THE EMISSION SPECTRUM OF DIATOMIC BISMUTH

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by

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ABSTRACT

The emission spectrum of Bi_2 was excited by irradiating bismuth vapor in a discharge tube by a high power microwave generator and photographed with a Bausch and Lomb dual grating spectrograph. Three new band systems have been observed and analyzed:

(i) The near infrared system (G - B) in the region λ 8820 - 8030 Å consists of 15 bands whose frequencies are represented by the quantum expression

$$\nu = 11869.5 + 107.0\,(v' + \tfrac{1}{2}) - 0.2\,(v' + \tfrac{1}{2})^2 - [132.3\,(v'' + \tfrac{1}{2}) - 0.6\,(v'' + \tfrac{1}{2})^2]\ .$$

(ii) The system (H - B) in the region λ 7050 - 6730 Å consists of a single long v" progression. The derived vibrational constants of this system are

$$\nu_{oo} = 14851.6\ \mathrm{cm}^{-1};\ \omega_e'' = 134.0\ \mathrm{cm}^{-1};\ \omega_e''x_e'' = 0.34\ \mathrm{cm}^{-1}\ .$$

(iii) The system (I - B) in the region λ 6570 - 6290 Å consists of over 10 bands. The frequencies of the band heads are expressed as

$$\nu = 15477.4 + 156.4\,(v' + \tfrac{1}{2}) - 6.1\,(v' + \tfrac{1}{2})^2 - [132.4\,(v'' + \tfrac{1}{2}) - 0.3\,(v'' + \tfrac{1}{2})^2]\ .$$

Since the lower state vibrational frequencies of these three systems agree closely with each other and also with the known upper

state frequency of the B - X system, it is concluded that state B is the common lower state of the new systems. The upper states of the new systems are designated as G, H, and I following the notation of Herzberg (1950) and Almy (1937) for the previously known electronic states of Bi_2.

The known B - X system of Bi_2 which was mainly studied in absorption (Almy and Sparks (1933); Nakamura and Shidei (1934)) has also been obtained in emission under the conditions mentioned above. Over 270 bands have been measured in the region λ 7980 - 4830 Å. The new emission data of this system are in general agreement with the data obtained in absorption. The following expression is derived from the analysis of the emission data:

$$\begin{aligned}\nu = {} & 17739.5 + 132.571\,(v' + \tfrac{1}{2}) - 0.3271\,(v' + \tfrac{1}{2})^2 \\ & + 0.5240 \times 10^{-3}\,(v' + \tfrac{1}{2})^3 - 0.5324 \times 10^{-4}\,(v' + \tfrac{1}{2})^4 \\ & + 0.154 \times 10^{-5}\,(v' + \tfrac{1}{2})^5 \\ & - [173.132\,(v'' + \tfrac{1}{2}) - 0.4156\,(v'' + \tfrac{1}{2})^2 \\ & + 0.2437 \times 10^{-2}\,(v'' + \tfrac{1}{2})^3 - 0.8356 \times 10^{-4}\,(v'' + \tfrac{1}{2})^4 \\ & + 0.72 \times 10^{-6}\,(v'' + \tfrac{1}{2})^5]\end{aligned}$$

In conclusion, a general summary of all the known electronic states of Bi_2 is given.

CHAPTER I

INTRODUCTION

1.1 Electronic Spectra of Homopolar Diatomic Molecules of Elements of the Fifth Group:

A great progress has been made in the last several decades in the experimental investigation and theoretical interpretation of the electronic band spectra of molecules. From a detailed investigation of the electronic spectrum of a molecule, one can derive, precisely, the electronic, vibrational and rotational levels of that molecule. From these again, one can obtain detailed information about the electronic structure (motion of electrons) and the vibration and rotation of the nuclei in the molecule. A knowledge of the electronic motions leads to the understanding of important properties such as chemical valence. From the vibrational frequencies and the corresponding anharmonicities, the forces between the atoms of the molecule and the heats of dissociation can be calculated. From a study of the rotational fine structure of the electronic bands of the molecule, the moments of inertia (hence the internuclear distances) and the nature of the coupling between the electronic and rotational motions of the molecule can be determined with great precision. The various properties of the individual molecules thus obtained by spectroscopic methods enable us to understand many of their physical and chemical properties.

Molecules formed by the union of two atoms in the same group of the periodic table should, to a first approximation, exhibit similar spectra. In each atom of the group, the outermost shell of electrons is the same except for the principal quantum number, and the type of molecular binding and the kind of molecular states depend largely upon these electrons. But the relative positions of the energy levels and the type of electronic coupling in the molecular spectra depend also on the inner shells of electrons. For a correlation of the electronic states and the nature of the electronic coupling in the spectra of a series of homologous molecules, it is therefore necessary to discover as many electronic states as possible for each of the individual molecules and do the rotational analysis of bands of the various electronic transitions of the molecule.

Considering the electronic band spectra of homopolar diatomic molecules of the elements of the fifth group of the periodic table, a great deal of experimental work has been done, both in emission and absorption, on the molecules N_2, P_2 and As_2. However, the work done on the heavier molecules Sb_2 and Bi_2 is not very extensive. Some work has been done mainly in absorption, but the work in emission is particularly very fragmentary. A knowledge of the electronic states so far identified for N_2, P_2 and As_2 suggests that there is a considerable scope for further work on the electronic spectra of Sb_2 and Bi_2 in emission as well as in absorption. In view of this, a study of the emission spectrum of Bi_2 was undertaken and the results of this study are presented in this thesis.

1.2 Previous Work on the Electronic Band Spectrum of Diatomic Bismuth:

Although the characteristic absorption spectrum of molecular bismuth has been observed by a number of earlier researchers, no analysis of any of the band systems has been carried out prior to the work of Almy and Sparks (1933) (see also Almy and Sparks for earlier references). Almy and Sparks have photographed the absorption spectrum of diatomic bismuth in the spectral region 2110 Å - 7900 Å 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. The spectrum has been analyzed into four discrete band systems. In addition, it consists of a continuum and a series of diffused bands. Following the notation used by Herzberg (1950) and Almy (1937), the details of the absorption spectrum of bismuth are briefly presented below. Table I-(a) summarizes mainly the results of the work of Almy and Sparks.

(1) The B ← X System: This system consists of over 300 bands in the region 4500 Å - 7900 Å. The bands in the region up to 7660 Å have been assigned vibrational quantum numbers v' = 59 and v" = 55. The wave-numbers ν of the band heads of the system are represented by the quantum expression,

$$\nu = 17742.3 + \left[132.205\,(v'+\tfrac{1}{2}) - 0.30090\,(v'+\tfrac{1}{2})^2 - 0.0004739\,(v'+\tfrac{1}{2})^3\right]$$
$$- \left[172.708\,(v''+\tfrac{1}{2}) - 0.3227\,(v''+\tfrac{1}{2})^2 - 0.0023209\,(v''+\tfrac{1}{2})^3 - 0.000013\,(v''+\tfrac{1}{2})^4\right].$$

TABLE I-(a)

Known Electronic Band Systems of Bi_2 Prior to the Present Work

Region (Å)	Transition*	T'_e	ω'_e	ω''_e	Remarks	References
			(cm^{-1})			
4500-7900	B ← X	17742.3	132.2	172.7	observed over 300 bands in the temperature range 850-1500°C	1,2
2950-3400	C ← X	~ 32000			C is a repulsive state. continuous absorption occurs at temperatures above 900°C	1
2600-2900	D ← X	36457	157	$(\Delta G''_{\frac{1}{2}} = 172.0)$	observed 40 bands at ~ 900°C	1,2
4000-4200	E ← B	42252	129	$(\Delta G''_{\frac{1}{2}} = 134.4)$	observed 15 bands at temperatures above 1000°C only	1
4200-4500					a series of diffused bands were observed	1
2060-2270	(F) ← X	~ 46000			only partially analyzed	1,2

*Designation of states is taken from Herzberg (1950) and Almy (1937).

[1] Almy and Sparks (1933).

[2] Nakamura and Shidei (1934)

The difference $\nu_{observed} - \nu_{calculated}$, the latter from the above formula, fluctuates from band to band. For some bands, this fluctuation is very small (less than 0.1 cm^{-1}), whereas for others it is as large as 5 cm^{-1}. At temperatures greater than 1000^oC, bismuth vapor becomes luminous and a part of this system appears in thermal emission in the red region.

(2) The C ← X System: This consists of a region of continuous absorption which appears faint at about 900^oC with a maximum of absorption at 3120 Å. At a temperature of 1050^oC, complete absorption occurs from 2600 Å to 3400 Å. This continuous absorption is explained as arising from a transition from the initial ground state X to a final repulsive state C.

(3) The D ← X System: This system extends from 2600 Å to 2900 Å and consists of 40 bands. It appears at about the same temperature as the B ← X system and the absorption is much more intense and does not greatly extend with increasing temperature as is the B ← X system. The lower state vibrational constants of this system agree closely with those of the B ← X system. The derived constants of the upper D state are $\omega_e' = 157$ cm^{-1}, $\omega_e'x_e' = 4.6$ cm^{-1}.

(4) The E ← B System: This system which appears only at temperatures greater than 1000^oC consists of 15 discrete bands in the region 4000 Å - 4200 Å. From the close agreement between the vibrational constants of the lower state of this system and those of the upper state of the B ← X system, it was concluded that the lower state is state B. Since the B - X system appears in thermal emission at temperatures above 1000^oC,

it is certainly possible to have many bismuth molecules in state B by thermal excitation. The derived upper state vibrational constants of this system are $\omega_e' = 129\ \mathrm{cm}^{-1}$, $\omega_e'x_e' = 9.7\ \mathrm{cm}^{-1}$.

(5) Diffuse Band in the Region 4200 Å - 4500 Å: These bands are probably due to a transition from a repulsive state, which is presumably crossed by state E, to the lower state B.

(6) The (F) ← X System: This system occurs at temperatures of about 825°C in the region 2060 Å - 2270 Å. The bands are diffuse in appearance and a partial analysis suggests that a presumably v" progression has the same vibrational intervals as state X. The data are insufficient to make any definite conclusion about the upper vibrational level.

Nakamura and Shidei (1934) also observed the band systems B - X, D - X and (F) - X of diatomic bismuth in absorption (Table I-(a)). Their independent analyses of systems B ← X and D ← X are in agreement in general with those of Almy and Sparks.

1.3 The Present Investigation:

In the present investigation, the emission spectrum of diatomic bismuth was excited by irradiating bismuth vapor by a high power microwave generator. The spectrum revealed the existence of three new band systems of Bi_2 which occur in the following regions: (i) λ 8820 - 8030 Å (system G ← B), (ii) λ 7050 - 6730 Å (system H ← B) and, (iii) λ 6570 - 6290 Å (system I ← B). Vibrational analyses of all the three systems have been carried out and the vibrational constants derived. In addition, the B - X system of Bi_2 which was studied previously in absorption

(Section 1.2) was also obtained in emission in the region λ 7980 - 4830 Å. Using the new emission data of this system which are in general agreement with the absorption data, accurate vibrational constants are derived. Finally, all the known electronic states of Bi_2 are summarized.

CHAPTER II

EXPERIMENTAL TECHNIQUE

The emission spectrum of diatomic bismuth was excited with the use of microwave radiation on a heated quartz discharge tube containing molten bismuth. A brief description of the apparatus used and of the experimental procedure adopted is given in the present chapter.

2.1 Bausch and Lomb Dual Grating Spectrograph:

All the spectra were photographed on a modified Bausch and Lomb Dual Grating Spectrograph. The schematic diagram of the spectrograph is shown in Fig. I. This instrument is of the littrow type with a large spherical mirror as collimator which has a radius of curvature of 200 cm. Two echelle-type plane gratings, having a ruled area of 102 mm x 128 mm each, one with 1200 and the other with 600 grooves per mm, are provided for the spectrograph. These gratings are mounted back to back in a rotatable turret. Light from a source (not shown in the Fig.) after passing through the adjustable slit S and getting reflected at the plane mirror M is incident on the collimator SM. It is then dispersed by the grating G and later focussed by the collimator onto the photographic plate P. Against a vertical scale fitted with the spectrograph, the plate holder can be raised or lowered either manually or by an automatic device co-ordinated with the opening and closing operations of the slit. The spectra were photographed with a slit width of 0.1 mm

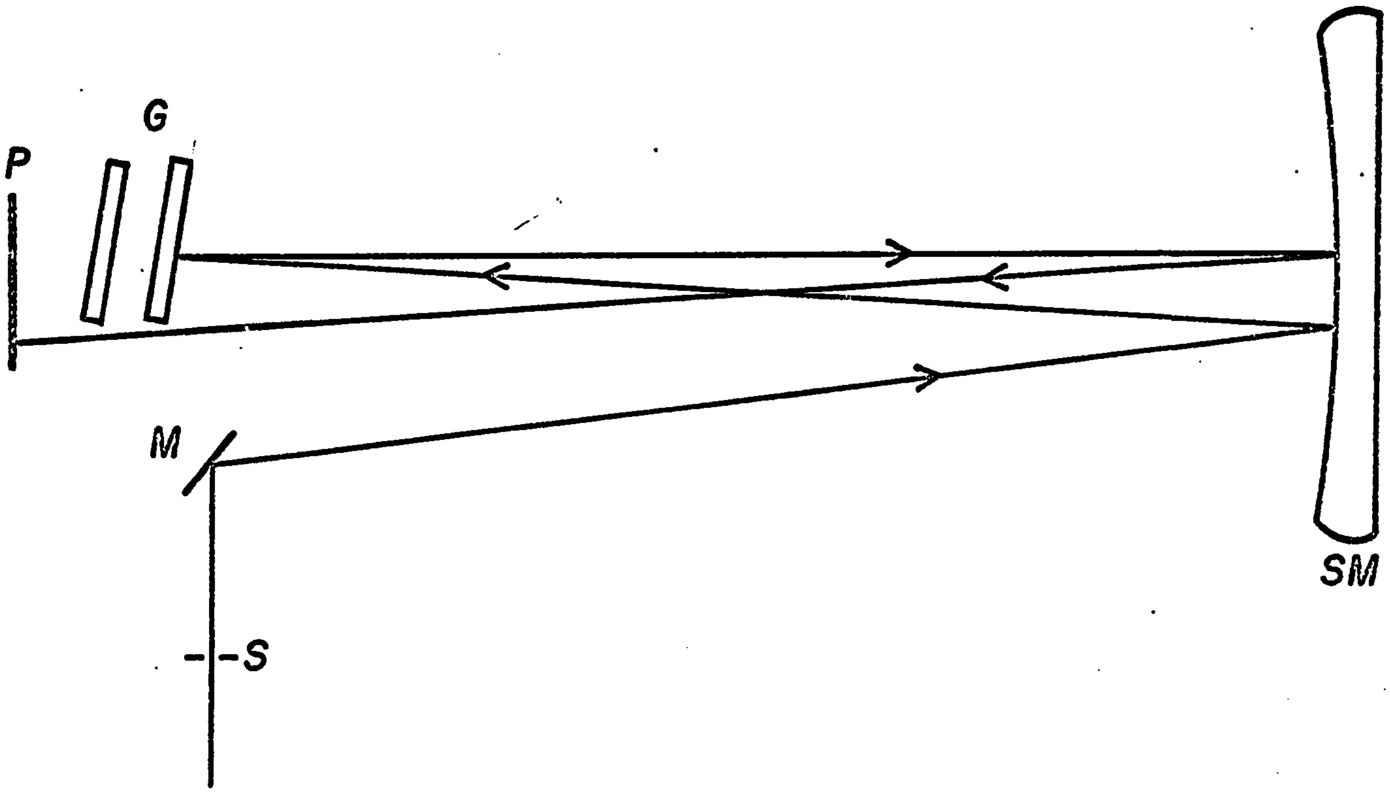


Fig. 1. Optical Arrangement of the Spectrograph.

