

THE ABSORPTION SPECTRUM OF BiBr

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INTRODUCTION

Howell and Rochester (1934) using a high frequency discharge obtained the emission band spectrum of BiBr molecule, but no vibrational analysis seems to have been done. Morgan (1936) obtained the absorption spectrum by using a long column of vapour formed by heating bismuth metal in a vapour of bromine in an open iron tube to a temperature of 900°C. Besides these no further information is available.

In view of the fact that a system of bands of BiCl molecule was observed by one of the authors (Sur, 1950) in the extreme ultraviolet region ($\lambda\lambda$ 2400–2200) in absorption, it was expected that a molecule of the same group might give a corresponding system in about the same region. With this purpose in view, the present investigation was undertaken.

EXPERIMENTAL

The experimental arrangement was essentially the same as was used by the author in previous investigation on BiCl (1950) and BiS (1951), and other molecules. A chemically pure sample of BiBr₃ salt was obtained from Eimer and Amend, New York, through the kindness of the Head of the Department of Chemistry, University of Cornell. A small quantity of the salt after being dried in an oven was introduced into a vitreous tube 15 cms. long and 1 cm. internal diameter. This tube was inserted into a closely fitting Acheson graphite tube heated electrically to a temperature ranging from 900°C. to 1020°C. within a water-cooled furnace provided with side windows for making observations. The substance is highly vaporisable and quickly effuses out of the absorbing tube. To prevent this the furnace chamber was kept filled with nitrogen at a pressure of about 30 cms. of mercury. It was not until the vapour had thinned out sufficiently that a spectrogram of measurable intensity was possible, for which a prolonged exposure lasting from two to two and a half, sometimes three hours was found necessary. The band systems, in spite of several try outs under varying conditions, could only be developed feebly. A temperature of about 990°C. was sufficient to bring out the bands to just a measurable intensity. Observations were taken on a E_2 quartz spectrograph on *B*, 20 Kodak plates. A copper arc was used for comparison spectra, and temperatures were estimated by an optical pyrometer of the vanishing filament type. A water-cooled hydrogen discharge provided with quartz windows was used for the continuum.

RESULTS

Figures I(a) and I(b), Plate VII, are a reproduction of the bands of the ultraviolet system *C*, and systems *D* and *E* respectively. The observed wavenumbers reduced to vacuum, the difference between the observed and calculated wavenumbers, the

estimated intensities on the scale of ten, and the vibrational quantum numbers are recorded in Tables I, II and III for the three systems of bands. Tables IV, V and VI give the Deslander's scheme. These band heads are represented within the experimental error by the following formulae:—

For the system *C*

$$\nu = 34362.9 + 503.8(v' + \frac{1}{2}) - 40(v' + \frac{1}{2})^2 - 209.3(v'' + \frac{1}{2}) + 40(v'' + \frac{1}{2})^2.$$

For the system *D*

$$\nu = 41633.3 + 652.5(v' + \frac{1}{2}) - 209.2(v'' + \frac{1}{2}) - 25(v' + \frac{1}{2})^2 + 60(v'' + \frac{1}{2})^2$$

and for the system *E*,

$$\nu = 43502.33 + 319(v' + \frac{1}{2}) - 5.5(v' + \frac{1}{2})^2 - 209.2(v'' + \frac{1}{2}) + 60(v'' + \frac{1}{2})^2$$

The last two systems overlap between the wavelengths $\lambda\lambda$ 2350–2336 Å, as the system origins are very close to each other.

TABLE I

λ in Å.	Int.	ν obs. cm. ⁻¹	ν cal. cm. ⁻¹	ν obs. - ν cal.	v'	v''
2968.5	0	33677.5	33681	- 3.5	0	4
2950.3	0	33885.0	33887	- 2	0	3
2932.0	2	34096.0	34094	2	0	2
2912.7	0	34310.6	34302	8.6	0	1
2893.0	4	34509.0	34510	- 1	0	0
2872.0	0	34808.0	34805	3	1	1
2856.0	10	35003.7	35013	- 9.3	1	0
2834.56	.	Atomic line				
2814.7	8	35517.3	35515	2.3	2	0
2794.8	6	35770.2	35778	- 7.8	5	6
2774.8	2	36028.0	36017	11	3	0
2747.0	4	36393.0	36394	- 1	5	3
2730.7	0	36609.8	36601	8.8	5	2
2709.9	0	36890.8	36893	- 2.2	6	3

