			23.41	20.90	42.68	40.17
22	80.36	77.78			22.84	20.19	42.11	39.46
23	79.78	77.03			22.22	19.46	41.45	38.69
24	79.08	76.27			21.61	18.70	40.84	37.93
25	78.42	75.47			20.90	17.91	40.13	37.10
26	77.78	74.66			20.19	17.08	39.46	36.26
27	77.05	73.91			19.46	16.25	38.67	35.43
28	76.27	73.01			18.70	15.36	37.87	34.52
29	75.59	72.07			17.91	14.45	37.05	33.60
30	74.70	71.13			17.08	13.50	36.26	32.61
31	73.91	70.33			16.25	12.54	35.39	31.65
32	73.01	69.22			15.36	11.55	34.48	30.63
33	72.17	68.18			14.45	10.53	33.53	29.57

Table II (continued)

J	(13−2)		(14−2)		(15−2)		(16−2)	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
34	34271.34	34267.17			34713.50	34709.46	34932.56	34928.47
35	70.33	66.11			12.54	08.38	31.57	27.41
36	69.39	65.06			11.55	07.26	30.57	26.27
37	68.34	63.85			10.53	06.13	29.49	25.10
38	67.31	62.76	34485.56		09.46	04.96	28.44	23.93
39	66.24	61.53	84.58	34479.72	08.38	03.75	27.32	22.69
40	65.17	60.36		78.63	07.26	02.53	26.17	21.46
41	64.08	50.13	82.49	77.40	06.13	01.25	24.99	20.18
42	62.91	57.85	81.40	76.26	04.96	34699.95	23.81	18.86
43	61.72	56.57	80.28	74.97	03.75	98.66	22.61	17.49
44	60.55	55.28	79.15	73.71	02.53	97.30	21.32	16.10
45	59.30	53.84	77.96	72.44	01.25	95.92	20.04	14.69
46	58.03	52.50	76.73	71.08	34699.95	94.53	18.74	13.27
47	56.75	51.07	75.45	69.73	98.66	93.08	17.36	11.83
48	55.44	49.66	74.15	68.27	97.30	91.61	15.99	10.30
49	54.06	48.20	72.87	66.86	95.92	90.12	14.59	08.78
50	52.73	46.63	71.55	65.41	94.53	88.59	13.13	07.26
51	51.29	45.14	70.15	63.96	93.08	87.06	11.67	05.66
52	49.85	43.64	68.77	62.43	91.61	85.46	10.17	04.04
53	48.41	42.04	67.33	60.90	90.12	83.84	08.60	02.36
54	46.88	40.38	65.86	59.32	88.59	82.21	07.07	00.72
55	45.39	38.76	64.38	57.72	87.06	80.53	05.51	34899.00
56	43.80	37.06	62.85	56.08	85.46	78.83	03.85	97.27
57	42.25	35.41	61.32	54.40	83.84	77.12	02.27	95.51
58	40.63	33.69	59.75	52.68	82.21	75.35	00.54	93.69
59	38.98	31.95	58.11	51.02	80.53	73.56	34898.83	91.89
60	37.34	30.11	56.41	49.17	78.83	71.77	97.05	90.03
61	35.66	28.29	54.80	47.40	77.12	69.89	95.34	88.12
62	33.94	26.46	53.07	45.58	75.35	68.02	93.47	86.20
63	32.16	24.59	51.36	43.76	73.56	66.12	91.65	84.31
64	30.37	22.70	49.56	41.84	71.77	64.18	89.86	82.32
65	28.60	20.81	47.79	39.94	69.89	62.14	87.91	80.25
66	26.72		45.93	37.99	68.02	60.25	86.01	78.24
67	24.87		44.06	36.07	66.12	58.22	84.01	76.16
68	22.99		42.21	34.01	64.18	56.19	82.07	74.07
69	21.08		40.28	31.96	62.24	54.11	79.97	71.91
70			38.31	29.90	60.25	51.97	77.97	69.72
71			36.34	27.79	58.22	49.87	75.93	67.54
72			34.31	25.67	56.19	47.69	73.79	65.33
73			32.28	23.50	54.11	45.49	71.50	63.07
74			30.17	21.30	51.97	43.25	69.48	60.74
75			28.09	19.11	49.87	41.02	67.23	58.32
76			25.94	16.88	47.33	38.71	65.01	56.16
77			23.82	14.57	45.53	36.39		
78			21.61	12.32	43.27	34.07		
79			19.40	09.97	41.08	31.67		
80			17.16	07.59	38.79	29.28		
81			14.90	05.22	36.46	26.87		
82			12.56	02.78	34.14	24.41		
83			10.22	00.35	31.79	21.94		
84			07.85	34397.86	29.39	19.42		
85			05.46	95.31	27.01	16.88		
86			03.06	92.75	24.56	14.35		
87			00.58	90.16	22.11	11.72		
88			34398.10	87.59	19.60	09.12		
89			95.56	84.92	17.07	06.49		
90			92.97	82.23	14.53	03.79		
91			90.42	79.54	11.95	01.12		
92			87.80	76.83	09.34	34598.42		
93			85.22	74.10	06.81	95.64		
94			82.52	71.29	04.09	92.82		
95			79.78	68.47	01.42	90.06		
96			77.06	65.66	34598.71	87.23		