(which corresponds to 10 divisions on the drum). Out of the two gratings, the one with 1200 grooves per mm and having the following specifications was used in the present investigation:

Blazed wave length	1.0 micron (first order)
Blaze angle	36°52'
Resolving Power	70% of the theoretical value (153600 in the first order)
Efficiency	62% at 9000 Å 66% at 1.0 micron 70% at 1.1 microns
Ghost intensity	1.0% of parent line in the 2nd order at 5461 Å.

The numerical aperture of the spectrograph is f/15.5 and the measured wavelength dispersions are as follows: 3.7 Å/mm at 7530 Å in the first order; 1.8 Å/mm at 4740 Å in the second order; and 1.3 Å/mm at 6420 Å in the second order.

2.2 Raytheon Microwave Power Generator:

Microwave radiation used in the present work for the excitation of the emission spectrum of bismuth was obtained from a microwave power generator model PGM-100 supplied by Raytheon Company, Waltham, Massachusetts, U. S. A. In Fig. 2 is represented a schematic diagram of the experimental set up which consists essentially of the microwave power generator PG, its accessories (filter unit F, waveguide G, and horn H),

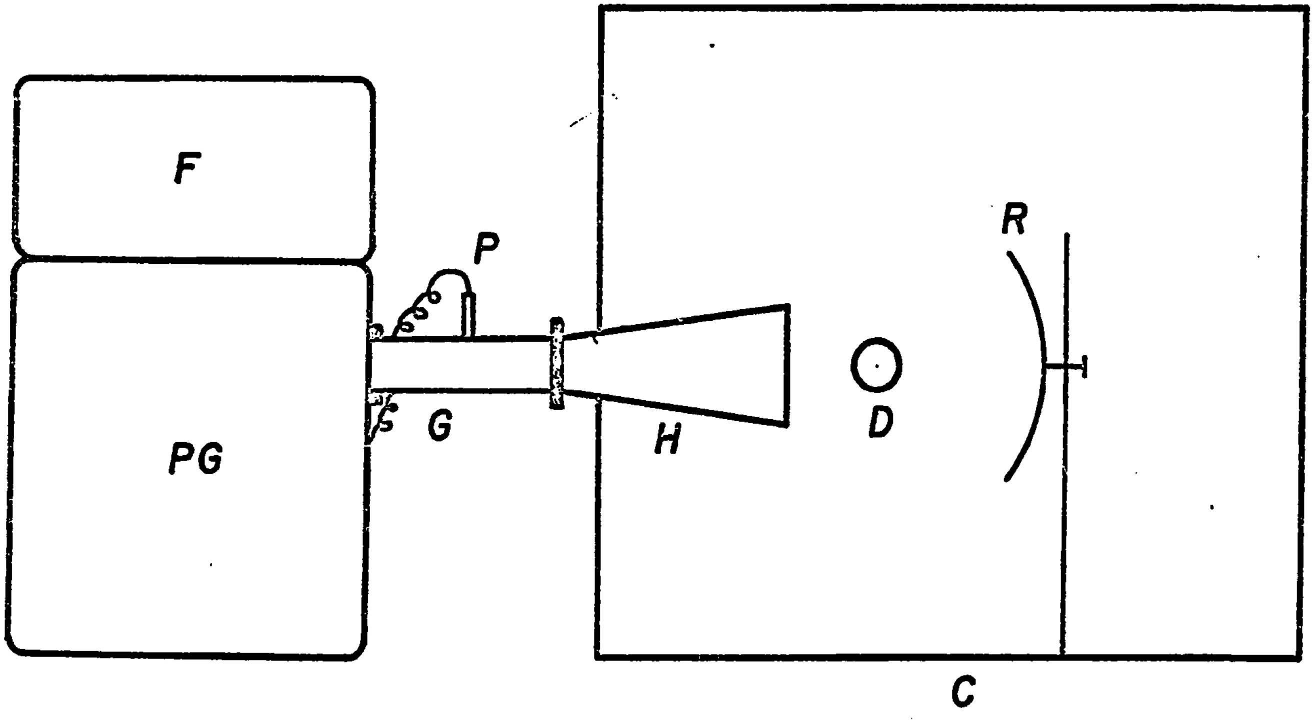


Fig. 2. Front View of the Experimental Set-Up.

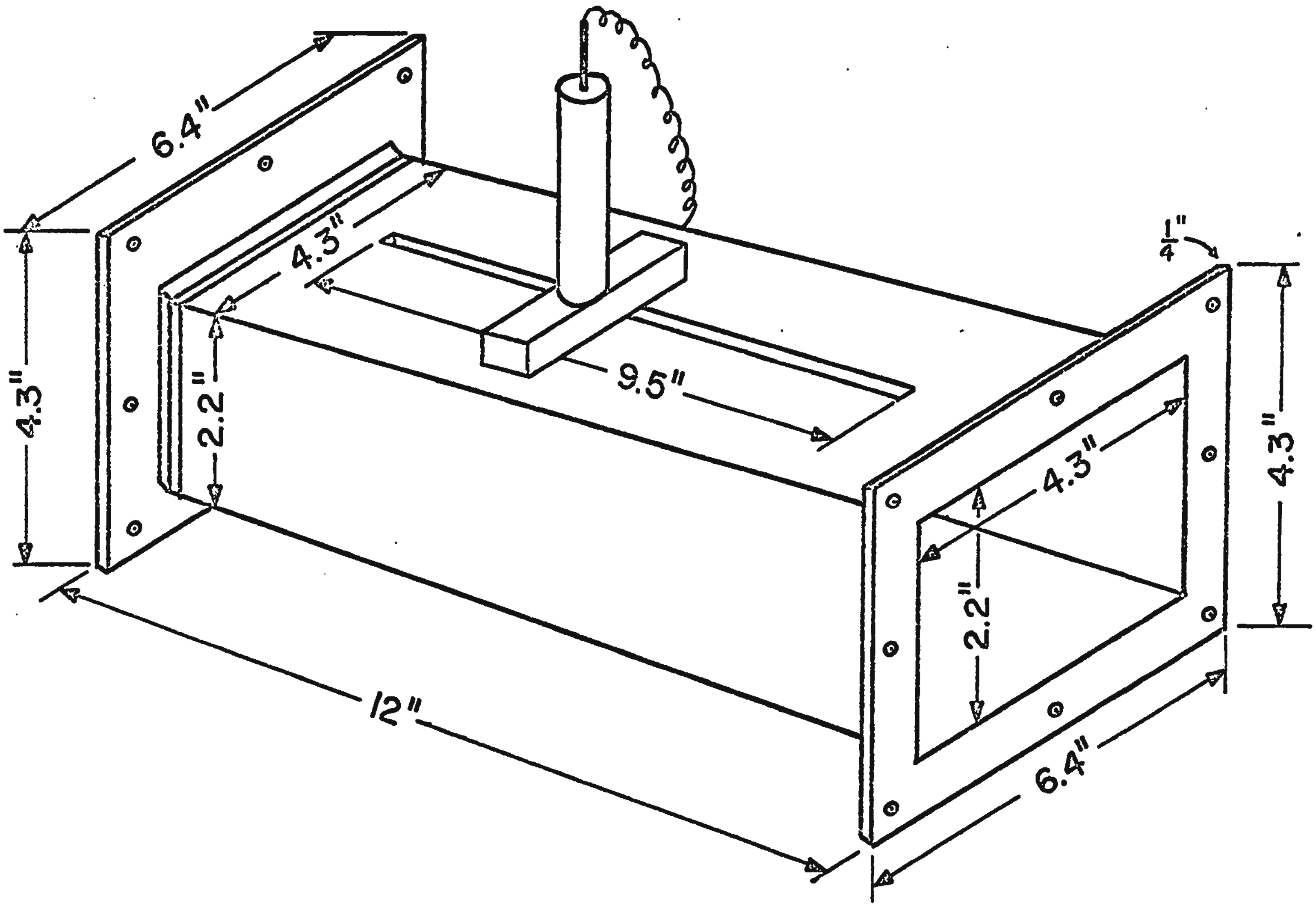


Fig. 3. Wave Guide for Microwave Radiation.

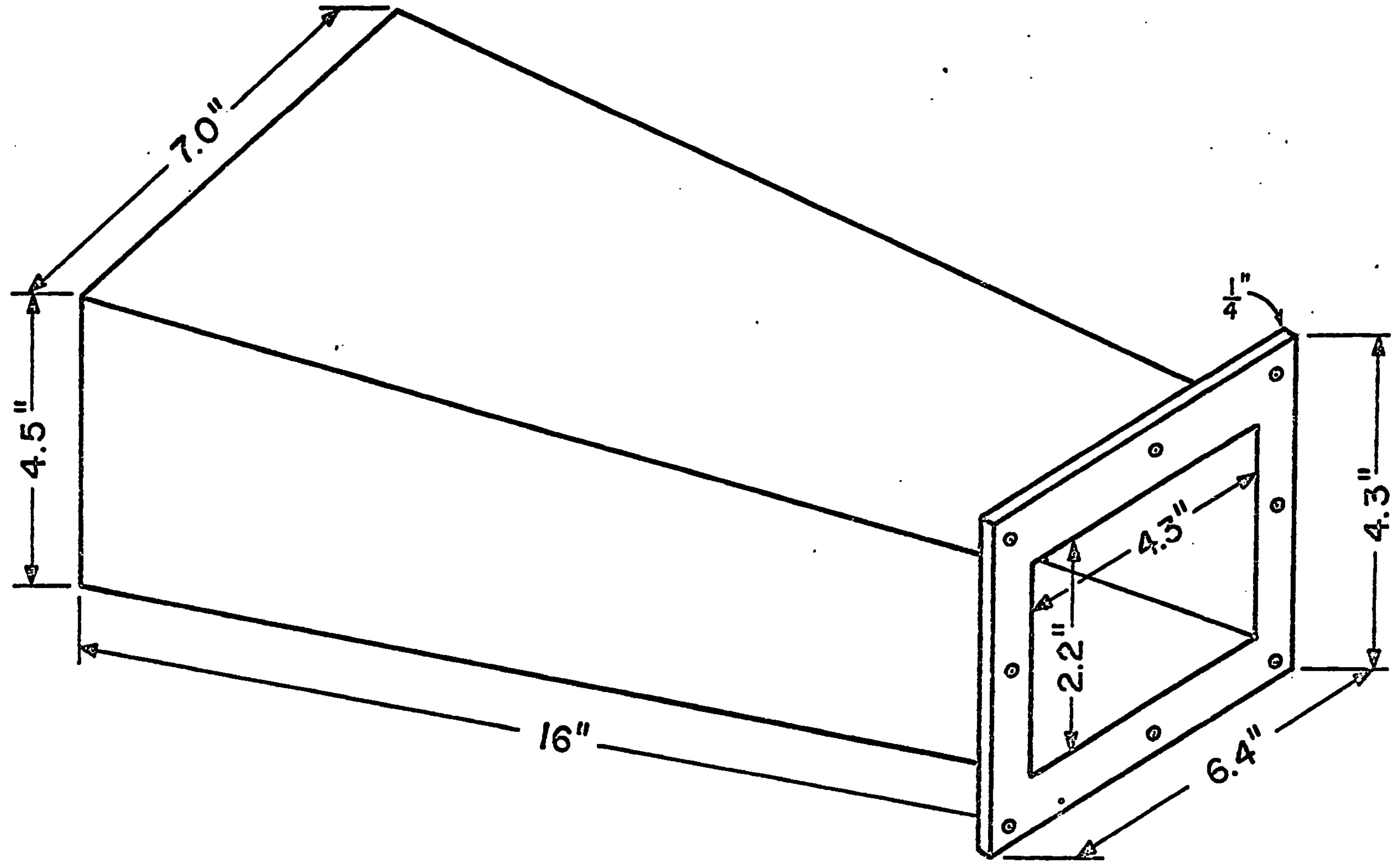


Fig. 4. Horn for Microwave Radiation.

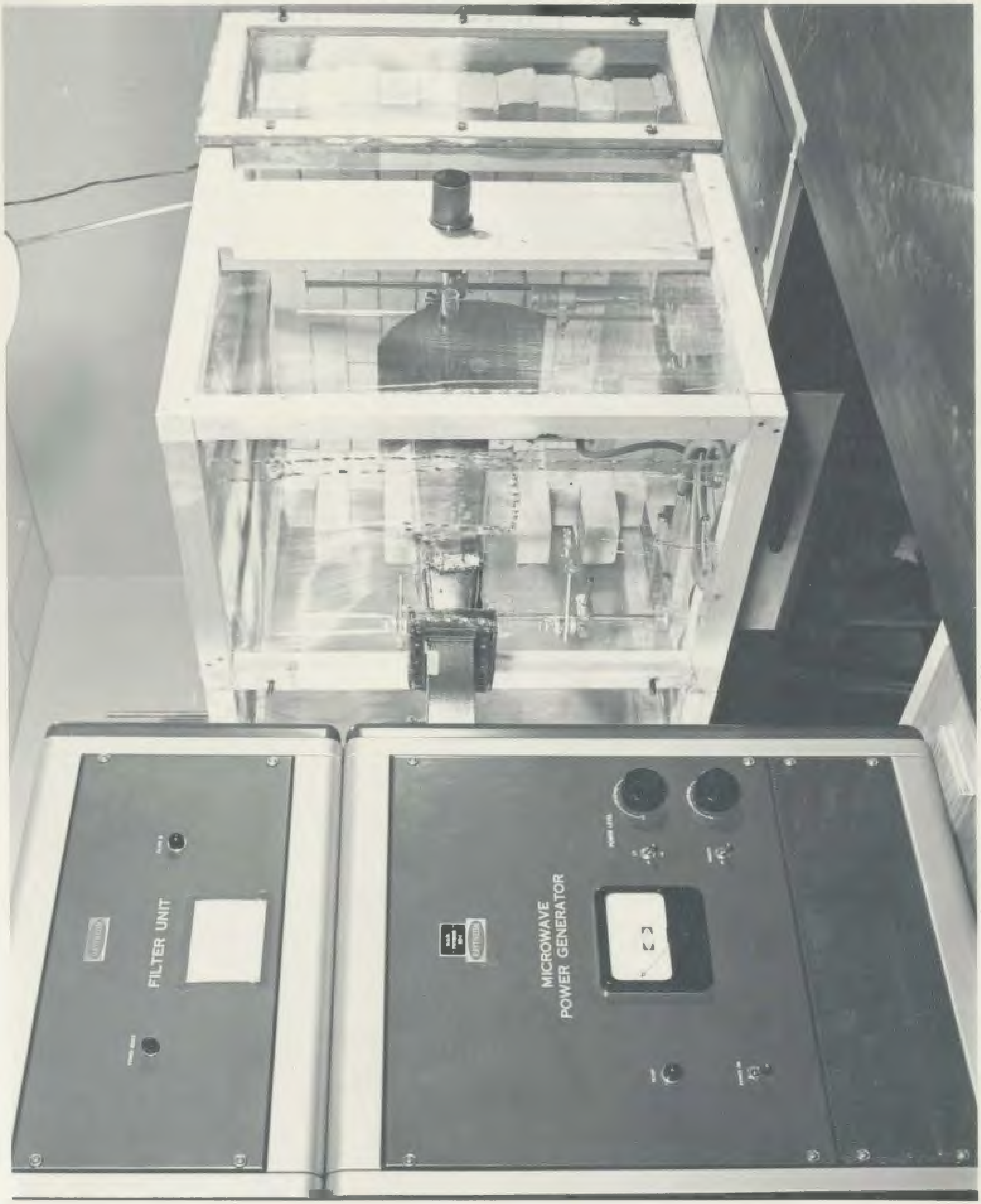


Fig. 5 A Photograph Of The Experimental Set Up

the discharge tube D, the metallic reflector R and the microwave radiation cage C. The microwave power generator is essentially comprised of a fixed frequency, air-cooled, CW-type magnetron oscillator. The magnetron is provided with a full wave rectified (120 cycles) power supply unit which employs a magnetic regulator to hold the average anode current. Consequently, the power output is virtually constant through normal line fluctuations and variations of magnetron impedence with load and life. The filter network F of the generator can be switched into the magnetron plate supply to provide a microwave power output with a modulation of about 10% in the detected R.F. envelope. The microwave power generator, with its filter in, has an output power supply in the range 250 to 800 watts at a frequency of 2450 ± 25 MHz. The generator PG is fitted with the waveguide G which in turn is connected with the horn H. The waveguide and the horn are constructed of brass plates of thickness 0.125" and 0.03", respectively. The details of construction of these are diagrammatically represented in Figs. 3 and 4, respectively. The wavelength of the radiation in the guide is 14.8 cm. A photograph of the experimental set up excluding the spectrograph is shown in Fig. 5.

