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Detection and characterization of singly deuterated silylene, SiHD, via optical spectroscopy

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Singly deuterated silylene has been detected and characterized in the gas-phase using high-resolution, two-dimensional, optical spectroscopy. Rotationally resolved lines in the 0_0^A→1_0^A^+ band are assigned to both c-type perpendicular transition and additional parallel, axis-switching induced bands. The extracted rotational constants were combined with those for SiH₂ and SiD₂ to determine an improved equilibrium bond length, r_{SiH}, and bond angle, θ, of 1.5137 ± 0.0003 Å and 92.04° ± 0.05°, and 1.4853 ± 0.0005 Å and 122.48° ± 0.08° for the ˜X^1A^0(0,0,0) and ˜A^1A^0(0,0,0) state respectively. The dispersed fluorescence consists of a long progression in the ˜X^1A^0(0,0,0) → ˜X^1A^0(0,0,0) emission which was analyzed to produce vibrational parameters. A strong quantum level dependence of the rotationally resolved radiative decay curves is analyzed. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4954702]

I. INTRODUCTION

Understanding the observed electronic state energy ordering for silylene, SiH₂, which is ˜X^1A_1 < ˜a^3B_1 < ˜A^1B_1 < ˜B^1A_1, relative to the energy ordering for methylene, CH₂, which is ˜B^1B_1 < ˜a^3A_1 < ˜b^5B_1 < ˜c^1A_1, has been of long standing theoretical interest, as has understanding the associated excited state unimolecular dynamics. Modelling the role of SiH₂ in the fabrication of amorphous silicon thin films and polycrystalline silicon has also attracted significant interest.¹⁻⁶ Motivated primarily by the desire to garner a fundamental understanding of the properties of this simplest of silicon containing polyatomic molecules, and in part by the desire to develop a real time, in situ SiH₂ monitoring scheme, there have been numerous reported experimental⁷⁻²⁸ and theoretical²⁹⁻⁴⁸ studies of gas-phase SiH₂ and to a lesser extent SiD₂. In addition, SiH₂ is predicted to be abundant in circumstellar envelopes of carbon rich stars⁴⁹ and has been tentatively identified⁵₀,⁵₁ via the detection of the 1₁₁⁻₀₀₀ pure rotational transition. In contrast to the extensive studies of the SiH₂ and SiD₂ isotopologues, the only previous experimental study of singly deuterated silylene (SiHD), which is the focus of this report, is the matrix isolated infrared spectroscopic study from which the fundamental vibrational frequencies of the ˜X^1A^0 state were determined.⁵² The reduced symmetry of SiHD as compared to SiH₂ and SiD₂ causes the permanent electric dipole moment, μ₀, to have non-vanishing components on both the a- and b-inertial axes. Consequently, the number of electric dipole allowed, pure rotational transitions, and the number of levels that strongly Stark tune are significantly more numerous. In addition, the reduced symmetry of SiHD causes the inertial axes of the ˜A^1A^0 state to be rotated relative to that of the ˜X^1A^0 state, phenomena referred to as “axis-switching.”⁵₃⁻⁵₈ This leads to additional branch features in the electronic spectrum of SiHD relative to those for SiH₂ and SiD₂. This richer spectrum facilitates the extraction of structural parameters, investigation of dynamics, and provides additional possibilities for optical Stark spectroscopy.

A brief synopsis of the previous studies of SiH₂ and SiD₂ is warranted. The visible spectrum of SiH₂ was first detected in the gas-phase in 1967 by Dubois, Herzberg, and Verma⁷ using conventional visible absorption spectroscopy and rotationally analyzed soon thereafter.⁶ The spectrum was assigned to a progression in the ν_2^B-bending mode of a c-type (Δ J = 0, ±1, ΔK_3 = ±1, ±3 ... ΔK_c = 0, ±2, ...) ˜X^1A_1 → ˜A^1B_1 electronic transition. The visible spectrum exhibits numerous local perturbations because of strong interactions amongst the ˜X^1A_1, ˜A^1B_1 (E₀ ≈ 1.9256 eV), ˜B^1A_1 (E₀ ≈ 3.37 eV), and ˜a^3B_1 (E₀ ≈ 0.9 eV) states, which correlate to the 1Σ^+, 3Σ^−, and 1Δ states arising from the ... configuration in a linear structure. Laser induced fluorescence (LIF) detection of the visible bands was first reported in 1980¹⁰,¹¹ and at about the same time by intracavity absorption.¹² The sample was prepared by photolysis and microwave discharge under bulb conditions. The fluorescence lifetimes of ˜A^1B_1(0, ν₂, 0) levels of a bulb sample were measured during this period both broad banded¹₀ and at rotational resolution.¹₀,¹₃⁻¹₅ The observed lifetimes varied widely depending upon the specific rovibrational level excited, and the decay curves were often biexponential.¹₄ The behavior was interpreted as coupling of the ˜A^1B_1(0, ν₂, 0) levels with background levels in the ˜X^1A_1 and ˜a^3B_1 states followed by predissociation. About the same time, the adiabatic ionization potential of the ˜X^1A_1 and ˜a^3B_1 states of SiH₂ were experimentally determined¹⁶ and the infrared

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The first LIF detection of a supersonic free-jet expansion sample of SiH$_2$ and SiD$_2$ was performed by Fukushima et al.$^{18}$ Both excitation and dispersed fluorescence spectra were measured for the $(0,0,0)\tilde{X}^1A_1 \rightarrow (0,y,0)\tilde{A}^1B_1$, $v_2 = 0-6$, bands. It was proposed that the observed anomalous branch intensities were due to rotational and vibrational level-dependent nonradiative processes. The same group recorded the LIF excitation spectra of numerous bands of the $\tilde{X}^1A_1 \rightarrow \tilde{A}^1B_1$ electronic transition of SiD$_2$, which is much richer in features, at relatively high resolution (0.03 cm$^{-1}$).$^{19}$ The spectra were analyzed to produce a precise set of spectroscopic parameters for the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ states. A similar LIF excitation and dispersed fluorescence study of a free-jet sample of SiH$_2$ but at lower spectral resolution was reported by Ishikawa and Kajimoto.$^{20}$ The developed LIF techniques were utilized for the detection of SiH$_2$ in a plasma similar to those used for fabrication of amorphous silicon thin films.$^{21-23}$

The most accurate spectroscopic parameters for SiH$_2$ are from experiments performed nearly 20 years ago. In the case of the $\tilde{A}^1B_1$ state, they were derived from the analysis of cw-intracavity laser absorption and cw-cavity ring down spectrum of the 0$^2_2$ and 2$^2_2 \tilde{X}^1A_1 \rightarrow \tilde{A}^1B_1$ bands.$^{24,25}$ In those studies, rotational information up to $J = 16$, $K_a = 9$ was obtained from the analysis of Doppler limited spectra. A combined fit with the previous visible$^{7,8}$ and infrared$^{17}$ absorption measurements was performed. The $\tilde{X}^1A_1$ state parameters were derived from the analysis of infrared diode laser spectroscopic measurements.$^{26}$ More recently, the stimulated emission pumping spectrum has also been recorded and interpreted$^{27}$ to establish that the (0,3,0) $\tilde{a}^3B_1$ state lies approximately 9640 cm$^{-1}$ above (0,0,0) $\tilde{X}^1A_1$. In addition, an optical-optical double resonance technique was used to detect the $\tilde{B}^1A_1$ states of SiH$_2$ and SiD$_2$.$^{28}$ The spectra were interpreted as quasilinear behavior in the $\tilde{B}^1A_1$ state with a very small barrier ($\simeq 125$ cm$^{-1}$) to linearity.

