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# Applied quantum chemistry: Spectroscopic detection and characterization of the $F_2BS$ and $Cl_2BS$ free radicals in the gas phase

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In this and previous work [D. J. Clouthier, J. Chem. Phys. **141**, 244309 (2014)], the spectroscopic signatures of the $X_2BY$ (X = H, halogen, Y = O, S) free radicals have been predicted using high level *ab initio* theory. The theoretical results have been used to calculate the electronic absorption and single vibronic level (SVL) emission spectra of the radicals under typical jet-cooled conditions. Using these diagnostic predictions, the previously unknown $F_2BS$ and $Cl_2BS$ free radicals have been identified and characterized. The radicals were prepared in a free jet expansion by subjecting precursor mixtures of $BF_3$ or $BCl_3$ and $CS_2$ vapor to an electric discharge at the exit of a pulsed molecular beam valve. The $\tilde{B}^2A_1$–$\tilde{X}\ ^2B_2$ laser-induced fluorescence spectra were found within 150 $cm^{-1}$ of their theoretically predicted positions with vibronic structure consistent with our Franck-Condon simulations. The $\tilde{B}^2A_1$ state emits down to the ground state and to the low-lying $\tilde{A}^2B_1$ excited state and the correspondence between the observed and theoretically derived SVL emission Franck-Condon profiles was used to positively identify the radicals and make assignments. Excited state Coriolis coupling effects complicate the emission spectra of both radicals. In addition, a forbidden component of the electronically allowed $\tilde{B}$–$\tilde{X}$ band system of $Cl_2BS$ is evident, as signaled by the activity in the $b_2$ modes in the spectrum. Symmetry arguments indicate that this component gains intensity due to a vibronic interaction of the $\tilde{B}^2A_1$ state with a nearby electronic state of $^2B_2$ symmetry. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4915126]

## I. INTRODUCTION

Free radicals of the general formula $X_2BY$ (X = H, D or halogen, Y = O, S) are little known, although boron-containing free radicals are important intermediates in a variety of contexts. For example, boron has been characterized as a key element in radical reactions where organoboron species are used as radical initiators, chain-transfer reagents, and radical precursors.[1] In addition, boron halides and simple boranes are used as boron sources in chemical vapor deposition processes for the production of boron nitrides, carbides, and amorphous boron thin films and boron-centered free radicals are likely intermediates in such processes. The high temperature chemistry of boron rocket fuel additives also involves free radical reactions.[2] Discoveries of new boron-containing free radicals are both relevant and significant in all these areas of chemistry. In the present work, aided by *ab initio* predictions of their spectroscopic properties, we report the first detection of two new species, the planar $F_2BS$ and $Cl_2BS$ free radicals.

The only $X_2BY$ radicals previously known were the $F_2BO$ and $H_2BO$ species. In 1965, Mathews and Innes[3] presented spectroscopic evidence that $F_2BO$ was the mostly likely source of an emission band system at 580 nm that was obtained from discharges through $BF_3/O_2$ mixtures. In 1966, Mathews[4] showed that a group of closely spaced red-degraded emission bands at 446.5 nm obtained in the same discharge was also due to $F_2BO$ (or possibly $F_2BO^+$). The author could not definitively establish if the 580 nm and 446.5 nm bands had a common electronic state or if either band system involved transitions to the ground state. Subsequently, Dixon *et al.*[5] compared these bands with those of $F_2CN$ and eliminated $F_2BO^+$ as a possible source of the 580 and 446.5 nm band systems. Finally, in 1988, Jacox[6] reconsidered Mathews' data and postulated that the 446.5 nm system was due to the $1^2A_1 \rightarrow \tilde{X}^2B_2$ transition and that the 580 nm bands were transitions from the same upper state to a low-lying excited state ($1^2A_1 \rightarrow 1^2B_1$), assignments which were subsequently supported by detailed *ab initio* calculations.[7]

In 2014, we reported the first laser-induced fluorescence (LIF) and emission spectra of jet-cooled $F_2{}^{11}BO$ and $F_2{}^{10}BO$ obtained by laser excitation of the bands near 446.5 nm.[8] $F_2BO$ was generated in a pulsed discharge jet apparatus, using a precursor mixture of 7% $BF_3$ and 7% $O_2$ in high pressure argon. The emission spectrum obtained by laser excitation of the 0-0 band clearly showed transitions down to the ground state and a second set of bands down to the low-lying excited state, precisely as postulated by Jacox.[6] Our combined experimental and *ab initio* results proved conclusively that the previously reported emission spectra[4,5] were due to $F_2BO$ and substantially extended our knowledge of the structure, vibrational frequencies, and electronic states of this interesting free radical.

The only other study of an $X_2BY$ radical was the 1976 report by Graham and Weltner[9] of the detection of the

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$H_2BO$ radical among the products produced by vaporizing and trapping elemental boron in solid argon at 4-10 K. It was identified by its ESR spectrum, which was very similar to that of the isoelectronic $H_2CN$ free radical.[10] No further experimental observations of $H_2BO$ species have been reported and the $Cl_2BO$, $Br_2BO$, $H_2BS$, $F_2BS$, $Cl_2BS$, and $Br_2BS$ free radicals have never been previously observed.

In anticipation of the possibility of finding new $X_2BY$ radicals, Clouthier[11] conducted an extensive *ab initio* study of the ground and first two excited electronic states of the $H_2BO$, $H_2BS$, $F_2BO$, and $F_2BS$ free radicals and their various isotopologues. The radicals were found to have planar $C_{2v}$ geometries in the $\tilde{X}^2B_2$ ground state, the low-lying $\tilde{A}^2B_1$ first excited state, and the higher $\tilde{B}^2A_1$ state. The most promising method of identifying these species in the gas phase was suggested to be absorption or laser-induced fluorescence spectroscopy through the allowed $\tilde{B} - \tilde{X}$ transitions which occur in the visible-near UV region of the electromagnetic spectrum. Complete basis set extrapolations of CCSD(T)/aug-cc-pVXZ (X = 3,4,5) energies were used to accurately predict the excited state energies. Franck-Condon profiles of the absorption and emission spectra and the rotational structure of the $\tilde{B} - \tilde{X}\ 0_0^0$ bands were simulated from the *ab initio* results. The calculated single vibronic level (SVL) emission spectra were found to provide a unique, readily recognizable fingerprint of each particular radical, facilitating the experimental identification of new $X_2BY$ species in the gas phase. These predictions were very successfully employed in the present work to identify $F_2BS$ and similar calculations led us to the $Cl_2BS$ radical.

## II. EXPERIMENT

$F_2BS$ and $Cl_2BS$ were generated in our pulsed discharge jet apparatus, which has been described elsewhere,[12] using precursor mixtures of 4% $BF_3$ or $BCl_3$ and 4% $CS_2$ in high pressure argon. In brief, the precursor gas was injected with a pulsed valve into an evacuated flow channel in a vacuum chamber. At the appropriate time, the gas pulse was subjected to a pulsed electric discharge between a pair of stainless steel ring electrodes placed in the flow channel, fragmenting the precursor molecules and producing products. A short 1 cm long reheat tube[13] was added to the flow channel downstream of the electrodes to increase the number of collisions and enhance the production of the radicals. Natural abundance $BF_3$ or $BCl_3$ (80% $^{11}B$ and 20% $^{10}B$, Matheson) were used to measure transitions for the boron-11 isotopologue, while isotopically enriched $^{10}BF_3$ (96%, Ceradyne Boron Products) was used for measurements on $F_2{}^{10}BS$. $^{10}BCl_3$ was synthesized by the reaction of gaseous $^{10}BF_3$ with powdered $AlCl_3$ at elevated temperatures, in a modified literature procedure,[14] and used for studies of $Cl_2{}^{10}BS$.

Approximately, 1 cm downstream of the reheat tube, the free jet expansion was interrogated with the beam of a tunable dye laser (Nd:YAG pumped Lumonics HD-500) to obtain modest resolution (~0.1 $cm^{-1}$) LIF spectra. The fluorescence was imaged onto the photocathode of a high-gain photomultiplier (EMI 9816QB), and the pulsed signals were processed with a gated integrator, digitized by a National Instruments A/D board, and recorded with LabVIEW based software. The LIF spectra were calibrated to ±0.1 $cm^{-1}$ using a portion of the laser beam to simultaneously record the neon and argon optogalvanic spectra using hollow cathode lamps.

For low-resolution SVL emission spectra, fluorescence was generated by pumping the maximum of an LIF band and then the emission was focused through $f/1.5$ optics onto the entrance slit of a scanning monochromator (Spex 500M). The spectra were calibrated to an estimated ±1 $cm^{-1}$ accuracy using emission lines from an argon-filled hollow cathode lamp. The monochromator was equipped with an 1800 lines/mm grating blazed at 400 nm and operated with a bandpass of 0.2-0.8 nm.