To avoid the hazards of microwave radiation, the horn, the discharge tube and the reflector were shielded in a rectangular radiation cage C (Figs. 2 and 5) of size 40" x 40" x 29" made of copper screen of mesh size 0.1 cm x 0.15 cm. To absorb scattered radiation inside the cage, a rubber pad was spread on the bottom surface of the cage and bricks made of clay were placed inside the cage along the wall behind the reflector R.

2.3 Discharge Tube:

The electrodeless quartz discharge tube D used in the present investigation is diagrammatically represented in Fig. 6. It is 18" long and 25 mm in inner diameter. One end of the discharge tube was joined with pyrex tubing through a graded seal. A circular quartz window W of thickness 2 mm was sealed to the other end. The pyrex tubing was connected to a high vacuum pumping system through a liquid nitrogen trap T. Before the pyrex tubing was sealed to the liquid nitrogen trap, a sufficient quantity of pure bismuth in the form of shots, supplied by American Smelting and Refining Company, New Jersey, was placed in the discharge tube.

2.4 Experimental Procedure:

The quartz discharge tube containing bismuth was optically aligned with respect to the slit of the spectrograph so that the radiation from the discharge tube filled the collimator uniformly. The pyrex tubing connected to the liquid nitrogen trap (Fig. 6) was ultimately joined to the pumping system with a small rubber pressure tubing. The discharge tube was continuously evacuated during the experiment. When the vacuum reached approximately 5×10^{-7} torr, the discharge tube was heated in the central portion over a length of 10" with a special bunsen burner to produce the requisite amount of bismuth vapor. It was then irradiated with microwave radiation from the generator. The position of the reflector was adjusted as described below to obtain maximum intensity of the discharge. The characteristic color of the discharge was bluish

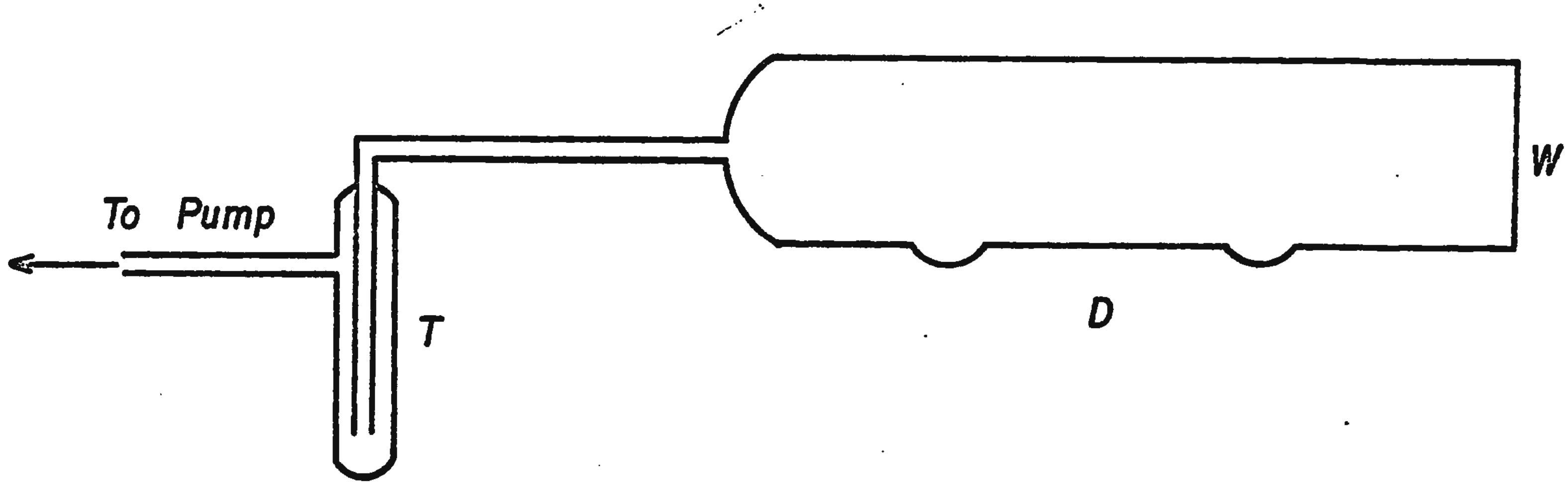


Fig. 6. Discharge Tube with Trap.

white. At times it was necessary to start the discharge with the help of a tesla coil. Condensation of bismuth on the window of the discharge tube was prevented by heating the window.

The details of finding a suitable position for the reflector which concentrates the microwave radiation on the discharge tube are as follows: A suitable position of the reflector with respect to the discharge tube and the horn was found so that the standing wave ratio VSWR (hereafter called ρ) in the wave guide was minimum when the discharge was on. To check ρ, a probe P (Figs. 2 and 3) which could be moved in the slot S of the wave guide was read on a Wheatstone bridge circuit. According to the manufacturer's instructions, ρ should not exceed 2 for the operation in the phase for the maximum power output. To find ρ in the wave guide, a graph was plotted between probe distances along the wave guide and the corresponding resistances required to balance the Wheatstone bridge. This graph had several maxima and minima positions. Since the probe was not calibrated, square roots of the ratios between the resistances corresponding to maxima and minima of the graph were used for ρ's. However, it must be mentioned here that this simplification is not entirely justified. The values of ρ's were found to lie between 1.26 and 1.31. Using a value of 1.31 for ρ, P_r the power received was calculated using the formula $P_r = P_a \left\{4\rho/(1+\rho)^2\right\}$ where P_a is the power available. The microwave power generator was used at an anode current of 260 ma which corresponded to P_a equal to 755 watts. This value of P_a was taken from a calibration curve obtained previously in our laboratories using a water load in conjunction with the microwave power generator. The corresponding value of P_r was of the order of 740 watts.

The spectra were photographed with the Bausch and Lomb Grating Spectrograph (described in section 2.1) in the first and second orders of the grating (1200 lines/mm). Kodak photographic plates of types 103a-O, panchromatic B and 1-N were used to record the spectra. The exposure times ranged from ½ hour to 2½ hours. A d.c. iron arc was used as a reference source and the iron lines were photographed in juxtaposition of the spectrum under investigation using a Hartmann diaphragm in front of the slit of the spectrograph.

2.5 Measurement of Spectra:

The spectra were measured using a linear comparator, Model 1205C, supplied by Gaertner Optical Instrumentation Company. Using iron arc lines as wavelength standards and the second order equation $\lambda = \lambda_0 + a(d_0 - d) + b(d_0 - d)^2$, the wavelengths of the band heads (λ_{air}) were calculated. In the above formula, d's stand for comparator scale readings and λ's for the corresponding wavelengths. Constants λ_0, a and b were determined by substituting in the above formula the λ's and d's of three known sharp reference lines. In a particular spectral region, the positions of band heads and a number of iron arc lines were measured. In a certain wavelength range, three sharp standard iron arc lines were used to calculate the constants λ_0, a and b. The accuracy of the constants was tested by calculating back the λ's of the other reference lines whose d's were measured in that range. When the calculated λ's started differing from the corresponding standard values by a factor more than 0.02 Å, another suitable set of three iron arc lines were used for calculating λ's of next band heads. The λ_{air} thus obtained was then converted to λ_{vac} by using the formula

$$\lambda_{vac} = \lambda_{air} + \lambda_{air}\left(2726.43 + \frac{12.288}{\lambda_{air}^{2}\times10^{-8}} + \frac{0.3555}{\lambda_{air}^{4}\times10^{-16}}\right) \times 10^{-7} .$$

This formula was used by Kayser (1944) to prepare the tables for λ_{air} and ν_{vac} cm^{-1}. The reciprocal of λ_{vac} gave ν_{vac} (cm^{-1}) for the band heads. These calculations were done using a Hewlett-Packard Calculator, Model 9100A. This procedure was found to be faster than obtaining the vacuum wave numbers from Kayser's tables when a large number of conversions is involved.

CHAPTER III

EXPERIMENTAL DATA AND ANALYSIS

3.1 Observed Emission Band Systems of Bi_2:

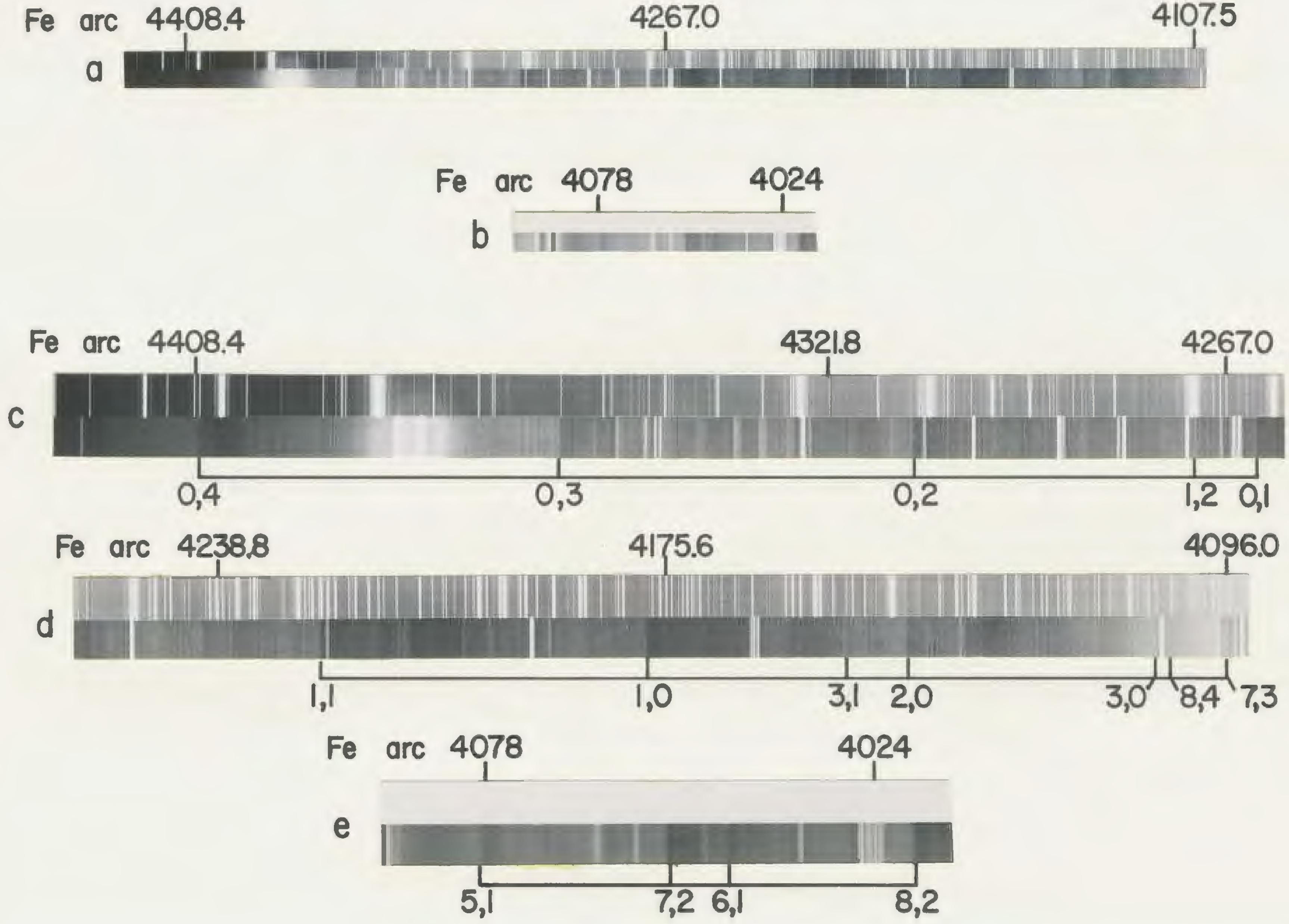
In this chapter, the new experimental data on the emission spectrum of Bi_2 and details of the vibrational analyses of three new band systems as well as thoseof system B - X will be presented. As mentioned in Chapter I, the new band systems are designated as G → B, H → B, and I → B. Equations which are applicable to the analysis of the vibrational structure of electronic band systems are summarized in the Appendix. The vibrational analyses of all band systems mentioned here were carried out by standard procedures described by Herzberg (1950) and Jevons (1932).

Most of the details of the experimental technique used in obtaining the band systems mentioned above are described in Chapter II. Details of recording the spectra are briefly summarized below. The G - B, H - B, and I - B systems which occur in the spectral regions λ 8820 - 8030 Å, λ 7050 - 6730 Å, and λ 6570 - 6290 Å, respectively, were photographed in the first order of the grating spectrograph using Kodak 1-N plates. Second order iron arc lines were used as standards for the G - B system and first order iron arc lines were used for the other two systems. Different parts of the B - X system which occur in the region λ 7980 - 4830 Å were photographed on Kodak 1-N, Panchromatic B, and 103 a-O plates; and both first order and second

PLATE I

THE G → B SYSTEM OF DIATOMIC BISMUTH

(a and b: contact spectrograms; c, d and e: enlarged spectrograms; Bi_2 spectrum: first order; Fe arc spectrum: second order.)



order iron arc lines were used as standards. To avoid overlapping of different orders of the grating, Corning filters CS-3-66 and CS-0-54 and Kodak filters 2A and 26 were used. The exposure time was approximately 2½ hours for system G - B and was 3/4 hour for systems H - B and I - B. For system B - X, the exposure time varied from ½ to 1 hour. The intensities of the bands of the four systems reported in this chapter are only visual estimates. These should not be considered very accurate since the sensitivities of different photographic plates in different wave length regions vary considerably from each other. For numerical calculations, an IBM 360 computer was used in addition to the Hewlett-Packard Calculator Model 9100.

3.2 The G → B System:

The near infrared G - B system which consists of about 15 bands degraded toward larger wavelengths is reproduced in plate I where strips a and b are contact spectrograms, and strips c, d, and e are enlarged spectrograms. A few second order wavelengths of iron arc lines are marked in the spectrum to indicate the spectral region. The wavelengths and the vacuum wave numbers of all band heads are listed in Table I. Vibrational quantum numbers assigned in this Table were obtained by fitting the wave numbers of band heads into a vibrational scheme. The vibrational scheme, extending to v' = 8 and v" = 4, is shown in Table II. The bands fall into the usual Franck-Condon parabola. The vibrational quantum numbers of band heads are also marked for the enlarged spectrograms of plate I.