Now turning to the theoretical studies, there have been numerous $ab$ $initio$ predictions of the properties of SiH$_2$, with particular emphasis on understanding the state ordering,$^{29-35,39-42,47}$ relative to that of CH$_2$, to gain insight into the unimolecular dynamics,$^{36,46,48}$ and aid in the interpretation of the spectra.$^{37,43-46}$ In addition to these electronic structure predictions, Duxbury et al.$^{38}$ reanalyzed the originally recorded $\tilde{X}^1A_1 \rightarrow \tilde{A}^1B_1$ absorption spectra of SiH$_2$$^{7,8}$ and rationalized the strong local perturbations and observed anomalous radiative lifetimes$^{44,15}$ using a semi-quantitative model. That model simultaneously accounted for the combined effects of Renner-Teller coupling of the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ states, direct spin-orbit coupling of the $\tilde{a}^3B_1$ and $\tilde{X}^1A_1$ states, and second order spin-orbit coupling of the $\tilde{a}^3B_1$ and $\tilde{A}^1B_1$ states. A more quantitative, theoretical-based analysis of the interacting $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ states of SiH$_2$ and SiD$_2$ was carried out by Yurchenko et al.$^{41}$ In that study, $ab$ $initio$ calculations of the potential energy surfaces (PESs), the electric dipole moments, and the electric dipole transition moment surfaces for the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ were performed. The PESs were used to calculate the rovibrionic energies which were compared with experimental values and subsequently the PESs were modified to improve the agreement. Using these refined PESs for the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ states, and accounting for the Renner-Teller coupling of these two states, the $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ emission spectrum was simulated. The agreement between the observed and calculated spectra was relatively poor, suggesting that accounting only for the Renner-Teller coupling and not spin-orbit interaction is insufficient. The same group used a similar approach to refine a predicted PES for the $\tilde{B}^1A_1$ state for SiH$_2$ and SiD$_2$. The optimized PESs were used to calculate the $\tilde{B}^1A_1$ term values and predict the rotation-vibration spectrum associated with the $\tilde{B}^1A_1$ state.

At about the same time, in an attempt to understand the $\tilde{X}^1A_1 \rightarrow \tilde{A}^1B_1 \rightarrow \tilde{B}^1A_1$ photoexcitation, the vibrational energies for the $\tilde{X}^1A_1$, $\tilde{A}^1B_1$, and $\tilde{B}^1A_1$ states of SiH$_2$ and SiD$_2$ were calculated, based on generated global PESs.$^{45}$ The vibrational levels, Franck-Condon factors (FCFs), and related transition probabilities were calculated. Renner-Teller effects were ignored. In a subsequent paper,$^{46}$ the same group investigated excited-state dynamics and the vibrational state dependence of the dissociations following the $\tilde{A}^1B_1 \rightarrow \tilde{B}^1A_1$ photoexcitation using three dimensional wave packet propagation methods. As part of that study, the vibronic energies for the $\tilde{X}^1A'$, $\tilde{A}^3A''$, and $\tilde{B}^1A'$ states of SiHD were also calculated. Interestingly, the photon energy dependence of the total photodissociation cross section was predicted to be fairly similar for SiH$_2$ and SiD$_2$, but very different from that predicted for SiHD. This marked difference in the photodissociation cross section was attributed to subtle differences in PESs for the $\tilde{A}$ and $\tilde{B}$ states and differences in vibrational wavefunctions. This is presumably associated with the fact that SiHD has C$_2$-symmetry compared to the C$_{2v}$-symmetry of SiH$_2$ and SiD$_2$.

Recently SiH$_2$ was selected as a venue for evaluation of the performance of time independent nonadiabatic transition state theory (NA-TST) relative to that of the more computationally demanding, quantum-based surface hopping method in an attempt to model spin-orbit induced intersystem crossing dynamics.$^{48}$ The $\tilde{X}^1A_1/\tilde{a}^3B_1$ system of SiH$_2$ was viewed as better suited for model studies of nonadiabatic dynamics of states involving different multiplicities than the $\tilde{X}^1B_1/\tilde{a}^1A_1$ system of CH$_2$, due to the larger spin-orbit coupling. The NA-TST and surface hopping methods predicted grossly different values for the $\tilde{X}^1A_1/\tilde{a}^3B_1$ intersystem crossing rates of SiH$_2$. There is no experimental information for the $\tilde{X}^1A_1/\tilde{a}^3B_1$ intersystem crossing, limiting assessment of the two methods employed. The effects of lowering the symmetry to that of SiHD were not considered, but should be large.

Here we report on the first LIF spectroscopic measurements of SiHD. Excitation and dispersed fluorescence spectroscopy and fluorescence decay curve measurements of the 0$^0_2\tilde{X}^1A' \rightarrow \tilde{A}^3A''$ band near 643 nm have been performed. The 0$^0_2\tilde{X}^1A' \rightarrow \tilde{A}^3A''$ band was selected instead of the more intense 2$^2_2\tilde{X}^1A' \rightarrow \tilde{A}^3A''$ band near 580 nm in the anticipation of fewer local perturbations resulting in a richer spectrum due to a lower predissociation rate.
II. EXPERIMENTAL

Singly deuterated silylene (SiHD) was generated via a supersonic, pulsed, d.c. discharge through a mixture of silane (SiH₄) (~2%), deuterium (D₂) (~5%), and argon (~93%) at a backing pressure of approximately 400 PSI and operated at 20 Hz. The supersonic d.c. discharge source has been previously described. The free-jet expansion was probed approximately 10 cm downstream. Four types of experiments were performed: (a) two dimensional (2D), medium resolution, excitation spectroscopy of the 01^1A′ → 31A″ band of SiHD, and corresponding bands of SiH₂ and SiD₂ using a Nd:YAG pumped pulsed dye laser; (b) two dimensional (2D), high resolution, excitation spectroscopy of the 01^1X′ → 31A″ band of SiHD using a single frequency cw-dye laser; (c) dispersed fluorescence (DF) resulting from the 01^3X′ → 31A″ excitation; and (d) rovibronic resolved fluorescent lifetime measurements. The two dimensional (2D) method⁶⁰,⁶¹ used to record the excitation spectra was previously described.⁶⁰ Briefly, a 75 nm wide spectral window in the dispersed fluorescence is simultaneously monitored using a cooled, gated, intensified CCD detector attached to a 2/3 m monochromator. The CCD detector gate for the pulsed dye laser 2D spectral measurements was typically set to a 1 µs width and delayed 20 ns from the laser. The CCD detector gate for the cw-dye laser 2D measurements was typically set to 30 µs, which approximately corresponds to the transit time of the pulsed free-jet expansion through the viewing region of the LIF collection optics. The central wavelength of the 75 nm wide monochromator spectral window was usually selected to look at the off-resonance 31A″(000) → 31A″(010) emission and was tracked with the wavelength of the laser excitation source. The entrance slit width of the monochromator was set to produce a spectral resolution of approximately ±2 nm for the DF. Typically, in the 2D measurements, 30 free-jet expansion pulses were averaged at a given laser excitation wavelength. A calibrated commercial wavemeter was used to determine the absolute wavenumber of the pulsed dye laser. The transition wavenumbers of the high-resolution 2D spectra were accurately determined by simultaneously measuring the sub-Doppler spectrum of iodine.⁶³ The pulsed or cw-dye laser 2D spectra were subsequently processed to produce excitation spectra by vertically summing of the pixels of the CCD detector along a horizontal slice (e.g., the 31A″(000) → 31A″(010) emission).