The $BS_2$ radical was also produced in our discharge and its strong fluorescence interfered with our studies of the LIF spectra. As in previous work,[8] we used both time-gating and synchronously scanning (sync-scan) LIF techniques to isolate the signals of the radicals of interest. The sync-scan LIF method used a monochromator as a tunable bandpass filter by synchronously scanning the monochromator and the excitation laser with a fixed wavenumber offset between the two. In this fashion, we were able to isolate fluorescence from the species of interest, largely free of impurity emission.

## III. RESULTS AND ANALYSIS

### A. *Ab initio* calculations on $Cl_2BS$

Our success in identifying $F_2BS$ based on a*b initio* predictions of the LIF and emission spectra[11] (*vide infra*) encouraged us to undertake similar theoretical studies of $Cl_2BS$. Due to the larger number of electrons, these were not as extensive as the complete basis set extrapolations previously performed for the smaller $H_2BO$, $H_2BS$, $F_2BO$, and $F_2BS$ radicals,[11] but were of sufficient quality to lead to unambiguous predictions of the expected spectra. In the present work, the ground and two lowest energy excited electronic states were examined with density functional theory (DFT) using the Becke 3-parameter exchange and Lee-Yang-Parr correlation (B3LYP) hybrid functional[15,16] and coupled cluster theory with singles, doubles, and perturbatively included triples [CCSD(T)] using Dunning's correlation consistent basis sets augmented with diffuse functions[17] (aug-cc-pVnZ). The basis sets for chlorine and sulfur included a further tight *d* function [aug-cc-pV(X+d)Z] which facilitated convergence.[18] All the *ab initio* calculations were done with the Gaussian 09 software package.[19] The three electronic states were calculated variationally by constraining the geometry to $C_{2v}$ symmetry, with each state exhibiting a minimum on the potential energy surface. The highest level CCSD(T)/aug-cc-pV(T+d)Z vibrational frequencies and $T_0$ values are presented in Table I, with the geometric parameters relegated to Table VII. As in previous work,[11] the vibrational frequencies are numbered conventionally such that the vibrations are segregated by symmetry species and numbered in order of decreasing frequency within each symmetry species, so that $\nu_1$, $\nu_2$, and $\nu_3$ are the $a_1$ modes, $\nu_4$ is the single $b_1$ mode, and $\nu_5$ and $\nu_6$ are the $b_2$ modes.

The *ab initio* calculations show that the ground state electronic configuration of $Cl_2BS$ is $\ldots(13a_1)^2\ (4b_1)^2\ (9b_2)^1$, which gives rise to a $^2B_2$ term. The $9b_2$ HOMO is essentially

TABLE I. Summary of the observed vibrational fundamentals and $T_0$ values and the corresponding *ab initio* (in parentheses) harmonic frequencies for the various electronic states of $F_2BS$ and $Cl_2BS$ (in $cm^{-1}$).

| | | $T_0$ | $\nu_1(a_1)$ | $\nu_2(a_1)$ | $\nu_3(a_1)$ | $\nu_4(b_1)$ | $\nu_5(b_2)$ | $\nu_6(b_2)$ |
|---|---|---|---|---|---|---|---|---|
| $\tilde{X}^2B_2$ | $F_2{}^{11}BS$ | ... | 1232 (1242)[a] | 683 (683) | 412 (410) | 578 (578) | ... (1398) | 276 (277) |
| | $F_2{}^{10}BS$ | ... | 1275 (1285) | 684 (687) | 413 (410) | 598 (602) | 1452 (1447) | 279 (279) |
| | $Cl_2{}^{11}BS$ | ... | 960 (966)[b] | 462 (464) | 237 (239) | ... (432) | 910 (922) | 179 (181) |
| | $Cl_2{}^{10}BS$ | ... | 1000 (1006) | 464 (464) | 240 (239) | ... (451) | 946 (959) | 180 (182) |
| $\tilde{A}^2B_1$ | $F_2{}^{11}BS$ | 3 517 (3 464) | 1224 (1236) | 657 (660) | 415 (420) | 545 (545) | ... (1412) | ... (316) |
| | $F_2{}^{10}BS$ | 3 520 (3 463) | 1248 (1277) | 659 (666) | 415 (420) | 562 (568) | ... (1462) | ... (318) |
| | $Cl_2{}^{11}BS$ | 4 862 (4 769) | 901 (909) | 443 (453) | 256 (255) | ... (409) | 932 (942) | 231 (232) |
| | $Cl_2{}^{10}BS$ | 4 865 (4 768) | 940 (947) | 448 (453) | 253 (256) | ... (427) | 968 (981) | 231 (233) |
| $\tilde{B}^2A_1$ | $F_2{}^{11}BS$ | 23 180 (23 175) | 1101 (1136) | 610 (617) | 395 (394) | 573 (579) | ... (1509) | 318 (319) |
| | $F_2{}^{10}BS$ | 23 180 (23 174) | 1135 (1167) | 621 (625) | 399 (394) | 599 (603) | ... (1564) | 324 (320) |
| | $Cl_2{}^{11}BS$ | 21 123 (21 271) | 746 (756) | 454 (453) | 243 (240) | ... (433) | 960 (986) | 256 (256) |
| | $Cl_2{}^{10}BS$ | 21 123 (21 269) | 774 (787) | 456 (454) | 246 (242) | ... (452) | 998 (1027) | 257 (256) |

[a]$F_2BS$ CCSD(T)/aug-cc-pV5Z results from Ref. 11.
[b]$Cl_2BS$ CCSD(T)/aug-cc-pVTZ results, present work.

an in-plane *p* orbital on the sulfur atom and can be labeled as nonbonding ($n_O$). The $4b_1$ second highest occupied molecular orbital (SHOMO) is the out-of-plane *p* orbital on the sulfur atom with some stabilization from the out-of-plane *p* orbital on the boron atom, and so can be termed a $\pi_{BS}$ orbital. Finally, the $13a_1$ third highest occupied molecular orbital (THOMO) is a slightly bonding orbital between the boron and sulfur atoms, which can be labeled $\sigma_{BO}$. Parenthetically, we note that the ground state dipole moment of $Cl_2BS$ is predicted to be about 0.4 D, which may make microwave observations difficult. The $\nu_1$ and $\nu_5$ fundamentals have appreciable infrared absorption intensities (175–270 km/mol), so it might be possible to detect $Cl_2BS$ in matrix isolation experiments in the 800–1000 $cm^{-1}$ region.

Promoting a single electron from the SHOMO to the HOMO produces the low-lying $\tilde{A}^2B_1$ state, which has a somewhat longer B–S bond length (increase of ~0.06 Å) due to the removal of an electron from an orbital with $\pi$ bonding character between these two atoms. The $\tilde{B}^2A_1$ state is formed from the promotion of an electron in the THOMO to the HOMO, which can be considered an $n$–$\sigma$ transition, which again increases the B–S bond length by 0.03–0.06 Å depending on the level of theory.

We have also used our CCSD(T)/aug-cc-pVTZ *ab initio* results to perform Franck-Condon simulations of the absorption and single vibronic level emission spectra of $Cl_2BS$, as an aid to the experimental identification. The simulation program, originally developed by Yang *et al.*,[20] and locally modified for the calculation of SVL emission spectra, requires input of the molecular structures, vibrational frequencies, and mass-weighted Cartesian displacement coordinates from the *ab initio* force fields of the two combining electronic states. Franck-Condon factors are then calculated in the harmonic approximation using the exact recursion relationships of Doktorov *et al.*[21] taking into account both normal coordinate displacement and Duschinsky rotation effects.

### B. Spectra of $F_2BS$

The LIF spectrum of $F_2{}^{11}BS$ is shown in Fig. 1. It commences with a strong 0-0 band centered at 23 178.5 $cm^{-1}$, fortuitously close to $T_0$ = 23 175 $cm^{-1}$ predicted in our previous *ab initio* study.[11] The inset in Fig. 1 shows that the calculated 0-0 band contour, obtained from the *ab initio* rotational constants, matches experiment very well and validates our prediction that the band should follow *b*-type

