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The electronic spectrum of the jet-cooled stibino (SbH₂) free radical

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ABSTRACT

The $\tilde{A}^2 A_1 - \tilde{X}^2 B_1$ electronic transition of the jet-cooled stibino (SbH₂ and SbD₂) free radical has been observed for the first time using laser induced fluorescence (LIF) detection. The radicals were produced by a pulsed electric discharge through a mixture of stibine (SbH₃ or SbD₃) in high pressure argon at the exit of a pulsed molecular beam valve. SbH₂ exhibits only three LIF bands, assigned as 2_1^0 , 0_0^0 , and 2_0^1 , with a fluorescence lifetime (τ), which decreases from ~50 ns for 0^0 to <10 ns for 2^1 . LIF transitions to the 0^0 ($\tau \sim 2 \mu$ s), 2^1 ($\tau \sim 400$ ns), and 2^2 ($\tau \sim 75$ ns) upper vibronic states of SbD₂ were also observed. High-resolution spectra exhibited large spin-rotation splittings and small resolved antimony hyperfine splittings due to a substantial Fermi contact interaction in the excited state. The experimentally determined rotational constants gave effective molecular structures of $r_0'' = 1.724(2)$ Å, $\theta_0'' = 90.38(7)^\circ$ and $r_0' = 1.693(6)$ Å, $\theta_0' = 120.6(3)^\circ$. The ground state bending vibrational levels up to eight quanta (6404 cm⁻¹) in SbH₂ and 12 quanta (6853 cm⁻¹) in SbD₂ were measured from dispersed fluorescence spectra. All indications are that SbH₂ undergoes a dissociative process at low vibrational energies in the excited electronic state.

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I. INTRODUCTION

Indium antimonide (InSb) is a crystalline narrow bandgap (0.23 eV at 80 K) semiconductor material used extensively in infrared detectors. Researchers have endeavored to use stibine (SbH₃) in the chemical vapor deposition growth of antimonide thin films and have shown that SbD₃ has suitable characteristics for carbon-free Sb deposition at temperatures below $300 \,^{\circ}C$.¹ Sugiura *et al.*² have also found that InSb can be grown by Metal-Organic Chemical Vapor Deposition (MOCVD) using triethylindium and stibine precursors at temperatures between 300 and 400 $^{\circ}C$. In such CVD processes, stibine is degraded to antimony atoms with the likely intermediacy of the SbH and SbH₂ reactive species.

Although diatomic SbH is well known, there is little information about triatomic SbH₂. In 1968, Basco and Yee³ reported new spectra attributed to SbH and SbH₂ obtained by flash photolysis of stibine. Seven blue degraded bands with prominent Q-heads, a very complex rotational structure, and a vibrational interval of ~698 cm⁻¹ were tentatively assigned as a progression involving the upper state bending vibration of the SbH₂ free radical. The 0-0 band was identified at 5143.1 Å (19 438 cm⁻¹). In 1986, Ni and coworkers⁴ reported emission spectra obtained by ArF laser photolysis of stibine (a few mTorr in a slow gas flow). They found a complicated spectrum between 480 nm and 530 nm, which they assigned to SbH₂ ($\tilde{A}^2A_1 - \tilde{X}^2B_1$). The radiative lifetime of SbH₂ at a stibine pressure of 22 mTorr was measured as 70 ± 20 ns. No further analysis was possible as the spectra were vibrationally hot and very congested.

In 2003, Wang, Souter, and Andrews⁵ reported the infrared spectra of antimony and bismuth hydrides in cryogenic matrices obtained by reacting hydrogen with laser-ablated metal atoms. SbH₂ (SbD₂) was detected with $v_1 = 1869.0$ (1341.8) cm⁻¹ and $v_3 = 1863.7$ (1337.6) cm⁻¹ in solid argon. The assignments were supported by theoretical (B3LYP/6-311++G^{**}) calculations of the $C_{2\nu}$ structure and vibrational frequencies, which also predicted an

 SbH_2 ground state bending frequency of 876 cm⁻¹. No further experimental information is available for SbH_2 .

In 2016, Ostojić *et al.*⁶ published a very detailed *ab initio* study of the ground and excited state rovibronic levels of the stibino free radical including Renner–Teller and spin–orbit coupling effects. As discussed by the authors, the ground and first excited states are components of a ${}^{2}\Pi_{u}$ state at linearity. In the $\tilde{X}^{2}B_{1}$ state, SbH₂ was found to have an equilibrium bond length of 1.719 Å and a bond angle of 90.5°, while in the $\tilde{A}^{2}A_{1}$ state, the equilibrium geometry was 1.681 Å and 121.3°. The band origin of 121 SbH₂ was calculated to be 19 459.840 cm⁻¹, in very good agreement with the Basco and Yee³ value of 19 438 cm⁻¹, and the calculations indicated a spectrum with a long Franck–Condon (FC) profile in the upper state bending mode. The authors included very detailed tables of their calculated rovibronic term values for the ground and excited states of 121 SbH₂, 121 SbH₂, and 121 SbHD.

In the present work, we have succeeded in producing jetcooled SbH_2 and SbD_2 by an electric discharge through a stibine/argon mixture. The free radicals have been detected by laser-induced fluorescence (LIF) and the resulting spectra have been rotationally analyzed to provide molecular constants for both states, which allowed the determination of the molecular geometries. Emission spectra have also been obtained and these have been used to establish the ground state vibrational frequencies in the gas phase.

II. EXPERIMENT

The SbH₂ reactive intermediate was generated by seeding the vapor of stibine (SbH₃ or SbD₃), cooled with a cold finger chiller (Neslab CC-100) to -84 °C (vapor pressure ~18 Torr), into high pressure argon (40–60 psi) and subjecting pulses of this gas mixture to an electric discharge. As described in detail elsewhere,^{7,8} a pulsed molecular beam valve (General Valve, series 9) injected the precursor mixture into a flow channel where an electric discharge between two stainless steel ring electrodes fragmented the precursor, producing the species of interest and a variety of other products. The reactive intermediates were rotationally and vibrationally cooled by free jet expansion into vacuum at the exit of the pulsed discharge apparatus. A 1.0 cm long reheat tube⁹ added to the end of the discharge apparatus increased the production of the stibino radicals and suppressed the background glow from excited argon atoms.