TABLE II

λ in Å.	Int.	ν obs. cm. ⁻¹	ν cal. cm. ⁻¹	ν obs. - ν cal.	v'	v''
2448.6	0	40827	40827	0	0	5
2436.5	2	41030	41030.4	- 0.4	0	4
2425.5	5	41233	41234.6	- 1.6	0	3
2412.5	7	41438	41440.2	- 2.2	0	2
2400.5	7	41645	41647	- 2	0	1
2388.5	7	41854.5	41855	- 0.5	0	0
2375.1	9	42090.6	42092	- 1.4	1	2
2363.5	9	42297	42299	- 2	1	1
2336.5	7	42786	42782	4	3	5

TABLE III

λ in Å.	Int.	ν obs. cm. ⁻¹	ν cal. cm. ⁻¹	ν obs. - ν cal.	ν'	ν''
2350.6	10	42529	42528	1	0	5
* 2327.8	1	42946	42935.6	10.4	0	3
2317.8	5	43131	43141.2	-10.2	0	2
2306.2	9	43348	43348	0	0	1
* 2295.2	2	43556	43556	0	0	0
2290.0	0	43655	43656	-1	1	1
2279.1	2	43864	43864	0	1	0
2264.0	2	44156	44161	-5	2	0
* 2246.1	0	44509	44514	-5	4	1
* 2232.4	0	44781	44778	3	5	1
* 2222.1	0	44988	44986	2	5	0

* Not quite visible under comparator..

TABLE IV

6				36891			
5		36610		36393			35770
4							
3	36028						
2	35517						
1	35004	34808					
0	34509	34310	34096	33885	33677		
ν'/ν''	0	1	2	3	4	5	6

System C

TABLE V

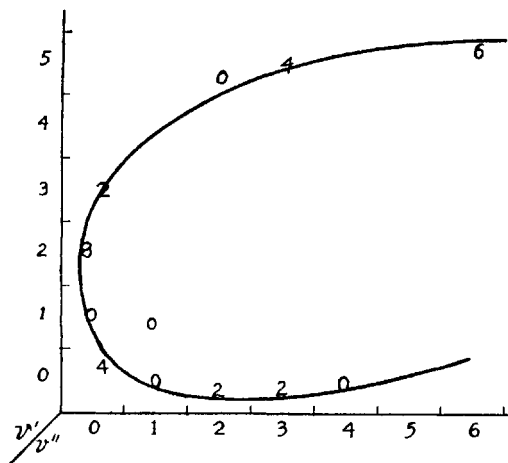
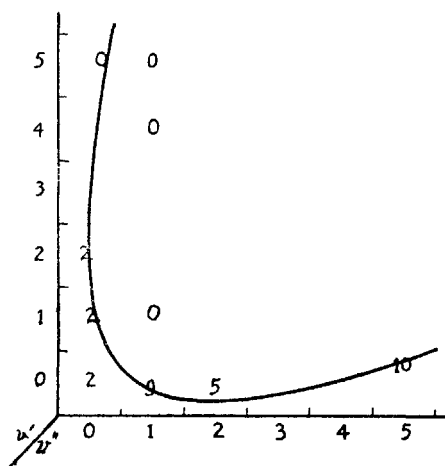
3						42786
2						
1		42297	42091			
0	41855	41645	41438	41233	41030	40827
ν'/ν''	0	1	2	3	4	5

System D

TABLE VI

6						
5	44988	44781				
4		44509				
3						
2	44156					
1	43864	43655				
0	43556	43348	43131	42946		42529
ν'/ν''	0	1	2	3	4	5

System E

FIG. 2. System *C*FIG. 3. System *E*

Figs. 2 and 3 show the Condon parabolas for the systems *C* and *E* respectively.

These parabolas are not well defined on account of few bands in each of the above systems. A parabola could not be drawn for system *D* on account of the same reason. These plots, however, indicate that the intensity plots of the band heads lie on open parabolas as expected from large differences in the values of w_s' and w_s'' in the above systems. The intensity observed for the (0, 5) bands of the system *E* is abnormally high.

