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# Barely fluorescent molecules. II. Twin-discharge jet laser-induced fluorescence spectroscopy of HSnBr and DSnBr

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#### ABSTRACT

HSnBr and DSnBr have been detected for the first time by a combination of laser-induced fluorescence (LIF), fluorescence hole-burning, and wavelength resolved emission spectroscopies. The transient molecules were produced in a twin-discharge jet using separate precursor streams of SnH<sub>4</sub>/SnD<sub>4</sub> and HBr/DBr, both diluted in high pressure argon. The  $\tilde{A}^1 A'' - \tilde{X}^1 A'$  spectrum of HSnBr only consists of the  $0_0^0$  and  $2_0^1$  cold bands that show clearly resolved subband structure with fluorescence lifetimes varying from 526 to 162 ns. The DSnBr LIF spectrum exhibits four bands  $(0_0^0, 2_0^1, 2_0^2, and 1_0^1)$  whose fluorescence lifetimes decrease from 525 ns  $(0^0)$  to 175 ns  $(1^1)$ . Single vibronic level emission spectra have provided extensive information on the ground state vibrations, including all the anharmonicities and the harmonic frequencies. Fluorescence hole-burning experiments have shown that a few higher HSnBr nonfluorescent levels are very short-lived but still detectable. The *ab initio* studies of Tarroni and Clouthier [J. Chem. Phys. **156**, 064304 (2022)] show that these molecules dissociate into SnBr + H on the excited state potential surface and this is the cause of the short fluorescence lifetimes and breaking off of the LIF spectra. HSnBr is a barely fluorescent molecule in the sense that only vibrational levels less than or equal to 317 cm<sup>-1</sup> in the excited state emit detectable photons down to the ground state.

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#### I. INTRODUCTION

As part of a new program to study the spectra of tin-containing polyatomic reactive intermediates, we have recently reported the detection and characterization of the jet-cooled tin dihydride (SnH<sub>2</sub>) species in the gas phase.<sup>1</sup> This molecule has a  $\tilde{A}^1B_1-\tilde{X}^1A_1$  band system near 630 nm and is readily detectable by laser-induced fluorescence (LIF) spectroscopy. As expected, based on the Walsh postulate, SnH<sub>2</sub> has a bent ground state with a bond angle of 91° that increases substantially to 122.9° on electronic excitation. As a result, the electronic spectrum should show long progressions in the bending mode, but we have found that fluorescence is only detectable from a few vibrational levels in the excited state due to a competitive photodissociation process.

Although  $SnH_2$  was produced in the conventional method by subjecting dilute precursor mixtures of  $SnH_4$  or tetramethylstannane in high pressure argon to a discharge at the exit of a pulsed supersonic expansion, production of HSnX (X = F, Cl, Br, I) necessitated a more sophisticated technique. Stable  $H_3SnX$  or  $HSnX_3$  precursors are not available,<sup>2</sup> so we resorted to a twindischarge jet method in which  $SnH_4$  and HX were introduced in separate discharge flow channels and the reactant streams were mixed just prior to expansion.

As detailed in Paper I,<sup>3</sup> efforts to detect HSnCl and DSnCl using SnH<sub>4</sub> (SnD<sub>4</sub>) and HCl (DCl) were successful. HSnCl was only barely fluorescent, exhibiting a single LIF  $0_0^0$  band, whereas the DSnCl spectrum contains  $0_0^0$ ,  $2_0^1$ , and  $2_0^2$  bands. The  $0^0$  level of HSnCl has a very short fluorescence lifetime (29 ns), but the zero-point level of DSnCl has a long lifetime (393 ns), decreasing to 380 ns for  $2^1$  and then plummeting to <10 ns for  $2^2$ . Clearly, a competitive nonradiative process, probably dissociative, occurs low down in the excited state potential, resulting in the breaking off of the fluorescence. A similar but somewhat different phenomenon occurs in SnH<sub>2</sub>, where LIF transitions are observed to the first few bending levels; however, each band is comprised of at most a few rotational lines, terminating on the very lowest rotational levels. All of the observed LIF bands

of  $\text{SnH}_2$  and  $\text{SnD}_2$  show evidence of a rotational-level-dependent predissociation process that rapidly decreases the fluorescence yield and lifetime with increasing rotational angular momentum in each excited vibronic level.

In an attempt to systematize our observations and make predictions for further experiments, Tarroni and Clouthier used high level *ab initio* theory to explore the excited state potential energy surfaces of the HSiX, HGeX, and HSnX (X = H, F, Cl, Br and I) molecules.<sup>4</sup> It was found that the dissociation of HMX  $\rightarrow$  H + MX limits fluorescence from the  $\tilde{A}^1 A''$  states of some of these molecules so that HGeF and HSnF should be nonfluorescent, as is found experimentally.<sup>3</sup> The calculations also indicated that HSnCl should only fluoresce from the very lowest excited state levels, with slightly more activity for DSnCl, due to the reduced excited state zero-point energy, precisely as we have found.<sup>3,4</sup> For HSnBr and DSnBr, the dissociation is predicted to occur somewhat higher up in the excited state, so the LIF spectra of these species should be more extensive but can still be classified as barely fluorescent.

