Absorption Spectrum of As_2

Further Analysis of the A→X System and Observation of New Electronic States

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Within the study of the interaction between A and B states of As_2 molecule, a high resolution analysis of 16 absorption bands with $11 \leqq v' \leqq 17$ in the $A \leftarrow X$ system has been performed. The following constants are proposed for the A state: $T_{00} = 40145.9\ cm^{-1}$, $\omega_e = 262.7\ cm^{-1}$, $\omega_e x_e = 0.48\ cm^{-1}$, $B_e = 0.0797\ cm^{-1}$, $D_e \cong 3\times10^{-8}\ cm^{-1}$, $\alpha_e = 0.00031\ cm^{-1}$, $r_e = 2.374$ Å. Three new vibronic levels have been discovered in the 42400–44500 cm^{-1} energy range, either directly or by the perturbations they induce in A levels.

Introduction

The absorption spectrum of the As_2 molecule in the ultraviolet region (2200 – 2750 Å) has been recorded for the first time in 1934 by Gibson and MacFarlane[1]. They have classified almost all the observed bands in one electronic system, namely $A \leftarrow X$, which on the analogy of the N_2 and P_2 molecules, was assigned to a ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$ transition. Recently, this absorption spectrum has been extended to the vacuum ultraviolet region by Topouzkhanian and Sibai[2], down to 1775 Å. Most of the new bands belong to the $A \leftarrow X$ system, and the others have been arranged into two new $F \leftarrow X$ and $G \leftarrow X$ systems. On the other hand, Donovan and Strachan[3] observed absorption bands of As_2 molecule as far as 1365 Å, following the flash photolysis of AsH_3. The latter have been ascribed to the $A \leftarrow X$ system and to seven others, two of them ($f \leftarrow X$ and $E \leftarrow X$) being identical, respectively, to the $F \leftarrow X$ and $G \leftarrow X$ systems of Topouzkhanian and Sibai. The corresponding transitions have been interpreted as Rydberg in type, except for $f \leftarrow X$ and $A \leftarrow X$.

This last system has been observed very strongly in emission between 2300 and 5600 Å by Almy and Kinzer[4, 5], but bands with $v' \geqq 10$ do not appear, except those for which $v = 14$. Accordingly, a predissociation of the A state is to be expected for vibrational levels beyond $v = 9$ ($T_{0(v=9)} = 42577.7\ cm^{-1}$). Another system, $B \rightarrow X$, lies in the same spectral region, but Almy and Kinzer assumed that the B state dissociates near 42600 cm^{-1}, i. e. the energy at which A predissociates. It must be emphasized that strong irregularities appear in ΔG intervals of the A and B states, which indicates the occurence of perturbations. A rotational analysis of numerous bands of $A \rightarrow X$ and $B \rightarrow X$ systems has been carried out by Perdigon, Martin and D'Incan[6, 7, 8]. It led to the conclusion that A and B states are of ${}^1\Sigma_u^+$ (or case c-0_u^+) symmetry, and confirmed that the observed perturbations are due to an interaction of these two states, as previously suggested by Almy and Kinzer.

As the treatment of this interaction requires as far as possible a complete knowledge of A and B levels, it appeared quite necessary to get information about the A levels with $v > 9$. The purpose of the present work was to perform a rotational analysis of absorption bands with $10 \leqq v \leqq 17$, which have been recorded under high resolution. During this investigation, three hitherto unknown vibronic levels have been discovered, directly or through the perturbations they induce in A levels.

Experimental Conditions

The absorption tube was prepared in a previously described way[2], and the source of continuous ultraviolet light was of the Finkelstein type[9]. Spectra have been photographed with the 4-m asymmetric Czerny-Turner grating vacuum spectrograph[10] of the University College London, on Kodak 101-01 or SWR films. The exposure times varied between 5 and 60 minutes. The slit width was 30 μ, which allowed a resolving power of about 300 000, the reciprocal dispersion being 0.1 Å/mm. The rotational lines have been calibrated against Fe atomic lines from a hollow cathode source. It is considered

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that, for sharp lines, the errors do not exceed $\pm 0.03\ \mathrm{cm}^{-1}$.