Low resolution (3–5 cm⁻¹) survey LIF spectra were recorded using a tunable optical parametric oscillator (OPO) pumped with the 355 nm output of a tripled neodymium:yttrium aluminum garnet (Nd:YAG) laser. The fluorescence was collected by a lens, focused through appropriate longwave pass filters, and onto the photocathode of a photomultiplier tube (RCA C31034A). The spectra were calibrated with optogalvanic lines from various argon- and neon-filled hollow cathode lamps. The laser-induced fluorescence and calibration spectra were digitized and recorded simultaneously on a homebuilt computerized data acquisition system. Higher-resolution, fully rotationally resolved spectra were recorded using a YAG pumped dye laser (Lumonics HD-500 0.05 cm⁻¹ FWHM) excitation source.

For emission spectroscopy, single rotational lines in the LIF spectrum were excited by the OPO or dye laser, and the resulting fluorescence was imaged with f/4 optics onto the entrance slit of a 0.5 m scanning monochromator (Spex 500M). The pulsed fluorescence signals were detected with a gated CCD camera (Andor iStar 320T) and recorded digitally. The emission spectra were calibrated to an estimated accuracy of ± 1 cm⁻¹ using emission lines from an argon filled hollow cathode lamp. A 1200 line/mm grating blazed at 750 nm was employed in this work, which gave a bandpass of 29.9 nm with an 18 mm effective active area on the CCD.

Stibine is a gas at room temperature (bp = -18 °C and $mp = -88 \degree C$) that has been reported to be unstable even at temperatures as low as -65 °C. Todd *et al.*¹ have published a high yield (77%) synthetic method, which involved the low-temperature $(-30 \degree C)$ reaction of SbCl3 with LiAlH4 in tetraethylene glycol dimethyl ether (tetraglyme). In our inexpert hands, this method gave very poor yields of stibine, so we resorted to a slight variation which we had previously found successful in producing stannane (SbH₄),¹⁰ a similarly unstable compound. LiAlH₄ or LiAlD₄ (2-3 g) was added to 250-300 mL of anhydrous diethylene glycol dimethyl ether (diglyme, Sigma-Aldrich 99.5%) in a 500 mL, 3-necked round bottom flask, equipped with a magnetic stirrer, a jacketed addition funnel, a cold finger condenser, and a thermocouple temperature monitor. The appropriate quantity of SbCl3 (Sigma-Aldrich ACS reagent >99%) was dissolved in 50 mL of anhydrous diglyme and contained in the addition funnel. The SbCl₃ solution was degassed by pumping and backfilling with 1 atm of argon. The reaction vessel was similarly degassed by pumping through two efficient liquid nitrogen cooled traps. Subsequently, the reaction vessel, addition funnel, and cold finger condenser were cooled to -30 °C (dry ice/methanol). With the system under dynamic vacuum, the SbCl₃ solution was added dropwise to the reaction flask, with rapid stirring, over a period of 1 h. Immediately, the pressure in the vacuum system rose to 1-2 Torr due to the formation of hydrogen from the decomposition of stibine, and the solution turned black from the liberation of antimony. The stibine that survived the reaction environment was frozen in the liquid nitrogen trap. After the addition was complete, the solution in the flask was slowly warmed to room temperature over a period of 1-2 h. The product (an estimated yield of ~1 mL) was transferred in vacuum to a container for storage and use. The identity and purity of the synthesized SbH₃ and SbD₃ were established by gas phase IR spectroscopy.

The compound was stored in a Pyrex U-tube cooled to $-92 \,^{\circ}$ C in a recirculating methanol bath (SP Scientific Vapor Trap VT490). Despite never warming the stibine above $-80 \,^{\circ}$ C, over time a thin film of metallic antimony deposited on the inside of the U-tube, indicating slow decomposition even at these very low temperatures. One mL of liquid stibine sufficed for all the experiments reported herein.

III. RESULTS AND ANALYSIS

A. Low-resolution LIF spectra

The stibino free radical from theory is expected to be of $C_{2\nu}$ symmetry with three vibrations conventionally labeled v_1 (a_1): symmetric Sb–H stretch, v_2 (a_1): HSbH bend, and v_3 (b_2): asymmetric Sb–H stretch. Molecular orbital theory predicts that the ground (${}^{2}B_{1}$) and first excited (${}^{2}A_{1}$) electronic states are components of what

would be the $1^2 \Pi_u$ state at linearity. Antimony has two naturally occurring isotopes ¹²¹Sb (57.21%) and ¹²³Sb (42.79%).

Our initial experiments on the SbH₃ precursor focused on the region identified by Basco and Yee³ as the 0-0 band of SbH₂ around 19 438 cm⁻¹. We immediately observed a variety of compact bands with a long $(4-6 \mu s)$ fluorescence lifetime, which were readily assigned as members of the *B*-*X* band system of Sb₂.¹¹ In addition, we noted some features with a very short lifetime (~50 ns) in the 19 400–19 575 cm⁻¹ region that were consistent with what little was known about SbH2. A long survey scan showed only three bands, as illustrated in Fig. 1. The central, strong feature we assign as the 0-0 band, with the 2_1^0 hot band ~820 cm⁻¹ to lower wavenumbers (predicted $v_2'' = 805$ cm⁻¹).⁶ To the blue, only a single, weak band some 690 cm^{-1} above the 0-0 band was observed with a very short fluorescence lifetime, approximately within the duration of the laser pulse (<10 ns). The correspondence with the vibrational interval observed by Basco and Yee³ ($\overline{698}$ cm⁻¹) and the predicted upper state bending frequency (696.5 cm⁻¹)⁶ leads to the assignment of this band as 2_0^1 . The limited number of observed vibronic bands in the LIF spectrum and rapidly decreasing fluorescence lifetimes indicate that a nonradiative, possibly dissociative, process opens at low energies in the upper state.

Theorizing that SbD₂, with lower upper-state vibrational frequencies, would be likely to exhibit more bands in its spectrum, we synthesized SbD₃ and repeated the experiment. The observed spectrum at moderate resolution ($\sim 3 \text{ cm}^{-1}$) is shown in the lower section of Fig. 1. In addition to a plethora of Sb₂ bands, which show up as closely spaced isotopic triplets (see Fig. 1, inset), we found several SbD₂ bands in the 19 350–21 100 cm⁻¹ region. The strongest features between 19 450 and 19 550 cm⁻¹ had the longest lifetime, estimated from oscilloscope traces to be $\sim 2 \mu s$, with steadily decreasing lifetimes for the higher bands. The three strongest bands, with an obvious interval of $\sim 490 \text{ cm}^{-1}$ (theory = 485 cm⁻¹),⁶ we assign as $0_0^0, 2_0^1$, and 2_0^2 , with hot bands 2_1^1 and 2_1^2 giving a ground state bending frequency of ~586 cm⁻¹ (predicted 573 cm⁻¹).⁶ With bands that are so spread out (100–125 cm⁻¹), consisting of a large number of rotational lines, the only way to get reasonable vibrational intervals is to identify a repeat feature (band head, *Q*-branch, etc.) in each band, which can be used as the "band center." In the present case, our rotational analysis showed that the ${}^rR_0(0)$ line between the J = 0.5 spin components in both states was readily assigned as it occurs in a gap near the middle of the spectrum. This is the value we have measured for each band in the low-resolution spectra of SbH₂ and SbD₂, as summarized in Table I.