DISCUSSION OF RESULTS.

Morgan could observe in absorption band systems due to each of the isotopic molecules BiBr⁷⁹ and BiBr⁸¹ which have practically the same abundance ratio. He had taken his spectrograms on a 21 ft. grating in the second order having a dispersion of .48 Å/mm. at 3900 Å. In our case no such isotopic separation in the

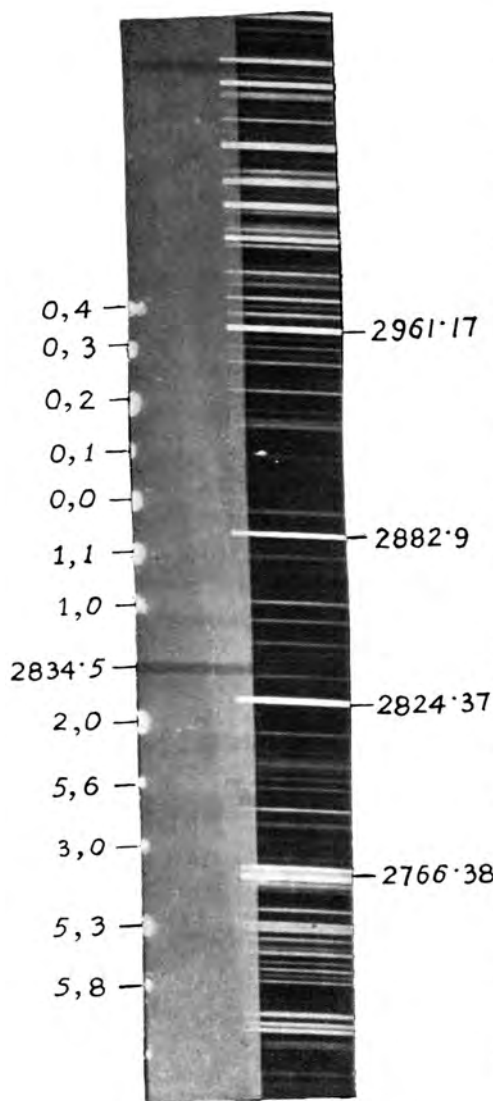


FIG. 1(a)
C System of BiBr

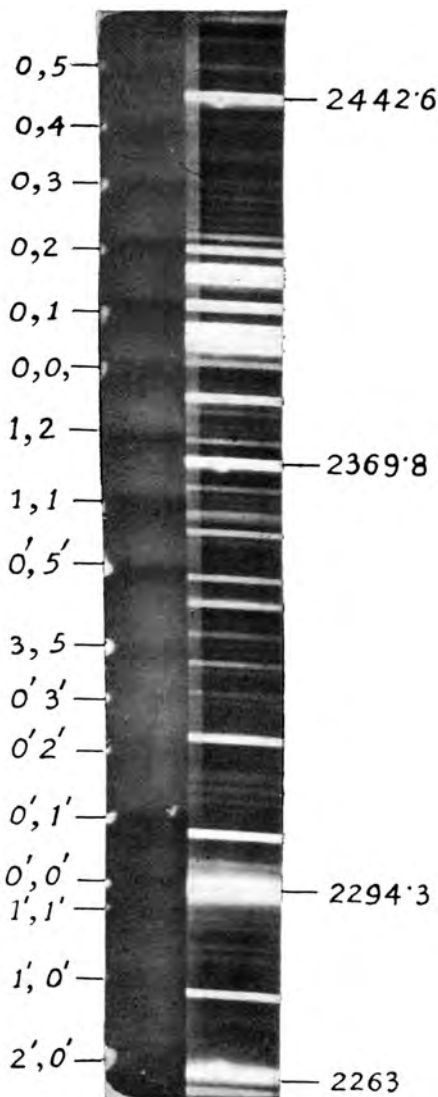


FIG. 1(b)
D and E Systems of BiBr
The bands of the E System are marked with a dash