TABLE I

Band Heads of the G - B System in the Region λ 8820 - 8030 Å

λ_{air}(A)	ν_{vac}(cm^{-1})	Intensity*	v'	v"	$\nu_{obs}-\nu_{calc}$
8815.44	11340.6	w	0	4	0.8
8717.75	11467.7	s	0	3	0.4
8620.93	11596.5	m	0	2	0.5
8542.49	11703.0	w	1	2	0.4
8525.68	11726.1	w	0	1	0.2
8448.77	11832.8	w	1	1	0.3
8356.87	11962.9	m	1	0	-0.7
8301.16	12043.2	m	3	1	-0.6
8283.30	12069.2	m	2	0	-0.6
8211.30	12175.0	vw**	3	0	-0.6
8207.10	12181.2	w	8	4	-0.2
8192.08	12203.6	w	7	3	-1.5
8158.70	12253.5	vw	5	1	-1.4
8107.38	12331.1	m	7	2	-2.7
8088.55	12359.8	vw	6	1	0.3
8039.19	12435.7	m	8	2	-1.9

* vs: very strong
s: strong
m: medium
w: weak
vw: very weak
** : superposed by an atomic line

TABLE II

Vibrational Scheme of the G-B System

v'' / v'	0		1		2		3		4	Mean $\Delta G'_{v+\frac{1}{2}}$
0			11726.1	129.6	11596.5	128.8	11467.7	127.1	11340.6	
			106.7		106.5					106.6
1	11962.9	130.1	11832.8	129.8	11703.0					
	106.3									106.3
2	12069.2									
	105.8									105.8
3	12175.0	131.8	12043.2							
4										
5			12253.5							
			106.3							106.3
6			12359.8							
7					12331.1	127.5	12203.6			
					104.6					104.6
8					12435.7				12181.2	
Mean $\Delta G''_{v+\frac{1}{2}}$		131.0		129.7		128.2		127.1		

Plots of the mean values of vibrational intervals $\Delta G_{v + \frac{1}{2}}$ against the corresponding $v + \frac{1}{2}$ values for various states of Bi_2 are shown in Fig. 7. The vibrational intervals of the lower and upper states of this system were obtained using only the frequencies of the bands (0,4), (0,3), (0,2), (1,2), (0,1), (1,1), (1,0), (3,1), (2,0), and (3,0) because the frequencies of the other bands are considered to be less accurate. The plots for the lower and upper states of this system indicate that the vibrational terms G(v) can be expressed as

$$(1) \qquad G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 \ .$$

The slopes and intercepts of the straight lines obtained by a least square fit for this system (Fig. 7) give the values of $- 2\omega_e x_e$ and $\omega_e - \omega_e x_e$, respectively (eq. 9, Appendix). The values of the vibrational constants thus obtained for the G - B system are

$$\omega_e' = 107.0 \text{ cm}^{-1} \qquad \omega_e'' = 132.3 \text{ cm}^{-1}$$

$$\omega_e' x_e' = 0.2 \text{ cm}^{-1} \qquad \omega_e'' x_e'' = 0.6 \text{ cm}^{-1} \ .$$

The system origin ν_e (eq. 2, Appendix) was determined individually by using the calculated values of G'(v) and G"(v) in conjunction with the frequencies ν of the 10 band heads mentioned above. The mean value of ν_e thus obtained was found to be 11869.5 cm^{-1}. Finally, the wave numbers of the band heads of the G - B system are represented by the formula

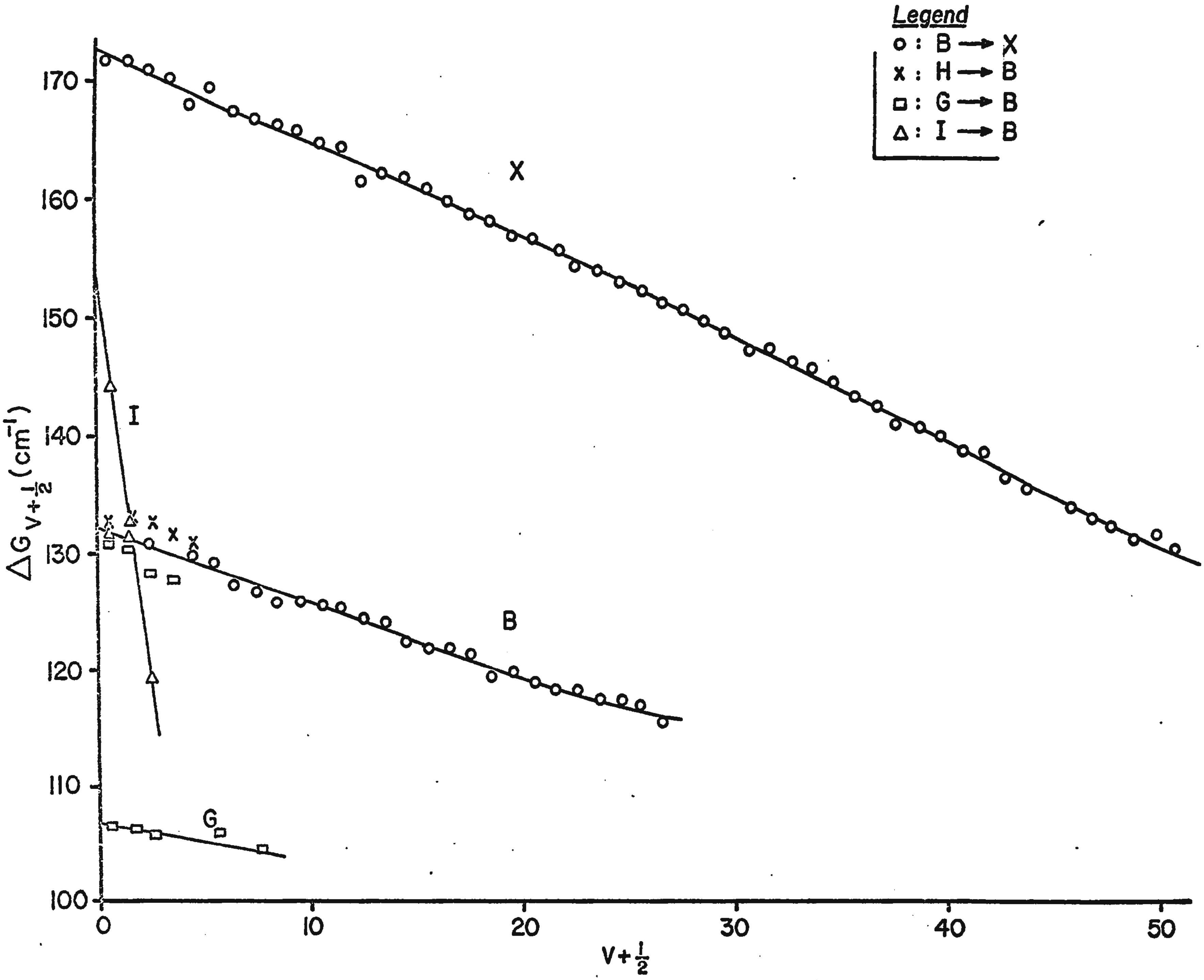
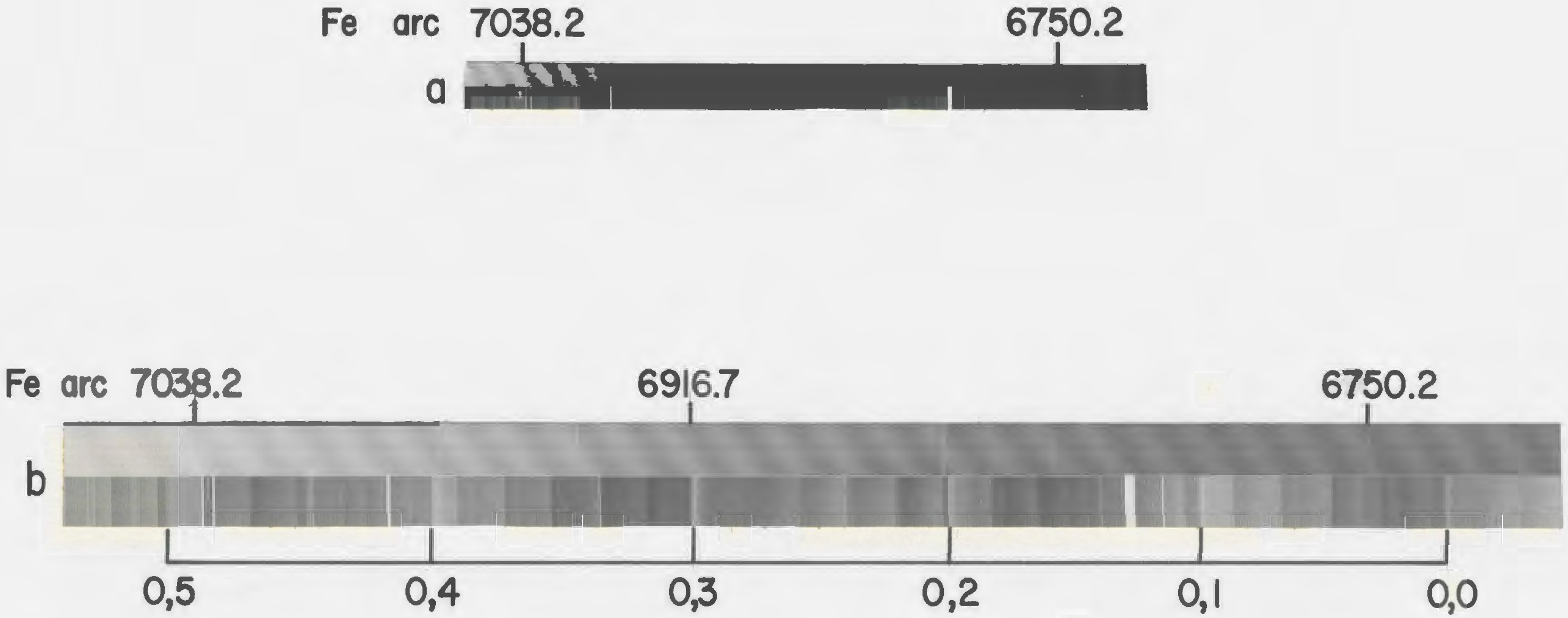


Fig. 7. Mean ΔG curves of observed states of diatomic bismuth (plotted against $V+\frac{1}{2}$)

PLATE II

THE H → B SYSTEM OF DIATOMIC BISMUTH

(a: contact spectrogram ; b: enlarged spectrogram. Both Fe arc and Bi_2 spectra are photographed in the first order of the grating. Bands degraded to longer wavelengths belong to the B → X system.)



$$\nu = 11869.5 + 107.0\,(v' + \tfrac{1}{2}) - 0.2\,(v' + \tfrac{1}{2})^2 - [132.3\,(v'' + \tfrac{1}{2}) - 0.6\,(v'' + \tfrac{1}{2})^2] \;. \tag{2}$$

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. (2). The last column of Table I gives the differences of the observed and calculated values. Except for three bands, these differences were less than 1 cm^{-1}. The measurements of these three bands are considered to be less accurate. Since the lower state vibrational frequency (132.3 cm^{-1}) of this system agrees very closely with the upper state frequency (132.571 cm^{-1}) of the B - X system (see section 3.5), it is concluded that the lower state of the G - B system is the upper state of the B - X system.

3.3 The H → B System:

The H - B system consists of a single progression of 6 sharp bands degraded to shorter wave lengths. The spectrograms of this system are shown in plate II where strip a is a contact spectrogram and strip b is an enlarged spectrogram. The wave lengths of a few iron arc lines are marked for comparison. The wave lengths, vacuum wave numbers and visual estimates of intensities of the bands are listed in Table III. The vibrational scheme is presented in Table IV and the values of the vibrational quantum numbers are included in Table III. The 0,4 and 0,1 bands of this system show anomalous

TABLE III

Band Heads of the H-B System in the Region λ7050-6730 Å *

λ_{air}(Å)	ν_{vac}	Intensity	v', v"
7044.45	14191.7	m	0, 5
6980.55	14321.6	s	0, 4
6916.91	14453.3	s	0, 3
6854.03	14585.9	s	0, 2
6792.07	14719.0	s	0, 1
6731.45	14851.6	m	0, 0

---

[*] The notation for the intensities is the same as the one given in Table I .

TABLE IV

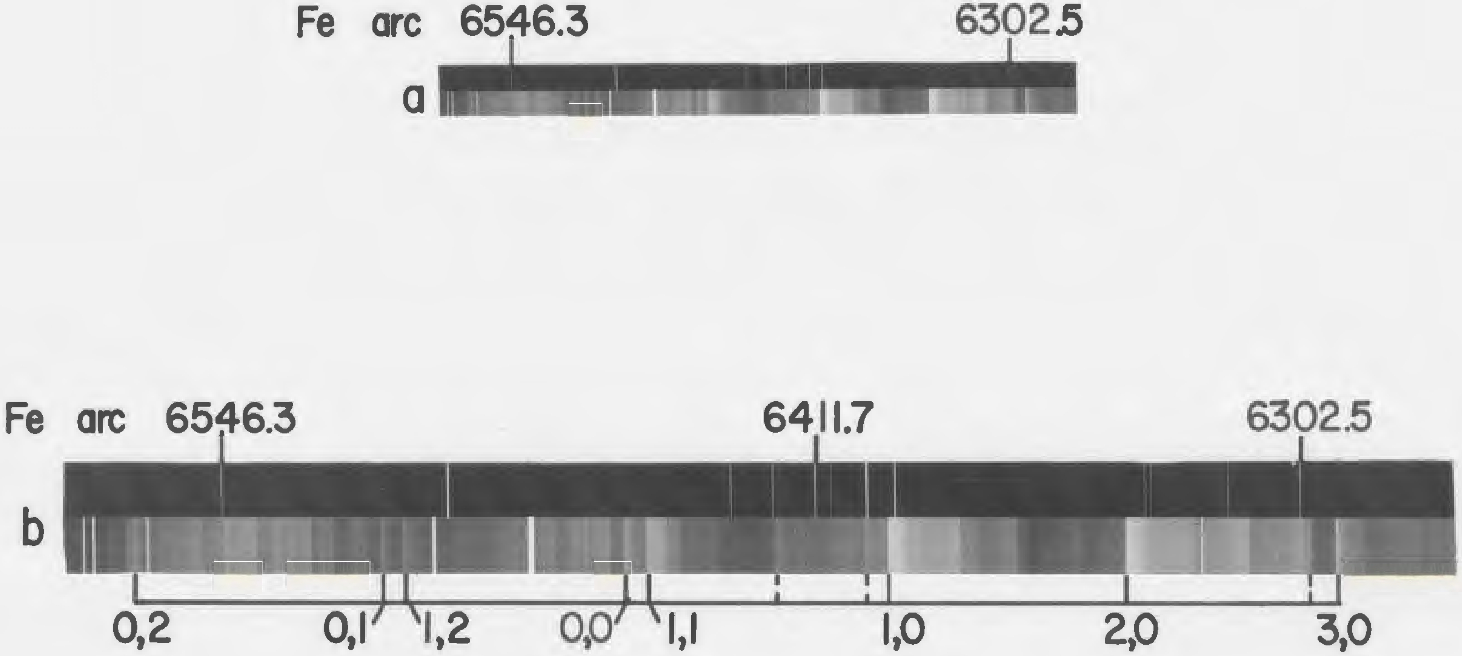
Vibrational Scheme of the H-B System

v'' / v'	0		1		2		3		4		5
0	14851.6	132.6	14719.0	133.1	14585.9	132.6	14453.3	131.7	14321.6	129.9	14191.7
$\Delta G''_{v+\frac{1}{2}}$		132.6		133.1		132.6		131.7		129.9	

THE I → B SYSTEM OF DIATOMIC BISMUTH

PLATE III

(a: contact spectrogram; b: enlarged spectrogram. Both Fe arc and Bi_2 spectra are photographed in the first order of the grating. Bands degraded to longer wavelengths belong to the B → X system.)



intensities because each of them is superposed by a band of the B - X system, degraded toward longer wave lengths. The vibrational constants of the upper state of this system could not be determined since all the six bands of this system belong to a single v"-progression. The constants of the lower state were obtained by a least squares straight line fit of $\Delta G''_{v+\frac{1}{2}}$ versus v + ½ (Fig. 7). The slope and intercept thus obtained were used to calculate $\omega''_e x''_e$ and ω''_e. The values of the constants of this system are

$$\nu_{00} = 14851.6 \text{ cm}^{-1}$$

$$\omega''_e = 134.0 \text{ cm}^{-1}$$

$$\omega''_e x''_e = 0.34 \text{ cm}^{-1}$$

We see here that the lower state vibrational constants of this system agree closely with the upper state constants of the B - X system (see section 3.5). It is therefore inferred that the lower state of this system is the upper state of the B - X system.

