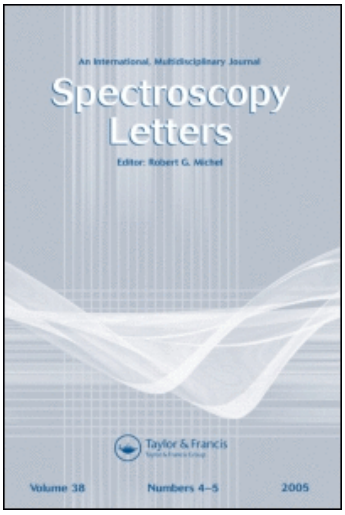

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Rotational Analysis of the 383.8 nm Band of the GeBr Molecule

J. Borkowska-burnecka[a]; W. Zyrnicki[a]; N. Badowski[a]
[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wrocław, Poland

To cite this Article Borkowska-burnecka, J. , Zyrnicki, W. and Badowski, N.(1989) 'Rotational Analysis of the 383.8 nm Band of the GeBr Molecule', Spectroscopy Letters, 22: 3, 307 — 314
To link to this Article: DOI: 10.1080/00387018908053879
URL: http://dx.doi.org/10.1080/00387018908053879

SPECTROSCOPY LETTERS, 22(3), 307-314 (1989)

ROTATIONAL ANALYSIS OF THE 383.8 nm BAND OF THE GeBr MOLECULE

KEY WORDS : rotational analysis, germanium monobromide isotopic molecules

J. Borkowska-Burnecka, W. Żyrnicki and N. Badowski
Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, 50-370 Wrocław, Poland

ABSTRACT

The 383.8 nm band of the GeBr molecule, recorded at high resolution, has been rotationally analyzed. Rotational constants of the upper and lower states have been determined from lines of six, main isotopic molecules of GeBr. The band has been proposed to be assigned as the $^4\Sigma^- - X^2\Pi_{3/2}$ 0-0 transition.

INTRODUCTION

An emission spectrum of germanium monobromide was observed for the first time by Jevons et al.[1] Observed bands, degraded to shorter wavelengths, have been attributed to the the $B^2\Sigma^+ - X^2\Pi$ transition. Several

other systems were discovered later and assigned as doublet-doublet transitions.[2] Only vibrational constants have been determined for some electronic states of the GeBr molecule, but these constants, obtained from measurements of band heads are of low accuracy. No rotational constants of germanium monobromide have been reported.

A system of red-degraded bands lying in the region 360-420 nm was suggested to result from transition $^2\Delta$-$X^2\Pi$ (or $^2\Pi$-$X^2\Pi$).[3] The bands can be easily attributed to two subsystems in which the most intense and prominent are the 0-0 bands at 383.8 and 368.9 nm. According to our study of the GeCl and SnCl spectra[4-5] one could expect that the band system at 360-420 nm arises from the $^4\Sigma^-$-$X^2\Pi$ transition. A high resolution study of the bands at 383.8 and 368.9 nm have been undertaken by us to establish the nature of the upper electronic state and to determine rotational constants of the lower and upper states, including coupling constants. As a part of this study, results of rotational analysis of the 383.8 nm band of six isotopic molecules of GeBr have been presented here.

EXPERIMENTAL DETAILS

An intense emission spectrum of the GeBr molecule was produced by a microwave discharge (2450 MHz) in a flowing continuously mixture of $GeBr_4$ vapor with argon at a low pressure. High resolution spectra of GeBr were photographed in the 15th and 16th orders of a 7 m Ebert-type spectrograph (in Herzberg Institute of Astrophysics, NRC, Ottawa) . A reciprocal dispersion was from 0.015 to 0.016 nm/mm. Exposure times up to 30 min were sufficient to record spectra at high resolu-

tion on Kodak 103a-O plates. A monochromator was applied to separate overlapping orders. Spectra were calibrated by reference to emission lines of an iron-neon hollow cathode discharge. The plates were measured manually on Hilger comparator. A computer program was then used to reduce measured data to vacuum wavenumbers of rotational lines.

The 383.8 nm BAND SPECTRUM

The band heads at 26049.84, 26049.49, 26049.19, 26048,84 and 26048.45 cm^{-1} could be measured and were identified as formed by the R branches of the $^{76}Ge^{81}Br$ $^{74}Ge^{81}Br$, $^{74}Ge^{79}Br$, $^{72}Ge^{79}Br$ and $^{70}Ge^{79}Br$ molecules.

