as indicated by the discussion of Fig. 13, is that the cosmic-ray ionization is due to electrical primaries approaching the earth with a threshold energy of about 7.5×10^9 ev. If atmospheric absorption is inadequate to account for this sharply defined threshold, what may be its origin? Vallarta's recent suggestion[17] of a limit imposed by the magnetic field of the sun may supply the answer. Or is there perhaps some sharply defined atmospheric barrier, analogous to a potential barrier, whose seasonal fluctuations may cause the seasonal fluctuations of the cosmic-ray ionization? To these questions, our observations have not supplied the answer.

ACKNOWLEDGMENTS

We wish to thank the Canadian Australasian Steamship Company for permitting us to build the cosmic-ray observatory on the R. M. S. Aorangi, and to use it for the year, the Union Carbide and Carbon Corporation for supplying the batteries required for operating the meter, and the Carnegie Institution of Washington for the use of the cosmic-ray meter. Mrs. Ardis Monk and Mr. Piara Gill have carried through most of the laborious calculations. Professor P. W. Burbidge of Auckland University College and Mr. F. L. Code of Vancouver have given valued help in the adjustments of the meter.

OCTOBER 15, 1937 PHYSICAL REVIEW VOLUME 52

The Emission Spectrum of Diatomic Arsenic. II

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(Received August 13, 1937)

The emission spectrum of diatomic arsenic, previously studied in the interval 2100A to 3700A, has been extended to 7000A. The two prominent systems have been greatly extended so that the ground state of the molecule has been followed to $v=70$, in energy to nearly 0.8 of the heat of dissociation, $D(X)$. $D(X)$ is 3.9 volts by extrapolation and the same value is obtained from analysis of predissociation occurring in the two most prominent systems. Two new systems have been found, one having the same lower state as those previously reported and the other forming a double array. The latter has been tentatively assumed to be due to As_2^+.

INTRODUCTION

A VIBRATIONAL analysis of the emission spectrum of As_2 found between 2100A and 3700A has been given by Almy and Kinzer in a previous report.[1] The spectrum, complex in appearance, consists of three overlapping systems having a common lower state. By careful control of the source consisting of a quartz discharge tube filled with arsenic vapor and heated in an oven or by a flame, it has been possible to extend the spectrum to 7000A (see Fig. 1). A more complete analysis of the reported systems has been made and two additional systems found. A brief abstract of the new results has been included in a recent paper comparing the spectra of elements of the fifth periodic group.[2]

VIBRATIONAL ANALYSIS

The three systems originally reported[1] as lying between 2100A and 3700A have been extended to about 5600A. These are designated as $A\rightarrow X$, $B\rightarrow X$, and $C\rightarrow X$. Another system $D\rightarrow X$ was also found between 3700A and 4500A. The wave numbers of the new band edges with an estimate of the intensities and sharpness of edges of bands in these four systems are given in Table I. The v', v'' arrays for the $A\rightarrow X$, $B\rightarrow X$, and $D\rightarrow X$ systems are shown in Fig. 2 and Fig. 3. System $C\rightarrow X$ consists of a single $(v'=0)$ progression. Averaged values of $\Delta G''(v+\frac{1}{2})$ are the same in these four systems, showing that they have a common lower state, X. In a study of the absorption spectrum of As_2, Gibson and MacFarlane[3] found the $A\rightarrow X$ system well developed in v' progressions, showing that the X state is

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

[2] G. M. Almy, J. Phys. Chem. **41**, 47 (1937). The designation of states in the present paper corresponds to that in reference 1.

[3] G. E. Gibson and A. MacFarlane, Phys. Rev. **46**, 1059 (1934).

