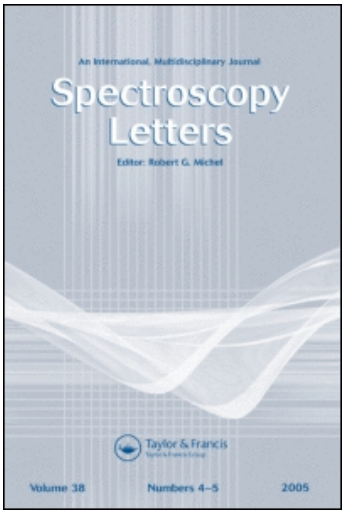

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Vibrational Analysis of the $A^3\Pi_0$-$X^1\Sigma$ and $B^3\Pi_1$-$X^1\Sigma$ Subsystems of the GaBr Molecule

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VIBRATIONAL ANALYSIS OF THE $A^3\Pi_0-X^1\Sigma^+$ and $B^3\Pi_1-X^1\Sigma^+$ SUBSYSTEMS OF THE GaBr MOLECULE

KEY WORDS: vibrational constants, gallium monobromide, emission spectra

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ABSTRACT

The emission band spectrum of gallium monobromide has been excited in a dc hollow cathode discharge. bands of the $^3\Pi_{0,1}-X^1\Sigma^+$ system, lying in the range from 340 to 370 nm have been recorded at high resolution and measured. The previous vibrational analysis has been revised and corrected. New vibrational assignment has been proposed and improved vibrational constants of the upper and lower electronic states have been determined.

INTRODUCTION

Knowledge of molecular constants is necessary for studying chemical reactions in plasma, in solving some

problems connected with spectrochemical analysis, calculations of Franck-Condon factors and potential curves and thermodynamic constants over high temperatures. In the present work investigation of GaBr spectra has been undertaken to obtain accurate vibrational constants.

A band spectrum of gallium monobromide was observed for the first time in absorption by Petrikaln and Hochberg[1]. Miescher and Wehrli[2] attributed the bands in the region 260-300 nm to the system C and the bands in the region 340-360 nm to two subsystems A and B, involving a $^3\Pi_{0,1}-X^1\Sigma$ transition. Savithry et al.[3] excited in high frequency discharge numerous new bands of the A-X and B-X subsystems and performed the vibrational analysis, using in vibrational energy formulae only the constants ω_e and $\omega_e x_e$, both for upper and the lower state. The rotational constants have been determined for the ground state ($X^1\Sigma^+$) on the base of microwave spectrum analysis[4] and for the $A^3\Pi_0$ and $B^3\Pi_1$ states by Borkowska-Burnecka et al.[5] Study of the analogous triplet systems of other monohalides of the III group elements[6,7] have shown that higher anharmonic constants (e.g. $\omega_e y_e$) are required for description of vibrational energies of the monohalide excited states. The constants reported previously[3] have been based on relatively low resolution band spectra measurements. In addition to that, calculation of vibrational constants performed here by means the least squares procedure[8] has shown some bands reported in Ref. 3 have not fitted well. Therefore, a reinvestigation of the GaBr spectrum under higher resolution than that employed earlier has been undertaken here.

EXPERIMENTAL

A demountable lamp with a hollow cathode operated at dc current was used here. A solid sample of gallium bromide ($GaBr_3$) was placed into the hollow cathode. Argon flowing continuously through the lamp was a carrier gas. More details of the apparatus are reported in Ref. 5. Excited spectra of gallium monobromide were recorded by means of a plane grating spectrograph PGS-2 on Kodak No 3 and 103a-O plates. Exposure times were varied from 2 to 4 hours. The high resolution spectra were recorded in the 8th order at reciprocal linear dispersion from 0.033 to 0.042 nm/mm. Argon and iron lines (with wavelengths known, mainly, with accuracy of 10^{-5} nm) produced by the hollow cathode discharge were used as standard lines for measurements of wavelengths of the GaBr band heads. Measurements of the lines and band heads have been made using a Hilger comparator in the usual way. The sharp band heads have been measured with accuracy of 0.05 cm^{-1}.

