

The Absorption Spectrum of Diatomic Bismuth

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The absorption spectrum of diatomic bismuth, previously observed but not analyzed, has been obtained by heating pure bismuth in an atmosphere of nitrogen in a carbon-tube furnace at temperatures from 850 to 1500°C and also by heating in an evacuated quartz tube up to 1200°C. Four systems of bands have been photographed and analyzed: (1) the visible system, 4500Å to 7900Å, which consists of over 300 bands which have been arranged in square array extending to $v' = 59$ and $v'' = 55$. (2) The ultraviolet system of 40 bands, 2600Å to 2900Å, which has its lower state in common with (1). (3) The far ultraviolet system, below 2250Å, which is very difficult to obtain and measure but almost certainly has the same lower state as (1) and (2). (4) The violet system, appearing

only at temperatures greater than 1000°C ((1), (2) and (3) appear below 900°C), which consists of 15 sharp band heads, 9 "continuous bands" and a series of closely spaced diffuse bands. Its lower state is the upper state of (1) and its upper state is presumably crossed by a repulsive state which accounts for the diffuse and continuous bands. There is also an extended continuum in the neighborhood of 3100Å. Assuming that the lowest state dissociates into two normal $^4S_{3/2}$ bismuth atoms, a set of potential energy curves for the molecular states has been drawn with satisfactory extrapolation into atomic states in all cases. The estimated heat of dissociation of the lowest state is 1.71 volts.

THERE have been a number of observations^{1, 2, 3, 4, 5, 6} on the absorption spectrum of molecular bismuth but no analysis of any of the band systems has been published.

There have been two studies of the fluorescence of Bi vapor with Hg radiation excitation. The first, by McLennan, Walerstein, and Smith⁷ showed a group of lines excited by $\lambda 4358$ which can be arranged in three series, each with an interval of about 300 cm^{-1} . The second, recently reported by Parys,⁸ shows a series of triplets excited by $\lambda 4358$ with an interval (from triplet to triplet) running from 309 cm^{-1} down and a series of doublets excited by $\lambda 5461$ in which the interval from doublet to doublet is 173 cm^{-1} at the beginning of the series. The correlation between fluorescence and absorption spectra will

be discussed later but it may be remarked here that the interval 173 is exactly that found in absorption for the normal state of Bi_2 whereas the interval 309 is nowhere to be found in the absorption spectrum.

EXPERIMENTAL METHODS

The absorption spectrum was obtained with the use of a carbon-tube resistance furnace. The tube was 127 cm long, had an inside diameter of 2.54 cm and 0.64 cm walls. It was heated electrically over a length of 92 cm by a stepdown transformer with induction-regulator control. The tube was supported inside, but insulated from, a 15.2 cm steel tube which was filled with carborundum for heat insulation. This tube was in turn supported in the center of a 9.1 cm steel tube fitted with end plates on which were mounted quartz windows. These end plates were kept cool by circulating water through coils wrapped around the ends of the 9.1 cm tube. The current was led through water-cooled brass conductors through insulating plugs in the end plates and into the tube by large cylindrical blocks of carbon clamped to the heating tube.

Temperatures were measured with an optical pyrometer. A temperature of 2000°C could be

¹ W. Grotrian, *Zeits. f. Physik* **18**, 169 (1923).

² R. K. Rao, *Proc. Roy. Soc. A* **107**, 760 (1925).

³ A. L. Narayan and R. K. Rao, *Phil. Mag.* **50**, 645 (1925).

⁴ A. L. Narayan and R. K. Rao, *Proc. Phys. Soc. A* **38**, 321 (1926).

⁵ J. G. Frayne and A. W. Smith, *Phil. Mag.* **1**, 732 (1926).

⁶ S. Barratt and A. R. Bonar, *Phil. Mag.* **9**, 519 (1930).

⁷ McLennan, Walerstein and Smith, *Phil. Mag.* **3**, 390 (1927).

⁸ J. Parys, *Zeits. f. Physik* **71**, 807 (1931).

maintained indefinitely and a temperature of 2200°C for an hour or more. The maximum temperature used with bismuth was 1500°C. To reduce the oxidation of the tube nitrogen was flowed slowly through the furnace. To test the possibility that some of the spectra obtained were due to compounds of bismuth and carbon, nitrogen, or other impurities, some exposures, were taken in which the bismuth was placed in an evacuated quartz tube which was inserted in the carbon tube. Temperatures up to 1100°C could be used. No essential difference appeared in the spectrum. With the quartz absorption tube the bands were somewhat sharper and there were therefore rather more of them than could be seen on the plates at atmospheric pressure.

The bismuth used contained, according to the analysis of the manufacturers, Coleman and Bell Company, less than 0.01 percent iron, 0.04 percent silver, 0.01 percent zinc, as impurities. This analysis was checked by photographing with a vacuum arc, containing argon at various pressures, the emission spectrum of a sample of the bismuth. Examination showed silver to be the only impurity detectable.