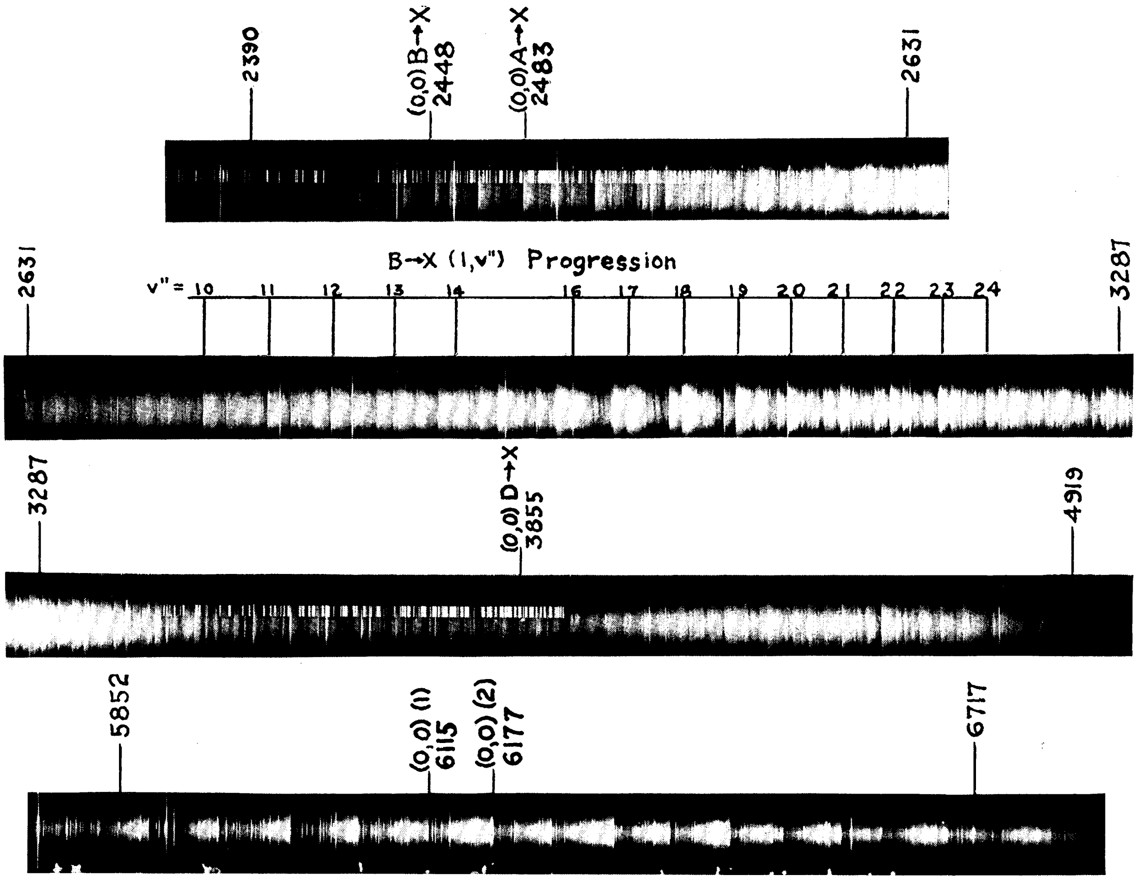

FIG. 1. Spectrum of discharge in arsenic vapor. The position and wave-length of the (0,0) band of each of four well-developed systems is shown, though actually observed only in the red system (bottom strip) due presumably to As_2^+. A part of a strong progression in the $B \rightarrow X$ system is indicated. The $A \rightarrow X$ and $B \rightarrow X$ systems extend with faint bands to 5600A though the reproduction shows them only to about 4900A.

the normal state of the molecule. Values of $\Delta G_X(v)$[4] are plotted in Fig. 4 against $G_X(v)-G_X(0)$, obtained by adding the averaged vibrational intervals. Attempts to obtain an equation for $G_X(v)$ over the entire range of v failed. Plotting $dG_X(v)/d\Delta G_X(v)$ against $\Delta G_X(v)$, as shown in Fig. 5, by the method of Birge,[5] indicated that there may be a sudden small change in the law of force between the two atoms of As_2 at $\Delta G_X(v) = 335\ \mathrm{cm}^{-1}$ or $v=40$. Two equations for $G_X(v)$, one to $v=40$ and the other from $v=41$ to $v=70$, have been calculated by least squares and are:

$v=0$ to $v=40$,

$$G_X(v)=429.44(v+\tfrac{1}{2})-1.120(v+\tfrac{1}{2})^2 +0.005091(v+\tfrac{1}{2})^3-0.00002563(v+\tfrac{1}{2})^4, \quad (1)$$

and, $v=41$ to $v=70$,

$$G_X(v)=-275.28+442.8437(v+\tfrac{1}{2}) -1.39913(v+\tfrac{1}{2})^2+0.00255646(v+\tfrac{1}{2})^3 -0.000025945(v+\tfrac{1}{2})^4. \quad (2)$$

That these equations accurately represent $G_X(v)$ is shown in Table II by the close agreement between values of $G_X(v)$ obtained by summing averaged vibrational intervals and values of $G_X(v)$ calculated from the equations. Following the method outlined in the first report,[1] these equations are used to calculate the wave numbers of the band heads in the $A \rightarrow X$, $B \rightarrow X$, $C \rightarrow X$, and $D \rightarrow X$ systems, giving a check on the assignment of the observed heads. (See obs.-calc. column in Table I.) The apparent perturbations in vibrational levels of the A and B states ob-

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[4] $\Delta G(v)=\frac{1}{2}[G(v+1)-G(v-1)]=\omega_e-2(v+\frac{1}{2})x_e\omega_e$.

[5] R. T. Birge, Trans. Faraday Soc. **25**, 707 (1929).