Results

All the investigated bands consist of only P and R branches, which present an intensity alternation, the lines with odd values of J being the strongest. As B_e, α_e, γ_e and D_e constants of the $X\,^1\Sigma_g^+$ state are well known [6], J-values of each P and R line have been assigned with the help of classical combination differences. Least-squares fittings on the term values of the upper levels of the transitions were used to determine the T_{0v}, B' and D' constants.

A(v = 10) level

Whereas (10-0), (10-1) and (10-2) heads were observed on low resolution spectrograms [2], they are not perceptible on high resolution films. At $42412.7\ \mathrm{cm}^{-1}$, the wavenumber at which the (10-1) head is to be expected, it seems that a very weak absorption occurs. But, as for (10-0), all the rotational lines which appear down to $42160\ \mathrm{cm}^{-1}$ have been attributed to other transitions. Therefore, it is likely that all the rotational levels of this ($v = 10$) level are strongly predissociated.

Table I. Wavenumbers for (11−0) and (11−1) bands of A ← X.

J	(11−0)		(11−1)	
	$P(J)$	$R(J)$	$P(J)$	$R(J)$
7	43 092.09			42 667.82
8			42 664.93	
9	90.83		64.37	67.15
10	89.84		63.61	
11			62.89	66.31
12	88.10		62.00	65.78
13	87.15		61.23	65.28
14	86.22		60.34	64.71
15	85.18		59.36	63.98
16	84.12		58.40	63.32
17	82.97		57.30	62.47
18	81.80	43 088.51	56.14	61.78
19	80.51		55.00	60.81
20	72.22	86.66	53.74	59.85
21	77.85	85.70	52.43	58.88
22	76.51	84.67	51.12	57.83
23	75.04	83.51	49.71	56.71
24		82.32	48.27	55.61
25		81.11	46.75	54.38
26			45.26	53.12
27		78.34	43.65	51.88
28		77.12	42.01	50.42
29		75.71	40.36	49.03
30		74.17	38.44	47.48
31		72.66	36.59	45.92
32			34.66	44.40
33			32.69	42.76
34			30.72	41.27
35			28.61	39.24
36				
37			23.89	

A(v = 11) level

(11-0) and (11-1) bands have been analyzed. Their heads are well defined and the structure is almost completely resolved. But it must be noted that all the lines are slightly diffuse, which indicates a weak predissociation, and they disappear completely for relatively low values of J. From $J = 0$ to 37, the B-value of the ($v = 11$) level is constant and equal to $0.0746\ \mathrm{cm}^{-1}$. Table I gives the measured wavenumbers for these two bands.

A(v = 12) and unidentified x_1 levels

Two series of lines, lying respectively near 43200 and $42700\ \mathrm{cm}^{-1}$, have been attributed to an unidentified x_1 level, which interacts with $A(v = 12)$. These series may be grouped in branches, which are observed from $R(78)$ and $P(77)$ for the first one, from $R(85)$ and $P(87)$ for the second, and which disappear when the quantum number J of the upper level reaches a value of about 100. Furthermore, in this range of J values, the behaviour of the curve $\frac{R(J) - P(J)}{4(J + 1/2)}$ versus J is characteristic of the occurence of an interaction with another level (Figure 1). Since no line arising from this latter could be observed, deperturbed constants T_0 and B of the perturbed and perturbing levels have been calculated with the help of a method described by Massot,

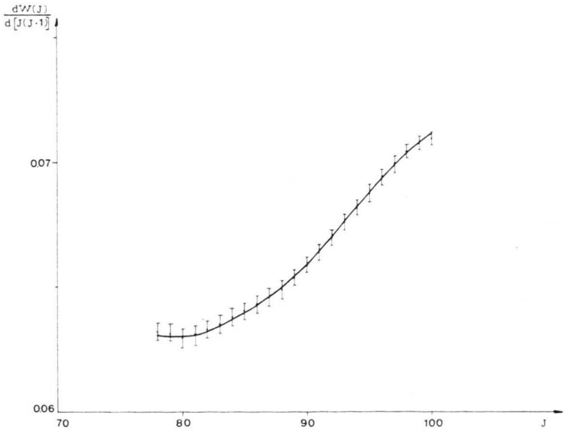

Fig. 1. $B(J) = \mathrm{d}W(J)/\mathrm{d}J(J+1)$ curve for x_1 level.

