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Hydroxysilylene (HSi–OH) in the gas phase ⊘

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ABSTRACT

The hydroxysilylene (HSiOH) molecule has been spectroscopically identified in the gas phase for the first time. This highly reactive species was produced in a twin electric discharge jet using separate precursor streams of ${}^{16}O_2/{}^{18}O_2$ and Si_2H_6/Si_2D_6 , both diluted in high pressure argon. The strongest and most stable laser induced fluorescence (LIF) signals were obtained by applying an electric discharge to each of the precursor streams and then merging the discharge products just prior to expansion into vacuum. Bands of the $\tilde{A}^1A-\tilde{X}^1A'$ electronic transition of HSiOH were found in the 455–420 nm region, and single vibronic level emission spectra showed only transitions attributable to the *trans*-hydroxysilylene ground state isomer. High resolution, rotationally resolved spectra were obtained for the 0-0 bands of HSi¹⁶OH and HSi¹⁸OH. The rotational constants were used to obtain ground and excited state molecular structures of HSiOH, with some necessary constraints. The derived ground state structure is *trans*-HSiOH, with geometric parameters similar to theoretical predictions from the literature. In the excited state, a *skew*-HSiOH structure was obtained with a dihedral angle of 102°. Our own CASSCF/aug-cc-pVTZ calculations predict a similar excited state *skew* geometry. The lack of odd quantum number changes in the torsional mode in emission and our difficulties in obtaining DSiOD spectra, despite considerable effort, all suggest that further experimental and theoretical efforts will be necessary to thoroughly understand the electronic spectrum of hydroxysilylene.

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I. INTRODUCTION

Three isomers of the general formula SiOH₂ have been identified both theoretically and experimentally, with the structures shown in Fig. 1. All three isomers are found theoretically to have similar energies, with $H_2SiO \le cis$ -HSiOH $\le trans$ -HSiOH. Silanone (H_2Si = O), a molecule of $C_{2\nu}$ symmetry, was first detected in matrices,¹ and the microwave spectrum has been thoroughly explored.² Although many silylenes (HSiX; X = H, F, Cl, Br, I) have been identified and characterized,⁴ gas phase hydroxysilylene (HSi-OH) has so far escaped detection by microwave, infrared, or UV-visible spectroscopy. However, this elusive species has been previously detected by mass spectrometry and in matrix isolation studies. In 1982, Margrave and co-workers⁵ reported the infrared spectra of the cis- and trans-HSiOH species prepared by the reaction of silicon atoms with water and concluded that the cis-isomer appeared to convert to the more stable trans-isomer upon annealing. In 1985, Withnall and Andrews¹ showed that HSiOH could be prepared in high yield by the reaction of SiH4 with oxygen atoms and

trapped in an argon matrix. In 1991, Schwarz and co-workers⁶ used neutralization-reionization mass spectrometry to show that H₂SiO, HSiOH, H₂SiOH, and H₃SiO could all be prepared in the gas phase and were stable during the microsecond transit time in the instrument. The O + SiH₄ reaction has been investigated by the crossedbeam method, and H₂SiOH, HSiOH, and SiOH have been suggested as the primary products.⁷ A similar subsequent study⁸ indicated that there are multiple dynamical pathways in this complicated reaction.

The SiOH₂ isomers have been studied theoretically by a variety of groups at levels of theory ranging from self-consistent-field to coupled-cluster methods.^{9–20} In a very thorough investigation, Martin¹⁸ has calculated the vibrational fundamentals and anharmonicities and reassigned the matrix infrared spectra of HSiOH to the *cis*-isomer based on his high level *ab initio* results and a previous reassignment by Ma and Schaefer.¹⁵ In some of the most recent and detailed calculations, Koput *et al.* have calculated the ground state vibration-rotation levels of silanone¹⁹ and the equilibrium structure and relative energies of the *cis*- and *trans*-hydroxysilylene isomers.²⁰



FIG. 1. Sketches of the geometric structures of silanone $(C_{2\nu})$, *cis*- and *trans*-hydroxysilylene (C_s) , and excited state *skew*-HSiOH (C_1) .

At 0 K, the *cis*-isomer was predicted to be more stable than the *trans*-isomer by as little as 0.04 ± 0.03 kcal/mol. The best available hydroxysilylene structural parameters and vibrational frequencies are summarized in Table I.

Although hydroxysilylene is known to be a product of the reactions of silanes with oxygen and water, it is puzzling that it was not detected in microwave experiments that readily detected silanone.^{2,3} In recent Fourier transform microwave work,²¹ the *cis*-and *trans*-isomers of dihydroxysilylene, HOSiOH, and the higher energy dioxasilirane c-H₂SiO₂ were abundantly produced by an electrical discharge through a dilute SiH₄/O₂ mixture, and one would expect that HSiOH would be generated under similar conditions. However, the microwave search was guided by *ab initio* predictions of the properties of the expected products and likely did not pursue the hydroxysilylene species.

With hydrogen, oxygen, and silicon being the first, third, and seventh most abundant elements in the universe, it is not surprising that Si–H–O species are of continuing interest as possible interstellar molecules. SiH₄ and SiO have been positively identified^{22,23} in

space, but no $H_x Si_y O_z$ species have been reported to date. With a predicted dipole moment of ~4 Debye, silanone¹⁵ has been suggested as a good radio astronomy candidate,²⁴ but no detections have been published. The hydroxysilylenes have rather smaller dipole moments¹⁵ than silanone with $\mu_B \sim 1.1(trans)-1.5$ (*cis*) D and $\mu_A \sim 0.4$ D, which is perhaps why they have not yet been detected by microwave spectroscopy.

Of course, Si–H–O molecules are also potentially important in combustion and chemical vapor deposition (CVD) processes. For example, the O(³P) reaction with SiH₄ has been extensively studied,^{25,26} and silanone has been predicted as a precursor in the deposition of silicon dioxide films produced by the CVD techniques.²⁷ Silane oxidation also often leads to the formation of silica and silica composites, although the mechanisms of such processes are poorly understood.^{14,16}

In the present work, we set out to study the laser induced fluorescence (LIF) spectra of species produced by the reactions of discharged oxygen and silanes in a supersonic expansion. The spectrum of hydroxysilylene has been identified based on the rotational structure of the LIF bands and on the frequencies of the vibrational fundamentals in the single vibronic level emission spectra of $\mathrm{HSi}^{16}\mathrm{OH}$ and $\mathrm{DSi}^{16}\mathrm{OD}$.

