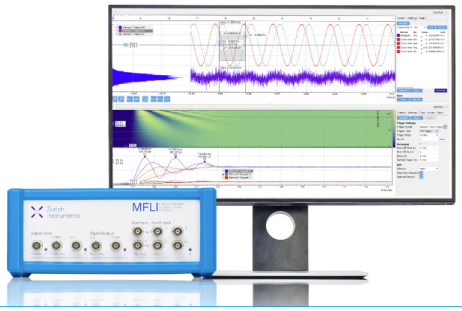
The Journal of Chemical Physics

Optical spectra of the silicon-terminated carbon chain radicals SiC_nH (n = 3,4,5)

Cite as: J. Chem. Phys. **141**, 044310 (2014); https://doi.org/10.1063/1.4883521
Submitted: 27 February 2014 . Accepted: 03 June 2014 . Published Online: 29 July 2014

D. L. Kokkin, N. J. Reilly, R. C. Fortenberry, T. D. Crawford, and M. C. McCarthy



Optical spectra of the silicon-terminated carbon chain radicals SiC_nH ($n = 3,4,5$)

D. L. Kokkin,[1,2,a)] N. J. Reilly,[1,2,b)] R. C. Fortenberry,[3,c)] T. D. Crawford,[3] and M. C. McCarthy[1,2,d)]
[1]*Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA*
[2]*School of Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge, Massachusetts 02138, USA*
[3]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA*

(Received 27 February 2014; accepted 3 June 2014; published online 29 July 2014)

The gas-phase optical spectra of three silicon-terminated carbon chain radicals, SiC_nH ($n = 3 - 5$), formed in a jet-cooled discharge of silane and acetylene, have been investigated by resonant two-color two-photon ionization and laser-induced fluorescence/dispersed fluorescence. Analysis of the spectra was facilitated by calculations performed using equation-of-motion coupled cluster methods. For SiC_3H and SiC_5H, the observed transitions are well-described as excitations from a $^2\Pi$ ground state to a $^2\Sigma$ state, in which vibronic coupling, likely involving a higher-lying Π state with a very large predicted *f*-value (close to unity), is persistent. The lowest $^2\Sigma$ states of both species are characterized by a rare silicon triple bond, which was identified previously [T. C. Smith, H. Y. Li, D. J. Clouthier, C. T. Kingston, and A. J. Merer, J. Chem. Phys. **112**, 3662 (2000)] in the lowest $^2\Sigma$ state of SiCH. Although a strong $\Pi - \Pi$ transition is predicted for SiC_4H, the observed spectrum near 505 nm more likely corresponds to excitation to a relatively dark Σ state which is vibronically coupled to a nearby Π state. In contrast to the chains with an odd number of carbon atoms, which exhibit relatively sharp spectral features and lifetimes in the 10–100 ns range, SiC_4H shows intrinsically broadened spectral features consistent with a ~100 fs lifetime, and a subsequent long-lived decay (>50 μs) which we ascribe to mixing with a nearby quartet state arising from the same electronic configuration. The spin-orbit coupling constants for both SiC_3H and SiC_5H radicals were determined to be approximately 64 cm^{-1}, similar to that of SiCH (69.8 cm^{-1}), suggesting that the unpaired electron in these species is localized on the silicon atom. Motivated by the new optical work, the rotational spectrum of linear SiC_3H was detected by cavity Fourier-transform microwave spectroscopy in the 13–34 GHz range. Each rotational transition from the $^2\Pi_{3/2}$ ground state exhibits well-resolved Λ-doubling and hyperfine structure; the derived rotational constant of $B = 2.605$ GHz is in excellent agreement with our calculations. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4883521]

I. INTRODUCTION

Both silicon and carbon are among the most abundant elements in circumstellar and interstellar environments and thus play vital roles in astrochemical processes. The carbon chain is a persistent structural motif among interstellar molecules: many hydrogen-terminated carbon chains (C_nH), including both neutral and ionized species, have been observed in a variety of astronomical sources.[1,2] Because small silicon-containing species are also quite conspicuous in circumstellar shells of certain evolved carbon stars, silicon-substituted analogues of known or postulated carbon chains may be plausible targets for astronomical detection; they are also likely to be highly polar and possess conjugated structures, implying that they have strong electronic transitions in the visible region of the spectrum. For these reasons, appropriately "doped" carbon chains are attractive as potential carriers of the elusive diffuse interstellar bands (DIBs),[3] for which carbon chains have been proposed as viable candidates (see, for example, Ref. 4 and references therein).

Motivated by this possibility, several silicon-terminated carbon chain radicals of the form SiC_nH ($n = 2, 4 - 6$), were identified in a jet-cooled silane-acetylene discharge by Fourier-transform microwave (FTMW) spectroscopy.[5] All were determined to have linear or nearly linear geometries with $^2\Pi$ ground states and exhibited well-resolved hyperfine structure, with regular ($^2\Pi_{1/2}$ lowest in energy) and inverted ($^2\Pi_{3/2}$ lowest) rotational ladders for n even and odd, respectively. While it should also have been possible to detect the rotational spectrum of the missing member of the series – SiC_3H – searches for its transitions were unsuccessful.

In light of the non-detection of the linear SiC_3H isomer, Sun *et al.* predicted in a recent theoretical study that several stable ring isomers should lie close in energy to the linear ground state, including a rhomboidal structure, located 11.2 kcal/mol above ground, in which the hydrogen atom

a)Current address: Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA.
b)Current address: Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA.
c)Current address: Department of Chemistry, Georgia Southern University, Statesboro, Georgia 30460, USA.
d)Author to whom correspondence should be addressed. Electronic mail: mccarthy@cfa.harvard.edu

is bonded *para* to silicon.[6] Both linear and rhomboidal isomers of SiC_3, as well as highly energetic isomers of other species – notably isofulminic acid (HONC), lying 84 kcal/mol above ground – have been detected using the same discharge source,[7–9] so it is not unreasonable to posit that energetic isomers of SiC_3H could be efficiently formed in the silane/acetylene discharge; however, the non-detection of the linear isomer remained surprising.

The electronic spectra of many C_nH chains have now been studied in connection with the DIBs using fluorescence, absorption (cavity ring-down), and mass-selective techniques.[10] By analogy with the C_4H and C_6H radicals, which exhibit fairly strong, well-resolved transitions in the visible region to excited states of Π symmetry (origin bands at 420 nm[11] and 526 nm,[12] respectively), it was suggested[5] that the isovalent *l*-SiC_3H and *l*-SiC_5H radicals should be good candidates for optical detection. In contrast to the well-characterized carbon chains, however, almost no optical data exists for the silicon-bearing radicals, the sole exception being the shortest member in the series, SiCH, whose $\widetilde{A}^2\Sigma^+ - \widetilde{X}^2\Pi_i$ transition was first observed in emission by Cireasa and Cossart[13] in a discharge through a flowing mixture of hexamethyldisilane and helium. This transition was subsequently investigated in the region 600–815 nm by Smith *et al.* using laser-induced fluorescence.[14] Detailed analysis of the rotationally resolved electronic spectrum yielded the first ever identification of a silicon triple bond – in the first excited state, which has Σ symmetry – with a bond length of ≈1.61 Å; in contrast, the triply bonded Σ state of isovalent CCH lies significantly below (by nearly 0.5 eV[15]) the excited Π state.

The unusual bonding in the excited state of SiCH in comparison to CCH serves to emphasize that, beyond their relevance to astrophysics, the investigation of such systems has intrinsic fundamental value in elucidating differences in bonding and electronic structure between carbon and silicon. In this paper, we report the optical spectra of the silicon-terminated carbon chains SiC_3H, SiC_4H, and SiC_5H, produced in a jet-cooled discharge of silane and acetylene, by means of resonant two-color two-photon ionization (R2PI) spectroscopy. Laser-induced fluorescence and dispersed fluorescence spectra were recorded for SiC_3H to confirm that the observed isomer has a linear geometry (the other chains are not amenable to fluorescence detection). Interpretation of the spectra has been facilitated by calculations of the ground and several excited states of SiC_nH radicals (for $n = 3 - 6$) using coupled cluster and equation-of-motion coupled-cluster (EOM-CC) methods. Motivated by the new optical data and high-level quantum chemical calculations, the rotational spectrum of *l*-SiC_3H has now been observed by FTMW spectroscopy in the 13–34 GHz range, and precise spectroscopic constants derived for its $^2\Pi_{3/2}$ ground state.

II. EXPERIMENTAL DETAILS

The silicon-terminated carbon chains (SiC_nH) were produced by applying an electric discharge to a 1%SiH_4/1%C_2H_2/Ar premix during the early stages of adiabatic expansion into a large source chamber (typical pressure with the gas expanding is 3×10^{-6} Torr). The expansion was skimmed 50 mm downstream by a 2 mm skimmer prior to passing into a differentially pumped extraction chamber (typical operating pressure 10^{-7} Torr). The skimmed beam was then probed between the extraction grids via a two color scheme, in which the resonant photon was produced by a Nd:YAG-pumped dye laser which operates in the 390–700 nm range. The resulting electronically excited molecules were subsequently ionized using 193 nm radiation from an excimer laser containing Ar/F_2 premix. The power of the excimer laser was adjusted such that non-resonant ion signal during scans was minimized. Each spectrum required the use of several laser dyes; while no attempt was made to normalize for laser power, the output was kept approximately constant ∼10 mJ per pulse throughout the entire 390–700 nm range by mixing overlapping dye solutions and/or adjusting the pump laser power as necessary. While the pure carbon chains C_nH often exhibit origin-dominated transitions,[16,17] the origin band of SiC_3H was relatively weak when 193 nm was used as the ionizing wavelength, leading us to suspect that ionization was occurring near threshold. Indeed, the relative strength of this band increased by a factor of almost two when higher energy 157 nm (F_2) radiation was used instead. No such dependence was observed for the longer chains, both of which have lower IPs and whose origin bands occur at higher energies.

Laser-induced fluorescence/dispersed fluorescence (LIF/DF) studies were undertaken in a separate experimental apparatus to determine ground state vibrational frequencies for comparison with calculations. In this experiment, jet-cooled SiC_3H was generated using the same gas premix and pulsed discharge source, and laser-induced fluorescence was imaged by *f*/1 optics and detected using a monochromator equipped with a photomultiplier tube (PMT). A small (14 cm) monochromator was used as a broad bandpass filter (FWHM 30 nm) during excitation scans to limit spectral contamination from metastable Ar and other abundant discharge products, notably C_2 and Si_2, which have strong transitions throughout this region.[18,19] For DF, a 1 m monochromator was operated with 0.5 mm slits to record moderate resolution emission spectra (FWHM ∼30 cm^{-1}) from electronically excited SiC_3H in the vibrationless level and the two lowest excited vibronic levels. A cursory search for SiC_5H by LIF/DF was unsuccessful, presumably owing to the much shorter lifetime of the upper state – ∼10 ns, compared to 100 ns for SiC_3H – which is comparable to the rise-time of the PMT used in this work (lifetimes were estimated by adjusting the time delay between the tunable and ionizing photons in R2PI). The SiC_4H spectrum appears to be intrinsically broadened and thus is not a good target for LIF detection; no obvious decay in R2PI signal for SiC_4H was observed even when the ionization laser was delayed by 50 μs relative to the tunable radiation, possibly indicating mixing with a quartet state.