Table II (continued)

	(13−2)		(14−2)		(15−2)		(16−2)		(l′−2)	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
97			34374.33	34362.78	34595.98	34584.40				
98			71.55	59.86	93.23	81.53				
99			68.71	56.98	90.50	78.63				
100			65.90	53.96	87.71	75.71				
101			63.00	50.99	84.93	72.78				
102			60.08	47.97	82.10	69.83				
103			57.19	44.90	79.24	66.69				
104			54.19	41.87	76.45	63.87				
105			51.21	38.72	73.63	60.87				
106			48.18	35.58	70.77	57.87				
107			45.12	32.43	67.96	54.84				
108			42.09	29.25	65.12	51.86				
109			38.96	25.98	62.25	48.83				
110			35.83	22.77	59.40	45.79				
111			32.66	19.40	56.34	42.80				
112			29.47	16.16	53.83	39.79				
113			26.21	12.83	51.08	36.83				
114			22.95	09.47	48.35	33.88				
115			19.66	06.03	45.58	30.95				
116			16.41	02.59	42.80	27.96				
117			13.01	34299.17	40.12	25.06				
118			09.65	95.64	37.31	22.07				
119			06.21	92.15	34.34					
120			02.78	88.61						
121			34299.36	85.00						
122			95.82	81.40						
123			92.34	77.78						
124			88.77	74.12					34505.12	
125			85.17	70.33					01.56	34486.24
126			81.54	66.69					34498.06	83.00
127			77.95	62.91					94.42	79.18
128			74.24	59.13					90.78	75.59
129			70.55	55.28					87.15	71.84
130			66.84	51.43					83.43	68.02
131			63.08	47.55					79.69	64.18
132			59.30	43.68					75.90	60.28
133			55.44	39.76					72.02	56.34
134			51.61	35.79					68.23	52.34
135			47.76	31.80					64.16	48.33
136			43.80	27.78					60.35	44.34
137			39.89	23.71					56.38	40.28
138			35.92						52.34	36.13
139			31.96						48.33	31.96
140			27.88						44.34	27.80
141			23.83						40.28	23.55
142									36.13	19.40
143									31.96	15.10
144									27.76	10.81
145									23.55	06.59
146									19.40	02.17
147									14.90	34397.72
148									10.57	93.26
149									06.26	88.77
150									01.85	84.09
151									34397.42	79.79
152									92.97	75.19
153									88.47	70.59
154									84.09	66.08
155									79.54	61.54
156									74.90	56.64
157									70.17	51.92
158										47.15
159										42.39

Determination of the Rotational Constants and the Interaction Parameters

Because of the occurrence of perturbations in almost all the bands studied, the upper and lower levels must be dealt with separately. We have calculated for each band the combination differences:

$$\Delta_2 F''(J) = \frac{R(J-1) - P(J+1)}{4(J+1/2)} = B'' - 2\,D''\,(J+1/2)^2 .$$

For the whole of the seven bands investigated, no systematic difference between the mean $\Delta_2 F''(J)$ values, calculated for the two progressions labelled $v''=0$ and $v''=2$, can be pointed out. Accordingly it is inferred that all these bands have, in fact, the same lower level, which can reasonably be regarded as the $(v''=0)$ level of the X ground state. The vibrational assignments by Naudé are thus certainly incorrect, which is confirmed by the observations made above, concerning the so-called (13,0) and (13,2) bands.