As sources of continuous radiation, a Point-o-lite lamp and a tungsten ribbon filament lamp were used in the infrared and visible regions. In the near ultraviolet, a tungsten electrode of a Corex-glass "sun lamp" supplied a continuous background which was satisfactory though crossed by strong Hg lines. Through the ultraviolet a water-cooled, quartz, hydrogen discharge tube of a special, compact type, constructed by Kistiakowsky, provided an excellent source of continuous radiation.

For most of the work an E1 Hilger spectrograph with interchangeable glass and quartz parts was used. This instrument was supplemented with a smaller Bausch and Lomb quartz spectrograph and an E185 Hilger (10 foot Littrow mount). Two to four plates of each region were measured. Every plate was measured by each of two observers.

OBSERVED BAND SYSTEMS OF Bi_2

The absorption spectrum of Bi_2 consists of four systems of bands with discrete structure and

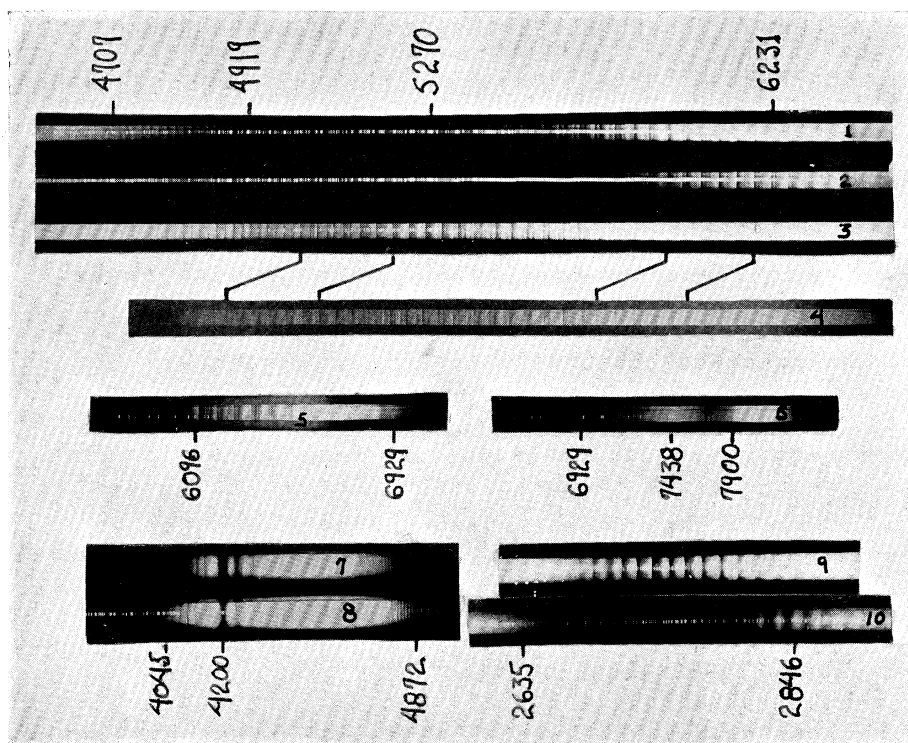
two regions of continuous absorption. Reproductions of three systems showing discrete bands and a region of narrow continuous bands appear in Fig. 1. The fourth discrete system, the far ultraviolet, is not reproduced. These various spectra and their analysis will be discussed in order in this section and in the following section a composite picture of the molecular states will be given by means of a potential energy diagram.

The visible system

The visible-infrared system extends from about 4500Å to 7910Å in which range 304 bands were measured. The visible part of the system appears first at a temperature of about 850°C and can be extended to the infrared by increasing the temperature, as shown in the first 6 photographs in Fig. 1. At the highest temperatures used, about 1500°C, the "red edge" of the system appears. It is, in fact, a double red edge at 7850Å and 7910Å and the separation is that to be expected if each edge is due to a sequence of bands (see Fig. 2). At high temperatures (above 1000°C) the bismuth vapor becomes luminous and a part of this system appears in emission in the red.

The wave numbers of the band edges are listed in Table I. The estimates of intensity are not of much significance except in a narrow range of wave numbers since no attempt was made to compare intensities in widely different regions. Vibrational quantum numbers, also in Table I, were assigned by fitting the observed wave numbers into a square array, testing continually for constant differences. The square array, extending to $v'=59$ and $v''=55$, is shown in Fig. 2. The assignments were easily made except near the violet end where there is some doubt. However, all but 6 bands, each of which was found on only one plate, fitted into the array. The bands fall into the usual parabolic order. The width of each branch of the parabola is quite small, indicating a close adherence to the Franck principle that the internuclear distance does not change much in a transition.

The mean values of the vibrational differences, $\Delta G(v+\frac{1}{2})$, for the various states are shown in Fig. 3. Curves *A* and *B* represent the lower and upper states, respectively, of the visible system. The data from which these curves were plotted

FIG. 1. Reproductions of photographs of Bi_2 band systems.

