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The Emission Spectrum of Diatomic Arsenic

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The emission spectrum of As_2 consists principally of an extensive group of bands in the ultraviolet, which have been analyzed into two overlapping band systems. These two systems have the same lower state. Their upper states lie at about the same electronic energy, have similar vibrational intervals and perturb one another strongly. In one system, called $A\rightarrow X$, predissociation sets in at two points in the upper state, namely, at $v'=9$ and $v'=14$. In the regions where predissociation is occurring absorption bands appear (for low v'') on the emission plates. The heat of dissociation obtained depends upon what assumption is made as to the pair of atomic states standing at the predissociation energy. If this pair is $^4S+^2D$, $D(X)$ is about 4.0 volts in agreement with the value obtained by extrapolation of the vibrational levels, but if this pair is $^2D+^2D$, as appears to be required by the Kronig rules for perturbations and predissociations, $D(X)$ is 2.6 volts.

INTRODUCTION

THE diatomic molecules of nitrogen, phosphorus, arsenic, antimony and bismuth, form an homologous group, each consisting of two atoms whose lowest state is . . . $p^3\ ^4S$. A comparative study of the spectra of these molecules should provide information as to the variation with mass and type of atomic coupling of the process of molecule formation. The spectrum of each of these molecules has been observed. In the case of N_2,[1, 2] and P_2,[3] the vibrational and rotational structure has been analyzed. A fairly complete vibrational analysis of the absorption spectrum of Bi_2 has been made,[4] and Naudé[5] has published a preliminary report of Sb_2 absorption spectrum. The absorption spectrum of As_2 is the subject of a recent paper by Gibson and MacFarlane.[6] The present paper is an account of the emission spectrum of the same molecule. The emission spectrum contains the system observed in absorption though much more extensively developed and other systems in addition. It yields, therefore, more information about the molecular states than the absorption spectrum.

Gibson and MacFarlane give a good summary of the previous work on the arsenic molecular spectrum as observed in absorption, emission and fluorescence. The only attempt to study the emission spectrum is that of Winand,[7] who used an electrodeless discharge in a tube containing metallic arsenic. The spectrum he obtains is entirely unlike that which we are describing in this paper. In fact, examination of his data makes it practically certain that the bands he reports are largely, if not entirely, due to CO. We have produced Winand's bands by simply heating slightly metallic arsenic in a bulb connected to a discharge tube by several inches of cold glass tubing. A considerable but limited amount of gas is driven from the arsenic and a discharge in this gas discloses the CO bands, attributed by Winand to arsenic. As discussed below we found it necessary to free the arsenic used in obtaining the As_2 bands from impurities by a preliminary heating.

In the present paper only the vibrational analysis of the As_2 bands and conclusions that can be drawn therefrom will be discussed. On the low dispersion plates so far obtained, the rotational structure is in some places partly resolved; we are hoping to secure plates with larger dispersion in order to perform the rotational analysis, which may establish or disprove some of the conclusions tentatively drawn in the following sections

EXPERIMENTAL METHOD

The spectrum was obtained by photographing an electrical discharge in a mixture of arsenic

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[1] See Jevons' *Report on Band-Spectra of Diatomic Molecules*, or Weizel, *Bandenspektren*, for work up to 1931.

[2] G. Herzberg and H. Sponer, Zeits. f. physik. Chemie **B26**, 1 (1934).

[3] G. Herzberg, Ann. d. Physik **15**, 677 (1932).

[4] G. M. Almy and F. M. Sparks, Phys. Rev. **44**, 365 (1933).

[5] S. M. Naudé, Phys. Rev. **45**, 280 (1934).

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

[7] Winand, Bulletin de la classe des sciences, Academie Royale de Belgique (5), **18**, 422 (1932). Results of this work also described in reference 6.

TABLE I. *Observed bands in order of wave number.* Assignment to system *A*, *B*, or *C* and to vibrational quantum numbers. Comparison with calculated wave numbers. Intensities; *s* = sharp, *d* = diffuse, *dd* = very diffuse, *at* = head obscured by atomic line. Bands marked *Abs.* in column 2 were obtained as absorption bands on emission spectrum plates.