Theoretically, it would be possible to derive B'' and D'' by fitting the experimental $\Delta_2 F''(J)$ values to the above formula. But this procedure is not quite applicable here, because of the magnitude of the constants involved ($B'' \cong 0.04\ \mathrm{cm}^{-1}$). This fact, together with the precision of the measurements on the spectrograms, leads to prohibitive relative uncertainties. To obtain reliable values of B'' and D'', we fitted the experimental wavenumbers of P and R lines for unperturbed bands or unperturbed portions of bands to the wavenumbers calculated from the expressions:

$$P(J) = \nu_0 + F'(J-1) - F''(J)\,,$$
$$R(J) = \nu_0 + F'(J+1) - F''(J)$$
$$\text{where}\quad F(J) = B\,J(J+1) - D\,J^2(J+1)^2 .$$

The following values have thus been adopted:

$$B'' = 0.044263\ \mathrm{cm}^{-1}\,,$$
$$D'' = 8 \times 10^{-9}\ \mathrm{cm}^{-1}\,.$$

It must be pointed out, that if some inaccuracy remains on these values, a corresponding uncertainty will be found on the rotational constants of the upper levels, since the parameters for the upper as well as lower levels are strongly correlated in such a calculation.

Starting from these B'' and D'' values, we have further calculated the $W(J)$ term-values for the upper levels of all the analyzed bands [above the $(v''=0)$ level of the X state]. Only the so-called (13,2) and (16,2) transitions exhibit no perturbation; a least-squares fitting on the corresponding upper level term-values gives the following parameters:

$$(13{,}2)\ \begin{cases} T_0 = 34286.29 \pm 0.02\ \mathrm{cm}^{-1}\,, \\ B' = 0.02990 \pm 0.00001\ \mathrm{cm}^{-1}\,, \\ D' = (9 \pm 4) \times 10^{-9}\ \mathrm{cm}^{-1}; \end{cases}$$

$$(16{,}2)\ \begin{cases} T_0 = 34948.36 \pm 0.02\ \mathrm{cm}^{-1}\,, \\ B' = 0.02935 \pm 0.00001\ \mathrm{cm}^{-1}\,, \\ D' = (23 \pm 2) \times 10^{-9}\ \mathrm{cm}^{-1} \end{cases}$$

with a root mean square (RMS) error of $0.02\ \mathrm{cm}^{-1}$.

As all the other bands are perturbed, the determination of deperturbed constants requires the building-up of a molecular model suited to the observed perturbations. It is represented by a hamiltonian matrix whose dimension equals the number of interacting levels, and in which the off-diagonal elements are the interaction parameters. When performing a numerical diagonalization of this matrix and fitting the corresponding eigenvalues to the experimental term-values by a non-linear least-squares technique, one can obtain the deperturbed constants and the interaction parameters. The shape of the B_v-curves on Figs. 2 and 3 led us to deal separately with the upper levels of each band through a 2×2 matrix, the interaction parameters being independent of J.

This method results directly in significant values in the case of the (13,0) and (15,2) bands. The following parameters have been obtained, the RMS errors being respectively 0.02 and $0.04\ \mathrm{cm}^{-1}$:

D ($v=13$) level	Perturbing level (l)
$T_0 = 34838.9 \pm 0.2\ \mathrm{cm}^{-1}$	$T_0 = 34835.46 \pm 0.10\ \mathrm{cm}^{-1}$
$B = 0.02946 \pm 0.00001\ \mathrm{cm}^{-1}$	$B = 0.03374 \pm 0.00004\ \mathrm{cm}^{-1}$
$D = (13.0 \pm 0.6) \times 10^{-9}\ \mathrm{cm}^{-1}$	$D = (20 \pm 6) \times 10^{-9}\ \mathrm{cm}^{-1}$

$$H = 5.33 \pm 0.04\ \mathrm{cm}^{-1}$$

D $(v=15)$ level
$T_0 = 34728.6 \pm 0.1\ \mathrm{cm}^{-1}$
$B = 0.02956 \pm 0.00001\ \mathrm{cm}^{-1}$
$D = (11.2 \pm 0.4) \times 10^{-9}\ \mathrm{cm}^{-1}$

Perturbing level (l')
$T_0 = 34673.9 \pm 1.2\ \mathrm{cm}^{-1}$
$B = 0.03382 \pm 0.00004\ \mathrm{cm}^{-1}$
$D = (11.2 \pm 1.2) \times 10^{-9}\ \mathrm{cm}^{-1}$

$$H = 5.22 \pm 0.03\ \mathrm{cm}^{-1}\,.$$

For the other levels the problem is indefinite, since no extra lines are observed, and this procedure failed. For the (14,2) band, however, we performed a set of least-squares fittings relative to the matrix eigenvalues. A systematic variation of T_0, B and D was carried out for each level, the interaction parameter H being taken as the only variable in each fitting. We were thus able to represent the experimental term-values within an RMS error of 0.05 cm^{-1}, which seems acceptable for such an indefinite problem. The adopted values are (in cm^{-1}):

