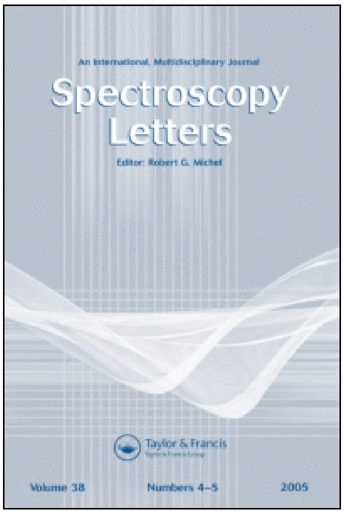

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Precise Vibrational Analysis of B-X System of BiI

Onkar N. Singh[a]; B. P. Asthana[a]; O. N. Singh[ab]
[a] Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi, INDIA [b] FOM Institute for Atomic and Molecular Physics, Amsterdam, HOLLAND

To cite this Article Singh, Onkar N. , Asthana, B. P. and Singh, O. N.(1975) 'Precise Vibrational Analysis of B-X System of BiI', Spectroscopy Letters, 8: 2, 101 — 111
To link to this Article: DOI: 10.1080/00387017508067312
URL: http://dx.doi.org/10.1080/00387017508067312

SPECTROSCOPY LETTERS, 8(2&3), 101-111 (1975)

PRECISE VIBRATIONAL ANALYSIS OF B-X SYSTEM OF BiI

Onkar N.Singh*, B.P.Asthana and O.N.Singh**
Spectroscopy Laboratory, Department of Physics
Banaras Hindu University
Varanasi 221005 (INDIA)

ABSTRACT

The bands of the B-X system of BiI have been photographed in the second order of a 35 ft concave grating spectrograph (with a dispersion of 0.33 Å/mm and resolution 2 X 180,000). A precise vibrational analysis of this system has been carried out and the vibrational constants $\omega_e y_e$ and $\omega_e z_e$ for the upper and lower states have been evaluated for the first time.

INTRODUCTION

The electronic spectra of bismuth halides have been the subject of numerous investigations by various workers[1-32]. A survey of the existing literature on the spectra of diatomic bismuth halides shows that our knowledge regarding the spectra of BiI molecule is meagre. Four electronic band systems in the visible region (4000-6000 Å) and one electronic band system in ultraviolet region (2300-2600 Å) of BiI are known with the B-X system lying in the

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* C.S.I.R. (India) Fellow.

**Present Address: FOM Institute for Atomic and Molecular Physics, Kruislaan - 407, Amsterdam (HOLLAND).

region 4150-4350 Å. Morgan[5] was the first to study the absorption spectra of BiI by passing light from a 500 watt incandescent lamp through the graphite tube containing bismuth and iodine at 600-700°C. He observed some bands in the region 4150-4350 Å which he attributed to the B-X system. Rao[7] using a high frequency discharge obtained the bands of B-X system in emission and also reported some weak bands of another system in the region 5650-5900 Å. He analysed these new bands (5650-5900 Å) and found that the vibrational frequencies of the upper and lower states are nearly the same as compared with the frequencies of the upper and lower states of B-X system. However, he attributed these to A-X system considering the ground state to be common and the upper state to be a new state 'A'. Singh[18] contradicted this suggestion and attributed these bands to a new system B-a. His main argument is that these bands could not be obtained in absorption and hence the ground state is not involved in this transition. Further, the closeness of the vibrational frequency of the upper state of these two systems (B-X and B-a) also supports his assignment. Joshi[8] photographed a group of BiI bands in absorption in the ultraviolet region (2300-2600 Å) and assigned these bands to three different systems. The bands of only one system were completely analysed and designated to the C-X system. Recently Yamdagni[19] has got the absorption bands of BiI in the region 4650-5300 Å by placing solid bismuth tri-iodide inside the 15 cm. graphite tube in a furnace with the optimum conditions of temperature about 1000°C in presence of nitrogen (pressure of 50 cm. of Hg). He assigned these bands to A-X and A'-X systems of BiI molecule.

So far as the high resolution study of bismuth halides is concerned, it is confined mainly to BiF (20-25) and BiCl (26-31).

