

Communications to the Editor

Spectroscopic Characterization of Silicon and Germanium Methylidyne: Fundamental Astrophysical and Organometallic Building Blocks

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Received March 5, 1999

There has been a great deal of recent interest in simple transition metal methylidyne, $M\equiv CH$, due primarily to their relevance in understanding catalytic processes. Several main group methylidyne are also known but in group 14 only the ethynyl radical, CCH , has been characterized.² After hydrogen and helium, silicon and carbon are among the most abundant elements in the universe. Small hydrogen-containing silicon–carbon species are thought to be important in the interstellar medium and may be the precursors of the SiC_n clusters found in stellar atmospheres.^{3,4} $SiCH$ and $GeCH$ are also fundamental building blocks in main group organometallic chemistry and are likely intermediates in the production of amorphous silicon and germanium semiconductor films and carbides.⁵ In the present work, we have used laser-induced fluorescence (LIF) spectroscopy to study the electronic spectrum of supersonic expansion-cooled silicon methylidyne and to determine its molecular structure. The corresponding germanium methylidyne has also been detected for the first time.

Neutral silicon methylidyne had previously been observed in neutralization–reionization mass spectrometry studies,⁶ proving that it is a viable species. While our work was in progress, two other reports identifying $SiCH$ appeared. Han et al.⁷ conducted a Fourier transform infrared study of the products of the vacuum ultraviolet photolysis of a mixture of silane and methane trapped in an argon matrix and detected the Si–C stretching fundamental of $SiCH$ at 1010.4 cm^{-1} . At about the same time, Cireasa et al.⁸ reported a new emission band system around 850 nm, generated by a DC discharge through a flowing mixture of helium and hexamethyldisilane, which they assigned to the $SiCH$ radical. The authors identified the 3_1^0 , 0_0^0 , and 3_0^1 bands and obtained rotational constants for the 0_0^0 band. A literature search has found no previous experimental or theoretical studies of the $GeCH$ radical.

In our studies, jet-cooled $SiCH$ and $GeCH$ were detected by LIF of the products from a pulsed discharge through tetramethylsilane (TMS) or tetramethylgermane (TMG) precursors, using techniques described elsewhere.^{9,10} The corresponding deuterated radicals were obtained using TMS- d_{12} and TMG- d_{12} , synthesized by literature methods. Since we have previously shown these

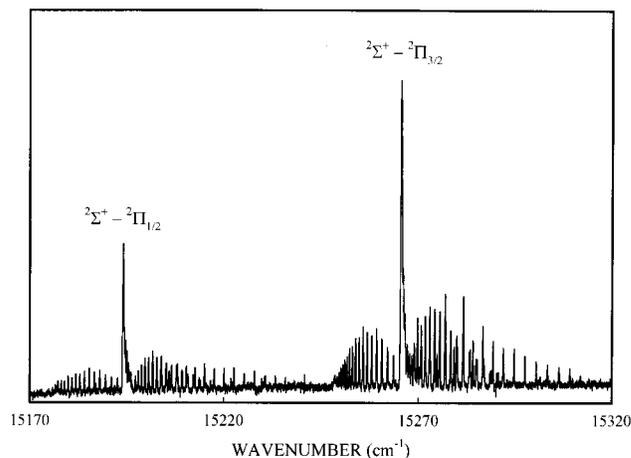


Figure 1. Laser-induced fluorescence spectrum of the $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi\ 3_0^3$ band of jet-cooled HCSi.

techniques to be rich sources of silylidene (H_2CSi) and germylidene (H_2CGe),¹¹ it is not surprising that they also yield the corresponding methylidyne radicals.