Building on our experience with the twin-jet discharge technique, our success in finding the spectrum of HSnCl, and encouraged by our *ab initio* findings, we set out to find the LIF spectra of HSnBr and DSnBr, as detailed in this paper. As predicted,<sup>4</sup> the HSnBr LIF spectrum is limited, accessing only the  $0_0^0$  and  $2_0^1$  cold bands, abruptly terminating due to the opening of the SnBr + H photodissociation channel. The spectrum of DSnBr is somewhat more extensive, ceasing just above three quanta of the bending mode. Both molecules have extensive single vibronic level (SVL) emission spectra, extending 5000–6000 cm<sup>-1</sup> in the ground state, providing a very detailed picture of the vibrational levels in the lower state.

#### **II. EXPERIMENT**

Most of the experimental details are the same as outlined in Paper I,<sup>3</sup> to which the reader is referred, and, here, we only summarize particulars important to the HSnBr/DSnBr experiments. HBr (Matheson, 99.8%) and DBr (Sigma-Aldrich, 99%) were used as received. The LIF spectra were obtained using the twin-discharge jet apparatus described previously. SnH<sub>4</sub> or SnD<sub>4</sub> liquid was cooled in a Pyrex U-tube to -110 °C (ethanol/liquid N<sub>2</sub> slush), pressurized with 55 psi of argon, and delivered through stainless steel tubing to one of the pulsed valves. One atmosphere of HBr or DBr gas was diluted with 400 psi of argon, and the mixture was delivered to the second pulsed valve through a regulator at a pressure of 120 psig. As in our HSnCl work, experiments showed that the best conditions were with an electric discharge in the HBr/DBr channel but no discharge in the stannane channel.

Nonfluorescent vibronic levels higher up in the excited state were probed using a two-laser fluorescence hole-burning technique. The PUMP laser (Lumonics HD-540) was fixed on a strong *Q*branch of an LIF transition and the PROBE laser (Lumonics HD-500), triggered 50–100 ns *before* the PUMP laser, was scanned to the blue. If the PROBE laser became resonant with a transition from the same ground state levels as the PUMPed *Q*-branch, the ground state levels were depleted and this action showed up as a dip or hole in the total fluorescence intensity. In this manner, transitions to higher vibronic states, broadened by the short excited state lifetimes, were identified and their decay rates estimated from the linewidths.

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#### III. RESULTS AND ANALYSIS

#### A. LIF spectra

We label the vibrations of HSnBr conventionally as  $v_1 = Sn-H$ stretch,  $v_2$  = bend, and  $v_3$  = Sn–Br stretch. Based on the experimental conditions used for the generation of the LIF spectrum of HSnCl,<sup>3</sup> we readily obtained the spectra shown in Fig. 1 using our tunable OPO source. The top panel shows two traces: the upper trace (short decay) is the spectrum obtained by gating the LIF signal for 100 ns immediately after the laser pulse and the lower trace (long decay) is that recorded with a 1  $\mu$ s wide gate delayed 1  $\mu$ s after the laser. The long-lived band system between 21 550 and 22 400 cm<sup>-1</sup> was readily identified because of tin(II) bromide,<sup>5,6</sup> as was the lengthy progression of SnBr bands<sup>7</sup> at lower energies. In addition, the short decay spectrum exhibits two strong bands centered at ~20030 and ~20 350 cm<sup>-1</sup> with clear subband structure even at this low resolution. Subsequent more detailed work shows that these are the  $0_0^0$  and  $2_0^1$  bands of the previously unknown  $\tilde{A}^1 A'' - \tilde{X}^1 A'$  electronic spectrum of HSnBr.

Using the Lumonics dye laser, we obtained the medium resolution spectra  $(0.1 \text{ cm}^{-1})$  of the complete band system of DSnBr, as illustrated in the bottom panel of Fig. 1. The strong bands form an anharmonic bending progression with an interval of ~228 cm<sup>-1</sup> and are partially overlapped by the weaker SnBr band system. It is evident that the DSnBr bands get rapidly broader and more complex with increasing energy, a trend not seen in the more limited HSnBr spectra. There are also weak bands on the red edges of  $2_0^1$  and  $2_0^2$ , which we assign as the  $3_1^2$  and  $3_1^3$  hot bands based on their vibrational interval (217 cm<sup>-1</sup>) and emission spectra (*vide infra*). At the high energy end of the spectrum, there is a weak band with sharp subband structure, much like that of the 0–0 band, which we assign, based on the vibrational interval of 816.7 cm<sup>-1</sup> above 0–0 (*ab initio*:



**FIG. 1.** LIF spectra of HSnBr and DSnBr. The top panel shows the low resolution  $(3-5 \text{ cm}^{-1})$  spectra obtained from a twin discharge jet with SnH<sub>4</sub> and argon in one channel and HBr and argon in the other. The upper trace (short delay spectrum) is that obtained with a gated integrator gate width of 100 ns, delayed 20 ns after the laser pulse. The lower trace (long delay spectrum) is that obtained with a gated integrator gate width of 1  $\mu$ s, delayed 1  $\mu$ s after the laser pulse. The bottom panel shows the medium resolution (0.1 cm<sup>-1</sup>) LIF spectrum of DSnBr with assignments.

 $v'_1 = 836 \text{ cm}^{-1})^4$  and the prominence of  $v''_1$  in the emission spectrum (*vide infra*), as  $1^1_0$ .