Further, Sreenivasa Murty and Rao[32] have reported the rotational analysis of (7, 0), (7, 4) and (1, 4) bands of A-X system of BiBr by photographing the bands in the first order of a 21 ft. concave grating spectrograph (dispersion 1.25 Å/mm) and have reported the rotational constants. Since none of the BiI band systems has so far been obtained on high resolution and dispersion instruments, it was considered worthwhile to record the visible (B-X) bands of BiI on a better resolution and dispersion instrument and to propose the fine structure analysis. The bands have been photographed in emission in the second order of a 35 ft. concave grating spectrograph We had originally intended to perform the rotational analysis of this band system but even in second order of our grating spectrograph, the rotational structure was not resolved. We failed to record these bands in higher orders because the grating is blazed for 7500 A in first order and hence for recording these bands in third order, one needs very strong source. Since it was not possible to propose a rotational analysis, we contended ourselves with a more accurate measurements of the band heads and more accurate determination of vibrational constants.

EXPERIMENTAL

A conventional Π-type discharge tube of pyrex glass was fitted with cylindrical nickel electrodes was used to obtain the spectrum. The narrow part in the middle of the discharge tube was 12 mm. in diameter and 150 mm. in length, whereas the ends were of larger diameter (25 mm.). Bismuth tri-iodide (purity - 99.9%) obtained from E.Merck (Germany) was spread in the middle of the discharge tube and was heated from below by an electric heater. The discharge tube was continuously evacuated from the rear end (away from the slit) by a Cenco. Hyvac. pump. The B-X bands of BiI have been developed in an uncondensed transformer discharge by using an 1 KW power transformer. To avoid deposition of bismuth iodide powder on the window facing the spectrograph, the front end of the tube was made considerably longer ($\simeq$ 150 mm.). Further, a piece of cotton soaked in water was wrapped around the tube at a distance of 50 mm. from the front window so that the vapour could condense at this cooler spot rather than getting deposited on the window.

The emission spectrum was recorded in the second order of the 35 ft. concave grating spectrograph (30,000 lines/inch, ruled area 6", blazed for 7500 Å in the first order) with a reciprocal dispersion of 0.33 Å/mm. Exposure time of 8 hours duration with a slit-width of 25 microns was found suitable to photograph the bands on Ilford HP3 plates. Iron lines were superposed for secondary standard. Wavelengths of iron lines were taken from M.I.T. wavelength table[33]. The measurements of the band-heads were made on a Russian comparator, Model EZA-2. Accuracy of the measurements is estimated to be ± 0.05 cm^{-1}. Wavelength of the band heads have been converted into vacuum wavenumbers from the National Bureau of Standards Wavenumber tables compiled by Coleman et al.[34].

STUDY OF THE SPECTROGRAM

The spectrogram showing a large number of intense and well developed emission bands obtained on a 35 ft. concave grating spectrograph is reproduced in Fig.1. The bands are single headed and degraded towards longer wavelength side. A few band heads (3, 1), (1, 0), (3, 3), (2, 2) which were superposed by atomic lines on the plates of lower dispersion instruments, are clearly resolved and well separated from the atomic lines. The band heads of the (4,1), (4,2), (4,3) and (4,4) bands are accompanied by atomic lines