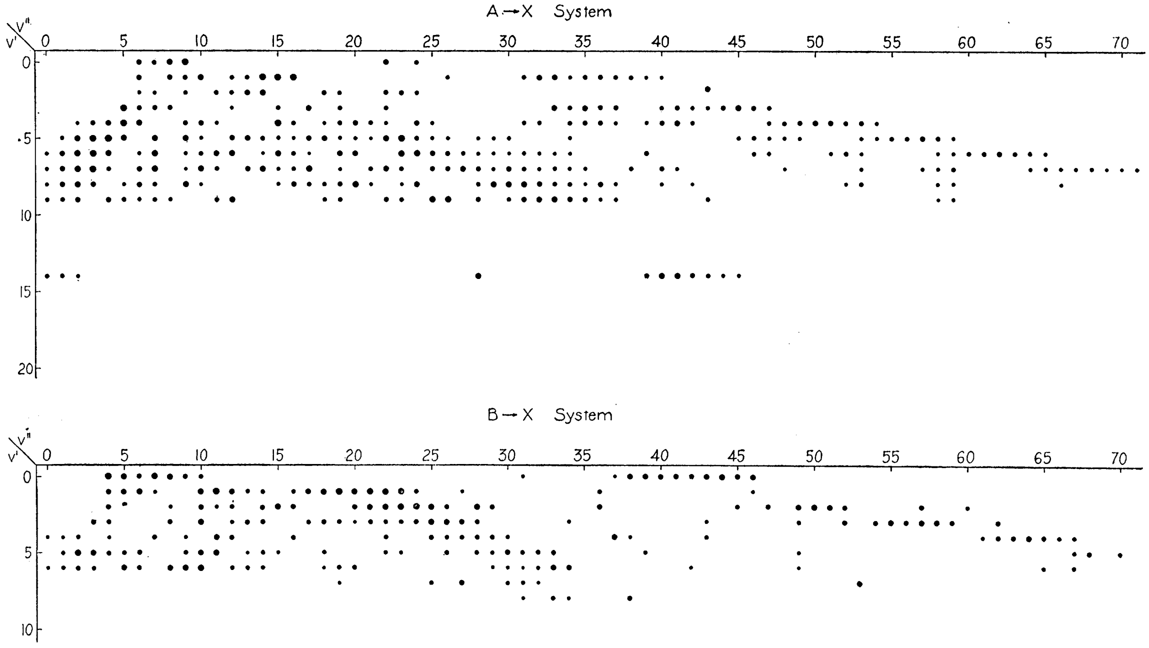

FIG. 2. Observed bands of $A\to X$ and $B\to X$ systems with intensities indicated by the size of dots.

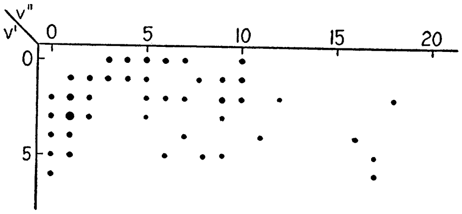

FIG. 3. Observed bands of $D\to X$ system with intensities indicated by size of dots.

served both in absorption[3] and in emission[1] prevents the calculation of any significant equations for $G_A(v)$ and $G_B(v)$. The few v' levels in the $D\to X$ system converge regularly, and by least squares calculation:

$$G_D(v)=337.0(v+\tfrac{1}{2})-0.83(v+\tfrac{1}{2})^2. \tag{3}$$

The bands in the $A\to X$, $B\to X$, $C\to X$, and

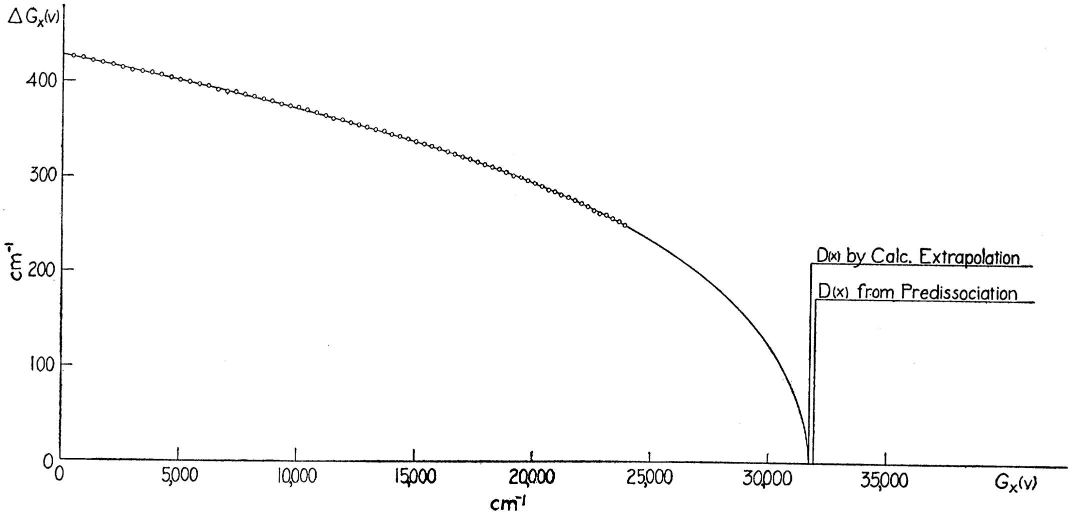

FIG. 4. Plot of $\Delta G_X(v)$ vs. $G_X(v)$ for the normal state of As_2. Vertical lines indicate values of $D(X)$ as calculated by two methods.

TABLE I. *Observed band heads not previously reported. Assignment to system A, B, C, and D and to vibrational quantum numbers. Comparison with calculated wave numbers. Under intensities: s = sharp, d = diffuse, dd = very diffuse.*