Exposure number	System	Temperature ($^{\circ}\text{C}$)	Time of exposure	Exposure number	System	Temperature ($^{\circ}\text{C}$)	Time of exposure
1	Visible	1075	40 sec.	6	Visible	1500	80 sec.
2	Visible	1155	15 sec.	7	Violet	1215	5 min.
3	Visible	1155	60 sec.	8	Violet	1215	2 min.
4	Visible	1250	16 min.	9	Ultraviolet	925	60 min.
5	Visible	1350	30 min.	10	Ultraviolet	900	4 min.

were used to obtain the molecular constants. Least squares calculations of $\Delta G'$ and $\Delta G''$ in powers of v' and v'' , respectively, were transformed into the following expression for the wave number of the edge of the (v', v'') band of the system:

$$\begin{aligned} \nu = & 17,742.3 + [132.205(v' + \frac{1}{2}) - 0.30090(v' + \frac{1}{2})^2 \\ & - 0.000,473,9(v' + \frac{1}{2})^3] - [172.708(v'' + \frac{1}{2}) \\ & - 0.322,72(v'' + \frac{1}{2})^2 - 0.002,320,9(v'' + \frac{1}{2})^3 \\ & + 0.000,013,18(v'' + \frac{1}{2})^4]. \quad (1) \end{aligned}$$

As a check on the calculations and on the assignments of v' and v'' , the wave numbers of all the bands were calculated by means of Eq. (1). The last column of Table I gives the difference of the

observed and the calculated values. Following down the "obs.-calc." column one sees that this difference moves slowly up and down through a variation greater than the average fluctuation from band to band. The fluctuation is due to errors of measurement. The reduction of the slow variation is a matter of using more terms in the power series. (A fourth power equation was necessary to represent state *A* as accurately as the cubic represents state *B*.) There is no wide departure, however, and the fit is good enough at the extreme wave numbers so that Eq. (1) is considered adequate to represent the visible system.

It is interesting to compare the expression for the energy of the lower state with the fluorescence

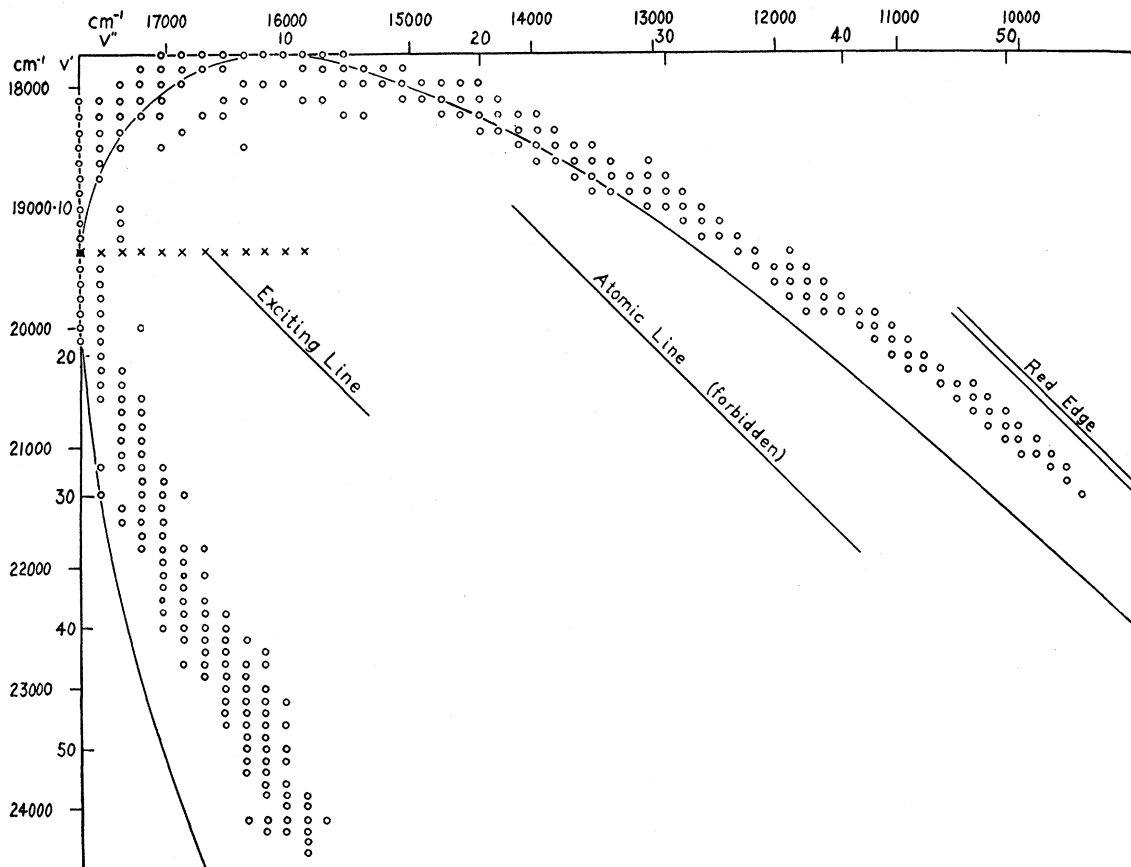


FIG. 2. Square array for the visible system. The circles represent measured band heads, plotted according to wave number. Projection to the upper, or left, axis at 45° gives the wave number of any band head. The red branch of the parabola shows a red edge, that is to say, it turns back on itself (on the wave number scale) beyond the point where measurements were obtained and leads almost certainly to dissociation with an atomic energy difference between upper and lower states of 15,437 cm⁻¹. The next eligible atomic energy is 21,600 cm⁻¹. The red edge appears to be double with a separation approximately equal to ΔG'' (=ΔG' at the red edge) indicating that each edge is formed by a sequence. The solid curve is the Franck-Condon parabola constructed from the potential energy curves in Fig. 4. The crosses indicate the bands in which Parys observed fluorescence. It is rather remarkable that the progression is so much longer than that readily observed in absorption.