System and v′, v″	Int.	Wave Number (obs.)	(obs.−calc.)
A 17,0	Abs.	44597.2	0.0
A 16,0	Abs.	44352.0	0.0
A 15,0	Abs.At	44102.9	−1.8
A 14,0	2s	43854.4	−2.5
A 13,0	Abs.	43603.9	−0.1
A 14,1	2s	43428.4	−0.6
A 12,0	Abs.	43350.2	−0.1
A 13,1	Abs.	43176.5	−0.3
A 11,0	Abs.	43095.3	+0.4
A 14,2	1s	43003.6	−0.2
A 12,1	Abs.	42926.0	+2.7
A 10,0	Abs.	42836.9	−0.3
A 11,1	Abs.	42670.0	+2.3
A 9,0 14,3	2s	42581.5	+2.8 +0.4
A 10,1	Abs.	42412.6	+2.6
B 6,0	0s	42392.5	−1.3
A 8,0	1s	42321.8	−1.0
	1d	42223.0	
A 9,1	2s	42151.0	−0.5
A 7,0	1s	42080.6	−1.0
B 6,1	1s	41965.0	−1.6
B 4,0	0d	41918.0	+0.1
A 8,1	3s	41895.0	−0.6
A 6,0	1d	41833.0	−2.8
A 14,5	2s	41743.6	+1.3
B 5,1	1d	41734.6	−0.2
A 9,2	3s	41726.1	−2.2
	0s	41671.3	
A 7,1	3s	41653.8	−0.6
B 6,2	2d	41543.0	+1.6
B 4,1	0s	41487.8	−2.9
A 8,2	4s	41470.6	+0.2
A 6,1	3s	41407.1	−1.5
B 5,2	4s	41308.1	−1.5
A 7,2	5s	41227.1	−2.1
A 5,1	1dd	41147.5	+0.2
B 6,3	1dd	41118.8	+0.1
B 4,2	1s	41063.6	−0.9
A 8,3	3s	41046.3	−1.4
A 6,2	5s	40981.6	−1.8
A 9,4 B 5,3	3d	40884.3	+1.2 −2.6
A 7,3	6s	40804.9	−1.6
A 5,2	4d	40721.1	−1.0
A 6,3	5s	40559.9	−0.8
A 9,5 B 5,4	2d	40465.3	+0.5 −0.9
A 4,2	0dd	40445.5	+3.0
A 7,4	2dd	40384.5	−1.5
B 3,3	2dd	40371.9	−1.1
A 5,3	5s	40298.6	−0.8
B 6,5	3s	40280.9	+1.0
B 4,4	0d	40223.1	+0.8
A 8,5	1d	40207.6	−1.3
	1d	40177.8	
A 6,4	4d	40139.4	−0.8
A 9,6 B 5,5	1dd	40048.0	−0.8 −0.1
A 4,3	2d	40017.5	−2.0
B 3,4	1dd	39950.0	−2.5
A 5,4	6s	39877.8	−1.1
B 6,6	2s	39863.6	−0.3
A 8,6	3d	39791.7	−1.2
	1d	39758.4	
	2s	39684.7	
B 2,4	2s	39667.9	−0.7
A 9,7 B 5,6	2d	39633.8	−1.2 +1.7
A 4,4	3s	39598.6	−0.4
A 7,6	3s	39551.6	−0.1
A 5,5	4s	39459.7	−0.9
A 8,7 B 1,4	2d	39378.9	−0.2 −1.8
	1s	39342.3	
A 6,6	1dd	39305.7	−0.2
B 2,5	1d	39252.4	+2.1
A 9,8	1dd	39224.6	+1.2
A 4,5	5s	39179.2	−1.5
A 7,7 B 0,4	5s	39137.4	−0.5 −0.0
B 6,8	3s	39037.7	−0.8
B 4,7	2s	38973.9	−0.3
B 1,5	3s	38961.5	−0.9
A 6,7	5d	38891.8	−0.3
A 3,5	5s	38876.3	−1.3
A 4,6	4s	38764.4	−0.3
B 0,5	3d	38718.5	−0.6
A 5,7 B 6,9	4s	38628.7	−2.1 −0.5
	4d	38618.6	
A 8,9	4s	38557.6	−0.6
B 1,6	3s	38545.5	−0.9
	0s	38513.6	
A 3,6	2s	38460.4	−1.3
B 5,9	1d	38398.9	+1.5
A 7,9	0d	38318.9	+1.9
B 0,6	2d	38303.0	−0.1
B 3,8	2dd	38294.1	+1.3
A 2,6	0s	38243.1	−3.0
B 6,10	4s	38219.7	−2.4
B 4,9 A 8,10	0s	38152.0	−1.3 +0.9
B 1,7	0d	38133.5	+0.9
A 6,9	1d	38071.1	−0.1
A 3,7	2s	38047.2	−0.7
B 2,8	0d	38008.3	−0.6
A 9,11	2d	38001.5	−0.7
A 1,6 B 5,10	3s	37990.1	+3.3 −0.2
A 7,10	4s	37909.9	−0.0
B 0,7	5s	37888.4	−0.9
A 2,7	0s	37834.3	+2.0
A 5,9	4s	37810.0	+0.1
A 0,6	3s	37728.8	−2.2
A 6,10	2s	37663.7	−0.4
A 3,8	2s	37635.8	−0.8
B 2,9 A 9,12	4s	37598.3	−1.3 −1.3
B 5,11	4d	37584.7	−0.8
A 4,9	2s	37529.9	−0.1
A 7,11	2s	37504.5	−0.6
B 0,8 B 3,10	3s	37477.7	−0.0 +1.3
B 6,12	1dd	37413.4	−1.3
A 5,10	0d	37402.2	−0.6
B 4,11	3s	37343.6	+2.2
A 0,7	2s	37316.1	−1.1
	2s	37288.3	
A 6,11	4s	37259.2	−0.1
B 2,10	2s	37192.1	−0.4
A 1,8	3s	37169.2	+1.2
A 4,10	3s	37124.5	+1.6
B 0,9	2s	37067.8	−0.6
A 2,9 B 6,13	1d	37011.5	+0.1 −2.8
B 4,12	2s	36942.6	+3.8
A 0,8 B 1,10	4s	36905.2	−0.4 +0.6
A 6,12	4s	36857.6	+0.9
B 2,11 B 5,13	0d	36785.6	−2.1 +3.1
A 1,9	2s	36760.2	+1.5
A 4,11	0s	36719.2	+1.1
A 7,13	3s	36701.6	−0.5
B 3,12	0dd	36669.1	+0.1
B 0,10	1d	36662.1	+0.8
B 6,14	1d	36617.6	+1.4
A 5,12	3s	36595.1	−0.3
A 0,9 B 1,11	5s	36500.1	+3.8 −0.3
B 2,12 B 5,14	1s	36386.0	+0.9 +1.6
A 1,10	3s	36354.0	+2.4
A 7,14	4s	36304.3	+0.3
B 3,13	2s	36268.6	0.0
A 2,11	1d	36198.3	−1.2
A 5,13	3d	36193.7	−1.3
A 8,15	1d	36151.3	+1.9
	1s	36122.5	
B 1,12	3s	36096.6	−0.6
A 6,14	0dd	36061.9	+3.7
A 3,12	0d	36012.0	−0.5
B 5,15	0d	35988.2	−0.4
A 7,15	1d	35909.4	+1.2
B 3,14	1s	35870.9	+0.4
B 6,16	1s	35825.9	−0.9
	1s	35804.7	
A 2,12 A 5,14	2d	35795.9	−1.0 −1.0
A 8,16	3d	35755.4	−0.4
	1s	35719.2	
B 1,13	3s	35696.5	−0.3
A 6,15	4s	35662.1	−0.3
B 2,14	2s	35586.9	+0.3
A 1,12	1s	35545.7	+1.5
A 7,16	2d	35517.5	+2.9
A 4,14			+0.5
	1d	35453.4	
A 5,15	1s	35402.1	+1.0
A 2,13	3d	35397.4	+0.9
A 8,17	2s	35365.0	+0.5
B 4,16	2s	35353.6	+2.7
B 1,14	1s	35299.8	+1.1
A 6,16	2s	35269.0	+0.2
A 9,18	2s	35230.7	−0.6
B 2,15	3s	35190.4	−0.4
	1d	35170.5	
A 1,13	1d	35146.4	+2.6
A 4,15 A 7,17	5s	35122.0	+0.8 −1.3
B 6,18	0d	35048.8	+2.4
A 5,16	0d	35004.4	−3.1
A 2,14	5d	34998.8	+0.4
A 8.18	2d	34975.4	0.0
A 6,17 B 7,19	0d	34880.3	+2.8 0.0
A 9,19	2d	34842.7	−1.9
A 3,15 B 5,18	1d	34815.5	−2.7 +0.9
B 2,16	2s	34797.8	+0.6
A 4,16	2d	34728.5	+0.9
B 3,17	1s	34689.9	+0.1
B 6,19	2d	34659.4	−0.3
A 5,17	3s	34616.8	+0.6
A 2,15	5s	34602.9	+0.3
A 8,19	3d	34587.3	−1.4
	0d	34556.1	
B 1,16	1s	34508.1	−1.2
A 7,19	1s	34346.6	−0.9
B 3,18	2s	34300.6	−0.1
B 6,20	2dd	34274.8	−0.4
	2d	34253.1	
A 5,18	3d	34225.9	−1.2
A 2,16	5s	34208.8	−0.2
A 8,20	5s	34203.0	−1.2
B 1,17	3s	34117.0	−1.0
A 6,19	4d	34101.7	0.0
A 9,21	1dd	34077.1	−0.8
	1d	34006.9	
A 4,18	0d	33947.1	−0.1
B 3,19	1s	33912.4	−1.6
	1s	33849.9	
A 5,19	1s	33839.7	−0.3
A 2,17	4s	33818.7	+1.0
B 1,18	4s	33729.1	+0.2
A 6,20	4s	33717.3	+0.1
A 9,22	3d	33698.0	+0.2
	1s	33621.4	
A 7,21	2s	33581.1	+0.3
A 4,19	2s	33559.2	−1.3
B 3,20	0d	33530.0	+0.5
C 0,21	1d	33502.1	−0.7
A 2,18	2 At	33429.7	+1.1
B 1,19	5s	33342.3	+0.1
A 9,23	2dd	33319.5	−1.2
B 5,22	1dd	33283.3	+1.8
B 2,20	2s	33244.5	−1.1
A 7,22	4s	33201.2	+0.1
A 4,20	3s	33176.8	+0.8
B 3,21	1d	33147.2	−0.1
C 0,22	1dd	33124.6	+0.9
A 5,21	0d	33075.0	+1.3
A 8,23	1d	33065.8	+1.0
A 2,19	1s	33043.4	+1.5
B 4,22	1d	33032.9	−4.5
B 1,20	4 At	32958.9	+1.2
B 5,23	0dd	32904.8	+0.8
B 2,21	3s	32863.0	−0.4
A 7,23	2s	32823.5	−0.1
A 4,21	2s	32794.6	−0.8
A 14,28 C 0,23	4s	32746.7	+0.9 +0.5
A 5,22 A 8,24	4d	32692.3	−1.3 +2.7
	1d	32658.5	
A 6,23 A 9,25 B 1,21	5s	32575.1	−2.7 +2.5 −0.4
B 2,22	4s	32483.2	−0.5
A 4,22	0d	32413.8	−0.3
B 3,23	1d	32391.1	+1.0
A 5,23	5s	32316.3	−0.2
A 9,26 A 6,24	5d	32201.6	−0.5 −1.0
B 1,22	5d	32195.6	−0.2
B 2,23	5s	32106.2	0.0
B 3,24	2s	32016.0	+1.1
A 5,24	2s	31942.2	+0.9
A 9,27 A 6,25	4d	31832.6	−1.5 +2.9
B 1,23	5d	31819.3	+1.0
B 2,24	5s	31731.0	0.0
A 7,26	3s	31705.6	+0.6
A 4,24	3s	31664.3	+2.9
B 3,25	4s	31643.1	+1.1
C 0,26	1d	31626.8	−0.8
A 5,25	1s	31568.2	−0.2
B 4,26	1s	31542.2	+0.9
A 6,26	3d	31460.4	+1.2
B 1,24	3d	31444.0	+0.9
B 2,25	4d	31359.9	+1.8
A 7,27	4s	31338.1	+1.1
	3s	31308.9	
B 3,26	3s	31272.0	+0.5
C 0,27	3s	31258.7	−0.9
A 8,28	2s	31213.2	+0.8
A 5,26	1s	31198.4	+0.5
B 4,27	2s	31172.9	−0.4
A 6,27	2s	31091.4	+0.2
B 5,28	1dd	31052.2	+0.6
B 2,26	2d	30987.7	+0.1
A 7,28	3s	30971.8	+0.6
B 3,27	3s	30905.5	+1.8
C 0,28	3d	30893.6	−0.2
A 8,29	4s	30850.1	+0.9
	1d	30834.2	
B 4,28	2s	30807.4	−0.1
B 7,30	1d	30781.3	+1.2
A 9,30	1d	30744.4	0.0
A 6,28	1s	30726.4	+1.0
B 5,29	1d	30688.9	+0.5
B 8,31	0d	30629.9	−1.3
A 7,29	1s	30609.0	+0.9
B 6,30	0s	30559.4	−0.1
B 3,28	2d	30538.7	+1.0
A 8,30	4s	30489.3	+0.8
	1d	30473.2	
A 5,28	1d	30464.4	+0.3
B 4,29	2s	30443.1	+1.2
B 7,31	1d	30421.9	+0.2
A 9,31	3s	30386.3	+0.3
A 6,29	1s	30363.3	+1.1
	1s	30349.0	
B 5,30	3s	30328.4	+0.7
B 2,28	4s	30255.7	+1.9
A 7,30	3d	30247.2	−0.1
B 6,31	0s	30201.5	+0.4
C 0,30	1dd	30169.9	0.0
A 8,31	4s	30131.1	+1.0
	1d	30117.0	
A 5,29	1dd	30103.7	+2.8
B 4,30	1d	30085.4	+1.8
B 7,32	0dd	30061.6	−4.4
A 9,32	4s	30030.3	0.0
A 6,30	0d	30003.0	+1.5
B 5,31	2s	29968.8	−0.5
B 8,33	2s	29922.2	+0.2
	3s	29909.4	
A 7,31 B 2,29	2s	29888.7	−0.2 −1.9
B 6,32	1d	29845.1	−0.3
A 8,32	3s	29774.7	+0.4
	1d	29759.8	
A 5,30	1dd	29743.8	+3.6
A 9,33	4s	29676.1	−0.7
A 6,31	1s	29643.1	0.0
B 5,32	2s	29612.4	−1.2
B 8,34	0d	29571.9	+0.9
	0d	29551.3	
A 7,32	1s	29533.1	−0.1
	2d	29498.6	
C 0,32	0d	29456.9	+1.1
A 8,33	2s	29420.6	−0.3
A 9,34	3s	29324.5	−1.3
A 6,32	0d	29288.7	+1.3
A 7,33	1s	29181.3	+1.6
A 8,34	2d	29069.6	−0.3
	2d	28995.5	
A 9,35	3d	28976.7	−0.5
A 6,33	0d	28933.9	+0.1
	0d	28910.8	
A 14,39	3s	28885.9	+0.1
A 7,34	1d	28831.1	+2.4
A 8,35	1s	28720.9	−0.4
A 9,36	1d	28631.1	−0.1
A 6,34	0d	28583.2	+0.3
A 14,40	4s	28550.0	0.0
	0s	28497.5	
	0s	28376.2	
A 9,37	1d	28289.8	+0.3
A 14,41	4s	28217.1	+0.3
A 14,42	3s	27886.3	0.0
A 14,43	2s	27558.4	+0.1
A 14,44	1s	27223.0	−0.1