Goure and Figuet[11], which requires the knowledge of the energies of only the perturbed level. The following values have been found:

$$T_{01} = 43354.6 \pm 1.6\ \text{cm}^{-1},$$
$$B_1 = 0.0764 \pm 0.0001\ \text{cm}^{-1},$$
$$T_{02} = 43469.4 \pm 1.6\ \text{cm}^{-1},$$
$$B_2 = 0.0633 \pm 0.0001\ \text{cm}^{-1}.$$

The interaction parameter H_{12} is $11.7 \pm 0.8\ \text{cm}^{-1}$ if the perturbation is homogeneous (H_{12} independent of J), which is the most probable case.

Comparison of these B-values with that obtained for the $A(v=11)$ level shows that B_1 is of the same magnitude as $B_{A(v=11)}$; furthermore, T_{01} is nearly equal to the value 43350 cm^{-1} previously determined for $T_{0A(v=12)}$. Therefore, there is no doubt that the two interacting levels labelled 1 and 2 are respectively $A(v=12)$ and a level x_1 which has not yet been observed. Figure 1 shows that the recorded rotational lines, which are listed in Table II, belong indeed to this x_1 level.

Table II. Wavenumbers for (x_1-0) and (x_1-1) bands.

J	(x_1-0) $P(J)$	(x_1-0) $R(J)$	(x_1-1) $P(J)$	(x_1-1) $R(J)$
77	43 228.79			
78	22.13	43 242.15		
79	15.99	36.07		
80		29.80		
81	03.24	23.83		
82		17.54		
83	190.51	11.61		
84	83.87	05.43		
85	77.30	199.14		42 774.63
86		92.88		
87	64.06	86.60	42 739.67	62.24
88	57.45	80.35		56.06
89	50.80	74.03	26.13	49.77
90	44.07	67.81	19.83	43.62
91	37.45	61.73	13.31	37.46
92	30.79	55.57	06.61	31.35
93	24.19	49.45	00.07	25.30
94	17.62	43.39	693.54	19.32
95	11.11	37.39	87.09	13.35
96	04.64	31.48	80.72	07.50
97	098.26	25.57	74.36	01.75
98	91.91	19.82	68.11	695.85
99	85.56	13.97	61.92	90.27
100	79.30	08.05	55.61	84.55
101	73.47		49.73	
102	66.89		43.67	

$A(v=13)$ level

The rotational structure of (13-0), (13-1) and (13-2) bands appears only from $R(59)$ and $P(61)$ on. The first three lines of these branches are broad; then the lines are sharp, and become broad again beyond $R(78)$ and $P(80)$. They disappear completely when the quantum number J of the upper level reaches about 85. For all the observed values of J in this level, B is constant (0.0755 cm^{-1}), the centrifugal distortion constant D being 3.8×10^{-8} cm^{-1}. Table III gives the wavenumbers of the measured lines for two of the three analyzed bands.

Table III. Wavenumbers for $(13-0)$ and $(13-1)$ bands of $A \leftarrow X$ (b=broad).