A renewed search for rotational transitions of linear SiC_3H was undertaken concurrently with the optical spectroscopy with the same FTMW spectrometer and discharge nozzle source as that used in our earlier work on silicon-terminated carbon chains.[5] Prior to undertaking the new search, the experimental conditions were optimized to produce SiC_4H in high yield. Lines of SiC_4H were observed

most intensely in a mixture of 0.1%SiH_4/0.2%C_2H_2 diluted in neon, and a voltage of 1 kV delivered to the inner electrode (closest to the valve orifice) of the discharge nozzle. SiC_3H has a $^2\Pi_{3/2}$ ground state with a large magnetic *g* factor, which causes its low-*J* rotational transitions to be easily split or broadened by even a small Zeeman field; for this reason, a search for a relatively high *J* transition ($J = 11/2 - 9/2$) was undertaken first. The search range covered ±1% in frequency of our best estimate, which was determined by scaling our calculated rotational constant by the ratio between that predicted (based on the same calculations) and measured (from Ref. 5) for SiC_5H.

III. COMPUTATIONAL DETAILS

Ground state geometries were optimized utilizing coupled cluster singles, doubles, and perturbative triples [CCSD(T)][20] making use of unrestricted Hartree-Fock reference wavefunctions (UHF)[21,22] with Dunning and coworkers' cc-pVTZ basis set[23,24] with silicon utilizing the cc-pV(T+d)Z basis set[25] simply called cc-pVTZ from here on. Computations of vertical excitation energies and oscillator strengths from these CCSD(T)/cc-pVTZ geometries were carried out at the CCSD level of theory[26] as well as energies with the approximate, iterative triples CC3 method[27–30] in the EOM formalism[31,32] using augmented forms of the aforementioned Dunning triple-zeta basis sets[25,33] and restricted open-shell reference (ROHF) wavefunctions[34–37] previously shown to provide superior treatment of excited states of closely related linear carbon radicals.[38]

Building from earlier studies involving excited states of silicon-containing interstellar molecules,[39–41] adiabatic excitation energies were computed from the energy differences between the optimized forms of the ROHF-CCSD/aug-cc-pVTZ ground and ROHF-EOM-CCSD/aug-cc-pVTZ excited state geometries. Harmonic vibrational frequencies were computed via finite differences of energies for each geometry which allowed for further refinement of the adiabatic excitation energies for zero-point vibrational energy (ZPE) corrections.[42] All computations of the linear radicals were undertaken in the C_{2v} point group, the largest Abelian subgroup of $C_{\infty v}$. The PSI3 suite of computational chemistry programs[43] was used for all of the computations, with the exception of the $\langle s^2 \rangle$ expectation values, which were calculated with the CFOUR quantum chemistry package.[44]

IV. RESULTS

A. Computational results

The SiC_nH radicals have $^2\Pi$ ground states as determined by rotational spectroscopy,[5] but the electronic configurations differ between two subclasses. Chains with an odd number of carbon atoms have three electrons in the π highest occupied molecular orbital (HOMO) while only one electron is present in the π HOMO for the chains with an even number of C atoms. Thus, SiC_3H has an electronic configuration of (core)$10\sigma^2\ 2\pi^4\ 11\sigma^2\ 3\pi^3$, and SiC_5H is (core)$14\sigma^2\ 2\pi^4\ 15\sigma^2\ 3\pi^4\ 4\pi^3$, whereas SiC_4H is (core)$11\sigma^2\ 12\sigma^2\ 2\pi^4\ 13\sigma^2\ 3\pi^4\ 4\pi^1$. Similar electronic configurations have been noted for the analogous carbon chains, including those with more than four heavy atoms.[10,38,45] Rotational constants derived from the optimized geometries (Table II) of each chain are in excellent agreement (<1.3%) with those obtained in the earlier microwave work,[5] and with the new microwave data on SiC_3H reported herein (see Sec. IV B 2).

The calculations indicate that chains within the respective isovalent odd and even *n* groupings have similar electronic excitation behavior. As listed in Table I, the strongest optical

TABLE I. Excitation energies (in eV) for the first few states of the $^2\Pi$ SiC_nH radicals ($n = 3 - 6$) from coupled cluster aug-cc-pVTZ computations.

					Vertical			Adiabatic		
Molecule	State	$\langle s^2 \rangle$	Excitation character		CCSD	f	CC3	CCSD	ZPE-CCSD	Expt.
SiC_3H	$1\ \Sigma^+$	0.839	$11\sigma \rightarrow 3\pi$	(0.88 β)	2.19	0.003	1.98	2.04	2.08	1.83
	$2\ \Pi$	2.799	$3\pi \rightarrow 4\pi^*$	(0.59 β; 0.45 α)	2.50	10^{-5}	2.51	…	…	…
			$3\pi \rightarrow 5\pi^*$	(0.39 β; 0.30 α)						
	$3\ \Pi$		$4\pi \rightarrow 5\pi^*$		5.36	1.06	…	…	…	…
SiC_4H	$1\ \Sigma^-$	3.320	$13\sigma \rightarrow 4\pi$	(0.64 β; 0.59 α)	2.66	10^{-5}	2.54	…	…	2.45
			$4\pi \rightarrow 4\pi\ 13\sigma \rightarrow 4\pi$	(0.21 $\alpha\beta$)						
	$2\ \Pi$	2.707	$3\pi \rightarrow 4\pi$	(0.43 β; 0.41 α)	3.18	0.012	3.06	2.84	2.73	…
			$3\pi \rightarrow 4\pi$	(0.31 β)						
			$4\pi \rightarrow 7\pi^*$	(0.25 α)						
SiC_5H	$2\ \Pi$	2.707	$4\pi \rightarrow 5\pi^*$	(0.63 β; 0.47 α)	2.25	10^{-6}	2.25	…	…	…
			$4\pi \rightarrow 6\pi^*$	(0.30 β; 0.23 α)						
	$1\ \Sigma^+$	0.856	$15\sigma \rightarrow 4\pi$	(0.89 β)	2.29	0.003	2.07	2.12	2.16	1.94
	$3\ \Pi$		$2\pi \rightarrow 5\pi^*$		4.91	0.68	…	…	…	…
SiC_6H	$1\ ^2\Sigma^-$		$17\sigma \rightarrow 5\pi$	(0.64 β; 0.58 α)	2.68	10^{-5}	2.56	…	…	…
			$5\pi \rightarrow 5\pi\ 17\sigma \rightarrow 5\pi$	(0.20 $\alpha\beta$)						
	$2\ ^2\Pi$		$4\pi \rightarrow 5\pi$	(0.40 β; 0.36 α)	2.71	0.015	2.57	…	…	
			$4\pi \rightarrow 5\pi$	(0.28 β)						
			$5\pi \rightarrow 7\pi^*$	(0.26 α)						

TABLE II. Bond lengths (in Å) and rotational constants B (in MHz, with experimental values from Ref. 5 and the present work in parentheses beneath) for relevant electronic states of SiC_nH ($n = 3 - 6$) from CCSD and EOM-CCSD calculations with an aug-cc-pVTZ basis.

		Electronic state		
Molecule	Parameter	$1\,^2\Pi$	$1\,^2\Sigma^+$	$2\,^2\Pi$
SiC_3H	Si–C1	1.692	1.611	1.853
	C1–C2	1.351	1.38	1.307
	C2–C3	1.225	1.211	1.251
	C3–H	1.062	1.062	1.063
	B	2594.70	2675.95	2427.12
		(2605.0528)		
SiC_4H	Si–C1	1.805	1.781	1.774
	C1–C2	1.231	1.22	1.303
	C2–C3	1.372	1.376	1.305
	C3–C4	1.21	1.209	1.256
	C4–H	1.063	1.062	1.063
	B	1398.23	1415.92	1392.24
		(1415.7035)		
SiC_5H	Si–C1	1.693	1.613	
	C1–C2	1.334	1.373	
	C2–C3	1.236	1.215	
	C3–C4	1.362	1.376	
	C4–C5	1.213	1.209	
	C5–H	1.062	1.062	
	B	878.69	890.98	
		(883.8539)		
SiC_6H	Si–C1	1.801		
	C1–C2	1.234		
	C2–C3	1.363		
	C3–C4	1.216		
	C4–C5	1.374		
	C5–C6	1.209		
	C6–H	1.063		
	B	571.40		
		(578.1810)		

transition of the odd-n chains is dominated by a single excitation from the σ HOMO-1 into the π HOMO creating a filled π orbital and a $^2\Sigma^+$ excited state. In contrast, the even n radicals do not have appreciably strong transitions to a Σ^+ state; instead, their visible spectra are predicted to be dominated by transitions to a Π state. These $\Pi - \Pi$ transitions are primarily composed of transitions out of the fully occupied π HOMO-1 into the singly occupied π HOMO (the second-highest occupied molecular orbital or SHOMO), though excitations out of the SHOMO into higher π^* orbitals also contribute to the overall excitation character.

The differences in excitation character for the two subclasses are reflected in geometry changes upon excitation. As indicated in Table II, a commonality between SiC_3H and SiC_5H is that the major changes in bond length are confined to the Si–C–C moiety, with a significant shortening (by 0.08 Å) of the Si–C bond upon excitation to create a nominal Si–C triple bond, while the neighboring C–C bond length increases slightly. Alternation in the C–C bond lengths in the ground state becomes more pronounced in the excited state. The net result for both is that the overall chain length decreases slightly upon excitation, with an accompanying increase in the rotational constant of a few percent; indeed, this behavior was confirmed experimentally for SiCH.[14] For the excited Π state of SiC_4H, the Si–C bond length decreases less markedly, while large (>0.05 Å), alternating increases/decreases in adjacent C–C bond lengths give an excited state that is essentially cumulenic, with a rotational constant that decreases very slightly with respect to the ground state geometry. Such differences are reflected in the experimental spectra: the odd-n spectra show conspicuous activity in the Si–C stretch and Si–C–C bending modes, while the strongest features in the SiC_4H spectrum are due to modes involving the carbon chain.