DF spectra having higher resolution than those associated with the 2D measurements were recorded using the software provided with the camera and pulsed dye laser excitation. In these measurements, the entrance slit on the monochromator was narrowed to produce a resulting spectral resolution of approximately ±0.7 nm. The DF signal at a given emission wavelength was obtained from vertical binning of the intensified CCD detector. Typically in this mode of operation, 10 000 averages were taken for each 75 nm monochromator transmission window. The multiple 75-nm-wide, one-dimensional arrays of intensity versus dispersed fluorescence wavelength were spliced together, and adjusted for wavelength variation of sensitivity, to produce the DF spectra. Wavelength calibration of the DF spectra was achieved by recording the emission of an argon pen lamp. The calibration lines also facilitated the splicing together of the 75-nm-wide segments.

The fluorescence decay curves were measured by tuning the laser wavelength to be resonant with a particular feature of the excitation spectra and recording the DF spectrum at variable time delays from the pulsed laser. The gate for the CCD detector was set to a large value (approximately 1 µs) and the time delay from the laser excitation stepped in 20 ns increments to produce a series of DF spectra. The

**FIG. 1.** Center: The pulsed dye laser, two dimensional (2D) spectrum of silylene radicals generated in a SiH₄ + D₂ supersonic, d.c. discharge expansion. Right: The off-resonance detected laser excitation spectra obtained from the vertical integration of the intensities of the three horizontal slices marked by the dashed red rectangles. Left: The dispersed fluorescence (DF) spectrum resulting from laser excitation of 5P(1) 01^3X′ → 31A″ transition of SiH₂ at 15 532 cm⁻¹. The spectrum was obtained from the horizontal integration of the intensities of the vertical slice marked by the dashed blue rectangle.
resulting DF spectra were integrated over the appropriate wavelength region to give the relative fluorescence intensity at a given delay from the laser excitation. The lower limit of the lifetime measurements of this experimental approach is set by the approximate 20 ns pulse width of the dye laser. Typically $10^4$ pulses at a given time delay were co-added resulting in a large background ($\sim 2 \times 10^6$) signal due to dark current.

FIG. 2. The observed and predicted spectra laser excitation spectrum for the $0^3\tilde{X}^1A' \rightarrow \tilde{A}^1A''$ band of SiHD and the associated assignment. The predicted stick spectrum and predicted spectrum assuming a Lorentzian line shape with a FWHM of 0.3 cm$^{-1}$ obtained using the optimized spectroscopic parameters (vide infra). The features marked with arrows were recorded at high-resolution and used in the analysis.

FIG. 3. Left: A 15 GHz region of the observed and predicted high-resolution LIF excitation spectrum near 15 523.0 cm$^{-1}$. A 200 MHz FWHM Lorentzian line was used in the prediction. Right: The associated energy levels, quantum assignment, and branch feature assignments right side of Figure 3. The three intense features are $c$-type whereas the weak, unresolved feature is an axis-switching induced transition.
III. OBSERVATIONS

The pulsed dye laser 2D spectrum in the 15 500 cm$^{-1}$ to 15 600 cm$^{-1}$ spectral region, which coincides with excitation of the $0^0\tilde{X}^1A'\rightarrow\tilde{A}^1A''$ band of SiHD and the $0^0\tilde{X}^1A_1\rightarrow\tilde{A}^1B_1$ bands of SiH$_2$ and SiD$_2$, is presented in the center panel of Figure 1. The laser excitation wavelength is indicated on the horizontal axis and the DF wavelength on the vertical axis. Tracking the monochromator causes the vertical axis (LIF Emission Wavelength) to vary nearly linearly as function of excitation wavelength; at the beginning of the scan (15 500 cm$^{-1}$), the center of the 75 nm spectral window is 677.5 nm whereas at the end of the scan (15 600 cm$^{-1}$), it is 681.7 nm. The widely spaced features in the middle of the 2D spectra correspond to the $\tilde{A}^1A''(000)\rightarrow\tilde{X}^1A'(010)$ and $\tilde{A}^1B_1(000)\rightarrow\tilde{X}^1A_1(010)$ emissions resulting from exciting the $0^0\tilde{X}^1A'\rightarrow\tilde{A}^1A''$ band of SiHD and the $0^0\tilde{X}^1A_1\rightarrow\tilde{A}^1B_1$ bands of SiH$_2$ and SiD$_2$, respectively. The DF near 710 nm is the $\tilde{A}^1B_1(000)\rightarrow\tilde{X}^1A_1(020)$ emission associated with the excitation of the SiH$_2$ $0^0\tilde{X}^1A_1\rightarrow\tilde{A}^1B_1$ band. The two compact, red-degraded bands in the DF spectra near 668 nm and 692 nm are tentatively identified$^{64}$ as the (7,1) $F\rightarrow X$ transitions.

![Figure 4](image-url)
and (7,2) $F \rightarrow X$ emissions resulting from the laser excitation of the (7,0) $F \leftarrow X$ band of SiH$_2$ near 15 572 cm$^{-1}$.

At the right side of Figure 1 are the off-resonance detected laser excitation spectra obtained from the vertical integration of the intensities of the three horizontal slices marked by the dashed red rectangles. The SiH$_2$ (top) and SiD$_2$ (bottom) spectra are very similar to previously reported LIF spectra of a jet-cooled sample. In those earlier studies, the spectral congestion was avoided by using either phenylsilane ($q$-SiH$_3$) or phenylsilane-$\alpha$-$d_3$ ($q$-SiD$_3$) as a precursor in a photolysis scheme for generating either a nearly pure SiH$_2$ or SiD$_2$ sample. Here DF wavelength selectivity of the 2D spectroscopic technique is exploited to extract the spectra of the individual isotopologues from the mixed isotopologue sample. The on-resonance excitation spectrum (not shown) obtained by vertical integration of the band near 642 nm in the 2D spectrum results in an unassignable, highly overlapped spectrum of SiH$_2$, SiD$_2$, SiHD, and Si$_2$. The 1 µs CCD detector gate width biases against the detection of levels that pre-dissociate on a short time scale. Hence, the excitation spectrum for SiH$_2$ (top) is very sparse compared to that of SiD$_2$ (bottom) where the predissociation is less extensive. Although the excitation spectrum of SiD$_2$ exhibits a recognizable pattern of branches, no such pattern is obvious in the corresponding spectrum of SiHD. On the left side of Figure 1 is the DF spectrum resulting from laser excitation of $^3$P$_1(1)$ 0$^0_0$$^2$X$_1$$^1$A$_1 \rightarrow$ $^3$B$_1$ transition of SiH$_2$ at 15 532 cm$^{-1}$. The spectrum was obtained from the horizontal integration of the intensities of the vertical slice marked by the dashed blue rectangle. The $^3$B$_1(0,0,0) \rightarrow$ $^2$X$_1(0,1,0)$ emission feature occurs at 687.6 nm.