II. EXPERIMENT

As the potential silicon hydride precursors silane (SiH₄) and disilane (Si₂H₆) are pyrophoric, we elected to use the twin jet technique, described in detail elsewhere,²⁸ in our attempts to produce hydroxysilylene in the gas phase. Briefly, this apparatus involves two pulsed valves (General Valve, series 9), each of which injects a precursor mixed with high pressure argon into a Delrin flow channel where an electric discharge between two stainless steel ring electrodes fragments the precursor. After the discharges, the flow

TABLE I. *Ab initio* values for the geometric parameters (Ref. 15) and vibrational fundamentals (Ref. 18, reassigned expt'l matrix values in parentheses) of ground state *cis*- and *trans*-hydroxysilylene (HSi¹⁶OH) and excited state *skew*-HSiOH (this work).

	Ground s	tate	Excited state s	kew-HSiOH
	cis	trans	CASSCF/pVTZ	CASSCF/pVQZ
r_e (SiO) Å	1.658	1.662	1.639	1.632
r_e (HSi) Å	1.536	1.521	1.566	1.560
r _e (OH) Å	0.957	0.958	0.940	0.939
θ_e (HSiO)°	98.0	94.8	116.95	117.0
θ_e (SiOH)°	118.2	114.3	120.1	120.6
θ_e (HSiOH)°	0	0	96.8	96.8
$T_0 ({\rm cm}^{-1})$	0	14	22 632	22 662
v_1 (a') (OH str.)	3676 (3677)	3673	4173[4159][3039] ^a	4178
v_2 (a') (SiH str.)	1891 (1882)	1950	1603[1603][1157]	1622
v_3 (a') (HSiO bend)	939 (938)	930	598[597][448]	606
v ₄ (a') (SiO str.)	841 (847)	837	939[921][908]	945
v_5 (a') (SiOH bend)	727 (723)	788	863[845][651]	854
v_6 (a") (torsion)	600 (596)	633	391[389][287]	387

^aExcited state vibrational freqs. of HSi¹⁶OH, [HSi¹⁸OH], and [DSi¹⁶OD].

channels are merged, allowing reactions to occur, and the mixture is expanded into a vacuum. In the present instance, a mixture of 75–100 Torr of disilane in 500–800 psi of argon passed through a pressure regulator at a delivery pressure of 110 psi through valve No. 1. An oxidizer mixture of 40 psi of oxygen in 800 psi of argon was delivered to valve No. 2 at a regulator pressure of 85 psi. The most stable and strongest LIF signals were obtained with modest electric discharges applied to both gas streams.

The merged jet-cooled discharge products were probed with the pulsed laser beam of either a broadly tunable optical parametric oscillator (Continuum Horizon OPO, 400–710 nm, linewidth $3-7 \text{ cm}^{-1}$, energy 10–50 mJ/pulse), a moderate resolution (0.1 cm⁻¹) neodymium: yttrium aluminum garnet (Nd:YAG) pumped dye laser (Lumonics HD-500), or a higher resolution narrow band (0.035 cm⁻¹) dye laser (Lambda-Physik Scanmate) as the excitation source. In each case, any resulting laser induced fluorescence (LIF) was imaged through appropriate long pass optical filters onto the photocathode of a red sensitive photomultiplier (RCA C31034A PMT).

Moderate resolution survey LIF spectra were calibrated with optogalvanic lines from a neon-filled hollow cathode lamp to an estimated absolute accuracy of 0.1 cm⁻¹. Absolute wavelength calibration of the high-resolution dye laser (± 0.003 cm⁻¹) was accomplished by simultaneously recording lines in the absorption spectrum of 130 Te₂ whose wavenumbers have been reliably measured.²⁹

Single vibronic level emission spectra were obtained by exciting a previously measured LIF band maximum with one of the lasers, and the resulting fluorescence was imaged with f/4 optics onto the entrance slit of a 0.5 m scanning monochromator (Spex 500M). These 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 holographic grating blazed at 400 nm was employed in this work, which gave a bandpass of 29.9 nm with an 18 mm effective active area on the CCD. A spectral resolution of 0.02 nm was typical, depending on the signal intensity.

Disilane (Si₂H₆, Aldrich, 97%) was used as received. Disilaned₆ (Si₂D₆) was synthesized by the lithium aluminum deuteride reduction of hexachlorodisilane.³⁰ The purity of the disilanes was verified by gas-phase infrared spectroscopy. Oxygen ($^{16}O_2$ Matheson gas 99%) and $^{18}O_2$ (Sigma-Aldrich 97% enrichment) were used as received. The precursor gas mixtures were stored in 2 L stainless steel sample cylinders in a fume hood and delivered to the pulsed valves through flexible 1/8 in. OD stainless steel tubing.

III. AB INITIO CALCULATIONS

The ground states of the SiOH₂ isomers have been thoroughly explored in previous theoretical studies,^{9–20} so we have concentrated our calculations on efforts to characterize the excited state. All computations were performed with the GAUSSIAN 16 suite of *ab initio* programs.³¹ Our preliminary studies on *cis*- and *trans*hydroxysilyenes of C_s symmetry indicated that both species devolve to lower symmetry on promotion of a HOMO electron to the LUMO, limiting the types of calculations that could be undertaken. A low-level configuration interaction singles (CIS) calculation on either isomer gave an identical excited state of C_1 symmetry with the O–H and Si–H bonds at ~90° to each other—a skewed or twisted geometry of C_1 symmetry, as illustrated in Fig. 1. Subsequent complete active space self-consistent field (CASSCF) studies involving four active orbitals and four electrons gave similar results. Dunning's correlation consistent basis sets augmented by diffuse functions (aug-cc-pVTZ and aug-cc-pVQZ)³² were employed for the CASSCF calculations. In each case the excited state geometry was optimized and the vibrational frequencies calculated for three isotopologues, and these quantities are summarized in Table I.