B. SiC_3H

1. Optical data

a. Identification of spectral carrier. Figure 1 shows the electronic spectrum recorded for $m/z = 65$ in the region 14 500–16 500 cm^{-1}. To confirm that the carrier contained silicon, the measurement was repeated using a discharge of pure acetylene, and as expected, none of the same spectral features were observed. The band at 197 cm^{-1} relative to the origin is close to the lowest bending frequency observed in the isovalent C_4H carbon chain (189 cm^{-1} for the $\tilde{B}$ state[11] and at 220 cm^{-1} for the $\tilde{A}$ state[46,47]), giving some confidence that the structure of the SiC_3H radical detected here is also a linear chain. Additionally, a frequency of 165 cm^{-1} is predicted for the SiCC bend of linear SiC_3H (in the ground state) by Sun *et al.*[6] However, owing to the earlier non-detection of this isomer by microwave spectroscopy, and to the number of low-lying nonlinear SiC_3H isomers predicted by theory,[6] LIF-DF spectroscopy was needed to firmly establish that the observed spectrum arises from the linear form.

A portion of the LIF spectrum containing the origin and several higher vibronic bands, compared to the R2PI spectrum, is shown in Fig. 2. The signal-to-noise (S/N) ratio is significantly worse than in the R2PI spectrum owing to both the short fluorescence lifetime (making rejection of scattered laser light difficult), and measures taken to reduce spectral interference by the C_2 Swan bands,[18] as well as Si_2[19] (a low discharge voltage, in comparison to the R2PI experiment, and a large nozzle-laser distance were required to prevent vibrationally and rotationally hot Si_2 and C_2 from obscuring the SiC_3H spectrum). Nevertheless, the LIF spectrum shows several clear coincidences with the R2PI spectrum recorded at $m/z = 65$, strongly suggesting that these features are good targets for further study by DF spectroscopy.

DF spectra recorded from the three lowest observed vibrational levels of electronically excited SiC_3H are shown in Fig. 3. For the purpose of identifying the structure of SiC_3H (the spectra are discussed in more detail in Sec. IV B 1 b), it suffices to note that the origin DF spectrum is dominated by a single feature at a Stokes-shift of 64 cm^{-1}, which cannot be plausibly assigned to a vibrational mode of any isomer calculated by Sun *et al.*[6] Rather, the only sensible assignment of this feature is to the upper spin-orbit component of the Π ground state of the linear chain. A value of 64 cm^{-1} for A_{so} is

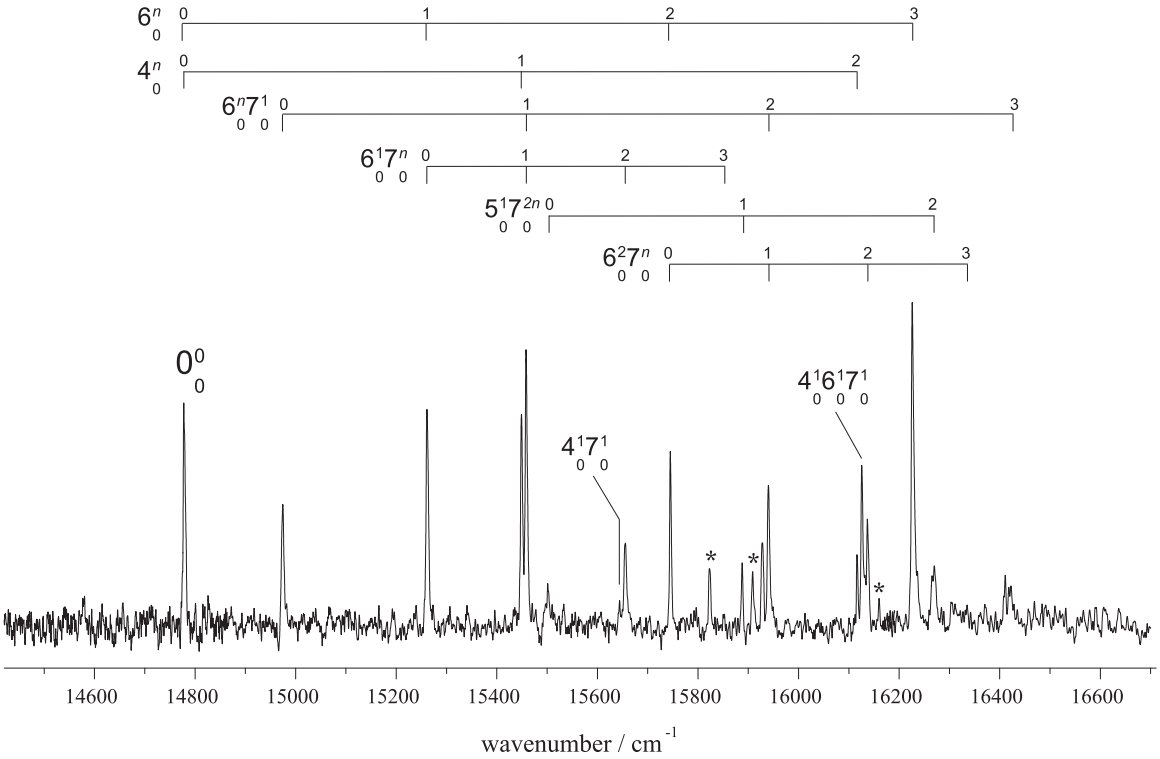


FIG. 1. R2PI spectrum of SiC_3H from an acetylene-silane discharge. Assignments are for the linear chain; features designated with asterisks are presently unassigned and may belong to another isomer.

consistent with that reported for SiCH (69.8 cm^{-1}[114]), SiC_2H (72.3 cm^{-1}[148]), and that derived herein for SiC_5H (64 cm^{-1}; see Sec. IV D). The stark contrast between the excitation spectrum – containing strong transitions involving several vibrational modes – and the emission spectrum – which is dominated by a single feature – suggests a fairly vertical transition in which off-diagonal vibrational transitions are largely brought about by vibronic coupling.

b. Spectral assignment. With confirmation that the observed spectrum arises from – or at least, is dominated by – the linear isomer, it is possible to proceed with an assignment based on the predicted transition energies, *f*-values, and vibrational frequencies given in Tables I and II. Owing to its comparatively high oscillator strength and close agreement between experimental and calculated excitation energies, it is reasonable to assume that the Σ state dominates the observed

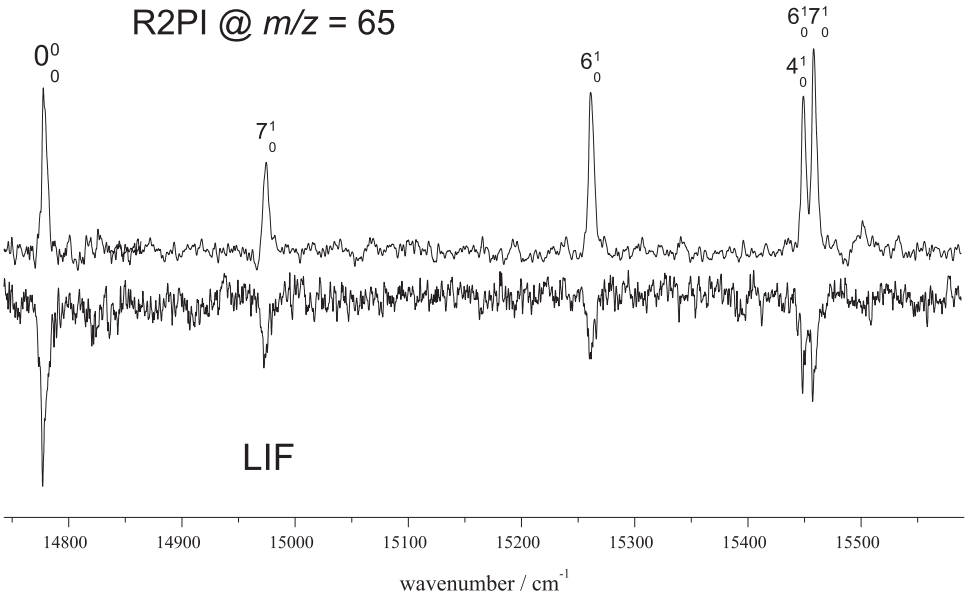


FIG. 2. Comparison between the laser-induced fluorescence and R2PI spectra (recorded at $m/z = 65$) of a silane-acetylene discharge. Intensity discrepancies between the two spectra result primarily from the bandpass used for fluorescence detection.

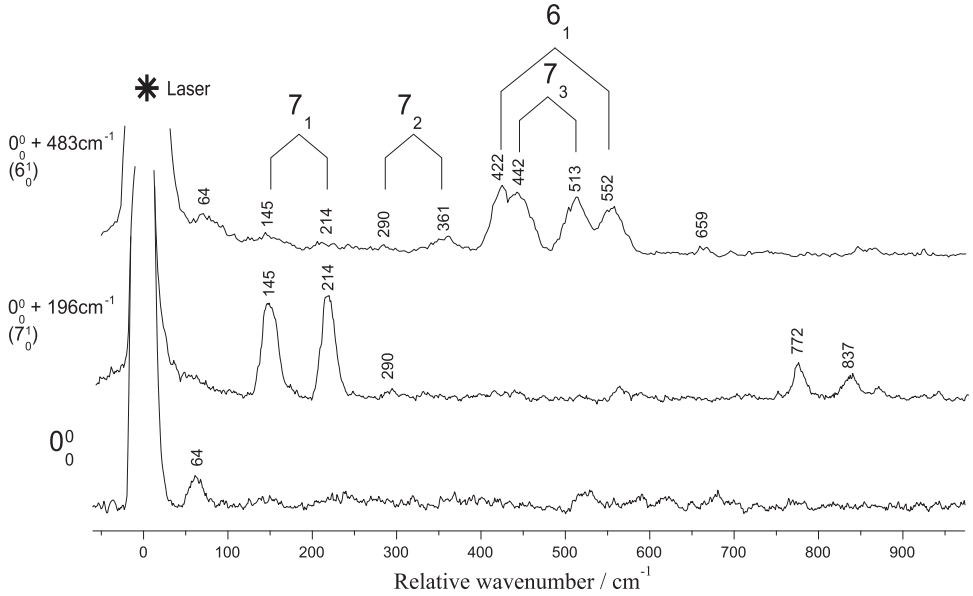


FIG. 3. Dispersed fluorescence spectra from the 0^0, 7^1 (Si–C–C bend), and 6^1 (C–C–C bend) levels of the $1\,^2\Sigma$ state of SiC_3H radical.

transition. As indicated in Fig. 1 and Table III, it is fairly straightforward to assign a large fraction of the observed bands to harmonic combinations involving a few vibrational modes with fundamental frequencies of 197 cm^{-1}, 483 cm^{-1}, and 672 cm^{-1}, which we ascribe to the SiCC and CCC bends and the Si–C stretch, respectively; the agreement with the predicted frequencies for these modes in the Σ state is compelling. In this assignment, both Herzberg-Teller-induced transitions and Franck-Condon-allowed transitions are present, reminiscent of the electronic spectrum of isovalent C_4H. Although an electronic state of Π symmetry is predicted to lie nearby (at 2.5 eV), the *f*-value for excitation to this state (10^{-5}) is almost certainly too small to explain the persistent vibronic coupling throughout the observed spectrum; rather, we believe that a higher-lying Π-state with an extremely strong predicted transition ($f = 1.026$ at 5 eV) is implicated. This conclusion is supported by EOM-CCSD computations of oscillator strengths at Si–C–C bond angles from 180° to 95°. While both the Σ and higher-lying Π transitions decrease in strength by a factor of several over this range, the latter transition remains at least two orders of magnitude stronger, while the transition strength to the lower Π-state near 2.5 eV remains negligible.