A more detailed pulsed dye laser excitation spectrum for SiHD is presented in Figure 2. Also presented are the predicted stick spectrum and predicted spectrum assuming a Lorentzian line shape with a FWHM of 0.1 cm$^{-1}$ obtained using the optimized spectroscopic parameters (vide infra). A rotational temperature of 20 K was used based upon a comparison of the observed and predicted intensities (vide infra) of the lines involving the lowest rotational levels, which do not predissociate. The FWHM of the predicted spectra is approximately half the observed width in order to emphasize overlapped character. A $^4$K$^a$J$^a$$^4$K$^c$$^4$J$^c$($J''$) designation is being used for branch feature assignment (vide infra). High-resolution 2D spectra of the features marked with arrows in Figure 2 were recorded by replacing the pulsed dye laser with a single frequency, cw-dye laser. The 15 GHz region of the observed and predicted high-resolution spectrum near 15 523.0 cm$^{-1}$ is presented on the left in Figure 3. A 200 MHz FWHM Lorentzian line was used in the simulation. The associated energy levels, quantum assignment, and branch feature assignments are given on the right side of Figure 3. The three intense features are c-type transitions, whereas the weak, unresolved feature is an axis-switching induced transition. The 40 measured transition frequencies and assigned quantum number assignments are given in Table I. Also given are the differences between the observed and calculated transition wavenumbers and the standard deviation of the fit.

The dispersed fluorescence spectra for SiH$_2$, SiHD, and SiD$_2$ resulting from pulsed dye laser excitation of the $^3$P$_1(1)$ ($\tilde{v} = 15 532.5$ cm$^{-1}$), $^3$P$_0(1)$ ($\tilde{v} = 15 538.3$ cm$^{-1}$), and $^3$R$_0(1)$ ($\tilde{v} = 15 542.3$ cm$^{-1}$) transitions, respectively, are presented in Figure 4. The DF spectra are primarily progressions in the (0, $\nu_2$, $\nu_3$) mode. Due to the near resonance of multiples of $\nu_1$, $\nu_2$, and $\nu_3$ vibrational frequencies for the $^2$X$_1$$^1$A$_1$ state of SiH$_2$, and to a lesser extent for the $^2$X$_1$$^1$A$_1$ state of SiD$_2$, the DF spectra of these two molecules exhibit additional features from the $^1$A$_2$-$^2$F$_2$ Fermi resonances as well as 2$\nu_1$-$\nu_3$ Darling-Denison resonance. The weaker feature on the red side of the SiHD emissions are most likely due to the $\nu_{10} \rightarrow \nu_{11}$ transition or caused by simultaneously pumping multiple transitions. Note that the DF spectral features for SiH$_2$ are sharp whereas those for SiHD, and more so for SiD$_2$ are broader and red-degraded. This is a consequence of the predissociation which is more prevalent in SiH$_2$ and the fact that the long detection gate of the CCD (1 µs) biases towards the detection of long-lived levels. The $^2$X$_1$$^1$A vibronic energies, $E(\nu_1, \nu_2, \nu_3)$, extracted from the observed spacing of the DF

![Fig. 5. The decay fluorescence curves resulting from excitation of the $^3$P$_0(1)$ ($\tilde{v} = 15 531.2283$ cm$^{-1}$) (top), $^3$R$_0(0)$ ($\tilde{v} = 15 560.2951$ cm$^{-1}$) (middle), and $^3$R$_0(1)$ ($\tilde{v} = 15 566.0411$ cm$^{-1}$) (bottom) transitions. The fluorescence from the $^3$R$_0(1)$ line exhibits bi-exponential behavior. The amplitudes of for the bi-exponential curve are 40 016 counts ($\tau_1$) and 5686 counts ($\tau_2$). The associated $A^1$$^1$A$''(0,0,0)$ energy level and resulting lifetimes are indicated in Figure 8.](image-url)
TABLE II. Fluorescence lifetimes (ns) and relative energies for the $A'^1A''(0,0,0)$ state.

<table>
<thead>
<tr>
<th>Line</th>
<th>Transition</th>
<th>Lifetime (ns)</th>
<th>Energy (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4$P$_{10}(1)$</td>
<td>0$_{07}^+$</td>
<td>1011 ± 13</td>
<td>0</td>
</tr>
<tr>
<td>$^4$R$_{10}(1)$</td>
<td>0$_{22}^+$</td>
<td>814 ± 4</td>
<td>17.25</td>
</tr>
<tr>
<td>$^4$R$_{00}(0)$</td>
<td>1$_{07}^+$</td>
<td>769 ± 6</td>
<td>17.58</td>
</tr>
<tr>
<td>$^4$Q$_{02}(2)$</td>
<td>2$_{12}^+$</td>
<td>739 ± 5</td>
<td>27.85</td>
</tr>
<tr>
<td>$^4$R$_{01}(1)$</td>
<td>2$_{13}^+$</td>
<td>835 ± 5</td>
<td>29.73</td>
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<tr>
<td>$^4$R$_{10}(1)^b$</td>
<td>2$_{20}^+$</td>
<td>335 ± 5</td>
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<td>2$_{20}^+$</td>
<td>1493 ± 93</td>
<td>63.14</td>
</tr>
</tbody>
</table>

$^a$Relative to the 0$_{00}$ level of the $A'^1A''(0,0,0)$ state.
$^b$Bi-exponential behavior.

Initial assignment of the $c$-type transitions in the excitation spectrum was readily accomplished by predicting the spectrum using estimated rotational parameters based upon the previously determined structure$^{25}$ of SiH$_2$. Combination/differences revealed that the energies were not severely perturbed. Once the assignment of the additional axis-switching transitions was obtained (vide infra), a direct fit to the precisely measured transition wavenumbers of Table I was performed using a non-linear least squares fitting procedure. The energies for both the $X'^1A'$ and $A'^1A''$ states were modelled using the standard Watson $A$-type Hamiltonian,

$$\hat{H}_{\text{rot}} = \frac{1}{2}(B + C)J^2 + \left[A - \frac{1}{2}(B + C)\right]J_z^2 + \frac{1}{4}(B - C)(J_z^2 + J_\perp^2)$$

$$- \Delta J_J^4 - \Delta J_K J_z^2 - \Delta_K J_\perp^2 \delta_J^4 (J_z^2 + J_\perp^2)$$