As an aid to understanding the experimentally observed LIF and single vibronic level emission spectra, Franck–Condon (FC) profiles of the transitions were calculated from the *ab initio* results using a locally modified version of the program of Yang *et al.*³³ The input involved the ground and excited state molecular structures, vibrational frequencies, and Cartesian displacement coordinates for each of the normal modes. The FC factors for each vibronic transition were calculated in the harmonic approximation, including normal mode displacements and Duschinsky rotations.³⁴ Simulations and fitting of the rotational structure of the LIF bands were performed with the PGOPHER program.³⁵

IV. RESULTS AND ANALYSIS

A. Identification of HSiOH

A low-resolution OPO scan of the twin jet effluent of disilane + O_2 exhibits a complex series of LIF bands in the 450–400 nm region as shown in Fig. 2. The resolution is just sufficient to suggest that several features throughout the spectrum exhibit similar subband structure. It is also evident from the figure that the spectrum contains a variety of other bands with different rotational contours that arise from as yet unidentified species produced in our twin discharge jet. A medium resolution scan of the LIF feature at 22 845 cm⁻¹, presented in Fig. 3, shows well-resolved rotational structure characteristic of a perpendicular band of an asymmetric top, and the other bands identified by the vertical leaders in Fig. 2 are found to be very similar. The LIF spectrum obtained using a mixture of 1% $^{16}O_2$ and 1% $^{18}O_2$ (see Fig. 3) clearly shows a doubling of the



FIG. 2. Low resolution LIF spectrum of the reaction products from twin discharges through Si₂H₆ and ¹⁶O₂. The vertical leaders identify features with similar rotational contours among the plethora of other intensely fluorescent species.



FIG. 3. (Top trace) Calculated absorption band of *trans*-HSiOH from the *ab initio* structures in Table I, with a rotational temperature of 15 K, a linewidth of 0.15 cm⁻¹, and an axis switching angle $\theta = 4^{\circ}$. (Middle trace) The medium resolution LIF spectrum (0.15 cm⁻¹ FWHM) of the reaction products of a twin discharge jet of Si₂H₆ and ¹⁶O₂. (Bottom trace) LIF spectrum obtained with the same conditions as the middle trace except using a 1% ¹⁶O₂ + 1% ¹⁸O₂ in argon gas mixture.

Q-branches, indicative of a single oxygen atom in the molecule. Substituting Si₂D₆ in the gas mixture produces substantial shifts in the LIF bands, proving that the molecule contains hydrogen. The calculated rotational structure of the band of HSi¹⁶OH (see Fig. 3), based on the *ab initio* rotational constants of the *trans* isomer (Table I), matches the experimental result very well, leaving little doubt as to the identity of the carrier of the spectrum.

Further confirmation that we have observed *trans*hydroxysilylene comes from the emission spectra shown in Fig. 4. The spectrum of HSi¹⁶OH shows low energy features attributable to the *trans* isomer [obs/calc (Table I)] at 784/788 cm⁻¹ (v_5), 849/837 cm⁻¹ (v_4), 926/930 cm⁻¹ (v_3), and 1234/1243 cm⁻¹ ($2v_6$) and higher energy combinations and overtones of these modes. The observed frequency intervals match the *trans* isomer theoretical and matrix values (Table I) better than those of the *cis* isomer. Similarly, the emission spectrum of DSi¹⁶OD shows *trans* bands¹⁸ at 710/718 cm⁻¹ (v_3) and 924/938 cm⁻¹ ($2v_6$) along with combinations of these modes.

The general agreement between the first prominent $HSi^{16}OH$ band centered at ~22 840 cm⁻¹ (assigned as 0_0^0 vide infra) and the calculated T_0 of 22 632/22 662 cm⁻¹ (pVTZ/pVQZ, Table I) further confirms that the electronic band system we have observed is due to the *trans*-HSiOH molecule.

B. Low resolution LIF and emission spectra

The LIF spectra of DSi¹⁶OD were disappointingly weak and largely obscured by other fluorescent impurities, although three bands of DSiOD were identifiable by their characteristic *Q*-branch intervals. The situation was somewhat better for HSi¹⁶OH, with five very weak features in the red end and five much stronger bands interspersed among the intensely fluorescent impurity features. The measured wavenumbers of the *Q*-branches of the observed bands



FIG. 4. Comparison of the emission spectra of HSi¹⁶OH and DSi¹⁶OD. The top panel shows the calculated FC profile for emission from the 0-0 band of HSi¹⁶OH. Calculated profiles from other upper state levels are very similar. The upper trace in the bottom panel is the emission spectrum obtained from laser excitation of the ${}^{\rho}Q_1$ (${}^{\Delta Ka}\Delta J_{K''_a}$) branch of the HSi¹⁶OH band at 23 470 cm⁻¹ (3¹₀ band in Fig. 5). The middle trace is the emission spectrum from the ${}^{r}Q_1$ branch of the same HSi¹⁶OH band showing doublets for transitions from $K'_a = 2$ down to $K''_a = 1$ and 3. The bottom trace is the weak emission spectrum recorded by laser excitation of the ${}^{\rho}Q_1$ branch of DSi¹⁶OD at 23 229 cm⁻¹ (6¹₀ band in Table II).

of both isotopologues and their assignments are summarized in Table II.

Figure 5 shows a comparison of the observed and calculated LIF spectra of HSi¹⁶OH. As shown by the FC profile, the first few bands in the trans-hydroxysilylene spectra are expected to be very weak, with long progressions involving v₆, gaining substantial intensity to higher energy. This is generally what is observed, although there appears to be an abrupt fluorescence cutoff above \sim 23 800 cm⁻¹, complicated by the increasing intensity of the impurity bands. In previous ab initio work,³⁶ Tarroni and Clouthier showed that the absence or extent of fluorescence in HMX (M = Si, Ge, and Sn; X = F, Cl, Br, I) molecules is predictable based on the energetic onset of the HMX \rightarrow H(²S) + MX(²\Pi) dissociation process relative to the \tilde{A} state zero point energy. Although we have not performed any detailed calculations, we suspect that the limited extent of the HSiOH LIF spectra is due to a competing excited state dissociation process. In this regard, we note that the hydroxsilylene fluorescence lifetimes observed on an oscilloscope, although complicated by the longer-lived impurity fluorescence, were of the order of tens of nanoseconds, much shorter than the measured 0-0 band ($T_0 = 23260 \text{ cm}^{-1}$) radiative lifetime of 175 ± 6 ns for the isoelectronic HSiF species.37