Weak features designated with asterisks – at 1046, 1132, and 1383 cm^{-1} above the origin – have no obvious assignment to the Σ state of SiC_3H. In this light, an alternative explanation is that the excited state of the observed transition is in fact the nearby Π state, which can be coupled to the brighter Σ state by π vibrational modes, and would have a richer spectrum owing to the Renner-Teller effect (potentially explaining the unassigned bands). We reject this notion, because (1) if it were true, one would expect to see the stronger $\Sigma - \Pi$ transition nearby; (2) with the exception of those few weak bands, the spectrum has a straightforward assignment in terms of harmonic combinations, reflecting the relative simplicity one tends to expect of a Σ state; (3) several

TABLE III. Excited state band positions (in cm^{-1}) and assignments for SiC_3H. Frequencies are given relative to the origin band at 14 778 cm^{-1}.

Frequency	Assignment
0	0^0_0
197	7^1_0
415	
462	
484	6^1_0
563	
672	4^1_0
681	$6^1_0 7^1_0$
724	5^1_0
869	$4^1_0 7^1_0$
878	$6^1_0 7^2_0$
967	6^2_0
1045	
1110	$5^1_0 7^2_0$
1131	
1150	$4^1_0 6^1_0$
1163	$6^2_0 7^1_0$
1201	
1339	4^2_0
1348	$4^1_0 6^1_0 7^1_0$
1359	$6^2_0 7^2_0$
1383	
1448	$6^3_0 + 3^1_0$
1492	$5^1_0 7^4_0$
1634	
1641	$6^3_0 7^1_0$
1645	$6^3_0 7^1_0$

TABLE IV. Vibrational energies (in cm^{-1}, from Fig. 3) and assignments for the $\widetilde{X}^2\Pi_i$ ground state of SiC_3H.

Vibrational energy (cm^{-1})	Assignment
0	0_0^0 ($^2\Pi_{1/2}$)
64	($^2\Pi_{3/2}$)
145	7_1 ($\mu\ ^2\Sigma_{1/2}$)
214	7_1 ($\kappa\ ^2\Sigma_{1/2}$)
290	7_2 ($\mu\ ^2\Pi_{1/2}$)
360	7_2 ($\kappa\ ^2\Pi_{3/2}$)
422	6_1 ($\mu\ ^2\Sigma_{1/2}$)
440	7_3 ($\mu\ ^2\Sigma_{1/2}$)
510	7_3 ($\kappa\ ^2\Sigma_{1/2}$)
552	6_1 ($\kappa\ ^2\Sigma_{1/2}$)
659	7_4 ($\mu\ ^2\Pi_{1/2}$)
772	$4_1 7_1$ ($\mu\ ^2\Sigma_{1/2}$)
837	$4_1 7_1$ ($\kappa\ ^2\Sigma_{1/2}$)

of the derived vibrational frequencies are in excellent agreement with the prediction for the Σ state; and (4) the Si–C bond length is predicted to increase significantly (0.11 Å) in the Π state, which would result in a reduced frequency for the Si–C stretch; in contrast, the Si–C stretch frequency increases upon excitation (see further discussion of DF spectra below), which is consistent with the prediction for the Σ state. On the basis of this analysis, we conjecture that these weak unassigned features belong to a different isomer (see Sec. V B).

Because our spectral resolution is insufficient to determine band types, and thereby distinguish upper state levels possessing Σ or Π vibronic symmetry, we use DF spectroscopy to seek qualitative insight into the vibronic bands at 197 cm^{-1} and 483 cm^{-1} above the origin. Ground state vibrational assignments are presented in Table IV. The spectrum from the 197 cm^{-1} level (Fig. 3) has a fairly simple interpretation, because it is dominated by a pair of features located at 145 cm^{-1} and 214 cm^{-1}. Both are in reasonable agreement with the predicted ν_7 (SiCC bend) π_x and π_y frequencies (153 cm^{-1} and 168 cm^{-1}), which are harmonic frequencies calculated with the unpaired electron forced into the π_x or π_y system (Table V); the small difference between the π_x and π_y vibrational frequencies suggests a small Renner-Teller interaction for this mode (π_x and π_y frequencies are degenerate in the absence of coupling with orbital angular momentum). The separation between the experimental bands (69 cm^{-1}) is also very close to the spin-orbit splitting (64 cm^{-1}) in the origin DF spectrum. The term symbols for vibronic levels of a $^2\Pi$ state take the form $^{2S+1}K_P$, where $K = |\Lambda + l|$ and $P = |\Lambda + l + \Sigma|$. According to an expression from Hougen,[49] when the Renner-Teller interaction is small, the two $^2\Sigma_{1/2}$ levels corresponding to $l = \pm 1$ are separated by approximately $\sqrt{A_{eff}^2 + \epsilon^2\omega^2(v+1)^2}$, where A_{eff} is an effective spin-orbit coupling constant. Thus, the observed separation is consistent with that expected from spin-orbit, and yields a Renner parameter of order $\epsilon_7 \sim 0.07$ cm^{-1}. Additionally, because 197 cm^{-1} is close to the calculated ν_7 frequency in the Σ-state (207 cm^{-1}), we assign the 197 cm^{-1} feature as the Herzberg-Teller-induced 7_0^1 transition. We interpret the features in the DF spectrum at 770 cm^{-1} and 833 cm^{-1} (also separated by approximately A_{so}) similarly: as combinations of the two ν_7 RT-components with the Si–C stretch (ν_4), yielding a Si–C stretch frequency (627 cm^{-1}) in excellent agreement with theory (632 cm^{-1}), and significantly smaller than the corresponding frequency in the excited state (672 cm^{-1}), as predicted.

The transition at $0_0^0 + 483$ cm^{-1} can also be assigned as a Herzberg-Teller-induced transition to the CCC bend (ν_6). Because ν_7 has a very small Renner-Teller splitting, its transitions should be fairly harmonic; indeed, bands can be found near 290 cm^{-1} and 360 cm^{-1} (2 quanta) and 440 cm^{-1} and 510 cm^{-1} (three quanta). We therefore assign the remaining strong bands, at 422 cm^{-1} and 552 cm^{-1}, as the lower ($\mu\ ^2\Sigma_{1/2}$) and upper ($\kappa\ ^2\Sigma_{1/2}$) components of ν_6, respectively. This assignment gives a zeroth-order ν_6 frequency near 480 cm^{-1}, in reasonable agreement with predicted harmonic π_x and π_y frequencies (433 cm^{-1} and 465 cm^{-1}), although the present assignment implies a larger Renner-Teller splitting in this mode than suggested from our calculations. The preponderance of the SiCC bend in the CCC bend emission spectrum probably results from mode mixing upon excitation (i.e., Duschinsky mixing).

Table I summarizes the calculated and observed band origins for SiC_3H – SiC_5H, in addition to preliminary calculations on SiC_6H. The experimentally determined band origin position for SiC_3H is 1.83 eV. The SiC_3H vertical CCSD $1^2\Sigma^+$ excited state over-estimates this excitation (2.19 eV) by 0.18 eV. The adiabatic CCSD excited state is much closer at 2.04 eV while the zero-point corrected adiabatic excitation energy (ZPE-CCSD) actually increases the excitation energy to 2.08 eV. The ZPE increase is simply a consequence of the predicted increase in the excited state vibrational frequencies; while this increase is indeed borne out for all of the assigned modes, it is probably an artifact for the highest frequency modes (particularly the CH stretch), which one would expect to be largely unaffected by electronic excitation within the Si–C moiety. The vertical CC3 computation gives a transition energy closest (within 0.15 eV) to the experimental value, probably owing to the inclusion of triples, which provides for a better description of the excitation.[38] The agreement between the experimental and theoretical vibrational frequencies is generally good for both the ground and excited states, with the exception of ν_5. While it is possible to assign combination bands involving this mode and ν_7, these assignments should be considered somewhat tentative, and may require higher resolution study to confirm their association with the $1^2\Sigma$ state of *l*-SiC_3H.

2. Microwave data

For an appreciably polar (calculated $\mu = 0.77$ D[6]) radical such as SiC_3H, it is surprising that optical detection precedes microwave detection. However, earlier searches for *l*-SiC_3H, under experimental conditions which favored the production

TABLE V. Experimental and theoretical harmonic vibrational frequencies (in cm^{-1}) of the ground ($^2\Pi$) and first excited ($^2\Sigma$) states of of SiC_3H. Experimental bending frequencies in the ground state are given for the lowest Renner-Teller component.

	Ground				Excited			
Mode	Description		Calc.	Expt.	Description		Calc.	Expt.
ν_1	σ (a_1)	C1–H stretch	3463		σ	C1–H stretch	3477	
ν_2	σ (a_1)	C2–C1 stretch	2016		σ	C2–C1 stretch	2191	
ν_3	σ (a_1)	C2–C3 stretch	1442		σ	C2–C3 stretch	1491	1492
ν_4	σ (a_1)	Si–C3 stretch	632	627	σ	Si–C3 stretch	683	672
ν_5	π (b_1)	C2–C1–H bend	655		π (b_2)	C2–C1–H bend	635	723
	π (b_2)	C2–C1–H bend	521		π (b_1)			
ν_6	π (b_2)	C3–C2–C1 bend	465		π (b_1)	C3–C2–C1 bend	514	483
	π (b_1)	C3–C2–C1 bend	433	422	π (b_2)			
ν_7	π (b_2)	Si–C3–C2 bend	168		π (b_1)	Si–C3–C2 bend	208	197
	π (b_1)	Si–C3–C2 bend	153	145	π (b_2)			

of similar chains, were unsuccessful. In light of the unambiguous optical data presented here, and our new theoretical calculations of its molecular structure, a second search for the rotational spectrum of *l*-SiC_3H was undertaken. Within 0.5% of our best prediction, a line with closely-spaced structure (see Fig. 4), characteristic of an open-shell molecule possessing both Λ-doubling and hydrogen hyperfine splitting, was observed. Subsequent chemical assays and other tests quickly confirmed that the carrier of these features requires both SiH_4 and HCCH, and that the carrier is paramagnetic, as expected for SiC_3H. On the assumption that this line is the $J = {}^{11}/_2 - {}^9/_2$ transition, searches were soon undertaken for other higher- and lower-*J* transitions. Ultimately, five lines were observed between 13 and 34 GHz (Table VI), each separated by approximately 5.2 GHz. Using a standard effective Hamiltonian for a molecule in an isolated $^2\Pi$ state with hyperfine structure,[50–52] it was possible to determine several spectroscopic constants, including the rotational constant to high precision (Table VII). The experimental rotational constant agrees to within 0.4% with our calculation, and to better than 0.2% by scaling from SiC_5H; other constants are in excellent agreement with those predicted from SiC_5H. Although it is not obvious why our earlier search for *l*-SiC_3H was unsuccessful, several factors may have conspired to prevent detection, including a search for a lower-*J* transition which is even more sensitive to the Zeeman effect, and the lack of a hydrocarbon precursor which is an especially good source for carbon chains with three carbon atoms.