B. Medium-resolution rotationally resolved spectra

We have recorded the 0_0^0 and 2_0^1 bands of SbH₂ at a laser step size of 0.05 cm⁻¹, giving measured linewidths of ≤ 0.1 cm⁻¹. The laser resolution is higher than this, and the widths can be attributed to unresolved Sb isotope and hyperfine and spin splittings. An example spectrum illustrating the rotational structure of the 0-0 band of SbH₂ is shown in Fig. 2. At first glance, this spectrum does not appear to have recognizable branch structure, although the low wavenumber end has some regular features that look like they might be Qbranches. The notation we shall use to label the rotational levels is $N_{Ka,Kc}$, J, and F, where N is the rotational angular momentum quantum number, K_a and K_c are the usual asymmetric top labels, and $J = N \pm S$ (S = electron spin quantum number of 1/2) is the quantum number for the total angular momentum including electron spin but excluding the nuclear spin. Conventionally, a state with J = N + 1/2 is labeled F_1 and J = N - 1/2 is F_2 . Finally, in cases where nuclear hyperfine effects are evident, we cite the total angular momentum quantum number, including the nuclear spin, as F = J + I, J + I - 1,... |J - F|. The isotopes ¹²¹Sb and ¹²³Sb have nuclear spin quantum numbers I = 5/2 and 7/2, respectively.



FIG. 1. Low resolution LIF spectra of SbH₂ (top) and SbD₂ (bottom). The inset shows a representative band of Sb₂ in more detail. The asterisks in the bottom spectrum identify Sb₂ bands whose intensity is strongly dependent on the discharge conditions.

TABLE I. Assignments, ${}^{r}R_{0}(0)$ transition frequency (cm	¹), and approximate fluorescence lifetimes (τ) of the observed
bands ^a in the medium resolution LIF spectra of SbH ₂ and S	bD ₂ .

	Sbl	H_2		Sb	D_2
Assign.	$rR_0(0)^{b}$	Comment	Assign.	$rR_0(0)^{\mathrm{b}}$	Comment
$\overline{2_{1}^{0}}$	18 634.0	$v_2'' = 819.4$	2_{1}^{1}	19 372.4	$v_2'' = 586.5$
0_{0}^{0}	19 453.4	$\tau \approx 50 \text{ ns}$	0_{0}^{0}	19 465.5	$\tau \approx 2 \ \mu s$
2_0^1	20 142.7	$v_2' = 707.3, \tau < 10 \text{ ns}$	2_{1}^{2}	19865.2	$2_0^2 - 2_1^2 = 586.3$
			2_{0}^{1}	19958.9	$\nu_2' = 493.4, \tau \approx 400 \text{ ns}$
			2_0^2	20 451.5	2_0^1 + 492.6, $\tau \approx 75$ ns

^aThere are a small number of very weak, unassigned fragments of bands, often obscured by stronger features of Sb_2 , throughout the SbD_2 spectrum.

^bThe rotational transition including the spin is (*N*_{Ka,Kc}, *J*), which is 1_{1,0}, 0.5–0_{0,0}, 0.5.

Symmetry considerations indicate that the transition must obey *c*-type rotational selection rules ($\Delta K_a = \pm 1, \pm 3$ and $\Delta K_c = 0, \pm 2$) and that the nuclear statistical weights for the $\widetilde{X}^2 B_1$ electronic state with the *b*-axis as the C_2 symmetry axis and two equivalent hydrogen atoms should follow the $K_a K_c$ parities as ee = 3, eo = 1, oo = 3, and oe = 1. This indicates that the central, presumably strong (due to the low rotational temperature), ${}^r R_0$ branch should have alternating intensities, with ${}^r R_0(0)$ strong (the lower state is $0_{0,0}$ with parity ee), ${}^r R_0(1)$ weaker (the lower state is $1_{0,1}$), etc.

A calculation of the ground state rotational constants from the *ab initio* structure⁶ (r = 1.719 Å and $\theta = 90.5^{\circ}$) gives A'' = 5.806, B'' = 5.6116, and C'' = 2.8535 cm⁻¹, making SbH₂ a near-oblate asymmetric top. Investigation of the ground state energetics showed that levels with N > 3 have little population at our typical rotational



FIG. 2. The medium resolution LIF spectrum of SbH₂ (labeled Experiment) showing the rotational structure of the 0-0 band. The bottom downgoing trace is the spectrum calculated using the constants from Table II with a linewidth of 0.1 cm⁻¹ and a rotational temperature of 20 K. Intensity differences in the experimental and simulated spectra can be ascribed to discharge instabilities and variations in laser power throughout the scan.

temperatures of ~20 K, so the branches are liable to be quite short. The theoretical excited state structure⁶ (r = 1.681 Å and $\theta = 121.3^{\circ}$) yields A' = 12.5251, B' = 3.8956, and C' = 2.9714 cm⁻¹, a near-prolate asymmetric top. Expecting from our previous work on AsH₂ that the spin-rotation splittings in the spectrum would be substantial,¹² we next estimated the major ε_{aa} spin-rotation constant (often abbreviated as the "spin constant") based on the following pure precession relationship:¹³

$$\varepsilon_{aa} \approx \frac{\pm 4A\zeta_{5p}}{\Delta E},$$
(1)

where A is the rotational constant, ζ_{5p} is the spin-orbit coupling constant of the Sb atom (2593 cm⁻¹),¹⁴ ΔE is the vertical excitation energy (taken as the calculated Q-branch head of the 2_0^6 band = 23540 cm⁻¹)⁶, and the \pm signs are for the excited and ground states, respectively. These yield $\varepsilon''_{aa} = -2.6$ and $\varepsilon'_a = +5.5$ cm⁻¹. Using these constants and a rotational temperature of 15 K, we simulated the spectrum using the PGOPHER program,^{15,16} which gave a good starting representation of the spectrum and allowed assignments to be made immediately. By varying the rotational constants, the band origin, and ε_{aa} in both states, we obtained a reasonable fit for many lines. It soon became apparent that all three spin constants (ε_{aa} , ε_{bb} , and ε_{cc}) were required for a proper fit of the observed transitions. Our final simulation of the spectrum along with the experimental result is shown in Fig. 2.