HSi ¹⁶ OH band	Comment	¹⁸ O ₂ - ¹⁶ O ₂ shift	$^{p}Q_{1}$	rQ_0	rQ_1
$\overline{6_{3}^{0}}$	$3v_6'' = 1811.4$	6.7	21 020.1	21 031.9	21 046.0
6^0_2	$2v_6'' = 1234.1$	5.1	21 597.9	21 609.2	21 624.0
6^{1}_{2}	1234.0	4.1	21 965.5	21 976.7	21 991.3
6_1^0	$v_6'' = 629.4$	3.4	22 202.5	22 213.9	22 228.5
6_1^1 ?	618.5 ^a	2.0	22 581.0	22 592.2	22 606.1
00	$T_{00} = 22836.765$	1.35	22831.4	22 843.3	22 857.5
6_0^1	$v_6' = 367.4$	0.4	23 199.1	23 210.7	23 224.8
3_0^1	$v'_3 = 638.4$	-0.04	23 469.9	23 481.7	23 496.0
6_0^2	$2v_6' = 772.6$	-2.6^{b}	23 603.8	23 615.9	23 630.8
5_0^1	$v'_{5} = 900.9$	-2.1	23731.7	23 744.2	23 7 58.7
DSi ¹⁶ OD band					
611?	$v_6'' = 466.7$		22762.6	22 768.6	22776.0
000?	$T_{00} \sim 23015$		23 013.9	23 019.4	23 026.9
6_0^1 ?	$v_6' = 215.9$		23 229.4	23 235.3	23 242.7

TABLE II. Measured wavenumbers (cm⁻¹) and assignments of the *Q*-branches for the observed LIF bands of HSi¹⁶OH and DSi¹⁶OH. ? denotes tentative or unknown assignment.

^aAssignment tentative as v_6'' interval is ~10 cm⁻¹ too low.

^bFrom ${}^{p}Q_{1}$ only, other branches appear perturbed.

We were able to make assignments of the LIF bands based primarily on the oxygen isotope shifts. For fundamentals and overtones of a single harmonic vibration k, the ¹⁸O–¹⁶O isotope shift Δ_{18-16} can be approximated as

$$\Delta_{18-16} = \Delta_{0-0} + \left(\omega'_{k18} - \omega'_{k16}\right)\mathbf{v}'_k - \left(\omega''_{k18} - \omega''_{k16}\right)\mathbf{v}'_k, \tag{1}$$



FIG. 5. (Top trace) Medium resolution LIF spectrum of the reaction products from twin discharges through Si₂H₆ and ¹⁶O₂. HSi¹⁶OH bands are identified by assignments, and the weaker bands are enlarged. (Bottom trace) The calculated absorption spectrum of HSi¹⁶OH, with the 0-0 band placed at 22.843 cm⁻¹ to match the experimental assignment. The calculated major progressions involve the torsional (v₆) and HSiO bending (v₃) modes.

where ω_k is the harmonic frequency and Δ_{0-0} is the 0-0 band isotope shift. In the usual case where all $\omega_{k16} > \omega_{k18}$, which applies to trans-HSiOH (see Table I and Ref. 18), then cold bands V_{k0}^n will have $\Delta_{18-16} < 0.0$, hot bands V_{kn}^0 have $\Delta_{18-16} > 0$, and the 0-0 band has Δ_{0-0} small and positive based on the *ab initio* frequencies (Table I and Ref. 18). Experimentally (see Table II), we find Δ_{18-16} is large and positive for the very weak bands in the red end of the spectrum, gradually decreasing and becoming negative at the blue end. The pattern of frequency intervals suggests the band with blue end. The pattern of frequency intervals suggests the band with ${}^{r}Q_{0} = 22\,843.3 \text{ cm}^{-1}$ and $\Delta_{18-16} = 1.3 \text{ cm}^{-1}$ as the 0-0 band with weak features 629.4 cm⁻¹ ($\Delta_{18-16} = 3.4 \text{ cm}^{-1}$), 1234.1 cm⁻¹ ($\Delta_{18-16} = 5.1 \text{ cm}^{-1}$), and 1811.4 cm⁻¹ ($\Delta_{18-16} = 6.7 \text{ cm}^{-1}$) to the red as 6_{1}^{0} , 6_{2}^{0} , and 6_{3}^{0} . The *ab initio* ω_{6}^{\prime} values are 632.7 (¹⁶O) and 630.6 (¹⁸O) cm⁻¹ with $\Delta_{18-16} = 2.1 \text{ cm}^{-1}$. Substituting the 6_{1}^{0} values into Eq. (1) and solving gives $\Delta_{0-0} = 1.2 \text{ cm}^{-1}$, in excellent agreement with the observed 0-0 band isotope shift of 1.3 cm⁻¹. The strong band just to the blue of 0-0 can be identified as 6_0^1 based on the FC simulation, the vibrational interval of 367.4 (*ab initio* = 391) cm^{-1} , and $\Delta_{18\cdot16} = 0.4 \text{ cm}^{-1}$ (calc. = -0.7 cm^{-1}). The 6_0^2 band is the weaker feature at 23 615.9 cm⁻¹ with $\Delta_{18\cdot16} = -2.6$ and a larger vibrational interval of 405.2 cm⁻¹, implying a large positive anharmonicity. The corresponding 6_1^1 and 6_2^1 hot bands were identified among the weak features in the red end of the spectrum with appropriate vibrational intervals and isotope shifts. Finally, two other cold bands above 0-0 were tentatively assigned as 3_0^1 and 5_0^1 , based primarily on the vibrational intervals and the corresponding emission spectra. The three observed DSi¹⁶OD LIF bands were tentatively assigned as listed in Table II.

The emission spectra obtained from the hydroxysilylene species were generally weak, due to the low intensity of the LIF signals, and only one DSi¹⁶OD spectrum was measurable. However, the observed ground state intervals were readily assigned to the *trans*-HSi¹⁶OH

and *trans*-DSi¹⁶OD species, based on the excellent calculations of the anharmonic frequencies of Martin.¹⁸ As expected based on the large change in geometry from *trans* to *skew* on electronic excitation, even quantum number changes of the torsional mode, $v_6''(a'')$, figure prominently in the spectra. In addition, intervals involving v_3'' (HSiO bend) and v_5'' (HOSi bend) were readily apparent in some of the spectra. However, the emission spectra do not show the long progressions involving even and odd quantum number changes in v_6'' predicted by the FC calculations (Fig. 4, top panel).