System and $v'v''$	Int.	Wave Number	
		(obs.)	(obs.-ca'c.)
A 3,17	3*d*	34034.3	−1.3
A 5,20	0*s*	33454.2	−0.9
A 3,19	1*d*	33257.7	−0.9
B 3,22	1*d*	32770.1	+3.4
A 8,24	2*s*	32688.8	+0.1
B 7,25	1*d*	32609.0	+1.6
A 0,20	3*d*	32142.3	+0.8
A 3,22	1*s*	32113.4	+3.2
A 7,25	2*d*	32072.9	−2.4
B 4,25	2*dd*	31912.1	+2.4
A 2,22	2*s*	31897.1	+2.5
B 7,27	3*s*	31869.6	+0.8
A 6,25	3*d*	31829.6	+0.9
B 5,26	2*s*	31784.9	+0.5
A 2,23	2*dd*	31515.0	−2.1
A 9,28	2*d*	31465.7	−1.5
A 0,22	3*d*	31380.4	+0.9
B 2,25	4*s*	31354.7	−2.4
A 2,24	1*dd*	31142.6	+0.7
B 6,29	0*dd*	30919.9	+0.8
A 4,26			+2.6
A 0,24	1*s*	30627.5	+0.7
A 2,26	0*s*	30400.7	+2.3
B 1,27	0*s*	30331.7	+1.0
A 1,26	1*d*	30146.7	+1.0
A 8,31	5*s*	30129.6	+0.6
B 6,33	3*s*	29492.1	+1.4
B 5,33	2*dd*	29259.7	−0.8
B 6,34	3*s*	29140.0	−0.1
A 4,31	1*s*	29100.0	+2.9
C 0,33			+1.1
C 0,34	0*d*	28752.3	−0.2
A 4,32	1*s*	28746.4	−1.1
B 0,31	0*s*	28637.4	+1.8
A 7,35	1*d*	28478.9	−0.1
B 3,34	0*d*	28392.2	+2.0
A 8,36	3*d*	28373.9	+0.1
A 1,31	1*s*	28330.1	−1.0
A 5,34	0*s*	28318.1	+2.5
B 8,38	2*s*	28186.5	+4.0
A 3,33	3*dd*	28086.5	+2.0
A 4,34	1*s*	28040.5	+0.5
A 8,37	1*dd*	28030.0	+0.6
A 1,32	3*d*	27972.6	+1.1
A 3,34	1*s*	27735.8	+1.9
A 4,35	2*s*	27692.7	−0.6
B 4,37	3*s*	27621.4	+4.2
A 2,34	0*dd*	27521.1	+1.0
A 7,38	2*d*	27448.1	+0.1
B 2,36	2*s*	27415.5	+3.5
A 3,35	3*s*	27387.5	+1.3
A 4,36	2*d*	27344.6	+1.5
B 4,38	0*s*	27288.4	−1.4
A 1,34	3*s*	27269.6	−0.2
B 5,39	1*dd*	27191.9	−1.7
B 1,36	1*dd*	27126.4	+1.1
A 3,36	2*d*	27042.3	−0.3
A 8,40	0*d*	27015.1	+0.1
A 4,37	0*s*	27001.0	+1.6
A 1,35	2*s*	26921.1	−0.6
A 14,45	4*s*	26908.1	+0.6
A 6,39	2*s*	26856.2	−2.8
A 7,40	2*s*	26777.4	−2.4
A 3,37	2*s*	36698.5	+0.8
C 0,40			−0.2
D 6,0	0*s*	26580.9	0.0
A 1,36	2*d*	26573.2	+1.3
B 0,37	0*s*	26539.2	+1.5
A 7,41	0*s*	26439.8	+1.0
B 6,42	0*d*	26422.1	+0.5
A 8,42	0*d*	26350.4	+1.2
A 4,39	0*d*	26323.8	−0.7
A 9,43	2*d*	26281.0	−1.2
D 5,0	1*dd*	26255.3	0.0
A 1,37	2*d*	26232.2	−1.2
B 0,38	3*s*	26199.0	+0.6
A 4,40	2*dd*	25987.3	0.0
D 4,0	2*dd*	25928.5	0.0
A 1,38	2*d*	25891.2	−2.4
B 0,39	3*s*	25862.0	−0.8
D 5,1	3*s*	25828.9	0.0
A 3,40	1*d*	25685.9	+0.6
A 4,41	3*s*	25656.7	−0.1
B 4,43	1*s*	25619.1	−0.1
D 3,0	1*d*	25597.6	+1.4
A 1,39	0*s*	25553.8	−2.3
B 0,40	3*s*	25525.8	−0.4
D 4,1	2*s*	25501.7	0.0
A 3,41	2*d*	25349.4	+1.4
A 4,42	1*d*	25323.0	+0.7
D 2,0	0*d*	25263.8	0.0
A 1,40	0*d*	25214.6	+1.1
B 0,41	3*s*	25189.9	+2.3
D 3,1	2*s*	25167.8	+3.8
A 3,42	1*d*	25022.7	0.0
B 0,42	3*s*	24864.2	0.0
D 3,2	1*s*	24745.5	+0.2
B 3,43	0*s*	24700.3	+0.1
A 3,43	1*s*	24692.6	−0.1
A 5,45	1*d*	24620.8	−0.3
A 6,46	1*d*	24570.0	+0.5
B 0,43	4*d*	24534.3	+0.2
D 1,1	1*d*	24504.2	−0.9
A 2,43	3*s*	24471.6	−1.0
B 2,45	1*d*	24415.9	−2.1
D 2,2			+0.2
A 3,44	2*d*	24367.2	+0.2
A 5,46	2*d*	24309.1	+0.9
A 6,47	1*s*	24249.6	+2.3
B 0,44	4*s*	24209.3	+0.9
A 7,48	0*d*	24183.7	+0.7
B 6,49			+0.6
D 1,2	1*s*	24080.7	+0.9
A 3,45	4*d*	24044.2	−1.2
A 5,47	0*s*	23991.0	+0.4
D 2,3			−0.2
B 5,49	0*d*	23952.0	0.0
B 0,45	3*s*	23884.2	−2.6
B 1,46	0*d*	23812.0	+0.2
B 2,47	2*s*	23777.8	−2.5
A 3,46	2*s*	23723.8	−1.5
A 4,47	1*s*	23710.7	−0.3
A 5,48	0*s*	23676.7	+0.8
D 1,3	2*s*	23658.0	+0.9
B 0,46	3*s*	23566.0	−0.6
D 3,5	1*d*	23485.1	+0.4
B 2,48	2*d*	23465.0	−0.6
B 3,49	1*d*	23438.9	+1.4
A 3,47	1*d*	23408.3	+0.6
A 4,48	1*s*	23395.7	−0.6
A 5,49	0*d*	23361.3	−2.6
D 0,3	1*s*	23321.6	−0.8

Table I (*Continued*).