The rotational structure of the GeBr bands has been dense and complex mainly for the following reasons:

- GeBr is a heavy molecule (it leads to small distances between rotational lines),
- a natural sample of $GeBr_4$ has been used in our experiment, so that germanium monobromide has consisted of ten isotopic molecules and a contribution of six of them to spectrum production is meaningful and can not be ignored,
- coupling phenomena (e.g. the Λ-type doubling) and/or multiplicity of electronic states of GeBr

Rotational lines of the six molecules of GeBr having very close line intensities (connected with their contributions in natural species ($^{74}Ge^{79}Br$ - 18.4%, $^{74}Ge^{81}Br$ - 18.0%, $^{72}Ge^{79}Br$ - 13.9%, $^{72}Ge^{81}Br$ - 13.6%, $^{70}Ge^{79}Br$ - 10.4% and $^{70}Ge^{81}Br$ - 10.2%) have been clearly identified and measured but most of the lines have overlapped each other. Two branches R and two branches P have been identified for every isotopic

Table 1
The J ranges of the rotational lines used for calculations

Molecule	R_{ee} and R_{ff}	P_{ee} and P_{ff}
$^{74}Ge^{79}Br$	14.5 - 90.5	1.5 - 110.5
$^{74}Ge^{81}Br$	14.5 - 90.5	1.5 - 111.5
$^{72}Ge^{79}Br$	14.5 - 90.5	1.5 - 110.5
$^{72}Ge^{81}Br$	14.5 - 90.5	1.5 - 110.5
$^{70}Ge^{79}Br$	15.5 - 86.5	1.5 - 99.5
$^{70}Ge^{81}Br$	1.5 - 87.5	1.5 - 104.5

molecule of germanium monobromide. No strong, long Q branch which is very characteristic for the $^2\Delta - {}^2\Pi$ transition could be found here.

ROTATIONAL CONSTANTS

Rotational lines of the six isotopic molecules have been used to calculate effective rotational constants of the upper and lower electronic states. The lowest and highest values of the rotational quantum numbers, J, are collected in Table 1.
Wavenumbers of the rotational lines represented by the fundamental equations

$$\nu = \nu_0 + F'(J') - F''(J'') \qquad (1)$$

$$F(J) = B\cdot J\cdot (J+1) - D\cdot J^2\cdot (J+1)^2 + H\cdot J^3\cdot (J+1)^3 \qquad (2)$$

have been used to calculate effective rotational constants of the upper and lower states of the molecules given in Table 1. Computer programs written in FORTRAN 77 have been applied to determine the constants by the direct fitting approach from line positions with the aid of IBM PC/XT microcomputer. Series of calculations were performed using the least squares method. In the first step ν_0 and the rotational constants B_0, D_0 and H_0 of both electronic states were fitted simultaneously. The constants obtained in a such way were not calculated precisely due to very strong correlation between some constants. On the other hand it was observed that the distortion constant H_0 must be taken into account at least for one (upper) electronic state. The constants H' and H'' were calculated by the approximate formula given in Ref. 5. The values of $-2.0 \cdot 10^{-12}$ and $4.0 \cdot 10^{-16}$ cm^{-1}, respectively were obtained for the $^{74}Ge^{79}Br$ molecule. It confirmed that the contribution of H' was meaniningful. Therefore to improve results of the calculations of the rotational constants, values of H_0', H_0'' and D_0'' have been calculated by means of approximate formulas[6] and fixed in the fitting procedure. The constant D_0'' and not D_0' was fixed because D_0'' could be determined more accurately than D_0'. Reliabity and accuracy of the vibrational constants, ω_e and $\omega_e x_e$, is higher for the ground state than for the upper state and in addition to that our consideration indicated that β_e' should be greater than β_e'' (β_e-the coefficient responsible for changes of D_v with v). The calculations have been performed for the $^{74}Ge^{79}Br$, $^{74}Ge^{81}Br$, $^{72}Ge^{79}Br$, $^{72}Ge^{81}Br$, $^{70}Ge^{79}Br$ and $^{70}Ge^{81}Br$ molecules, separately for the levels e and f. The rotational constants with their standard deviation