vapor and hydrogen. The discharge tube was constructed so that a continuous flow of hydrogen through it could be maintained when necessary. Its electrodes were hollow nickel cylinders lying along the axis of the discharge column. The spectrum was photographed through a quartz window which was waxed to one end of the discharge tube. In the center of the discharge a side tube containing metallic arsenic was so placed that, by heating it, arsenic vapor could be driven into the hydrogen discharge.

In the procedure used, the tube was exhausted of gas and then a steady flow of hydrogen pumped through it. A discharge in the hydrogen was then maintained and the tube and arsenic heated for a time sufficient to eliminate impurities from the walls and electrodes of the tube as well as the surface impurities such as AsO and carbon compounds from the arsenic. This washing and baking process was essential for eliminating OH, CO, NO and N_2 bands from the spectrum. Finally, the flow of hydrogen was stopped, the pressure in the tube adjusted to between 15 and 40 mm Hg and the arsenic vapor driven into the discharge. It was necessary to heat constantly the discharge column as well as the side tube in order to prevent the arsenic from condensing. The discharge in the arsenic vapor was nearly colorless in contrast to the blue of the discharge in hydrogen.

The bands were most intense at the highest pressure of hydrogen that could be used. The exposure time on a Hilger E1 spectrograph with Eastman I–0 plate was from 10 min. to $1\frac{1}{2}$ hours, the longest time being used in photographing the shortest wavelength portion of the spectrum, because of the loss in the sensitivity of the photographic plates in that region.

The metallic arsenic used in this investigation was tested spectroscopically for impurities and was found to contain traces of Fe, Sb and Bi. The hydrogen used was very carefully dried by passing it through P_2O_5 and then through a liquid air trap. Another liquid air trap was placed between the exhausting oil pump and the discharge tube for collecting any arsine which might have been formed.

A method quite similar to this was used by Pearse[8] in photographing PH bands, but in this investigation no trace of bands was found which could be attributed to AsH.