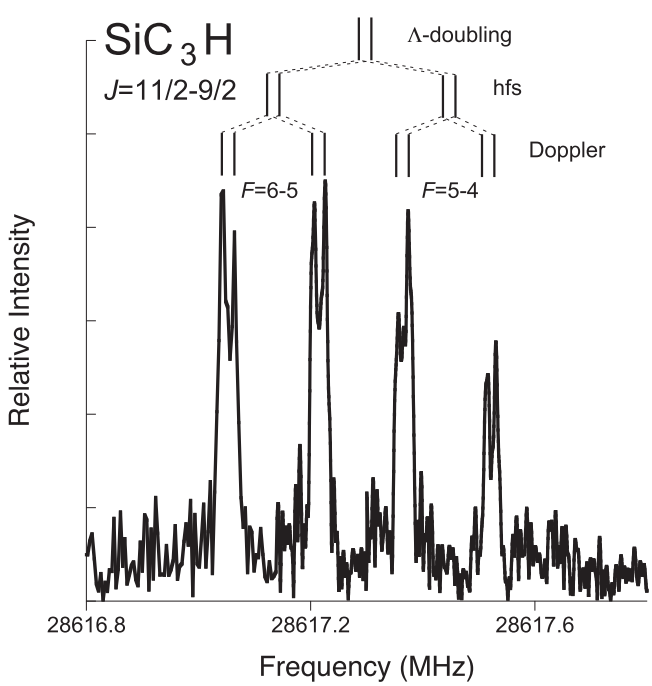


FIG. 4. The FTMW spectrum of the J = $^{11}/_2 - {}^9/_2$ transition in the $^2\Pi_{3/2}$ ground state of SiC_3H radical.

TABLE VI. Hyperfine-split rotational transitions of SiC_3H in the $\widetilde{X}^2\Pi_{3/2}$ state.

Transition[a]		*e*/*f*[b]	Frequency[c]	O–C[d]
$J' \rightarrow J$	$F' \rightarrow F$	Λ-component	(MHz)	(kHz)
2.5→ 1.5	3 → 2	*f*	13 007.447	− 1.8
		e	13 007.454	0.3
3.5→ 2.5	4 → 3	*f*	18 210.774	− 1.0
		e	18 210.787	2.9
	3 → 2	*f*	18 211.485	3.6
		e	18 211.485	− 5.3
4.5→ 3.5	5 → 4	*f*	23 413.977	− 4.9
		e	23 414.001	3.7
	4 → 3	*f*	23 414.415	− 3.3
		e	23 414.437	4.0
5.5→ 4.5	6 → 5	*f*	28 617.128	0.9
		e	28 617.149	− 0.4
	5 → 4	*f*	28 617.438	4.5
		e	28 617.453	− 2.6
6.5→ 5.5	7 → 6	*f*	33 820.227	− 0.7
		e	33 820.259	0.9
	6 → 5	*f*	33820.461	0.3
		e	33 820.489	− 1.8

[a]The coupling scheme is $F = J + I(\mathrm{H})$.
[b]Designation of *e* and *f* levels is based on the assumption that the lambda-type doubling constant *q* is negative. See Table VII.
[c]Estimated 1σ measurement uncertainties are 2 kHz.
[d]Observed minus calculated frequencies O–C are derived from the best-fit constants in Table VII.

TABLE VII. Spectroscopic constants of SiC_3H in the $\widetilde{X}^2\Pi_i$ state (in MHz).

Constant	Expt.[a]	Predicted
A_{eff}	1 950 000[b]	...
B	2605.0528(3)	2610[c]
$10^6 D$	209.(5)	127[d]
q	−0.092(11)[e]	<0.2[f]
$a + (b + c)/2$	4.9(5)	2.1[f]
b	−41.5(10)	−30[f]

[a]Uncertainties (in parentheses) are 1σ in the last significant digit. Constants derived from hyperfine-split rotational transitions in Table VI.
[b]Derived from optical data (see text).
[c]Theoretical rotational constant scaled by ratio of measured value to that calculated for SiC_5H.
[d]Value for C_5H (Ref. 68).
[e]Sign assumed to be negative. See Ref. 68.
[f]From SiC_5H (Ref. 5).

C. SiC_4H

The R2PI spectrum of SiC_4H ($m/z = 77$) is shown in Fig. 5. Owing to the low S/N ratio and large linewidths of the spectral features, as well as the wide variety of possible isomers of SiC_4H,[53] we restrict our attention only to the coarse vibronic structure of the most conspicuous bands. In contrast to SiC_3H, the spectrum shows activity in fewer vibrational modes, and significantly broader (>30 cm^{-1}) band profiles which were found to be independent of the expansion conditions; they are therefore likely intrinsic to the radical. This behavior is qualitatively similar to that found for the isovalent chain C_5H, whose optical spectrum was also observed by R2PI spectroscopy.[17] Although calculations indicate that the spectrum of SiC_4H should be dominated by a modestly strong ($f = 0.012$) transition to a Π electronic state with an origin near 2.8 eV, we suspect instead that the upper state is more likely the Σ state predicted near 2.6 eV, which the calculated $\langle s^2 \rangle$ value indicates has predominantly quartet character. Several considerations justify such an assignment. First, the difference between the observed (2.45 eV) and predicted (3.06 eV) CC3 energy for the Π state seems unacceptably large in comparison to the discrepancy observed for the Σ states of the odd-n chains (≤0.15 eV). Second, the predicted $\Pi - \Pi$ transition should be several times stronger than the observed $\Pi - \Sigma$ transitions of SiC_3H and SiC_5H, yet resonant SiC_4H signal was found to be nearly an order of magnitude weaker, under the same experimental conditions, and independent of the ionization wavelength. Third, the calculated geometry and frequencies for the Σ state indicate two acetylenic bonds, consistent with the observed spectrum (note bands at 2038 cm^{-1} and 2300 cm^{-1} above the origin, which have similar widths to the origin band), while the excited Π state is calculated to be more cumulenic, with only one acetylenic stretching frequency.

More generally, the spectrum appears qualitatively consistent with a transition to a "dark" Σ state which can be vibronically coupled to a brighter Π state. It contains three 2000 cm^{-1} progressions: a short, weak one associated with the origin; a much stronger one blue-shifted from the origin by 595 cm^{-1}, which shows even broader (FWHM > 70 cm^{-1}) features; and a moderately intense one, apparently associated with the latter progression, blue-shifted by a further 515 cm^{-1} and with still-broader bands, which are not built onto the origin band. It therefore seems natural to interpret the weaker 2000 cm^{-1} progression as belonging to the "pure" Σ state, with the stronger two possibly arising from vibronic coupling to the higher-lying bright Π state via a 595 cm^{-1} mode.

If one accepts this tentative assignment, a good candidate for the 595 cm^{-1} coupling mode would be the CCC bend (ν_6), which is calculated to have a frequency of 653 cm^{-1} in the Σ state. The progression blue-shifted by 515 cm^{-1} would then likely correspond to the Si–C stretch, which has a predicted frequency of 507 cm^{-1}, although $2\nu_8$ (570 cm^{-1}), ν_7 (464 cm^{-1}), and ν_4 (1038 cm^{-1}, built onto the origin) could also contribute to the large widths of features within this progression; the complicated band profiles of the corresponding features near 22 950 cm^{-1} and 24 900 cm^{-1} suggests the presence of multiple components. Several features, including one near 1870 cm^{-1}, resist obvious assignments at present. The lack of activity in the low frequency region of the spectrum makes it difficult to assign features at higher energy with confidence. Because transitions to the Π state likely become

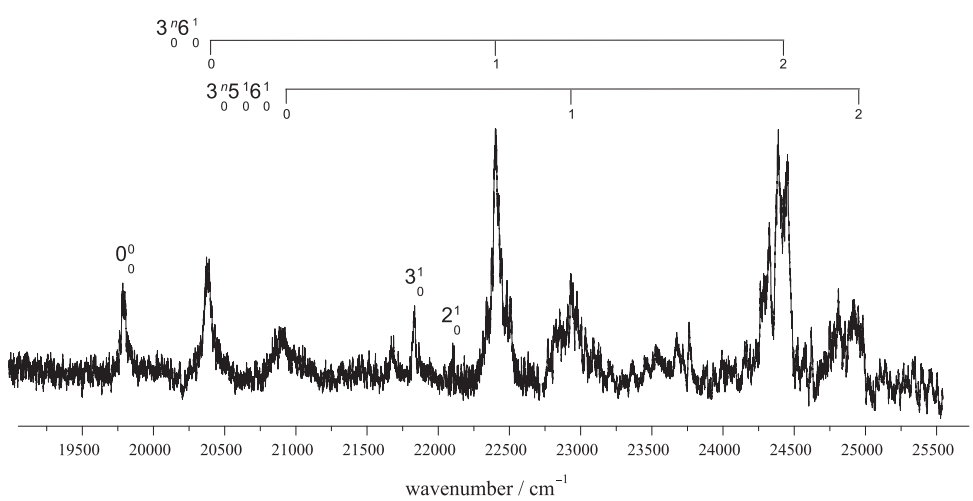


FIG. 5. R2PI spectrum of SiC_4H from an acetylene-silane discharge. Assignments are for the linear isomer.

TABLE VIII. Experimental excited state band positions (in cm^{-1} relative to the origin at 19 803 cm^{-1}) and assignments for *l*-SiC_4H.