3.4 The I → B System:

The I - B system consists of over 10 sharp bands which are degraded to shorter wave lengths. As can be seen from strip a or b of plate III, two of the bands (1,1 and 1,0) of this system are superposed by bands of the B - X system which are degraded toward longer wave lengths. The wave lengths, vacuum wave numbers and intensities of the bands are listed in Table V and the vibrational scheme is displayed in

TABLE V

Band Heads of the I-B System in the Region λ6570-6295 Å *

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
6566.25	15225.2	m	0, 2	0.3
6510.23	15356.2	m	0, 1	0.1
6505.22	15368.0	m	1, 2	-1.1
6455.11	15487.3	m	0, 0	-0.6
6449.91	15499.8	vs	1, 1	-0.5
6420.67	15570.4	m	— —	—
6400.54	15619.4	w	— —	—
6395.18	15632.5	vs	1, 0	0.4
6341.32	15765.2	vs	2, 0	1.1
6300.18	15868.2	w	— —	—
6293.63	15884.7	m	3, 0	0.8

---

* The notation for the intensities is the same as the one given in Table I .

TABLE VI

Vibrational Scheme of the I-B System

v'' v'	0		1		2	Mean $\Delta G'_{v+\frac{1}{2}}$
0	15487.3	131.1	15356.2	131.0	15225.2	
	145.2		143.6		142.8	143.9
1	15632.5	132.7	15499.8	131.8	15368.0	
	132.7					132.7
2	15765.2					
	119.5					119.5
3	15884.7					
Mean $\Delta G''_{v+\frac{1}{2}}$		131.9		131.4		

THE B→X SYSTEM OF DIATOMIC BISMUTH PLATE IV

(contact spectograms a,b and c: first order; d,e,f,g and h: second order.)

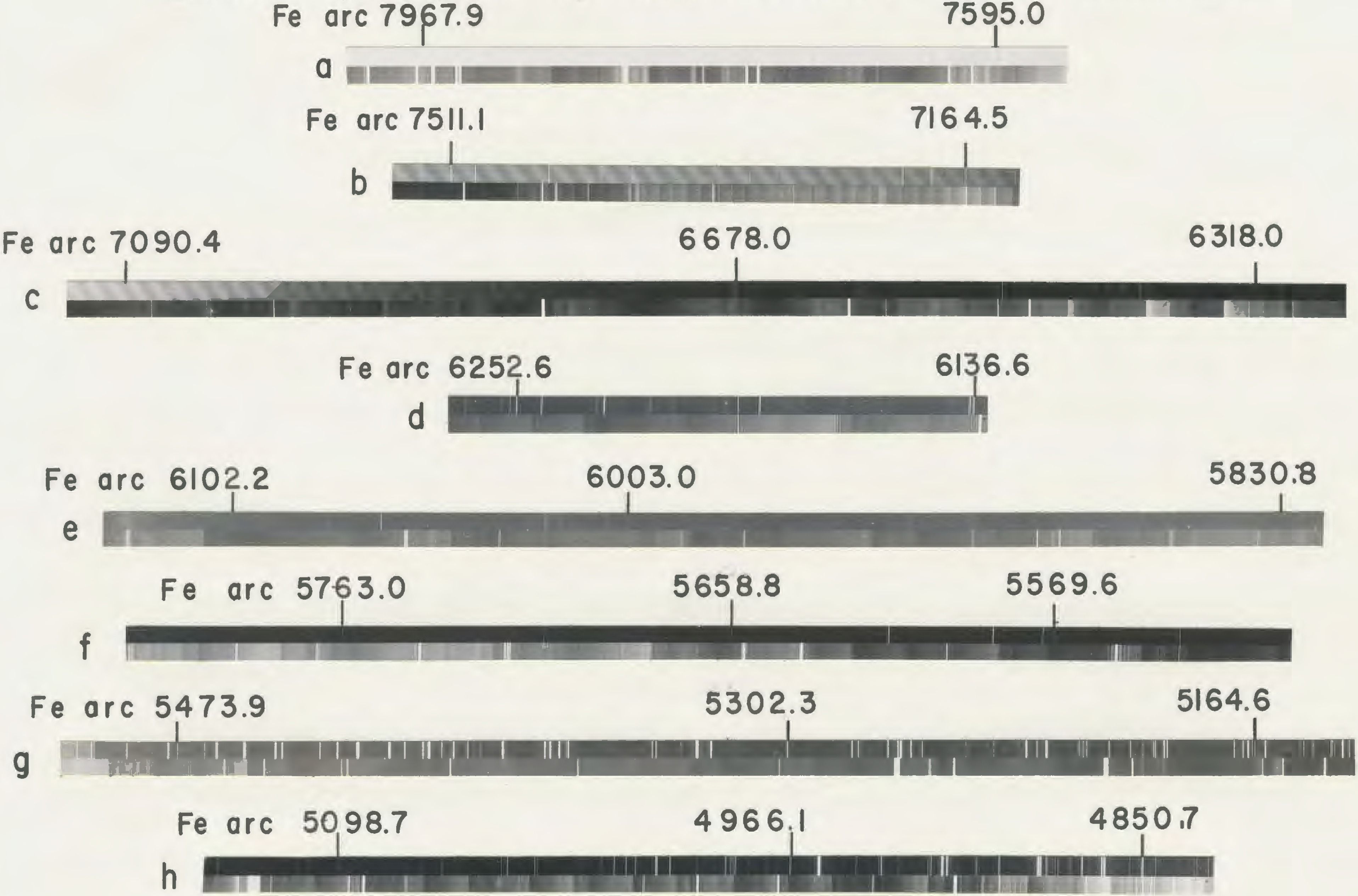


Table VI. The method of obtaining the vibrational constants of the upper and lower states of this system is essentially the same as the one described for the G - B system (section 3.2). The least squares straight line fits of $\Delta G_{v+\frac{1}{2}}$ versus $v + \frac{1}{2}$ for the upper and lower states of this system are also shown in Fig. 7. Finally, frequencies of the band heads of this system are represented by the expression

$$(3) \qquad \nu = 15477.4 + 156.4\,(v' + \tfrac{1}{2}) - 6.1\,(v' + \tfrac{1}{2})^2 - [132.4\,(v'' + \tfrac{1}{2}) - 0.3\,(v'' + \tfrac{1}{2})^2] \;.$$

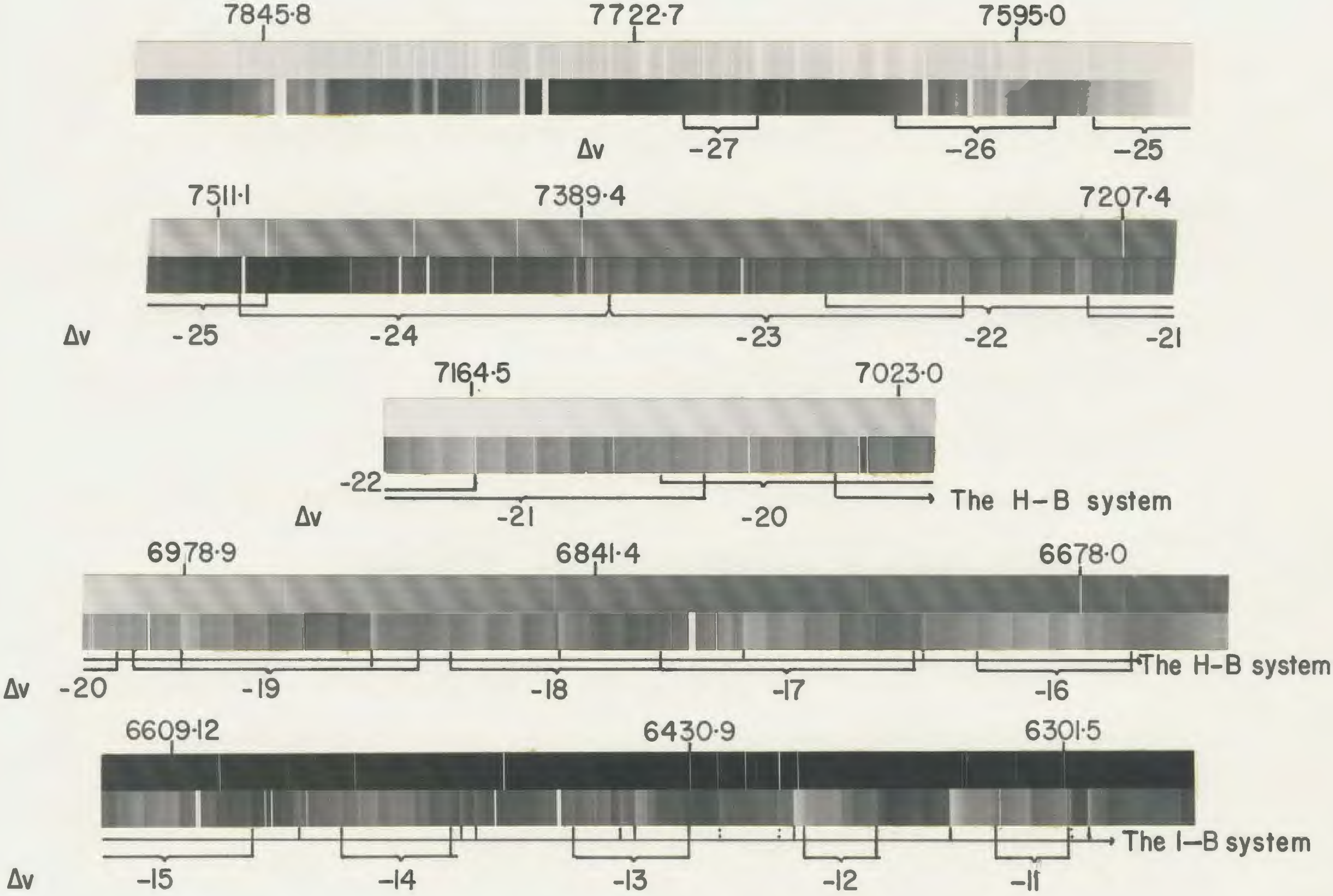
The differences between the observed frequencies and the calculated frequencies (using eq. (3)) are listed in Table V. The values of v' and v" are also included in the same Table. A glance at this table indicates that the differences, $\nu_{obs}-\nu_{cal}$, are $\gtrsim 1$ cm^{-1}. Such a good agreement between the observed and calculated values of ν's is a proof of the correctness of the vibrational assignments and the calculations. It is apparent from the values of the lower state vibrational constants of this system that this system and the G - B and H - B systems have a common lower state which is the upper state of the B - X system.

3.5 The B → X System:

The emission bands of the extensive B - X system which were previously studied by earlier workers in absorption occur in the spectral region from about 8000 Å to 4830 Å. The contact spectrograms of this system are given in plate IV and the enlarged spectrograms are

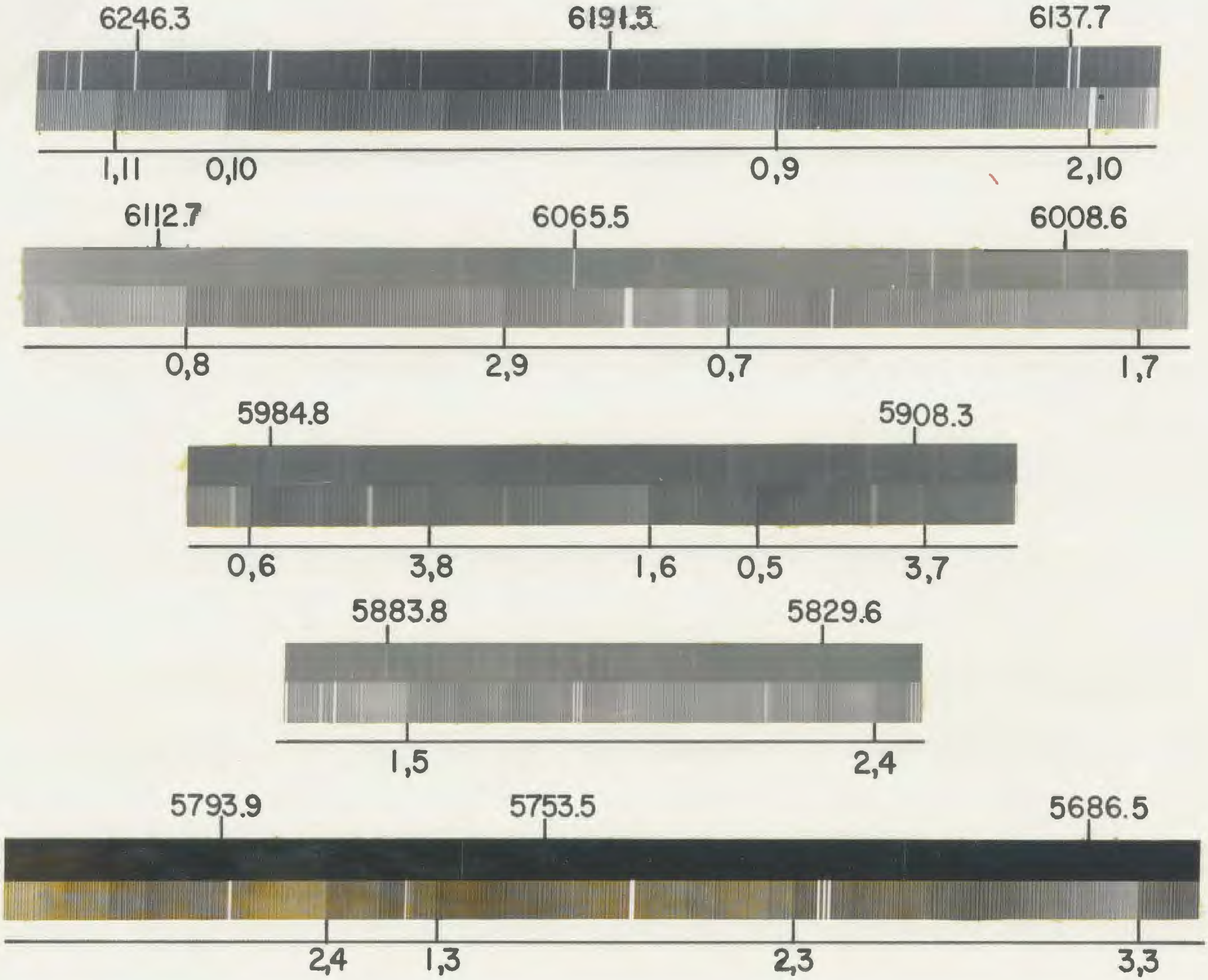
THE B→X SYSTEM OF DIATOMIC BISMUTH PLATE V