$$- \frac{1}{2} \delta_K [J_z^2, (J_z^2 + J_\perp^2)],$$

where $[.]$ is the anti-commutator. The eigenvalues and eigenvectors were obtained by diagonalization of a prolate symmetric top basis set representation of $\hat{H}_{\text{rot}}$. In the end, 39 of the 40 precisely measured lines were used as input to a non-linear least squares fitting procedure. In addition to the optimized rotational parameters ($A_0$, $B_0$, and $C_0$) and the origin ($\ell_{00}$), fits including various combinations of the centrifugal distortion parameters were attempted. Only $\Delta J_K$ for the $X'^1A'$ state and $\Delta_K$ and $\delta_J$ for the $A'^1A''$ state were required. The difference between the observed and calculated transition wavenumbers given in Table I does not exhibit any systematic pattern. The standard deviation of the fit ($\approx 0.0027$ cm$^{-1}$) is commensurate with the estimated measurement uncertainty. The residual for the excluded $^4$Q$_{13}(3)$ ($\ell$ 15 548.2339 cm$^{-1}$) line was 0.0186 cm$^{-1}$. No other transitions associated with the 3$_{13}$ rotational level of the $A'^1A''$ state were observed. The optimized parameters for SiH$_2$ as well as those for the previously determined values for the $X'^1A'$ and $A'^1A''$ states of SiH$_2^{25,26}$ and SiD$_2^{19}$ are given in Table III.

IV. ANALYSIS

A. Energies and transition frequencies

The SiHD DF spectrum, which exhibited a $A'^1A''(0,0,0) \rightarrow X'^1A'(0,v_2,0)$ progression, was fit to the simple anharmonic expression

$$G(0,v_20) = \omega_2(v_2 + 1/2) + x_{22}(v_2 + 1/2)^2$$

(1)

to give $\omega_2 = 872.9(11)$ cm$^{-1}$ and $x_{22} = -3.2(4)$ cm$^{-1}$ and a standard deviation of the fit = 2.0 cm$^{-1}$. The value derived from the analysis of the infrared absorption measurement of a matrix isolation sample$^{32}$ is 854.3 cm$^{-1}$.

B. Intensities and spectral simulation

Modeling the spectrum was critical for assignment and analysis. These calculations were performed by generating
the electric dipole transition moment matrix, $\mu$, and then cross multiplying with the upper and lower state eigenvectors, $\alpha(A''',X')$, to obtain the appropriate transition moment, $\text{TM}$,

$$\text{TM}(A'' \leftrightarrow X') = \alpha(A''') \cdot \mu \cdot g(X').$$  \hspace{1cm} (3)

The TM was then squared and multiplied by the Boltzmann factors appropriate for the approximate 20 K internal temperature. A Lorentzian line shape was superimposed to give the predicted spectra as in Figures 1-3.

Initial simulations used the principal axis systems of the $X' A$ and $A'' A'$ states to calculate the eigenvectors, $\alpha(\text{principal})(A''',X')$ and transition moment matrix, $\mu$, to predict the relative intensities of the $c$-type transitions. The method was checked by comparing observed and predicted relative intensities for the spectral features of the $X' A' \rightarrow A'' A''$ band of SiH$_2$ and SiD$_2$. It became clear that there were many additional, non-$c$-type, spectral features in the $0^0_0 X' A' \rightarrow A'' A''$ band of SiHD. Due to the $C_{2v}$-symmetry of SiH$_2$ and SiD$_2$, the orientation of the principal axes is unaltered upon excitation, whereas for the lower symmetry SiHD molecules, the orientation of inertial axes of the ground and excited states do not coincide. The molecule-fixed axis system is defined by the Eckart conditions, which approximately separates the rotational motion from the vibrational motion. The Eckart conditions depend upon the instantaneous geometry for the electronic state in question.$^{66}$

In order to describe an electronic transition of the molecule, two equilibrium configurations, and so two sets of moving axes must be considered. Hougen and Watson$^{53}$ showed that when a molecule undergoes an electronic transition accompanied by a geometry change, it is necessary to consider molecule-fixed axis systems of both electronic states. These axes have coincident center of mass origins, but one set is usually rotated with respect to the other. The two molecular fixed axis systems are related by a $3 \times 3$ rotation matrix $T$ ("axis switching matrix").$^{53,55,67}$ The equilibria locations of the nuclei (vide infra) in the principal axes for the $A'' A''$ and $X' A'$ states are shown in Figure 6. A rotation angle, $\Omega_0$, that produces the rotation matrix, $T$, which fulfills the Eckart condition is $21.7^\circ$ (Appendix). The location of the $A'' A''$ state nuclei in this rotated axis system (the Eckart axis system) is also shown in Figure 6, as are the angles that the principal and Eckart axes systems make relative to ones that bisect a line joining the D and H nuclei. The relative orientation of the H, D, and, 

![FIG. 6. The location of the nuclei in the principal axis system of the $X' A'$ state (bottom), the principal axis system of the $A'' A''$ state (middle), and the Eckart axis system of the $A'' A''$ state (upper). Also shown are the angles that the principle axes system make relative to one that bisects a line joining the D and H nuclei.](image-url)
The relative orientation of the H, D, and Si nuclei in the principal axis of the $\tilde{X}A'$ and $\tilde{A}A''$ states, as well as that for the $\tilde{A}A''$ state in an Eckart axis. Note that the 21.7° rotation of the principal axis of the $\tilde{A}A''$ state (see text) produces a geometry in the Eckart axis that approximately achieves a mass-weighted shift of the H and D nuclei relative to that of the $\tilde{X}A'$ state.

Si nuclei in the principal axes of the $\tilde{X}A'$ and $\tilde{A}A''$ states, as well as that for the $\tilde{A}A''$ state in the Eckart axis system, is given in Figure 7. Here the principal axes of the three are made to be coincident.

The inertial tensor in the Eckart axis system is non-diagonal and produces rotational parameters $A_0$, $B_0$, $C_0$, and $D_0$ of approximately 12.496 cm$^{-1}$, 4.683 cm$^{-1}$, 2.601 cm$^{-1}$, and 3.698 cm$^{-1}$, respectively (Appendix). These values were used to calculate the eigenvalues and eigenvectors for the $\tilde{A}A''$ state as described in Appendix. The Eckart axis system eigenvectors, $\vec{a}(\text{Eckart})(\tilde{A}A'')$, were then used in Eq. (3) to predict the transition moments and subsequently simulate the spectra.

V. DISCUSSION

A comparison of the observed and predicted spectra in Figure 2 reveals that numerous branch features were not observed even after accounting for the axis switching induced lines. Most obvious is the predicted $^{9}\text{R}_{02}(2)$ transition ($3_{12} \leftarrow 2_{02}$) near 15 571.66 cm$^{-1}$. As other transitions originating from the $2_{02}$ rotational level of the $\tilde{X}A'$ state are observed, it was concluded that the $3_{12}$ rotational level of the $\tilde{A}A''$ state is pre-dissociative. It is also noteworthy that the $3_{13}$ level of $\tilde{A}A''$ state, which is approximately 4 cm$^{-1}$ lower in energy than the $3_{12}$ level, is the upper energy terminus of the perturbed $^{9}\text{Q}_{13}(3)$ transition (Table I). The fluorescence lifetimes of the observed branch features provide additional insight into the predissociation process. The energy level pattern with the observed lifetimes and indicated perturbed and non-observed levels is given in Figure 8. The determined lifetime of 1011 ± 3 ns for the $0_{00}$ level of the $\tilde{A}A''$ state is similar to the 1.1 ± 0.17 µs and 0.93 ± 0.38 µs values for the same rotational level of SiH$_2$ and SiD$_2$, respectively.