System and $v'v''$	Int.	Wave Number		System and $v'v''$	Int.	Wave Number	
		(obs.)	(obs.-calc.)			(obs.)	(obs.-calc.)
D 1,4	1*s*	23234.7	−1.9	*D* 1,9	1*s*	21171.2	+3.8
A 8,52	1*d*	23193.9	+0.5	*A* 8,59	1*d*	21150.4	+0.5
B 7,53	4*s*	23183.8	−0.6	*D* 2,10	1*d*	21096.7	+2.3
B 2,49	3*d*	23152.8	−0.8	*B* 3,57	3*s*	21044.0	−0.4
D 2,5			+0.3	*A* 5,57	3*d*	20971.3	+0.5
A 4,49	2*s*	23084.2	−0.1	*A* 6,58	1*s*	20946.7	+0.7
D 4,6	1*dd*	23056.0	0.0	*A* 7,59	2*s*	20908.1	−0.6
A 6,51	1*s*	23009.1	−0.7	*B* 3,58	3*s*	20762.1	+3.8
D 4,7	0*d*	22986.8	−0.2	*A* 5,58	2*s*	20684.4	−0.3
D 0,4	2*s*	22902.6	+0.6	*A* 6,59	1*s*	20662.8	−0.1
A 8,53	2*d*	22892.7	−0.1	*B* 6,61			0.0
D 5,8			+0.7	*D* 3,12	0*d*	20619.6	0.0
B 2,50	4*d*	22844.6	+0.1	*B* 3,59	2*s*	20473.3	−1.9
D 1,5	2*d*	22817.8	−0.3	*D* 0,10	1*s*	20429.5	+3.9
D 6,9			−0.6	*A* 5,59	0*s*	20402.7	+1.1
A 4,50	3*d*	22765.3	+0.1	*A* 6,60	2*s*	20283.2	+0.4
D 2,6	1*s*	22738.1	−0.5	*D* 2,12	0*d*	20287.4	+0.5
A 6,52	2*d*	22706.5	+0.1	*D* 3,13	0*d*	20219.2	0.0
B 6,54	1*s*	22666.1	+0.1	*B* 4,61	1*d*	20186.4	−1.3
A 7,53	1*d*	22650.2	−1.4	*A* 6,61	2*d*	20106.0	−0.4
B 2,51	3*s*	22537.7	−0.5	*B* 2,60	1*d*	19911.6	+0.4
B 3,52	2*d*	22516.6	−2.1	*B* 4,62			−2.1
D 0,5	2*s*	22854.3	+0.6	*A* 6,62	3*s*	19831.6	0.0
A 4,51	3*s*	22468.8	−0.1	*B* 4,63	2*s*	19641.3	−1.2
A 6,53	1*d*	22406.3	+0.5	*B* 3,62			−2.6
D 2,7	1*s*	22326.8	+0.5	*B* 6,65	1*s*	19590.2	+4.6
B 2,52	2*s*	22235.5	+0.7	*A* 6,63	2*d*	19561.1	+0.7
A 4,52	2*s*	22165.3	−0.2	*A* 7,64	0*d*	19538.6	+0.3
D 4,9			−0.7	*B* 4,64	3*s*	19372.6	−2.0
A 5,53	1*s*	22144.6	+0.1	*D* 4,16	0*d*	19362.0	+2.0
D 0,6	1*s*	22068.2	+0.7	*B* 6,66	1*d*	19325.1	+1.2
B 3,54	2*s*	21919.4	−0.9	*D* 5,17	0*d*	19299.4	−2.4
A 4,53	2*s*	21864.5	−0.4	*A* 6,64	1*d*	19293.6	+1.1
A 5,54	1*s*	21846.9	+0.2	*A* 7,65	0*d*	19273.8	+0.4
A 9,58	0*d*	21690.9	+2.0	*A* 8,66	0*d*	19253.4	+0.5
D 0,7	0*s*	21653.0	−0.7	*B* 4,65	2*s*	19109.1	−0.6
B 3,55	3*d*	21625.6	+0.1	*B* 6,67	1*d*	19064.4	−1.0
D 1,8	0*d*	21576.9	+0.2	*A* 6,65	1*s*	19027.5	−0.1
A 4,54	1*d*	21567.2	+0.1	*A* 7,66	1*d*	19011.0	−0.7
A 5,55	2*s*	21551.9	0.0	*B* 4,66	1*d*	18850.4	−2.4
D 2,9	0*d*	21499.0	−2.5	*B* 5,67	1*d*	18833.9	+0.3
A 7,57	1*s*	21498.2	+0.3	*A* 7,67	1*s*	18752.5	−0.7
A 8,58	1*d*	21433.1	+0.1	*B* 4,67	1*d*	18588.4	−1.1
A 9,59	0*d*	21405.8	0.0	*B* 5,68	2*d*	18576.9	−1.2
D 4,11	0*d*	21354.6	+0.7	*A* 7,68	1*s*	18297.6	−0.1
B 3,56	2*d*	21334.8	+1.4	*A* 7,69	0*s*	18245.3	−0.2
A 5,56	2*d*	21260.6	+1.0	*B* 5,70	1*s*	18077.3	+0.4
A 7,58	1*s*	21191.2	−0.6	*A* 7,70	0*s*	17994.9	−1.6
				D 2,18	0*d*	17920.4	+0.2

$D \rightarrow X$ systems (2100A to 5600A) are degraded to the red, but the bands from 5600A to 7000A are degraded to the violet and have sharp edges on the red side. These bands form two arrays, Table III, in which corresponding bands, i.e., bands with identical values of v', v'', are matched in intensity and separated by a nearly constant interval of 162 cm^{-1}. The bands can be represented by the equation:

$$\nu = \begin{matrix}(16359)\\(16197)\end{matrix} + \{336.8(v'+\tfrac{1}{2}) - 1.04(v'+\tfrac{1}{2})^2\} - \{314.8(v''+\tfrac{1}{2}) - 1.25(v''+\tfrac{1}{2})^2\}. \quad (4)$$