First order spectrograms



THE B → X SYSTEM OF DIATOMIC BISMUTH

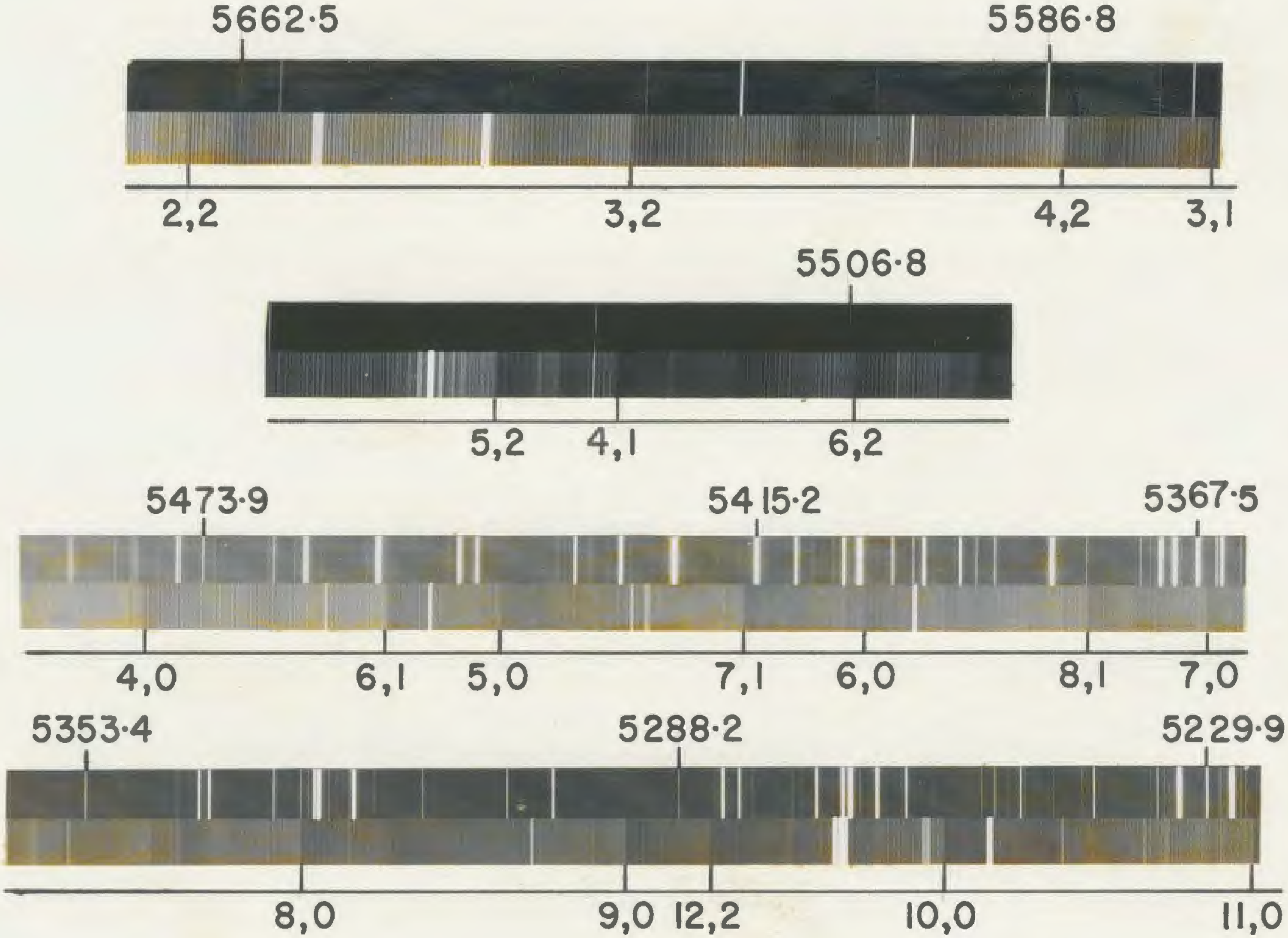
Second order spectrograms



THE B → X SYSTEM OF DIATOMIC BISMUTH

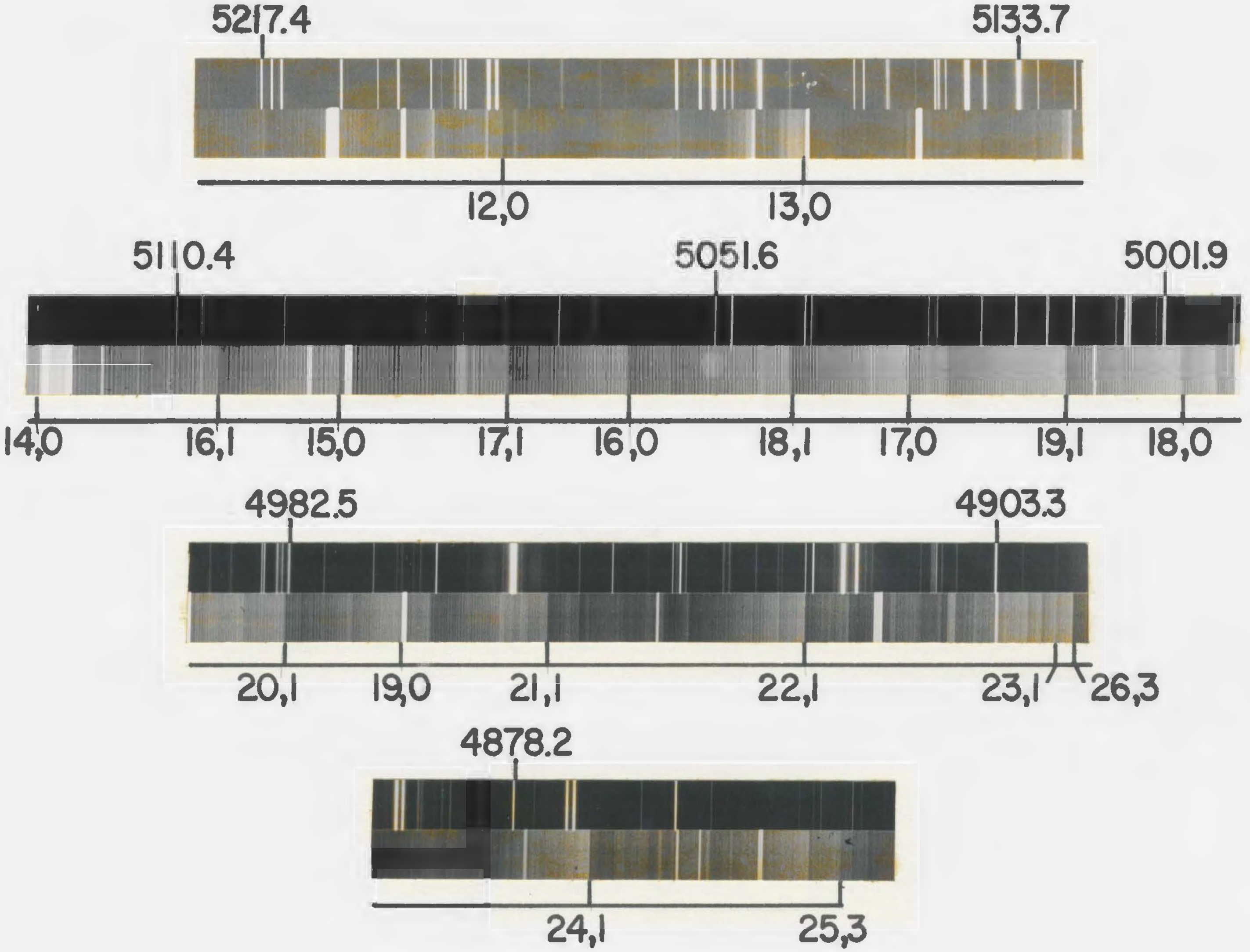
PLATE VII

Second order spectrograms



THE B → X SYSTEM OF DIATOMIC BISMUTH

Second order spectrograms



given in plates V to VIII. Altogether, about 270 bands which are degraded toward longer wave lengths were measured in the above spectral region. The wave lengths, vacuum wave numbers and intensities of the bands are listed in Table VII. The emission data are in general agreement with the data obtained in absorption. The intensity estimates of the bands of this system are not of much significance except in a narrow spectral region because three types of plates were used to photograph different parts of this system. It was not attempted in the present work to compare the intensities in widely different regions. The vibrational scheme extending to $v' = 28$ and $v'' = 51$ is shown in Table VII which spreads over six pages in this thesis. The bands fall into the usual parabola. The fact that the width of each branch of the parabola is quite small agrees with the Franck-Condon principle that the internuclear distance does not change much in a transition. The mean values of the vibrational intervals $\Delta G_{v+\frac{1}{2}}$ of about 210 discrete bands of this system are plotted against $v + \frac{1}{2}$ in Fig. 7. A fourth order polynomial fit (see eq. 6, Appendix) was found to be necessary to obtain a smooth relation between the values of $\Delta G_{v+\frac{1}{2}}$ and the corresponding values of $v + \frac{1}{2}$ for the upper as well as the lower states of this system. The constants b, c, d, e, and f in eq. 6, Appendix, obtained from this fit were used to calculate the vibrational constants of this system using eq. 8, Appendix. The value of ν_e was obtained as described in section 3.2 using frequencies of the above-mentioned 210 bands. The following expression is derived from the frequencies of the band heads:

$$\begin{aligned}\nu = {} & 17739.5 + 132.571\ (v' + \tfrac{1}{2}) - 0.3271\ (v' + \tfrac{1}{2})^2 \\ & + 0.5240 \times 10^{-3}\ (v' + \tfrac{1}{2})^3 - 0.5324 \times 10^{-4}\ (v' + \tfrac{1}{2})^4 \\ & + 0.154 \times 10^{-5}\ (v' + \tfrac{1}{2})^5 \\ & - [173.132\ (v'' + \tfrac{1}{2}) - 0.4156\ (v'' + \tfrac{1}{2})^2 \\ & + 0.2437 \times 10^{-2}\ (v'' + \tfrac{1}{2})^3 - 0.8356 \times 10^{-4}\ (v'' + \tfrac{1}{2})^4 \\ & + 0.72 \times 10^{-6}\ (v'' + \tfrac{1}{2})^5] \ .\end{aligned}$$

The vibrational assignments v', v" and the differences (ν_{obs}-ν_{cal}) are also included in Table VII. For at least 85% of the band heads of this system, these differences are less than 1 cm^{-1}. It is claimed that the vibrational constants obtained for the B - X system in the present work are the most accurate available so far for this system.

In conclusion of this chapter, it may be necessary to comment briefly on the values of ω_e and $\omega_e x_e$ of state B obtained independently from the analyses of the four different band systems described here. A comparison of these values indicate that all the values of ω_e agree well with each other; the values of $\omega_e x_e$ also agree well with each other, except the one obtained for the G-B system ($\omega_e'' x_e''$ = 0.6 cm^{-1}). This apparently larger value of $\omega_e'' x_e''$ may be due to uncertainty in the measurement of the band heads.

TABLE VII

Band Heads of the B-X System in the Region λ7980-4830 Å*

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
7971.70	12540.9	m	— —	—
7968.77	12545.5	w	— —	—
7952.47	12571.3	vw	— —	—
7908.17	12641.7	m	— —	—
7889.62	12671.4	m	— —	—
7844.40	12744.5	s	— —	—
7835.54	12758.9	m	— —	—
7812.15	12797.1	vw	— —	—
7795.18	12824.9	s	— —	—
7744.30	12909.2	vw	— —	—
7707.23	12971.3	vw	24, 51	-1.9
7699.27	12984.7	vw	23, 50	-0.9
7690.88	12998.8	vw	22, 49	0.5
7684.10	13010.3	w	21, 48	-0.9
7656.25	13057.6	vw	— —	—

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs} - \nu_{calc}$
7635.67	13092.8	w	25, 51	2.7
7629.81	13102.9	w	24, 50	-0.1
7621.69	13116.9	m	23, 49	0.7
7614.61	13129.0	s	22, 48	-0.7
7606.57	13142.9	s	21, 47	-0.5
7598.35	13157.1	s	20, 46	-0.3
7590.14	13171.4	m	19, 45	-0.3
7582.02	13185.5	w	18, 44	-0.8
7569.73	13206.9	w	26, 51	0.4
7562.11	13220.2	m	25, 50	0.3
7554.40	13233.7	w	24, 49	0.1
7546.25	13248.0	vw	23, 48	0.4
7538.77	13261.1	s	22, 47	-0.8
7530.70	13275.3	s	21, 46	-1.2
7522.30	13290.2	s	20, 45	-1.2
7513.77	13305.2	s	19, 44	-1.4
7504.14	13322.3	m	18, 43	0.2
			27, 51	-0.2

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v''	$\nu_{obs}-\nu_{calc}$
7495.87	13337.0	m	17, 42	-0.9
			26, 50	0.7
7487.83	13351.3	m	25, 49	0.8
7480.18	13365.0	w	24, 48	0.0
7472.23	13379.2	w	23, 47	-0.6
7463.75	13394.4	w	22, 46	-0.6
7455.09	13410.0	w	21, 45	-0.5
7446.41	13425.6	w	20, 44	-0.6
7437.61	13441.5	w	19, 43	-0.8
7428.57	13457.8	w	18, 42	-0.9
7419.37	13474.5	vw	17, 41	-0.9
7410.04	13491.5	vw	16, 40	-0.9
7400.53	13508.8	vw	15, 39	-0.9
7390.44	13527.3	m	14, 38	0.0
7380.98	13544.6	m	13, 37	-0.5
			21, 44	-0.7
7372.09	13561.0	m	20, 43	-0.9
7362.80	13578.1	m	19, 42	-0.9
7353.35	13595.5	m	18, 41	-0.9

TABLE VII (Continued)

Band Heads of the B - X System

$\lambda_{air}(\mathring{A})$	$\nu_{vac}(cm^{-1})$	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
7343.84	13613.1	m	17, 40	-0.8
7334.07	13631.3	w	16, 39	-0.5
7324.26	13649.5	m	15, 38	-0.5
7314.47	13667.8	m	14, 37	-0.7
7308.37	13679.2	w	21, 43	-1.8
7304.34	13686.7	m	13, 36	-0.6
7298.48	13697.7	w	20, 42	-1.1
7294.37	13705.4	m	12, 35	-0.9
7289.00	13715.5	m	19, 41	-1.2
7284.48	13724.0	m	11, 34	-1.5
7279.17	13734.1	m	18, 40	-0.9
7273.64	13744.5	w	10, 33	-0.9
7269.28	13752.7	m	17, 39	-0.6
7265.80	13759.3	m	— —	—
7262.71	13765.2	m	9, 32	0.0
7259.36	13771.5	m	16, 38	-0.6
7249.30	13790.6	s	15, 37	-0.7
7239.02	13810.2	s	14, 36	-0.5
7228.78	13829.8	s	13, 35	-0.6
7218.32	13849.8	s	12, 34	-0.6
7207.71	13870.2	m	11, 33	-0.5

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
7197.09	13890.7	m	17, 38	-2.9
			10, 32	-0.5
7185.74	13912.6	m	16, 37	-0.8
			9, 31	0.6
7175.15	13933.2	s	15, 36	-0.3
			8, 30	0.2
7164.64	13953.6	s**	14, 35	-0.2
			7, 29	-0.7
7153.98	13974.4	s	13, 34	-0.1
7143.29	13995.3	m**	12, 33	-0.1
7132.48	14016.5	m	11, 32	-0.1
7121.58	14038.0	m	10, 31	0.0
7110.52	14059.8	w	9, 30	0.1
7102.14	14076.4	w	15, 35	-0.2
7099.37	14081.9	w	8, 29	0.2
7091.10	14098.5	w	14, 34	0.6
7088.34	14103.8	w	7, 28	-0.1
7080.38	14119.7	m	13, 33	0.2
7069.52	14141.3	m	12, 32	0.0
7058.52	14163.4	m	11, 31	0.0

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
7047.35	14185.8	m	10, 30	0.0
7036.10	14208.5	m	9, 29	0.1
7024.90	14231.2	m	8, 28	-0.1
7013.62	14254.1	m	7, 27	-0.3
6986.18	14310.0	m	11, 30	-1.2
6974.24	14334.5	m	10, 29	0.1
6970.13	14343.0	w	— —	—
6962.85	14358.0	m	9, 28	0.0
6951.43	14381.6	m	8, 27	0.1
6939.91	14405.4	m	7, 26	-0.3
6928.13	14429.9	m	6, 25	-0.1
6916.36	14454.5	m	5, 24	0.4
6890.59	14508.6	m	9, 27	0.2
6878.97	14533.1	s	8, 26	0.0
6867.27	14557.8	s	7, 25	-0.2
6855.49	14582.8	m	6, 24	-0.3
6843.49	14608.4	m	5, 23	0.1
6831.54	14634.0	m	4, 22	0.1
6824.87	14648.3	w	— —	—

TABLE VII (Continued)