series formula given by Parys³:

$$\nu = 19,422.4 - 173.30(v'' + \frac{1}{2}) + 0.324(v'' + \frac{1}{2})^2 - 0.0074(v'' + \frac{1}{2})^3.$$

The agreement is satisfactory. The constant 19,422.4 is not to be compared with the electronic frequency given in Eq. (1) but is the wave number of $v'' = -\frac{1}{2}$ level for a higher v'' progression, probably the one for which $v' = 13$. This probable correlation of the fluorescence series and the absorption bands is indicated by the series of crosses in Fig. 2.

The ultraviolet system

The ultraviolet system extends from 2600A to 2900A. It appears at about the same temperature as the visible system but the absorption is much more intense. The system is not greatly extended with increasing temperatures as is the visible system. Table II gives in square array the wave numbers, intensities and differences of the bands to which quantum numbers could be assigned. *s* indicates a band with a sharp edge, *d* a diffuse edge. The vibrational differences are plotted as crosses in Fig. 3. It is obvious that the lower state is state A, also the lower state of the

TABLE II. *The ultraviolet system.*

v''	0	1	2	3	4	5	6	7						
0	36447.0 d3	171.9	36275.1 d4	171.0	36104.1 d7	172.5	35931.6 d4	171.6	35760.0 d1					
	150.1	149.9		151.0	152.8									
1	36597.1 s9	172.1	36425.0 s6		36082.6 s1	169.8	35912.8 s5	169.2	35743.6 s7	169.0	35574.6 s5	167.0	35407.6 s3	165.5
	146.8			144.2				142.9			142.0			
2	36743.9 d7			36226.8 d2					35717.5 d3	167.9	35549.6 d3	166.0		
	141.5													
3	36885.4 d5													
	141.1													
4	37026.5 d4													
Mean $\Delta G''$	172.0		171.0		172.5		170.7		169.2		169.0		167.4	165.7

v''	8	9	10	11	12	13	Mean $\Delta G'$					
0							150.9					
1	35242.1 s0	170.2	35071.9 d0				143.5					
	141.5		143.8									
2	35383.6 d1	167.9	35215.7 d0				141.4					
			141.3									
3		35357.0 d1	163.6	35193.4 d1	168.2	35025.2 d0						
				(125.0)		132.6	136.8					
4			35318.4? d1	(160.6)	35157.8 s1	160.8	34997.0 s1	162.7	34834.3 s0			
Mean $\Delta G''$	169.0		163.6		168.2		160.8		162.7			

visible system. The upper state, marked *C* in Fig. 3, behaves in an erratic manner. Five vibrational levels are fairly definite, whereupon the bands become diffuse and their positions indefinite. Farther to the violet there are some fairly

TABLE III. *Unassigned bands of the ultraviolet system. Wave-number (cm^{-1}), with intensity in parentheses.*

ν (cm^{-1})	ν (cm^{-1})
37167.1 (s5)	37300.0 (d2)
37340.0 (d3)	37446.2 (d0)
37611.0 (00)	37682.0 (00)
37789.0 (00)	37867.0 (00)

definite edges, listed in Table III, to which no satisfactory assignments could be made. It seems likely that some form of predissociation is occurring in this state but exposures under a wide

variety of conditions of pressure, temperature and exposure time did not give enough data to disclose the process in detail. It may be noted that all bands with $v' = 0$ are diffuse, those with $v' = 1$ are sharp and most of those with v' greater than 1 are diffuse. From the graph in Fig. 3 the constants of state *C* were estimated as $\omega_e = 157 \text{ cm}^{-1}$, $x_e \omega_e = 4.6 \text{ cm}^{-1}$.

The far ultraviolet system

The far ultraviolet system extends from about 2250Å to the violet and appears at a temperature of about 825°C. The bands are diffuse and accurate measurements were impossible. The mean of several measurements of the wave numbers is given in Table IV. What appears to be a v'' progression with the same vibrational interval as state *A* is fairly well developed as