$SiCH$ and $SiCD$ exhibit extensive band systems in the 855–605 nm region; each band consists of two sub-bands with a spin–orbit splitting of about 70 cm^{-1} , as illustrated in Figure 1. The bands have simple rotational structures which are readily assigned as the $2\Sigma^+ - 2\Pi_i$ electronic transitions of linear silicon methylidyne. The isotope shifts on deuteration are entirely consistent with this assignment. The spectrum cannot be due to the $HSiC$ isomer which is predicted¹² to be about 50 kcal/mol less stable than $SiCH$, and to have a bent geometry which is inconsistent with the observed rotational structure. Rotational analysis of the 3_0^3 bands of $SiCH$ and $SiCD$ (at 15233 and 15056 cm^{-1} , respectively,) gives the ground-state structure of silicon methylidyne, assuming that the CH bond length is the same for both isotopomers. The rotational constants and structural information are given in Table 1.

Experiments with $Ge(CH_3)_4$ revealed a new, weak system of bands starting at 550 nm and extending into the near-infrared which can be assigned with confidence to the germanium methylidyne radical, a previously unknown species. Deuterium substitution gave the expected isotope shifts, and medium-resolution (0.04 cm^{-1}) spectra, illustrated in Figure 2, show the unambiguous germanium isotope pattern of a molecule with a single Ge atom. The separation of the $2\Sigma^+ - 2\Pi_{3/2}$ and $2\Sigma^+ - 2\Pi_{1/2}$ sub-bands of $GeCH$ was found to be 335 cm^{-1} , consistent with the much larger spin–orbit splittings expected for germanium compounds. Our spectra of $GeCH$ are too complicated for a detailed rotational analysis, but higher resolution collaborative studies with Anthony Merer's group at the University of British Columbia are currently in progress.

The valence isoelectronic C_2H radical has a $2\Sigma^+$ ground state ($\dots\pi^4\sigma^1$) represented by the Lewis structure $H-C\equiv C\cdot$. Electronic excitation involves promotion of a π electron to the σ orbital, resulting in a low-lying 2Π electronic state about 3800 cm^{-1} above the ground state. Electronic excitation lowers the $C\equiv C$ bond order,

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Table 1. Experimental and ab Initio Spectroscopic Parameters of Silicon Methylidyne

	experimental ^a		ab initio ^b	
	$\tilde{X}^2\Pi$	$\tilde{A}^2\Sigma^+$	$\tilde{X}^2\Pi$	$\tilde{A}^2\Sigma^+$
$r(\text{C-H}) \text{ \AA}$	1.069(2)	1.044(2) ^c	1.078	1.080
$r(\text{SiC}) \text{ \AA}$	1.6913(3)	1.6316(3) ^c	1.702	1.587
$B \text{ cm}^{-1}$	0.581045(63)	0.623130(78) ^c	0.5737	0.652
$T_0 \text{ cm}^{-1}$	0	11766.7205(9) ^d	0	12454
$\nu_1 (\text{C-H stretch}) \text{ cm}^{-1}$	3260.2	3249.6
$\nu_2 (\text{bend}) \text{ cm}^{-1}$...	715	469.9	848.7
$\nu_3 (\text{C-Si stretch}) \text{ cm}^{-1}$	1013 ^d	1171	1011.9	1150.9
spin-orbit coupling constant $A \text{ cm}^{-1}$	-69.7361(25)	...	-41.0	...

^a This work except as noted. ^b References 12 and 13. ^c Parameters for the $\nu_3 = 3$ vibrational level in the excited state. ^d From the analysis of the 0_0^0 band emission spectrum, ref 8.

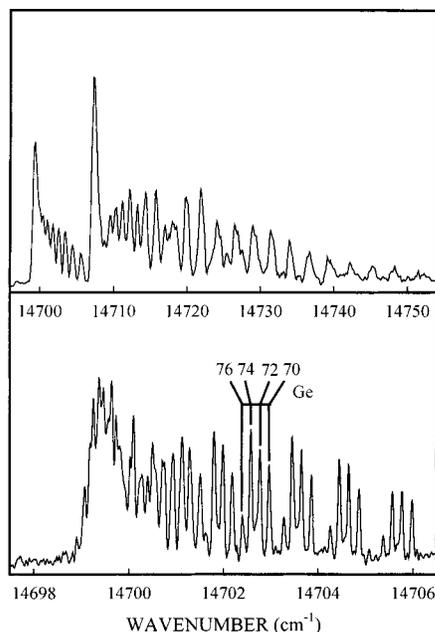


Figure 2. Laser-induced fluorescence spectrum of a $2\Sigma^+ - 2\Pi_{3/2}$ sub-band of the near-infrared system of HCGe. The bottom panel is a higher-resolution scan of part of the band showing the pattern of germanium isotopic lines.

