

Band Spectra of BiBr, BiCl, BiF, and BiI in Absorption

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The band spectra of BiBr, BiCl, BiF, and BiI have been examined in absorption and a vibrational analysis made for each of the observed systems. For BiBr there are two systems for each of the isotopes Br⁷⁹ and Br⁸¹ with origins at 4045.7A and 4869.1A. The lower frequency system degrades to the red, but the direction in which the other degrades is in doubt. In BiCl a band system lying between

$\lambda\lambda 3600$ and $4000A$ has been found for each of the isotopes Cl³⁵ and Cl³⁷ in addition to the system at $\lambda\lambda 4300$ – $5500A$ reported by Saper. The vibrational analyses are confirmed by the respective isotope shifts. One band system between $\lambda\lambda 4150$ and $4900A$ for BiF and one between $\lambda\lambda 4150$ and $4300A$ for BiI have been observed and analyzed.

INTRODUCTION

EDER and Valenta¹ photographed the flame spectrum of various compounds of bismuth and found band systems lying in the region of $\lambda\lambda 4300$ – $6700A$, which they ascribed to BiO. Their photographs also show a group of lines in the neighborhood of $3900A$. Mecke and Guillery,² using previous data, arranged some of these bands in a Deslandres' scheme in which the constants correspond to those expected for BiO. Ghosh³ rephotographed the bands lying between 4300 and $6700A$ in a flaming arc fed with metallic bismuth or bismuth trichloride and made a vibrational analysis of the observed heads. He attributed them to BiO. Saper⁴ had previously studied the band system lying between 4300 and $5500A$, having excited it by introducing bismuth trichloride vapor into active nitrogen. His vibrational analysis of this band system is nearly identical with that given by Ghosh for the systems he assigned to BiO. The assignment of Saper is, however, reinforced by the fact that he observed an isotope shift in agreement with the expected shift for Cl=35 and Cl=37. Howell and Rochester⁵ using a high frequency electrical discharge have produced emission band spectra in BiBr and BiF, but no analysis of the observed systems seems to have been made.

In view of the apparent disagreement between Saper and Ghosh and the meagerness of data and analysis of the band systems of the bismuth halides, the present investigation was undertaken.

¹ Eder and Valenta, *Atlas Typischer Spektren*.

² Mecke and Guillery, *Physik. Zeits.* **28**, 514 (1927).

³ C. Ghosh, *Zeits. f. Physik* **86**, 241 (1933).

⁴ Saper, *Phys. Rev.* **37**, 1710A (1931).

⁵ Howell and Rochester, *Univ. Durham Phil. Soc. Proc.* **9**, 196 (1934).

EXPERIMENTAL

To obtain these absorption spectra, light from a 500-watt incandescent lamp was passed through the vapor under investigation in an electric furnace heated to a temperature ranging from $700^{\circ}C$ to $1400^{\circ}C$ and then focused on the slit of the spectrograph. The spectrograms were taken with four different types of spectrographs according to experimental needs. An E-1 Hilger quartz spectrograph was used essentially to explore the region under consideration and to determine suitable experimental conditions. Some of the measurements on the bands of bismuth chloride were made on photographic plates taken on a Hilger-185 quartz spectrograph. This instrument has a dispersion of about $9.5A/mm$ at $4500A$ and $7A/mm$ at $3900A$. The lower frequency system of bismuth chloride was photographed in the first order of a 21-ft. concave grating with 30,000 lines to the inch, giving a dispersion of $1.25A/mm$ at $4500A$. The other system in bismuth chloride was photographed both in the first and second order of this grating. The dispersion in the second order is $0.48A/mm$ at $3900A$. The remainder of the spectrograms from which measurements were made were taken on a 10-ft. concave grating on a Littrow mounting. This instrument has a dispersion of about $5.7A/mm$ in the first order. Both the first and second orders were used.

A standard iron arc was used as a comparison spectrum and measurements of wave-lengths were made on a Geneva Society comparator.

Two types of electric furnaces were used, one a Hoskins carbon resistor furnace giving temperatures up to $1600^{\circ}C$, the other a Hoskins

resistance furnace with which temperatures up to 1000°C can be attained.

To get the band systems of BiBr, bromine was passed over molten bismuth in an iron tube in the resistance furnace heated to about 900°C. The tube was open to the air at atmospheric pressure.