Band Heads of the B-X System

$\lambda_{air}(\mathring{A})$	$\nu_{vac}(cm^{-1})$	Intensity	v′, v″	$\nu_{obs}-\nu_{calc}$
6819.87	14659.0	w	3, 21 9, 26	-0.6 -0.8
6795.93	14710.6	s	7, 24	-0.5
6783.77	14737.0	s	6, 23	0.0
6772.07	14762.5	s	5, 22	-0.7
6759.76	14789.4	s	4, 21	-0.1
6751.53	14807.4	w	— —	—
6747.88	14815.4	m	— —	—
6747.45	14816.3	m	3, 20	0.2
6743.26	14825.5	w	— —	—
6735.66	14842.3	w	2, 19	-0.5
6726.13	14863.3	w	7, 23	-1.7
6713.35	14891.6	m	6, 22	-0.2
6701.34	14918.3	s	5, 21	-0.5
6696.45	14929.2	w	— —	—
6692.84	14937.2	m	— —	—
6689.04	14945.7	s	4, 20	-0.3
6681.42	14962.8	s	— —	—
6676.91	14972.9	m	3, 19	-0.5
6671.07	14986.0	w	— —	—

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v''	$\nu_{obs}-\nu_{calc}$
6664.56	15000.6	w	2, 18	-0.3
6631.93	15074.4	w	5, 20	-1.0
6619.50	15102.7	s	4, 19	-0.7
6607.22	15130.8	s	3, 18	-0.8
6594.85	15159.2	m	2, 17	-0.7
6582.35	15188.0	m	1, 16	-0.4
6550.98	15260.7	s	4, 18	-0.8
6538.42	15290.0	s	3, 17	-0.5
6526.07	15318.9	s	2, 16	-0.8
6520.91	15331.1	m	— —	—
6513.47	15348.6	m	1, 15	-0.4
6470.85	15449.7	s	3, 16	-0.6
6466.01	15461.2	m	— —	—
6461.30	15472.5	m	— —	—
6458.25	15479.8	s	2, 15	-0.5
6445.48	15510.5	s	1, 14	0.2
6432.47	15541.8	m	0, 13	1.2
6391.48	15641.5	m	2, 14	-0.1
6378.88	15672.4	s	1, 13	-0.1

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
6375.01	15681.9	m	— —	—
6366.36	15703.2	s	0, 12	-0.3
6363.95	15709.2	w	— —	—
6354.35	15732.9	w	— —	—
6337.61	15774.5	m	3, 14	2.3
6325.18	15805.5	m	2, 13	1.7
6313.13	15835.6	m	1, 12	0.2
6300.37	15867.7	m	0, 11	0.5
6286.55	15902.6	w	4, 14	0.4
6273.30	15936.2	vw	3, 13	1.8
6261.51	15966.2	vw	2, 12	-0.5
6248.69	15998.9	w	1, 11	-0.2
6235.74	16032.2	m	0, 10	0.5
6223.77	16063.0	w	4, 13	-1.4
6210.73	16096.7	w	3, 12	-0.6
6185.01	16163.7	m	1, 10	0.1
6172.11	16197.4	s	0, 9	0.5
6168.12	16207.9	w	— —	—
6163.37	16220.4	w	— —	—
6147.56	16262.1	m	3, 11	1.1

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v' v''	$\nu_{obs}-\nu_{calc}$
6135.57	16293.9	m**	2, 10	-1.0
6109.43	16363.6	s	0, 8	0.6
6073.59	16460.2	m	2, 9	0.1
6056.50	16506.6	w	— —	—
6051.69	16519.8	s	5, 11	-0.5
6047.79	16530.4	m	0, 7	0.6
6043.31	16542.7	w	— —	—
6038.62	16555.5	w	4, 10	0.0
6018.29	16611.4	m	7, 12	-1.9
6012.86	16626.4	m	2, 8	0.2
6004.86	16648.6	m	6, 11	-0.4
6000.00	16662.1	m	1, 7	0.4
5994.94	16676.1	w	— —	—
5987.15	16697.8	m	0, 6	0.5
5978.58	16721.8	w	4, 9	1.1
5966.11	16756.8	w	3, 8	0.0
5953.26	16792.9	w	2, 7	-0.1
5940.35	16829.4	m	1, 6	0.2
5927.29	16866.5	w	0, 5	0.8

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
5907.34	16923.4	w	3, 7	-0.2
5880.94	16999.4	s	1, 5	1.8
5869.16	17033.5	w	0, 4	-1.3
5862.45	17053.0	w	4, 7	-0.5
5837.43	17126.1	m	— —	—
5835.53	17131.7	m	2, 5	2.8
5831.03	17144.9	w	6, 8	0.2
5823.39	17167.4	m	1, 4	0.7
5804.99	17221.8	w	4, 6	0.7
5779.33	17298.3	m	2, 4	0.3
5766.14	17337.8	w	1, 3	1.2
5761.54	17351.7	w	5, 6	1.3
5736.13	17428.5	w	3, 4	-0.1
5732.68	17439.0	w	7, 7	-0.5
5726.11	17459.0	m	— —	—
5723.19	17467.9	m	2, 3	0.0
5710.00	17508.2	w	1, 2	0.9
5705.90	17520.7	w	5, 5	1.9
5680.59	17598.9	m	3, 3	0.4

TABLE VII (Continued)

Band Heads of the B-X System

$\lambda_{air}(\AA)$	$\nu_{vac}(cm^{-1})$	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
5667.37	17640.0	w	2, 2	1.4
5649.15	17696.9	w	9, 7	3.3
5637.25	17734.2	w	8, 6	-0.3
5626.07	17769.5	w	3, 2	0.3
5607.80	17827.4	w	— —	—
5601.87	17846.2	vw	— —	—
5597.50	17860.3	vw	5, 3	2.5
5585.22	17899.4	m	4, 2	0.2
5570.98	17945.2	w	3, 1	4.5
5545.14	18028.8	m	5, 2	0.3
5538.33	18051.0	w	— —	—
5531.88	18072.0	w	4, 1	1.3
5519.20	18113.6	w	3, 0	0.6
5506.17	18156.4	w	6, 2	-0.7
5492.90	18200.3	w	5, 1	0.3
5480.00	18243.1	w	4, 0	0.1
5454.00	18330.1	w	6, 1	1.5
5441.61	18371.8	vw	5, 0	-0.5
5419.09	18448.2	w	11, 4	-1.9

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
5416.76	18456.1	w	7, 1	-0.6
5403.84	18500.2	vw	6, 0	-0.8
5395.44	18529.0	vw	13, 5	-0.8
5379.43	18584.2	w	8, 1	0.2
5374.94	18599.7	w	— —	—
5366.49	18629.0	w	7, 0	0.0
5356.10	18665.1	vw	10, 2	-0.2
5346.35	18699.2	w	13, 4	0.3
5343.90	18707.7	w	— —	—
5333.38	18744.6	vw	12, 3	-0.1
5330.13	18756.1	w	8, 0	-0.2
5320.18	18791.1	vw	11, 2	0.4
5294.35	18882.8	w	9, 0	-0.2
5285.04	18916.1	w	12, 2	0.7
5259.17	19009.1	w	10, 0	0.0
5242.99	19067.8	vw	16, 4	0.6
5224.84	19134.0	w	11, 0	-0.5
5190.84	19259.4	w	12, 0	0.2
5170.21	19336.2	vw	14, 1	1.8

TABLE VII (Continued)

Band Heads of the B-X System

$\lambda_{air}(\mathring{A})$	$\nu_{vac}(cm^{-1})$	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
5164.16	19358.9	w	— —	—
5157.65	19383.3	m	13, 0	0.0
5137.70	19458.6	w	15, 1	1.4
5131.77	19481.0	w	18, 3	1.5
5124.60	19508.3	w**	14, 0	1.6
5119.05	19529.5	vw	17, 2	0.2
5105.90	19579.8	w	16, 1	0.5
5092.74	19630.3	w	15, 0	0.8
5074.30	19701.7	w	17, 1	0.9
5061.29	19752.3	w	16, 0	0.7
5056.46	19771.2	vw	19, 2	0.7
5043.20	19823.2	w	18, 1	1.5
5030.33	19873.9	m	17, 0	0.8
5025.84	19891.6	vw	20, 2	1.5
5012.94	19942.8	w	19, 1	0.8
4999.70	19995.7	w	18, 0	1.7
4995.98	20010.5	w	21, 2	1.3
4982.87	20063.2	w	20, 1	1.6
4970.33	20113.8	w**	19, 0	-0.5

TABLE VII (Continued)

Band Heads of the B-X System

λ_{air}(Å)	ν_{vac}(cm^{-1})	Intensity	v', v"	$\nu_{obs}-\nu_{calc}$
4966.85	20127.9	w	22, 2	0.3
4953.68	20181.4	w	21, 1	0.7
4950.15	20195.8	vw	24, 3	3.6
4937.92	20245.8	vw	23, 2	0.2
4924.82	20299.7	w	22, 1	0.6
4899.71	20403.7	w	— —	—
4898.12	20410.3	w	— —	—
4896.52	20417.0	w	23, 1	-0.1
4894.62	20424.9	w	26, 3	-0.6
4868.42	20534.8	w	24, 1	0.4
4840.88	20681.7	w	25, 1	0.4
4839.65	20656.9	w	28, 3	-0.1

---

[*] The notation for the intensities is the same as the one given in Table I .

TABLE VIII

Vibrational Scheme of the B - X System

v″ v′	0		1		2		3		4		5		6		7		8		9		10		11		12
0									17033.5	167.0	16866.5	168.7	16697.8	167.4	16530.4	166.8	16363.6	166.2	16197.4	165.2	16032.2	164.5	15867.7	164.5	15703.2
									133.9		132.9		131.6		131.7						131.5		131.2		132.4
1					17508.2	170.4	17337.8	170.4	17167.4	168.0	16999.4	170.0	16829.4	167.3	16662.1						16163.7	164.8	15998.9	163.3	15835.6
					131.8		130.1		130.9		132.3				130.8						130.2				130.6
2					17640.0	172.0	17467.9	169.6	17298.3	166.6	17131.7				16792.9	166.5	16626.4	166.2	16460.2	166.3	16293.9				15966.2
					129.5		131.0		130.2						130.5		130.4								130.5
3	18113.6	168.4	(17945.2)	175.7	17769.5	170.6	17598.9	170.4	17428.5						16923.4	166.6	16756.8						16262.1	165.4	16096.7
	129.5		126.8		129.9										129.6										
4	18243.1	171.1	18072.0	172.6	17899.4								17221.8	168.8	17053.0				16721.8	166.3	16555.5				
	128.7		128.3		129.4								129.9												
5	18371.8	171.5	18200.3	171.5	18028.8						17520.7	169.0	17351.7										16519.8		
	128.4		129.8		127.6																		128.8		
6	18500.2	170.1	18330.1	173.7	(18156.4)												17144.9						16648.6		
	128.8		126.0																						
7	18629.0	172.9	18456.1												17439.0										16611.4
	127.1		128.1																						
8	18756.1	171.9	18584.2										17734.2												
	126.7																								
9	18882.8														17696.9										
	126.3																								
10	19009.1				18665.1																				
	124.9				126.0																				
11	19134.0				18791.1				18448.2																
	125.4				125.0																				
12	19259.4				18916.1																				
	123.9																								
13	19383.3								18699.2	170.2	18529.0														
	125.0																								
14	19508.3	172.1	19336.2										18490.0												
	122.0		122.4																						

TABLE VIII (Continued)

Vibrational Scheme of the B - X System

v" v'	0		1		2	3	4	5	6
15	19630.3	171.7	19458.6						
	122.0		121.2						
16	19752.3	172.5	19579.8				19067.8		
	121.6		121.9						
17	19873.9	172.2	19701.7	172.2	19529.5				
	121.8		121.5						
18	19995.7	172.5	19823.2			19481.0			
	118.1		119.6						
19	20113.8	171.0	19942.8	171.6	19771.2				
			120.4		120.4				
20			20063.2	171.6	19891.6				
			118.2		118.9				
21			20181.4	170.9	20010.5				
			118.3		117.4				
22			20299.7	171.8	20127.9				
			117.3		117.9				
23			20417.0	171.2	20245.8				
			117.8						
24			20534.8			20195.8			
			116.9						
25			20651.7						
26						20424.9			

TABLE VIII (Continued)

Vibrational Scheme of the B - X System

v'' / v'		13		14		15		16		17		18		19		20		21		22		23		24
0	161.4	15541.8																						
		130.6																						
1	163.2	15672.4	161.9	15510.5	161.9	15348.6	160.6	15188.0																
		133.1		131.0		131.2		130.9																
2	160.7	15805.5	164.0	15641.5	161.7	15479.8	160.9	15318.9	159.7	15159.2	158.6	15000.6	158.3	14842.3										
		130.7		133.0				130.8		130.8		130.2		130.6										
3	160.5	15936.2	161.7	15774.5				15449.7	159.7	15290.0	159.2	15130.8	157.9	14972.9	156.6	14816.3	157.3	14659.0						
		126.8		128.1								129,9		129.8		129.4		130.4						
4		(16063.0)	160.4	(15902.6)								15260.7	158.0	15102.7	157.0	14945.7	156.3	14789.4	155.4	14634.0				
																128.7		128.9		128.5				
5																15074.4	156.1	14918.3	155.8	14762.5	154.1	14608.4	155.1	14453.3
																				129.1		128.6		129.5
6																				14891.6	154.6	14737.0	154.2	14582.8
																						126.3		127.8
7																						14863.3	152.7	14710.6

TABLE VIII (Continued)

Vibrational Scheme of the B - X System

v″ v′	24		25		26		27		28		29		30		31		32		33		34		35		36
5	14453.3																								
	129.5																								
6	14582.8	152.9	14429.9																						
	127.8		127.9																						
7	14710.6	152.8	14557.8	152.4	14405.4	151.3	14254.1	150.3	14103.8	150.2	13953.6														
					127.7		127.5		127.4		128.3														
8					14533.1	151.5	14381.6	150.4	14231.2	149.3	14081.9	148.7	13933.2												
					125.9		127.0		126.8		126.6		126.6												
9					14659.0	150.4	14508.6	150.6	14358.0	149.5	14208.5	148.7	14059.8	147.2	13912.6	147.4	13765.2								
											126.0		126.0		125.4		125.5								
10											14334.5	148.7	14185.8	147.8	14038.0	147.3	13890.7	146.2	13744.5						
													124.2		125.4		125.8		125.7						
11													14310.0	146.6	14163.4	146.9	14016.5	146.3	13870.2	146.2	13724.0				
																	124.8		125.1		125.8				
12																	14141.3	146.0	13995.3	145.5	13849.8	144.4	13705.4		
																			124.4		124.6		124.4		
13																			14119.7	145.3	13974.4	144.6	13829.8	143.1	13686.7
																					124.1		123.8		123.5
14																					14098.5	144.9	13953.6	143.4	13810.2

TABLE VIII (Continued)

Vibrational Scheme of the B - X System

v" v'	36		37		38		39		40		41		42		43		44		45		46		47		48
13	13686.7	142.1	13544.6																						
	123.5		123.2																						
14	13810.2	142.4	13667.8	140.5	13527.3																				
	123.0		122.8		122.2																				
15	13933.2	142.6	13790.6	141.1	13649.5	140.7	13508.8																		
			122.0		122.0		122.5																		
16			13912.6	141.1	13771.5	140.2	13631.3	139.8	13491.5																
					119.2		121.4		121.6																
17					(13890.7)	138.0	13752.7	139.6	13613.1	138.6	13474.5	137.5	13337.0	138.0	(13199.0)										
									121.0		121.0		120.8		123.3										
18									13734.1	138.6	13595.5	137.7	13457.8	135.5	13322.3	136.8	(13185.5)								
											120.0		120.3		119.2		119.7								
19											13715.5	137.4	13578.1	136.6	13441.5	136.3	13305.2	133.8	13171.4						
													119.6		119.5		120.4		118.8						
20													13697.7	136.7	13561.0	135.4	13425.6	135.4	13290.2	133.1	13157.1				
															118.2		119.0		119.8		118.2				
21															13679.2	134.6	13544.6	134.6	13410.0	134.7	13275.3	132.4	13142.9	132.6	13010.3
																	113.8				119.1		118.2		118.7
22																	(13658.4)				13394.4	133.3	13261.1	132.1	13129.0
																							118.1		119.0
23																							13379.2	131.2	13248.0

TABLE VIII (Continued)

Vibrational Scheme of the B - X System

v" v'	48		49		50		51
21	13010.3						
	118.7						
22	13129.0	130.2	12998.8				
	119.0		118.1				
23	13248.0	131.1	13116.9	132.2	12984.7		
	117.0		116.8		118.2		
24	13365.0	131.3	13233.7	130.8	13102.9	131.6	12971.3
			117.6		117.3		121.5
25			13351.3	131.1	13220.2	127.4	(13092.8)
					116.8		114.1
26					13337.0	130.1	13206.9
							115.4
27							13322.3

The figures in parentheses are less accurate than the others.