band heads could be detected, even for the more refrangible systems using a medium quartz spectrograph, having a dispersion of 11 Å/mm. Possibly another reason for its non-appearance may be that a wide slit had to be used for photographing the bands in the extreme ultraviolet region because of the very poor intensity of the continuum in this region from the hydrogen discharge tube. If the slit width was narrowed down below a certain limit, it was observed that no continuum could be recorded on the plates. As a result the band heads were very diffuse, and possibly isotopic heads were lost in the general diffusiveness of the band heads. The increasing diffusiveness of the heads, however, as they move out from the system origin leads one to suspect that there are unresolved bands due to isotopic molecules (BiBr⁷⁹ and BiBr⁸¹). An isotopic separation could, however, be observed in the case of BiCl molecule by one of the authors. The three systems observed by the authors as well as the two observed by Morgan in the visible region appear to have the same ground state as can be judged by a comparison of the values of the ground state constants for the different systems observed by the authors, and those determined by Frank Morgan.

For the lower frequency system of BiBr⁷⁹

Morgan	Authors
	System <i>A</i> (lower frequency)
w_e'' 209.50	w_e'' 209.30
$w_e'' x_e''$ 0.466	$w_e'' x_e''$.40

For the higher frequency system of BiBr⁷⁹

	Authors
	Systems <i>D</i> and <i>E</i> (higher frequency)
w_e'' 209.17	209.20
$w_e'' x_e''$.469	.60

Besides the agreement of these constants, higher frequency system *B* of Morgan's bands in the visible region were always recorded on the plates, though as a very narrow absorption region (under the small dispersion of a medium quartz spectrograph) with a sharp edge at about λ 4040-45*, which is practically the same as the origin of the system reported by Morgan, thus confirming the assignment of the new systems obtained by the authors to BiBr molecule.

Morgan observed in both the band systems obtained by him in the visible region, a rapid convergence of the band heads. As the number of band heads in each of the systems is sufficiently large, it was possible to obtain the convergence limit at about λ 4520 Å, and to determine the dissociation energy D_0 . In the present case, the number of bands observed is very few, and the heads do not show any convergence at all, even to extrapolate and determine the limit. Thus it is not possible from the existing data to calculate the dissociation energy of the molecule.

Summing up the following schematic diagram Fig. 4 (not drawn to scale) gives an idea of the various electronic levels of the molecule obtained by the authors in relation to those observed by Morgan.

* Actual Head at ν 24738.6, i.e. λ 4041 Å. On closer examination of the Morgan's bands as recorded on the plates of the authors, it is easily possible to identify the fairly strong bands of the sequence $\Delta v = 0$, which lie on the shorter wavelength side of λ 4041, (0,0,) band.

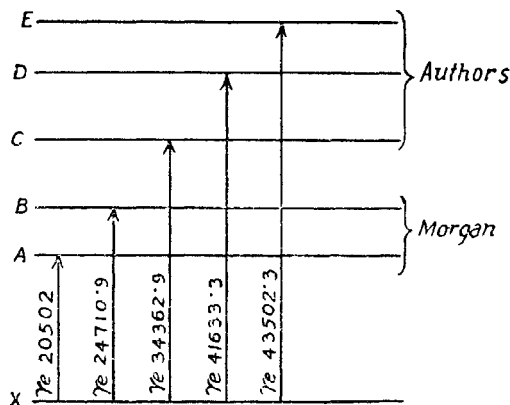


FIG. 4.

SUMMARY

Morgan observed two systems of bands in absorption for BiBr molecule in the visible regions with origins at 4045.7 Å and 4869.1 Å. The lower frequency system degrades to the red, but the direction in which the other system degrades is in doubt. In the present paper are reported three new systems observed in absorption in the ultraviolet regions $\lambda\lambda$ 2968–2709, $\lambda\lambda$ 2450–2336 and $\lambda\lambda$ 2350–2200 respectively. The bands are degraded to the violet in each case, and the band heads fit in the following formulas:

$$\text{System C, } \nu = 34362.9 + 503.8u' - 0.40u'^2 - 209.3u'' + 0.40u''^2$$

$$\text{System D, } \nu = 41633.3 + 652.5u' - 0.25u'^2 - 209.2u'' + 0.60u''^2$$

$$\text{System E, } \nu = 43502.33 + 319u' - 5.5u'^2 - 209.2u'' + 0.60u''^2$$

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

Band heads due to the isotopic molecule BiBr⁸¹ were not recorded.

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