The BiCl bands were obtained by heating solid BiCl₃ in an open iron or quartz tube in the resistance furnace until the temperature was sufficiently high to vaporize the bismuth trichloride and dissociate it to form BiCl. They were also obtained by heating metallic bismuth in one of these tubes to the desired temperature and passing pure chlorine gas over the molten metal. Similarly the bands of BiI were produced by heating bismuth and iodine together at a temperature of 600 to 700°C and the same band

system was obtained when BiI₃ was heated to the necessary temperature.

To develop the band systems of BiF a higher temperature is required. Hence bismuth trifluoride was heated in the Hoskins carbon resistor furnace to a temperature of about 1200°C. At this temperature a well-defined band system is developed in absorption.

BiBr BANDS

In BiBr two band systems have been observed for each of the two isotopes of bromine, Br = 79 and Br = 81. The intensities of the corresponding bands are nearly equal as might be expected from the fact that the abundance of the isotopes is essentially the same. The lower frequency band system for each of the isotopes degrades

TABLE I. *BiBr band systems.*

LESS REFRANGIBLE SYSTEM					MORE REFRANGIBLE SYSTEM									
<i>v'</i>	<i>v''</i>	<i>I</i>	<i>ν</i> _{obs.}	<i>ν</i> _{calc.}	<i>v'</i>	<i>v''</i>	<i>I</i>	<i>ν</i> _{obs.}	<i>ν</i> _{calc.}	<i>v'</i>	<i>v''</i>	<i>I</i>	<i>ν</i> _{obs.}	<i>ν</i> _{calc.}
1	11	0	18385.6*	-1.1	3	3	1	268.8*	1.6	6	10	00	24209.3*	0.9
		0	404.6	-0.9								00	213.8	0.6
0	10	1	450.8*	-0.6	2	2	8	347.8*	1.8	7	11	00	246.9*	-0.6
		1	469.2	-0.6								00	251.6	-0.2
1	10	2	585.0*	-0.9	3	2	6	476.7*	2.8	2	4	2	431.8*	1.6
		2	603.4	0.3								2	434.2	1.4
0	9	4	652.2*	0.7	2	1	5	555.3*	1.6	3	5	2	480.0*	0.5
		4	668.1	-0.2								2	482.1	1.2
1	9	0	786.8*	0.8	4	2	3	600.9*	-1.7	4	6	1	525.3*	-0.2
		0	802.2	0.6								1	527.0	-0.2
0	8	6	852.6*	-0.1	3	1	6	683.3*	-0.2	0	1	0	530.0*	-0.3
		6	867.5	-0.1								1	568.3*	-0.4
2	9	0	917.4*	-1.1	4	1	5	809.9*	0.0	5	7	1	569.6	-0.4
		0	19054.6*	-0.1								2	585.0*	0.5
0	7	10	067.9	0.0	5	1	4	930.8	1.1	1	2	2	585.9	0.2
		9	257.6*	-0.2				21018.3*	-0.5	6	8	0	608.5*	-0.4
0	6	9	268.6	-0.5	4	0	2	015.9	0.3	6	8	0	609.6	-0.4
		1	320.9*	-0.8				047.6	0.2	2	3	2	636.2	-0.2
2	7	1	330.5	-0.1	5	0	4	140.7*	-0.8					
		8	461.4*	-0.3				135.6	-1.8	3	4	2	683.9*	0.0
0	5	8	470.5	-0.7	7	1	1	163.1	-1.6	4	5	1	728.5	-0.6
		7	596.3*	0.1				258.0*	-2.0	0	0	10	738.6*	0.0
1	5	7	604.6	0.1	6	0	5	254.1	-0.9	5	6	2	770.8*	-0.5
		4	666.8*	0.1				372.5*	-0.8	1	1	10	792.1*	0.3
0	4	4	674.5	0.3	7	0	5	365.7	-1.8	6	7	3	810.5*	-0.4
		5	801.3*	0.3				480.1*	-0.6	2	2	9	842.0*	-0.1
1	4	5	807.8	0.3	8	0	5	473.1	1.6					
		0	932.7*	-0.8				582.4*	0.5	8	6	4	484.2*	-0.8
2	4	0	937.6	-0.2	9	0	4	574.2	-1.2				478.1	-1.0
		4	20007.6*	0.8				678.1*	1.9	1	1	10	511.1*	-0.1
1	3	4	012.6	1.1	10	0	3	670.4	0.8	6	7	3	504.5	0.3
		0	079.1*	0.1				763.1*	0.2	4	1	2	552.9*	0.3
0	2	0	140.0*	1.1	11	0	1	756.0	-0.3				545.6	0.4
		5	143.4	1.6						7	8	2	846.2*	-0.7
2	3	5	215.5	2.0						8	9	1	877.8*	-2.3
		2								3	3	8	889.1*	0.2
1	2	2										7	933.0*	-0.5
										4	4	7	931.3	-0.3
												5	974.3*	-0.6
										5	5	5	972.4	-0.2
												5	999.8*	-0.2
										1	0	5	997.0	-0.5
										6	6	3	25012.7*	-0.4
										7	7	3	010.6	-0.2
												7	overlapped by (2,1)	
										2	1	7	049.2*	-0.2
												7	046.0	-0.2
												8	856.1	1.3
												2	865.7*	1.2
												2	856.1	1.3
												2	892.9*	-0.1
												2	883.4	-0.1