CHAPTER IV

DISCUSSION ON THE ELECTRONIC STATES OF Bi_2

4.1 Summary of the Electronic States of Bi_2:

As described in Chapter III, the present work contributed considerably to the spectroscopic knowledge of the Bi_2 molecule. Three band systems, observed for the first time, have been analyzed and vibrational constants derived. Accurate vibrational constants for one of the known systems of Bi_2 have also been derived from the present emission data. It is therefore considered worthwhile to summarize the existing data on the Bi_2 molecule. This information is presented in the following table and in Fig. 8.

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	Observed transition	References
	cm^{-1}					
	In addition a series of diffuse bands near 40200 cm^{-1}.					
(F)	~46000	only partially analyzed			(F) ← X	Almy and Sparks (1933)
E	42252	129	9.7		E ← B	Almy and Sparks (1933)
D	36457	157	4.6		D ← X	Almy and Sparks (1933)
I	33216.9	156.4	6.1		I → B	This thesis
H	(32591)	only one v" progression			H → B	This thesis
C	~32000	continuous absorption, repulsive state			C ← X	Almy and Sparks (1933)
G	29609.0	107.0	0.2		G → B	This thesis
B	17739.5	132.571	0.3271	0.000524	B ↔ X	This thesis
$X^1\Sigma_g^+$	0	173.132	0.4156	0.002437		This thesis

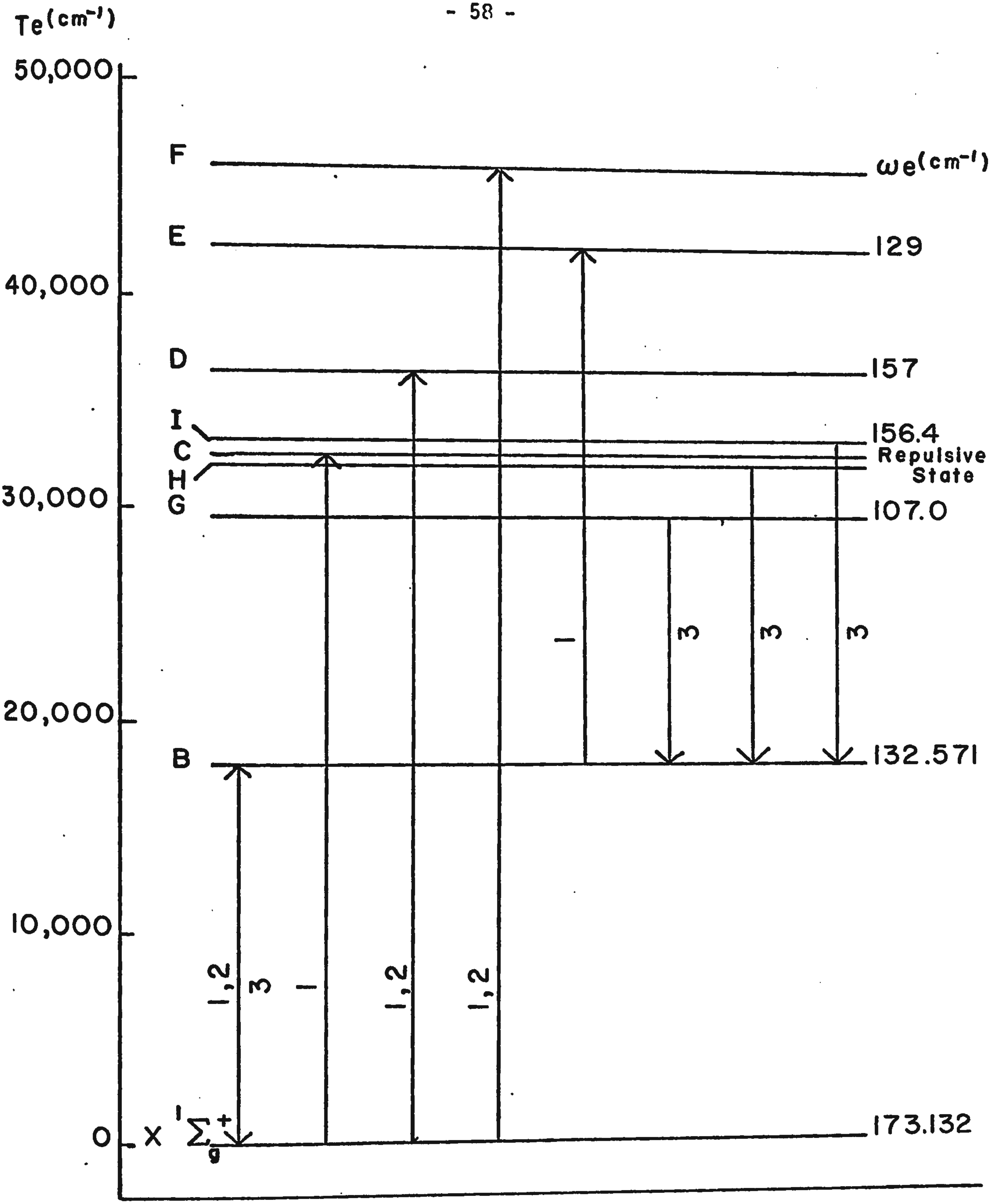


Fig. 8 Energy level diagram of the Bi_2 molecule. [1] Almy and Sparks (1933); [2] Nakamura and Shidei (1934); [3] This thesis.

4.2 Electronic Configurations and Molecular Terms of Bi_2:

To determine the nature of the electronic states of the observed transitions, it is necessary to do the rotational fine structure analyses of bands belonging to these transitions. Moderate dispersion used in the present work is not quite adequate to make such an analysis possible for the Bi_2 molecule. However, one can predict the possible electronic states of a molecule from the molecular orbital theory as well as from the separated atoms. We shall now consider, first, the number of low-lying states of Bi_2 which may be predicted by the molecular orbital theory and, second, the number of states of Bi_2 which can be formed from two bismuth atoms in their low-lying electronic states.

(i) From the molecular orbital theory:

The electron configuration of the Bi atom is $KLMNO_{spd}6s^2 6p^3$. In deriving the possible molecular electronic states of the Bi_2 molecule, we need not take into account the electrons of the inner K, L, M, N, O shells of the individual Bi atoms since these atomic shells are unaffected in the molecular formation. The 'united atom' method of writing the electron configuration for molecules is therefore not a good approximation in this case. Using the standard notation (Herzberg, 1950, Chapter VI), the electron configuration and the term type of the lowest electronic state of Bi_2 may be written as

$$\text{(1)} \qquad KKLLMMNN\ O_{spd}O_{spd}(\sigma_g 6s)^2(\sigma_u 6s)^2(\pi_u 6p)^4(\sigma_g 6p)^2 \ : \ {}^1\Sigma_g^+ \ .$$

Therefore, the ground electronic state X of Bi_2 is a $^1\Sigma_g^+$ state. The first excited electron configurations of Bi_2 are

(2) $$\mathrm{KK} \text{-------} (\sigma_g 6s)^2(\sigma_u 6s)^2(\pi_u 6p)^4(\sigma_g 6p)(\pi_g 6p) : {}^3\Pi_g,\ {}^1\Pi_g,$$

and

(3) $$\mathrm{KK} \text{-------} (\sigma_g 6s)^2(\sigma_u 6s)^2(\pi_u 6p)^3(\sigma_g 6p)^2(\pi_g 6p) : {}^1\Sigma_u^+,\ {}^3\Sigma_u^+,\ {}^1\Sigma_u^-,\ {}^3\Sigma_u^-\ {}^1\Delta_u,\ {}^3\Delta_u\ .$$

Higher excited states are obtained by bringing the emission electron taken from the $\sigma_g 6p$ or the $\pi_u 6p$ or the $\sigma_u 6s$ shells to higher and higher orbitals. The number of states resulting even from a few of these configurations is very large and does not allow a unique correlation with the numerous observed states. However, if the molecule under consideration is very simple, for example, H_2 or He_2, a unique correlation is possible. In the case of Bi_2, the observed low excited states B, G, C, H, I, D (Fig. 8) may probably be identified with those derived from the configurations (2) and (3).

(ii) From the States of Separated Bi Atoms:

If L_1 and L_2 are the quantum numbers of the orbital angular momenta of the two atoms and M_{L_1} and M_{L_2} their components in the direction of the internuclear axis, then the resultant orbital angular momentum $M_{L_1} + M_{L_2}$ and the quantum number Λ of the molecule is

(4) $$\Lambda = \left|M_{L_1} + M_{L_2}\right| \ .$$

The possible Λ values are obtained from all possible combinations of the individual M_L values. States with different Λ values correspond to different molecular electronic states. States which differ only in the sign of both M_{L_1} and M_{L_2} have equal energies if $M_{L_1} + M_{L_2} \neq 0$ and are said to be degenerate with each other. For $\Lambda = 0$, each combination corresponds to a different molecular state (Σ^+ or Σ^-). The resulting spin quantum number of the molecule is obtained from the two spin vectors S_1 and S_2 of the separated atoms as

$$(5) \qquad S = (S_1 + S_2),\ (S_1 + S_2 - 1),\ \text{---------},\ |S_1 - S_2|\ .$$

Each molecular state having a specific Λ value occurs with each of the multiplicities $2S + 1$ where S is given by (5).

Making use of the above considerations as well as the so-called Wigner-Witmer correlation rules (see Herzberg, 1950, Chapter VI) the number of states of the Bi_2 molecule which can be formed from two Bi atoms in their low-lying ^4S_u, ^2D_u, and ^2P_u states may be written in the following way:

$$(6) \qquad {}^4S_u + {}^4S_u \rightarrow {}^1\Sigma_g^+,\ {}^3\Sigma_u^+,\ {}^5\Sigma_g^+,\ {}^7\Sigma_u^+;$$

$$(7) \qquad {}^4S_u + {}^2D_u \rightarrow {}^3\Sigma_g^+,\ {}^3\Pi_g,\ {}^3\Delta_g,\ {}^5\Sigma_g^+,\ {}^5\Pi_g,\ {}^5\Delta_g,$$

$${}^3\Sigma_u^+,\ {}^3\Pi_u,\ {}^3\Delta_u,\ {}^5\Sigma_u^+,\ {}^5\Pi_u,\ {}^5\Delta_u;$$

(8) $^4S_u + {}^2P_u \rightarrow {}^3\Sigma_g^-, {}^3\Pi_g, {}^5\Sigma_g^-, {}^5\Pi_g,$

$^3\Sigma_u^-, {}^3\Pi_u, {}^5\Sigma_u^-, {}^5\Pi_u;$

(9) $^2D_u + {}^2D_u \rightarrow {}^1\Sigma_g^+(3), {}^1\Sigma_u^-(2), {}^1\Pi_g(2), {}^1\Pi_u(2), {}^1\Delta_g(2),$

$^1\Delta_u, {}^1\Phi_g, {}^1\Phi_u, {}^1\Gamma_g,$

$^3\Sigma_u^+(3), {}^3\Sigma_g^-(2), {}^3\Pi_u(2), {}^3\Pi_g(2), {}^3\Delta_u(2),$

$^3\Delta_g, {}^3\Phi_u, {}^3\Phi_g, {}^3\Gamma_u .$

Similarly, the states arising from the combinations $^2D_u + {}^2P_u$ and $^2P_u + {}^2P_u$ may also be obtained. The ground electronic state X of Bi_2 may be identified as the $^1\Sigma_g^+$ state arising from two normal Bi(^4S) atoms. The excited states B, G, C, H, I, etc., may correspond to those states which can be derived from the atomic states ^4S, ^2D, and ^2P as shown above.

APPENDIX

VIBRATIONAL STRUCTURE OF ELECTRONIC SPECTRA

The total energy E of a molecule can be expressed, to a good approximation, as the sum of three component parts, $E = E_e + E_v + E_r$, where E_e is the electronic energy, E_v is the vibrational energy and E_r is the rotational energy. The translational energy E_t, and the energy of the nuclei E_n, of the molecule are assumed to be zero and hence neglected in the above sum. When our interest is in the vibrational structure of electronic spectra, the rotational energy term E_r can also be omitted. Then the frequency $\nu(\mathrm{cm}^{-1})$ of a band head in an electronic band system is represented as

$$(1) \qquad \nu = (T'_e - T''_e) + (G'(v) - G''(v))$$

where $T_e = \frac{E_e}{ch}$, $G(v) = \frac{E_v}{ch}$, h is Planck's constant and c is the velocity of light. Here the single-primed letters refer to the upper electronic state and the double-primed letters refer to the lower electronic state. Putting $T'_e - T''_e = \nu_e$, eq. (1) can be written as

$$(2) \qquad \nu = \nu_e + G'(v) - G''(v) \quad ,$$

$$(3) \qquad \text{or } \nu_e = \nu - [G'(v) - G''(v)] \quad .$$

For an anharmonic oscillator, the vibrational term value G(v) for an electronic state is given by

$$(4) \qquad G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \omega_e z_e(v + \tfrac{1}{2})^4 + a(v + \tfrac{1}{2})^5 + \text{- - - - - - - - -} \quad .$$

Substituting eq. (4) in eq. (2) and retaining terms of $v + \frac{1}{2}$ up to the 5th power, we get

$$(5) \qquad \nu = \nu_e + \omega_e'(v' + \tfrac{1}{2}) - \omega_e'x_e'(v' + \tfrac{1}{2})^2 + \omega_e'y_e'(v' + \tfrac{1}{2})^3 + \omega_e'z_e'(v' + \tfrac{1}{2})^4 + a'(v' + \tfrac{1}{2})^5 - [\omega_e''(v'' + \tfrac{1}{2}) - \omega_e''x_e''(v'' + \tfrac{1}{2})^2 + \omega_e''y_e''(v'' + \tfrac{1}{2})^3 + \omega_e''z_e''(v'' + \tfrac{1}{2})^4 + a''(v'' + \tfrac{1}{2})^5] \quad .$$

The vibrational quanta $\Delta G_{v + \frac{1}{2}}$ for a given electronic state aredefined by the relation

$$(6) \qquad \Delta G_{v + \frac{1}{2}} = G(v + 1) - G(v) \ ,$$

$$= b - c(v + \tfrac{1}{2}) + d(v + \tfrac{1}{2})^2 + e(v + \tfrac{1}{2})^3 + f(v + \tfrac{1}{2})^4 ,$$

where $b = \omega_e - \omega_e x_e + \omega_e y_e + \omega_e z_e + a$

$c = 2\omega_e x_e - 3\omega_e y_e - 4\omega_e z_e - 5a$

(7) $d = 3\omega_e y_e + 6\omega_e z_e + 10a$

$e = 4\omega_e z_e + 10a$

$f = 5a$.

From relations (7) we get the following expressions for the vibrational anharmonicities and the vibrational frequency:

$$\begin{aligned}
a &= f/5 \\
\omega_e z_e &= e/4 - f/2 \\
\omega_e y_e &= \tfrac{1}{3}(d + f) - e/2 \\
\omega_e x_e &= \tfrac{1}{2}(c + d) - e/4 \\
\omega_e &= b + c/2 + d/6 - f/30 \, .
\end{aligned}$$

If we put $\omega_e y_e = \omega_e z_e = a = 0$ in eq. (4), eq. (6) reduces to

$$\Delta G_{v+\frac{1}{2}} = \omega_e - \omega_e x_e - 2\omega_e x_e(v + \tfrac{1}{2}) \quad . \tag{9}$$

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