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Author(s)	Xia, Y; Liao, Z; Yang, M; Chan, MC; Cheung, ASC
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Laser spectroscopy of the $C^1\Sigma^+ - X^1\Sigma^+$ transition of ScBr

Y. Xia¹, Zhenwu Liao², Mei Yang², Man-Chor Chan² and A.S.C. Cheung^{1*}

¹Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

²Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Proposed running head: LIF spectrum of ScBr

*Correspondence to:

Prof. A.S.C. Cheung
Department of Chemistry
The University of Hong Kong
Pokfulam Road
Hong Kong

Fax : (852) 2857 1586
Tel : (852) 2859 2155
Email : hrscsc@hku.hk

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Abstract

The laser induced fluorescence spectrum of scandium monobromide (ScBr) between 795 and 845 nm has been recorded and analyzed. ScBr was produced by reacting laser vaporized Sc atoms with ethyl bromide ($\text{C}_2\text{H}_5\text{Br}$). Spectra of six vibrational bands of both Sc^{79}Br and Sc^{81}Br isotopomers of the $\text{C}^1\Sigma^+ - \text{X}^1\Sigma^+$ transition were observed. A least-squares fit of the measured line positions yielded accurate molecular constants for the $v = 0 - 3$ levels of the $\text{C}^1\Sigma^+$ state and the $v = 0 - 2$ levels of the $\text{X}^1\Sigma^+$ state. The equilibrium bond length of the $\text{C}^1\Sigma^+$ state has been determined to be 2.4776 Å

I. Introduction

Electronic transitions of scandium (Sc) monohalide molecules have been the subject of studies since the sixties [1]. This is because the scandium metal is particularly simple with only one electron in the d shell; the monohalides are model systems for understanding the role played by d electrons in chemical bonding [2]. As far as the studies of molecular spectra of scandium monohalides are concerned, ScF [3-9], ScCl [9-17] and ScI [18-24] have received considerable attention, however, only very limited work was performed on the ScBr molecule [25-27].

Experimental observation of scandium monobromide was first reported by Fischell *et al.* [18] using laser induced fluorescence (LIF) spectroscopy and two electronic transition systems were recorded with low resolution between 410 and 430 nm. Using Fourier transform microwave spectroscopy, Lin *et al.* [25] measured the pure rotational spectrum of ScBr and reported ground state molecular constants with high precision. Using the complete active space self-consistent field (CASSCF) method and multireference configuration interaction (MRCI) calculations, Langhoff *et al.* [26] obtained spectroscopic constants for the $X^1\Sigma^+$ and $a^3\Delta$ states. Using a similar method of calculation, Korek and Hamdan [27] predicted molecular properties of 23 low-lying electronic states of ScBr.

In this work, we report a high resolution laser induced fluorescence (LIF) study of the $C^1\Sigma^+$ - $X^1\Sigma$ system of ScBr in the near infrared region. Six vibrational bands of both Sc⁷⁹Br and Sc⁸¹Br isotopomers were observed and analyzed. Line positions of all the vibrational bands of the individual molecules were fit simultaneously to retrieve molecular constants for both the $C^1\Sigma^+$ and $X^1\Sigma^+$ states.

II. Experiment

The experimental setup for studying transition metal halides using LIF spectroscopy has been discussed in detail in a previous publication [28], therefore only a brief description of the experimental conditions will be provided here. ScBr molecules were produced by the reaction of laser vaporized scandium atoms with ethyl bromide (C_2H_5Br) under supersonic free jet conditions. Pulses from a Nd:YAG laser at a wavelength of 1064 nm and a laser power of 10 mJ were focused onto the surface of a scandium rod to produce the Sc atoms in the gas-phase. A pulsed valve, synchronized with an appropriate delay, released a gas mixture of 3% C_2H_5Br in argon to react with Sc atoms. The jet-cooled ScBr molecules were excited by a continuous wave ring Ti:sapphire laser that was pumped by a diode pump solid state (DPSS) laser with the wavelength set at 532 nm. A lens system collected the LIF signal which was then sent through a monochromator, and the signal was eventually detected by a photomultiplier tube (PMT). Two functions were performed by the monochromator: it was used to record the resolved fluorescence spectrum of the ScBr molecule, and it also acted as an optical filter for removing unwanted laser scatter. The wavelength of the dye laser was measured using a wavemeter with an accuracy of one part in 10^7 . The absolute accuracy of a measured line position is generally about 0.002 cm^{-1} . Many individual scans were made and then connected together using the wavemeter readings.