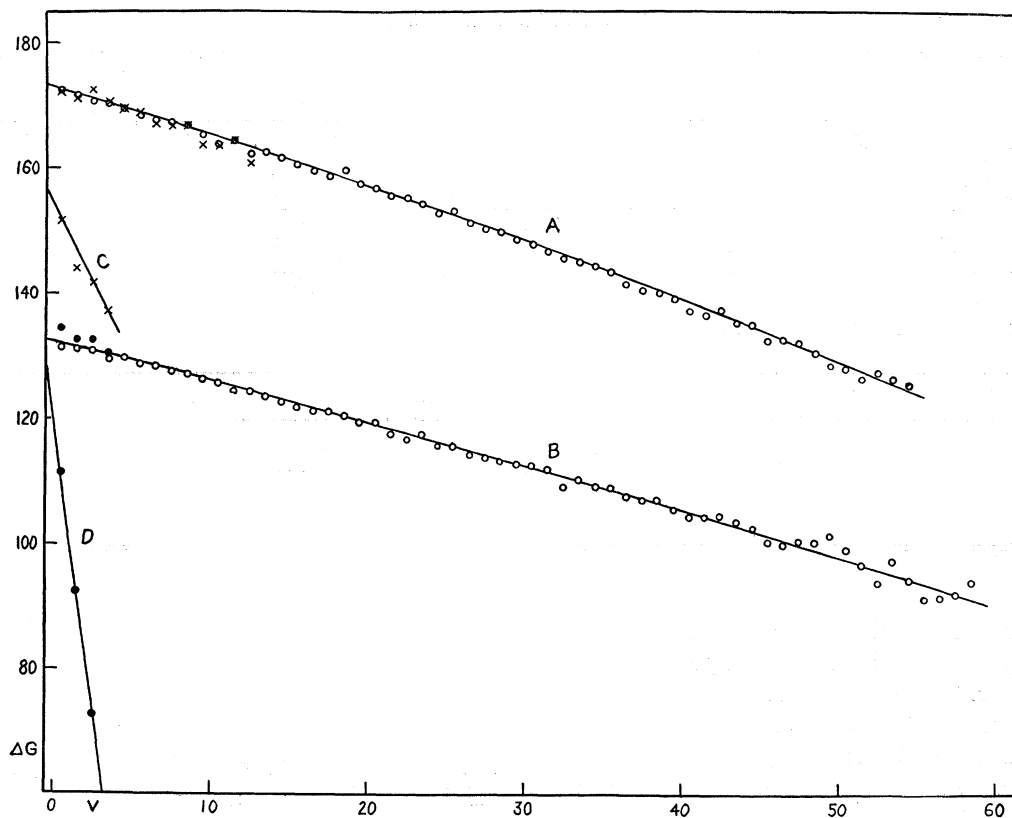


FIG. 3. Mean vibrational level differences of all observed states. Open circles are data from the visible system, crosses from the ultraviolet system, solid circles from the violet system. The intersection at the vertical axis gives ω_e . The areas under the curves, extrapolated to $\Delta G=0$, give the heats of dissociation.

TABLE IV. *The far ultraviolet system.*

Int.	ν (cm^{-1})	$\Delta\nu$	Int.	ν (cm^{-1})	$\Delta\nu$
0	44941		0	46176	164
0	45104	163	1	46522	2×173
0	45164		1	46650	
1	45330	166	1	46806	
1	45498	168	0	46932	
2	45673	175	0	47022	
1	45847	174	0	47090	
1	46012	165	0	47192	

indicated by the column of differences. This, together with the fact that the system appears at low temperatures, indicates that it has the same lower state as the visible and ultraviolet systems. The data are insufficient to justify any statement about the upper vibrational level.

The violet system

The violet system, which appears only at temperatures greater than 1000°C , consists of

three parts, (1) a group of sharp-edged bands extending from 4050\AA to 4200\AA , (2) a series of diffuse "continuous bands" from 4200\AA to 4500\AA and (3) a group of closely spaced bands from 4000\AA to 4050\AA so weak and diffuse that no adequate measurements could be made. The wave numbers of the discrete bands are arranged in square array in Table V. The lower state of this system is state *B*, the upper state of the visible system. This is shown by the close agreement of the vibrational interval (see the solid circles on Fig. 3, state *B*). It is clearly possible, moreover, to put many molecules into state *B* by thermal excitation since the visible bands (*B*→*A*) appear in emission at temperatures greater than 1000°C . The upper state of this system appears to be a very rapidly converging series of vibrational levels with $\omega_e=129\text{ cm}^{-1}$, $x_e\omega_e=9.7\text{ cm}^{-1}$ as shown by curve *D* in Fig. 3.

TABLE V. *The violet system.*

ν''	0		1		2		3		4		Mean $\Delta G'$
0	24485.3	134.6	24350.7	132.7	24218.0	132.6	24085.4	130.4	23955.0		
	s1		s4		s5		s4		s1		
	110.8		111.7		109.2		111.7				110.9
1	24596.1	133.7	24462.4	135.2	24327.2	130.1	24197.1				
	s2		s1		00		d0				
	92.5		90.3				94.1				92.3
2	24688.6	135.9	24552.7				24291.2				
	s1		d0				d0				
	72.2		74.8				71.0				72.7
3	24760.8	133.3	24627.5				24362.2				
	00		00				00				
Mean $\Delta G''$	134.4		134.0		131.4		130.4				
<i>Continuous Bands</i>											
			22069		22654		23350				
			22246		22877		23578				
			22440		23104		23797				

Moreover, it breaks off rather suddenly, indicating predissociation into some perturbing state lying near. The existence of such a state is also suggested by the series of continuous bands (wave numbers in Table V) lying to the red of the discrete bands. These continuous bands are intense, rather narrow, symmetrical, regions of continuous absorption (see reproductions 7 and 8, Fig. 1). The intensity decreases rapidly as the series progresses to the red. An explanation of the origin of these bands will be given in the section on potential energy curves.