DESCRIPTION OF BAND SYSTEMS AND VIBRATIONAL ANALYSIS

The bands observed consisted of an extensive complex group of bands degraded to the red between 2100A and 3700A and a few weak bands similarly degraded in the visible violet region. The latter group is not as yet certainly identified or analyzed and the discussion of them will be deferred until they have been more completely studied experimentally. The wave numbers of the band heads of the ultraviolet group are given in Table I, together with an eye estimate of intensity and sharpness of edge, and vibrational quantum assignment. This group has been arranged into two systems, designated *A* and *B* in Table I, which overlap one another almost completely. There is some indication of a weak,

TABLE IIa. *Values of* ΔG_X.

v	ΔG_X (obs.) Ave. from $A\rightarrow X$, $B\rightarrow X$	ΔG_X (calc. from Eq. (1))	Obs.–Calc.	v	ΔG_X (obs.) Ave. from $A\rightarrow X$, $B\rightarrow X$	ΔG_X (calc. from Eq. (1))	Obs.–Calc.
1	428.1	427.2	+0.9	23	377.3	377.5	−0.2
2	425.4	425.0	+0.4	24	374.5	375.2	−0.7
3	423.3	422.7	+0.6	25	373.2	372.9	+0.3
4	419.8	420.5	−0.7	26	370.9	370.5	+0.4
5	418.4	418.3	+0.1	27	368.3	368.0	+0.3
6	416.0	416.0	0.0	28	365.9	365.8	+0.1
7	413.3	413.8	−0.5	29	361.9	363.2	−1.3
8	410.9	411.6	−0.7	30	360.9	360.7	+0.2
9	409.4	409.3	+0.1	31	358.8	358.4	+0.4
10	407.2	407.1	+0.1	32	355.9	355.7	+0.2
11	405.4	404.8	+0.6	33	353.4	353.5	−0.1
12	402.1	402.6	−0.5	34	350.9	351.0	−0.1
13	400.1	400.4	−0.3	35	348.6	348.6	0.0
14	398.1	398.1	0.0	36	346.1	346.0	+0.1
15	396.0	395.8	+0.2	37	343.5*	343.5	0.0
16	394.1	393.6	+0.5	38	341.0*	341.0	0.0
17	389.1	391.3	−2.2	39	338.4*	338.4	0.0
18	389.6	389.1	+0.5	40	335.9	335.8	+0.1
19	387.6	386.7	+0.9	41	333.5	333.2	+0.3
20	385.1	384.5	+0.6	42	331.0	330.5	+0.5
21	382.5	382.2	+0.3	43	327.7	328.0	−0.3
22	380.7	379.7	+1.0	44	325.4	325.2	+0.2

*Smoothed in, not observed.

TABLE IIb. *Term values of states A and B.*

v'	T_A+G_A $(=\nu_A(v',0))$	ΔG_A	T_B+G_B $(=\nu_B(v',0))$	ΔG_B	v'	T_A+G_A $(=\nu_A(v',0))$	ΔG_A
0	40260.9		40833.0		9	42578.7	255.9
1	40523.3	262.4	41076.3	243.3	10	42837.2	258.5
2	40776.0	252.7	41364.2	287.9	11	43094.9	257.7
3	40991.6	215.6	41648.1	283.9	12	43350.5	255.6
4	41294.9	303.3	41917.9	269.8	13	43604.0	253.5
5	41574.5	279.6	42162.0	244.1	14	43856.2	252.2
6	41835.8	361.3	42393.8	231.8	15	44104.7	249.3
7	42081.6	245.8	42614.4	220.6	16	44352.0	247.3
8	42322.8	241.2	42823.9	209.5	17	44597.2	245.2

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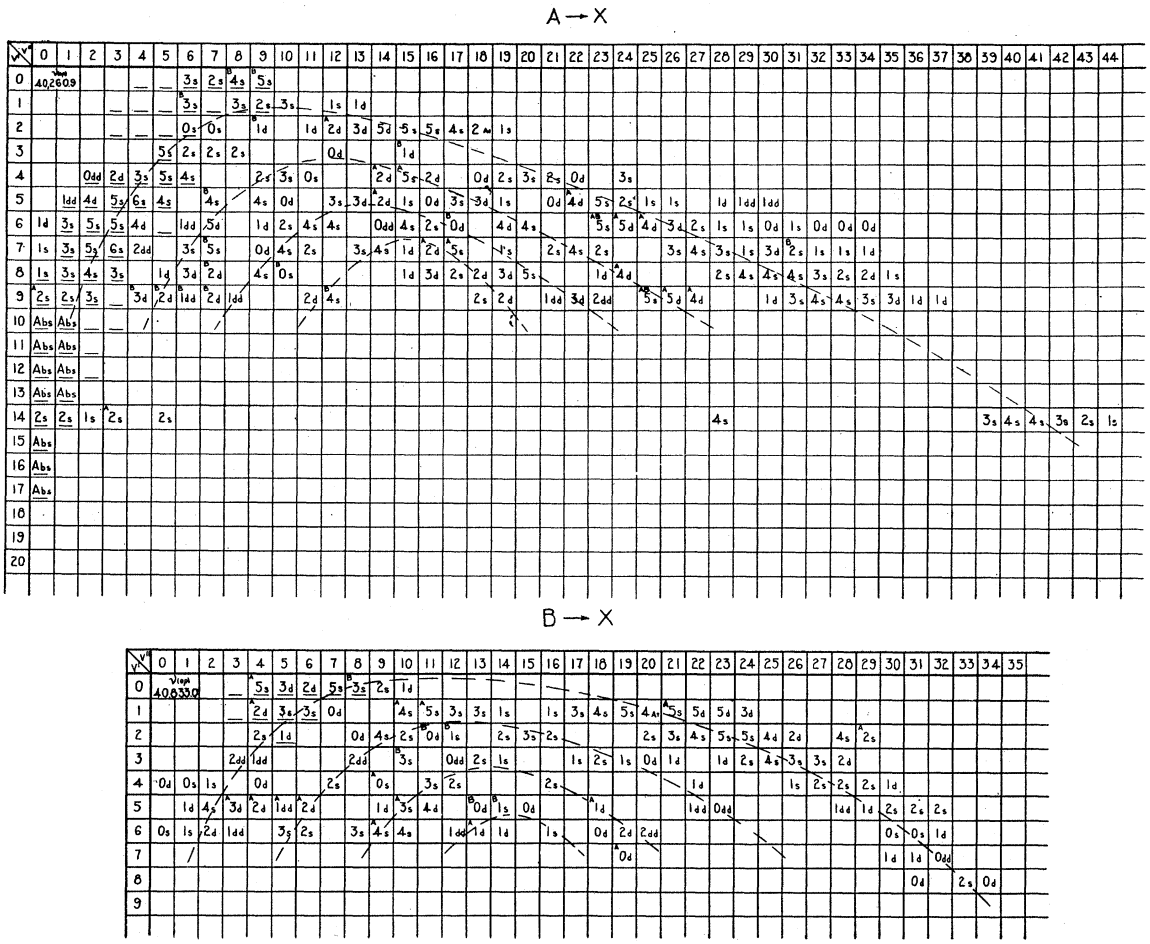
[8] R. W. B. Pearse, Proc. Roy. Soc. **A129**, 328 (1930).



A → X

v′ \ v″	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
0	ν(op) 40,260.9				—	—	3s	2s	^{B}4s	^{B}5s																																			
1				—	—	—	^{B}3s	—	3s	2s	3s		1s	1d																															
2				—	—	—	0s	0s		^{B}1d		1d	^{A}2d	3d	5d	5s	5s	4s	2m	1s																									
3						5s	2s	2s	2s				0d			^{B}1d																													
4			0dd	2d	3s	5s	4s			2s	3s	0s			^{A}2d	^{A}5s	2d		0d	2s	3s	2s	0d		3s																				
5		1dd	4d	5s	6s	4s		^{B}4s		4s	0d		3s	3d	^{A}2d	1s	0d	3s	3d	1s		0d	^{A}4d	5s	2s′	1s	1s		1d	1dd	1dd														
6	1d	3s	5s	5s	4d	—	1dd	5d		1d	2s	4s	4s		0dd	4s	2s	^{B}0d		4d	4s			^{AB}5s	^{A}5d	^{A}4d	3d	2s	1s	1s	0d	1s	0d	0d	0d										
7	1s	3s	5s	6s	2dd		3s	^{B}5s		0d	4s	2s		3s	4s	1d	^{A}2d	^{A}5s		1s		2s	4s	2s			3s	4s	3s	1s	3d	^{B}2s	1s	1s	1d										
8	1s	3s	4s	3s		1d	3d	^{B}2d		4s	^{B}0s					1d	3d	2s	2d	3d	5s			1d	^{A}4d				2s	4s	4s	4s	3s	2s	2d	1s									
9	^{A}2s	2s	3s	—	^{B}3d	^{B}2d	^{B}1dd	^{B}2d	1dd			2d	^{B}4s						2s	2d		1dd	3d	2dd		^{AB}5s	^{A}5d	^{A}4d			1d	3s	4s	4s	3s	3d	1d	1d							
10	Abs	Abs	—	—																																									
11	Abs	Abs	—																																										
12	Abs	Abs	—																																										
13	Abs	Abs																																											
14	2s	2s	1s	^{A}2s		2s																							4s											3s	4s	4s	3s	2s	1s
15	Abs																																												
16	Abs																																												
17	Abs																																												
18																																													
19																																													
20																																													

