

CHARACTERIZATION OF THE $B^3\Pi(O^+)$ STATE OF BrF BY HIGH RESOLUTION SPECTROSCOPY

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Introduction. While the low-lying $B^3\Pi(O^+)$ excited states of ClF(1) and IF (2) have been characterized in detail from their B-X visible band systems, the only data available for BrF are from vibrational analyses of low resolution absorption (3) and afterglow (4) spectra and from a recent study (5) of the laser excitation spectrum over a limited wavelength range. There is considerable interest in probing rotationally-dependent lifetime and predissociation phenomena in the $B^3\Pi(O^+)$ states of the interhalogens (6), and in the B-X systems as possible visible and near infrared laser transitions. Primary spectroscopic data are essential to the interpretation and design of such experiments. The present work overcomes the difficulties associated with a conventional study of the absorption spectrum of BrF at high resolution, and the results of a rotational analysis of 18 bands of ^{79}BrF and ^{81}BrF in the ranges $1 \leq v' \leq 9$ and $0 \leq v'' \leq 2$ are reported.

Experimental. The absorption cell was a 51 mm diameter 1 m long tube constructed of Monel metal and fitted with calcium fluoride windows. The cell was electrically heated to 160°C, and BrF was produced by carefully controlled mixing of pure Br_2 and F_2 at total pressures up to ~ 160 Torr. Continuum radiation from a 500 W xenon arc lamp was reflected back and forth along the cell axis with a White-cell arrangement of three concave mirrors to give absorption path lengths of 8 or 16 m. Spectra were recorded in the range $\lambda 4500\text{--}5700\text{\AA}$ using a 3.5 m Ebert spectrograph in the 2nd order of a 1200 line/mm grating.

Results. The short wavelength region contains the single $v'' = 0$ progression and is simple in appearance. Each band contains single P and R branches as found by laser excitation spectroscopy. At longer wavelengths the spectrum is weaker and more complex owing to overlapping of bands of the $v'' = 0$ and $v'' = 1$ progressions, and at the longest wavelengths of the $v'' = 1$ and $v'' = 2$ progressions. Except for one band, the 9-0 band, the rotational analysis was straightforward, and was facilitated by comparisons of trial sets of combination differences with calculated values from the rotational constants derived from the microwave spectrum. The measured line frequencies of individual bands were fitted by least squares to obtain estimates of the band origins and ground and excited state rotational constants. However B_0'' values were constrained to the microwave results (7,8), and D_v'' were constrained to values calculated from the RKR potential energy curve. The results from individual bands were then merged (9,10) to obtain a final set of vibrational term values and rotational constants for each state (Table 1).

TABLE 1. Merged^a Vibrational Term Values and Rotational Constants for the $B^3\Pi(O^+)$ and $X^1\Sigma^+$ States of ^{79}BrF and ^{81}BrF

	^{79}BrF	^{81}BrF	
$B^3\Pi(O^+)$	T_8'	20704.836 (3)	20700.446 (3)
	T_7'	20437.3947(27)	20433.1613(28)
	T_6'	20148.3931(25)	20144.5458(28)
	T_5'	19842.2413(41)	19838.8861(37)
	T_4'	19521.3476(25)	19518.6102(27)
	T_3'	19187.2728(31)	19185.2085(34)
	T_2'	18841.0606(61)	18839.7508(55)
	T_1'	18483.652 (17)	18483.109 (20)
	B_1'	0.252451 (42)	0.251381 (49)
	B_2'	0.249114 (16)	0.2479805(134)
	B_3'	0.2455456(62)	0.2444027(68)
	B_4'	0.2416846(53)	0.2405532(56)
	B_5'	0.2374974(83)	0.2364252(75)
	B_6'	0.2327472(50)	0.2316938(57)
	B_7'	0.2271310(102)	0.2261552(98)
	B_8'	0.2197656(141)	0.2188760(123)
	$10^7D_1'$	4.81 (24)	5.77 (25)
	$10^7D_2'$	5.325(82)	5.531(68)
	$10^7D_3'$	5.718(26)	5.722(28)
	$10^7D_4'$	6.195(21)	6.089(22)
	$10^7D_5'$	6.898(30)	6.879(28)
	$10^7D_6'$	7.842(19)	7.708(22)
	$10^7D_7'$	9.177(89)	9.134(86)
	$10^7D_8'$	11.370(144)	11.140(124)
$10^{11}H_7'$	-1.348(209)	-1.087(205)	
$10^{11}H_8'$	-8.66 (40)	-8.40 (33)	
$X^1\Sigma^+$	G_2''	1316.9731(28)	1313.8852(32)
	G_1''	662.2851(17)	660.7190(17)
	G_0''	[0.0]	[0.0]
	B_1''	0.3519418(15)	0.3502548(16)
	B_2''	0.3493105(28)	0.3476355(31)

a) All values are in units of reciprocal wavenumbers (cm^{-1}). Values in parentheses are $(\hat{V}_{ii}^M)^{1/2}$, from the diagonal elements of the output merge dispersion matrices, \hat{V}^M , in units of the last significant figures, of the corresponding constant. Standard errors are approximately $3(\hat{V}_{ii}^M)^{1/2}$.

The 9-0 bands of both isotopic species could be followed only to $J' \sim 28$ owing to considerable line-broadening with increasing J' . At $J' = 28$, the linewidths were $\sim 1.0 \text{ cm}^{-1}$, corresponding to lifetimes of about 5 ps. This predissociation is very much stronger than that found by Clyne and McDermid (6) from lifetime measurements in the $v' = 6, 7$ and 8 levels for which line-broadening is not detectable.

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