Continuous absorption

In the ultraviolet is a short series of continuous bands whose appearance is similar to that of the continuous bands of the violet system just described. Only 3 bands are observed, with wave numbers 40115, 40275 and 40467 cm^{-1} .

In addition to the continuous bands just described there is a region of continuous absorption which appears to be independent of any of the band systems. It appears, quite faint, at about 900°C with a maximum absorption at 3120Å. At 1000°C it extends roughly from 2950 to 3350Å. At 1050°C it overlaps the ultraviolet system and complete absorption occurs from 2600Å to 3400Å. At 1215°C it extends almost to the violet system as can be seen in reproductions 7 and 8 in Fig. 1.

POTENTIAL ENERGY CURVES AND HEATS OF DISSOCIATION

Although there are not enough data available to plot accurately the potential energy curves, it is worth while to go as far as possible in obtaining such a picture of the collection of molecular states. For this purpose the Morse expression for potential energy has been used. It may be stated

$$U(r) = E_e + D_e [1 - e^{-a(r-r_e)}]^2,$$

where E_e is the electronic energy, D_e the heat of dissociation, r_e the equilibrium internuclear distance and $a = [(8\pi^2\mu c x_e \omega_e)/h]^{\frac{1}{2}}$. The values of $x_e \omega_e$ and D_e may be obtained from the vibrational analysis but r_e , since there is no rotational analysis, can be estimated only by using the empirical fact that the product $r_e^3 \omega_e$ is practically a constant for most molecules. The constant usually adopted is 3000×10^{-24} , an average value for several of the lighter symmetrical molecules. For the heaviest molecules known, however, (K_2 , Br_2 , I_2) the constant seems to be nearer 4000×10^{-24} . Bi_2 is, of course, much heavier than these but this constant was adopted in the hope that it would lead, at the least, to a consistent set of values of r_e for the four attractive states. Thus the values of r_e used here, in 10^{-8} cm, are, for state *A*, 2.85; for *B*, 3.10; for *C*, 2.95; for *D*, 3.15.

The heats of dissociation of the various states were obtained from the rates of convergence of the vibrational levels and the possible atomic energies of the products of dissociation. To begin with it was assumed that the lowest state (*A*) dissociated into two normal $^4S_{3/2}$ Bi atoms, in analogy with the lowest states of N_2 and P_2 , the atoms of which have similar electronic configurations. Then state *B* was extrapolated to convergence, since the vibrational difference is more nearly linear (with increasing v) than in state *A*. The value of D_e obtained for state *B* was $11,516\text{ cm}^{-1}$. This was added to the electronic frequency $17,742\text{ cm}^{-1}$ and the most likely atomic energy difference, $15,437\text{ cm}^{-1}$ (see Fig. 2) subtracted to give $13,821\text{ cm}^{-1}$ as the heat of dissociation of the lowest state *A*. This is equivalent to about 1.71 volts. As a check, direct extrapolation of state *A* gave $14,900\text{ cm}^{-1}$ as its heat of dissociation.

Since the Morse formula assumes a linear rate of convergence of ω_v , a value of $x_e\omega_e$ was determined from the mean slope of the curves *A* and *B* in Fig. 3 for v less than 30, rather than from the least squares calculation. This gave for *A*, $x_e\omega_e = 0.41$; and for *B*, $x_e\omega_e = 0.33$. With these constants, the potential energy curves for states *A* and *B* were calculated with the results shown in Fig. 4. These curves were used to locate the theoretical Franck-Condon parabola drawn in Fig. 2. While the fit is by no means perfect it indicates that the potential energy curves as drawn have considerable significance.

For state *C* the value of the heat of dissociation obtained by extrapolation is 2500 cm^{-1} , while the nearest available atomic levels $^2D_{3/2} + ^2D_{5/2}$ indicate a dissociation energy of 4300 cm^{-1} . It is very likely that there is another curve such as *N* crossing *C* and perturbing it because, first, the vibrational levels of state *C* become diffuse and end prematurely and, second, such a perturbation would probably indicate an apparent heat of dissociation lower than the actual, as is the case here. It appears futile, then, to apply any particular form of potential energy expression. Assuming that dissociation occurs into the first available atomic states, the curve in Fig. 4 is a reasonable one passing through two known points, one at the minimum, one at dissociation. Its curvature near the minimum was obtained