B → X

v′ \ v″	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
0	ν(op) 40,833.0			—	^{A}5s	3d	2d	5s	^{B}3s	2s	1d																									
1				—	^{A}2d	3s	3s	0d			^{A}4s	^{A}5s	3s	3s	1s		1s	3s	4s	5s	4At	^{A}5s	5d	5d	3d											
2					2s	1d			0d	4s	2s	^{B}0d	^{B}1s		2s	3s	2s				2s	3s	4s	5s	5s	4d	2d		4s	^{A}2s						
3				2dd	1dd				2dd		^{B}3s		0dd	2s	1s			1s	2s	1s	0d	1d		1d	2s	4s	3s	3s	2d							
4	0d	0s	1s		0d			2s		^{A}0s		3s	2s				2s						1d				1s	2s	2s	2s	1d					
5		1d	4s	^{A}3d	^{A}2d	^{A}1dd	^{A}2d			1d	^{A}3s	4d		^{B}0d	^{B}1s	0d			^{A}1d				1dd	0dd					1dd	1d	2s	2s	2s			
6	0s	1s	2d	1dd		3s	2s		3s	^{A}4s	4s		1dd	^{A}1d	1d		1s		0d	2d	2dd										0s	0s	1d			
7																				^{A}0d											1d	1d	0dd			
8																																0d		2s	0d	
9																																				

FIG. 1. Observed bands of $A \rightarrow X$ and $B \rightarrow X$ systems, indicated by intensity symbols. A, B, indicates superposed band in A or B system. Underlined bands observed by Gibson and MacFarlane in absorption. "Abs" indicates observed as absorption bands on emission plates.

third, C system overlapping the long wave end of the A and B systems. The (v', v'') arrays of the A and B systems are shown in Fig. 1 where the presence of a band is indicated by its intensity symbol. The values of $\Delta G''$ obtained from this assignment show that the two strong systems (as well as the C system) have a common lower state, which is undoubtedly the normal state of As_2, since the A system is identical with the absorption spectrum observed by Gibson and MacFarlane. Hereafter, therefore, the common lower state will be designated X and the three systems, $A \rightarrow X$, $B \rightarrow X$, $C \rightarrow X$, respectively. In Table IIa values ΔG_X (averages from $A \rightarrow X$ and $B \rightarrow X$) are listed, together with a comparison with ΔG_X calculated by Eq. (1) (below). In Fig. 2 ΔG_X is plotted against G_X. Through the range of observation the lower state follows a normal course. Values of ΔG_X were fitted to a power series by least squares (Birge-Shea method), from which was obtained for ΔG_X,

$$\Delta G_X = 428.32 - 2.238(v+\tfrac{1}{2}) + 0.001374(v+\tfrac{1}{2})^2 - 0.0001025(v+\tfrac{1}{2})^3. \quad (1)$$

From Eq. (1) G_X was obtained,

$$G_X = 429.44(v+\tfrac{1}{2}) - 1.120(v+\tfrac{1}{2})^2 + 0.0005091(v+\tfrac{1}{2})^3 - 0.00002563(v+\tfrac{1}{2})^4. \quad (2)$$

In every v'' progression the observed values of

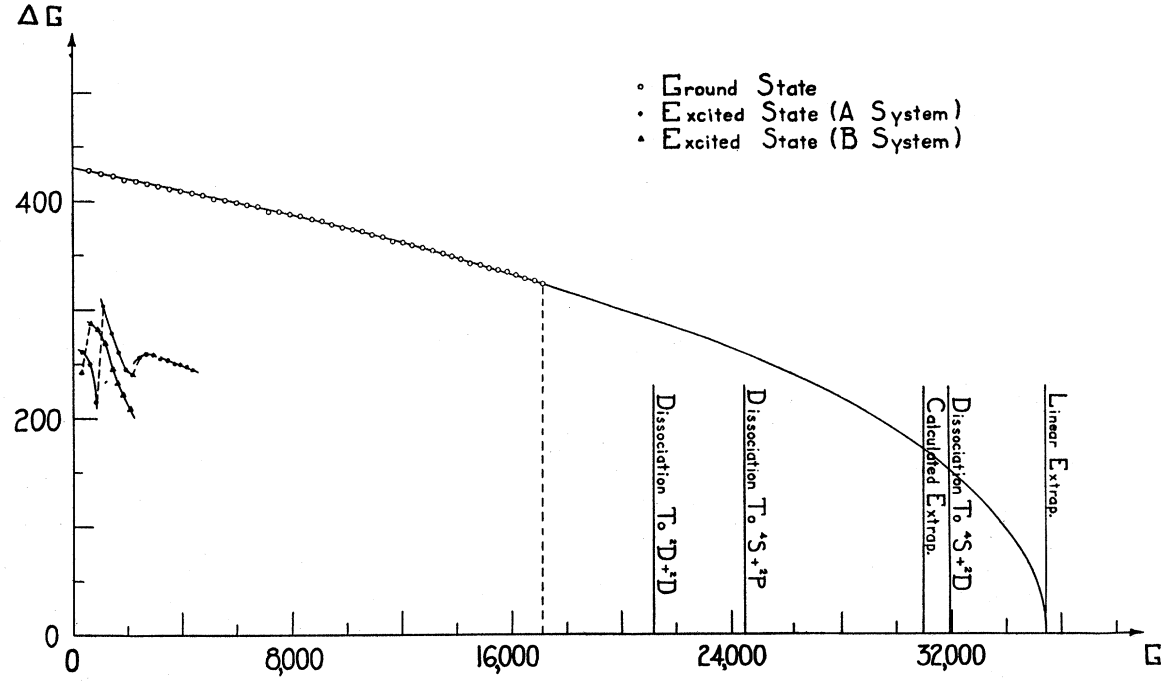


FIG. 2. Plot of ΔG *vs.* G for states X, A, B. Vertical lines indicate values of $D(X)$ as calculated by different methods. For example, the value labeled "Dissociation to ${}^2D+{}^2D$" assumes state B dissociates into ${}^2D+{}^2D$. It is probably the correct $D(X)$.

ΔG_X fit Eq. (1) sufficiently well that the relative v'' numbering is entirely definite; the progressions cannot be shifted with respect to one another even by one. This was important in making the vibrational anslysis, because of the irregular behavior of the intervals in the upper states. In fact, the analysis was made by arranging practically all of the bands into v'' progressions, then fitting these as smoothly as possible into two systems. The absolute numbering of v'' was secured by the absence of any bands of v'' lower than that of the long first v' progression in system $A\rightarrow X$.