The vibronic emission bands obtained by laser excitation of the ${}^{p}Q_{1}$ branch show single features attributable to the unresolved $K'_{a} = 0 \rightarrow K''_{a} = 1$ subband (Fig. 4, top trace). However, excitation of ${}^{r}Q_{1}$ yields closely spaced doublets (Fig. 4, middle trace) corresponding to the $K'_{a} = 2 \rightarrow K''_{a} = 1$ and $K'_{a} = 2 \rightarrow K''_{a} = 3$ subbands, with a measured doublet separation of 48 ± 1 cm⁻¹. In the simplest approximation, the ground state energy levels of a near-prolate asymmetric top are given by

$$F(J, K_a) = \overline{B}J(J+1) + (A-\overline{B})K_a^2,$$
(2)

HSi¹⁶OH

784.3

848.9

926.8

1232.5

1626.5

1681.1

1769.8

1837.3

2116.0

2362.6

2386.3

2519.2

2569.6

 $[\overline{B} = (B + C)/2]$ which yields $F(3,3) - F(1,1) = 12\overline{B} - 2\overline{B} + 9(A - \overline{B}) - (A - \overline{B}) = 8A + 2\overline{B}$ for the subband origins. Employing the ground state *ab initio* constants,¹⁵ one obtains $\Delta E = 48.1 \text{ cm}^{-1}$, in good agreement with the experimental measurement.

In the presence of so much impurity emission, the ${}^{r}Q_{1}$ and ${}^{r}Q_{0}$ emission spectra provided a strong check on which features could be assigned to HSi¹⁶OH. Single features in the ${}^{p}Q_{1}$ spectra had to

Assignment

51

 4_1

31

6₂ 4₁5₁

 3_15_1

3141

3162

4152

 3_25_1

 $3_14_15_1$

32

 6_4

exhibit doublets with the correct splitting when $K'_a = 1$ or 2 was pumped. In this fashion we weeded out suspect emission bands and confirmed bands assigned to hydroxysilylene. The measured vibrational intervals and their assignments are summarized in Table III. The HSi¹⁶OH emission bands beyond 2700 cm⁻¹ were very weak and could not be verified as due to hydroxysilylene, so they were omitted from the table. The emission spectra have been included as pdf files in the supplementary material.

C. High resolution LIF spectra

HSi¹⁶OH and HSi¹⁸OH bands centered at ~22 480 cm⁻¹ (0_0^0 band in Fig. 5) were sufficiently free of overlapping impurity features to permit the acquisition of high resolution, rotationally resolved LIF spectra. In both the ground and first excited singlet states, HSiOH is predicted to be a near-prolate asymmetric top, with a large *A* rotational constant and smaller, nearly equal *B* and *C* values. The electronic transition involves promotion of an electron from the HOMO (a', in-plane lone electron pair centered on silicon) to the LUMO (a'', out-of-plane Si *p* orbital), so the transition moment is along the out-of-plane or *c*-axis. In HSiOH, the *a*-inertial axis is oriented almost coincident with the Si–O bond, so the *A* rotational constant is determined primarily by the off-axis hydrogen atoms. The HSiO bond angle is predicted to increase substantially on electronic excitation (see Table I), which should be reflected in a concomitant increase in the *A* constant.

The medium resolution spectrum of the $HSi^{16}OH 0_0^0$ band is shown in Fig. 3, and a portion of the high-resolution spectrum of the same band is given in Fig. 6. The branches are fairly well resolved

Notes

 $\begin{array}{l} \nu_3=709.5\\ \nu_6\approx 462 \end{array}$

 $3_1 + 690.8$ $6_2 + 685.2$

 $6_2 + 871.7$

DSi¹⁶OD

. . .

. . .

709.5

924.1

1400.3

1609.3

1795.8

TABLE III. Measured ground state vibrational energies (cm⁻¹) of *trans*-HSi¹⁶OH and *trans*-DSi¹⁶OD. ? denotes tentative or unknown assignment.

Notes

 $v_5 = 784.3$

 $v_4 = 848.9$

 $v_3 = 926.8$

 $\nu_6\approx 616$

 $4_1 + 777.6$

 $3_1 + 754.3$

 $4_1 + 920.9$

 $3_1 + 910.5$

 $6_2 + 883.5$

 $6_2 + 1130.1$

 $4_15_1 + 759.8$

 $3_14_1 + 749.4$

 $3_15_1 + 888.5$

Obs.-Calc.^a

-4.1

12.1

-3.1

-10.4

-20.7

-7.4

-5.4

-32.6

-34.0

-16.5

-10.9

-28.6

5.5

 $3_14_1 + 902.7$ 3_24_1 2672.5 1.6 $3_2 + 903.1$ 33 2740.4 1.9 2085.0 $3_2 + 684.7$ 3262 2282.0 $3_16_2 + 672.7$ $3_{1}6_{4}$ 2449.3 $6_4 + 653.5$ 3362 2939.1 $3_26_2 + 657.1$ 2 2975.3 3088.9 $3_{2}6_{4}$ $3_16_4 + 639.6$ 3108.4 2 ^aCalculated values obtained from the *trans*-HSi¹⁶OH *ab initio* harmonic frequencies and anharmonicity constants given in Table 3 of Ref. 18.

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FIG. 6. Portion of the high resolution LIF spectrum of HSi¹⁶OH. The downward trace is the calculated spectrum at a rotational temperature of 20 K. The inset on the bottom left shows an expanded view of the axis switching branches. The vertical leaders on the top right identify perturbed lines and extra lines in the $^{r}R_{0}$ branch.

and were readily assigned. The $K'_a = 1 - K''_a = 0$ subband lines were used to calculate the combination defect³⁸ as

$$\Delta_{CD} = R(J'') - Q(J'') - [Q(J''+1) - P(J''+1)].$$
(3)

 $\Delta_{CD} = (B - C)' (J'' + 1)^2 \text{ or positive for a } c\text{-type band and } \Delta_{CD} = (C - B)' (J'' + 1)^2 \text{ or negative for a } b\text{-type band. In this case the combination defect is positive, confirming that the band follows <math>c\text{-type selection rules with } \Delta K_a = \pm 1, \Delta K_c = 0, \pm 2. \text{ Once a set of initial assignments was made, the PGOPHER program was used to fit the data to an asymmetric top model, fitting the ground and excited state rotational constants and the band origin. The analysis of the analogous band of HSi¹⁸OH proceeded in a similar fashion, and the resulting constants are summarized in Table IV. The measured transitions, assignments, and least squares residuals are reported in Table V.$

TABLE IV. Ground and excited state rotational constants (cm⁻¹) of HSi¹⁶OH and HSi¹⁸OH.