J	$(13-0)$ $P(J)$	$(13-0)$ $R(J)$	$(13-1)$ $P(J)$	$(13-1)$ $R(J)$
59		43 519.64 b		43 094.05
60		16.55 b		90.94
61	43 495.04 b	13.47 b	43 069.45	87.71
62	91.55 b	10.29	65.93	84.76
63	88.02 b	07.07	62.58	81.68
64	84.48	03.77	59.14	78.74
65	80.82	00.47	55.49	75.08
66	77.15	497.06	51.81	71.76
67	73.40	93.63	48.13	68.35
68	69.61	90.12	44.36	64.87
69	65.75	86.57	40.56	61.39
70	61.87	82.99	36.69	57.87
71	57.94	79.35	32.83	54.23
72	53.92	75.65	28.84	50.57
73	49.88	71.86	24.84	46.87
74	45.78	68.07	20.81	43.10
75	41.60	64.22	16.69	39.26
76	37.38	60.25	12.54	35.38
77	33.09	56.30	08.29	31.45
78	28.77	52.28 b	04.01	27.48 b
79	24.41	48.18 b	42 999.63	23.45 b
80		44.02 b	95.32 b	19.32 b
81		39.78 b	90.83 b	15.17 b
82		35.52 b		10.97 b
83		31.23 b	81.82 b	06.78 b
84		26.84 b		02.40 b
85			72.43 b	42 998.27 b
86				93.66 b
87			67.67 b	89.08 b
88				
89				79.69 b

$A(v=14)$ level

(14-0), (14-1), (14-2) and (14-3) bands have been analyzed. Unlike the previously mentioned ones, their structure is quite developed and they are very intense, except (14-2). All the lines are sharp, even for the highest observed values of J, and no variation of the B-value of the upper level is found. This constant has been deduced accurately from the measurements, since a great number of rotational levels are present: $B_{A(v=14)} = 0.07530$ cm^{-1}, with $D = 3.3 \times 10^{-8}$ cm^{-1}. Wavenumbers of the (14-0) and (14-1) lines may be found in Table IV.

$A(v=15)$ level

In bands arising from this level, rotational lines appear from R(49) and P(51) on; the first ones

Table IV. Wavenumbers for (14−0) and (14−1) bands of A ← X.

J	(14−0)		(14−1)	
	P(*J*)	*R*(*J*)	*P*(*J*)	*R*(*J*)
7		43 853.27		
8	43 850.41	52.97		
9	49.77	52.63		43 425.84
10	49.08	52.28	43 422.27	
11	48.38	51.81	21.55	25.02
12	47.56	51.29	20.76	
13	46.72	50.80	19.98	24.00
14	45.85	50.17	19.02	23.43
15	44.91	49.53	18.13	22.75
16	43.88	48.84		22.07
17	42.83	48.07	16.09	21.34
18	41.73	47.24		20.55
19	40.55	46.42	13.81	19.73
20	39.35	45.49	12.60	18.79
21	38.07	44.56	11.40	17.87
22	36.76	43.50	10.09	16.83
23	35.41	42.47	08.74	15.82
24	33.94	41.33	07.32	
25	32.46	40.20	05.85	13.49
26	30.92	38.88	04.33	12.31
27	29.39	37.61	02.73	11.00
28	27.72	36.27		09.70
29	26.00	34.88	399.43	08.33
30	24.29	33.46	97.74	06.91
31	22.47	31.96	95.97	05.43
32	20.60	30.40	94.11	03.93
33	18.74	28.80	92.24	02.33
34	16.75	27.13	9032.	00.69
35	14.73	25.44	88.31	398.97
36	12.71	23.66	86.29	97.24
37	10.58	21.83	84.19	95.48
38	08.41	19.98	82.04	93.62
39	06.18	18.05	79.87	91.74
40	03.91	16.11	77.59	89.78
41	01.58	14.05	75.30	87.77
42	799.19	11.97	72.96	85.70
43	96.76	09.85	70.53	83.66
44	94.29	07.62	68.08	81.44
45	91.74	05.39	65.56	79.25
46	89.09	03.14	63.03	76.96
47	86.46	00.79	60.38	74.67
48	83.76	798 39	57.70	72.28
49	81.02	95.90	55.02	69.82
50	78.20	93.42	52.25	67.39
51	75.33	90.82	49.37	64.86
52	72.41	88.21	46.53	62.26
53	69.44	85.57	43.57	59.64
54	66.45	82.80	40.56	57.02
55	63.40	80.06	37.49	54.23
56	60.26	77.20	34.45	51.51
57	57.07	74.33	31.29	48.54
58	53.84	71.38	28.03	45 62
59	50.56	68.40	24.83	42.74
60	47.22	65.36	21.52	39.62
61	43.75	62.32	18.09	36.66
62	40.40	59.15		33.48
63	36.86	55.96		30.35
64	33.30	52.70		27.22
65	29.70	49.39		23.92
66	26.01	46.02		20.53
67	22.35	42.60		
68	43 718.61	43 739.20		
69	14.78	35.63		
70	11.01	32.12		
71	07.01	28.43		
72	03.04	24.80		
73	699.04	21.04		
74	95.00	17.31		
75	90.90	13.47		
76	86.62	09.58		
77	82.41	05.70		
78	78.15	01.62		
79		697.65		
80		93.43		
81		89.38		
82				
83		80.93		