A general trend of decreasing lifetime with increasing upper state energy is observed (Table II), similar to that observed for the other isotopologues. The correlation with $K_a$ values is more pronounced with the $0_{00}$, 1$_{10}$, and 2$_{20}$ lifetimes being 1011 ns, 769 ns, and 335 ns, respectively. The 2$_{11}$ level has a significantly longer lifetime than the 1$_{10}$ level, which is 12 cm$^{-1}$ lower in energy indicating that energy and/or $K_a$ is not the only factor dictating pre-dissociation rate. The bi-exponential decay curve for the 2$_{20}$ level is dominated by the fast component (amplitude = 40 016 counts). The lifetime of the weaker (amplitude = 5686 counts) slow component is comparable to that of the 0$_{00}$ level. The most obvious explanation for the observed bi-exponential behavior is that two or more different transitions were simultaneously excited due to a blending of lines.

The LIF excitation data set for SiHD (Table I) is less extensive than the data sets associated with the previous visible or infrared absorption spectra of SiH$_2$. The fluorescence lifetimes are given in parentheses. The dashed lines indicate levels that were not detected due to low fluorescence quantum yield. The 3$_{13}$ level is slightly perturbed.

![Figure 7](image-url) FIG. 7. The relative orientation of the H, D, and Si nuclei in the principal axis of the $\tilde{X}A'$ and $\tilde{A}A''$ states, as well as that for the $\tilde{A}A''$ state in an Eckart axis. Note that the 21.7° rotation of the principal axis of the $\tilde{A}A''$ state (see text) produces a geometry in the Eckart axis that approximately achieves a mass-weighted shift of the H and D nuclei relative to that of the $\tilde{X}A'$ state.

![Figure 8](image-url) FIG. 8. The energy level pattern for the $\tilde{A}A''(0,0,0)$ state of SiHD. The fluorescence lifetimes are given in parentheses. The dashed lines indicate levels that were not detected due to low fluorescence quantum yield. The 3$_{13}$ level is slightly perturbed.
of three parts, resulting from vibration and electronic motion and centrifugal distortions.\textsuperscript{68,69} The centrifugal distortion part is usually negligible for low rotational levels. The vibrational part, $\Delta_0^{\text{vb}}$, is a Coriolis effect; the electronic part, $\Delta_0^{\text{el}}$, results from off diagonal elements of the orbital angular momentum operator. The expression for $\Delta_0^{\text{vb}}$ for molecules having $C_{2v}$-symmetry (e.g., SiH$_2$ and SiD$_2$) is well documented.\textsuperscript{69} The expression for $C_s$-symmetry molecule (e.g., SiHD) is readily obtained from the general expression\textsuperscript{68} and symmetry constraints\textsuperscript{70} to be

$$\Delta_0^{\text{vb}} = \frac{\hbar}{\pi^2 c} \left[ \frac{1}{n_1 + 1} \left( \frac{\omega_1^2}{\omega_1(\omega_1^2 - \omega_2^2)} (\xi_{13}^{(c)} - \omega_1(\omega_1^2 - \omega_2^2)) \left( \frac{\omega_1^2}{\omega_1(\omega_1^2 - \omega_2^2)} (\xi_{13}^{(c)} - \omega_1(\omega_1^2 - \omega_2^2)) \right) \right) + \left( \frac{V_2 + 1}{2} \right) \left( \frac{\omega_2^2}{\omega_2(\omega_2^2 - \omega_3^2)} (\xi_{23}^{(c)} - \omega_2(\omega_2^2 - \omega_3^2)) \left( \frac{\omega_2^2}{\omega_2(\omega_2^2 - \omega_3^2)} (\xi_{23}^{(c)} - \omega_2(\omega_2^2 - \omega_3^2)) \right) \right) + \left( \frac{V_3 + 1}{2} \right) \left( \frac{\omega_3^2}{\omega_3(\omega_3^2 - \omega_1^2)} (\xi_{31}^{(c)} - \omega_3(\omega_3^2 - \omega_1^2)) \left( \frac{\omega_3^2}{\omega_3(\omega_3^2 - \omega_1^2)} (\xi_{31}^{(c)} - \omega_3(\omega_3^2 - \omega_1^2)) \right) \right) \right].$$

(4)

In Eq. (4), $\xi_{ij}^{(c)}$ are the $c$-principal axis component of Coriolis coupling constants between the “$i$-th” and “$j$-th” vibrational mode and $\omega_i$ is the harmonic frequency of the “$i$-th” mode. Theoretical predictions for $\xi_{ij}^{(c)}$ are only available for the ground states SiH$_2$, SiD$_2$, and SiHD.\textsuperscript{37} As part of the present study, density functional theory\textsuperscript{71} (DFT) and time dependent density functional theory\textsuperscript{72} (TDDFT) employing the B3LYP hybrid functional\textsuperscript{73} and the 6-311G+(3df, 3pd) basis set were used to predict $\xi_{ij}^{(c)}$, $\omega_i$, and vibration-rotation parameters, $\alpha_i$, needed for equilibrium structure determination\textsuperscript{(vide infra)}. The DFT-B3LYP and TDDFT-B3LYP calculations were implemented using the GAUSSIAN 03 quantum chemistry program package.\textsuperscript{74} It is not the objective to produce the best set of predicted values, but instead reasonably accurate values obtained at nearly the same level of theory for both the ground and excited states. The results are presented in supplementary material.\textsuperscript{75} The predicted $\xi_{ij}^{(c)}$ and $\omega_i$ values were input into Eq. (4) to predict the $\Delta_0^{\text{vb}}$ values for the ground and excited states of SiH$_2$, SiD$_2$, and SiHD, and are given in Table IV. The predicted $\Delta_0^{\text{vb}}$ values for the ground states of the three isotopologues are in excellent agreement with the observed $\Delta_0$ values. In contrast, the predicted $\Delta_0^{\text{vb}}$ values for the excited states are in relatively poor agreement with the observed $\Delta_0$ values. It is reasonable that the electronic contribution to $\Delta_0$ will be large for the excited states because of the proximity of the $\tilde{a}B_1$, $\tilde{A}^1B_1$, and $\tilde{B}^1A_1$ states in the case of SiH$_2$ and SiD$_2$ and the $\tilde{A}^1A''$, $\tilde{a}^1A'$, and $\tilde{B}^1A'$ states in the case of SiHD. Local perturbations in the excited state could also affect the interpretation of the rotational parameters.