Two further aspects of the rotational analysis of these bands should be emphasized. The first is that for a molecule of such low symmetry (C_s in the \widetilde{X} state, C_1 in the \widetilde{A} state), there is the possibility of axis switching,³⁹ in which there is a rotational axis tilt on electronic excitation, which in this case induces extra $\Delta K_a = 0$ lines in the spectrum. These are identified in Fig. 6, and their intensity is consistent with a tilt angle of $\theta \sim 4^{\circ}$. Several of the axis switching lines in the HSi¹⁶OH spectrum were included in the least squares analysis. The second point is that there is an obvious perturbation in the $K'_a = 1$ stack of levels, as highlighted in Fig. 6. The ^{*r*} R_0 branch lines are progressively displaced from their expected positions and are accompanied by a group of weaker extra lines. Since the $^{r}Q_{0}$ lines (as well as one component of the asymmetry-split ${}^{r}R_{2}$ and ${}^{p}P_{2}$ branches) are unperturbed, it is apparent that only the upper asymmetry component $(J_{1,J-1})$ of $K'_a = 1, J' = 3-7$ is observed to be shifted from their expected positions. Although the number of transitions is very limited, the perturbation appears to go through a resonance and changes sign from J' = 6 to 7. A similar perturbation was found in the HSi¹⁸OH spectrum (see Table V), although the evidence for a resonance is less clear in this isotopologue. A perturbation in the 0_0^0 band is unusual and is likely attributable to a nearby level of the lower excited triplet state.

V. DISCUSSION

A. Molecular structure

Unfortunately, because we were unable to obtain high resolution spectra of DSiOD, the number of rotational constants determined experimentally (see Table IV) was insufficient to derive ground and excited state molecular structures free of constraints. Despite this limitation, we note that the experimental A'' values are very close to those calculated¹⁷ for *trans*-HSiOH with a maximum error of -0.06%, whereas the error in comparison to the *cis* values is 1.8%, 30 times larger. The HSi¹⁶OH ground state inertial defect Δ (amu Å²) is

$$\Delta = I_C - I_B - I_A,\tag{4}$$

		Groun	id state			Excite	ed state	
	HSi ¹⁶ C	Н	HSi ¹⁸ C	ЭН	HSi ¹⁶ OF	ł	HSi ¹⁸ OF	Н
	Expt.	Theory ^a	Expt.	Theory ^a	Expt.	Theory ^b	Expt.	Theory ^b
A	5.881 07(45)	5.88445	5.860 53(37)	5.863 23	7.043 24(39)	7.041 50	7.011 76(36)	7.01414
В	0.548 538(91)	0.541 45	0.513 841(96)	0.507 56	0.51781(10)	0.52479	0.485 90(11)	0.493 05
С	0.500 57(10)	0.494 65	0.472 33(12)	0.46613	0.50007(11)	0.505 77	0.470 89(10)	0.47627
T_0	0	0	0	0	22 836.764 7(14)	22 632	22838.1179(12)	
# ^c	90		67					
σ^{d}	0.006		0.004					

^bCASSCF/pVTZ this work.

^cNumber of transitions fitted.

^dOverall standard deviation of fit (cm^{-1}).

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with a small positive value of 0.079 amu Å², as it should be for a planar molecule. In the excited state, $\Delta = -1.24$ amu Å², indicative of a nonplanar structure. For the *trans* ground state, we fixed the O–H bond length at a 0.958 Å value predicted in a previous high quality *ab initio* study,¹⁵ assumed planarity, and fitted four geometric parameters to the observed moments of inertia (fitting planar moments did not yield any improvement). The resulting zero-point parameters (see Table VI) are in general accord with *ab initio* predictions, although the dearth of experimental data led to rather large errors for the bond angles. Attempts to fit either a nonplanar or a *cis* structure led to much larger errors, significant deviations from *ab initio* values, and a poorer overall rms deviation.

In the excited state, our *ab initio* studies predicted a nonplanar *skew*-structure (Fig. 1), so we were forced to constrain r(O-H)and r(H-Si) in order to determine the dihedral angle. The results in Table VI (obtained by fitting to the moments of inertia) are in reasonable accord with our only modest quality *ab initio* values, suggesting that the predicted excited state *skew* structure is correct. Attempts were made to fit the data to *trans* and *cis* planar structures, with little success.

In Table VII, we have compared the structural parameters and their changes on electronic excitation for various silvlenes. The HSiOH ground state Si-H bond length is similar, although less precise, to those of the other HSiX species and comparable to the 1.520 Å ground state bond length of the silicon hydride diatomic molecule.43 The Si-OH bond length is comparable to the Si-F bond length of HSiF but substantially longer than the 1.510 Å ground state bond length of SiO.43 However, the present Si-OH bond length of 1.654(14) Å is the same within the respective errors as the much more precise microwave determination of the 1.647(2) Å bond length of the Si-OH molecule.44 Finally, the ground state HSi-OH bond angle of $94.5(46)^{\circ}$ is very similar to the $92-98^{\circ}$ bond angles of the simple triatomic silvlenes. It is abundantly evident that the hydroxysilylene geometric parameters determined in the present work are in accord with those of other silylenes and with previous *ab initio* values^{15,18} for the *trans* isomer.

SiH₂ and the triatomic halosilylenes undergo a substantial increase in bond angle (Table VII, 18°–30°) on promotion to the \tilde{A}^1A'' excited state, and the 24° H–Si–OH bond angle increase is consistent with this trend. The finding of relatively small changes in the bond lengths on electronic excitation is also replicated in HSiOH. The energies of the $\tilde{A}^1A''-\tilde{X}^1A'$ electronic transitions of the triatomic silylenes depend strongly on the electronegativity of the substituents, with T_0 of HSiF at 23 338 cm⁻¹ and the origin of the SiH₂ spectrum some 7800 cm⁻¹ to the red. It is thus not surprising that the electronic transition of HSiOH occurs at about the same energy (~23 000 cm⁻¹) as that of HSiF, since the Pauling electronegativities of oxygen (3.44) and fluorine (3.98) are similar.