are broad, then they become sharper and well defined after *R*(63) and *P*(65). The two branches can be observed until *J* ≅ 115 for the upper level, but

Table V. Wavenumbers for (15−0) band of A ← X (b=broad).

J	*P*(*J*)	*R*(*J*)	*J*	*P*(*J*)	*R*(*J*)
49		44 044.16 b	83	43 902.45	43 927.36
50		41.66 b	84	897.78	23.00
51	44 023.67 b	39.08 b	85	93.04	18.56
52	20.41 b	36.40 b	86	88.26	14.03
53	17.66 b	33.66 b	87	83.42	09.51
54	14.68 b	30.97 b	88	78.59	04.93
55	11.51 b	28.11 b	89	73.64	00.28
56	08.37 b	25.27 b	90	68.58	895.55
57	05.15 b	22.36 b	91	63.50	90.79
58	01.83 b	19.35 b	92	58.40	86.00
59	43 998.54 b	16.32 b	93	53.27	81.14
60	95.13 b	13.25 b	94	48.07	76.15
61	91.73 b	10.09 b	95	42.82	71.22
62	88.21 b	06.83 b	96	37.53	66.21
63	84.70 b	03.63	97	32.01	61.13
64	81.10 b	00.38	98	26.64	55.94
65	77.38	43 997.01	99	21.15	50.79
66	73.73	93.59	100	15.56	45.49
67	69.93	90.08	101	09.97	40.20
68	66.12	86.57	102	04.38	34.88
69	62.24	82.99	103	798.66	29.40
70	58.29	79.37	104	92.92	23.91
71	54.35	75.71	105	87.10	18.49
72	50.29	71.96	106	81.22	12.90
73	46.23	68.14	107	75.33	07.24
74	42.08	64.32	108	69.41	01.60
75	37.90	60.41	109	63.40	795.89
76	33.65	56.47	110	57.18	90.09
77	29.34	52.53	111	51.12	84.20
78	24.97	48.43	112	44.93	78.30
79	20.61	44.31	113	38.53	72.41
80	16.16	40.19	114	32.18	66.43
81	11.65	35.94	115	26.03	60.26
82	07.05	31.65	116	19.49	

no broadening of the last lines occurs. The B-value of the $A(v=15)$ level is found to be constant and equal to $0.0749\ \mathrm{cm}^{-1}$, the D constant being of the same magnitude as for $A(v=14)$. Wavenumbers of the (15-0) band are listed in Table V.

A(v = 16) level

Wavenumbers of rotational lines of the (16-0) band are given in Table VI. The structure reveals a number of characteristic features:

Table VI. Wavenumbers for (16 − 0) band of A ← X (b = broad).