States A and B lie at about the same electronic energy, the $A\rightarrow X$ (0,0) head being at 40,260.9 cm^{-1}, the $B\rightarrow X$ (0,0) head at 40,833.0. The two states have also approximately the same vibrational intervals with the result that one set of levels strongly perturbs the other giving erratic series of values of ΔG (Fig. 2). On account of these irregularities no attempt was made to represent states A and B by equations such as Eq. (1). To test the validity of the quantum assignments the following procedure was adopted for comparing observed and calculated wave numbers of the bands. To each observed $\nu(v', v'')$, $G_X(v'')$, as calculated by summing the ΔG_X's calculated from Eq. (1), was added, giving a value of $\nu(v', 0)$. These values were averaged for each v'' progression and are listed in Table IIb, together with the first differences. Finally, the position of each band was calculated according to

$$\nu(v', v'') = \nu(v',0)_{\text{ave}} - G_X(v''). \qquad (3)$$

The difference between observed and calculated values is listed in column 4 of Table I. Although the difference is larger in some cases than the probable experimental error (0.5 to 2 cm^{-1} depending on diffuseness and superposition), the calculation, on the whole, strongly supports the assignment.

Certain band heads of the $A\rightarrow X$ system appeared in absorption on the emission plates. These are marked "Abs" in the intensity column of Table I and in Fig. 1. The wave numbers of these absorption bands were not calculated in the same way as the wave numbers of the emission bands, since only two v' progressions were observed. Since ΔG_A decreases linearly for $v'>9$, the smoothed values of ΔG_A were read from a plot of ΔG_A *vs.* v, and added successively to the calculated positions of (9,0) and (9,1) (emission bands) to give the calculated positions of the first two v' progressions. Since in the v'' progression for which $v'=14$ bands of high v'', as well as low, were observed, the bands (14,0) and (14,1) were calculated by both methods giving values differing by only 0.8 cm^{-1}.

There are several features of intensity distribution among the bands that deserve remark.

(1) As mentioned above, the $A\rightarrow X$ system is the one found in absorption by Gibson and MacFarlane, who reported the bands underlined in Fig. 1. These authors also found a few bands of the $B\rightarrow X$ system (also called B bands by them), noted a fairly constant difference between them and suitably chosen A bands and speculated on the probable association of the two sets of heads into one band system. With the two systems completely developed in emission it seems clear that they are independent.[9] The $B\rightarrow X$ bands observed in absorption are also underlined in Fig. 1.

(2) In each band system there is a fairly definite principal Franck-Condon parabola and several subsidiary parabolas. These are sketched in Fig. 1. This behavior is compatible with the progressive overlapping or "interference" of the wave functions of a given upper vibrational state with those of a progression of lower states. Similar intensity variations were found in the emission spectrum of P_2 by Herzberg.[3]

(3) There is, in the $A\rightarrow X$ system, a pronounced intensity perturbation in the neighborhood of $v'=3$, near which the most violent energy perturbation occurs. At low v'' the intensity minimum along the parabola comes at $v'=2$ with $v'=3$ also quite weak. At higher v'', on the right branch of the parabola, the progression for $v'=2$ is very strong and the minimum is at $v'=3$. The intensity distribution in both systems would be somewhat improved if the strong, A, $v'=2$, progression were interchanged with the B, $v'=0$, progression (see Fig. 1). The wave number displacements are then less pronounced in state B but more so in A. It may be that in this region of greatest perturbation one cannot say definitely that one particular set of rotational levels (associated with a vibrational state) belongs to the A state and the other set of levels to the B state. This difficulty calls for rotational analysis.

(4) Every $A\rightarrow X$ band for which $v'=8$, which is not superposed on another band, shows a very characteristic peculiarity in the partially resolved rotational structure. The head is sharp, and at 15 to 25 cm^{-1} from the head the intensity drops suddenly, beyond which, after a narrow gap, almost resolved but irregularly spaced rotational lines appear. These lines look something like a new head, much weaker than the main head. In Table I several of these subsidiary heads are listed following $A(8,v'')$ heads, but are unassigned.

(5) The $A\rightarrow X$ bands at $v'=9$ which are not obscured by other bands show a sharp drop in intensity at approximately 25 cm^{-1} from the head indicating a break off in the unresolved rotational structure.

(6) $A\rightarrow X$ bands for which $v'=10$, 11, 12, 13 do not appear in emission. But on the emission photographs absorption bands do occur in the first two v' progressions at the proper positions for the emission bands. These progressions were observed by Gibson and MacFarlane. At $v'=14$ a strong emission progression occurs not only for

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[9] According to our classification of the $B\rightarrow X$ bands the lowest vibrational state is the one labeled $v'=2$ by Gibson and MacFarlane. Accurate measurements on four sharp heads making up what is apparently their B, $v'=1$, $v''=4$ to 7 progression cannot fit in that position but must range from $v''=5$ to $v''=8$. Thus restricted it fits best in the $A\rightarrow X$ system with $v'=3$, where it implies, however, a large perturbation in state A (cf. ΔG_A in Table IIb and Fig. 2). Their B (0,3) and B (0,4) at 39,034 and 38,611, may be our B (6,8) and B (6,9) (or possibly A (5,6) and A (5,7)) although we also list an unassigned band at 38,618.6 cm^{-1}. Their assignment of these two bands would isolate them in our square array, while our assignment separates them from their other observed bands. Although our disposal of these last two bands is not as satisfactory as we should like, we assume, because of lack of data pushing it farther down, that the B, $v'=0$, state lies about two vibrational intervals above the A, $v'=0$, state.

The additional evidence against associating each B band with an A band to form a single system may be summarized as follows: (1) There is no regular intensity relation between corresponding A and B bands. Both may be strong, both weak, or one strong and the other weak. (2) Visual inspection of the plates indicates that the association is erroneous. For example, a strong B head, lying to the violet of the associated A head fades out completely before it gets half-way to the A head. (3) To understand the strong perturbations in either system, it is necessary to assume a nearly coincident state with similar vibrational and rotational constants. The other system provides just such a state.

low v'' but for $v''=39$ to 44, in exactly the positions demanded by the intervals, ΔG_X (extrapolated), and by the intensity distribution. The $(14,v'')$ bands have sharp heads but break off suddenly at about 15 cm^{-1} from the head. Finally the first v' progression ($v''=0$) appears again in absorption and can be followed visually to $v'=26$ on a low dispersion plate although the measurements have not been extended beyond $v'=17$ on the Hilger E1 plates.

(7) In the $B \rightarrow X$ system the general intensity distribution is similar to that of the $A \rightarrow X$ system except that the parabolas are shifted somewhat toward larger v''. The system was not pushed beyond $v'=6$ at low v'' or $v'=8$ at high v''. At low v'' where the structure is fairly well resolved the rotational lines of the $B \rightarrow X(6,v'')$ bands appear diffuse. The structure does not appear to break off suddenly.

PERTURBATIONS, PREDISSOCIATION, HEAT OF DISSOCIATION

In this section we shall first draw what conclusions we can without making any assumptions as to the kinds of electronic molecular states involved in the band systems. Then we shall discuss, largely by means of the analogy with P_2, the probable electronic molecular states and their parent atomic states.

The vibrational analysis shows that in state A there are large perturbations in the positions and intensities of the band heads. These perturbations seem to center near $v'=3$ and $v'=7$. In the B state there are large perturbations at about the same total energies, or at $v'=0$ or 1 and $v'=4$ or 5. It is therefore probable that the interaction of states A and B is responsible for the perturbations and that their potential energy curves cross in the regions of greatest displacement. Such a relation of the two curves is shown in Fig. 3. The vibrational levels are shown, as well as the directions of their apparent displacements in the lower regions of great perturbation. It is not clear just what the displacements are at the higher perturbation.

To explain such large perturbations as occur, with whole bands apparently displaced, it seems necessary that the sets of rotational levels of close-lying A and B vibrational levels should very nearly parallel one another, since one of the selection rules is that $\Delta J=0$. Such approximate coincidence of rotational levels is quite likely in As_2 since (1), each A vibrational level lies just below the nearest B level and (2), the rotational constant $B(=h/8\pi c\mu r^2)$ of an A state is probably slightly greater than the rotational B of a B state. This last is true if the relative positions of the minima of the curves assumed in Fig. 3 are correct; it is also consistent with the intensity distribution in the square array (Fig. 1) where, as mentioned above, the Franck-Condon parabolas are shifted to higher v'', for a given v', in B than in A. Therefore the rotational levels of a vibrational state of A should gradually overtake and pass the rotational levels of corresponding J in the nearby vibrational state of B. A rotational analysis is necessary in order to discuss the perturbations with more certainty and completeness.