Two further complications were noted. First, many of the weaker lines in the spectrum involve $\Delta K_a = \pm 3$ transitions, a direct consequence of the large change in the asymmetry parameter ($\kappa'' = 0.877$ and $\kappa' = -0.798$) on electronic excitation. As these involve transitions to levels with K'_a as high as 4, it was necessary to include the Δ'_K centrifugal distortion constant in the analysis. The second interesting effect is that some of the low *N* lines in the spectrum show small hyperfine splittings, as shown in Fig. 3. A similar phenomenon is found in the spectrum of AsH₂ and can be attributed to a substantial Fermi contact interaction in the excited state. The hyperfine energies are given by

$$E_{HF} = \frac{a_F}{2} [F(F+1) - I(I+1) - J(J+1)], \qquad (2)$$



FIG. 3. A small segment of the medium resolution LIF spectrum of the 0-0 band of SbH₂. The four features are the spin and hyperfine components of the $0_{0,0}-1_{1,0} {}^{p}P_{1}(1)$ rovibronic transition. The spin-rotation and hyperfine splittings are identified. The nuclear spin has been assumed to be that of ¹²¹Sb with *I* = 5/2.



FIG. 4. The central portion of the medium resolution LIF spectrum of SbD₂ (top) showing the rotational structure of the 0-0 band. The bottom trace is the spectrum calculated using the constants from Table II with a linewidth of 0.08 cm⁻¹ and a rotational temperature of 15 K. Differences in the experimental and simulated spectra can be ascribed to discharge instabilities and variations in laser power throughout the scan.

where a_F is the Fermi contact parameter. The separation of the $0_{0,0}$, 0.5 F = 3 – F = 2 levels (assuming the more abundant ¹²¹Sb I = 5/2 isotope) is $\Delta E = \frac{a_F}{2}[3(3 + 1) - 2(2 + 1)] = 0.31 \text{ cm}^{-1}$, which yields an estimate of $\sim a_F = 0.1 \text{ cm}^{-1}$, providing a good starting point for fitting the hyperfine-split lines.

With the above preliminaries in mind, we used the PGOPHER program to fit 127 SbH₂ assignments, varying 15 constants to obtain an overall standard deviation of 0.054 cm^{-1} . Care was taken to eliminate badly overlapped or blended lines from the least squares fitting. We were unable to detect any evidence of Sb isotope splittings in the SbH₂ spectrum. The ground and excited state constants are summarized in Table II. The 2_0^1 band is weaker and exhibits fewer lines, so only 31 transitions were assigned and fitted to an overall standard

deviation of 0.052 cm^{-1} , varying only 9 excited state constants, with the ground state constants fixed at the 0-0 band values, as shown in Table II.

The 0-0 band spectrum of SbD₂ was acquired with a smaller laser step size (0.02 cm^{-1}) and more averaging than that of SbH₂ as the smaller rotational constants make the line density substantially higher. The central portion of the band is shown in Fig. 4, along with our simulation from the final constants. The analysis followed the same process as outlined for SbH₂, and in the final fitting, 218 assignments were fitted with a 0.041 cm⁻¹ weighted rms standard deviation and 17 constants were determined, as summarized in Table II.

TABLE II. The molecular constants (in cm⁻¹) of SbH₂ and SbD₂.^a

$ ilde{X}^2B_1$		$ ilde{A}^2A_1$			
Parameter	SbH ₂ 0 ₀	SbD ₂ 0 ₀	SbH ₂ 0 ⁰	$SbH_2 2^1$	$SbD_2 0^0$
$\overline{T_0}$			19 440.773(12)	20 128.962(20)	19 459.185 7(76)
Α	5.8658(31)	2.951 9(41)	12.6797(40)	14.216 5(379)	6.400 9(32)
В	5.6801(38)	2.833 3(21)	3.911 5(25)	3.961 5(58)	1.9746(20)
С	2.8401(26)	1.4297(21)	2.9267(43)	2.883(12)	1.475 2(26)
Δ_K		$-0.00426(44)^{b}$	0.010 37(28)	0.039 18(780)	$0.00111(28)^{c}$
ε_{aa}	-1.917(14)	-0.9573(97)	7.137(15)	8.826(40)	3.550(11)
ε_{bb}	-0.606(19)	-0.353 9(99)	0.272(12)	0.300(22)	0.0722(83)
Ecc	0.044(12)	0.0173(79)	-0.387(17)	-0.433(29)	-0.166(11)
a_F			0.1147(66)	0.112(11)	0.1225(37)

^aThe numbers in parentheses are 1σ error limits.

^bFor SbD₂, this constant is Δ_{JK} .

^cIn addition, $\Delta_{JK} = 0.000\,94(21)$.

C. Emission spectra

Single rotational level (SRL) excitation of various lines in the 0-0 band of SbH₂ results in characteristic rotationally resolved emission bands, as shown in Fig. 5. We have chosen to record emission spectra down to levels such as $(v_1'', v_2'', v_3'') = (0, 3, 0)$ or (0, 5, 0) as they are the strongest and offered the best signal-to-noise. These are compared in Fig. 5 to the calculated emission spectra, using the constants in Table II, from the assigned upper state SRL down to all possible rotational levels in the (0, 0, 0) vibrational level of the ground state. The comparison is not exact but should be similar as the rotational and spin-rotation constants are not expected to vary substantially with vibrational excitation in the ground state.

Figure 5 illustrates two important points. First, the emission spectra from the upper states $N_{Ka,Kc}$, $J = 1_{1,0}$, 0.5, $2_{2,1}$, 2.5, and $3_{3,0}$, 2.5, are sufficiently different to provide diagnostic evidence of the validity of our rotational analysis. It is clear from these and other similar spectra that our rotational assignments must be correct. Second, the center panel in Fig. 5 shows two closely spaced transitions down to the $3_{3,1}$, 3.5 and $3_{3,2}$, 2.5 levels, which differ only by the *J* quantum number. It is clearly evident that the J = N - 1/2 or F_2 level is above the J = N + 1/2 or F_1 level, which can only be the case if the major spin constant $\varepsilon''_{aa} < 0$, as argued previously.