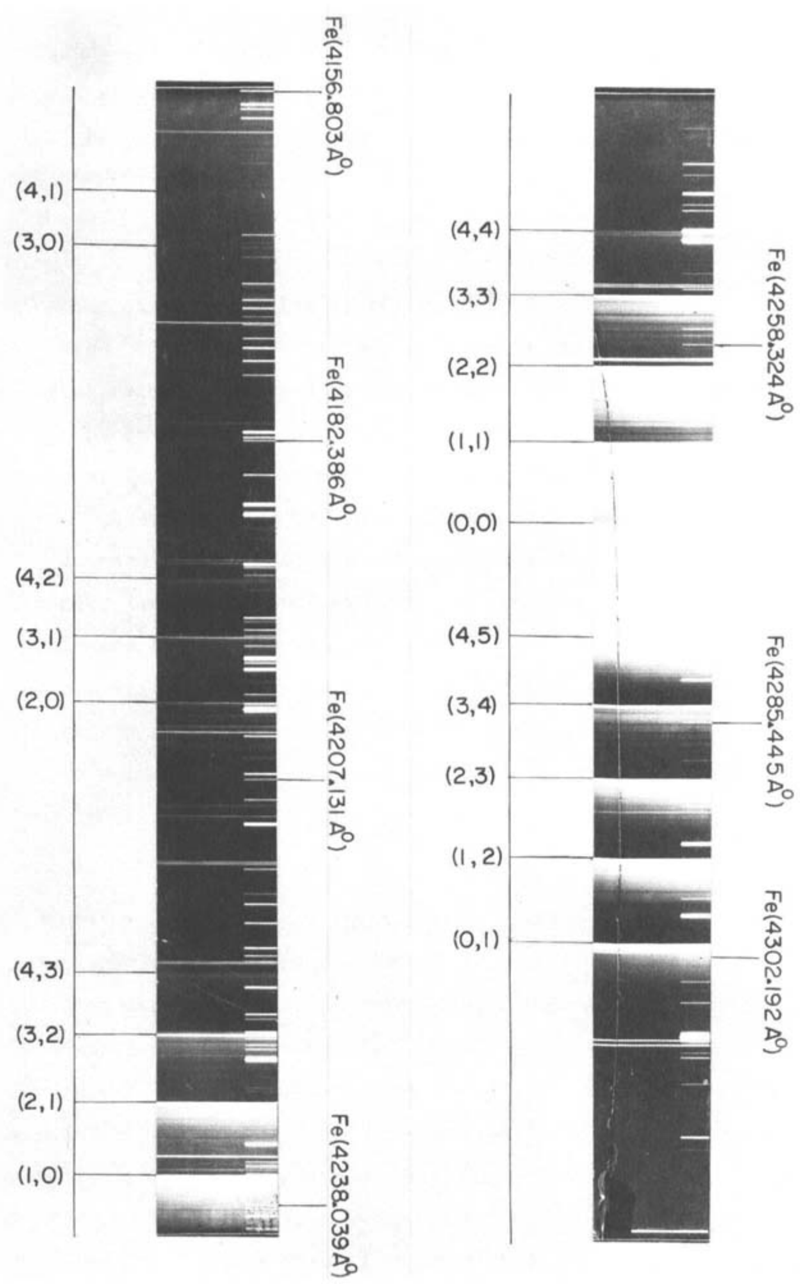

Figure 1. The B-X system of BiI.

(very close to heads) towards the longer wavelength side and give the impression that these bands are double headed. However, a careful observation of the plate reveals that it is not so.

The precisely measured band heads with estimated intensities and the vibrational assignments are listed in Table 1.

RESULTS AND DISCUSSION

All the bands of the B-X system of BiI reported in the emission and absorption spectra by earlier workers[5,7,18] have been recorded and measured accurately in the present case. A vibrational analysis has been carried out which confirms the previous vibrational assignments. The Deslandres scheme is given in Table 2. In Table 3 the measurements of the band heads reported by earlier workers and those obtained in the present work are listed for comparison. The precise vibrational constants for the upper and lower states have been evaluated and alongwith the vibrational constants obtained earlier are collected in Table 4. All the band heads are very well represented by the following equation (shown in Table 1)

$$\nu = 23389.064 + 198.087\,(v' + 1/2) - 1.444\,(v' + 1/2)^2 + 0.092\,(v' + 1/2)^3 - 0.015\,(v' + 1/2)^4 - 163.876\,(v'' + 1/2) - 0.280\,(v'' + 1/2)^2 - 0.005(v'' + 1/2)^3$$

It is found that the vibrational constants obtained in the present case for the ground state are almost the same as reported earlier but there is a significant difference in the constants of the upper state. Further, the precise measurements of these well resolved band heads have been compared with the earlier data shown in Table 3. It has been found that in most of the cases difference is at first place of decimal but in few cases it is quite appreciable (e.g. in 4,1 band the difference is over 1 cm.$^{-1}$ and in 3,0 band