III. Results and Discussion

The laser induced fluorescence spectrum of ScBr in the near infrared region between 798 and 866 nm was recorded and analyzed. Six vibrational bands: (0, 0), (1, 0), (2, 0), (3, 0), (2, 1) and (2, 2) were studied. Each vibrational band shows resolved P and R branches only, which

confirms the nature of a $^1\Sigma - ^1\Sigma$ transition. Following the labeling of electronic states in scandium monohalides in the near infrared region, we label the observed transition as the $C^1\Sigma^+ - X^1\Sigma^+$ transition. Figure 1 shows the (3, 0) band in which the R heads of both the $Sc^{79}Br$ and $Sc^{81}Br$ isotopomers, and a portion of their P branches are clearly displayed. The observed line positions were fit to a standard formula [29]:

$$\nu_o = T_o + B' J' (J' + 1) - D' [J' (J' + 1)]^2 - \{B'' J'' (J'' + 1) - D'' [J'' (J'' + 1)]^2\} \quad (1)$$

where the ' and '' refer to the upper and the lower states respectively. We initially performed least squares fit to individual vibrational bands, but, in the final fit, all bands were merged together to yield only one set of molecular constants for each vibrational level and each isotopic molecule. Since the microwave work of Lin *et al.* [25] reported rotational constants of the $v = 0$ and 1 levels with high precision, these constants were fixed in our fit. Molecular constants determined for individual vibrational levels are reported in Table 1; the overall RMS error of the merged fit was about 0.002 cm^{-1} . The molecular constants for the $C^1\Sigma^+$ state are obtained for the first time and the equilibrium bond length, r_e , was determined to be 2.4776 \AA . The vibrational separations for the $C^1\Sigma^+$ state of the $Sc^{79}Br$ isotope are respectively $\Delta G_{1/2} = 286.95$, $\Delta G_{3/2} = 285.46$ and $\Delta G_{5/2} = 283.98 \text{ cm}^{-1}$. For the $X^1\Sigma^+$ state, the ω_e was determined to be 339.21 and 337.69 cm^{-1} for the $Sc^{79}Br$ and $Sc^{81}Br$ isotopic molecules respectively, and the B and D values for the $v = 2$ level were also determined in this work. A list of the measured line positions of the observed bands of the $C^1\Sigma^+ - X^1\Sigma^+$ transition is available from the Journal archive.

Molecular parameters for the $Sc^{79}Br$ and $Sc^{81}Br$ isotopomers are related by different powers of the mass dependence parameter $\rho = (\mu/\mu_i)$ where μ and μ_i are the reduced mass of an isotope and its more abundant isotope $Sc^{79}Br$ [29]. The measured equilibrium molecular

parameters for the two isotopomers are listed in Table 2. The agreement between the calculated and measured molecular constants for Sc⁸¹Br is excellent.

Since the scandium monohalides are considered as simple model systems, it is important to compare results from earlier calculations to establish the credibility of the theoretical computational treatment. Both Langhoff *et al.* [26] and Korek *et al.* [27] performed CASSCF and MRCI calculations on the ScBr molecule, a comparison of their predictions and our equilibrium molecular constants are given in Table 2. The agreement between experimental and calculated value is generally very good.

Langhoff *et al.* [26] discussed the electronic configurations and electronic states of scandium monohalides using the molecular orbitals (MO) formed from atomic orbitals (AO) of the scandium and the halide elements. The ground and low-lying electronic states for ScBr are similar to those for other monohalides. The electronic configurations giving rise to the ground X¹Σ⁺ and other low-lying electronic states are as follows:

$$1\sigma^2 1\pi^4 2\sigma^2 \quad X^1\Sigma^+ \quad (2)$$

$$1\sigma^2 1\pi^4 2\sigma^1 1\delta^1 \quad A^1\Delta, a^3\Delta \quad (3)$$

$$1\sigma^2 1\pi^4 2\sigma^1 2\pi^1 \quad B^1\Pi, b^3\Pi \quad (4)$$

$$1\sigma^2 1\pi^4 2\sigma^1 3\sigma^1 \quad C^1\Sigma^+, c^3\Sigma^+ \quad (5)$$

$$1\sigma^2 1\pi^4 2\sigma^1 3\pi^1 \quad D^1\Pi, d^3\Pi \quad (6)$$

The molecular orbital (MO) energy level diagram formed from the Sc atom's 4s, 3d and 4p atomic orbitals and the halogen np orbitals would be similar to those discussed in earlier publications [18, 26]. The observed C¹Σ⁺- X¹Σ⁺ transition in this study corresponds to the promotion of an electron from the 2σ MO to the 3σ MO as indicated in (5). The dominant

configuration for the $C^1\Sigma^+$ state has one electron in predominantly the $(2p\sigma+3d\sigma)$ orbital and another one in either a $4s\sigma$ or $2p\sigma$ orbital [18].

Table 3 lists equilibrium molecular constants for the ground and low-lying singlet electronic states of the four scandium monohalides. We can easily notice that the energy of the corresponding electronic state decreases from ScF to ScI. For the $C^1\Sigma^+-X^1\Sigma^+$ transition in scandium monohalides, the electron was taken from a closed 2σ shell and placed in the slightly anti-bonding 3σ MO. The bond length and vibrational frequency of the $C^1\Sigma^+$ state are respectively longer and weaker than that of the $X^1\Sigma^+$ state. In addition, similar trends in increasing bond length, r_e , and decreasing vibrational frequency, ω_e , can also be found in the other electronic states of the scandium monohalides, which imply a weakening of the chemical bond between the scandium metal and the halogen elements going down the group. As far as the electronic configurations mentioned in expressions (3) to (6) are concerned, triplet states are always accompanying the singlet states. We have work in progress to study the triplet states of ScBr, as it would be interesting to find out whether the trend that shows in the singlet states will also be true for the triplet states in ScBr.