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
66		44 240.98 b	94	44 092.27 b	44 119.93 b
67		37.16 b	95		14.69 b
68		33.37	96		09.91 b
69	44 209.29 b	29.56	97		04.70 b
70	05.18	25.72	98		099.56 b
71	00.93	21.82	99		94.11 b
72	196.73	17.96			
73	92.36	13.93			
74	88.05	09.99			
75	83.70	05.92	118		43 984.10
76	79.31	01.85	119		77.59
77	74.85	197.69 b	120	43 935.92	71.32
78	70.40	93.50 b	121	28.99	64.73
79	65.85 b	89.30 b	122	22.15	58.29
80	61.25 b	85.02 b	123	15.22	51.63
81	56.62 b	80.75 b	124	08.32	44.96
82	51.95 b	76.38 b	125	01.28	38.27
83	47.14 b	71.95 b	126	894.25	31.63
84	42.38 b	67.48 b	127	87.14	24.77
85	37.58 b	62.91 b	128	79.99	17.84
86	32.69 b	58.37 b	129	72.68	10.92
87	27.76 b	53.80 b	130	65.49	03.95
88	22.85 b	49.06 b	131	58 32	896.92
89	17.81 b	44.37 b	132	50.80	89.70
90	12.54 b	39.61 b	133		82.63
91	07.39 b	34.75 b	134	34.88	75.39
92	02.41 b		135	28.14	
93	097.29 b	24.98 b	136	20.60	

i) The head does not appear in the spectrograms, and rotational lines are observed only beyond $R(66)$ and $P(69)$. The lines from $R(66)$, $R(67)$ and $P(69)$ are broad; the following ones are sharp, and the lines become broad again from $R(77)$ and $P(79)$ on.

ii) Between $J = 100$ and $J = 119$ concerning the rotational quantum number of the upper level, the lines are very diffuse and no measure can be performed. But for $120 \leqq J \leqq 135$ sharp lines are observed, with intensities decreasing regularly.

iii) The B-value of the upper level cannot be regarded as constant versus J, even if its variation is fairly slow (see Figure 2). As for the x_1 level, deperturbed constants for $A(v=16)$ as well as for the perturbing level, (noted x_2), have been calculated. The following values are obtained:

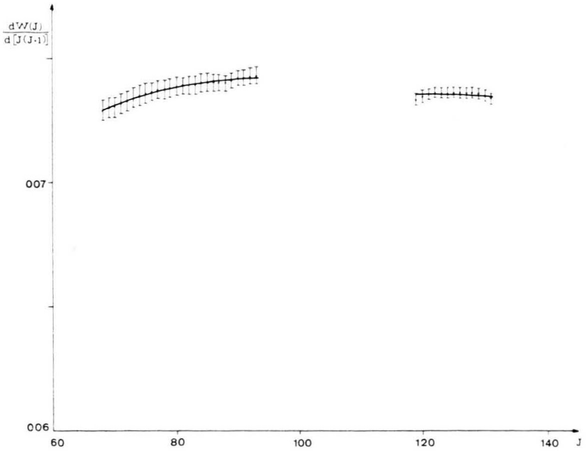

Fig. 2. $B(J) = \mathrm{d}W(J)/\mathrm{d}J(J+1)$ curve for $A(v=16)$ level.

$$T_{0(A,\,v=16)} = 44349.4 \pm 0.1\ \mathrm{cm}^{-1},$$
$$B_{(A,\,v=16)} = 0.0746 \pm 0.0001\ \mathrm{cm}^{-1},$$
$$T_{0x_2} = 44357.8 \pm 0.1\ \mathrm{cm}^{-1},$$
$$B_{x_2} = 0.0732 \pm 0.0001\ \mathrm{cm}^{-1},$$

the interaction parameter being $0.7 \pm 0.1\ \mathrm{cm}^{-1}$ if the interaction is of the homogeneous type. $T_{0(A,\,v=16)}$ is in good accordance with the expected value [2], and T_{0x_2} indicates the occurence of a hitherto unknown level, lying just above $A(v=16)$.

A(v = 17) level

Table VII. Wavenumbers for (17 − 0) band of A ← X.