Table 1

Band-head Data of B-X System of BiI

Intensity	v', v''	λ(Å)	$\nu_{vac.}$ (cm^{-1})	Calculated $\nu_{vca.}$ (cm^{-1})	Observed Calculated
8	0,1	4301.260	23242.46	23242.59	- 0.13
8	1,2	4295.188	275.32	275.31	0.01
8	2,3	4289.497	306.20	306.16	0.04
7	3,4	4284.216	334.93	334.98	- 0.05
6	4,5	4279.410	361.16	361.22	- 0.06
10	0,0	4271.227	405.89	405.89	0.00
9	1,1	4265.369	438.03	438.01	0.02
8	2,2	4259.882	468.22	468.22	0.00
7	3,3	4254.787	496.32	496.37	- 0.05
4	4,4	4250.167	521.86	521.93	- 0.07
8	1,0	4235.887	601.16	601.31	- 0.15
7	2,1	4230.562	630.87	630.92	- 0.05
6	3,2	4225.641	658.39	658.43	- 0.04
4	4,3	4221.205	683.25	483.32	- 0.07
4	2,0	4201.529	794.16	794.22	- 0.06
3	3,1	4196.777	821.10	821.13	- 0.03
2	4,2	4192.510	845.34	845.38	- 0.04
1	3,0	4168.190	984.47	984.43	0.04
1	4,1	4164.263	24008.09	24008.08	0.01

it is $\simeq$ 7 cm.$^{-1}$).

The vibrational constants $\omega_e y_e$ and $\omega_e z_e$ for the upper and lower states have been evaluated for the first time and it has been found that the contribution of these constants are significant for

Table 2

Deslandres Table for the Bands of B-X System of BiI

$v' \backslash v''$	0		1		2		3		4		5	$\Delta G'$	$\Delta^2 G'$	$\Delta^3 G'$	$\Delta^4 G'$
0	23405.89	163.43	23242.46												
	195.27		195.57									195.42			
1	23601.16	163.13	23438.03	162.71	23275.32								-2.51		
	193.00		192.84		192.90							192.91		-0.19	
2	23794.16	163.29	23630.87	162.65	23468.22	162.02	23306.20						-2.70		-0.37
	190.31		190.23		190.17		190.12					190.21		-0.56	
3	23984.47	163.37	23821.10	162.71	23658.39	162.07	23496.32	161.39	23334.93				-3.26		
			186.99		186.95		186.93		186.93			186.95			
4			24008.09	162.75	23845.34	162.09	23683.25	161.39	23521.86	160.70	23361.16				
$\Delta G''$		163.30		162.70		162.06		161.39		160.70					
$\Delta^2 G''$			-0.60		-0.64		-0.67		-0.69						
$\Delta^3 G''$				-0.04		-0.03		-0.02							

Table 3

Band-head Positions of B-X Bands by Different Workers

v', v''	ν in cm^{-1}		
	Morgan[5]	Singh[18]	Present Work
0,1	23242.5	23242.3	23242.46
1,2	275.5	274.7	275.32
2,3	308.5	306.2	306.20
3,4	335.2	333.2	334.93
4,5	361.5	360.7	361.16
0,0	406.1	405.5	405.89
1,1	438.3	437.9	438.03
2,2	468.5	467.6	468.22
3,3	496.6	496.3	496.32
4,4	522.3	521.1	521.86
1,0	601.3	600.6	601.16
2,1	631.1	630.7	630.87
3,2	658.8	658.1	658.39
4,3	683.9	683.3	683.25
2,0	794.5	793.8	794.16
3,1	821.6	820.4	821.10
4,2	845.8	844.8	845.34
3,0	-	977.5	984.47
4,1	24008.2	24006.9	24008.09

the vibrational term values of the upper state whereas their contribution to the ground state vibrational energy terms is negligible.

Table 4

Molecular Constants in the X and B States BiI

X State	B State
$\omega_e = 163.876\ \text{cm}^{-1}$ (163.9)	$\omega_e = 198.087\ \text{cm}^{-1}$ (198.6)
$\omega_e x_e = 0.280\ \text{cm}^{-1}$ (0.31)	$\omega_e x_e = 1.444\ \text{cm}^{-1}$ (1.44)
$\omega_e y_e = -0.005\ \text{cm}^{-1}$	$\omega_e y_e = 0.091_6\ \text{cm}^{-1}$
$\omega_e z_e \simeq 0$	$\omega_e z_e = 0.015_4\ \text{cm}^{-1}$
$\nu_e = 23389.064\ \text{cm}^{-1}$ (23388.9)	

The values given in parenthesis are by earlier workers.

ACKNOWLEDGEMENTS

The authors are thankful to Dr.I.S.Singh for his helpful suggestions and valuable discussions. Two of us (Onkar N. Singh and B.P.Asthana) are also thankful to C.S.I.R.(India) for financial assistance during the course of this work.

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Received December 17, 1974

Accepted February 4, 1975