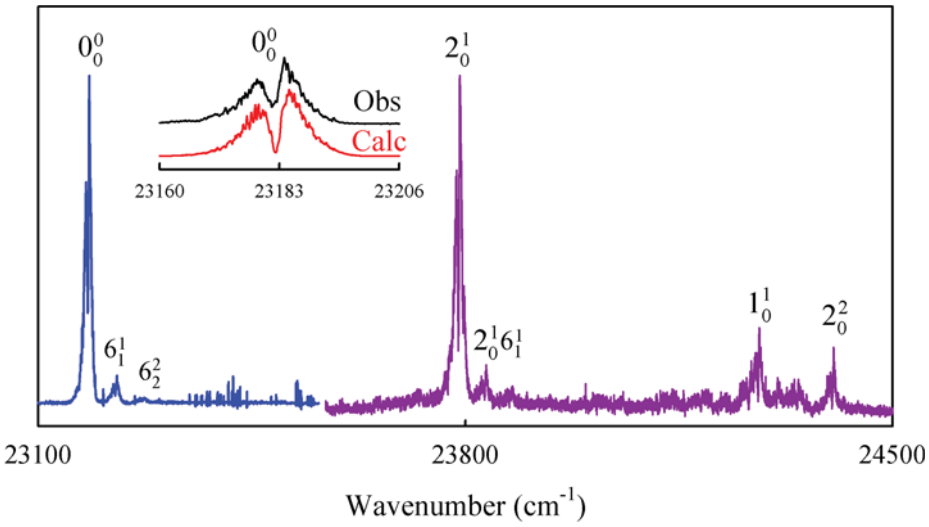


FIG. 1. The low resolution LIF spectrum of the $\tilde{B}$–$\tilde{X}$ transition of $F_2BS$. The spectrum was recorded in two sections with different laser dyes so the relative intensities of the two segments are not meaningful. The inset shows the observed and calculated (from our B3LYP/aug-cc-pV5Z results) rotational contours of the $F_2{}^{11}BS$ 0-0 band.

selection rules.[11] Our Franck-Condon simulation[11] of the LIF cold band spectrum shows a very strong 0-0 band, and weaker $2_0^1$ and $1_0^1$ bands along with a few very weak transitions and this is essentially what is observed. In addition, the experimental spectrum exhibits a few weak hot bands ($2_1^1$, $3_1^1$, $6_1^1$, $6_2^2$, $2_0^1 3_1^1$, and $2_0^1 6_1^1$, not all identified in Fig. 1), analogous to those found in the spectrum of $F_2BO$.[8] The LIF spectrum of $F_2{}^{10}BS$ is very similar to that shown in Fig. 1, although the $1_0^1$ band is shifted 30 cm$^{-1}$ to higher energy, in complete agreement with the *ab initio* isotope shift of 30 cm$^{-1}$. There can be little doubt that the observed LIF spectrum is the $\tilde{B}^2A_1$–$\tilde{X}^2B_2$ band system of $F_2BS$. A list of the observed LIF bands is given in Table II.

Unequivocal proof that $F_2BS$ is the carrier of the LIF spectrum in Fig. 1 comes from the comparison of the observed and calculated 0-0 band emission spectra, shown in Fig. 2. In fact, the correspondence between the experimental spectrum and the Franck-Condon simulation is so good that the majority of the bands were assigned directly from their simulation counterparts. The $\tilde{B}$–$\tilde{X}$ emission spectrum of $F_2{}^{11}BS$ consists of a relatively small number of bands (11) with a prominent progression in $\nu_1''$ out to $1_2^0$, consistent with the 0.06 Å difference in the BS bond length in the two states. The arrows in Fig. 2 highlight three features not reproduced in the simulation. Bands #2 and #3 are the $1_1^0$ and $1_2^0$ transitions of $F_2{}^{10}BS$ present in 20% natural abundance, which are resolved from the $F_2{}^{11}BS$ bands due to the relatively large $\nu_1''$ (B–S stretching) isotope effect (see Table I). Both show up prominently in the spectrum of isotopically enriched $F_2{}^{10}BS$. Band #1 cannot be attributed to $F_2{}^{10}BS$, although a similar very weak band occurs 50 cm$^{-1}$ higher in energy in the spectrum of $F_2{}^{10}BS$. The only other ground state vibration with frequency lower than $\nu_1$ and with a significant boron isotope effect is $\nu_4$ with a calculated $^{11}B$ frequency of 578 cm$^{-1}$ and isotope shift of 24 cm$^{-1}$ (see Table I). We therefore tentatively assign this transition to the $4_2^0$ band, with half the interval giving

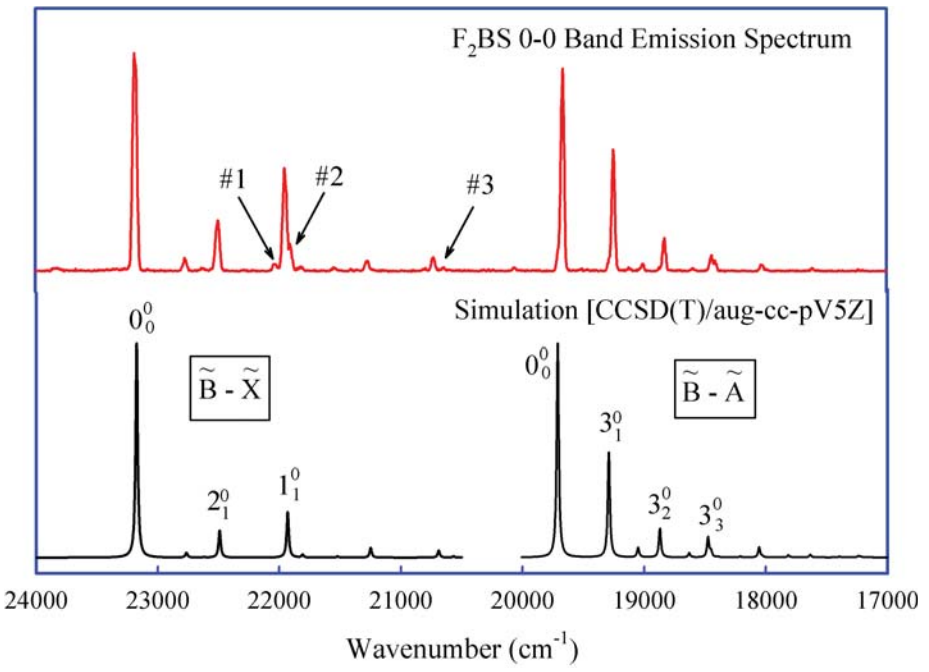


FIG. 2. The observed 0-0 band emission spectrum of $F_2BS$ (top panel) and the corresponding harmonic Franck-Condon simulation (bottom panel). The simulations involved calculating the $\tilde{B}$-$\tilde{X}$ and $\tilde{B}$-$\tilde{A}$ spectra, separately, so there is a break in the spectrum near 20 300 cm$^{-1}$. The relative intensities of the two calculated spectra have been normalized to the strongest feature in the corresponding emission spectrum.

TABLE II. Observed vibronic bands in the LIF spectra of the $\tilde{B}\ ^2A_1$–$\tilde{X}\ ^2B_2$ transition of the boron isotopologues of $F_2BS$.

| | $F_2{}^{11}BS$ | | $F_2{}^{10}BS$ | |
|---|---|---|---|---|
| Assignment | Transition ($cm^{-1}$) | Interval ($cm^{-1}$) | Transition ($cm^{-1}$) | Interval ($cm^{-1}$) |
| $2_1^1$ | ... | ... | 23 116.3 | $0_0^0-58.5$ |
| $3_1^1$ | 23 161.3 | $0_0^0-17.2$ | 23 160.8 | $0_0^0-14.0$ |
| $0_0^0$ | 23 178.5 | ... | 23 174.8 | ... |
| $6_1^1$ | 23 220.9 | $0_0^0+42.4$ | 23 220.1 | $0_0^0+45.3$ |
| $6_2^2$ | 23 266.1 | $6_1^1+45.2$ | ... | ... |
| $2_0^1 3_1^1$ | 23 771.0 | $3_1^1+609.7$ | 23 777.7 | $3_1^1+616.9$ |
| $2_0^1/4_0^1$ | 23 788.6 | $0_0^0+610.1$ | 23 795.8 | $0_0^0+621.0$ |
| $2_0^1 6_1^1$ | 23 831.7 | $6_1^1+610.8$ | 23 838.1 | $6_1^1+618.0$ |
| $1_0^1$ | 24 279.7 | $0_0^0+1101.2$ | 24 309.9 | $0_0^0+1135.1$ |
| $2_0^2$ | 24 400.9 | $2_0^1+612.3$ | 24 417.0 | $2_0^1+621.2$ |

TABLE III. Emission bands (in $cm^{-1}$) observed by pumping the $0_0^0$ and $2_0^1$ absorption bands of the $\tilde{B}$–$\tilde{X}$ transition of $F_2BS$. Unassigned lines: $F_2{}^{10}BS$: 0-0 band spectrum 20 063(vw); 2(1,0) band spectrum 20 028 (w).