It appears improbable that these bands arise from transitions to or between any of the states *A*, *B*, *C*, *D*, or *X*, and the existence of the 162 cm^{-1} interval suggests that the system may be due to a molecule of even multiplicities, probably

TABLE II. *Term values of normal state. In column 3 $G_X(0)$ is subtracted from $G_X(v)$ as calculated from Eq. (1), or Eq. (2).*

v	$G_X(v)$ (ave. obs.)	$G_X(v)$ (calc.)	obs. − calc.
0	0.0	0.0	—
1	428.1	427.4	+0.7
2	853.5	852.7	+0.8
3	1276.8	1275.4	+1.4
4	1696.6	1695.9	+0.7
5	2115.0	2114.1	+0.9
6	2531.0	2530.3	+0.7
7	2944.3	2944.1	+0.2
8	3355.2	3355.8	−0.6
9	3766.4	3765.1	+1.3
10	4171.8	4172.2	−0.4
11	4577.2	4577.2	0.0
12	4979.3	4979.7	−0.4
13	5379.4	5380.1	−0.7
14	5777.5	5778.2	−0.7
15	6173.5	6174.1	−0.6
16	6567.6	6567.7	−0.1
17	6956.7	6956.0	+0.7
18	7346.3	7348.2	−1.9
19	7733.9	7734.8	−0.9
20	8119.0	8119.4	−0.4
21	8501.5	8501.6	−0.1
22	8882.2	8881.4	+0.8
23	9259.5	9258.9	+0.6
24	9634.0	9634.1	−0.1
25	10007.2	10007.1	+0.1
26	10378.1	10377.6	+0.8
27	10746.4	10745.6	+0.8
28	11112.3	11111.5	+0.8
29	11474.2	11474.7	−0.5
30	11835.1	11835.4	−0.3
31	12193.9	12193.8	+0.1
32	12549.8	12549.6	+0.2
33	12903.2	12903.1	+0.1
34	13254.1	13253.9	+0.2
35	13602.7	13602.8	−0.1
36	13948.8	13948.8	0.0
37	14292.3	14292.3	0.0
38	14633.3	14633.4	−0.1
39	14971.7	14971.8	−0.1
40	15307.6	15307.3	+0.3
41	15641.1	15640.8	+0.3
42	15972.1	15971.2	+0.9
43	16299.8	16298.9	+0.9
44	16625.2	16624.6	+0.6
45	16947.4	16946.2	+1.2
46	17267.8	17266.3	+1.5
47	17584.6	17583.9	+0.7
48	17898.6	17898.6	0.0
49	18210.5	18210.6	−0.1
50	18520.1	18519.7	+0.4
51	18826.8	18826.0	+0.8
52	19130.3	19129.4	+0.9
53	19430.9	19430.0	+0.9
54	19728.6	19727.8	+0.8
55	20022.8	20022.6	+0.2
56	20313.9	20314.7	−0.8
57	20603.5	20603.7	−0.2
58	20890.5	20889.8	+0.7
59	21174.0	21172.9	+1.1
60	21453.6	21453.0	+0.6
61	21729.8	21730.2	−0.4
62	22003.4	22004.2	−0.8
63	22274.8	22275.4	−0.6
64	22542.9	22543.3	−0.4
65	22807.6	22808.2	−0.6
66	23069.8	23069.9	−0.1
67	23329.2	23328.4	+0.8
68	23585.2	23583.9	+1.2
69	23836.8	23836.1	+0.7
70	24085.2	24085.1	+0.1

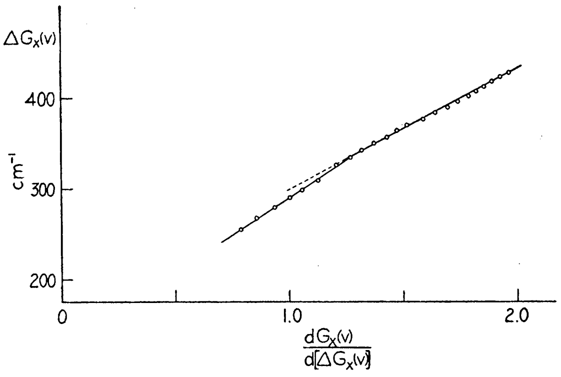

FIG. 5. $dG_X(v)/d[\Delta G_X(v)]$, obtained graphically from Fig. 3, plotted against $\Delta G_X(v)$. The point of intersection of the straight lines shows approximately the position of a change in the law of force between the two atoms in As_2.

$As_2{}^+$,[6] since As_2 should have only odd multiplicities.

It is unlikely that these bands are due to an impurity. When the arsenic used was excited in an arc, the only impurities detected were Fe, Sb, and Bi, and in the discharge the atomic lines of these elements were absent. In the spectrographs of the discharge the only molecular spectra which appeared were those described in this paper. No known spectra of molecules containing oxygen, nitrogen, hydrogen or carbon appeared.