D $(v=14)$ level
$T_0 = 34507.66$
$B = 0.02971$
$D = 9.2 \times 10^{-9}$

Perturbing level
$T_0 = 34506.66$
$B = 0.03385$
$D = 9.2 \times 10^{-9}$

$$H = 4.96 \pm 0.02\,.$$

Attempts to deal with the perturbations in the (11,0) and (12,0) bands have been unsuccessful, even with the method described by Massot, Goure and Figuet[9]. A least-squares fitting on the $W(J)$ term-values lying far from the crossing point gives:

$$\begin{array}{l} (11,0)\ \text{band} \\ 10 < J < 70 \end{array} \left\{ \begin{array}{l} T_0 = 34397.31 \pm 0.02\ \mathrm{cm}^{-1}, \\ B = 0.02981 \pm 0.00006\ \mathrm{cm}^{-1}, \\ D = \text{negligible}; \end{array} \right.$$

$$\begin{array}{l} (12,0)\ \text{band} \\ 20 < J < 120 \end{array} \left\{ \begin{array}{l} T_0 = 34617.77 \pm 0.02\ \mathrm{cm}^{-1}, \\ B = 0.029679 \pm 0.000004\ \mathrm{cm}^{-1}, \\ D = (10.0 \pm 0.2) \times 10^{-9}\ \mathrm{cm}^{-1} \end{array} \right.$$

with RMS errors of 0.03 and 0.02 cm^{-1} respectively.

Re-analysis of the (2,2) Band Belonging to the B → X System

As it has been pointed out above, the analysis given in[8] should be reconsidered. This is possible now, since correct values of the rotational constants B_0'' of the ground state have been determined. The attributions proposed in[8] must be corrected in the following manner-all the J-values must be raised by one unit for the P branch and lowered by the same quantity for the R branch. The corresponding constants are listed in Table III. The relative positions of the origins for the three isotopic molecules are consistent with the isotopic effect. For $^{123}\mathrm{Sb}-{}^{123}\mathrm{Sb}$, the B_2''-value is found to be lower than the adopted one for B_0'', as expected.

Table III. Rotational constants for the (2,2) band of the $B \rightarrow X$ system relative to the three isotopic molecules of diatomic antimony (in cm^{-1}).

	$^{121}\mathrm{Sb}-{}^{121}\mathrm{Sb}$	$^{121}\mathrm{Sb}-{}^{123}\mathrm{Sb}$	$^{123}\mathrm{Sb}-{}^{123}\mathrm{Sb}$
v_0	18937.80 (2)	18938.29 (2)	18938.78 (2)
B_2'	0.03936 (8)	0.03899 (6)	0.03867 (8)
B_2''	0.04496 (6)	0.04454 (6)	0.04417 (8)
$10^9 \times D_2'$	8.9 (15)	8.9 (15)	8.9 (15)
$10^9 \times D_2''$	9.1 (15)	9.1 (15)	9.1 (15)
RMS error	0.06	0.05	0.06

Note: Uncertainties (in units of the last figure given) have been taken as two standard deviations.

Discussion

Within the assumption made about the v''-numbering of the analyzed bands, the deperturbed $W(J)$ term-values are drawn versus $J(J+1)$ on Fig. 4, which gives rise, together with the above results, to the following observations:

1) The three perturbing levels which have been displayed belong certainly to the same electronic state, hitherto unknown, which we propose to label L. If their vibrational numbers are $v+1$, $v+2$, and $v+3$, we have the scheme (in cm^{-1}):

	T_0	B	$10^9 \times D$
$v+1$	34506.7	0.03385	9.2
	166.8		
$v+2$ (l' level)	34673.5	0.03380	11.2
	162.0		
$v+3$ (l level)	34835.5	0.03374	20

Apart from the D parameters, which are very sensitive to possible second order effects, these values are consistent. This L state would be $^1\Sigma_u^+$ or case $c - 0_u^+$.

2) If this hypothesis is assumed, the perturbation in the (12,0) band should be due to the $v + 1$ level of the L state. Therefore we dealt with this interaction using the 2×2 matrix procedure already described, starting from the vibronic scheme obtained, and taking H as a variable parameter. A satisfactory fit on all the observed term-values (RMS error = 0.04 cm^{-1}) of the (12,0) band was obtained for H = 7.77 cm^{-1}, with slight corrections on T_0 and D constants of the D ($v = 12$) level: the value of D should be taken as 13.1×10^{-9} cm^{-1}, and that of T_0 reduced by 0.58 cm^{-1}. This is not surprising, since the above-determined T_0 did not take the perturbation into account. On the other hand, this value of 0.58 cm^{-1} agrees with the calculated displacement for $J = 0$ (0.54 cm^{-1}).