VIBRATIONAL ANALYSIS OF GALLIUM MONOBROMIDE

The bands of the $^3\Pi_{0,1}-X^1\Sigma^+$ transitions have been degraded to shorter wavelengths and their P heads have usually been sharp and easy for measurements. Only for some bands of the $^3\Pi_1-X^1\Sigma^+$ transition, their Q heads have been identified. Bands of four isotopic molecules of gallium monobromide have been observed. Total number of the observed bands has been lower than that reported by Savithry et al.[3] Bands with a very low intensity, not classified by them in the scale from 1 to 10, have not been recorded here. However, some new, unobserved so far bands have been found and measured in the neighborhood of the A-X $\Delta v = +1, +2, +3$ and B-X $\Delta v = \pm 1, +2$ sequence heads.

Bands belonging to the sequences $\Delta v = 0, \pm 1, \pm 2, +3, +4$ have been observed both for the $A^3\Pi_0-X^1\Sigma^+$ and $B^3\Pi_1-X^1\Sigma^+$ electronic transitions. Analysis of band intensities and vibrational isotopic shifts was helpful in vibrational assignments of bands.

In the $A^3\Pi_0-X^1\Sigma^+$ band system, the well developed sequences $\Delta v = +1, +2, +3$ made possible a univocal determination of vibrational numbers of the upper and lower states of the analyzed bands. For the most bands of these sequences, there has been found that the previous vibrational numbers should be increased by unity both for the upper and lower states. The present measurements and assignments and those performed by Savithry et al.[3] have been compared for the A-X band system in Table 1. Using constants derived from the A-X bands measured here, wavenumbers of other A-X bands were calculated. The calculated wavenumbers were in a quite good agreement with those reported[3] for further weak bands of the sequences $\Delta v = 0, \pm 1, \pm 2, +3$. Bands of the sequence $\Delta v = -3$ differed by about 100 cm^{-1} (likely misprinting) and for bands of $\Delta v = -4$ a new vibrational assignment was performed here (see Table 2).

Bands of the B-X system have been of less intensity and not so well developed as the A-X bands. The routine of analysis was similar to that used for the A-X system. Wavenumbers of the 1-0, 2-1, 0-0, 1-1 and 0-1 bands measured here have been well consistent with previous results[3]. For the 3-1, 4-2, 5-3, 3-2, 4-3, 5-4, 6-5, 1-2, 3-4, 4-5 and 5-6 bands new wavenumbers have been found here. For bands reported earlier as the 6-4, 7-5, 8-6 and 7-6 bands their vibrational quantum numbers (lower and upper) must be increased by unity. The measured bands of the B-X transition and

TABLE 1

The P heads of bands of the $A^3\Pi_0 - X^1\Sigma^+$ subsystem of the $^{69}Ga^{79}Br$ molecule, ν - wavenumbers in cm^{-1}

v'-v''	ν [Ref.3]	ν [author]
3-0	28966.2	28969.64
4-1	28958.5	28964.88
5-2	28948.2	28957.69
6-3	28935.2	28947.88
7-4	28919.5	28935.32
8-5	28900.3	28919.62
2-0	28705.4	28705.60
3-1	28701.1	28704.51
4-2	28696.0	28701.17
5-3	28686.8	28695.37
6-4	28675.8	28687.05
7-5	28661.5	28675.95
8-6	28644.5	28661.97
9-7	28623.0	28644.63
1-0	28437.7	28537.91
2-1	28440.0	28440.39
3-2	28437.7	28440.74
4-3	28434.3	28438.76
5-4	28427.4	28434.33
6-5	28417.4	28427.46
7-6	28404.8	28417.81
8-7	28388.9	28405.32
9-8	28370.2	28389.67
10-9	28348.5	28370.47
0-0	28166.6	28166.72
1-1	28172.7	28172.64
0-1	27901.5	27901.48
1-2	27908.8	27908.75

TABLE 2

New vibrational assignment of the A-X $\Delta v=-4$ bands of the $^{69}Ga^{79}Br$ molecule.