The overall emission spectra of SbH₂ and SbD₂ are dominated by a very long progression in the bending mode, as illustrated in Fig. 6 for SbD₂. This is exactly what is expected for a molecule that changes its bond angle from nearly 90° in the ground state to about 121° in the excited state. There is also a weak progression of bands of the type $1_1^0 2_n^0$ although the 1_1^0 band was only observed in the SbD₂ emission spectrum obtained by pumping the 2_0^1 band, and it was very weak.



FIG. 6. The emission spectrum (top) of SbD₂ obtained by laser excitation of the 1_{1,0}, 0.5–0_{0,0}, 0.5 rotational transition of the 0-0 band. The bottom trace is the calculated Franck–Condon simulation of the spectrum from B3LYP vibrational frequencies and Cartesian displacement coordinates in the strictly harmonic approximation. Although the simulation is reasonable for the bending progression, it overestimates the intensity of the $1^0_12^0_n$ progression. The inset shows the rotational structure of the 2^0_6 band.

To compare with experiment, we have performed a series of Franck–Condon (FC) calculations of the single vibronic level emission spectra of SbH₂ and SbD₂. For this purpose, we have used our own density functional theory (DFT) Gaussian 09 results¹⁷ using the Becke 3-parameter exchange and Lee–Yang–Parr correlation



FIG. 5. Single rotational level (SRL) emission spectra of SbH₂. Each panel shows the emission spectrum (top trace) obtained by laser pumping of the 0-0 band rotational transition denoted in bold at the bottom of the panel. In each case, the vibronic transition detected in emission is labeled in bold in the upper left hand corner and the lower state rotational levels ($N_{Ka,Kc}$, J) are assigned above and below the spectra. The bottom, downgoing traces are the calculated emission spectra from the pumped SRL down to the 0₀ vibrational state.

(B3LYP) hybrid functional^{18,19} (aug-cc-pVTZ basis on hydrogen, with an aug-cc-pVTZ-pp basis for the Sb atom²⁰) to perform FC simulations of the absorption and single vibronic level emission spectra in the strictly harmonic approximation. The simulation program, originally developed by Yang *et al.*²¹ 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. FC factors are then calculated using the exact recursion relationships of Doktorov *et al.*²² taking into account both the normal coordinate displacement and Duschinsky rotation effects.

As expected from theory and our FC calculations, the 0-0 band emission spectra of SbH₂ and SbD₂ are free of nodes (see Fig. 6), whereas the 2_0^1 band emission (not shown) exhibits a single node at 2_r^1 , precisely as predicted by our FC results. As is often the case in simulations of the emission spectra of MHX (M = Si, Ge and X = F, Cl, Br) molecules, whose bond angle opens substantially on electronic excitation, the bending progression is usually predicted with high fidelity, but the FC calculations overestimate the intensity of the $1_1^0 2_n^0$ bands,²³⁻²⁶ perhaps due to the neglect of anharmonicity.

In order to get the most reliable information on the ground state vibrational intervals, we have recorded a series of emission spectra by exciting the $1_{1,0}$, 0.5– $0_{0,0}$, 0.5 rovibronic transition, which

TABLE III. Vibrational levels of the $\bar{X}^2 B_1$ state of SbH₂ and SbD₂ [in cm⁻¹ relative to the lowest (v₁, v₂, v₃, $N_{Ka,Kc}$, J) = (0,0,0, 0₀₀, 1/2) level].

	SbH_2			SbD ₂	
Level	Energy	Theory ^a	Level	Energy	Theory ^a
20	0	0	20	0	0
21	820	805	21	584	573
22	1635	1628	22	1170	1160
23	2445	2462	1_1	1341	1340
2_{4}	3250	3293	23	1751	1757
25	4049	4106	$1_1 2_1$	1926	1912
1_12_3	4279	4321	2_{4}	2331	2349
26	4842	4889	1_12_2	2505	2495
1_12_4	5069	5139	25	2908	2941
27	5627	5648	$1_{1}2_{3}$	3077	3088
$1_{1}2_{5}$	5852	5938	26	3482	3529
28	6404		$1_{1}2_{4}$	3651	3676
1_12_6	6629		27	4052	4103
			$1_{1}2_{5}$	4219	4263
			28	4620	
			1_12_6	4786	
			29	5184	
			$1_{1}2_{7}$	5349	
			2_{10}	5744	
			$1_{1}2_{8}$	5910	
			211	6300	
			1129	6467	
			212	6853	

^aReference 6.

provides a direct measure of the vibrational intervals between the lowest 0_{0,0}, 0.5 rotational levels (see Fig. 5). These spectra were individually calibrated and then concatenated into a single continuous record (see Fig. 6 for SbD₂). The emission spectra were converted into displacement vs intensity by subtracting the emission wavenumber from the laser excitation wavenumber. In this fashion, the wavenumber (in cm⁻¹) of each feature in the displacement spectrum gives a direct measure of the lower state energy relative to $(v''_1, v''_2, v''_3, N_{Ka,Kc}, J) = (0,0,0, 0_{00}, 0.5)$, the lowest energy level in the ground electronic state. Although we were able to calibrate our emission spectra to better than 0.5 cm⁻¹, the emission lines were quite broad (5–7 cm⁻¹) due to unresolved hyperfine and Sb isotope effects, so the displacements were not reproducible to better than $\pm 1-2$ cm⁻¹. The results are summarized in Table III where they are also compared to the theoretical predictions of Ref. 6.

IV. DISCUSSION

A. The molecular structure of SbH₂

The rotational constants of SbH₂ and SbD₂ (Table II) were used to calculate the molecular structures of the stibino radical in the ground and excited states. Planar moments ($P_{A, B, \text{ or }C}$) rather than the raw rotational constants or moments of inertia were used for the least squares analysis to minimize correlations between the geometric parameters. Since the out-of-plane planar moment P_C must, by definition, be zero, the dataset included only P_A and P_B of each isotopologue. A slight diminution (Laurie correction²⁶) in the bond length of 0.003 Å on deuteration was included in the analysis. The resulting structures are summarized in Table IV. The ground state r_0 bond length of the SbH₂ free radical is only 0.015 Å longer than the corresponding bond length of the closed shell SbH₃ molecule.²⁷

In Table IV, we compare the geometries and changes on electronic excitation for the isoelectronic SbH₂, AsH₂, and PH₂ free radicals. In all cases, the X–H bond length of the triatomic species is very close to that of the corresponding diatomic molecule. On

TABLE IV. Comparison of the ground and excited state geometric parameters of SbH_2, AsH_2, and PH_2.