Table 2
Rotational constants of $^{74}Ge^{79}Br$ molecule
(the a-$X^2\Pi_{3/2}$ 0-0 band at 383.8 nm, levels e and f)

		I	II
level e	ν_0	26047.671(2)	26047.672(1)
	B'_0	0.078013(11)	0.077994(6)
	$D'_0 \cdot 10^7$	0.563(1)	0.562(1)
	$^*H'_0 \cdot 10^{12}$	-0.22	-0.22
	B''_0	0.082497(11)	0.082494(6)
	$^*D''_0 \cdot 10^7$	0.257	0.257
	$^*H''_0 \cdot 10^{15}$	0.40	0.40
	SD	0.016	0.022
	n	177	1060
level f	ν_0	26047.653(3)	26047.648(1)
	B'_0	0.078027(13)	0.078012(6)
	$D'_0 \cdot 10^7$	0.531(2)	0.534(1)
	$^*H'_0 \cdot 10^{12}$	-0.22	-0.22
	B''_0	0.082477(13)	0.082459(6)
	$^*D''_0 \cdot 10^7$	0.257	0.257
	$^*H''_0 \cdot 10^{15}$	0.40	0.40
	SD	0.020	0.022
	n	184	1109

* - the constants fixed in the fitting procedure.
n - the number of fitting rotational lines
SD - standard deviation
I - from lines of the $^{74}Ge^{79}Br$ molecule
II- from lines of six isotopic molecules

uncertainties, obtained for the $^{74}Ge^{79}Br$ molecule are given in Table 2.

Using the relations for isotopic molecules given by Dunham (see e.g. Ref. 6) and under the assumption that

$$B_e(i)/B_e \simeq B_0(i)/B_0,$$

$$D_e(i)/D_e \simeq D_0(i)/D_0$$

and $H_e(i)/H_e \simeq H_0(i)/H_0$

at an accuracy much higher than the accuracy of determination of these constants here, the "best", and recommended rotational constants of the $^{74}Ge^{79}Br$ molecule have been calculated from all the R and P lines of the six main isotopic molecules for the levels e i f and given in Table 2. Vibrational shifts have been taken into acount in the calculation.

DISCUSSION

The rotational analysis of the 383.8 nm band of GeBr has shown that this band can not belog to the $^2\Delta$-$X^2\Pi$ transition (absence of strong Q branch). In connection with an initial analysis of the 363.9 nm band (made by us) it indicates that the 383.8 nm band is the $^4\Sigma_{3/2}$-$X^2\Pi_{3/2}$ 0-0 transition. Both the upper and lower electronic states have shown relatively large splittings into the levels e and f, considerably greater than those observed in the corresponding states of SnCl and GeCl.

The rotational analysis of the 363.9 nm band (the $^4\Sigma_{1/2}$-$X^2\Pi_{1/2}$ 0-0 transition) of germanium monobromide and calculations of rotational constants of the $^4\Sigma$ and $X^2\Pi$ staes (including coupling constants) are in progress and results should be published soon.

ACKNOWLEDGEMENTS

One of us (W.Ż.) would like to express his thanks to Dr. D.A. Ramsay for the kind hospitality and excelent facilities in laboratory of Herzberg Institute of Astrophysics (NRC) and to National Research Council for support. The assistance of Mr. M. Barnett in the photographing of the spectra is gratefully acknowledged.

REFERENCES

1. Jevons W., Bashford L.A.,Briscoe H.V.A., Proc. Phys. Soc. 1937; 49: 532.
2. Huber K. P.and Herzberg G., Molecular Spectra and Molecular Structure, IV, Constants of Diatomic Molecules, Van Nostrand-Reinhold, New York, 1979.
3. Andrews E. B. ,Barrow R. F., Proc. Phys. Soc. 1950; 63A: 957.
4. Żyrnicki W. Spectroscopy Lett. 1978; 11: 913.
5. Badowski N., Żyrnicki W., Borkowska-Burnecka J., J. Phys. B: At. Mol. Phys. 1987; 20: 5931.
6. Herzberg G., Spectra of Diatomic Molecules. Van Nostrand Co., New York 1950.

Date Received: 11/08/88
Date Accepted: 12/13/88