$\nu(cm^{-1})$	[Ref. 3] v'-v''	[This study] v'-v''
27115.2	10-14	0-4
27126.3	9-13	1-5
27136.8	8-12	2-6
27143.7	7-11	3-7
27148.6	6-10	4-8
27149.6	5-9	7-11
27145.1	3-7	8-12
27137.5	2-6	9-13

TABLE 3

The P heads of bands of the $B^3\Pi_1 - X^1\Sigma^+$ subsystem of the $^{69}Ga^{79}Br$ molecule, ν - wavenumbers in cm^{-1}

v'-v''	ν	v'-v''	ν
3-1	29066.58	5-4	28790.54
4-2	29060.36	6-5	28780.25
5-3	29051.50	7-6	28767.09
6-4	29039.81	0-0	28536.54
7-5	29025.07	1-1	28540.07
8-6	29006.92	0-1	28271.32
1-0	28805.26	1-2	28276.27
2-1	28805.26	3-4	28279.47
3-2	28802.81	4-5	28277.70
4-3	28797.96	5-6	28273.31

TABLE 4

Vibrational isotopic shifts ($\Delta\nu_c$ - calculated, $\Delta\nu_o$ - observed) for the A-X band system with respect to the $^{69}Ga^{79}GaBr$ molecule, in cm^{-1}

v'-v''	$^{69}Ga^{81}Br$		$^{71}Ga^{79}Br$		$^{71}Ga^{81}Br$	
	$\Delta\nu_c$	$\Delta\nu_o$	$\Delta\nu_c$	$\Delta\nu_o$	$\Delta\nu_c$	$\Delta\nu_o$
3-0	4.53	4.47	5.93	5.88	10.50	10.48
4-1	4.43	4.39	5.79	5.72	10.26	10.16
5-2	4.29	*	5.61	5.66	9.94	9.81
6-3	4.12	4.04	5.39	5.27	9.54	9.44
7-4	3.90	3.85	5.10	5.02	9.05	8.94
8-5	3.65	3.55	4.77	4.68	8.46	8.27
2-0	3.07	3.09	4.02	4.09	7.11	7.03
3-1	3.01	3.02	3.94	3.91	6.97	6.87
4-2	2.92	2.93	3.82	3.78	6.77	6.71
5-3	2.80	2.76	3.66	3.61	6.49	6.39
6-4	2.64	2.63	3.46	3.44	6.13	6.07
7-5	2.45	2.42	3.20	3.15	5.68	5.60
8-6	2.22	2.16	2.89	2.81	5.12	4.98
9-7	1.93	1.85	2.51	2.40		
1-0	1.57	1.56	2.05	2.01	3.62	3 57
2-1	1.55	1.53	2.02	2.01	3.58	3.54
3-2	1.50	1.52	1.97	1.98	3.48	3.46
4-3	1.43	1.44	1.87	1.87	3.32	3.28
5-4	1.33	1.29	1.74	1.70	3.08	2.96
6-5	1.19	1.19	1.56	1.53	2.76	2.69
7-6	1.01	0.98	1.33	1.36	2.35	2.26
8-7	0.80	0.78	1.04	1.01	1.84	1.72
9-8	0.52	0.49	0.68	0.57	1.10	1.22
10-9	0.19	0.15	0.25	0.15	0.47	0.28
0-0	0.02	0.00	0.03	0.00	0.05	0.00
1-1	0.04	0.00	0.06	0.00	0.10	0.00
0-1	-1.50	-1.51	-1.97	-1.96	-3.48	-3.48
1-2	-1.46	-1.46				

*Superposed by atomic line

TABLE 5

Vibrational isotopic shifts ($\Delta\nu_c$ - calculated, $\Delta\nu_o$ - observed) for the B-X band system with respect to the $^{69}Ga^{79}GaBr$ molecule, in cm^{-1}

v'-v''	$^{69}Ga^{81}Br$		$^{71}Ga^{79}Br$		$^{71}Ga^{81}Br$	
	$\Delta\nu_c$	$\Delta\nu_o$	$\Delta\nu_c$	$\Delta\nu_o$	$\Delta\nu_c$	$\Delta\nu_o$
3-1	2.95	2.86				
4-2	2.84	2.80				
5-3	2.69	2.65	3.53	3.48	6.25	6.16
6-4	2.51	2.45	3.28	3.20	5.82	5.70
7-5	2.28	2.21	2.99	2.85	5.29	5.17
1-0	1.54	1.50	2.02	2.02	3.57	3.51
2-1	1.51	1.50	1.98	2.02	3.50	3.51
3-2	1.45	1.44	1.89	1.83	3.35	3.26
4-3	1.35	1.35	1.77	1.75	3.14	3.11
5-4	1.22	1.22	1.60	1.56	2.84	2.75
6-5	1.05	0.98	1.38	1.34	2.45	2.35
7-6	0.84	0.88				
0-0	0.01	0.00	0.02	0.00	0.03	0.00
1-1	0.02	0.00	0.03	0.00	0.05	0.00
0-1	-1.51	-1.54	-1.97	-1.99	-3.50	-3.50
1-2	-1.48	-1.45				
4-5	-1.58	-1.60				

their vibrational assignments are listed in Table 3. The differences between the previous and the present band wavenumbers are mainly connected with assignments of bands. Due to low resolution Savithry et al.[3] could not observed some bands recorded here. This led to missing these bands and incorrect interpretation.