Frequency	Assignment
0	0_0^0
595	6_0^1
1113	$5_0^1 6_0^1$
1871	
2031	3_0^1
2300	2_0^1
2600	$3_0^1 6_0^1$
3130	$3_0^1 5_0^1 6_0^1$
4574	$3_0^2 6_0^1$
5101	$3_0^2 5_0^1 6_0^1$

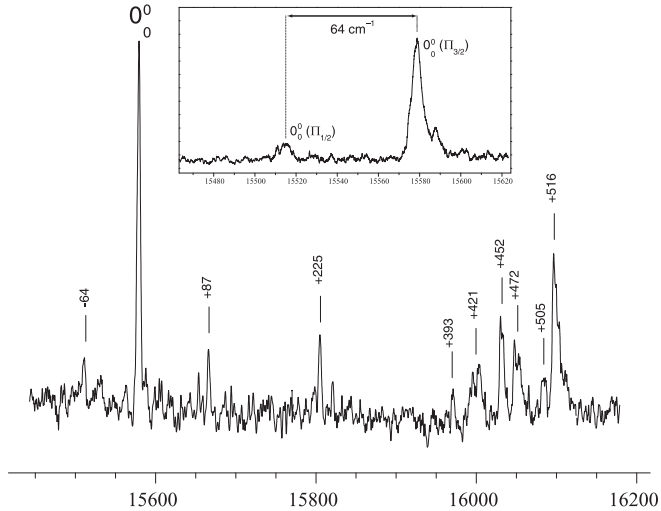


FIG. 6. R2PI spectrum of SiC_5H from an acetylene-silane discharge, and (inset) spin-orbit separation observed for the origin band under hotter expansion conditions.

important at higher energy, it seems imprudent to proffer a more detailed assignment of the increasingly congested region above ~23 000 cm^{-1}. In addition – like SiC_3H – SiC_4H can also adopt several stable cyclic structures[53] which also contain optical chromophores and can be expected to have transitions within the very broad spectral range covered in our experiments.

Measured vibronic band positions and excited state frequencies based on our tentative assignments are given in Table VIII. Table IX summarizes the calculated ground and excited state frequencies for SiC_4H in addition to the experimentally determined excited state frequencies. Because of the intrinsic broadening in the spectrum, dispersed fluorescence was not attempted to measure ground state frequencies. Extremely long-lived decay of the R2PI signal from this radical suggests mixing with a quartet state (see Sec. V A).

D. SiC_5H

The spectrum of SiC_5H (m/z = 89) is shown in Fig. 6. Only a relatively short region of the spectrum was surveyed; at increasing excitation energy, the upper state lifetime (~5 ns) becomes significantly shorter than the temporal jitter of our ionization laser. Consequently, the measurement of higher vibronic bands was increasingly difficult; for the same reason, fluorescence detection was not attempted. The experimental origin for SiC_5H is 1.93 eV; as was found for SiC_3H, the vertical CC3 excitation energy (2.07 eV) gives the closest agreement with experiment for excitation to the $1^2\Sigma^+$ state of SiC_5H. The adiabatic excitation energy for this state is 2.12 eV and, as for the $1^2\Sigma^+$ state of SiC_3H, the ZPE-corrected adiabatic CCSD excitation energy for the $1^2\Sigma^+$ state of SiC_5H is slightly higher, owing to the predicted increase in the excited state vibrational frequencies, and thus compares less favorably with experiment.

Spectral assignments and experimental and theoretical vibrational frequencies are given in Tables X and XI. As with the SiC_3H spectrum, a Herzberg-Teller transition involving the SiCC bend (87 cm^{-1} above the origin) is apparent, while both Herzberg-Teller and Franck-Condon allowed transitions involving the lowest CCC bend are present. Our

TABLE IX. Experimental and theoretical harmonic vibrational frequencies of the lowest three electronic states of SiC_4H.

	Ground ($1^2\Pi$)			2Π			1Σ		
Mode	Description		Calc.	Description		Calc.	Description		Calc.	Expt.
ν_1	σ (a_1)	C1–H stretch	3469	σ (a_1)	C1–H stretch	3446	σ	C1–H stretch	3472	
ν_2	σ (a_1)	C2–C1 stretch	2208	σ (a_1)	C2–C3 stretch	2099	σ	C2–C3 stretch	2266	2308
ν_3	σ (a_1)	C3–C4 stretch	2050	σ (a_1)	C3–C4 stretch	1646	σ	C3–C4 stretch	2106	2032
ν_4	σ (a_1)	C2–C3 stretch	1022	σ (a_1)	C2–C1 stretch	1098	σ	C2–C1 stretch	1038	
ν_5	σ (a_1)	Si–C4 stretch	477	σ (a_1)	Si–C4 stretch	498	σ	Si–C4 stretch	508	515
ν_6	π (b_2)	C2–C1–H bend	689	π (b_1)	C2–C1–H bend	387	π	C2–C1–H bend	653	595
	π (b_1)	C2–C1–H bend	615	π (b_2)	C2–C1–H bend	386				
ν_7	π (b_2)	Carbon chain bend	522	π (b_2)	Carbon chain bend	289	π	Carbon chain bend	464	
	π (b_1)	Carbon chain bend	460	π (b_1)	Carbon chain Bend	259				
ν_8	π (b_1)	Carbon chain bend	303	π (b_2)	Carbon chain bend	162	π	Carbon chain bend	285	
	π (b_2)	Carbon chain bend	264	π (b_1)	Carbon chain bend	117				
ν_9	π (b_1)	Si–C4–C3 bend	112	π (b_2)	Si–C4–C3 bend	72	π	Si–C4–C3 bend	122	
	π (b_2)	Si–C4–C3 bend	93	π (b_1)	Si–C4–C3 bend	70				

TABLE X. Excited state band positions (in cm^{-1}) and assignments for SiC_5H. Frequencies are given relative to the origin band at 15 579 cm^{-1}.

Frequency	Assignment
– 64	0_0^0 ($\Sigma \leftarrow \Pi_{1/2}$)
0	0_0^0 ($\Sigma \leftarrow \Pi_{3/2}$)
74	
87	11_0^1
115	
226	10_0^1
242	
324	
394	$10_0^1 11_0^2$
421	9_0^1
452	10_0^2
473	8_0^1
506	$10_0^2 11_0^1$
516	6_0^1

calculations indicate that the vibronically induced transitions in this radical probably result from coupling to a higher-lying (by ∼2 eV) Π state with an *f*-value near unity, which is also similar to that found for SiC_3H.

Because the Si–C bond is predicted to significantly shorten upon excitation, we assign the strong band at 516 cm^{-1} as the Si–C stretch, which gives a frequency in good agreement with theory (511 cm^{-1}), while moderately intense bands at 474 cm^{-1} and 426 cm^{-1} probably correspond to the CCC bending modes (predicted frequencies of 518 cm^{-1} and 452 cm^{-1}, respectively). Most of the bands in this region can subsequently be assigned to these few modes and combinations thereof; weaker bands associated with the very close-lying (0.03 eV), dark Π state might arise from vibronic coupling to the brighter Σ state.

Under "hotter" expansion conditions – high discharge voltage, low backing pressure, reduced nozzle-skimmer distance – it was possible to enhance the relative intensity of features lying 10 cm^{-1} to the blue and 64 cm^{-1} to the red of the origin band (see inset in Fig. 6). While the former is probably a vibrational sequence band (several vibrational modes could cause the observed blue-shift, on the basis of our calculations) the 64 cm^{-1} band is most readily interpreted as the transition from the upper spin-orbit component ($^2\Pi_{1/2}$) of the ground state to the vibrationless excited state, which yields a spin-orbit splitting which is close in magnitude with that derived previously for SiCH (69.8 cm^{-1}[14]), SiC_2H (73.2 cm^{-1}[48]), and SiC_3H (64 cm^{-1}, this work). The very small variation of the spin-orbit separation with chain length suggests that the unpaired electron in these radicals resides predominantly on the silicon atom, as was suggested in the earlier rotational study.[5]

V. DISCUSSION

A. Comparison with isovalent C_nH chains

For the isovalent carbon chain radicals, a roughly linear relationship between chain length and excitation wavelength has been observed both for the odd- and even-*n* numbered chains, for electronic transitions which have the same excitation character (e.g., the transitions for the odd-*n* chains which involve excitation from the σ HOMO-1 to the partially filled π HOMO). This behavior has been rationalized in terms of the free-electron model, whereby π electrons are delocalized over the length of the chain, yielding a decrease in T_e with increasing chain length. With the earlier detection of SiCH by Smith *et al.*,[14] and the detections of SiC_3H and SiC_5H herein, it would seem that sufficient data now exists to establish whether a similar trend occurs for the optical transitions of the odd-*n* silicon-terminated chains. However, the electronic states of the isovalent carbon chains which correspond to the present optical transitions are not the high-lying Π states, but rather the nearly degenerate lowest Σ and Π

TABLE XI. Experimental and theoretical harmonic vibrational frequencies (in cm^{-1}) of the ground ($^2\Pi$) and first excited ($^2\Sigma$) states of of SiC_5H. radical.

	Ground			Excited			
Mode	Description		Calc.	Description		Calc.	Expt.
ν_1	σ (a_1)	C1–H stretch	3469	σ	C1–H stretch	3475	
ν_2	σ (a_1)	C2–C1 stretch	2157	σ	C3–C2 stretch	2349	
ν_3	σ (a_1)	C3–C4 stretch	2029	σ	C2–C1 stretch	2161	
ν_4	σ (a_1)	C4–C5 stretch	1548	σ	C4–C5 stretch	1541	
ν_5	σ (a_1)	C3–C2-Stretch	971	σ	C3–C4 stretch	1014	
ν_6	σ (a_1)	Si–C5 stretch	487	σ	Si–C5 stretch	509	516
ν_7	π (b_1)	C2–C1–H bend	676	π	C2–C1–H bend	651	
	π (b_2)	C2–C1–H bend	604				
ν_8	π (b_1)	Carbon chain bend	515	π	Carbon chain bend	518	473
	π (b_2)	Carbon chain bend	497				
ν_9	π (b_2)	Carbon chain bend	430	π	Carbon chain bend	452	418
	π (b_1)	Carbon chain bend	398				
ν_{10}	π (b_1)	Carbon chain bend	203	π	Carbon chain bend	245	226
	π (b_2)	Carbon chain bend	203				
ν_{11}	π (b_1)	Si–C5–C4 bend	75	π	Si–C5–C4 bend	98	87
	π (b_2)	Si–C5–C4 bend	74				

states. The energy separation of these states (Σ minus Π) for the chains $C_{2n}H$ ($n = 1 - 3$) is, respectively, −0.45 eV,[15] 0.026 eV,[48] and 0.181 eV.[47] The Σ states can be generated by removing an electron from a non-bonding orbital on the terminal carbon and placing it in the highest occupied π orbital, which is a bonding orbital. Consequently, the terminal C–C bond significantly shortens in the Σ state,[54] approaching the acetylenic value of 1.21 Å.