* The bands marked with an (*) are bands due to BiBr⁷⁹.

toward the red. It was not possible to determine unambiguously in which direction the bands of the other system degrade. In some cases they appear to degrade to the red, but ordinarily they have the appearance of lines. This uncertainty may arise because of branches that rise almost vertically on a Fortrat diagram. According to the rule of Birge and Mecke they should degrade toward the violet since $\omega_e' > \omega_e''$.

The observed wave numbers, the difference between the observed and calculated wave numbers, the estimated intensities, and the vibrational quantum numbers are recorded in Table I for the bands corresponding to each of the isotopes of bromine.

These band heads are represented within the experimental error by the following formulas:

For the lower frequency system:

$$\begin{aligned} \text{BiBr}^{79}: \nu &= 20,532.0 + [135.91u' - 0.534u'^2 \\ &\quad - 0.1030u'^3] - [209.50u'' - 0.466u''^2]; \\ \text{BiBr}^{81}: \nu &= 20,532.0 + [134.69u' - 0.524u'^2 \\ &\quad - 0.1002u'^3] - [207.61u'' - 0.458u''^2], \end{aligned}$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

For the higher-frequency system:

$$\begin{aligned} \text{BiBr}^{79}: \nu &= 24,710.9 + [265.34u' - 1.956u'^2] \\ &\quad - [209.17u'' - 0.469u''^2]; \\ \text{BiBr}^{81}: \nu &= 24,710.9 + [262.95u' - 1.921u'^2] \\ &\quad - [207.29u'' - 0.461u''^2], \end{aligned}$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

The constants for BiBr^{81} were derived from the constants for BiBr^{79} from the well-known formula,

$$G(v) = \rho\omega_e(v + \frac{1}{2}) - \rho^2x_e\omega_e(v + \frac{1}{2})^2 + \rho^3y_e\omega_e(v + \frac{1}{2})^3 \dots,$$

for the vibrational terms of different isotopes, where ρ^2 is the ratio of the reduced masses of BiBr^{79} and BiBr^{81} . It will be observed from the vibrational formula for the system toward the red that the coefficient of the third-degree term of the excited level is large. It has been necessary to introduce this third-degree term with a large coefficient to take account of the rapid convergence of the band heads (Fig. 1b). That this convergence is very rapid is immediately evident from the second-order grating plates. The convergence point, as calculated from the band-head formula, is at about 4520A.

TABLE II. Intensities of BiBr bands.

LESS REFRACTILE												MORE REFRACTILE															
v'	v''	0	1	2	3	4	5	6	7	8	9	10	11	v'	v''	0	1	2	3	4	5	6	7	8	9	10	11
0														0		10	0										
1														1		5	10	2									
2														2		3	7	9	2	2							
3														3		1	5	6	8	2	2						
4														4			2	6	5	7	1	1					
5														5			0	3	6	4	5	2	1				
6														6				1	4	6	3	3	0	00			
7														7					2	4	5	2	* 2		00		
8														8						2	3	4	0	1	1		
9																											
10																											
11																											

* Overlapped by (2,1).