Parameter	SbH ₂ expt.	SbH ₂ theory ^a	AsH ₂ expt. ^b	PH ₂ expt. ^c
r'' (X–H) (Å) θ'' (deg)	1.724(2) 90.38(7)	1.719 90.5	1.519 90.75	1.418 90.7
r'' XH diatomic (Å) ^d	1.710		1.522	1.422
$ \begin{array}{l} r' (X-H) (Å) \\ \Delta r (X-H) (Å)^{e} \\ \theta' (deg) \\ \Delta(\theta) (deg)^{e} \end{array} $	$1.693(6) \\ -0.031 \\ 120.6(3) \\ 30.22$	$1.681 \\ -0.038 \\ 121.3 \\ 30.8$	$1.487 \\ -0.032 \\ 123.0 \\ 32.25$	$ \begin{array}{r} 1.389 \\ -0.029 \\ 123.2 \\ 32.5 \end{array} $

^aReference 6.

^bReference 35.

^cReference 36.

 $^{\rm d}{\rm SbH}\ r_e$ calculated from $B_{\rm e}$ of Ref. 37, AsH approx. r_e from Ref. 38, and PH r_e from Ref. 39.

^eChange in the geometric parameter on electronic excitation.

electronic excitation, the bond length decreases by ~0.03 Å and the bond angle increases by ~30° despite the differences in the valence shell orbitals as one goes down the group from phosphorus to antimony. It is noteworthy that exactly the same trend with almost identical changes in the geometries is found for the series SiH₂, GeH₂, and SnH₂.¹⁰

B. Rotational analysis

1. Isotope effects

The lack of any observable Sb isotope effect deserves some comment. The Sb atom is very close to the center of mass in both states, so the isotope effect would be expected to be very small. Our own B3LYP calculations of the ground and excited state structures and vibrational frequencies of ¹²¹SbH₂, ¹²³SbH₂, ¹²¹SbD₂, and ¹²³SbD₂ provided us with the necessary theoretical data. Calculation of the Sb vibrational isotope effect for the 0-0 band showed a shift of less than 0.01 cm⁻¹ in both the hydrogen and deuterium radicals. The differences in the rotational constants were typically in the 4th or 5th decimal place. PGOPHER simulations of the spectra, using the vibrational and rotational data, assuming the same spin-rotation constants for both Sb isotopologues, indicated that Sb isotope splittings would not be expected to be resolved for the typical linewidths (0.08–0.1 cm⁻¹) observed in our spectra.

2. Spin constants and T₀ values

A variety of ground and excited state molecular constants for NH₂, PH₂, AsH₂, and SnH₂ are compared in Table V. In all cases, the major spin constants ε_{aa} and ε_{bb} are negative in the ground state and positive in the excited state, in accord with expectations based on Eq. (1). In the pure precession approximation that leads to relations similar to Eq. (1), the ε_{xx} (x = a, b, or c) spin-rotation constant is proportional to the rotational constant for the moment of inertia about the *x* axis and the ratio of the spin constant to the rotational constant should be the same for the two isotopologues. For example, ε_{aa}''/A'' for SbH₂ is -0.327 and -0.324 for SbD₂, a difference of 0.9%. For SbH₂/SbD₂, the ratios for ε_{bb}'' and ε_{cc}'' are

-0.107/-0.125 and 0.015/0.012, differing by 16% and 25%, respectively. In the excited state, the percent differences of the ratios for the various spin constants range from 1% to 62%, still in reasonable agreement considering the approximations inherent in the pure precession formulation and the substantial error limits on most of the molecular constants in Table II. The larger spin constants of SbH₂ relative to PH₂ and AsH₂ are due to the much larger spin–orbit coupling constant of the Sb atom.

Table V also compares the T_0 values for the electronic excited states of PH₂, AsH₂, and SbH₂, which are found to lie in a narrow window around 19 100 ± 825 cm⁻¹. A similar trend was found for the SiH₂, GeH₂, and SnH₂ species whose 0-0 bands occur at 15 900 cm⁻¹ ± 425 cm⁻¹. In most aspects, the ground and excited states of the radicals and the corresponding closed shell molecules are remarkably similar, despite having central atoms that range from the 2nd row to the 4th row of the periodic table.

A plausible explanation for these similarities comes from a consideration of the combining electronic states. For the PH₂, AsH₂, and SbH₂ radicals, the \tilde{X}^2B_1 and \tilde{A}^2A_1 states are components of a ${}^2\Pi_u$ electronic state at linearity. The interaction with higher electronic states splits the degenerate Π state into two components with bent geometries, and the observed T_0 values measure the differences of the zero-point levels. The striking similarities in the changes in the geometry on electronic excitation and the T_0 values across the three radicals suggest that similar vibronic coupling with higher electronic states of similar energies is responsible for the observed trends.²⁸ A similar mechanism would account for the splitting of the ${}^1\Delta$ state at linearity into bent \tilde{X}^1B_1 and \tilde{A}^1A_1 states in the SiH₂, GeH₂, and SnH₂ species. *Ab initio* explorations of such vibronic coupling effects would be most welcome.

3. Hyperfine structure

In the absence of any detectable isotope effects, we have ascribed the observed hyperfine splittings to the more abundant ^{121}Sb isotope. However, ^{123}Sb has a substantial magnetic moment ($\mu_I=2.5498$ Bohr magnetons) and nuclear spin (I = 7/2) and must also contribute. Here, we calculate the effect of the ^{123}Sb Fermi

TABLE V. A comparison of various molecular constants (in cm⁻¹) of the group 15 dihydrides MH₂.^{10,35,36,40,41}