| | $0_0^0$ band emission spectrum | | | | $2_0^1$ band emission spectrum | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $F_2{}^{11}BS$ | | $F_2{}^{10}BS$ | | $F_2{}^{11}BS$ | | | $F_2{}^{10}BS$ | |
| Assign | Transition | Interval | Transition | Interval | Assign | Transition | Interval | Transition | Interval |
| | | | | $\tilde{B}-\tilde{X}$ transitions[a] | | | | | |
| $0_0^0$ | 23 181 | ... | 23 180 | ... | $2_0^1$ | 23 796 | $\nu'_2=615$ | 23 802 | $\nu'_2=622$ |
| $3_1^0$ | 22 769 | $\nu_3=412$ | 22 767 | $\nu_3=413$ | $4_1^1$ | 23 181 | ... | 23 183 | ... |
| $6_2^0$ | 22 629 | $2\nu_6=552$ | 22 621 | $2\nu_6=559$ | $2_1^1$ | 23 113 | $\nu_2=683$ | 23 117 | $\nu_2=685$ |
| $2_1^0$ | 22 500 | $\nu_2=681$ | 22 496 | $\nu_2=684$ | $2_1^1 3_1^0$ | 22 711 | $\nu_3=402$ | 22 710 | $\nu_3=407$ |
| $4_2^0$? | 22 031 | $2\nu_4=1150$ | 21 981 | $2\nu_4=1199$ | $2_1^0 4_1^1$ | 22 506 | $\nu_2=675$ | 22 501 | $\nu_2=682$ |
| $1_1^0$ | 21 949 | $\nu_1=1232$ | 21 904 | $\nu_1=1276$ | $2_2^1$ | 22 438 | $2_1^1-675$ | 22 436 | $2_1^1-681$ |
| $2_2^0$ | 21 811 | $2_1^0-689$ | ... | ... | $1_1^0 4_1^1$ | 21 956 | $4_1^1-1225$ | 21 904 | $4_1^1-1279$ |
| $1_1^0 3_1^0$ | 21 546 | $1_1^0-403$ | 21 504 | $1_1^0-400$ | $1_1^0 2_1^1$ | 21 884 | $2_1^1-1229$ | 21 846 | $2_1^1-1271$ |
| $1_1^0 2_1^0$ | 21 273 | $1_1^0-676$ | 21 227 | $1_1^0-677$ | $2_3^1$ | 21 752 | $2_2^1-686$ | ... | ... |
| $1_1^0 4_2^0$? | ... | ... | 20 711 | $1_1^0-1193$ | $1_1^0 2_2^1$ | 21 214 | $2_2^1-1224$ | 21 168 | $2_2^1-1268$ |
| $1_2^0$ | 20 728 | $1_1^0-1221$ | 20 642 | $1_1^0-1262$ | $1_2^0 4_1^1$ | ... | ... | 20 641 | $4_1^1-2542$ |
| $5_2^0$? | ... | ... | 20 275 | $2\upsilon_5=2905$ | $1_2^0 2_1^1$ | 20 657 | $2_1^1-2456$ | 20 584 | $2_1^1-2533$ |
| $1_2^0 2_1^0$ | 20 061 | $1_2^0-667$ | ... | 2 ... | $1_2^0 2_1^0 4_1^1$ | 20 028 | ... | ... | ... |
| | | | | $\tilde{B}-\tilde{A}$ transitions[b] | | | | | |
| $0_0^0$ | 19 664 | $\tilde{X}0_0+3517$ | 19 660 | $\tilde{X}0_0+3520$ | $2_0^1$ | 20 278 | $\nu'_2=614$ | 20 283 | $\nu'_2=623$ |
| $3_1^0$ | 19 249 | $\nu_3=415$ | 19 245 | $\nu_3=415$ | $2_0^1 3_1^0$ | 19 862 | $\nu_3=416$ | 19 865 | $\nu_3=418$ |
| $2_1^0$ | 19 004 | $\nu_2=660$ | 19 006 | $\nu_2=654$ | $4_1^1$ | 19 695 | ... | 19 699 | ... |
| $3_2^0$ | 18 829 | $3_1^0-420$ | 18 828 | $3_1^0-417$ | $2_1^1$ | 19 620 | $\nu_2=658$ | 19 624 | $\nu_2=659$ |
| $2_1^0 3_1^0$ | 18 592 | $2_1^0-412$ | ... | ... | $3_1^0 4_1^1$ | ... | ... | 19 281 | $4_1^1-418$ |
| $1_1^0$ | 18 440 | $\nu_1=1224$ | 18 412 | $\nu_1=1248$ | $2_1^1 3_1^0$ | 19 206 | $2_1^1-414$ | 19 207 | $2_1^1-417$ |
| $3_3^0$ | 18 410 | $3_2^0-419$ | ... | ... | $2_1^0 4_1^1$ | ... | ... | 19 037 | $4_1^1-662$ |
| ... | ... | ... | ... | ... | $2_2^1$ | 18 962 | $2_1^1-658$ | 18 966 | $2_1^1-658$ |
| ... | ... | ... | ... | ... | $3_2^0 4_1^1$ | ... | ... | 18 863 | $4_1^1-836$ |
| $1_1^0 3_1^0$ | 18 028 | $1_1^0-412$ | 17 990 | $1_1^0-422$ | $2_1^1 3_2^0$ | 18 792 | $2_1^1-828$ | 18 791 | $2_1^1-833$ |
| ... | ... | ... | ... | ... | $1_1^0 4_1^1$ | ... | ... | 18 442 | $4_1^1-1257$ |
| ... | ... | ... | ... | ... | $1_1^0 2_1^1$ | 18 398 | $2_1^1-1222$ | 18 371 | $2_1^1-1253$ |
| $1_1^0 3_2^0$ | 17 612 | $1_1^0 3_1^0-416$ | ... | ... | $1_1^0 2_1^1 3_1^0$ | 17 987 | ... | ... | ... |

[a]Vibrational intervals are for the $\tilde{X}$ state unless otherwise noted.
[b]Vibrational intervals are for the $\tilde{A}$ state unless otherwise noted.

$\nu_4'' = 575\ cm^{-1}$ and a 25 $cm^{-1}$ isotope shift. The 0-0 band emission spectrum of $F_2{}^{10}BS$ has many of the same features but has additional very weak bands tentatively assigned as $1_1^0 4_2^0$ and $5_2^0$. Since transitions involving two quanta of non-totally symmetric modes are expected to be very weak, all such assignments are only tentative as they could also be due to impurities or emission from higher levels excited through sequence bands overlapping the 0-0 band. A complete list of the $\tilde{B}$–$\tilde{X}$ emission band assignments is given in Table III.

The 0-0 band $\tilde{B}$–$\tilde{A}$ emission band systems of $F_2{}^{11}BS$ and $F_2{}^{10}BS$ were very easy to assign as they matched the simulations almost perfectly, with no extraneous features. The major progression involves $\nu_3$ (out to $3_3^0$) with a small amount of activity in $\nu_1$. Animations show that in the $\tilde{A}$ state both of these modes involve substantial contributions from the BS stretching and FBF symmetric bending internal coordinates. The assignments are summarized in Table III.

We also recorded the SVL emission spectra of the $2_0^1$ bands, which harbored a surprise. In this case, the emission spectra were much more complicated than the initial simulation, with some bands consisting of closely spaced doublets (particularly for $F_2{}^{10}BS$) along with a few extraneous features. Examining the $\tilde{B}$ state calculated vibrational frequencies (Table I), it is apparent that $\nu_2$ and $\nu_4$ are almost degenerate, differing by 38 $cm^{-1}$ in $F_2{}^{11}BS$ and only 22 $cm^{-1}$ in $F_2{}^{10}BS$ and that Coriolis coupling between the $\tilde{B}$ state $2^1$ and $4^1$ levels is the likely reason for the complexity. The $2_0^1$ band emission spectrum of $F_2{}^{10}BS$ is shown in Fig. 3, along with a simulation constructed by adding together Franck-Condon simulations from the $2^1$ and $4^1$ levels and normalizing the intensities to those of the observed $4_1^1$ and $2_1^1$ bands in each case. The agreement is excellent, confirming that the upper state pumped by the laser has $2^1/4^1$ character. The bands in the spectra of both isotopologues were assigned based on observed and calculated vibrational intervals and on the relative intensities predicted by the composite simulations. These results are summarized in Table III.

### C. Spectra of $Cl_2BS$

Our best CCSD(T)/aug-cc-pVTZ calculations predicted the $\tilde{B}$–$\tilde{X}$ $T_0$ of $Cl_2{}^{11}BS$ to be 21 271 $cm^{-1}$. Substituting $BCl_3$ for $BF_3$ and using similar experimental conditions, we readily found a strong 0-0 band at 21 123 $cm^{-1}$, 148 $cm^{-1}$ lower than predicted. The Franck-Condon simulation of the $Cl_2BS$ cold band absorption spectrum indicates that there should be more bands than observed in the LIF spectra of $F_2BO$ and $F_2BS$, which is what is found, as shown in Fig 4. In addition to the very strong 0-0 band, there are weaker $3_0^1$, $2_0^1$, $1_0^1$, and combination bands. Furthermore, the spectra of both isotopologues exhibit weak hot bands below 21 000 $cm^{-1}$ which can only be assigned as $3_1^0$ and $6_1^0$. The latter is unprecedented in the LIF spectra of the fluorinated radicals and must be vibronically induced through mixing with another excited state. The corresponding $6_0^1$ cold band is calculated to lie within the rotational envelope of the noticeably broad $3_0^1$ band (FWHM: $0_0^0 \approx 9\ cm^{-1}$, $3_0^1 \approx 19\ cm^{-1}$). In addition, $Cl_2{}^{11}BS/Cl_2{}^{10}BS$ shows a weak band 960/998 $cm^{-1}$ above the $0_0^0$ band which is assigned as the vibronically induced $5_0^1$ band, based on detailed consideration of the emission data (*vide infra*). Of course, $\nu_5'$ has the same vibrational symmetry as $\nu_6''$, so it is perhaps not too surprising that $5_0^1$ also appears in the $Cl_2BS$ spectrum. Finally, the $Cl_2BS$ least moment of inertia ($I_a$) is in the molecular plane perpendicular to the B–S bond, so the bands should follow *a*-type selection rules and not exhibit the central minima found for $F_2BS$ (see Fig. 1), and this is what is observed. The assignments of the LIF spectra are given in Table IV along with some derived vibrational intervals.