The $A_\theta$, $B_\theta$, and $C_\theta$ rotational parameters of SiHD, SiH$_2$, and SiD$_2$ (Table III) were used to determine the equilibrium rotational constants, $A_e$, $B_e$, and $C_e$ for the ground and excited states of the three isotopologues. The required

**TABLE IV.** Inertial defects (amu·Å$^2$).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta_0(X)\textsuperscript{\alpha}$</th>
<th>$\Delta_0^{\text{vb}}(X)\textsuperscript{\beta}$</th>
<th>$\Delta_0(A)\textsuperscript{\gamma}$</th>
<th>$\Delta_0^{\text{vb}}(A)\textsuperscript{\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiHD</td>
<td>0.083 4(2)</td>
<td>0.0884</td>
<td>0.095 4(2)</td>
<td>0.1035</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>0.072 75(3)</td>
<td>0.0771</td>
<td>0.115 49(4)</td>
<td>0.0897</td>
</tr>
<tr>
<td>SiD$_2$</td>
<td>0.102 29(7)</td>
<td>0.1071</td>
<td>0.137 75(6)</td>
<td>0.1243</td>
</tr>
</tbody>
</table>

$\alpha$ The numbers in parenthesis represents a 1σ error estimate.

$\beta$ Calculated using Eq. (4) and the DFT predicted Coriolis constants and vibrational frequencies (supplementary material).

**TABLE V.** Equilibrium rotational parameters.

<table>
<thead>
<tr>
<th>X$^1$A$^1$ or X$^1$A$'_1$</th>
<th>SiH$_2$</th>
<th>SiHD</th>
<th>SiD$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.005 81</td>
<td>0.040 36</td>
<td>0.140 02</td>
</tr>
<tr>
<td>$\nu = 0^\theta$</td>
<td>8.098 98</td>
<td>7.023 63</td>
<td>3.702 57</td>
</tr>
<tr>
<td>Equal$^5$</td>
<td>8.101 88</td>
<td>7.043 81</td>
<td>3.772 58</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X$^1$A$''$ or X$^1$B$^1$</th>
<th>SiH$_2$</th>
<th>SiHD</th>
<th>SiD$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>-1.495 40</td>
<td>0.057 05</td>
<td>0.151 87</td>
</tr>
<tr>
<td>$\nu = 0^\theta$</td>
<td>18.324 10</td>
<td>4.899 51</td>
<td>3.766 11</td>
</tr>
<tr>
<td>Equal$^5$</td>
<td>17.576 40</td>
<td>4.928 04</td>
<td>3.842 05</td>
</tr>
</tbody>
</table>

$\alpha$ The predicted rotation-vibration parameters (see text).

$\beta$ The experimentally determined $A_\theta$, $B_\theta$, and $C_\theta$ values from Table III.

$\gamma$ The equilibrium rotational parameters $A_e$, $B_e$, and $C_e$. 
rotation-vibration parameters, \( \alpha \), were obtained from the aforementioned electronic structure prediction. The resulting values are presented in Table V. The equilibrium geometrical parameters (\( r_e \) and \( \theta_e \)) for the ground and excited states of SiHD, SiH\(_2\), and SiD\(_2\) were calculated from the determined \( \alpha \), \( R_e \), and \( C_e \) parameters using the STRFIT program.\(^{76}\) Fits for the individual isotopologues, as well as a global fit to all three isotopologues, are presented in Table VI. The determined \( r_e \) and \( \theta_e \) for the \( \tilde{X}^1A_1 \) states are 1.5137(3) Å and 92.04(5)\(^{\circ} \), which compares to the most recent wavefunction-based prediction\(^{55}\) of 1.5187 Å and 92.27\(^{\circ} \). The determined \( r_e \) and \( \theta_e \) for the \( \tilde{A}^1B_1 \) state are 1.4853(6) Å and 122.48(10)\(^{\circ} \), which compares to the most recent wavefunction-based prediction\(^{45}\) of 1.4904 Å and 122.70\(^{\circ} \). Other recent high-level multireference wavefunction calculations\(^{42}\) give \( r_e \) and \( \theta_e \) values for the \( \tilde{X}^1A_1 \) state that range from 1.5112 Å to 1.5171 Å and 92.52\(^{\circ} \) to 92.84\(^{\circ} \), and for the excited \( \tilde{A}^1B_1 \) state that range from 1.4839 Å to 1.4890 Å and 121.68\(^{\circ} \) to 122.26\(^{\circ} \) depending upon the basis set employed.

### VI. CONCLUSION

The LIF spectrum of the 0\( \tilde{0}^0 \tilde{X}^1A' \rightarrow \tilde{A}^1A'' \) band of a cold sample of SiHD has been analyzed and combined with existing data for SiH\(_2\) and SiD\(_2\) to produce an experimentally determined structure. The LIF spectrum of SiHD is significantly more complex than that of either SiH\(_2\) or SiD\(_2\) mainly due to the presence of axis-switching induced transitions. The observed relative intensities of the axis-switching transitions have been successfully modeled. The inertial defects in the \( \tilde{X}^1A_1 \) states of SiH\(_2\) and SiD\(_2\) and the \( \tilde{X}^1A' \) state of SiHD have been successfully modelled assuming a dominant vibronic contribution, whereas those for the excited state are inconsistent with such a model. Similar to SiH\(_2\) and SiD\(_2\), the fluorescence lifetimes rapidly decrease as a function of \( K_a \) from a nominal value of 1 \( \mu \)s for the 0\( _00 \) level. The analysis of the optical spectrum of SiHD performed here will be relevant to future experimental and theoretical investigations of unimolecular dynamics. Optical Stark spectroscopic studies of SiHD based upon the observations presented here are being pursued in our laboratory. The determined ground state rotational parameters for SiHD will facilitate laboratory and radio telescope searches for the \( a \)-type (\( \Delta K_a = \text{even} \), \( \Delta K_c = \text{odd} \)) and \( b \)-type (\( \Delta K_a = \text{odd} \), \( \Delta K_c = \text{even} \)) pure rotational transitions.

### APPENDIX: RELATIVE INTENSITIES AND ECKART AXES

The objective is to predict the relative intensities when the effects of axis switching are considered. The 3 \( \times \) 3 rotation matrix, \( \mathbf{T} \), associated with the 0\( \tilde{0}^0 \tilde{X}^1A' \rightarrow \tilde{A}^1A'' \) transition is defined by Eckart conditions.\(^{55}\)

\[
\sum_{\alpha} m_{\alpha}(\mathbf{T} \cdot \mathbf{r}_{\alpha}(\hat{X})) \times (\mathbf{p}_{\alpha}(\hat{A}) + \mathbf{r}_{\alpha}(\hat{A})) = 0,
\]

where \( \mathbf{r}_{\alpha}(\hat{X}) \) and \( \mathbf{r}_{\alpha}(\hat{A}) \) are the equilibrium position of the \( \alpha \)-th nuclei having mass \( m_{\alpha} \) in the \( \tilde{X}^1A' \) and \( \tilde{A}^1A'' \) electronic state. \( \mathbf{p}_{\alpha}(\hat{A}) \) is the Cartesian displacement vector of the \( \alpha \)-th nuclei in the \( \tilde{A}^1A'' \) electronic state. For strongly bound molecules with low vibrational excitation, the displacement vectors are small. Under these circumstances, it is often possible to use the “zeroth order axis switching” method\(^{33,55}\) that assumes that \( \mathbf{p}_{\alpha}(\hat{A}) = 0 \), in which case \( \mathbf{T}(\mathbf{p}_{\alpha}(\hat{A}) = 0) = \mathbf{T}_0 \). The rotation matrix \( \mathbf{T}_0 \) depends upon the equilibrium location of the nuclei in the principal axes for the \( \tilde{A}^1A'' \) and \( \tilde{X}^1A' \) states, which are given in Figure 6. Under the “zeroth order axis switching” assumption, the Eckart conditions (Eq. (A1)) gives

\[
\mathbf{T}_0 = \begin{bmatrix}
\cos \Omega_0 & \sin \Omega_0 & 0 \\
-\sin \Omega_0 & \cos \Omega_0 & 0 \\
0 & 0 & 1
\end{bmatrix},
\]

where the rotation angle \( \Omega_0 \) is defined by\(^{55}\)

\[
\tan \Omega_0 = \frac{\sum_{\alpha} m_{\alpha}(a_{\alpha}(X)b_{\alpha}(A) - b_{\alpha}(X)a_{\alpha}(A))}{\sum_{\alpha} m_{\alpha}(a_{\alpha}(X)b_{\alpha}(A) + b_{\alpha}(X)a_{\alpha}(A))}.
\]