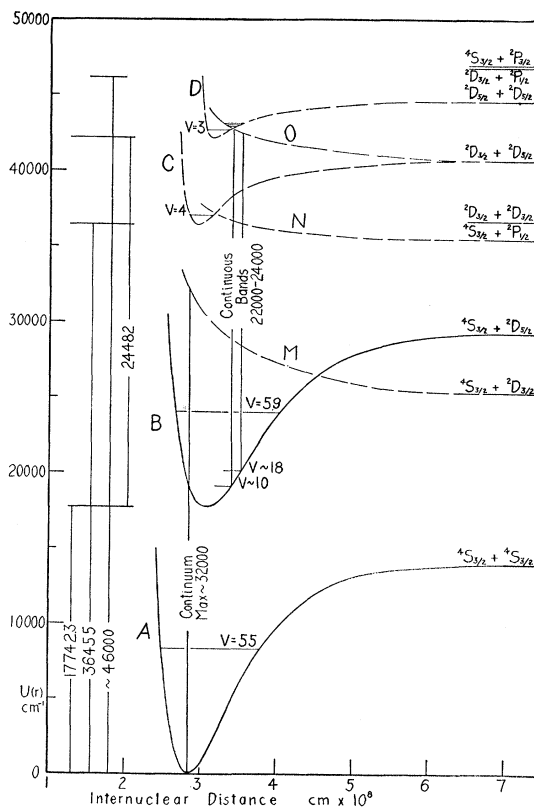


FIG. 4. Potential energy curves for states of Bi_2 molecule. *A* is the lower state of the visible, ultraviolet and far ultraviolet systems (electronic wave numbers shown at left). *B* is the upper state of the visible system and the lower state of the violet system. Curves *C* and *D* represent the upper states of the ultraviolet and violet systems, respectively. The continuous bands in the violet are supposed to be due to the transition from *B* to the repulsive state *O*. *N* is introduced to explain what appears to be predissociation in the ultraviolet system ($C \leftarrow A$). *M* would account for a broad continuum appearing around 3100 \AA . The list of pairs of atomic states of Bi at the right contains all possible combinations of known states arising from the $6p^3$ atomic configuration. The dashed curves are less certain than the solid curves.

by using $x_e\omega_e = 2.3$ (from Fig. 3) and $D = 2500\text{ cm}^{-1}$ in the Morse formula. The relative positions of *A* and *C* indicate, upon application of the Franck principle, a distribution of intensity like that actually found in the ultraviolet system, as described in Table II.

In state *D* the heat of dissociation from Fig. 3 appears to be only 400 cm^{-1} . The first available atomic energy, $^2D_{5/2} + ^2D_{5/2}$, requires a heat of dissociation of about 2500 cm^{-1} . As in the case of state *C*, a reasonable curve is drawn in for state *D*. The curvature near the minimum lies between

that to be expected if D_e were 400 cm^{-1} and that if D_e were 2500 cm^{-1} . There is again qualitative agreement between the positions of the curves B and D and the distribution of intensity in the violet system (Table IV).

The premature breaking off of the upper levels of the violet system and the apparent depression of the heat of dissociation strongly suggests a crossing perturbing state such as O . Such a repulsive state as O provides, moreover, a satisfactory explanation of the closely-spaced diffuse bands between 4000Å and 4050Å and the continuous bands appearing above 4200Å . The first group (4000Å – 4050Å) may arise from the formation of a narrow attractive state formed above the crossing of states O and D . Such an explanation has been offered by Brown and Gibson⁹ and by Brown¹⁰ for similar bands observed in iodine chloride and iodine bromide. The continuous bands may well be due to transitions from B to O for, if O is not steep, and if the Franck principle of small change of internuclear distance in a transition is enforced each transition would give a narrow continuum. The width of each continuous band is of the order of magnitude of 200 cm^{-1} which is also about the width of one branch of the parabola in the square array of the visible system. The length of the vertical line from B to O near the crossing of D and O corresponds closely to the observed frequency of the first continuous band. Finally, the slope of this curve O was estimated by subtracting from the successive intervals between the continuous bands the proper vibrational intervals of state B . Extrapolation of state O indicates that it should approach infinity some 1000 cm^{-1} below the crossing of D and O . The first available atomic energy (${}^2D_{3/2} + {}^2D_{5/2}$) is about 2000 cm^{-1} below the crossing point, which is satisfactory agreement since any error in the extrapolation of state B , the point of departure in locating the dissociation ends of the curves, would appear here. Thus if the extrapolated value of D_e ($14,900\text{ cm}^{-1}$) for state A is used to fix the starting point, the state O would extrapolate exactly into ${}^2D_{3/2} + {}^2D_{5/2}$.

There is what appears to be a similar set of

⁹ W. G. Brown and G. E. Gibson, *Phys. Rev.* **40**, 529 (1932).

¹⁰ W. G. Brown, *Phys. Rev.* **42**, 355 (1932).

continuous bands, though much weaker, in the far ultraviolet. These may arise from a similar transition to a repulsive curve above any of the curves in Fig. 4.

State M is drawn in to provide for the origin of the intense extended continuum in the near ultraviolet (about 3100Å) which begins to appear at 900°C . The difference in character of this continuum and those just described is probably due to the steepness of curve M as compared with O . Any continuum is a series of overlapping continuous bands. The steeper the repulsive curve, the greater the overlapping.