The intensity distribution in the $A \rightarrow X$ and $B \rightarrow X$ systems was described in the first report.[1] The extension of these systems to higher v'' quantum numbers brings out an additional locus of maximum intensity in each system. The suggestion[1] that the intensity distribution in both systems would be improved if the $v'=2$ progression of the $A \rightarrow X$ system were interchanged with the $v'=0$ progression of the $B \rightarrow X$ system is supported by the intensity distribution in the extensions of both systems. If this were done the vibrational intervals in the B state would be more regular but those in the A state less regular. In fact, in such an arrangement the break in ΔG_A (vibrational interval) at $v=2$ is so large that the $v'=0, 1, 2$ progressions seem to form a separate system. The assignments in Fig. 2 have, however, been left as in the previous account. With the present data one cannot with certainty classify the bands of small v' of either system. It is clear, however, that there are at least two systems and

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[6] $N_2{}^+$ bands appear in electrical discharge through nitrogen.

TABLE III. *Superimposed arrays of the bands degraded to the violet showing correspondence in intensity distribution and constant interval of separation, 162 cm^{-1}. Numbers in parentheses give estimated intensities.*

v' \ v''	0		1		2		3		4
0	16348.2(2*s*)	312.6	16035.6(2*s*)	306.7	15728.9(2*s*)	306.5	15422.4(2*s*)		
	163.2		160.3		161.8		160.7		
	16185.0(2*s*)	309.7	15875.3(2*s*)	308.2	15567.1(2*s*)	305.4	15261.7(2*s*)		
	334.3		335.6				334.5		
	335.9		334.8				333.6		
1	16682.5(3*s*)	311.3	16371.2(1*s*)				15756.0(1*s*)	305.6	15450.4(1*s*)
	161.6		161.1				159.8		160.7
	16520.9(3*s*)	310.8	16210.1(0*s*)				15596.2(1*s*)	306.5	15289.7(1*s*)
	331.4		331.4						
	330.2		330.3						
2	17013.9(3*s*)	311.3	16702.6(0*s*)	307.9	16394.1(1*s*)				
	162.8		162.2		161.0				
	16851.1(2*s*)	310.7	16540.4(0*s*)	307.2	16233.1(1*s*)				
	330.0		330.1						
	329.1		329.0						
3	17343.9(1*s*)	311.3	17032.7(2*s*)						
	163.5		163.3						
	17180.2(1*s*)	310.8	16869.4(2*s*)						
	326.8								
			328.8						
4	17670.7(0*s*)		17198.2(1*s*)						
5					17376.7(0*s*)				
					161.5				
					17215.2(0*s*)				
					322.7				
6					17699.4(0*s*)				

that they both exhibit perturbations. The uncertainty with regard to states A and B does not, of course, affect the conclusions drawn with regard to the ground state.

PREDISSOCIATION, HEATS OF DISSOCIATION

The drop in intensity and possibly complete breaking off of rotational structure of the bands with $v'=8$, 9 of the $A\rightarrow X$ system has been ascribed to predissociation at a total energy of about 42,700 cm^{-1} ($\nu_A(9,0)=42{,}579$ cm^{-1}, $\nu_A(10,0)=42{,}837$ cm^{-1}). The state to which radiationless transitions occur has been assumed to be C since $\nu_C(0,0)=42{,}006$, and with only one v' progression in the $C\rightarrow X$ system the potential energy curve of C must be quite shallow. To satisfy these conditions there must be a pair of atomic states having an energy of around 42,700 cm^{-1} (with respect to $G_X(0)$) into which C dissociates and A predissociates. It is probable that state B predissociates into the same atomic pair since the $B\rightarrow X$ system extends only to $v'=8$ with $\nu_B(8,0)=42{,}824$ cm^{-1}, at which point the vibrational interval is still 210 cm^{-1}.

The heat of dissociation in the normal state (X) can be determined in two ways, (1) by extrapolation of the vibrational levels using Eqs. (2) and (2) by analysis of predissociation. The extrapolation using Eq. (2) was carried out by finding the value of v for which $G_X(v)$ is a maximum, i.e., finding the v for which the vibrational intervals vanished. This gives $G_X(v)$(convergence) $=D(X)=31{,}726$ cm^{-1}. Since $G_X(v)$ was observed to be 24,300 cm^{-1}, nearly 0.8 of the energy of dissociation, this extrapolation of $D(X)$ should be fairly reliable.

When using the data of predissociation to calculate $D(X)$ one must assume a particular pair of atomic states at an energy of 42,700 cm^{-1} with respect to $G_X(0)$. Atomic states of As arising from the $4p^3$ configuration are the normal ^4S, ^2D at 10,785 cm^{-1} (center of gravity), and ^2P at 18,493 cm^{-1}. Atomic states from other configurations are too high to come into considerations. With $G_X(v)$ followed to 24,300 cm^{-1} (see Fig. 4) and predissociation occurring at 42,700 cm^{-1}, the energy of the atomic pair at 42,700 cm^{-1} cannot be more than $42{,}700-24{,}300=18{,}400$ cm^{-1} above $^4S+{}^4S$. (As in N_2 and P_2, the ground state of the molecule, undoubtedly $^1\Sigma_g{}^+$, is assumed to arise from the $^4S+{}^4S$ atomic pair.) This restriction excludes all pairs of atomic states except $^4S+{}^2D$ and $^4S+{}^4S$. The latter pair requires that $D(X)$ be 42,700 cm^{-1}, much higher than the extrapolated value. The former pair gives $D(X)=42{,}700-10{,}787=31{,}915$ cm^{-1}, in good agreement with the calculated extrapolated value, 31,726 cm^{-1}, and is taken to be the correct pair. The mean of the two determinations of $D(X)$, by extrapolation and from predissociation, is 3.93 volts.