The intensities of the band heads lie on well-defined Franck-Condon parabolas (Table II). For the system lying toward the red the parabola is much more open than for the other system as might be expected from the magnitude of the constants. The matrix scheme for the more refrangible system closely resembles that given by M. Wehrli and E. Miescher⁶ for the indium halides.

BiCl BANDS

For bismuth chloride two band systems were also observed for each of the isotopes of chlorine, Cl=35 and Cl=37. One of these systems, the one lying toward the red, has already been reported and analyzed by Saper.⁴ The other seems not to have been previously observed. The intensity of the bands for BiCl^{35} is about three times the intensity of the corresponding bands for BiCl^{37} as might be expected from the abundance of the isotopes. As in the band systems due to bismuth bromide the longer wave-length system degrades toward the red and the behavior of the other band system in this respect is uncertain.

Table III gives the observed wave numbers, the differences between observed and calculated wave numbers, the estimated intensities and the vibrational quantum numbers for the band systems due to BiCl^{35} and BiCl^{37} .

Within experimental error the vibrational analyses of these heads are given by the following formulas:

For the longer wave-length system:

⁶ M. Wehrli and E. Miescher, *Helv. Phys. Acta.* **7**, 298 (1934).

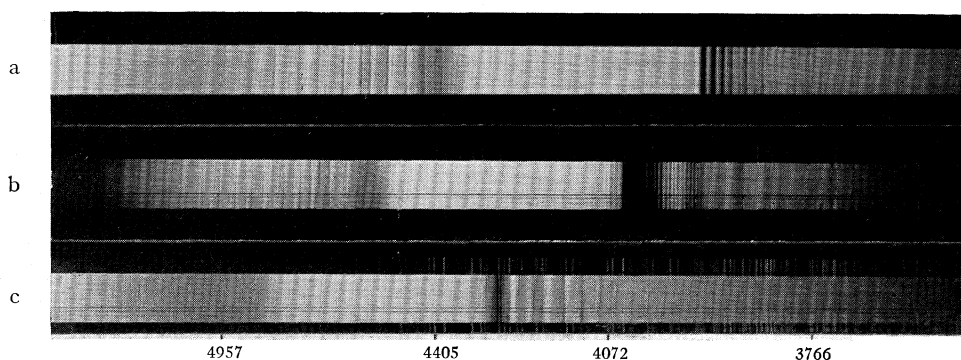


FIG. 1. Comparison of spectra: (a) BiCl; (b) BiBr; (c) BiI. Between $\lambda\lambda 4500$ and 4570 in (b), the absorption appears to be continuous. The band heads of the longer wave-length system converge to a point in this region. In (c), the bands to the extreme left are due to diatomic bismuth. The same bands appear in the case of BiBr, BiCl, or BiF, but at progressively higher temperatures. It is possible, of course, that there may be BiI bands mixed in with the Bi_2 bands.

TABLE III. *BiCl* band systems.