There is not much basis for speculation on the kind of molecular states found in Bi_2 . Assuming that the lowest state dissociates into two ${}^4\text{S}$ atoms and that Λ is a real quantum number in molecules of this weight the lowest state is probably ${}^1\Sigma$, in analogy with N_2 and P_2 . However, transitions occur from state A to state B and B must dissociate into ${}^4\text{S}$ and ${}^2\text{D}$ atoms (if state A goes into two ${}^4\text{S}$ atoms), which atoms would ordinarily combine to form a triplet state. A triplet-singlet transition would not be surprising in such a heavy molecule. It is possible that further information about states A and B may be obtained from rotational analysis of high dispersion photographs of the visible system. There appears to be some resolution of fine structure on our plates.

There have been at least two determinations of the heat of dissociation of bismuth by molecular ray methods. The first, by Leu,¹¹ led, when corrected by Fraser,¹² to the result 1.15 ± 0.5 volts. The second determination, recently announced by Cheng Chuan Ko,¹³ who used presumably a more accurate method, gave a much higher value, 3.21 ± 0.14 volts. Now our most probable value of the heat of dissociation of the lowest state of Bi_2 (state A) is 1.71 volts obtained

¹¹ A. Leu, *Zeits. f. Physik* **49**, 504 (1928).

¹² R. G. J. Fraser, *Molecular Rays*, Cambridge (1931).

¹³ Cheng Chuan Ko, *Bull. Amer. Phys. Soc.* **8**, No. 3, June 1, 1933. While we are not certain what bearing it has on Ko's result, it seems worth while to point out that at the temperatures used in his experiment (827°C to 947°C) many Bi_2 molecules are in the excited state B . At 1000°C the vapor is distinctly luminous, emitting the visible band system. In the molecular beam, then, there must be two kinds of Bi_2 molecules, differing in electronic energy by more than two volts.

by extrapolation of the upper state of the visible system and subtracting the proper atomic energy. The levels of state A were observed to extend above the nonvibrating state 1.0 volt (at $v=55$, where ΔG has dropped from 173 cm^{-1} to 126 cm^{-1}). Direct extrapolation of state A gave 1.84 volts for D_e ; this process usually gives too high a value. It seems to us, therefore, extremely unlikely that the heat of dissociation of Bi_2 should be more than 2 volts or less than 1.5 volts.

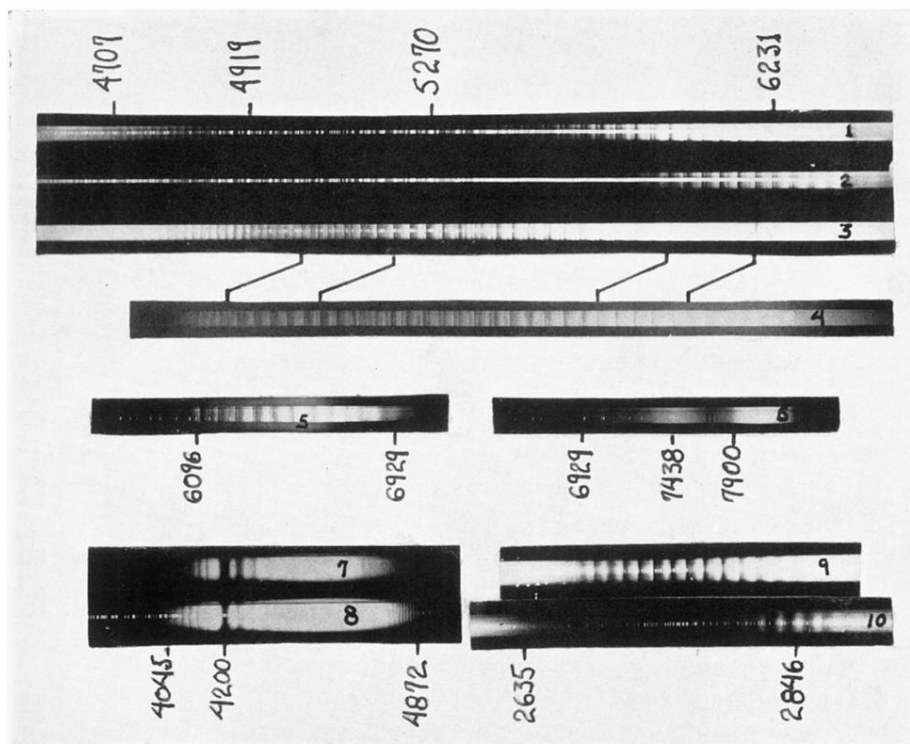


FIG. 1. Reproductions of photographs of Bi_2 band systems.

Exposure number	System	Temperature ($^{\circ}\text{C}$)	Time of exposure	Exposure number	System	Temperature ($^{\circ}\text{C}$)	Time of exposure
1	Visible	1075	40 sec.	6	Visible	1500	80 sec.
2	Visible	1155	15 sec.	7	Violet	1215	5 min.
3	Visible	1155	60 sec.	8	Violet	1215	2 min.
4	Visible	1250	16 min.	9	Ultraviolet	925	60 min.
5	Visible	1350	30 min.	10	Ultraviolet	900	4 min.