Figure 2 shows the rotational contours of the 0-0 bands of both isotopologues. These are clearly perpendicular bands of an asymmetric top and the obvious axis-switching Q-branches ( ${}^{q}Q_{0}$  and  ${}^{q}Q_{1}$ ) are as expected for molecules of  $C_{S}$  symmetry with a large change in the bond angle on electronic excitation.<sup>4</sup> Buried in the HSnBr contour are a series of weak Q branches, which we subsequently identified, based on emission spectra, as features of the  $3_1^1$  hot band. The bottom panel of Fig. 2 shows the contour of the DSnBr 0-0 band and our PGopher<sup>8,9</sup> simulation based solely on the *ab initio* geometries and the expected *c*-type rotational selection rules.<sup>4</sup> The agreement is obviously very good and confirms the identity of the fluorescent species. There are no bromine or tin isotope splittings evident in either spectrum. The 0-0 band isotope shift upon deuterium substitution of  $+104 \text{ cm}^{-1}$  is very similar to the calculated value of  $\pm 106 \text{ cm}^{-1}$ , and the upper state bending frequencies of 317 (HSnBr) and 228 cm<sup>-1</sup> (DSnBr) cm<sup>-1</sup> are in accord with the *ab initio* values of 342 and 258 cm<sup>-1</sup>. The individual rovibronic lines of these bands are not resolvable even at our highest available resolution (vide infra), so no detailed rotational analysis was possible. The measured band origins, assignments, and intervals in the LIF spectra of HSnBr and DSnBr are summarized in Table I.

#### **B.** Hole-burning measurements

In an attempt to obtain further information about the excited state vibronic energy levels and their lifetimes, we obtained holeburning spectra for HSnBr. The hole-burning technique has three significant advantages. First, it allows the experimentalist to detect nonfluorescent states, and it is species specific since the PROBE laser can only deplete the fluorescence of the molecular species being PUMPed. Second, if one PUMPs a cold band, hot band transitions are automatically eliminated. Third, the selection rules can be used to advantage to generate hole-burning spectra that access specific excited state rotational levels, depending on the ground state



**FIG. 2.** Medium resolution (0.1 cm<sup>-1</sup>) short delay LIF spectra of the 0–0 bands of HSnBr (top panel) and DSnBr (bottom panel). Both bands exhibit weak axisswitching Q-branches ( ${}^{q}Q_{0}$  and  ${}^{q}Q_{1}$ ) as identified in the upper panel. The HSnBr band is overlapped by the much weaker  $3_{1}^{1}$  band whose Q-branches are identified. The DSnBr spectrum is accompanied by a simulation of the expected band contour (0.25 cm<sup>-1</sup> FWHM, 20 K rotational temperature, and an axis switching angle of 1.3°) based on the *ab initio* geometries.<sup>4</sup>.

levels being PUMPed. For example, as shown in Fig. 3, the upper trace illustrates the result of PUMPing the  $0_0^0$  band  ${}^rQ_0$  branch and scanning the PROBE laser between 20 500 and 20 700 cm<sup>-1</sup>. A single hole-burning feature of a transition not detected in LIF is observed, in which the selection rules mandate must be the  ${}^rQ_0$  branch. The lower trace in Fig. 3 is a composite hole-burning spectrum over two laser dyes obtained by PUMPing the 0–0 band  ${}^pQ_1$  branch. Since the lower state is  $K_a'' = 1$ , two strong *Q*-branches ( ${}^pQ_1$  and  ${}^rQ_1$ ) should be

TABLE I. Assignments and approximate band origins of the observed bands (cm<sup>-1</sup>) in the LIF and hole-burning spectra of HSnBr and DSnBr. *Ab initio* values<sup>4</sup> are in square parentheses.

-				
Assign.	HSnBr	Comment	DSnBr	Comment
$\overline{3_1^1}$	200 01.3	v <sub>3</sub> ' = 234 [246]		
000	200 11.4	$^{q}Q_{0}$ [20 478]	20 115.6	$^{q}Q_{0}$ [20 584] D-H = 104.2 [106]
$3_1^2$			$\sim 20.321^{a}$	
$2_0^1$	203 28.5	${}^{q}Q_{0} v_{2}' = 317.1 [342]$	$\sim 20.344^{a}$	$v_2' = 228.4 \ [258]$
$3_1^3$			$\sim 20538^{a}$	v <sub>3</sub> <sup>'</sup> ~ 217 [238]
$2_0^2$	20 622.4 <sup>b</sup>	$2_0^2 - 2_0^1 = 293.9$	$\sim 20572^{a}$	$2_0^1 + 228$
$2_0^2 3_0^1$	20 850.5	$2_0^2 3_0^1 - 2_0^2 = 228.1$		
$2_0^3$	20 891.1	$2_0^3 - 2_0^2 = 268.7$	$\sim 20.778^{a}$	$2_0^2 + 206$
$1_{0}^{1}$			20 932.3	${}^{q}Q_{0} v_{1}' = 816.7 [836]$

<sup>a</sup>These bands are broad, with poorly defined rotational structure, so the band origins are only approximate.

<sup>b</sup>Transitions in boldface are from hole-burning spectra. Band origins are estimated as  ${}^{p}Q_{1} + 5.4 \text{ cm}^{-1}$  (from the  ${}^{q}Q_{0} - {}^{p}Q_{1}$  or  $[K_{a}'' = 1 - K_{a}'' = 0]$  interval of the 0–0 band).