The new proposed here vibrational assignment has been clearly confirmed by a good agreement between calculated and observed vibrational isotopic shifts for the $^{69}Ga^{79}Br$, $^{69}Ga^{81}Br$, $^{71}Ga^{79}Br$ and $^{71}Ga^{81}Br$

TABLE 6

Vibrational constants of the $^{69}Ga^{79}Br$ molecule obtained from the A-X and B-X transitions, in cm^{-1}

	$A^3\Pi_0-X^1\Sigma^+$		$B^3\Pi_1-X^1\Sigma^+$	
	[author]	[Ref.3]	[author]	[Ref.3]
ω'_e	274.31(5)	275.75	271.98(8)	274.6
$\omega'_e x'_e$	1.56(1)	2.25	1.60(2)	2.58
$\omega'_e y'_e$	-0.028(1)		-0.033(1)	
ω''_e	266.71(4)	266.9	266.75(5)	266.9
$\omega''_e x''_e$	0.728(4)	0.83	0.733(7)	0.89
ν_0	28163.18(8)	28162.53	28534.22(8)	28532.92
S.D.	0.09		0.08	

molecules what has been presented in Tables 4 and 5 for the A-X and B-X systems, respectively.

The following expression has been used to describe wavenumbers of the A-X and B-X bands :

$$\nu_{v'v''} = \nu_e + \omega'_e(v+\tfrac{1}{2}) - \omega'_e x'_e(v+\tfrac{1}{2})^2 + \omega'_e y'_e(v+\tfrac{1}{2})^3 - \omega''_e(v+\tfrac{1}{2}) + \omega''_e x''_e(v+\tfrac{1}{2}) - \omega''_e y''_e(v+\tfrac{1}{2})^3$$

The least squares method and program written in TurboPascal 5.0 (see Ref. 8) have been applied. The calculations of the constants have been performed for the $^{69}Ga^{79}Br$ molecule using all bands listed in Table 1 and 3. The calculated value of $\omega''_e y''_e$ has found to

be smaller than its standard deviation uncertainty and negligible. The final vibrational constants given with their standard deviation uncertainties are compared with previous results in Table 6. A very good agreement between the ground state constants calculated from both the analyzed here subsystems is an evidence for accuracy of measurements and correctness of the analysis. The vibrational constants obtained using the bands measured here (at their weights equal to unity) and some bands reported in Ref.3 (at weights equal to 0.1 and new vibrational assignments) were in a very good agreement with those presented in Table 6 (the differences are smaller than their standard deviation uncertainties).

CONCLUSION

The new vibrational constants of the $A^3\Pi_0$, $B^3\Pi_1$ and $X^1\Sigma^+$ states of gallium monobromide are a significant improvement of the previous results. A very good agreement between the ground state constants obtained from two subsystems (A–X and B–X) and consistence between observed and calculated vibrational isotopic shifts have confirmed new vibrational assignment proposed here.

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REFERENCES

1. Petrikaln A., Hochberg J., Z.Phys. 1933; 86: 214.
2. Miescher E., Wehrli M., Helv. Phys. Acta 1934; 7: 331.
3. Savithry T., Rao D.V.K., Murty A.A.N., Rao P.T., Physica 1974; 75: 386.
4. Pfaffe S., Tiemann E., Hoeft J., Z. Naturforch. 1978; 33a:1386.
5. Borkowska-Burnecka J., Żyrnicki W., Physica 1980; 100C: 124.
6. Huber K.P., Herzberg G.,Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules. Van Nostrand-Reinhold. New York, 1979.
7. Borkowska-Burnecka J., Żyrnicki W., Phys. Scr. 1987; 35: 141.
8. N. Badowski, W. Żyrnicki, Report "Program Packet ANALYSIS". Technical University of Wrocław. Wrocław 1989.

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