J	$P(J)$	$R(J)$	J	$P(J)$	$R(J)$
12	44 590.21		30	44 565.69	44 574.31
13	89.33		31	63.74	72.70
14	88.40		32	61.80	71.04
15	87.40		33	59.77	69.29
16	86.34		34	57.69	67.51
17	85.23	44 590.21	35	55.57	65.69
18	84.09	89.33	36	53.38	63.74
19	82.86	88.40	37	51.13	61.80
20	81.58	87.40	38	48.78	59.77
21	80.23	86.34	39	46.43	57.69
22	78.86	85.23	40	44.05	55.57
23	77.40	84.09	41	41.59	53.38
24	75.88	82.86	42	39.04	51.13
25	74.31	81.58	43	36.47	48.78
26	72.70	80.23	44	33.80	46.43
27	71.04	78.86	45	31.12	
28	69.29	77.40	46	28.37	
29	67.51	75.88			

Unlike most of the investigated branches, the head of the (17-0) band is readily observed on the spectrograms. P and R lines, though fsairly diffuse, can be followed up to $R(44)$ and $P(46)$. $P(J)$ and $R(J+5)$ are superposed, as it may be seen in Table VII. No variation of the B-value in the $A(v=17)$ level is observed.

Unidentified x_3 level

Between 42 360 and 42 460 cm^{-1}, two series of lines have been displayed, which may be interpreted as the $R(31)$ to $R(55)$ and $P(33)$ to $P(57)$ components of a transition between an unknown x_3 level and the $(v=0)$ level of the ground state $X\,^1\Sigma_g^+$. No significant variation of the B-constant for the x_3 level is observed within this range of J values ($B=0.0627\ cm^{-1}$), and the T_0 value (42 500.1 cm^{-1}) shows that x_3 lies between $B(v=6)$ and $A(v=9)$ levels. To check this assignment, the rotational structure of the (x_3-1) band has been calculated, and the corresponding lines have been easily recognized on the plates; their wavenumbers are given in Table VIII, together with those for the (x_3-0) band.

Table VIII. Wavenumbers for (x_3-0) and (x_3-1) bands.

J	(x_3-0)		(x_3-1)	
	$P(J)$	$R(J)$	$P(J)$	$R(J)$
31		42 465.10		42 038.55
32				36.12
33	42 451.91	60.07	42 025.41	33.67
34		57.48	22.61	31.09
35	46.14	55.07	19.73	28.86
36	43.57	52.52	16.79	26.00
37	40.20	49.65	13.80	23.26
38	37.20	46.76	10.77	20.45
39	33.96	43.98	07.55	17.64
40	30.72	40.88	04.25	14.53
41	27.49	37.72	01.03	11.48
42	23.93		41 997.59	08.13
43	20.46	31.25	94.04	04.96
44	16.91	28.23	90.72	01.62
45	13.14	24.77	86.90	41 998.59
46	09.75	21.31	83.39	95.14
47	05.81	17.75	79.73	91.64
48	01.86	14.09	75.93	88.05
49	397.98	10.44	71.94	84.35
50	93.95	06.57	67.95	80.62
51	89.85	02.77	63.90	76.79
52	85.63	399.17	59.72	72.82
53	81.38	94.97	55.51	69.08
54		90.84	51.31	64.96
55	72.77	86.50	46.98	60.86
56	68.29		42.54	
57	63.59		37.96	

Discussion

Term values T_0 as well as rotational B and D constants of all the studied vibronic levels are collected in Table IX. The vibrational spacings ΔG for the A state show a more regular behaviour with respect to v than for $v \leqq 9$. Nevertheless, it must be pointed out that $\Delta G(v=11)$ is too high compared to the other values, which shows that $A(v=11)$ is displaced by an interaction not displayed here. Besides, its B-value is smaller than what can be expected from an extrapolation of those belonging to levels ($v=12$ to 16), which decrease regularly with v. Despite of these rather small deviations, the achieved results are of great interest, since they allow the determination of deperturbed vibrational and rotational constants for the A state. A least-squares fitting on T_0 and B values for $v=12$ to 16 leads to:

$$T_{00} = 40145.9\ cm^{-1}\,,$$
$$\omega_e = 262.7\ cm^{-1}\,,$$
$$\omega_e x_e = 0.48\ cm^{-1}\,,$$

Table IX. Term values and rotational constants for the studied levels (in cm^{-1}).