The substantial number of bands in the LIF spectra provided the opportunity to obtain many more SVL emission

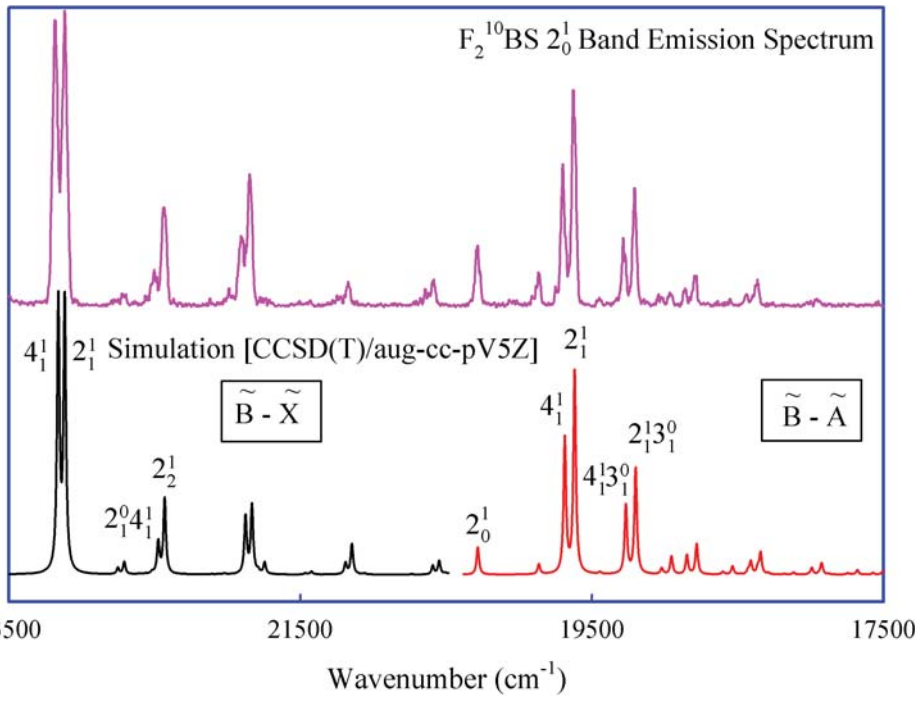


FIG. 3. The $F_2{}^{10}BS$ $2_0^1$ band emission spectrum (top panel) and the corresponding harmonic Franck-Condon simulation (bottom panel). The simulation was obtained by adding together Franck-Condon simulations of emission spectra from the $2^1$ and $4^1$ levels and normalizing the intensities to those of the observed $4_1^1$ and $2_1^1$ bands in each case.

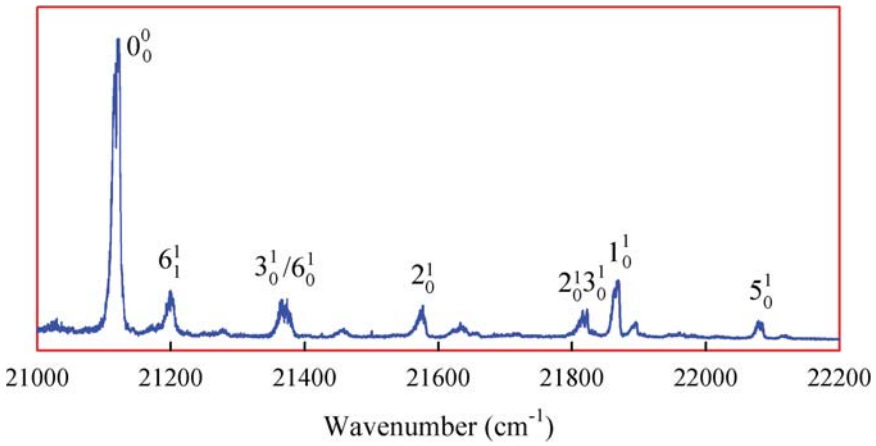


FIG. 4. A portion of the low resolution LIF spectrum of the $\tilde{B}$-$\tilde{X}$ transition of $Cl_2BS$. The 3(1,0) and 6(1,0) bands are overlapped, giving rise to a feature that appears to be broader than any other in the spectrum.

spectra than in the $F_2BO$ and $F_2BS$ cases. For each isotopologue, we recorded dispersed emission spectra by pumping the $3_1^0$, $6_1^0$, $0_0^0$, $6_1^1$, $3_0^1/6_0^1$, $6_1^1 3_0^1$, $2_0^1$, $1_0^1$, and $5_0^1$ LIF bands, along with the $2_0^1 3_0^1$ band of $Cl_2{}^{11}BS$ and the $6_0^2$ band of $Cl_2{}^{10}BS$. We will not discuss the details of all these spectra but simply refer to a few cases which illustrate the salient points of the analysis.

The 0-0 band emission spectrum of $Cl_2{}^{11}BS$ is shown in Fig. 5 along with our Franck-Condon simulation. It is readily apparent that the simulation is substantially at odds with experiment for the $\tilde{B}$–$\tilde{X}$ band system but is in quite good agreement for the $\tilde{B}$–$\tilde{A}$ transitions. The small features labeled #1, #2 and #3 are the key to understanding this behavior. Transitions #1 and #2 are to higher energy than the 0-0 band that was pumped by the laser and are readily assigned as $3_0^1$ and $6_1^1$, both bands that are also observed in the LIF spectra. We conclude that the 0-0 band is overlapped by the $3_1^1$ sequence band (it is calculated from the known vibrational frequencies to occur within the rotational contour of the 0-0 band) and that the $3^1$ ($\nu_3$ = 244 cm$^{-1}$) and $6^1$ ($\nu_6$ = 259 cm$^{-1}$) levels are Coriolis coupled. A similar complication was found in the spectrum of $F_2BO$.[8] This conclusion is buttressed by the fact that pumping the $Cl_2BS$ $6_1^1$ band yields an emission spectrum that includes a weak $3_0^1$ band. Thus, the 0-0 band emission spectrum in Fig. 5 contains contributions from the $\tilde{B}$ state $0^0$, $3^1$, and $6^1$ levels, accounting for the deviations from the harmonic Franck-Condon simulation. In addition to the bands predicted by the Franck-Condon simulation, we have also assigned a weak vibronically induced $6_1^0$ band and an even weaker $1_1^0 6_1^0$ band.

Initially, further $Cl_2{}^{11}BS/Cl_2{}^{10}BS$ zero-point $\tilde{B}$–$\tilde{X}$ emission bands of medium intensity with ground state intervals of 907/949 cm$^{-1}$ were difficult to assign. However, once it was recognized that the strongest features of the emission spectra of the LIF bands at 22 078.3/22 114.3 cm$^{-1}$ (Table IV) had the same intervals, it became apparent that these were the $\nu_5''$ frequencies, with a boron isotope shift of 42 cm$^{-1}$, comparable to the *ab initio* value of 37 cm$^{-1}$. This assignment was confirmed by the presence of weak transitions down to the $1_1 5_1$ level in the $0_0^0$ and $1_0^1$ band emission spectra with observed $\nu_1 + \nu_5$ frequency isotope shifts of 79 cm$^{-1}$ in both spectra. The expected isotope shift (from combining the observed shifts of

TABLE IV. Observed vibronic bands in the LIF spectra of the $\tilde{B}\ ^2A_1$–$\tilde{X}\ ^2B_2$ transition of the boron isotopologues of $Cl_2BS$.