LESS REFRACTILE SYSTEM						MORE REFRACTILE SYSTEM													
v'	v''	I	$\nu_{obs.}$	$\nu_{obs.} - \nu_{calc.}$	$\nu_{obs.} - \nu_{calc.}$	v'	v''	I	$\nu_{obs.}$	$\nu_{obs.} - \nu_{calc.}$	$\nu_{obs.} - \nu_{calc.}$	v'	v''	I	$\nu_{obs.}$	$\nu_{obs.} - \nu_{calc.}$			
3	13	0	18552*	-2	0	2	8	146.7*	0.2	1	3	0	25024.9*	0.7	3	1	3	399.7*	1.2
4	13	0	754*	0	2	4	0	162.2	-0.5	2	4	0	113.5*	1.4	9	8	00	379.0	0.4
3	12	1	837*	-1	3	5	0	361.5*	-0.3	3	5	0	197.5*	3.0	9	8	00	441.5*	-0.6
2	11	1	917*	0	1	2	7	372.1	0.0	4	6	0	273.8*	2.3	4	2	4	467.9*	0.0
5	13	1	947*	-3	0	1	5	450.8*	-0.2	1	2	0	328.6*	2.5	4	2	1	446.2	-0.8
1	10	1	994*	0	0	1	2	459.5	0.3	5	7	0	344.4*	1.1	5	3	4	530.9*	-1.1
4	12	1	19037*	1	3	3	4	475.4*	0.9	2	3	0	415.7*	3.6	6	4	2	508.3	-2.2
3	11	0	124*	1	2	2	0	572.1*	-0.2	3	4	0	417.2	2.8	6	4	3	588.7*	-2.0
2	10	2	204*	0	1	1	10	576.2	-1.4	0	0	10	539.9*	-0.6	7	5	3	642.1*	-2.1
1	9	2	262	-1	1	1	3	670.4	0.9	0	0	5	537.9	-1.4	7	5	1	618.4	-3.9
4	11	0	322*	0	0	0	1	756.2*	-1.2	4	5	1	568.5*	0.7	8	6	3	690.7*	-1.1
0	8	1	360*	1	2	1	10	876.4*	0.0	1	1	2	632.0*	2.0	3	0	2	666.8	-0.3
3	10	2	410*	0	1	0	5	972.3*	-0.4	5	6	0	628.1	1.1	3	0	0	705.9*	1.7
2	9	2	494*	0	3	1	1	22081.7*	0.0	5	6	0	636.6*	-0.9	9	7	2	678.0	0.4
1	8	2	548	2	2	0	7	071.4	-4.5	6	7	1	702.7*	-0.7	9	7	1	733.8*	-0.7
0	7	2	575*	0	2	0	7	182.8*	0.0	2	2	1	700.2	-0.3	10	8	1	710.4	-2.6
2	8	3	653.5*	0.8	3	0	2	176.7	2.3	7	8	0	716.4*	2.4	10	8	10	770.5*	-1.1
5	10	1	702.2	-0.5	5	1	4	374.5	-0.7	7	8	0	710.9	1.5	4	1	2	747.5	-3.3
1	7	3	785.0*	0.1	4	0	3	476.0*	-1.5	3	3	4	759.1*	-1.9	4	1	1	772.1*	0.3
4	9	0	805*	-1	5	1	8	588.4*	0.4	3	3	7	794.0*	1.3	5	2	2	783.1*	-0.6
0	6	4	868.3*	-0.4	6	1	2	571.5	0.2	8	9	0	787.2	0.4	8	3	1	803.6	-1.9
5	9	1	911.2	-0.8	8	2	1	665.2*	0.8	4	4	3	812.9*	-1.8	6	3	2	889.2*	-1.5
1	6	2	948.2*	0.6	5	0	4	647.1	-2.7	5	5	2	808.4	-4.3	7	4	1	859.2	-3.0
4	8	1	991.1	1.1	8	2	1	727.0*	0.7	4	4	6	808.4	-4.3	7	4	2	940.6*	-1.7
0	5	6	20095*	0	5	0	0	706.6	-4.5	4	4	3	858.0	-0.9	7	4	1	910.3	-2.3
4	8	1	163.5*	0.6	5	0	4	783.4*	-0.5	5	5	2	932.4	-1.4	8	5	2	987.2*	-0.9
0	5	3	191*	0	7	1	1	760.1	-2.6	1	0	6	937.0*	1.3	8	5	1	956.7	-2.8
6	9	0	244.5*	0.1	7	1	3	849.6*	-2.5	6	6	0	926.2	0.6	9	6	2	27028.7*	0.0
0	4	7	280.6	0.3	9	2	0	828.1	-3.5	6	6	1	993.8*	-2.4	9	6	1	26998.5	-2.1
3	6	0	284.3*	0.3	9	2	1	906.0*	5.0	2	1	2	984.1	-4.0	10	7	1	27063.2*	-0.8
2	5	1	543.1*	0.0	6	0	3	882.1	-1.3	2	1	3	26020.0*	2.1	10	7	0	034.0	-2.4
0	3	3	572.2	-0.1	6	0	1	971.1*	-1.7	7	7	1	007.6	1.4	4	0	00	477.7*	0.2
3	6	0	578.3*	0.0	8	1	0	946.0	-3.1	7	7	2	051.5*	-1.9	5	1	1	137.3*	-0.5
2	5	1	669.6*	-0.2	8	1	2	23031.0*	0.2	3	2	2	041.1	-3.8	5	1	00	100.7	-1.6
0	3	9	843.9*	0.1	10	2	1	005.7	-2.9	8	8	1	096.0*	0.4	6	2	1	191.6*	-1.0
2	4	1	866.0	-0.1	7	0	1	071.3*	0.6	4	3	2	082.2	0.4	6	2	0	154.4	-2.6
1	3	2	969.8*	1.3	7	0	0	158.3*	-0.2	8	8	1	103.8*	-1.4	7	3	1	240.8*	-1.6
		1	21058.3*	-0.8	9	0	1	125.1	-5.8	4	3	4	166.0*	0.0	8	3	0	203.8	-2.1
			074.6	-1.8	9	0	1	512.6*	0.7	5	4	2	151.2	-0.9	8	4	1	27285.7*	-0.6
										5	4	3	26230.7*	-2.1	8	4	0	248.3	-2.5
										6	5	2	215.0	-2.5	9	5	2	325.4*	0.4
										6	5	3	290.5*	-2.0	10	6	0	288.3	-1.7
										2	0	4	274.2	-3.3	10	6	1	358.0*	-0.2
										7	6	2	325.7*	2.1	8	3	1	586.0*	-0.3
										7	6	1	306.3	1.7	8	3	00	543.3	-0.7
										8	7	0	345.7*	-1.9	9	4	0	623.7*	0.5
										8	7	1	328.9	-3.6	9	4	00	579.8	-1.5
										8	7	0	396.6*	-1.0	10	4	00	654.7*	0.2