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Figure captions:

Figure 1. The (3, 0) band of the $C^1\Sigma^+ - X^1\Sigma^+$ transition of ScBr

Table legends:

Table 1. Molecular constants for the $C^1\Sigma^+$ and $X^1\Sigma^+$ states of ScBr (cm^{-1})[†]

[†] Numbers in parentheses are one standard deviation (in unit of the last figure)

* Rotational constants for the $v = 0$ and 1 levels of the $X^1\Sigma^+$ state are from Ref. 25

Table 2. Equilibrium molecular constants for the $C^1\Sigma^+$ and the $X^1\Sigma^+$ states of ScBr (cm^{-1})[†]

[†] Numbers in parentheses are one standard deviation (in unit of the last figure)

Table 3. Molecular constants for the singlet states of scandium monohalides (cm^{-1})

Table 1. Molecular constants for the $C^1\Sigma^+$ and the $X^1\Sigma^+$ states of ScBr (cm^{-1})[†].

State	v	Sc ⁷⁹ Br			Sc ⁸¹ Br		
		T ₀	B	10 ⁷ D	T ₀	B	10 ⁷ D
X ¹ Σ ⁺	0	0.0	0.10362137*	0.390*	0	0.10269389*	0.386*
	1	337.135(3)	0.10319109*	0.381*	335.631(3)	0.10226940*	0.389*
	2	672.196(4)	0.102767(3)	0.49(6)	669.207(5)	0.101840(4)	0.42(6)
C ¹ Σ ⁺	0	11667.4421(3)	0.095678(1)	0.387(8)	11667.5515(3)	0.094825(1)	0.414(9)
	1	11955.6839(2)	0.095296(1)	0.45(1)	11954.5069(3)	0.094441(2)	0.42(3)
	2	12242.4269(3)	0.094900(1)	0.43(1)	12239.9754(3)	0.094055(1)	0.44(1)
	3	12527.6710(3)	0.094509(1)	0.42(1)	12523.9583(4)	0.093668(2)	0.41(2)
No. of lines		363			361		
RMS error		0.0025			0.0021		

[†] Numbers in parentheses are one standard deviation (in unit of the last figure)

* Rotational constants for the v = 0 and 1 levels of the X¹Σ⁺ state are from Ref. 25

Table 2. Equilibrium molecular constants for the $C^1\Sigma^+$ and the $X^1\Sigma^+$ states of ScBr^\dagger

State	Param.	Sc^{79}Br	Sc^{81}Br		Theoretical		Expt.
			Observed	Calculated	KH[27]	LBP[26]	
$X^1\Sigma^+$	T_e	0.0	0.0	0.0	0.0	0.0	0.0
	ω_e	339.209(4)	337.686(5)	337.686	343.7	329	338.8
	$\omega_e\chi_e$	1.037(2)	1.028(2)	1.028			1.099
	B_e	0.10385(1)	0.10295(1)	0.10292	0.10186		0.10384
	$10^4\alpha_e$	4.50(1)	4.48(1)	4.46			4.30
	r_e (Å)	2.3806			2.3985	2.430	2.3806
$C^1\Sigma^+$	T_e	11692.105(1)	11692.104(1)		12113		
	ω_e	289.740(1)	288.439(3)	288.438	297.7		
	$\omega_e\chi_e$	0.750(2)	0.743(1)	0.7425			
	B_e	0.09588(1)	0.09502(1)	0.9502	0.09392		
	$10^4\alpha_e$	3.91(2)	3.87(2)	3.87			
	r_e (Å)	2.4776			2.4979		

[†] Numbers in parentheses are one standard deviation (in unit of the last figure)

Table 3. Molecular constants for the singlet states of scandium monohalides (cm^{-1}).

State	E.C.*	Parameter	ScF ^a	Sc ³⁵ Cl ^b	Sc ⁷⁹ Br	ScI ^c
X ¹ Σ ⁺	2σ ²	ω _e	735.3	447.5	339.2	277.1
		r _e (Å)	1.7874	2.3303	2.3806	2.608
A ¹ Δ	2σ1δ	T _e	4587.1	3555.7		2868.5
		ω _e	645.2	388.1		250.0
		r _e (Å)	1.860	2.337		2.718
B ¹ Π	2σ2π	T _e	9555.6	6020.5		
		ω _e	593.0	381.0		
		r _e (Å)	1.907	2.351		
C ¹ Σ ⁺	2σ3σ	T _e	[16091.9] [†]	12427.4	11692.1	
		ω _e		377	289.7	
		r _e (Å)	1.907	2.3305	2.4776	
D ¹ Π	2σ3π	T _e	20383.378	[17390.06] [†]		15630.1 ^d
		ω _e	622.506	374.3		237.9
		r _e (Å)	1.864	2.348		2.715

[†]Numbers in parenthesis are T₀ values

*E.C. – electronic configuration

^aRef. [6]

^bRef. [11]

^cRef. [21]

^dRef. [24]

Figure 1.