Figure 6 gives a term scheme showing the relative positions of atomic and molecular levels. By extrapolation, $D(A)$ is roughly 19,000 cm^{-1} and on this basis A is shown dissociating into $^2D+{}^2P$ atoms with $D(A)=20{,}500$ cm^{-1}. State B converges more rapidly than A and is shown dissociating into $^2D+{}^2D$ atoms giving $D(B)=10{,}600$ cm^{-1}. Closer agreement with the extrapolated energy of dissociation (uncertain because of perturbations) is obtained however if B is assumed to dissociate into $^4S+{}^2P$. The D state converges very slowly, and $D(D)$ by linear extrapolation is around 30,000 cm^{-1}, probably much too high. In Fig. 6 D is drawn as dissociating into $^4S+{}^2D$ atoms giving $D(D)=17{,}800$ cm^{-1}. With the assumption that state C causes the predissociation in A and dissociates into $^4S+{}^2D$ atoms at 42,700 cm^{-1}, $D(C)=700$ cm^{-1}. Almy,[2] in making a comparison between As_2 and other molecules of the same group, has made a tentative classification of the molecular states of As_2.

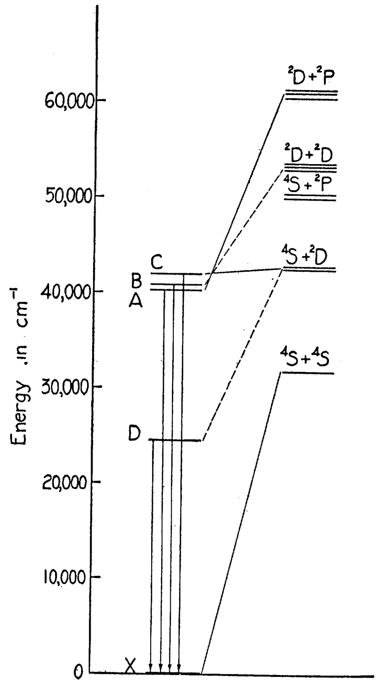

FIG. 6. Term scheme of As_2. Dissociation products indicated by dotted lines are uncertain.

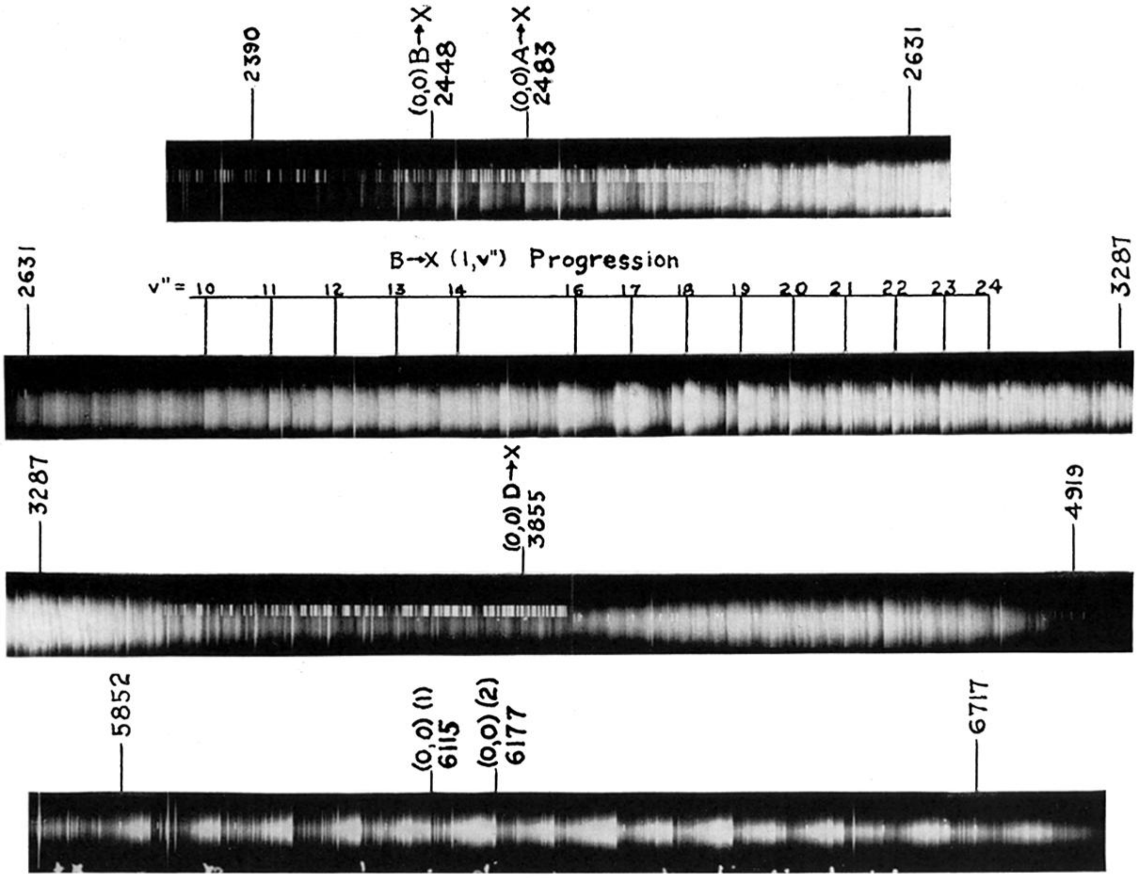

FIG. 1. Spectrum of discharge in arsenic vapor. The position and wave-length of the (0,0) band of each of four well-developed systems is shown, though actually observed only in the red system (bottom strip) due presumably to As_2^+. A part of a strong progression in the $B \to X$ system is indicated. The $A \to X$ and $B \to X$ systems extend with faint bands to 5600A though the reproduction shows them only to about 4900A.