**FIG. 3.** Fluorescence hole-burning spectra of HSnBr. The top trace shows a PROBE laser scan from 20 500–20 700 cm<sup>-1</sup> while PUMPing the 0–0 band  ${}^{r}Q_{0}$  branch. The single observed feature is the  ${}^{r}Q_{0}$  branch of the  $2_{0}^{2}$  band of HSnBr not detected in LIF experiments. The bottom trace is a composite spectrum over two laser dyes obtained by PUMPing the 0–0 band  ${}^{p}Q_{1}$  branch. Each observed vibronic band consists of two features assigned as  ${}^{p}Q_{1}$  and  ${}^{r}Q_{1}$ . The  $2_{0}^{2}3_{0}^{1}$  band has a further weak feature, marked "?," which may be the  ${}^{q}Q_{1}$  axis switching branch.

evident for each vibronic band. Near 20 600 cm<sup>-1</sup>, two such features are observed and they bracket the upper trace  ${}^{r}Q_{0}$  branch, precisely as expected. Two further doublets with much broader linewidths are observed at higher energies. We assign the 20 600 cm<sup>-1</sup> band as  $2_0^2$  and that near 20 900 cm<sup>-1</sup> as  $2_0^3$  based on the measured band separations of 317.1 cm<sup>-1</sup>  $[2_0^1 - 0_0^0]$ , 293.9 cm<sup>-1</sup>  $[2_0^2 - 2_0^1]$ , and 268.7 cm<sup>-1</sup>  $[2_0^3 - 2_0^2]$ , which are quite anharmonic as expected for a molecule near dissociation. The  ${}^{r}Q_{1} - {}^{p}Q_{1}$  branch separations are 25.4 (0<sup>0</sup><sub>0</sub>), 26.3 (2<sup>1</sup><sub>0</sub>), 26.6  $(2_0^2)$ , and 26.0  $(2_0^3)$  cm<sup>-1</sup>, reflecting the general increase  $(2_0^3)$  is anomalous) in A' as  $v'_2$  increases. The other band at 20 850.5 cm<sup>-1</sup> (Fig. 3) has a Q-branch separation of 26.8 and is 228.1 cm<sup>-1</sup> above  $2_0^2$ , leading to the assignment of  $2_0^2 3_0^1$ . This band has an extraneous feature marked in Fig. 3 with a question mark that is in about the right place for the  ${}^{q}Q_{1}$  axis-switching branch, although this weaker feature does not show up in any of the other hole-burning bands, so the assignment must remain questionable. The assignments and measured frequencies of the hole-burning bands have been added to Table I.

It is apparent in Fig. 3 that the linewidths of the  $2_0^2 3_0^1$  and  $2_0^3$ *Q*-branches (3–15 cm<sup>-1</sup>) are much greater than those of the  $2_0^2$  band (0.4–0.5 cm<sup>-1</sup>). We can crudely estimate the excited state lifetimes for these higher levels from the time-energy uncertainty relationship as  $\tau = 1/(2\pi c \Delta \overline{\nu}) \sim 1.8-0.4$  ps, entirely consistent with the notion that the higher levels are broadened due to dissociation in the excited state.

#### C. Emission spectra

Single vibronic level emission spectra were obtained by pumping the  $0_0^0$ ,  $2_0^1$ , and  $3_1^1$  bands of HSnBr and the  $0_0^0$ ,  $2_0^1$ ,  $2_0^3$ ,  $3_1^2$ ,  $3_1^3$ , and  $1_0^1$  LIF bands of DSnBr. Where feasible, we chose to pump the  ${}^rQ_0$  branch, yielding resolvable doublets in the emission spectra down to ground state levels with  $K''_a = 2 ({}^pQ_2 \text{ branch})$  and  $0 ({}^rQ_0 \text{ branch})$ . The differences between the  ${}^rQ_0$  branch maxima of any two vibronic bands in a progression gave the ground state vibrational interval directly, without the need for corrections due to  $K_a$  subband structure. In DSnBr, where the LIF subbands were often broad and badly overlapped, the  ${}^pQ_1$  features were identified by the unsplit emission transitions down to  $K''_a = 1$ , and these lines were used, with an approximate  $(A-\overline{B})''$  correction.

As shown by the examples in Fig. 4, the spectra consist primarily of an extensive bending  $(v''_2)$  progression with weaker features involving Sn–H  $(v''_1)$  and Sn–Br  $(v''_3)$  stretches. The emission spectra were quite intense, with excellent signal-to-noise ratios, so even very weak bands were readily measured and identified. The DSnBr  $1_0^1$ band emission spectrum (Fig. 4) was especially helpful as it included transitions down to  $1_1$ ,  $1_2$ ,  $1_3$  and the  $1_22_n$  and  $1_32_n$  progressions. As a result, a rather complete and regular set of ground state levels of both isotopologues have been measured, as summarized in Table II. These were fitted to the standard anharmonic expansion of the form<sup>10</sup>

$$G_0(\mathbf{v}) = \sum_{i=1}^3 \omega_i^0 \mathbf{v}_i + \sum_{i=1}^3 \sum_{j \ge i}^3 \omega_i^0 \mathbf{v}_j, \tag{1}$$

and the harmonic frequencies were calculated using the relation- ${\rm ship}^{10}$ 

$$\omega_i = \omega_i^0 - x_{ii}^0 - \sum_{j \neq i} \frac{1}{2} x_{ij}^0.$$
 (2)

The resulting constants are presented in Table III.