NH_2	PH_2	AsH ₂	SbH_2	SbD_2
	Grour	nd state		
23.693 053 5	9.132 437	7.549 667 5	5.8658	2.9519
-0.30876751	-0.28115	-1.1051846	-1.917	-0.9573
-0.04568177	-0.08199	-0.395023	-0.606	-0.3539
0.000 999 93	-0.00026	0.004 271 2	0.044	0.0173
0.000 936 01	0.006 915	0.001 928 8		
	Excite	ed state		
	20.401 2	17.206 5	12.6797	6.400 9
	1.178	4.7179	7.137	3.550
	0.041	0.082 61	0.272	0.0722
	-0.059	-0.2028	-0.387	-0.166
	0.05828	0.0512	0.1147	0.122 5
	18 276.59	19 909.453	19 440.773	19 459.186
	NH ₂ 23.693 053 5 -0.308 767 51 -0.045 681 77 0.000 999 93 0.000 936 01 	NH2 PH2 Grour 23.693 053 5 9.132 437 -0.308 767 51 -0.281 15 -0.045 681 77 -0.081 99 0.000 999 93 -0.000 26 0.000 936 01 0.006 915 Excite 20.401 2 1.178 0.041 0.058 28 18 276.59	NH2 PH2 AsH2 Ground state 23.693 053 5 $9.132 437$ $7.549 667 5$ $-0.308 767 51$ $-0.281 15$ $-1.105 184 6$ $-0.045 681 77$ $-0.081 99$ $-0.395 023$ $0.000 999 93$ $-0.000 26$ $0.004 271 2$ $0.000 936 01$ $0.006 915$ $0.001 928 8$ Excited state \dots $20.401 2$ $17.206 5$ \dots 1.178 $4.717 9$ \dots 0.041 $0.082 61$ \dots 0.059 $-0.202 8$ \dots $0.058 28$ $0.051 2$ \dots $18 276.59$ $19 909.453$	NH2 PH2 AsH2 SbH2 Ground state 23.693 053 5 9.132 437 7.549 667 5 5.865 8 -0.308 767 51 -0.281 15 -1.105 184 6 -1.917 -0.045 681 77 -0.081 99 -0.395 023 -0.606 0.000 999 93 -0.000 26 0.004 271 2 0.044 0.000 936 01 0.006 915 0.001 928 8 Excited state 17.206 5 12.6797 1.178 4.717 9 7.137 0.041 0.082 61 0.272 -0.059 -0.202 8 -0.387 0.058 28 0.051 2 0.114 7 18 276.59 19 909.453 19 440.773

contact interaction on the $0_{0,0}$, 0.5 excited state splitting (see Fig. 3). Neglecting higher order effects, the Fermi contact parameter a_F is given by²⁹

$$a_F(\text{cm}^{-1}) = 0.003\,186\,25\,\text{cm}^{-1}\left(\frac{\mu_I}{I}\right)\left(\frac{8\pi}{3}\right)\left(\frac{1}{2S}\right)\sum_i \langle \Psi_i^2(0) \rangle_{\text{nl}}, \quad (3)$$

where μ_I is the magnetic moment of the nucleus of interest with nuclear spin *I*, *S* is the spin quantum number of the unpaired electron, and the summation term is the total unpaired electron spin density at the nucleus. The ratio of the Fermi contact parameters for ¹²¹Sb and ¹²³Sb is then the ratio of their nuclear *g* values ($g = \mu_I/I$), yielding a_F (¹²³Sb) $\approx 0.062 \text{ cm}^{-1}$. From Eq. (2), the separation of the $0_{0,0}$, 0.5 F = 4 - F = 3 levels ($F = I + J = 7/2 \pm 1/2$ for the ¹²³Sb isotope) is $\Delta E = \frac{a_E}{2} [4(4 + 1) - 3(3 + 1)] = 0.25 \text{ cm}^{-1}$. This small difference in the hyperfine splittings would not be resolved at the resolution shown in Fig. 3 but likely accounts for the widths of the observed hyperfine lines.

The ground state molecular orbital configuration of SbH₂ is primarily $|... 12a_1^2 6b_2^2 13a_1^2 6b_1^1\rangle$, where $6b_1$ is predominantly an outof-plane 5p orbital on the Sb atom. The $13a_1$ σ -type molecular orbital is Sb-H antibonding but has substantial bonding electron density between the hydrogen centers, and $6b_2$ is a Sb-H σ -bonding orbital. Since only s orbitals can have significant electron density at the nucleus, the isotropic Fermi contact parameter a_F provides a measure of the s character of the orbital containing the unpaired electron. In the ground state, the Sb Fermi contact parameter would be expected to be very small (as in AsH₂, PH₂, and NH_2 ; see Table V) as the unpaired electron is in the $6b_1$ orbital. On $13a_1 \rightarrow 6b_1$ electronic promotion, the excited state unpaired electron occupies the $13a_1 \sigma$ -type orbital, which should have substantial 5s character and a much larger Fermi contact interaction. A comparison of the atomic Fermi contact value (35, 100 MHz)³⁰ with our excited state experimental value of 3298 MHz gives 9.4% atomic 5s character for the $13a_1$ molecular orbital, continuing the trend toward lower s character for heavier central atoms ($PH_2 = 13.1\%$ and $AsH_2 = 10.5\%$). The excited state Fermi contact parameter of SbH_2 is much larger than that of PH2 and AsH2, a direct consequence of the more than two times greater atomic Fermi contact term in SbH₂.

C. Excited state dynamics

It is of interest to compare the excited state dynamics of $\hat{A}^2 A_1$ PH₂, AsH₂, and SbH₂ (NH₂ will not be considered as it is linear in the excited state). Zero-pressure fluorescence lifetimes³¹ of PH₂ measured for groups of rotational levels from $v'_2 = 0$ to 5 show a slow monotonic decrease from 5.69 µs to 0.8 µs, with no obvious dependence on K'_a. At $v'_2 = 6$, the fluorescence lifetime drops to ~30 ns with a value of ~3 ns for $v'_2 = 7$, which the authors interpret as the evidence of the opening of a predissociation channel at about $v'_2 = 6$. In sharp contrast, He and Clouthier¹² found that the fluorescence lifetimes of jet-cooled AsH₂ varied widely with both rotational and vibrational levels, from a maximum of ~1.4 µs [$v'_2 = 0$, $3_{3,0} (F_2)$] to values less than 10 ns. The very short lifetimes occur occasionally in $v'_2 = 0$ but exclusively in $v'_2 = 2-4$. The authors concluded that the seemingly random fluctuations in the excited state fluorescence lifetimes reflected the accidental couplings of

laser-populated states with the sparse manifold of predissociation broadened \tilde{X} state rovibrational levels. In PH₂, AsH₂, and the isoelectronic H₂S⁺ species, theoretical studies along with thermodynamic and symmetry arguments suggest that the photodissociation occurs through coupling of the \tilde{A}^2A_1 rovibronic states with mixed states generated by spin–orbit coupling of isoenergetic \tilde{X}^2B_1 states with the dissociative \tilde{a}^4A_2 state, leading to the production of a ground state central atom and ground state molecular hydrogen.^{12,31}

In SbH₂, the excited-state dynamics are rather different. Although we have not performed any precise measurements, oscilloscope traces and the lack of substantial variations with the integrator gate width suggest that the fluorescence lifetimes do not vary significantly with rotational level. In addition, the excited-state bending levels beyond 2¹ do not yield detectable fluorescence. Despite a calculated absorption intensity substantially greater than the 0-0 band,⁶ the 2_0^1 band detected by LIF is quite weak. Although this anomaly may be due to the short fluorescence lifetime (~10 ns) and difficulties with detecting emission very near the time profile of the laser, we suspect that the onset of photodissociation is the major contributor. In our rotational analysis of the 2_0^1 band, we were unable to assign any transitions to $K'_a = 3$ or 4 levels, although such transitions are readily detected in the 0-0 band. The first $K'_a = 3$ level is ~120 cm⁻¹ above the lowest rotational level in 2^1 , which may be just enough energy to enable the onset of dissociation.