| | $Cl_2{}^{11}BS$ | | $Cl_2{}^{10}BS$ | |
|---|---|---|---|---|
| Assignment | Transition (cm$^{-1}$) | Interval (cm$^{-1}$) | Transition (cm$^{-1}$) | Interval (cm$^{-1}$) |
| $3_1^0$ | 20 881.3 | $\nu_3'' = 237.3$ | 20 878.8 | $\nu_3'' = 237.5$ |
| $6_1^0$ | 20 943.9 | $\nu_6'' = 174.7$ | 20 940.0 | $\nu_6'' = 176.3$ |
| $0_0^0$ | 21 118.6 | ... | 21 116.3 | ... |
| $6_1^1$ | 21 199.4 | $\nu_6 = 255.5$ | 21 195.2 | $\nu_6 = 255.2$ |
| $6_2^2$ | ... | ... | 21 278.1 | $6_1^1 + 82.9$ |
| $3_0^1$ and $6_0^1$ | 21 370.5 | ... | 21 368.9 | ... |
| $3_0^1 6_1^1$ | 21 453.5 | $6_1^1 + 254.1$ | 21 452.9 | $6_1^1 + 257.7$ |
| $2_0^1$ | 21 572.2 | $\nu_2 = 453.6$ | 21 572.3 | $\nu_2 = 456.0$ |
| $6_0^2$ and $3_0^2$? | 21 633.9 | ... | 21 632.6 | ... |
| $2_0^1 3_0^1$ | 21 817.2 | $2_0^1 + 245.0$ | 21 814.1 | $2_0^1 + 241.8$ |
| $1_0^1$ | 21 863.9 | $\nu_1 = 745.3$ | 21 889.8 | $\nu_1 = 773.5$ |
| $5_0^1$ | 22 078.3 | $\nu_5 = 959.7$ | 22 114.3 | $\nu_5 = 998.0$ |
| $2_0^2 3_0^1$? | 22 266.3 | $2_0^1 3_0^1 + 449.1$ | ... | ... |
| $1_0^1 2_0^1$ | 22 311.6 | $2_0^1 + 739.4$ | ... | ... |

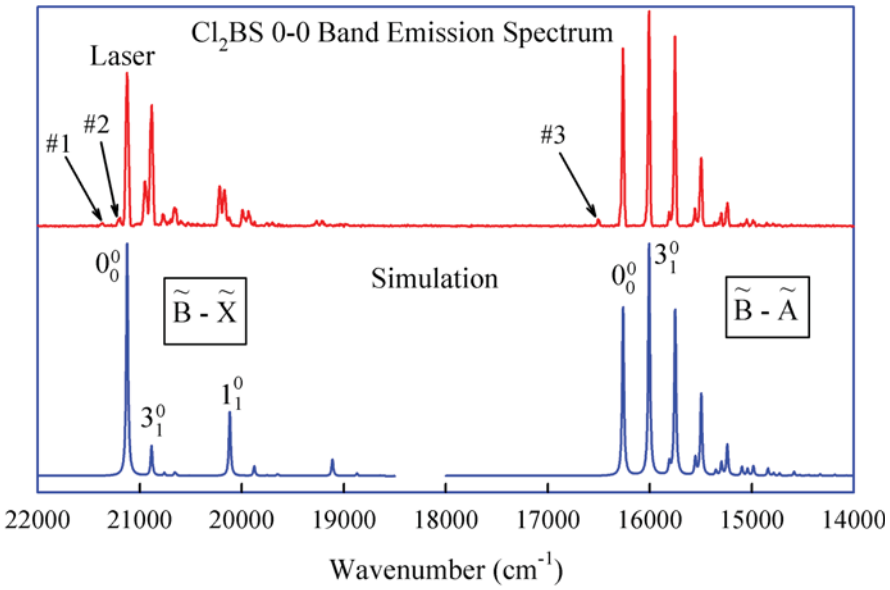


FIG. 5. The observed 0-0 band emission spectrum of $Cl_2BS$ (top panel) and the corresponding harmonic Franck-Condon simulation (bottom panel). The simulations involved calculating the $\tilde{B}$-$\tilde{X}$ and $\tilde{B}$-$\tilde{A}$ spectra, separately, so there is a break in the spectrum near 18 500 $cm^{-1}$. The relative intensities of the two calculated spectra are not meaningful.

TABLE V. Emission bands observed by pumping the $0_0^0$ band of the $\tilde{B}$–$\tilde{X}$ transition of $Cl_2BS$.

| | $Cl_2{}^{11}BS$ | | $Cl_2{}^{10}BS$ | |
|---|---|---|---|---|
| Assignment | Transition ($cm^{-1}$) | Interval ($cm^{-1}$) | Transition ($cm^{-1}$) | Interval ($cm^{-1}$) |
| | | $\tilde{B}-\tilde{X}$[a] | | |
| $3_0^1$ | 21 367 | $\nu'_3 = 244$ | 21 374 | $\nu'_3 = 251$ |
| $6_1^1$ | 21 203 | $\nu'_6 = 259$ | 21 200 | $\nu'_6 = 259$ |
| $0_0^0$ | 21 123 | ... | 21 123 | ... |
| $6_1^0$ | 20 944 | $\nu_6 = 179$ | 20 942 | $\nu_6 = 181$ |
| $3_1^0$ | 20 886 | $\nu_3 = 237$ | 20 883 | $\nu_3 = 240$ |
| $6_2^0$ | 20 768 | $6_1^0 - 176$ | 20 764 | $6_1^0 - 178$ |
| $2_1^0$ | 20 654 | $\nu_2 = 469$ | 20 658 | $\nu_2 = 465$ |
| $5_1^0$ | 20 216 | $\nu_5 = 907$ | 20 174 | $\nu_5 = 949$ |
| $1_1^0$ | 20 167 | $\nu_1 = 956$ | 20 121 | $\nu_1 = 1002$ |
| $1_1^0 6_1^0$ | 19 992 | $1_1^0 - 175$ | 19 945 | $1_1^0 - 176$ |
| $1_1^0 3_1^0$ | 19 927 | $1_1^0 - 240$ | 19 884 | $1_1^0 - 237$ |
| $1_1^0 5_1^0$ | 19 263 | $1_1^0 - 904$ | 19 184 | $1_1^0 - 937$ |
| $1_2^0$ | 19 209 | $1_1^0 - 958$ | 19 135 | $1_1^0 - 986$ |
| $1_1^0 3_1^0 5_1^0$ | ... | ... | 18 954 | $1_1^0 5_1^0 - 230$ |
| | | $\tilde{B}-\tilde{A}$[b] | | |
| $3_0^1$ | 16 504 | $\nu'_3 = 243$ | 16 504 | $\nu'_3 = 246$ |
| $0_0^0$ | 16 261 | $\tilde{X}\ 0_0 + 4862$ | 16 258 | $\tilde{X}\ 0_0 + 4865$ |
| $3_1^0$ | 16 005 | $\nu_3 = 256$ | 16 005 | $\nu_3 = 253$ |
| 2(0,1) | 15 809 | $\nu_2 = 452$ | 15 813 | $\nu_2 = 445$ |
| $3_2^0$ | 15 753 | $3_1^0 - 252$ | 15 750 | $3_1^0 - 255$ |
| $2_1^0 3_1^0$ | 15 557 | $3_1^0 - 448$ | 15 555 | $3_1^0 - 450$ |
| $3_3^0$ | 15 495 | $3_2^0 - 258$ | 15 494 | $3_2^0 - 256$ |
| $2_1^0 3_2^0$ | 15 301 | $3_2^0 - 452$ | 15 303 | $3_2^0 - 447$ |
| $3_4^0$ | 15 239 | $3_3^0 - 256$ | 15 238 | $3_3^0 - 256$ |
| $2_1^0 3_3^0$ | 15 045 | $3_3^0 - 450$ | 15 051 | $3_3^0 - 443$ |
| $3_5^0$ | 14 986 | $3_4^0 - 253$ | 14 986 | $3_4^0 - 252$ |

[a]Vibrational intervals are for the $\tilde{X}$ state unless otherwise noted.
[b]Vibrational intervals are for the $\tilde{A}$ state unless otherwise noted.

$\nu_1''$ and $\nu_5''$) is 78 $cm^{-1}$ whereas the *ab initio* value is 77 $cm^{-1}$, both in good agreement with experiment. The $0_0^0$ band $\tilde{B}$–$\tilde{X}$ emission assignments are summarized in Table V.

Although the excellent agreement between Franck-Condon simulation and experiment (Fig. 5) shows that most of the intensity of the $\tilde{B}$–$\tilde{A}$ band system originates from the $0^0$ level, the weak feature labeled #3 is not in the calculated spectrum, but was readily assigned as the $3_0^1$ band. There is no evidence for any vibronically induced features in the $\tilde{B}$–$\tilde{A}$ spectrum. The most intense bands form a progression in $\nu_3''$ out to $3_5^0$, along with weaker bands involving $\nu_2''$ and $\nu_2'' + \nu_3''$ combinations. These are listed in Table V.