B. Cis, trans, and skew structures

Our emission data and the constants obtained from the rotational analysis strongly support the conclusion that *trans*-HSiOH is the isomer being probed in our LIF/supersonic expansion experiments. This is rather surprising, as previous matrix isolation infrared spectra have been interpreted^{15,18} as arising primarily from the *cis*-HSi¹⁶OH isomer, although some of the IR bands obtained on ¹⁶O/¹⁸O and H/D isotopic substitution were only assignable as *trans*.

spectra of HSi¹⁶OH and HSi¹⁸OH.^a

resolution LIF

cm⁻¹) from the high

103

Calc. ×

(Obs.

and least squares residuals

assignments,

each entry),

cm⁻¹ to

Rotational line frequencies (add 22 800

LE <

TABL

		$K'_a = 0 \cdot$	$\leftarrow K_a'' = 1$				$K'_a = 1 \leftarrow$	- $K''_{a} = 0$		
	Id	R1	d	P_1	r _F	Ro	^r	0	r P	0
J'	¹⁶ O ^b	081	$^{16}O^{b}$	¹⁸ O	16O ^{b,c}	$^{18}O^{d}$	¹⁶ O ^b	¹⁸ O	16Ob.c	$^{18}O^{d}$
0			30.328(-7)	31.742(-2)						
Ч			29.197(-9)	30.675(-11)	44.323(-3)	45.621(5)	43.260(1)	44.617(2)	41.178(-1)	42.661(3)
7	33.388(0)	34.615(1)	28.021(-3)	29.568(-11)	45.335(5)	46.555(-3)	43.183(4)	44.542(1)	40.093(7)	41.635(7)
б	34.292(-4)	35.467(-3)	26.786(1)	28.421(-2)	46.308(-4)	47.478(-1)	43.061(1)	44.436(5)	38.977(4)	40.582(3)
4	35.146(-2)	36.281(4)	25.494(2)	27.219(4)	47.266(-8)	48.375(-4)	42.901(-2)	44.292(6)	37.840(-1)	39.515(3)
5	35.946(1)	37.033(1)	24.146(1)	25.961(2)	$^{*}48.181(-33)$	49.246(-11)	42.707(-2)	44.107(1)	*36.677(-15)	38.408
9	36.677(-10)	37.743(4)	22.753(9)	24.651(-2)	$^{*}49.061(-74)$	*50.074(-43)	42.485(6)	43.892(-1)	* 35.454(-72)	*37.283(-36
7	37.383(9)	38.408	21.286(-3)	23.296(-3)	*50.124(85)	*51.074(116)	42.215(0)	43.650(2)	*34.437(90)	*36.328(129
8	38.008(1)	38.997			*51.006(85)		41.916(-5)	43.371(-2)	*33.241(81)	
6	38.588(2)	39.561(1)					41.580(-17)	43.068(0)		
10	39.107(-3)							42.737(-1)		
11	39.578(-4)									

			$K'_a = 1 \leftarrow K''_a = 2$	5				$K'_a = 2 \not \leftarrow$	$\leftarrow K_a'' = 1$		
	pR2 ^e) _d	22	^p P	2	<i>I</i> ,	R1	r (Qı	I ₁	-
J'	$^{16}\mathrm{Ob}$	$^{16}\mathrm{O}^\mathrm{b,c}$	$^{18}\mathrm{O}^\mathrm{d}$	¹⁶ O ^{b,c}	$^{18}O^{d}$	$^{16}O^{b}$	¹⁸ O	$^{16}O^{b}$	¹⁸ O	$^{16}O^{b}$	¹⁸ O
_				19.754	21.180						
		21.808(3)	23.115(-1)	19.754 18.661(4)	21.180 20.162(6)	59.527(1)	60.746(-1)			54.156(-5)	
7		21.751	23.059	18.610(5)	20.119(7)	59.566(-8)	60.785(-4)	57.387(7)		54.448(0)	
6	24.875(-11)	21.751	23.059	17.528(-10)	19.106(4)	60.435(1)	61.600(-4)			52.922(-1)	54.553(-3)
n	24.782(2)	21.647	22.959	17.441(5)	19.018(2)	60.579(2)	61.727(-2)	57.216(2)	58.581(-2)	53.406(4)	54.966(-5)
~	25.834(-10)	21.647	22.959	16.390(-3)	18.028(4)	61.287(0)	62.408(-3)			51.626(-5)	
4	25.672(3)	21.477(10)	22.807(-2)	16.231(4)	17.883(1)	61.572(-1)	62.662(2)	56.995(1)	58.385(2)	52.340(-9)	
U	* 26.787(8)	*21.525(-13)	22.851(-3)	*15.205(-18)	16.917(-4)	62.085(0)	63.164(-4)			50.284(0)	
n	26.511(-6)	21.266(5)	22.617(-4)	14.980(1)	16.714(2)	62.564(1)	63.589(7)	56.721(1)	58.129(-5)	51.285(-6)	
9	÷	*21.345(-60)	* 22.695(-28)		*15.761(-31)	62.825(-4)	63.878(2)				
D	27.331(5)	21.005(-5)	22.391(0)		15.505(-2)	63.538(-8)	64.523	56.392(1)	57.837(3)		
1		÷	÷			63.538	:				
-		20.712(-2)	22.116(-5)			64.530(7)	÷	56.008(0)	57.493(7)		
0						64.163(4)	65.150(5)				
0						65.489(-4)			57.091(1)		
d						64.752(9)					
ע						66.466(7)			56.642(-3)		
^a In case perturb ^b Additi These ^q , ^c HSi ¹⁶ C	ss where the asymm ed lines (the calcula onal axis switching Q ₁ lines all end up i)H extra lines (in or	the provided set of the p	ved, the transition with the expected line position $_{3}(3) = 22.836.579, q_{20}(2_{30})$ and parity in the upper odd parity in the upper $_{7}N_{0}$: 22.846.616, 22.847	the ven parity $(J + K_a + K_a)$ ion is given in parenth $(4) = 22836.463, q Q_0(5)$ (4) = 22848.388, 22848 7.518, 22848, 28, 2284	$+ K_c$) in the upper st eses) and in bold for (5) = 22 836.309, ^{<i>q</i>} $Q_0($ (<i>p</i> .258, 22 849.867; ^{<i>T</i>}	ate is listed first. L. the overlapped line $6) = 22 836.130, {}^{q}C_{0}$	ines not included i es. 21 (5) = 22 837.707, 38.093, 22 836.868,	n the least square ^q Q ₁ (6) = 22 837. 22 835.648.	es analysis are den 622, ${}^{q}Q_{1}(7) = 228$	oted by a leading a 37.508 , and $^{q}Q_{1}(9)$	sterisk for the = 22 837.235.
^e The ^p K	JH extra lines (in o. 2 lines were too we:	rder of increasing <i>j</i>): ak to be assigned in th	R ₀ : 22 848.640, 22 84: he HSi ¹⁸ OH spectrum	9.455, 22 850.2618; 70 I.	: 22 839.770, 22 838.0	021, 22 85/.4/5.					