In SbD₂, with a lower zero-point energy, the 0⁰ level has a lifetime of about 2 μ s, which is probably the radiative lifetime, which drops rapidly to ~75 ns at 2². Comparing the zero-point (zpt) energies (from *ab initio* theory)⁶ of SbH₂ = 2017.7 cm⁻¹ and SbD₂ = 1479.2 cm⁻¹ and adding in the energy of the observed bands above zpt, we obtain the excited-state energy of the last observed fluorescent level as SbH₂ = 2725 cm⁻¹ and SbD₂ = 2465 cm⁻¹ above T_e . It is perhaps not surprising that these two numbers are very similar as the dissociation limit should be the same for both isotopologues.

Table VI shows the possible SbH₂ photodissociation products and the various enthalpies of reaction.^{32–34} It is readily apparent that the production of Sb + 2H or SbH + H is not energetically feasible from the excited state with $T_0 = 19441$ cm⁻¹.

TABLE VI. Heats of formation (0 K, kJ/mol, primarily from *ab initio* theory) and reaction enthalpies for ground state SbH₂ and possible photochemical products.

Species or reaction	$\Delta_{\rm f} {\rm H}$ (0K) (kJ/mol)
SbH ₂ (g)	211.9
SbH(g)	344.3
$H_2(g)$	0.0
H(g)	216.02
$Sb(^{4}S_{3/2})$	278.8
$Sb(^{2}D_{3/2})$	380.6
$SbH_2(g) \rightarrow SbH(g) + H(g)$	$348.4 (29124 \text{ cm}^{-1})$
$SbH_2 \rightarrow Sb(^4S_{3/2})(g) + H_2(g)$	$66.9 (5592 \text{ cm}^{-1})$
$SbH_2(g) \rightarrow Sb(^2D_{3/2})(g) + H_2(g)$	$168.7 (14102 \text{ cm}^{-1})$
$SbH_2(g) \to Sb(^4S_{3/2})(g) + 2H(g)$	498.9 (41705 cm^{-1})

Considering the spin and symmetry, the products $\text{Sb}({}^4S_{3/2})$ + $\text{H}_2({}^1\Sigma_{\text{g}}^+)$ correlate with the \tilde{a}^4A_2 excited state of SbH₂, whereas the formation of excited $\text{Sb}({}^2D_{3/2})$ + $\text{H}_2({}^1\Sigma_{\text{g}}^+)$ is allowed, and energetically feasible, from both the ground and excited states of SbH₂.

The situation is shown in Fig. 7 in which we have calculated 1-dimensional cuts through the ground and excited state potential energy surfaces by fixing the bond angle at each point and varying the bond length to minimize the energy using the Gaussian 09 CCSD method with the aug-cc-pVTZ basis set for the hydrogen atoms and the Sb aug-cc-pVTZ-pp with an effective core potential.²⁰ It is apparent that the ground state dissociation correlates with the production of $Sb(^{2}D_{3/2}) + H_{2}$ and that direct dissociation does not occur low down on the excited-state potential. We suspect that coupling to dissociative levels of the ground state occurs in the region of the 2^2 level of SbH₂, accounting for the abrupt breaking off of the fluorescence. Since the interaction is with a true dissociative continuum, the fluorescence lifetimes do not show the accidental couplings of laser-populated states with the sparse manifold of predissociation broadened \tilde{X} state rovibrational levels that is found in AsH₂.

D. Comparison to theoretical predictions

The present SbH₂ experimental data can be compared to the extensive *ab initio* calculations of Ostojić *et al.*⁶ in a variety of ways, with reference to Tables I–IV. First of all, the experimental and theoretical ground and excited state geometric parameters are in good agreement. The ground state vibrational levels (where known experimentally) are in good accord up to about 2000 cm⁻¹, but then the calculated energies of both the bending and bend-stretch combinations deviate more and more from experiment. Our vibrational data, which extend to 8 bending quanta for SbH₂ and 12 quanta for SbD₂, will provide a stringent test for future theoretical potentials. Theory predicts the band origin of ¹²¹SbH₂ to be $T_0 = 19459.84$ cm⁻¹, only 19.07 cm⁻¹ higher than experiment, which is in excellent agreement. However, the isotope shift on full deuteration is predicted



FIG. 7. Calculated bending potential energy curves for the ground and first excited electronic states of SbH₂. The relative energies of the various dissociation products are given on the RHS.

to be +45.75 cm⁻¹ rather larger than the observed +18.41 cm⁻¹ value. Of most concern are the calculated spin-rotation splittings of the $K_a = 1$ levels, which have been reported in Ref. 6 to be $F_1 > F_2$ in the ground state and the reverse in the excited state. This ordering is in direct contradiction to our experimental observations, and we suspect that it is simply a persistent tabulation error in Ref. 6.

V. CONCLUSIONS

The stibino free radical has now been conclusively identified and characterized in the gas phase. The jet-cooled SbH₂ and SbD₂ species have been studied by LIF and resolved emission techniques, and the tentative identification of the electronic spectrum in 1968 by Basco and Yee³ has been confirmed. Rotational analysis of the 0-0 bands of both isotopologues has provided rotational constants from which molecular structures of r''_0 (Sb–H) = 1.724(2) Å, θ''_0 = 90.38(7)° and r'_0 (Sb–H) = 1.693(6) Å and θ'_0 = 120.6(3)° have been derived. The changes in the geometric parameters on electronic excitation are very similar to those of the isoelectronic PH₂ and AsH₂ free radicals. A rapid diminution of the fluorescence lifetimes and an abrupt breaking off of the emission indicate that the stibino radical dissociates from low-lying vibrational levels in the excited state.

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