Level	T_0 *	B	$10^8 \times D$
x_3	42 500.11 ± 0.05	0.0627 ± 0.0001	3.6 ± 0.4
$A(v=11)$	43 095.84 ± 0.04	0.0746 ± 0.0001	—
	258.8		
x_1	43 469.4 ± 1.6	0.0633 ± 0.0001	∼12
$A(v=12)$	43 354.6 ± 1.6	0.0764 ± 0.0001	∼12
	250.3		
$A(v=13)$	43 604.94 ± 0.05	0.0755 ± 0.0001	3.8 ± 0.5
	248.59		
$A(v=14)$	43 853.53 ± 0.01	0.07530 ± 0.00009	3.1 ± 0.4
	249.21		
$A(v=15)$	44 102.74 ± 0.04	0.0749 ± 0.0001	3.0 ± 0.6
	246.7		
$A(v=16)$	44 349.4 ± 0.1	0.0746 ± 0.0001	3.1 ± 0.2
	246.9		
x_2	44 357.8 ± 0.1	0.0732 ± 0.0001	—
$A(v=17)$	44 596.33 ± 0.05	0.0734 ± 0.0001	—

* measured above $(v=0)$ level of the ground state $X\,^1\Sigma_g^+$.

$$B_e = 0.0797\ \text{cm}^{-1}\,,$$
$$\alpha_e = 0.00031\ \text{cm}^{-1}\,,$$
$$r_e = 2.374\ \text{Å}\,.$$

Besides, D_e is approximately equal to $3 \times 10^{-8}\ \text{cm}^{-1}$. These results should give reliable initial values for the treatment of the interaction between A and B states.

Two of the three new discovered levels, namely x_3 and x_1, may reasonably be thought of as belonging to the same electronic state, since their B-values are of the same magnitude. This state should be $^1\Sigma_u^+$ or case $c - 0_u^+$. If the vibrational quantum numbers of x_3 and x_1 were v and $v+3$, the ΔG vibrational spacings would be about $320\ \text{cm}^{-1}$, and if they were v and $v+4$, about $240\ \text{cm}^{-1}$, which is the same magnitude as for the A state. No definitive inference can be made for this point, since trials to display intermediate levels between x_3 and x_1 have not been yet successful. On the other hand, it may be noted that x_2 does not belong to the same electronic state as x_1 and x_3, since its B-value is of a quite different magnitude. Hence, two hitherto unknown electronic states are shown to occur in the energy range $40\,000 - 50\,000\ \text{cm}^{-1}$.

A great number of lines, which appear on our plates in the same spectral region as those studied here, are not attributed. Their classification is now in progress. It should lead to a better knowledge of this rather complex portion of the As_2 spectrum. On the other hand, a quite detailed investigation of the broadening of the lines, which has been displayed in most of the vibronic levels investigated here, will be undertaken, in order to explain the predissociation of the A state.

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[1] G. E. Gibson and A. MacFarlane, Phys. Rev. **46**, 1058 [1934].

[2] A. Topouzkhanian and A. M. Sibaï, Spectrochim. Acta **28 A**, 2197 [1972].

[3] R. J. Donovan and P. Strachan, Trans. Far. Soc. **67**, 3407 [1971].

[4] G. M. Almy and G. D. Kinzer, Phys. Rev. **47**, 721 [1935].

[5] G. D. Kinzer and G. M. Almy, Phys. Rev. **52**, 814 [1937].

[6] P. Perdigon and J. D'Incan, Can. J. Phys. **48**, 1140 [1970].

[7] P. Perdigon, F. Martin and J. D'Incan, J. Mol. Spectr. **36**, 341 [1970].

[8] F. Martin, P. Perdigon, and J. D'Incan, J. Mol. Spectr. to be published.

[9] N. A. Finkelstein, Rev. Sci. Instrum. **21**, 509 [1950].

[10] J. H. Callomon and G. G. Chandler, Appl. Opt. **8**, 1133 [1969].

[11] J. N. Massot, J. P. Goure, and J. Figuet, J. Phys. B, Atom. Mol. Phys. **6**, 1308 [1973].