**FIG. 4.** Example emission spectra of HSnBr (top trace, 0–0 band,  ${}^{r}Q_{0}$  excitation) and DSnBr (bottom trace,  $1_{0}^{1}$  band,  ${}^{r}Q_{0}$  excitation). Each vibronic transition appears as a partially resolved doublet due to transitions from the upper state  $K_{a} = 1$  down to  $K_{a}^{rr} = 0$  and 2. These spectra were obtained by concatenating several CCD images, each taken with the laser fixed on the Q-branch and a static monochromator wavelength. The spectra were individually calibrated with argon emission lines and then plotted as displacement (in cm<sup>-1</sup>) from the laser line, giving a direct measure of the ground state energy of each feature in the spectrum.

TABLE II. Vibrational energy	levels and assignments from	the SVL emission spectra
of HSnBr and DSnBr (in cm-	relative to the $0_0$ level).	

## TABLE II. (Continued.)

Assignment	HSnBr	DSnBr
11	1667	1198
12	3274	2365
13		3503
21	572	410
22	1143	819
23	1712	1227
24	2279	1635
25	2842	2041
26	3405	2446
27	3963	2851
28	4520	3253
29	5074	3654
210	5624	4054
211		4453
212		4851
213		5246
214		5640
2,15		6032
216		6425
217		6815
31	244	244
32	487	484
3.	726	727
3.	720	967
3-		1206
1.2.	1667	1200
1,2,	2226	2004
1,2,	2220	2004
1123	2703	2400
1124	2802	2007
1125	3892	3200
1126	4444	3603
1127	4992	4002
1128		4399
1129		4/91
I <sub>1</sub> 2 <sub>10</sub>		5185
11211		5577
I <sub>1</sub> 2 <sub>12</sub>		5969
11213		6357
$1_{1}2_{14}$		6746
$1_2 2_1$	3821	2762
1222	4365	3159
1223	4908	3554
$1_2 2_4$	5448	3949
1225		4342
$1_2 2_6$		4733
$1_2 2_7$		5123
1321		3894
1322		4284
1323		4673
1324		5061
1325		5448
· · · ·		

Assignment	HSnBr	DSnBr
1132		1687
112131	2472	1847
$1_1 2_2 3_1$	3028	2247
$1_1 2_3 3_1$	3581	2648
$1_1 2_4 3_1$	4133	3047
$1_1 2_5 3_1$	4683	3446
112631	5228	3845
$1_1 2_7 3_1$	5772	4240
$1_1 2_8 3_1$		4635
112931		5030
$1_1 2_{10} 3_1$		5422
2131	816	655
$2_23_1$	1385	1063
2 <sub>3</sub> 3 <sub>1</sub>	1953	1469
2 <sub>4</sub> 3 <sub>1</sub>	2518	1876
2531	3080	2281
2 <sub>6</sub> 3 <sub>1</sub>	3641	2686
2 <sub>7</sub> 3 <sub>1</sub>	4199	3089
2831	4753	3490
2931	5306	3890
$2_{10}3_1$	5855	4289
21131		4687
$2_{12}3_1$		5083
2 <sub>13</sub> 3 <sub>1</sub>		5477
$2_{14}3_1$		5871
21531		6263
2 <sub>16</sub> 3 <sub>1</sub>		6651
2132	1057	898
2 <sub>2</sub> 3 <sub>2</sub>	1626	1304
2332	2190	1710
2 <sub>4</sub> 3 <sub>2</sub>	2754	2116
2 <sub>5</sub> 3 <sub>2</sub>	3315	2520
2 <sub>6</sub> 3 <sub>2</sub>	3874	2923
2 <sub>7</sub> 3 <sub>2</sub>		3324
2832		3725
2932		4125
$2_{10}3_2$		4523
21132		4918
2133		1138
$2_23_3$		1546
2333		1952
2433		2356
2533		2757
2 <sub>8</sub> 3 <sub>2</sub> 2 <sub>9</sub> 3 <sub>2</sub> 2 <sub>10</sub> 3 <sub>2</sub> 2 <sub>13</sub> 3 2 <sub>2</sub> 3 <sub>3</sub> 2 <sub>3</sub> 3 <sub>3</sub> 2 <sub>4</sub> 3 <sub>3</sub> 2 <sub>5</sub> 3 <sub>3</sub>		3725 4125 4523 4918 1138 1546 1952 2356 2757

#### **D.** Fluorescence lifetimes

Fluorescence lifetimes were measured by laser excitation of a variety of *Q*-branches in the observed LIF bands. Since a group of upper state levels was excited in each case, the measured lifetimes just give a general trend as a function of  $K'_a$ . In most cases, the decays were good single exponentials over 1–2 lifetimes and were found to be reproducible to about  $\pm 5$  ns, although the statistical errors of

TABLE IV Measured fluorescence lifetimes (ns) of HSnBr and DSnBr

TABLE	III. Vibrational	constants	for	the	Ñ	~	$^{1}A'$	states of HSnBr and DSnBr (in	
$cm^{-1}$ ).								,	