3) The perturbation in the (11,0) band should be caused by the v level of the L state. A rough extrapolation of the results already obtained for L leads to T_0 and B values for the v level, which can be taken as a starting point for a calculation similar to that performed for (12,0). One cannot expect here a precise determination of the parameter, since lines in the vicinity of the maximum perturbation point have not been observed (Figure 2). An RMS error of 0.06 cm^{-1} has thus been obtained for the v level of L, together with the following results:

$$T_0 = 34335.9\ \text{cm}^{-1},\quad B = 0.0339\ \text{cm}^{-1},$$
$$D = 9 \times 10^{-9}\ \text{cm}^{-1}.$$

The value determined for H is thus 6.66 cm^{-1}. However, for the $D(v = 11)$ level, T_0 has been taken 0.78 cm^{-1} below the value calculated above, which agrees with the expected displacement (0.74 cm^{-1}). D is found to be 10×10^{-9} cm^{-1}.

4) This L(v) level would cross the upper level of the so-called (13,2) band for $J < 0$, which explains why no variation of the B_v-value is observed for this level. In the same manner the $L\,(v + 4)$ level, extrapolated from $L\,(v + 3)$, lies 44 cm^{-1} above the upper level of the so-called (16,2) band. This fact accounts for the absence of anomaly in the B_v-curve for the latter level (Figure 3).

All these results confirm the assumption made about the lower level of the analyzed bands. But a problem remains with regard to the attribution of the upper levels and their vibrational numbering. From Fig. 5, it could be supposed that the seven investigated bands would have the same upper electronic state, with vibrational assignments from v to $v + 6$, and a ΔG-value of about 110 cm^{-1}. This is consistent with the observed B_v-values for these levels. But we are inclined to prefer another attribution, in which the two analyzed progressions are

Table IV.
Proposed assignments
for the analyzed bands.

Naudé	This work
D (11,0)	D (v, 0)
D (12,0)	D (v+1,0)
D (13,0)	D (v+2,0)
D (13,2)	D' (v, 0)
D (14,2)	D' (v+1,0)
D (15,2)	D' (v+2,0)
D (16,2)	D' (v+3,0)

Table V.
Interaction parameters
between observed
vibronic levels of D,
D′ and L states.

Pair of interacting levels	H (cm^{-1})
L(v) ~D (v)	6.66
L(v+1) ~D (v+1)	7.77
L(v+3) ~D (v+2)	5.33
L(v+1) ~D′(v+1)	4.96
L(v+2) ~D′(v+2)	5.22

Table VI. Vibronic energies and rotational constants for the observed levels.

Vibrational quantum number	T_0	B_v	$10^9 \times D_v$
D state			
v	34396.53 (2)	0.02981 (6)	10
v+1	34617.19 (2)	0.029679 (4)	13.1
v+2	34838.9 (2)	0.02946 (2)	13.0 (6)
D′ state			
v	34286.29 (2)	0.02990 (1)	9 (4)
v+1	34507.66	0.02971	9.2
v+2	34728.6 (1)	0.02956 (1)	11.2 (4)
v+3	34948.36 (2)	0.02935 (1)	23 (2)
L state			
v	34335.9	0.0339	9
v+1	34506.66	0.03385	9.2
v+2	34673.9 (12)	0.03382 (4)	11.2 (12)
v+3	34835.46 (10)	0.03374 (4)	20 (6)

Note: Uncertainties (in units of the last figure given) have been taken as two standard deviations. Errors are not listed when the corresponding value is fixed in the deperturbation technique.

regarded as arising from two different electronic states. The following reasons may be advanced:

1) If the B_v-values are plotted for the successive observed levels (Fig. 5), a better consistency is obtained for the hypothesis of two electronic states than for merely one.

2) Upon examination of low-resolution spectrograms of the so-called $D \leftarrow X$ system, one easily notes several progressions with a distance of about 220 cm^{-1} between the successive band-heads, whereas it is impossible to observe systematic spacings of about 110 cm^{-1}.

Therefore, we propose to consider provisionally the two studied progressions as belonging to $D \leftarrow X$ and $D' \leftarrow X$ systems, the correspondence between Naudé's assignments and ours being given in Table IV. The results obtained in this work are collected in Tables V and VI.

Analysis of the same bands belonging to the $^{121}Sb - ^{121}Sb$ molecule is now in progress. Comparison with the results obtained for $^{123}Sb - ^{123}Sb$ would allow us to check the validity of the assumptions made about the upper electronic states, and propose an absolute v'-numbering for the bands involved.

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