Other emission spectra with upper states involving either $\nu_3'$ or $\nu_6'$ have similar complications due to the Coriolis coupling of these two modes. Most of the remaining emission spectra were understandable and assignable based on the assumption of laser excitation of a single uncompromised vibrational level, such as $1^1$ or $2^1$, with only modest deviations from the calculated spectra in the harmonic approximation, due to vibronically induced bands. Generally, it was found that the strongest features in the emission spectra of LIF bands involving an upper state fundamental ($1_0^1$, $2_0^1$, etc.) were down to one quantum of the same fundamental in the ground state, in accord with expectations based on the Franck-Condon principle. Thus, the most intense $\tilde{B} - \tilde{X}$ emission bands from laser excitation of the $1^1$, $2^1$, $3^1$, $5^1$, and $6^1$ levels were $1_1^1$, $2_1^1$, $3_1^1$, $5_1^1$, and $6_1^1$, respectively.

From the analysis of the LIF and emission spectra, we have obtained most of the fundamental frequencies in the three combining states, as reported in Table I. Some of these values deserve further comment. The $\tilde{B}$ state $\nu_6$ frequencies were obtained from the $6_1^1$ to $6_1^0$ LIF band intervals and the ground state $\nu_6$ from the emission $0_0^0$ to $6_1^0$ differences. The $\tilde{A}$ state $\nu_6$ values were calculated from the emission spectra as $0_0^0$ ($\tilde{B} - \tilde{A}$) + $\nu_6'$ – $6_1^1$ ($\tilde{B} - \tilde{A}$) and the $\nu_5$ values were derived in a similar fashion. The $\tilde{B}$ state $\nu_3$ values were taken as the differences between the $\tilde{B}$–$\tilde{A}$ $3_0^1$ and $0_0^0$ bands observed in the 0-0 band emission spectra, as the LIF values are compromised by the overlap of the $3_0^1$ and $6_0^1$ bands. In addition, a variety of $Cl_2BS$ $\tilde{X}$ and $\tilde{A}$ state overtone and combination levels were measured and assigned and these are collected in Table VI.

TABLE VI. The observed overtone and combination vibrational intervals (in $cm^{-1}$) for the $\tilde{X}$ and $\tilde{A}$ electronic states of $Cl_2BS$.

| | $\tilde{X}^2B_2$ | | $\tilde{A}^2B_1$ | |
|---|---|---|---|---|
| | $Cl_2{}^{11}BS$ | $Cl_2{}^{10}BS$ | $Cl_2{}^{11}BS$ | $Cl_2{}^{10}BS$ |
| $2\nu_6$ | 355 | 355 | ... | ... |
| $2\nu_3$ | 476 | 487 | 510 | 509 |
| $\nu_3+2\nu_6$ | ... | 596 | ... | ... |
| $\nu_2+\nu_6$ | 631 | 633 | ... | ... |
| $\nu_2+\nu_3$ | 700 | 702 | 704 | 703 |
| $3\nu_3$ | ... | ... | 766 | 764 |
| $2\nu_2$ | 930 | 933 | 893 | 904 |
| $\nu_2+2\nu_3$ | 935 | ... | 960 | 958 |
| $4\nu_3$ | ... | ... | 1021 | 1020 |
| $\nu_5+\nu_6$ | 1088 | 1121 | ... | ... |
| $\nu_3+\nu_5$ | 1153 | 1181 | 1212 | 1249 |
| $\nu_1+\nu_6$ | 1136 | 1178 | ... | ... |
| $2\nu_2+\nu_3$ | ... | ... | 1150 | 1155 |
| $\nu_1+\nu_3$ | 1197 | 1244 | 1155 | 1195 |
| $\nu_2+3\nu_3$ | ... | ... | 1216 | 1216 |
| $5\nu_3$ | ... | ... | 1275 | 1272 |
| $\nu_2+\nu_5$ | 1368 | 1400 | ... | ... |
| $\nu_1+\nu_2$ | 1417 | 1460 | 1351 | 1390 |
| $2\nu_2+2\nu_3$ | ... | ... | 1398 | ... |
| $\nu_1+2\nu_3$ | ... | ... | 1412 | 1453 |
| $\nu_2+4\nu_3$ | ... | ... | 1460 | ... |
| $2\nu_3+\nu_5$ | ... | ... | 1464 | 1517 |
| $\nu_2+\nu_3+\nu_5$ | 1600 | 1636 | 1661 | ... |
| $\nu_1+\nu_2+\nu_3$ | 1654 | 1698 | 1605 | 1649 |
| $\nu_1+3\nu_3$ | ... | ... | 1665 | 1708 |
| $3\nu_3+\nu_5$ | ... | ... | 1720 | 1753 |
| $2\nu_5$ | 1811 | 1875 | ... | ... |
| $\nu_1+\nu_2+2\nu_3$ | ... | ... | 1857 | ... |
| $\nu_1+\nu_5$ | 1859 | 1933 | ... | ... |
| $2\nu_1$ | 1914 | 1991 | ... | ... |
| $\nu_1+4\nu_3$ | ... | ... | 1919 | 1960 |
| $4\nu_3+\nu_5$ | ... | ... | 1969 | ... |
| $\nu_3+2\nu_5$ | 2044 | 2116 | ... | ... |
| $2\nu_1+\nu_6$ | 2084 | 2165 | ... | ... |
| $2\nu_1+\nu_3$ | 2153 | 2228 | ... | ... |
| $3\nu_1$ | 2853 | 2971 | ... | ... |

## IV. DISCUSSION

### A. Comparison to theory

The theoretical and experimental results are compared in Table I. It is apparent that the calculated band origins for the two electronic excited states are in excellent agreement with experiment, differing by a minimum of 5 $cm^{-1}$ (0.02%) for the $\tilde{B}$ state of $F_2BS$ and a maximum of 148 $cm^{-1}$ (0.70%) for the $\tilde{B}$ state of $Cl_2BS$. We have previously[11] attributed a similar fortuitously good level of agreement in $F_2BO$ to the small geometry changes on electronic excitation, the lack of spin contamination, and the predominantly single reference character of the wavefunctions, factors which also apply in the present cases. The measured vibrational fundamentals are very consistent with our CCSD(T)/aug-cc-pVnZ harmonic vibrational frequencies, with a maximum deviation of 35 $cm^{-1}$ (3%) and an average error of only 7 $cm^{-1}$. The observed isotope shifts are also in excellent agreement with those calculated experimentally. Most importantly, the harmonic Franck-Condon simulations, which hinge on reliable molecular geometries, vibrational frequencies, and normal mode Cartesian displacement coordinates of the two combining electronic states, mimic experiment so well that they provide unambiguous identification of the emitting species and reliable assignments for the great majority of the emission bands.

### B. Molecular structures

Since the spectra of $F_2BO$, $F_2BS$, and $Cl_2BS$ are too congested for detailed rotational analysis, we must rely on the *ab initio* results to compare molecular geometries. The fact that the calculated rotational contours of the $F_2BO$ and $F_2BS$ $\tilde{B}$–$\tilde{X}$ $0_0^0$ bands match experiment very well and that the Franck-Condon simulations agree so well with experiment in cases uncomplicated by extensive Coriolis or vibronic

TABLE VII. The *ab initio* ground state molecular structures of the known gas phase $X_2BY$ free radicals and the calculated changes in geometry on electronic excitation.

| Parameter | | $F_2BO$ [a] | $F_2BS$ [a] | $Cl_2BS$ [b] |
|---|---|---|---|---|
| | BY (Å) | 1.3639 | 1.8019 | 1.7801 |
| $\tilde{X}^2B_2$ | BX (Å) | 1.3135 | 1.3168 | 1.7544 |
| | XBX (°) | 119.29 | 120.56 | 120.89 |
| | Δ[BY] (Å) | +0.042 | +0.048 | +0.068 |
| $\tilde{A}^2B_1$ | Δ[BX] (Å) | +0.002 | +0.004 | −0.007 |
| | Δ[XBX] (°) | +1.44 | −0.69 | −2.23 |
| | Δ[BY] (Å) | +0.011 | +0.058 | +0.064 |
| $\tilde{B}^2A_1$ | Δ[BX] (Å) | −0.006 | −0.018 | −0.021 |
| | Δ[XBX] (°) | −0.09 | +2.57 | +4.93 |

[a]CCSD(T)/aug-cc-pV5Z values from Ref. 11.
[b]CCSD(T)/aug-cc-pVTZ values from this work.

coupling suggest that the *ab initio* structures are reasonably reliable. The structures obtained from theory are compared in Table VII. It is important to emphasize that each radical is predicted to be planar and of $C_{2v}$ symmetry in all three electronic states.