Constant	HSnBr	DSnBr
$\overline{\omega_1^0}$	1695.68(72)	1211.10(53)
$\omega_2^0$	574.51(12)	411.637(79)
$\omega_3^0$	245.92(56)	244.82(40)
$x_{11}^0$	-29.34(36)	-14.53(18)
$x_{22}^0$	-1.197(13)	-0.630(55)
$x_{33}^0$	-1.30(22)	-0.68(10)
$x_{12}^{0}$	-13.153(82)	-6.487(46)
$x_{13}^{0}$	1.37(49)	1.09(42)
$x_{23}^0$	-1.413(56)	-0.902(35)
$\omega_1$	1730.91	1228.34
$\omega_2$	582.99	415.96
ω3	247.24	245.40

fitting individual decays were much smaller. Some examples of the observed HSnBr fluorescence decay curves are shown in Fig. 5 and the results are summarized in Table IV. The fluorescence lifetimes of the zero-point levels are quite long (520-565 ns) with a slight discernible pattern as a function of upper state  $K_a$ . The 2<sup>1</sup> level of HSnBr shows a substantial decrease in lifetime that progresses from 450 ns for  $K'_a = 0$  to 160 ns for  $K'_a = 4$ . The 3<sup>2</sup> level of DSnBr (from the weak  $3_0^2$  hot band) has about the same lifetime as  $0^0$ , but the  $1^1$ lifetimes are much shorter, with an average value of about 190 ns and a slight trend of more rapid decays with increasing  $K'_a$ . It proved difficult to obtain reproducible lifetimes for the DSnBr  $2^1-2^3$  levels due to the broadness of the Q-branches and contamination from underlying SnBr bands  $(2_0^1 \text{ and } 2_0^3)$ . We measure the SnBr fluorescence lifetime at 20 974 cm<sup>-1</sup> as 4.38  $\pm$  0.05  $\mu$ s, so any overlap with the diatomic bands contributes a long-lived component to the HSnBr or DSnBr fluorescence decays.



**FIG. 5.** Fluorescence decay curves of HSnBr, plotted as the natural logarithm of the fluorescence intensity vs time for various upper state vibrational and  $K_a$  levels.

Upper state	Q-branch	HSnBr	Upper state	Q-branch	DSnBr
00	${}^{p}Q_{1}$	526 <sup>a</sup>	00	$^{p}Q_{2}$	525
$0^{0}$	$rQ_0$	536	$0^0$	$p_{Q_1}$	527
$0^{0}$	$rQ_1$	565	$0^0$	$rQ_1$	528
$0^{0}$	$rQ_2$	520	$0^0$	$rQ_2$	531
$2^{1}$	${}^{p}Q_{1}$	450	$0^0$	$rQ_3$	550
$2^{1}$	$^{r}Q_{1}$	205	3 <sup>2</sup>	$p_{Q_1}$	562
$2^{1}$	$^{r}Q_{2}$	215	$1^1$	$p_{Q_1}$	214
$2^{1}$	$^{r}Q_{3}$	162	$1^1$	$rQ_0$	191
			$1^1$	$rQ_1$	179
			$1^1$	$rQ_2$	175

 $^{\rm a}Estimated$  errors of all lifetimes based on reproducibility of duplicate determination are  $\pm 5$  ns.

#### **IV. DISCUSSION**

#### A. The molecular structure of HSnBr

In the absence of experimentally determinable rotational constants, we must rely on the *ab initio* structures<sup>4</sup> of HSnBr that give r''(SnH) = 1.788 Å, r''(SnBr) = 2.523 Å,  $\theta''(HSnBr) = 93.08^{\circ}$ , r'(SnH) = 1.816 Å, r'(SnBr) = 2.511 Å, and  $\theta'(HSnBr) = 113.52^{\circ}$ . These parameters are compared to the experimentally determined structures, vibrational fundamentals, and changes in geometry on electronic excitation of similar molecules in Table V. As in HSnCl,<sup>3</sup> we see that the calculated ground state SnH bond length is only slightly longer than that of SnH<sub>2</sub>  $(1.768 \text{ Å})^1$  and comparable to the ground state bond length of the SnH diatomic molecule (1.781 Å).<sup>11</sup> Although the bond length of diatomic SnBr ( $X^2\Pi$ ) does not appear to be known, a complete basis set extrapolation of coupled cluster singles, doubles, and triples included perturbatively (CCSD(T)/augccpVnZ) calculation gives 2.495 Å,<sup>12</sup> only 0.028 Å shorter than in HSnBr. The 93.0° bond angle is slightly larger than that of SnH<sub>2</sub>  $(91.0^{\circ})$  and follows the trend of decreasing calculated bond angle in HSiBr (94.5°) and HGeBr (94.1°).<sup>4</sup>

The changes in HSnBr structural parameters on  $\tilde{A}^1 A'' - \tilde{X}^1 A'$  electronic excitation follow those found experimentally for HSiBr and HGeBr (Table V), with a small decrease in the M-Br length and a 20°-23° increase in the bond angle. Perhaps the most compelling argument for the validity of the *ab initio* structures is the good agreement between calculated (*ab initio* rotational constants) and experimental HSnBr and DSnBr LIF 0–0 band contours (Fig. 2 shows this for DSnBr).