In Eq. (A3), \( a_{\alpha}(X) \) is the \( a \)-principal axis location of the \( \alpha \)-th nuclei in the \( \tilde{X}^1A' \) electronic state and \( b_{\alpha}(A) \) is the \( b \)-principal axis location of the \( \alpha \)-th nuclei in the \( \tilde{A}^1A'' \) electronic state. A rotation angle, \( \Omega_0 \), of 21.7\(^{\circ} \) is predicted using the \( a \)-principal axis and \( b \)-principal axis coordinates shown in Figure 6. The angles \( \theta_{X} \) and \( \theta_{A} \) shown in Figure 6 are of orientation of the Si–D bond relative to the \( a \)-principal axis for the \( \tilde{A}^1A'' \) and \( \tilde{X}^1A' \) states, respectively. The relative orientation of the H, D, and Si nuclei in the principal axes of the \( \tilde{X}^1A' \) and \( \tilde{A}^1A'' \) states, as well as that for the \( \tilde{A}^1A'' \) state in an Eckart axes, is given in Figure 7. Note that the 21.7\(^{\circ} \) rotation of the principal axis of the \( \tilde{A}^1A'' \) state produces an orientation in the Eckart axis that approximately achieves a mass-weighted shift of the H and D nuclei relative to that of the \( \tilde{X}^1A' \) state. Also note that \( \Omega = \Omega_0 + (\theta_X - \theta_A) \), where \( \Omega \) is the angle between the \( \tilde{A}^1A'' \) state structure in an Eckart axes and the \( \tilde{X}^1A' \) structure in the principal axis system when the two systems are made to be coincident (see Figure 7).

### ACKNOWLEDGMENTS

This research has been supported by the National Science Foundation, Division of Chemistry, CHE-1265885 (ASU).
The inertial tensor, \( \mathbf{I} \), for the \( A^1A'' \) state expressed in the Eckart axis system is (amu Å²),
\[
\mathbf{I} = \begin{bmatrix}
1.761 & -1.390 & 0 \\
-1.390 & 4.698 & 0 \\
0 & 0 & 6.458
\end{bmatrix}.
\] (A4)

Taking the inverse of \( \mathbf{I} \) and multiplying by the appropriate constant gives the rotational Cartesian tensor (in cm⁻¹),
\[
\mathbf{B} = \begin{bmatrix}
12.496 & 3.698 & 0 \\
3.698 & 4.683 & 0 \\
0 & 0 & 2.601
\end{bmatrix}.
\] (A5)

It is convenient to write the matrix elements of \( \mathbf{H}^\text{rot} \) (= \( \mathbf{J} \times \mathbf{B} \times \mathbf{J} \)) in spherical tensor form and express these elements in a type \( \Gamma \) convention axis system (i.e., a right-handed system with the \( a \)-principal axis = molecular fixed \( \alpha \)-axis) prolate symmetric top basis set,
\[
\langle J',k_\alpha|\mathbf{H}^\text{rot}|J,K_a\rangle = \delta_{J,J'}(-1)^{J-J'}(2J+1)(J+1)J \times \sum_{k=0}^{\min(J,J')} (-1)^{J}(2k+1)^{1/2} \begin{bmatrix} \mathbf{J} & \mathbf{J} & \mathbf{J} \\
\mathbf{k} & \mathbf{k} & \mathbf{k}
\end{bmatrix} \times \begin{bmatrix} \mathbf{J} & \mathbf{k} & \mathbf{k} \\
\mathbf{k} & \mathbf{k} & \mathbf{k}
\end{bmatrix} T_{\text{tr}}^{k_\alpha}(B).
\] (A6)

In Eq. (A6), \( k_\alpha \) is the projection of the rotational angular momentum on the \( a \)-principal axis and \( T_{\text{tr}}^{k_\alpha=0,1,2}(B) \) are the molecular fixed axis spherical tensor components of the rotational constant tensor \( \mathbf{B} \). The non-zero values of \( T_{\text{tr}}^{k_\alpha=0,1,2}(B) \) are
\[
T_{00}^{\alpha}(B) = -\frac{1}{\sqrt{3}} (A + B + C),
\] (A7)
\[
T_{02}^{\alpha}(B) = \frac{1}{\sqrt{6}} (2A - B - C),
\] (A8)
\[
T_{22}^{\alpha}(B) = \frac{1}{2} (B - iC),
\] (A9)
\[
T_{21}^{\alpha}(B) = \mp D.
\] (A10)

It is evident from the \( 3j \)-symbol in Eq. (A6) that the off-diagonal term, \( D \), produces a \( \Delta k_\alpha = \pm 1 \) mixing of prolate symmetric top basis functions. As a consequence, in addition to the “perpendicular,” \( c \)-type \( (\Delta J = 0, \pm 1, \Delta K_a = \pm 1, \pm 3, \ldots \Delta K_c = 0, \pm 2, \ldots) \) transitions, there are “parallel” \( \Delta J = 0, \pm 1, \Delta K_a = 0, \pm 2 \) transitions. The mixing of prolate symmetric top basis functions, and hence the intensities of the axis-switching induced transitions, is relatively large due to the relatively large value \( D \). For example, the eigenvector for the \( |1_{11} \rangle \) rotational level of the \( A^1A'' \) state in the principal axis system is
\[
|1_{11} \rangle = \frac{1}{\sqrt{2}} \left[ |J = 1, k_\alpha = +1 \rangle - |J = 1, k_\alpha = -1 \rangle \right],
\] (A11)

whereas in the Eckart axis system it is
\[
|1_{11} \rangle = c_1|J = 1, k_\alpha = +1 \rangle - c_1|J = 1, k_\alpha = -1 \rangle + c_2|J = 1, k_\alpha = 0 \rangle,
\] (A12)
with \( c_1 = 0.657 \) and \( c_2 = 0.370 \).
43. See supplementary material at http://dx.doi.org/10.1063/1.4954702 for tables of: (a) the calculated ground state vibration rotation parameters, experimental and equilibrium rotational constants; (b) calculated excited state vibration rotation parameters, experimental and equilibrium rotational constants, and (c) calculated harmonic frequencies (cm⁻¹) and Coriolis constants.