It is immediately evident that the ground state bond angles in all three radicals are very similar and very close to the 120° value expected in the simplest approximation of $sp^2$ hybridization on the central boron atom. The BF bond lengths are almost identical in $F_2BO$ and $F_2BS$, but the BS bond length of $Cl_2BS$ is 0.02 Å shorter than that of $F_2BS$. The BF (1.31-1.32 Å) and BCl (1.754 Å) bond lengths are comparable to the bond lengths of $BF_3$ (1.307 Å) and $BCl_3$ (1.74 Å), respectively.[22,23]

Our LIF spectra reflect the changes in the molecular structure between the ground state and the $\tilde{B}^2A_1$ electronic excited state. Table VII shows that $F_2BO$ undergoes very little geometry change and the LIF and absorption spectra consist of a prominent $0_0^0$ band and little else. In $F_2BS$, the BS bond length elongates by about 0.06 Å and the bond angle opens by about 2.5°, resulting in additional absorption transitions to the $2^1$ and $1^1$ states, vibrations which both involve substantial BS stretching motions. In $Cl_2BS$, the changes are more global with a 0.06 Å elongation of the BS bond, a 0.02 Å decrease in the BCl bond length and an increase in the bond angle by 5°, which leads to activity in $\nu_1'$ (BS stretch), $\nu_2'$ (BCl stretch), and $\nu_3'$ (ClBCl bend).

The observed $\tilde{B}$-$\tilde{A}$ emission spectra reflect the geometric changes between the $\tilde{B}$ and $\tilde{A}$ states. These can be determined from the data in Table VII by taking the difference between the Δ values of the two states. For example, for $F_2BS$, we have $\Delta BS = \Delta[BY]\tilde{A} - \Delta[BY]\tilde{B} = 0.048 - 0.058 = 0.01$ Å. It is then immediately apparent that the only significant change is in the $F_2B$ or $Cl_2B$ bond angle, which accounts for the pronounced activity in the $\tilde{A}$ state $\nu_3$ (symmetric bend or scissors) mode in all the spectra.

### C. Vibronic coupling

Although the observed spectra of $F_2BO$ and $F_2BS$ show no evidence of vibronic coupling, the $\tilde{B}^2A_1$–$\tilde{X}^2B_2$ allowed electronic transition of $Cl_2BS$ clearly contains forbidden components which gain intensity by vibronic coupling through the $b_2$ vibrations. Vibronic coupling can only occur between states that differ by no more than the species of one of the normal vibrations.[24] The involvement of the $b_2$ vibration implies that the $^2A_1$ state is coupled to a nearby $^2B_2$ state. Although it is, in principle, possible for the vibronic coupling to occur with the $\tilde{X}^2B_2$ ground state, it is so energetically distant (2.6 eV) that it is unlikely to be involved. Therefore, it must be that there is an excited $^2B_2$ electronic state of $Cl_2BS$ sufficiently close to the $\tilde{B}$ state to cause the vibronic perturbations and that such a state does not substantially perturb the second excited state in the fluorinated compounds. Although no detailed calculations are available for the higher excited electronic states of $Cl_2BS$, MRCI calculations on the vertical spectrum of the isoelectronic $H_2CO^+$ species[25] predict a $2^2B_2$ ($2b_2 \leftarrow 1b_2$) state about 1 eV above the $\tilde{B}^2A_1$ state, ideally situated for vibronic coupling. Similarly, in $F_2CO^+$, the $2^2B_2$ state is within 0.3 eV of the $1^2A_1$ state (calculated at the optimized ground state geometry of $F_2CO$) and within 0.8 eV according to the adiabatic ionization potentials from the photoelectron spectrum.[26] Of course, the $2^2B_2$–$\tilde{X}^2B_2$ transition is also electronically allowed and so the forbidden component of the $\tilde{B}$-$\tilde{X}$ system of $Cl_2BS$ can, at least in theory, gain intensity from the former by Herzberg-Teller intensity stealing. Detailed calculations of the identities and energies of the higher excited states of the $X_2BY$ radicals will be required to further elaborate this point.

The $\tilde{A}^2B_1$ state cannot have a vibronic interaction with the nearby $\tilde{X}^2B_2$ state as $C_{2v}$ molecules do not have a normal mode of $a_2$ symmetry.[24] In a similar fashion, although the evidence shows that the $\tilde{B}^2A_1$ state has an admixture of another $^2B_2$ state, this vibronic perturbation cannot lead to the occurrence of forbidden components in the $\tilde{B}^2A_1$–$\tilde{A}^2B_1$ emission band system and no such vibronically induced bands have been observed in the spectra of $F_2BO$, $F_2BS$, or $Cl_2BS$.

## V. CONCLUSIONS

In the present case, high level *ab initio* theory has proven to be a powerful tool for predicting the spectroscopic signatures of new $X_2BY$ free radicals, leading to their experimental detection in the gas phase. The Franck-Condon simulations of the emission spectra, in particular, were used to provide unambiguous identification of the radicals and, in most cases, reliable assignments of the observed transitions. The observed spectra of $F_2BS$ are complicated by Coriolis coupling of the $\nu_2$ and $\nu_4$ modes in the excited state, so the $2_0^1$ band emission spectrum exhibits transitions from both upper state levels. Even here, theory does very well—a composite Franck-Condon simulation of emission from $2^1$ and $4^1$ matches experiment very satisfactorily.

The LIF spectrum of $Cl_2BS$ exhibits more vibronic activity than those of $F_2BO$ and $F_2BS$, a necessary consequence of the larger geometric distortion of $Cl_2BS$ on $\tilde{B}^2A_1$–$\tilde{X}^2B_2$ electronic excitation predicted by the *ab initio* calculations. In addition, $Cl_2BS$ exhibits clear evidence of the existence of a forbidden component of the allowed electronic transition in

the experimental spectrum, involving activity in the $b_2$ modes, $\nu_5$ and $\nu_6$. This subset of the observed bands gains intensity by Herzberg-Teller intensity stealing from a nearby allowed transition, which is most likely $2^2B_2$–$\tilde{X}^2B_2$. Finally, the $Cl_2BS$ emission spectra are complicated by Coriolis coupling of $\nu_3$ and $\nu_6$ in the $\tilde{B}$ state. Both the excited state Coriolis coupling and vibronic interactions lead to complications in the $\tilde{B}$–$\tilde{X}$ emission spectra that cannot be accounted for in the harmonic Franck-Condon simulations. However, the $\tilde{B}$–$\tilde{A}$ band systems are largely free of such complexity and are reproduced by the simulations with gratifying fidelity.

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[1]P. Renaud, A. Beauseigneur, A. Brecht-Forster, B. Becattini, V. Darmency, S. Kandhasamy, F. Montermini, C. Ollivier, P. Panchaud, D. Pozzi, E. M. Scanlan, A.-P. Schaffner, and V. Weber, Pure Appl. Chem. **79**, 223 (2007).
[2]S. H. Bauer, Chem. Rev. **96**, 1907 (1996).
[3]C. W. Mathews and K. K. Innes, J. Mol. Spectrosc. **15**, 199 (1965).
[4]C. W. Mathews, J. Mol. Spectrosc. **19**, 203 (1966).
[5]R. N. Dixon, G. Duxbury, R. C. Mitchell, and J. P. Simons, Proc. R. Soc. A **300**, 405 (1967).
[6]M. E. Jacox, J. Phys. Chem. Ref. Data **17**, 398 (1988).
[7]I. Baraille, C. Larrieu, A. Dargelos, and M. Chaillet, Chem. Phys. **282**, 9 (2002).
[8]R. Grimminger, P. M. Sheridan, and D. J. Clouthier, J. Chem. Phys. **140**, 164302 (2014).
[9]W. R. M. Graham and W. Weltner, Jr., J. Chem. Phys. **65**, 1516 (1976).
[10]E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. **36**, 1938 (1962).
[11]D. J. Clouthier, J. Chem. Phys. **141**, 244309 (2014).
[12]W. W. Harper and D. J. Clouthier, J. Chem. Phys. **106**, 9461 (1997).
[13]D. L. Michalopoulos, M. E. Geusic, P. R. R. Langridge-Smith, and R. E. Smalley, J. Chem. Phys. **80**, 3556 (1984).
[14]E. L. Gamble, H. S. Booth, and H. Halbedel, *Inorganic Syntheses* (Wiley, 1950), Vol. 3.
[15]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[16]C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[17]T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[18]D. Feller, K. A. Peterson, and J. G. Hill, J. Chem. Phys. **135**, 044102 (2011).
[19]M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
[20]D.-S. Yang, M. Z. Zgierski, A. Bérces, P. A. Hackett, P.-N. Roy, A. Martinez, T. Carrington, Jr., D. R. Salahub, R. Fournier, T. Pang, and C. Chen, J. Chem. Phys. **105**, 10663 (1996).
[21]E. V. Doktorov, I. A. Malkin, and V. I. Man'ko, J. Mol. Spectrosc. **64**, 302 (1977).
[22]T. Masiello, A. Maki, and T. A. Blake, J. Mol. Spectrosc. **243**, 16 (2007).
[23]T. Wentink, Jr. and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).
[24]G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
[25]P. J. Bruna, M. R. J. Hachey, and F. Grein, Mol. Phys. **94**, 917 (1998).
[26]F. Grein, J. Phys. Chem A **102**, 10869 (1998).