#### **B.** Vibrational analysis

The vibrational fundamentals of various molecules are compared to those of HSnBr/DSnBr in Table V. The Sn–H/Sn–D stretches of SnH, SnH<sub>2</sub>/SnD<sub>2</sub>, and HSnBr/DSnBr differ by only a few percent, and the Sn–Br stretches of the diatomic and polyatomic molecules are very similar. The validity of our experimentally derived harmonic frequencies can also be tested with the Teller–Redlich product rule<sup>10</sup>

	Ground state	properties		
	HSnBr/DSnBr	SnH <sub>2</sub> /SnD <sub>2</sub>	SnH	SnBr
r(SnH) Å	1.788	1.768	1.78	
$v_1$ (SnH str) cm <sup>-1</sup>	1667/1198 [1677/1206]	1679/1204	1715	
r(SnBr) Å	2.523			2.495
$v_3$ (SnBr str) cm <sup>-1</sup>	244/244 [256/254]			254
$\theta$ (HSnBr) <sup>°</sup>	93.1	91.0		
$v_2$ (bend) cm <sup>-1</sup>	572/410 [612/440]	770/549		
References	This work and Ref. 4	1	11	12
	Structural changes on e	lectronic excitation		
	HSnBr	HGeBr	HSiBr	SnH <sub>2</sub>
Δr(MH) Å	[0.028]	0.002	-0.021	-0.039
∆r(MBr) Å	[-0.012]	-0.018	-0.029	
$\Delta \theta (HMBr)^{\circ}$	[20.4]	22.2	23.0	31.9
References	4	4	4	1

TABLE V. Comparison of ground state geometry,	vibrational fundamentals	(ab initio values in square	e brackets), and changes
in structure on electronic excitation of related mol	ecules.		

$$\frac{\omega_1^* \omega_2^* \omega_3^*}{\omega_1 \omega_2 \omega_3} = \sqrt{\left(\frac{C}{C^*}\right) \left(\frac{M^*}{M}\right)^2 \left(\frac{m_H}{m_D}\right)^2},\tag{3}$$

where an asterisk denotes DSnBr, the  $\omega$ 's are the *harmonic* frequencies, *C* is the rotational constant for the largest moment of inertia, *M* is the total molecular mass, and  $m_H$  and  $m_D$  are the masses of the hydrogen and deuterium atoms, respectively. Using the *ab initio* rotational constants and the masses of the <sup>120</sup>Sn and <sup>79</sup>Br isotopes, the RHS mass ratio gives 0.5076 and the LHS frequency ratio gives 0.5025. Given that the experimental frequencies include contributions from the various Sn and Br isotopes, the agreement is reasonable.

We have used the *ab initio* geometry and experimentally derived harmonic vibrational frequencies (Table III) to obtain a ground state harmonic force field for  $H^{120}Sn^{79}Br$ . The normal coordinate analysis was set up using internal coordinates and the force constants were refined using the ASYM20PC program of Hedberg and Mills.<sup>13</sup> The results are summarized in Table VI. Only the three diagonal force constants were determinable, but these reproduce the harmonic frequencies of HSnBr and DSnBr to well within their estimated errors of 1.0 cm<sup>-1</sup>. Since the experimental frequencies are actually averages over the natural abundances of all ten isotopes of tin and two of bromine and the input geometry was necessarily derived from theory rather than experiment, the results must be treated with some degree of caution.

Franck–Condon simulations of the emission spectra, based solely on *ab initio* values of the ground and excited state geometries, vibrational frequencies, and mass-weighted Cartesian displacement coordinates, showed good agreement with experiment, similar to the results for DSnCl (Ref. 3, Fig. 5). The correspondence of theory and

experiment provides further proof that the observed spectra are due to the new transient HSnBr/DSnBr molecules.

#### C. Comparison with ab initio predictions

The *ab initio* study of Tarroni and Clouthier<sup>4</sup> predicted that the LIF spectrum of HSnBr would be limited by the dissociation to form H + SnBr in the excited state. This is, in fact, the case that is shown by the attenuated extent of the spectra, terminating at  $2_0^1$  (317 cm<sup>-1</sup> above  $0_0^0$ ) for HSnBr and  $1_0^1$  (817 cm<sup>-1</sup> above  $0_0^0$ ) for DSnBr, rather smaller than the *ab initio* maximum energies<sup>4</sup> of 1366 and 1577 cm<sup>-1</sup>. The latter values provide an upper limit to the energy range of the vibrational levels in the  $\tilde{A}$  state, which are below the barrier to dissociation and, therefore, can potentially fluoresce

TABLE VI. The ground state harmonic force field of H<sup>120</sup>Sn<sup>79</sup>Br.

Value	
1.7631(14) <sup>a</sup>	
0.6316(15)	
1.7132(83)	
0.0 <sup>b</sup>	
0.0 <sup>b</sup>	
0.0 <sup>b</sup>	
	Value 1.7631(14) <sup>a</sup> 0.6316(15) 1.7132(83) 0.0 <sup>b</sup> 0.0 <sup>b</sup> 0.0 <sup>b</sup>

<sup>a</sup>Standard errors of 1 $\sigma$  are given in parentheses. The internal coordinates are R<sub>1</sub> =  $\Delta r$ (H–Sn), R<sub>2</sub> =  $\Delta \theta$ (H–Sn–Br), and R<sub>3</sub> =  $\Delta r$ (Sn–Br). The input *ab initio* geometry was r(HSn) = 1.7884 Å, r(SnCl) = 2.5225 Å, and  $\theta$ (HSnBr) = 93.082°. <sup>b</sup> Fixed in least squares refinement.

back down to the ground state. The fluorescence lifetime and holeburning experiments confirm that the higher observed excited state levels are shorter lived as they approach the predicted dissociation limit. In this sense, monobromostannylene is a barely fluorescent molecule, much like the chlorinated analog.