* The bands marked with an asterisk are BiCl₂.

$$\text{BiCl}^{35}: \nu = 21,801.8 + [220.3u' - 2.50u'^2] \\ - [308.4u'' - 0.96u''^2];$$

$$\text{BiCl}^{37}: \nu = 21,801.8 + [215.1u' - 2.38u'^2] \\ - [301.2u'' - 0.92u''^2].$$

For the shorter wave-length system:

$$\text{BiCl}^{35}: \nu = 25,493.7 + [402.55u' - 3.650u'^2] \\ - [307.66u'' - 0.954u''^2];$$

$$\text{BiCl}^{37}: \nu = 25,493.7 + [393.12u' - 3.481u'^2] \\ - [300.45u'' - 0.910u''^2],$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

As in the case of the BiBr bands, the coefficients for the equation for BiCl³⁷ were calculated from theory involving the isotope shift.

The constants for the longer wave-length system differ only slightly from those reported by Saper.⁴ They also differ only slightly from those given by Ghosh³ for BiO if the origin used by Ghosh is properly displaced. In view of the agreement between these results and those of Saper, the similarity of this band system to the corresponding band systems of BiBr and BiF, and the satisfactory confirmation of isotope theory, it seems that Ghosh has incorrectly assigned this band system to BiO. In this connection it may be of interest to recall that Barratt⁷ has shown that much confusion may arise in the identification of band systems because of the presence of chlorine as an impurity.

It is evident that the deviation of the calculated from the observed wave numbers for the higher frequency system is much greater for BiCl than for BiBr. This deviation apparently originates in perturbation of the upper levels because in the Deslandres' arrangement the values of $\Delta G''$ are quite consistent with what might be expected while $\Delta(\Delta G')$ first decreases and then increases as one goes to higher values of v' . The constants for the upper level are only average ones and only approximately fit the data. The error in observed frequencies should be less in this system than in any of the others because the heads were relatively sharp and the dispersion in the second order was only a little more than 3 cm⁻¹/mm. There is also a rather consistent, but unexplained, deviation between

the observed and calculated isotope displacement of the bands of this system.

Even in the second order of the 21-ft. grating, no rotational structure was resolved. The bands appeared essentially as lines somewhat diffuse on the red side.

The intensities of band heads of both systems lie on Franck-Condon parabolas quite similar to those shown in Table II for BiBr.

BiF BANDS

With bismuth fluoride (BiF), one strong and one weak band system were found. The weaker system lying toward the violet was not developed sufficiently well for measurement and analysis. The other system lying toward the red was similar to the corresponding system found for BiBr and BiCl except for the absence of the bands due to isotopes. Like the bands due to BiBr and BiCl, these bands degrade to the red.