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TABLE VI. Ground and excited state molec	cular structures of hydroxsilylene.
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	Ground	d state	Excited	state
	Expt.	Theory ^a	Expt.	Theory ^b
r ₀ (H–Si) Å	1.531(52)	1.521	1.5655°	1.5655
r0 (Si-O) Å	1.654(14)	1.662	1.6497(9)	1.6385
r ₀ (О–Н) Å	0.958^{d}	0.958	0.958^{d}	0.940
θ_0 (HSiO)°	94.5(46)	94.8	118.52(43)	116.95
θ_0 (SiOH)°	116.7(98)	114.3	116.8(15)	120.10
$\theta_0 (\text{HSiOH})^\circ$	0.0	0.0	102.5(25)	96.78

^a r_e values from Ref. 15.

^bCASSCF/pVTZ r_e values, this work.

^cFixed at the CASSCF/pVTZ theoretical value.

^dFixed at the theoretical value from Ref. 15.

The 0 K energy difference between *cis*- and *trans*-HSiOH has been calculated²⁰ to be as little as 0.04 ± 0.03 kcal/mol, and the barrier to interconversion along the torsional mode is predicted¹⁵ to have an activation energy of 8.3 kcal/mol. Deuterium substitution was found theoretically to shift the *cis-trans* isomerization equilibrium in favor of the *trans* form, although a semiclassical dynamics study concluded⁴⁵ that the probability of tunneling through the barrier was negligible. Clearly, the dynamics of the formation of HSiOH in our supersonic expansion/twin discharge jet is rather different than in previous matrix experiments.

Our *ab initio* finding of a *skew*-HSiOH structure in the excited state is supported by our rotational analysis. The excited state theoretical *A* values differ from the experiment by a maximum of only 0.034%, and the *ab initio* structural prediction is in good accord with the derived experimental structure. Despite these reassuring facts, Marcellus would have to conclude that "something is rotten in the state of Denmark"⁴⁶ since our FC simulations of the absorption and particularly the emission spectra, based on the *ab initio* ground and

TABLE VII. Comparison of ground state geometry and changes in structure on electronic excitation of various silylenes (HSiX).

	Ground state properties								
	HSiOH (r_0)	HSiF (r_0)	$HSiCl(r_0)$	$SiH_2(r_e)$					
r(SiH) Å	1.531(52)	1.548(3)	1.5214(8)	1.514					
r(SiX) Å	1.654(14)	1.606(1)	2.0729(4)						
θ (HSiX) [°]	94.5(46)	97.0(6)	95.0(2)	91.98					
	Structural chang	ges on electron	nic excitation						
	HSiOH	HSiF	HSiCl	SiH ₂					
Δr (SiH) Å	0.035	0.009	-0.016	-0.029					
$\Delta r(SiX) \text{ Å}$	-0.004	-0.004	-0.026						
$\Delta\theta$ (HSiX)°	24.0	17.4	21.5	30.5					
$T_0 ({\rm cm}^{-1})$	≈22 600	23 338	20718	15 548					
Reference	This work	40	41	42					

excited state structures, vibrational frequencies, and Cartesian displacement coordinates, do not match the experimental reality. In particular, a transition from a *skew*-HSiOH structure of C_1 symmetry to a *trans* structure of C_s symmetry would be expected to exhibit pronounced progressions in ν'_6 , the torsional mode, with the reduced symmetry allowing both odd and even quantum number changes in v₆. This is exactly what is predicted by our FC calculations, but the emission spectra only show transitions to the 6_2 and 6_4 levels (Table III) with no evidence of 6_1 or 6_3 .

One might argue that the molecule does not adopt a rigid molecular structure in the excited state but is freely rotating. Indeed, we found it difficult to get the CASSCF geometry optimizations to converge in the excited state, requiring very tight convergence criteria and step-by-step calculation of the force constants near the minimum, suggesting a fairly flat potential. However, medium resolution spectra of the LIF cold bands (Table II) do not show any evidence of subbands⁴⁷ or resolvable torsional splittings that might be expected under such circumstances, although the splittings may not be detectable except at much higher resolution. Although there may not be free rotation, it is likely there is a large amplitude torsional motion that includes the ground state trans geometry. At present, we do not understand the dearth of torsional bands in the emission spectra of HSiOH, the prevalence of the trans isomer in our spectra, and the exact nature of the excited state potential but expect that this new gas phase molecule will be fertile ground for future theoretical and experimental investigations.

VI. CONCLUSIONS

The hydroxysilylene (HSiOH) molecule has been spectroscopically detected in the gas phase through a combination of laser induced fluorescence and wavelength resolved emission techniques. All the evidence indicates that the observed transitions involve the planar, *trans* isomer in the ground state. High resolution, rotationally resolved LIF spectra have been obtained for the 0_0^0 bands of HSi¹⁶OH and HSi¹⁸OH. The derived rotational constants have been used to obtain ground and excited state molecular structures, with some constraints. The ground state structure is *trans*-HSiOH, whereas the excited state geometry is a nonplanar, *skew* molecule with a 102.5(25)° dihedral angle. Our own CASSCF calculations of the excited state geometry are in good agreement with the experimental results. Further work needs to be performed to thoroughly understand the vibronic structure of the LIF and emission spectra of hydroxysilylene.

SUPPLEMENTARY MATERIAL

See the supplementary material for pdf copies of the emission spectra of HSi¹⁶OH and DSi¹⁶OD.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tyler J. Herman: Data curation (supporting); Investigation (equal); Writing - review & editing (equal). Fumie X. Sunahori: Formal analysis (equal); Writing - review & editing (equal). Tony C. Smith: Conceptualization (lead); Formal analysis (supporting); Funding acquisition (lead); Investigation (supporting); Methodology (lead); Writing - review & editing (supporting). Dennis J. Clouthier: Data curation (supporting); Formal analysis (equal); Investigation (lead); Supervision (lead); Writing - original draft (lead); Writing review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and in the supplementary material.

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