In contrast to the $C_{2n}H$ chains, which have closely spaced electronic ground states of Σ or Π symmetry, the ground electronic states of $SiC_{2n+1}H$ always have Π symmetry, and they are well-separated from the excited Σ states. This is due to unfavourable hybridization of the Si 3*s* and 3*p* orbitals in comparison to the carbon 2*s* and 2*p* orbitals,[55] which raises the energy of the highest partially filled, bonding π HOMO relative to the fully occupied, non-bonding σ MO centered on silicon. Nevertheless, the electronic configurations of the excited Σ states in the silicon-terminated chains are analogous to those of the low-lying Σ states of the isovalent carbon chains. The first excited Σ states arise from promotion of an electron in a σ non-bonding MO into the highest-lying partially occupied Π MO. In SiC_3H, this corresponds to excitation from the HOMO-1 to the HOMO, while for SiC_5H, it is a HOMO ← HOMO-2 transition. As for the C_nH analogues, the highest σ MO continues to drop in energy relative to the partially filled π orbital with increasing chain length, shifting the Σ ← Π transition further to the blue (we predict a vertical transition near 2.5 eV for SiC_7H). The calculations indicate that this transition should produce a rare SiC triple bond (length ≈ 1.61 Å), which is borne out by the available experimental evidence. Analysis of the rotationally resolved SiCH electronic spectrum by Smith *et al.*[14] gave ground and excited state SiC bond lengths of 1.693 Å, and 1.612 Å, respectively;[14] while for SiC_3H, our LIF and DF spectra suggests that the Si–C stretching frequency increases significantly upon electronic excitation, from 630 cm^{-1} to 672 cm^{-1}. That the triply-bonded states of these species lie several tens of kcal/mol above the doubly-bonded ground states underscores the well-known reluctance of silicon to form multiple bonds.

The main difference between the optical spectra of the two C_nH "families" – specifically, that the spectra of the odd-*n* chains are intrinsically broadened,[17] while those of the even-*n* chains (for chains shorter than C_8H) are sharp – persists also for their silicon-terminated analogues. Intrinsic broadening in the optical spectra of carbon chain radicals has been ascribed to internal conversion, owing to a high density of vibrational states in the ground electronic state;[56] vibronic coupling between low-lying Σ and Π states, particularly for longer chains (e.g., C_8H[57]); and to intersystem crossing.[58] While the upper state lifetime for the odd-*n* chains indeed decreases with chain length (from 100 ns to 10 ns), the "lifetime" that we infer from intrinsic broadening in the SiC_4H spectrum – approx. 100 fs – would seem to suggest a different relaxation mechanism. Because the first excited Σ states of all the species studied herein are all well-separated from the Π ground electronic states, it is not obvious why internal conversion should not be similarly persistent for both odd-*n* and even-*n* chains.

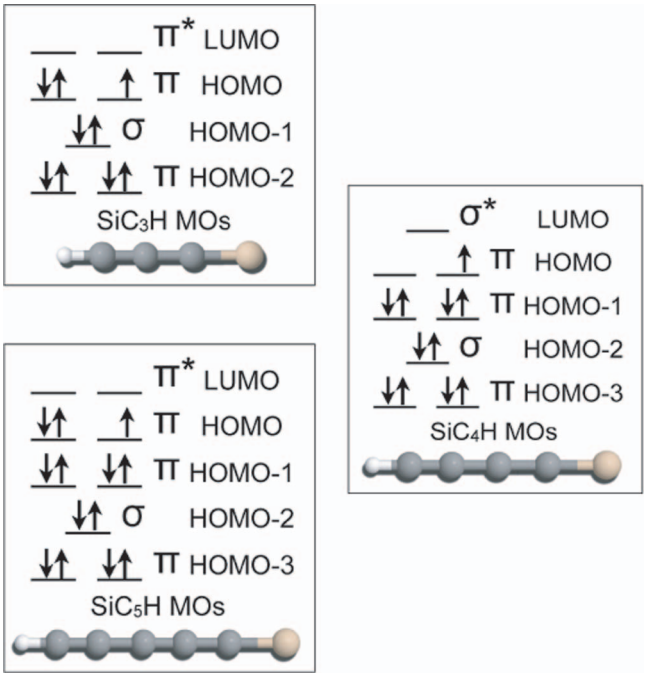


FIG. 7. Frontier orbital occupancies for the linear isomers of SiC_3H, SiC_4H, and SiC_5H.

Rather, we believe that intersystem crossing is the dominant broadening mechanism in the SiC_4H spectrum, and likely takes place in other members of the series. Figure 7 shows schematic electronic configurations which apply for the odd-*n* (left) and even-*n* (right) SiC_nH chains. For the odd-*n* chains, the lowest quartet state arises from promotion of an electron in the π-bonding HOMO into the anti-bonding LUMO. The HOMO-LUMO gap in these species lies in the near UV, significantly higher than the lowest Σ states. In contrast, for the even-*n* chains, the first excited Σ (σ HOMO-2 to the π HOMO) and Π (π HOMO-1 to the π HOMO) states are both generated from excitations within bonding MOs, and can give rise to quartets with similar energies; consequently, the potential for doublet-quartet mixing is significantly increased in these systems relative to the odd-*n* chains. The excited state relaxation dynamics of SiC_4H were probed in R2PI by delaying the ionizing photon relative to the resonant photon. Even with a delay of 50 μs (the longest delay possible with our detection geometry, because species in longer-lived states exit the extraction region), no significant decay in resonant signal was observed. The lifetime broadening in the spectrum can be reconciled with the very long excited state lifetime inferred from our experimental timings by noting that former can arise from rapid crossing to a nearby quartet state following electronic excitation, while the latter is due to subsequent slow, spin-forbidden decay to the ground state.

B. Longer chains, nonlinear isomers, and prospects for interstellar detection

In anticipation of optical detection, calculations were also performed on the ground and first two excited states of SiC_6H. The electronic spectrum of this species is expected to be similar to that of SiC_4H, with analogous transitions to a dark Σ

state ($f = 10^{-5}$) and a nearby bright Π state ($f = 0.015$) predicted near 2.6 eV. However, while this species was facilely detected in the rotational band, searches for its optical spectrum were unsuccessful. Renewed searches for this and still longer chains in a jet-cooled discharge may be feasible using diacetylene as a precursor, as was found for the earlier microwave measurements. While the even-n SiC_nH chains should be detectable by R2PI through ionization from long-lived quartet states, increasingly rapid internal conversion of the excited states of odd-n chains – the isovalent chain C_8H has an inferred lifetime of 8 ps[57] – may necessitate detection of longer members of the series by cavity-ringdown spectroscopy.

All of the electronic transitions reported herein for the SiC_nH radicals lie in the DIB region, but these transitions (i.e., to the first excited states) are almost certainly too weak to merit consideration in connection with this longstanding unsolved mystery. However, these chains are predicted to have extraordinarily strong ($f \approx 1$) $\pi^* \leftarrow \pi$ transitions; while these transitions lie deep in the UV for SiC_3H (5.36 eV) and SiC_5H (4.91 eV), they should enter the DIB region for longer chains. If one also considers the analogous transition of SiC_7H (predicted at 4.46 eV with $f = 0.82$), there is a clear linear decrease in the transition energy as a function of the number of carbon atoms, as expected from the free-electron model. On the basis of this linear trend, the shortest chain whose strong $3\Pi \leftarrow 1^2\Pi$ transition overlaps the DIB region will have to contain at least 13 carbon atoms. While such long silicon-containing chains are unlikely to be highly abundant in space, the strength of these transitions is encouraging and warrants their investigation in the laboratory.

Multiple low-lying cyclic structures are possible for SiC_nH where $n \geq 2$.[6,54,59,60] Of particular interest are those isomers which are structurally similar to interstellar c-SiC_2 and rhomboidal SiC_3. The former species is so abundant in IRC+10216 that several of its rare silicon isotopologues have been detected;[61] it is also the carrier of the well-known blue-green Merrill-Sanford bands observed in emission in carbon stars.[62] For SiC_3, one chain and two rhomboidal forms have been detected in the laboratory,[8,9] and one of them so far in space.[63] Several quite stable isomers of SiC_3H and SiC_4H incorporating all three motifs have been predicted[6,54] to lie within only 85 kcal/mol of the linear ground states – similar to the energy difference between HNCO, HONC, and HCNO, all of which have now been detected in the laboratory and in space.[7,64–67]

Ring-containing SiC_nH species may also possess electronic transitions in the visible because they contain at least one optical chromophore (e.g., c-SiC_2, and carbon chain moieties C_3H and C_4H). Indeed, there is some evidence to suggest the presence of a ring-containing isomer in our SiC_3H spectrum (see Fig. 1). There remain three weak bands designated with asterisks—at 1046, 1132, and 1383 cm^{-1} above the origin. Our ROHF-EOM-CCSD/aug-cc-pVTZ calculations on the isomer designated F1 by Sun *et al.*,[6] which is similar in structure to the rhomboidal SiC_3 isomer that contains a transannular Si–C bond[9] (see Fig. 8), indicate an A' ground state only 6.9 kcal/mol above the linear ground state, and a vertical transition to an excited A' state with f-value (0.003 at 2.06 eV) very similar to that of the observed Σ state. If one tentatively assigns the lowest "unexplained" band (at 1046 cm^{-1} above the l-SiC_3H origin) as the origin transition of this isomer, the other unassigned features correspond to vibrational energies of 85 cm^{-1} and 340 cm^{-1}, both of which can plausibly be assigned as 7_0^1 (95 cm^{-1}, predicted for the lowest a' mode) and 9_0^2 (370 cm^{-1}, for 2 quanta of the lowest a'' mode); most of the higher frequency modes fall outside the range of our scan. Regrettably, these bands were too weak under our experimental conditions for meaningful DF spectra to be recorded; our hypothesis might be better tested by visible-visible hole-burning spectroscopy. It will also be of interest to detect the rotational spectra of this and other nonlinear isomers: the laboratory and astronomical detection of related SiC_3 isomers augurs well for their detection in the rotational band; additionally, because they are predicted to have significantly larger dipole moments than the linear isomers,[6,54] ring-containing species may be good targets for future searches in the radio band, either in the laboratory, in space, or both.