The experimental  $T_0$  values are lower than calculated<sup>4</sup> by 476 cm<sup>-1</sup> (HSnBr) and 468 cm<sup>-1</sup> (DSnBr) (see Table I), although the *ab initio* deuterium isotope effect of 106 cm<sup>-1</sup> agrees very well with the experimental value of 104.2 cm<sup>-1</sup>. As shown in Table V, the calculated ground state fundamental frequencies are all slightly higher than the experimental values and the agreement is very satisfactory. Similar trends are found for the experimental and *ab initio* excited state vibrational frequencies as illustrated in Table I.

#### D. Prospects for rotational analysis

If the rotational lines of all ten tin isotopes were coincident, as they are in the 0–0 band of  $SnH_2$ , it might be feasible to record and analyze rotationally resolved spectra of HSnBr and DSnBr. To test this idea, we used our Lambda-Physik etalon-equipped Scanmate dye laser (0.035 cm<sup>-1</sup> resolution) to record a segment of the LIF spectrum of DSnBr (the worst case, with the smallest rotational constants). The result is shown in the top panel of Fig. 6 where it is evident that the spectrum is insufficiently resolved to enable a line-by-line rotational analysis. In an effort to understand the effect of the various isotopologues on the spectrum, we have calculated the



**FIG. 6.** Top panel: high resolution spectrum of the  $K'_a = 1 - K''_a = 0$  subband of DSnBr showing the intense  ${}^{\prime}Q_0$  branch and lack of resolvable rotational structure in the  ${}^{\prime}P_0$  and  ${}^{\prime}R_0$  branches. Directly below the experimental spectrum is the calculated spectrum, including the  ${}^{120}$ Sn,  ${}^{118}$ Sn,  ${}^{116}$ Sn,  ${}^{79}$ Br, and  ${}^{81}$ Br isotopologues at a resolution of 0.035 cm<sup>-1</sup> and a rotational temperature of 10 K. Bottom panel: calculated spectra for D ${}^{120}$ SnBr at two different resolutions and a rotational temperature of 10 K. The top plot is for a resolution of 0.035 cm<sup>-1</sup>, typical of our etalon-narrowed Scanmate dye laser, showing the unresolved Q-branch and partially resolved P- and R-branches. The bottom plot was calculated at a resolution of 0.01 cm<sup>-1</sup> and shows the bromine isotope splitting of the Q-branch and well-resolved rotational lines in the P- and R-branches.

expected rotational structure of the 0-0 band *ab initio*, including the vibrational and rotational effects for the six isotopologues of greatest abundance ( $^{116}$ Sn = 14.54%,  $^{118}$ Sn = 24.22%, and  $^{120}$ Sn = 32.58%, each with  $^{79}$ Br = 50.69% and  $^{81}$ Br = 49.31%). This involved a density functional theory (B3LYP/aug-cc-pVTZ basis sets with effective core potential for tin) calculation of the ground and excited state rotational and vibrational constants for each isotopologue. These were combined in a simulation of the overall spectrum<sup>8,9</sup> weighted by the appropriate isotopic abundances, with the results shown in the top panel of Fig. 6. It is apparent that the simulation matches the experiment reasonably well and that the incomplete rotational resolution is due to the many isotopes in the molecules at natural abundance. The most experimentally viable option would be to use isotopically enriched <sup>120</sup>Sn in the synthesis of stannane, eliminating the complications from the ten naturally abundant isotopes of tin. In fact, it is most probably the increasing spread of lines from various isotopologues that account for the observed congestion and broadening of the higher members of the bending progression in the LIF spectrum of DSnBr (Fig. 1). The calculated spectrum of D<sup>120</sup>SnBr at  $0.035 \text{ cm}^{-1}$  (see Fig. 6, bottom panel) is still only partially resolved, but an increase in resolution to 0.01 cm<sup>-1</sup> would be sufficient to provide spectra suitable for analysis (see Fig. 6) and the prospects are even more promising for the lighter  $H^{120}SnCl$  and  $D^{120}SnCl$ molecules. We hope to be able to attempt such studies in the future.

#### **V. CONCLUSIONS**

The previously unknown molecules HSnBr and DSnBr have been detected and characterized spectroscopically. These species were prepared by reacting the products of an electric discharge through an HBr/DBr and argon mixture with SnH<sub>4</sub>/SnD<sub>4</sub> in a supersonic expansion. Both molecules exhibit attenuated LIF spectra and fluorescence lifetime measurements gave values ranging from 565–162 ns, with a general trend toward faster decays at higher rovibronic energies. Fluorescence hole-burning studies identified a few even higher vibronic levels in the excited state of HSnBr with lifetimes of 1.8–0.4 ps. All the data indicate the onset of a dissociation low down in the  $\tilde{A}^1 A''$  state, which the *ab initio* study of Tarroni and Clouthier<sup>4</sup> indicates leads to the production of hydrogen atoms and SnBr molecules.

HSnBr and DSnBr gave extensive emission spectra, which allowed the determination of the harmonic frequencies and all the anharmonicities for the three ground state vibrations. A ground state force field has been determined based on the *ab initio* molecular structure. Good agreement was found for the experimentally measured vibrational frequencies and excitation energies and previous *ab initio* predictions.<sup>4</sup>

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#### AUTHOR DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

#### **Author Contributions**

All authors contributed equally to this work.

#### DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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