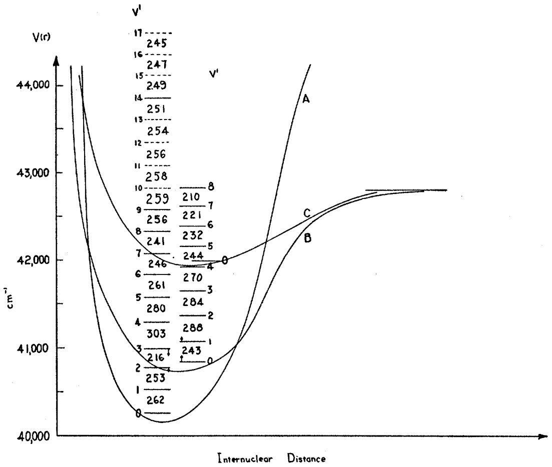

FIG. 3. An assumed set of potential energy curves for states A, B, C, which is consistent with the observed perturbations and predissociations; also vibrational energy levels of these states. Large perturbations are at $v'=3$ and $v'=7$ in state A and at the same total energy in state B; curves are assumed to cross in these regions. Departure of levels from smooth behavior at lower perturbation is indicated by arrows. B dissociates by rotation; A predissociates into B from $v'=9$ to 13, and into C from $v'=14$ on. Dotted levels are upper states of absorption bands on emission plates.

Bands of the A system for which $v'=8$ and 9 show, as described above, a sudden drop in intensity if not a complete break-off in rotational structure. This behavior is undoubtedly due to predissociation at a total energy of about 42,600 cm^{-1} ($\nu_A(9,0)=42{,}579$ cm^{-1}). At about the same or slightly greater energy the B system

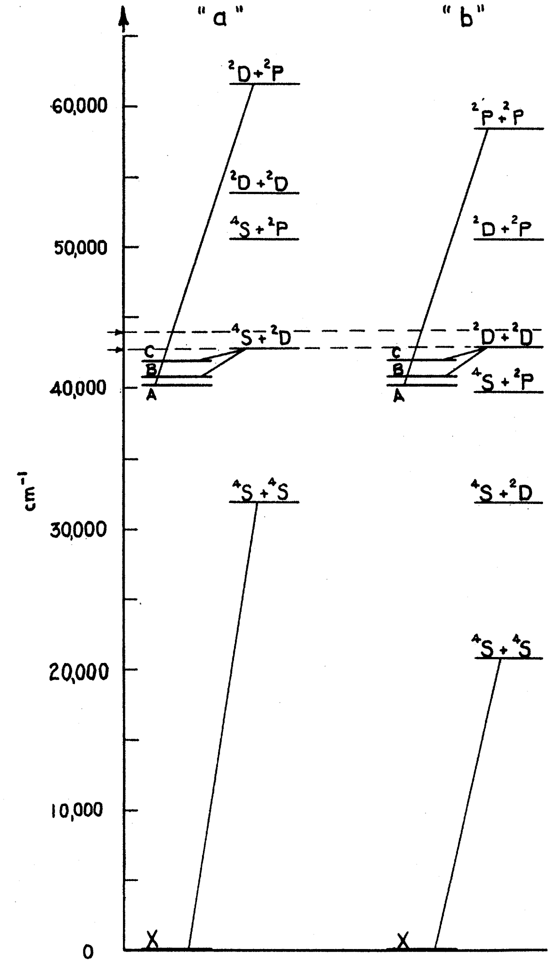

FIG. 4. Term schemes based on assumptions that predissociation occurs at, and B and C dissociate into, atomic states (a) $^4S+^2D$, (b) $^2D+^2D$. The latter is probably correct. Dashed lines indicate predissociation energies.

disappears entirely ($\nu_B(8,0)=42{,}824$ cm^{-1} is the last level observed). This disappearance together with the rapid convergence of the B levels as compared with the A levels and the scarcity of atomic states (Fig. 4) makes it likely that state B dissociates into a pair of atomic states having an energy of about 42,800 cm^{-1}. (It is possible, of course, for stable rotational states to exist having energies somewhat greater than the dissociation energy, as one can see by constructing the effective potential energy curve in which the potential energy is corrected by the rotational kinetic energy.) Finally, the only observed level of the questionable C system has only a little less energy than the predissociation energy of A and the dissociation energy of B. Thus, for example,

$$\nu_c(0,0)=\nu_c(0,22)+G_X(22)$$
$$=33{,}123+8880=42{,}003 \text{ cm}^{-1}.$$

It seems fairly certain, then, that a pair of atomic states stands at about 42,700 cm^{-1} (measured from $v''=0$ of the ground state) and that from these atomic states arise molecular states B and C, as shown in Fig. 3. B dissociates by rotation when its total energy exceeds sufficiently its dissociation energy. From $v'=9$ to $v'=13$ state A predissociates into the continuum of state B. At $v'=14$ A is reappearing in emission, but in the same vibrational level, at not very high J, it predissociates again, this time into C, and continues to go over into C as far as the bands are observed, that is, to $v'=26$. The bands from $v'=10$ to 13 and $v'=15$ to 26 are absorption bands on emission plates, the continuous background being supplied presumably[10] by continuous radiation from transitions $C\rightarrow X$ and $B\rightarrow X$. Finally, it may be remarked that even if the $C\rightarrow X$ bands do not actually represent a third system, there must be at least a repulsive state in the neighborhood to account for the second onset of predissociation in A (at $v'=14$).

We may determine the heat of dissociation of the ground state in two ways, (1) by extrapolating the vibrational levels, and (2) by assuming a particular pair of atomic states at total energy 42,700 cm^{-1}. The extrapolation of the ground state has been done in two ways. First, ΔG_X was plotted against v and the curve extrapolated linearly to $\Delta G_X=0$. The area under the curve gave $D(X)$, equal to 35,500 cm^{-1}. Second, in Eq. (1) the lowest v which made $\Delta G_X=0$ was found by trial and substituted in Eq. (2) to give $G_{X(\text{conv})}=D(X)=31{,}050$ cm^{-1}.[11]

The 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}. Since G_X was followed to 17,260 cm^{-1} and since the predissociation occurs at 42,700, the excitation energy of the pair of atoms at 42,700 cannot

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[10] Some of the continuum may come from the hydrogen in the tube, but probably not much of it, for there is little continuum on the better plates in the region 2500A to 3500A where the H_2 continuum is ordinarily strongest.

[11] In our preliminary report of this work (Phys. Rev. **47**, 199 (1935)), we gave $D(X)=27{,}500$ cm^{-1}, obtained by extrapolation. We have since discovered an error in the calculation of the frequencies of the $v'=14$ progression, which has increased this earlier value considerably.

be greater than 42,700–17,260 = 25,440 cm^{-1}. Thus this pair of atoms must be $^4S+^4S$, $^4S+^2D$, $^4S+^2P$, or $^2D+^2D$. The first pair is ruled out by the fact that it would require that $D(X)$ be 42,700 cm^{-1}, or more than a volt *higher* than the extrapolated value. The other three possibilities give, respectively, for $D(X)$, $42{,}700-10{,}785=31{,}915$ cm^{-1}, $42{,}700-18{,}493=24{,}207$ cm^{-1}, and $42{,}700-21{,}580=21{,}120$ cm^{-1}. The first of these is in good agreement with the extrapolated value obtained above (from Eq. (1)), supporting the conclusion that the rounded figure for $D(X)$ is 4.0 volts. The relative positions of atomic and molecular levels according to this scheme is shown in Fig. 4a.