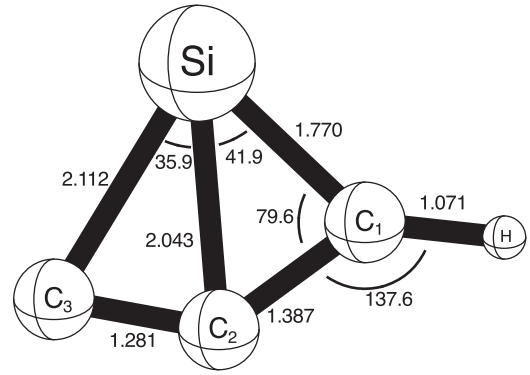


FIG. 8. A cyclic isomer of SiC_3H, predicted to lie only 7 kcal/mol above the linear ground state, and which has a moderately intense transition near 2 eV. The rhomboidal SiC_3 moiety is similar in structure to one of the two known rhomboidal forms of SiC_3.[9]

VI. CONCLUSION

The gas-phase optical detection and characterization of the silicon-terminated carbon chains SiC_nH ($n = 3 - 5$) has been carried out, as has the rotational detection of the missing member of the series, SiC_3H. Coupled cluster calculations indicate that, for the odd-n chains, the transitions are dominated by excitation to a $^2\Sigma$ state which is vibronically coupled to a higher-lying Π state; while for SiC_4H, the observed excited state appears to be strongly mixed with a quartet state, as evidenced by its long-lifetime (significantly longer than 50 μs) determined by R2PI spectroscopy. The lowest $^2\Sigma$ states of the odd-n chains, which lie approximately 2 eV above ground, are analogues of the very low-lying Σ states of the isovalent C_nH chains: both theory and experiment suggest that these states are characterized by a rare Si–C triple bond (with a predicted length of 1.61 Å), which was observed previously for the excited Σ state of SiCH. Transitions to the first excited states in all chains are too weak to be astronomically important; however, extremely strong transitions (with f-values near unity) are predicted for the odd-n chains, and should overlap the DIB

region for chains containing 13 or more carbon atoms. The best prospects for the astronomical detection of the silicon-terminated carbon chain radicals of intermediate size appear to lie in the rotational band, for which accurate rest frequencies are now in hand for $n = 2 - 6$. Because the SiC_3H optical spectrum suggests the presence of multiple isomers, further investigation at rotational resolution or by visible-visible hole-burning spectroscopy is warranted.

ACKNOWLEDGMENTS

The work in Cambridge is supported by NSF Grant No. CHE-1058063 and NASA Grant No. NNX13AE59G. Support for T.D.C. and R.C.F. is provided by the U.S. National Science Foundation Award No. CHE-1058420 and by Award No. CHE-0741927 (T.D.C.): a Multi-User Chemistry Research Instrumentation and Facility (CRIF:MU). The molecular structures in Fig. 7 were generated with the JMOL program, and Fig. 8 was generated with the CheMVP program developed at the Center for Computational and Quantum Chemistry at the University of Georgia. R.C.F. also wishes to thank the Virginia Space Grant Consortium for a Graduate Research Fellowship part of which was allocated during the time of this research. The authors would like to thank John Stanton for helpful discussions of this work.

[1] P. Thaddeus and M. C. McCarthy, Spectrochim. Acta A **57**, 757 (2001).
[2] H. Gupta, C. A. Gottlieb, M. C. McCarthy, and P. Thaddeus, Astrophys. J. **691**, 1494 (2009).
[3] G. H. Herbig, Annu. Rev. Astron. Astrophys. **33**, 19 (1995).
[4] C. A. Rice and J. P. Maier, J. Phys. Chem. A **117**, 5559 (2013).
[5] M. C. McCarthy, A. J. Apponi, C. A. Gottlieb, and P. Thaddeus, J. Chem. Phys. **115**, 870 (2001).
[6] H. Sun, N. Tan, H. Q. He, X. M. Pan, Z. M. Su, and R. S. Wang, Theor. Chem. Acc. **119**, 501 (2008).
[7] M. Mladenovic, M. Lewerenz, M. C. McCarthy, and P. Thaddeus, J. Chem. Phys. **131**, 174308 (2009).
[8] M. C. McCarthy, A. J. Apponi, and P. Thaddeus, J. Chem. Phys. **110**, 10645 (1999).
[9] M. C. McCarthy, A. J. Apponi, and P. Thaddeus, J. Chem. Phys. **111**, 7175 (1999).
[10] E. B. Jochnowitz and J. P. Maier, Ann. Rev. Phys. Chem. **59**, 519 (2008).
[11] K. Hoshina, H. Kohguchi, Y. Ohshima, and Y. Endo, J. Chem. Phys. **108**, 3465 (1998).
[12] H. Linnartz, T. Motylewski, O. Vaizert, J. P. Maier, A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, J. Mol. Spectrosc. **197**, 1 (1999).
[13] M. V. R. Cireasa and D. Cossart, Eur. Phys. J. D **2**, 199 (1998).
[14] T. C. Smith, H. Y. Li, D. J. Clouthier, C. T. Kingston, and A. J. Merer, J. Chem. Phys. **112**, 3662 (2000).
[15] P. G. Carrick, A. J. Merer, and R. F. Curl, J. Chem. Phys. **78**, 3652 (1983).
[16] F. J. Mazzotti, R. Raghunandan, A. M. Esmail, M. Tulej, and J. P. Maier, J. Chem. Phys. **134**, 164303 (2011).
[17] H. Ding, T. Pino, F. Güthe, and J. P. Maier, J. Chem. Phys. **117**, 8362–8367 (2002).
[18] J. G. Phillips and S. P. Davis, "The Swan system of the C_2 molecule," *The Berkeley Analysis of Molecular Spectra* (University of California Press, Berkeley, CA, 1968).
[19] K. S. Ojha and R. Gopal, Spectrochim. Acta A **71**, 1003 (2008).
[20] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[21] J. Gauss, J. F. Stanton, and R. J. Bartlett, J. Chem. Phys. **95**, 2623 (1991).
[22] J. D. Watts, J. Gauss, and R. J. Bartlett, Chem. Phys. Lett. **200**, 1 (1992).
[23] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[24] K. A. Peterson and T. H. Dunning, J. Chem. Phys. **102**, 2032 (1995).
[25] T. H. Dunning, K. A. Peterson, and A. K. Wilson, J. Chem. Phys. **114**, 9244 (2001).
[26] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (Cambridge University Press, Cambridge, 2009).
[27] H. Koch, O. Christiansen, P. Jørgensen, A. M. S. de Merás, and T. Helgaker, J. Chem. Phys. **106**, 1808 (1997).
[28] O. Christiansen, H. Koch, and P. Jørgensen, J. Chem. Phys. **103**, 7429 (1995).
[29] K. Hald, P. Jørgensen, O. Christiansen, and H. Koch, J. Chem. Phys. **116**, 5963 (2002).
[30] C. E. Smith, R. A. King, and T. D. Crawford, J. Chem. Phys. **122**, 054110 (2005).
[31] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
[32] A. I. Krylov, Ann. Rev. Phys. Chem. **59**, 433 (2008).
[33] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[34] J. S. Binkley, J. A. Pople, and P. S. Dobosh, Mol. Phys. **28**, 1423 (1974).
[35] J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **182**, 207 (1991).
[36] W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **187**, 21 (1991).
[37] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
[38] R. C. Fortenberry, R. A. King, J. F. Stanton, and T. D. Crawford, J. Chem. Phys. **132**, 144303 (2010).
[39] R. C. Fortenberry and T. D. Crawford, J. Chem. Phys. **134**, 154304 (2011).
[40] R. C. Fortenberry and T. D. Crawford, J. Phys. Chem. A **115**, 8119 (2011).
[41] R. C. Fortenberry, Mol. Phys. **111**, 3265 (2013).
[42] R. C. Fortenberry and T. D. Crawford, Annu. Rep. Comput. Chem. **7**, 195 (2011).
[43] T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, J. P. Kenny, E. T. Seidl, and W. D. Allen, J. Comput. Chem. **28**, 1610 (2007).
[44] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer *et al.* For the current version, see http://www.cfour.de.
[45] J. P. Maier, J. Phys. Chem. **102**, 3462 (1998).
[46] T. R. Taylor, C. S. Xu, and D. M. Neumark, J. Chem. Phys. **108**, 10018 (1998).
[47] J. Zhou, E. Garand, and D. M. Neumark, J. Chem. Phys. **127**, 154320 (2007).
[48] A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, Astrophys. J. **536**, L55 (2000).
[49] J. T. Hougen, J. Chem. Phys. **36**, 519 (1962).
[50] J. Brown, M. Kaise, C. Kerr, and D. Milton, Mol. Phys. **36**, 553 (1978).
[51] J. Brown, E. Colbourn, J. Watson, and F. Wayne, J. Mol. Spectrosc. **74**, 294 (1979).
[52] C. Amiot, J.-P. Maillard, and J. Chauville, J. Mol. Spectrosc. **87**, 196 (1981).
[53] H.-Y. Zhao, L. Wang, J. Li, Y. Liu, Y.-C. Li, and S.-L. Qin, Comput. Theor. Chem. **994**, 19 (2012).
[54] D. E. Woon, Chem. Phys. Lett. **244**, 45 (1995).
[55] W. Kutzelnigg, Angew. Chem., Int. Ed. **23**, 272 (1984).
[56] H. Kohguchi, Y. Ohshima, and Y. Endo, Chem. Phys. Lett. **254**, 397 (1996).
[57] P. Birza, D. Khoroshev, A. Chirokolava, T. Motylewski, and J. P. Maier, Chem. Phys. Lett. **382**, 245 (2003).
[58] A. E. Boguslavskiy and J. P. Maier, J. Chem. Phys. **125**, 094308 (2006).
[59] J. R. Flores, Chem. Phys. Lett. **392**, 196 (2004).
[60] D. Han, C. M. L. Rittby, and W. R. M. Graham, J. Chem. Phys. **106**, 6222 (1997).
[61] D. L. Kokkin, S. Brünken, K. H. Young, N. A. Patel, C. A. Gottlieb, P. Thaddeus, and M. C. McCarthy, Astrophys. J., Suppl. Ser. **196**, 17 (2011).
[62] P. J. Sarre, M. E. Hurst, and T. L. Evans, Mon. Not. R. Astron. Soc. **319**, 103 (2000).
[63] A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, Astrophys. J. **516**, L103 (1999).
[64] W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, Astrophys. J. **174**, L93 (1972).
[65] L. E. Snyder and D. Buhl, Astrophys. J. **177**, 619 (1972).
[66] M. Winnewisser and B. P. Winnewisser, Z. Naturforsch. **26a**, 128 (1971).
[67] N. Marcelino, J. Cernicharo, B. Tercero, and E. Roueff, Astrophys. J. **690**, L27 (2009).
[68] M. C. McCarthy, W. Chen, A. J. Apponi, C. A. Gottlieb, and P. Thaddeus, Astrophys. J. **520**, 158 (1999).