The data for this system together with the vibrational analysis are recorded in Table IV. The band heads are represented by the equation:

$$\nu = 22,958.5 + [383.6u' - 3.28u'^2] \\ - [512.0u'' - 2.25u''^2],$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

TABLE IV. *BiF bands.*

v'	v''	I	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	v'	v''	I	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
3	7	00	20548.0	0.5	4	4	00	360.2	0.3
2	6	00	664.6	0.5	0	1	7	386.5	-0.1
1	5	00	780.3	1.6	3	3	4	494.4	-2.1
4	7	0	906.3	1.4	2	2	3	630.6	-0.5
3	6	1	21027.0	-1.0	0	0	10	894.2	0.1
2	5	2	148.5	-0.5	3	2	0	992.6	-2.5
1	4	3	268.2	0.1	2	1	5	23132.9	-1.2
0	3	3	385.1	0.0	1	0	9	271.2	0.1
3	5	0	512.3	-0.7	4	2	4	351.2	-1.2
2	4	4	637.4	-1.2	3	1	8	497.2	-0.8
1	3	5	761.8	-0.3	2	0	9	641.2	-0.3
0	2	6	883.4	-0.2	5	2	1	706.9	3.7
2	3	000	22134.6	2.0	4	1	1	854.7	-0.7
1	2	4	260.3	-0.3	3	0	4	24003.8	-1.6

BiI BANDS

With bismuth iodide only one band system was observed. It corresponds to the system lying farther toward the violet in the other bismuth halides. As in the corresponding system in BiBr and BiCl the direction in which the bands degrade is uncertain.

It might be expected that there should be another system corresponding to the longer

⁷ Barratt, Trans. Faraday Soc. 25, 758 (1929).

TABLE V. *BiI bands.*

v'	v''	I	$\nu_{\text{obs.}}$	$-\nu_{\text{calc.}}$	v'	v''	I	$\nu_{\text{obs.}}$	$-\nu_{\text{calc.}}$
4	6	0	23202.0	0.9	4	4	4	522.3	0.2
5	7	0	220.5	-5.2	1	0	4	601.3	-0.4
0	1	1	242.5	0.0	2	1	4	631.1	-0.1
1	2	2	275.5	-0.2	3	2	3	658.8	0.3
2	3	4	308.5	2.0	4	3	2	683.9	0.4
3	4	4	335.2	0.1	5	4	0	706.9	0.6
4	5	4	361.5	0.2	2	0	2	794.5	-0.1
0	0	10	406.1	0.1	3	1	2	821.6	-0.6
1	1	9	438.3	-0.1	4	2	1	845.8	0.3
2	2	6	468.5	0.0	5	3	0	864.0	-3.7
3	3	4	496.6	0.1	4	1	0	24008.2	0.0

wave-length bands of BiBr and BiCl, but such a system was not observed. Judging from the way this system shifts in going from BiF to BiCl to BiBr, it would be expected in BiI at wave-lengths greater than 4500Å, but if it appeared in that region it would be completely masked by the strongly developed diatomic bismuth bands. It may be that BiI is too unstable at the temperature used in these experiments to obtain this system in absorption.

Table V, together with the following equation, gives the data and vibrational analysis of this system:

$$\nu = 23,388.9 + [198.6u' - 1.44u'^2] - [163.9u'' - 0.31u''^2],$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$.

The distribution of intensities is represented by a Franck-Condon parabola closely resembling the parabola for the corresponding system in BiBr and BiCl.

DISCUSSION OF RESULTS

Vibrational constants

According to the rule of Rosen⁸ $\omega_e'^{1/2}Z_1Z_2$ should be constant for these halides where Z_1 and Z_2 are the atomic numbers of the atoms in the molecule, and according to Mecke⁹ $\omega_e'^{1/2}\mu(Z_1 + Z_2)$ is constant for molecules of this type, where μ is the reduced mass of the molecule.

TABLE VI.

MOLECULE	$\mu 10^{24}$	ω_e''	$\omega_e'^{1/2}Z_1Z_2 10^{-7}$	$\omega_e'^{1/2}\mu(Z_1 + Z_2) 10^{16}$
BiF	28.7	512.0	19.6	6.9
BiCl	50.0	308.0	13.5	4.8
BiBr	95.3	209.4	12.8	4.9
BiI	130.2	163.9	11.8	4.8

⁸ B. Rosen, *Naturwiss.* **14**, 978 (1926).

⁹ R. Mecke, *Zeits. f. Physik* **42**, 390 (1927).

From Table VI it is evident that $\omega_e'^{1/2}Z_1Z_2$ decreases with increasing molecular weight and that $\omega_e'^{1/2}\mu(Z_1 + Z_2)$ is nearly constant if BiF is excluded.