So far we have made no assumptions as to the kind of molecular states involved. It is worth while to discuss the possible states, for such consideration raises some serious objections to the scheme just proposed (Fig. 4a). We may reasonably assume that, as in N_2 and P_2, the ground state of As_2 is $^1\Sigma_g{}^+$ arising from two normal ^4S As atoms. It is also probable that, as in P_2, the principal system, $A\rightarrow X$, is $^1\Sigma_u{}^+\rightarrow{}^1\Sigma_g{}^+$. Now if state B perturbs A, and if radiationless transitions occur from A to B and A to C, the relations of B and C to A should satisfy the Kronig selection rules for such perturbations or transitions, namely, $\Delta J=0$; $\Delta\Lambda=0,\ \pm1$; $\Delta S=0$; $g\rightarrow g$ or $u\rightarrow u$, $+\rightarrow+$ or $-\rightarrow-$. Of all possible states arising from the three combinations of atoms permitted by energy considerations, namely, $^4S+^2D$, $^4S+^2P$, $^2D+^2D$, there are only two that could interact with a $^1\Sigma_u{}^+$ state (A) without violating the selection rules. These are the two $^1\Pi_u$ states arising from two ^2D atoms; these must be states B and C if the selection rules are to be satisfied.[12] But if B and C dissociate into $^2D+^2D$ at 42,700 cm^{-1} the heat of dissociation of the ground state must be $42{,}700-21{,}580=21{,}120$ cm^{-1}, which is much below the value given and disconcertingly close to the maximum observed G_X (17,260 cm^{-1}), when one considers the nearly linear course of ΔG_X as far as observed. The relative positions of the atomic and molecular states according to this scheme are shown in Fig. 4b.

If $^4S+^2D$ stands at 42,700, $D(X)$ is equal to 31,915 cm^{-1}, in good agreement with the value obtained by extrapolating G_X. This assumption, however, implies the violation of the Kronig rules since this pair, $^4S+^2D$, supplies no singlet states to perturb our assumed $^1\Sigma_u{}^+$ A state. It does provide $^3\Sigma_u{}^+$ and $^3\Pi_u$ states, which break only the rule $\Delta S=0$; such an intersystem perturbation is of course possible. The third possibility for the pair of states at 42,700 cm^{-1} is $^4S+^2P$, giving $D(X)=24{,}207$ cm^{-1}. $^4S+^2P$ yields no singlet states but does yield two triplet states, $^3\Sigma_u{}^-$ and $^3\Pi_u$, which might perturb $^1\Sigma_u{}^+$ though violating the restriction, $\Delta S=0$. In Fig. 2 we have indicated the values of $D(X)$ which would result from the various assumptions as to the products of dissociation of the molecular states.

The situation is very like that found in the case of P_2, by Herzberg.[3] He preferred the choice corresponding to Fig. 4a in which the perturbing state dissociates into $^4S+^2D$, because of the satisfactory agreement then obtained between the values of the heat of dissociation as determined by extrapolation and by predissociation. In P_2 perturbations and predissociation occurred in the system observed but no transitions from the perturbing state were observed and there was no evidence for the presence of a third state such as C. As noted above, the Kronig selection rules are broken if this scheme of states is correct.

For As_2 we are inclined to prefer, in spite of the low value of $D(X)$ which it yields, the situation of states represented in Fig. 4b, in which states B and C dissociate into $^2D+^2D$, for two reasons: (1) It seems very unlikely that such large perturbations should occur between states not satisfying the selection rules, and (2) the recent work on the heat of dissociation of the similar molecule N_2 shows the danger of placing much weight on the extrapolation of ΔG_X. In N_2 the ground state has been followed to more than 5 volts, and extrapolated to 11.5 volts, but recent evidence independent of extrapolation pretty definitely places D very near to 7.3 volts.[2, 13, 14] In As_2 a successful rotational analysis, showing what kind of electronic states A, B and

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[12] Although we have in this discussion assumed, for definiteness, state A to be $^1\Sigma_u{}^+$, the argument requires only that states A, B, C be identified in any order with $^1\Sigma_u{}^+$, $^1\Pi_u$, $^1\Pi_u$.

[13] R. S. Mulliken, Phys. Rev. **46**, 744 (1934).

[14] W. Lozier, Phys. Rev. **45**, 840 (1934).

C are, should aid the fixing of the scheme of levels and thereby the determination of $D(X)$.

State *A* appears to be following a normal course in the latter part of its observed range. Extrapolation gives about 19,000 cm^{-1} as its heat of dissociation, which places its total energy of dissociation at $40,260+19,000=59,260$ cm^{-1}. In both schemes in Fig. 4 it is assumed that this extrapolated value of $D(A)$ is approximately correct in determining which pair of atoms give *A*. In either case, however, if state *A* were assumed to dissociate into the next lower atomic pair, the values of $D(A)$ would not be impossibly low.

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A Note on the Diffraction of Cathode Rays by Single Crystals

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The black and white line parabolas and circles observed in the diffraction patterns of electrons are shown to be a kind of envelope of the family of Kikuchi lines due to a set of co-zonal planes. That the parabolas appear isolated from the generating Kikuchi lines is due to an effect similar to that which in the case of x-rays accounts for the reduction in density observed at the intersection of two lines in the diffraction pattern. The circle is in fact the envelope of a family of parabolas, its appearance isolated from the generating lines being accounted for in the manner mentioned above. It is shown that the circle is the boundary of a region within which occur no Kikuchi lines of a certain set.

1. INTRODUCTION

When a beam of high voltage cathode rays is sent against a surface of a single crystal at a grazing angle and the scattered beam received on a photographic plate, a diffraction pattern, consisting of Kikuchi lines and spots,[1] is obtained. As the envelopes of certain families of these Kikuchi lines there are observed several parabolas and sometimes also circles. In a previous paper,[2] an account of an investigation on the parabolas in the diffraction patterns for rocksalt and calcite was given. The present paper is concerned with a more general investigation of these curves. The energy of the rays used was of the order of 70 kv.

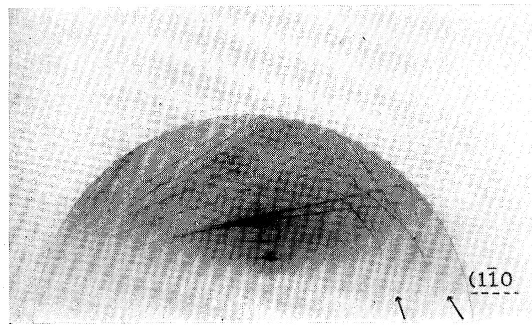

FIG. 1. Zincblende λ=0.043A (75 kv).

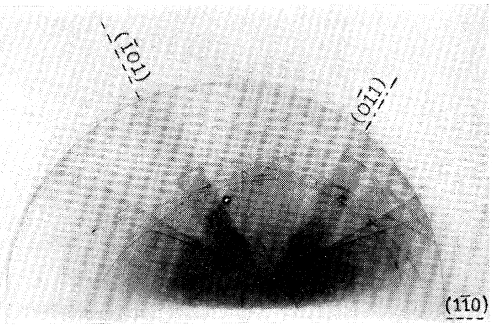

FIG. 2. Zincblende λ=0.044A (71 kv).

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[1] S. Kikuchi, Jap. J. Phys. **5**, 83 (1928–29). S. Nishikawa and S. Kikuchi, Proc. Imp. Acad. Japan **4**, 475 (1928).

[2] K. Shinohara, Sci. Papers, Inst. Phys. and Chem. Res. **20**, 39 (1932).