elongating the bond. As anticipated by ab initio studies,^{12,13} the situation is completely reversed in silicon methylidyne and must be similar in germanium methylidyne. In SiCH, the nonbonding σ orbital on the terminal silicon is lower in energy than the π orbitals, so that the ground-state configuration is $\dots\sigma^2\pi^3$ or 2Π , with Lewis structure $\text{H}-\dot{\text{C}}=\text{Si}$:. This difference has been attributed to the smaller hybridization of silicon relative to carbon, so that the 3s orbital remains doubly occupied in silicon-carbon compounds.¹³ Electronic excitation of a σ electron to the π orbital ($\dots\sigma^1\pi^4$) gives a $2\Sigma^+$ excited state, and the CSi bond length contracts on excitation.

The derived Si-C bond length of 1.691 Å is only slightly smaller than the 1.706 Å bond length we obtained previously for the ground state of silylidene ($\text{H}_2\text{C}=\text{Si}$),¹⁰ providing a range of reliable experimental values for the length of the silicon-carbon

double bond. The comparison of our SiCH experimental data with the ab initio predictions of Robbe et al.¹² is generally good, although a few discrepancies are apparent. The ground-state geometries are consistent with experiment, but the spin-orbit splitting is predicted to be about 40% lower than is observed. The ab initio values for the vibrational frequencies and the electronic excitation energy are in accord with experiment. Although our excited-state structural parameters from the $\nu_3 = 3$ vibronic level are not directly comparable with the ab initio r_e values, the theoretical and experimental geometry changes on electronic excitation should be qualitatively similar. However, this is not the case.¹⁴ The predicted 0.115 Å decrease in the Si-C bond length on excitation is clearly much too large, with experiment suggesting a change of the order of 0.060 Å. Although theory predicts an increase in the CH bond length on excitation, experiment indicates a decrease. Some evidence for the validity of the SiCH results can be obtained from literature data on the isoelectronic HCP^+ species, which also has a low-lying $2\Sigma^+ - 2\Pi$ electronic transition.¹⁵ From the reported B_0 values, we calculate that $r(\text{CP})$ decreases by 0.056 Å and $r(\text{CH})$ decreases by 0.042 Å on excitation. Although these values are quite imprecise, due to the large uncertainty in the reported rotational constants, the trend is clearly the same in both SiCH and HCP^+ .

Cireasa et al.⁸ noted that two of their emission bands correspond to bands assigned by Grutter et al.¹⁶ to the $\text{B}^3\Sigma^+ - \text{X}^3\Pi$ transition of matrix isolated SiC, and have reassigned them to SiCH. We confirm this reassignment by the observation that the four bands found in the matrix spectrum have the same vibrational interval and anharmonicity as the strong 3_0^n ($n = 0-3$) progression of bands observed in our jet spectra, with a matrix shift of about 50 cm^{-1} to lower energy. The weaker bands that we observe involving ν_2 and combinations of $\nu_2 + \nu_3$ are not apparent in the published matrix spectrum.

Further high-resolution LIF and fluorescence lifetime studies of both radicals are in progress.

Acknowledgment. We are grateful to Dr. Anthony Merer for many useful discussions and for critically reading the manuscript prior to publication. This research was supported by the National Science Foundation.

JA990713L

(14) Note added in proof: Our more recent excited state r_0 structure is in better agreement with the theoretical predictions.

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