Dissociation energies

It is not in general possible to calculate the dissociation energies of these halides from the vibrational constants, because the band systems do not converge rapidly enough. In the case of the longer wave-length band system in BiBr the convergence of the excited levels is sufficiently rapid to permit the necessary extrapolations to be made with some accuracy. Both band systems in BiCl converge very slowly so that long extrapolations are necessary and the accuracy of the calculated dissociation energies is small. Table VII shows the dissociation energies for BiBr and

TABLE VII.

BiBr			BiCl		
LEVEL	DISSOCIATION* ENERGY D (volts)	$D - Dx$	LEVEL	DISSOCIATION* ENERGY D (volts)	$D - Dx$
C	4.1	1.2	C	4.5	1.5
B	2.7	-0.2	B	3.3	0.3
X	2.9	0	X	3.0	0
ATOMIC EXCITATION			ATOMIC EXCITATION		
PROBABLE PRODUCTS	ENERGY** (volts)		PROBABLE PRODUCTS	ENERGY** (volts)	
Br(² P _{3/2}) + Bi(² D _{3/2})	1.9		Cl(² P _{3/2}) + Bi(² D _{3/2})	1.9	
Br(² P _{3/2}) + Bi(² D _{5/2})	1.4		Cl(² P _{3/2}) + Bi(² D _{5/2})	1.4	
Br(² P _{1/2}) + Bi(⁴ S _{3/2})	0.45		Cl(² P _{1/2}) + Bi(⁴ S _{3/2})	0.1	
Br(² P _{3/2}) + Bi(⁴ S _{3/2})	0		Cl(² P _{3/2}) + Bi(⁴ S _{3/2})	0	

* For states C and B, $D = D' + E_{\text{mole}}$.

** Calculated from values given in *Atomic Energy States* by Bacher and Goudsmit.

BiCl calculated in the usual way¹⁰ from the vibrational constants. Two of these atomic energy differences, *viz.*, 1.2 volts for BiBr and 1.5 volts for BiCl, suggest that in these cases the dissociation products are Br(²P_{3/2}) + Bi(²D_{3/2}) and Cl(²P_{3/2}) + Bi(²D_{3/2}), respectively, although the more probable¹¹ energy difference would be 1.9 volts if the ²D_{5/2} state of bismuth is more probable than the ²D_{3/2} state.

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¹⁰ Jevons, *Band Spectra of Diatomic Molecules*.

¹¹ G. M. Almy and F. M. Sparks, *Phys. Rev.* **44**, 365 (1933).

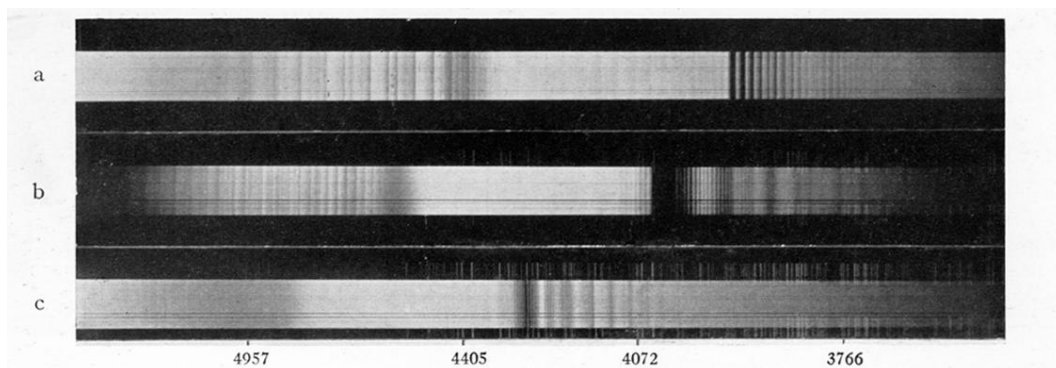


FIG. 1. Comparison of spectra: (a) BiCl; (b) BiBr; (c) BiI. Between $\lambda\lambda 4500$ and 4570 in (b), the absorption appears to be continuous. The band heads of the longer wave-length system converge to a point in this region. In (c), the bands to the extreme left are due to diatomic bismuth. The same bands appear in the case of BiBr, BiCl, or BiF, but at progressively higher temperatures. It is possible, of course, that there may be BiI bands mixed in with the Bi_2 bands.