

## AN EXPERIMENTAL AND THEORETICAL STUDY OF THE IONIZATION ENERGIES OF $\text{SiC}_2\text{H}_x$ ( $x = 0, 1, 2$ ) ISOMERS

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### ABSTRACT

We present a combined experimental and theoretical study on the formation processes and ionization energies of small organo-silicon molecules of the formula  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ). These organic molecules are considered important benchmark systems in understanding the formation of silicon- and carbon-bearing grains in the outflow of carbon stars. The studies identify four distinct (hydrogenated) silicon-carbon molecules together with their ionization energies: c- $\text{SiC}_2$  [ $9.75 \pm 0.10$  eV;  $9.83 \pm 0.05$  eV], 1-HCCSi [ $7.00 \pm 0.05$  eV], c- $\text{SiC}_2\text{H}$  [ $7.27 \pm 0.05$  eV], and c- $\text{SiC}_2\text{H}_2$  [ $9.05 \pm 0.05$  eV;  $8.96 \pm 0.05$  eV] with numbers in italics depicting computed data. Implications of these results to the non-equilibrium chemistry in shocked regions of circumstellar envelopes of carbon stars are also discussed.

*Key words:* astrochemistry – ISM: abundances – ISM: molecules – molecular processes

*Online-only material:* color figure

### 1. INTRODUCTION

During the last decade, organo-silicon molecules of various degrees of hydrogenation such as the  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ) family have received considerable attention. This is due to their potential role as benchmark systems in understanding the formation of silicon- and carbon-bearing interstellar grains and rationalizing the chemical evolution of distinct interstellar environments (Viti et al. 2000; Yasuda & Kozasa 2012) such as circumstellar envelopes of dying carbon stars like IRC + 10216. In these environments, temperatures can rise to a few thousand K close to the photosphere of the central star (Charnley et al. 2001). In the circumstellar envelope of IRC + 10216, the presence of the hydrocarbons methane ( $\text{CH}_4$ ), acetylene ( $\text{C}_2\text{H}_2$ ), and ethylene ( $\text{C}_2\text{H}_4$ ) together with silane ( $\text{SiH}_4$ ) (Goldhaber & Betz 1984) is of particular importance since these molecules are thought to be key ingredients in forming reactive intermediates via photolytically generated hydrocarbon radicals such as  $\text{CH}_x$  and  $\text{C}_2\text{H}_x$  ( $x = 1, 2, 3$ ) and also silicon-bearing species  $\text{SiH}_x$  ( $x = 0, 1, 2, 3$ ) (Agundez et al. 2008). The carbon- and silicon-bearing photofragments might undergo bimolecular reactions forming more complex organo-silicon molecules with various degrees of hydrogenation via ion-molecule reactions and/or bimolecular reactions of neutral species (Woodall et al. 2007).

These considerations have led to the development of astrochemical models of the circumstellar silicon chemistry of the carbon star IRC + 10216 (MacKay & Charnley 1999; Herbst et al. 1989; Bettens et al. 1995; Millar & Herbst 1994). It is remarkable that, based on reasonable alternatives for the unknown reaction dynamics and branching ratios, the models show inconsistent mechanisms for the principal routes leading to the build-up of organo-silicon molecules. A major set-back of these chemical reaction networks is that, for instance, calculated fractional abundances of the prominent cyclic  $\text{SiC}_2$  molecule, which was first identified in the circumstellar envelope of the carbon star IRC + 10216 almost 30 years ago via nine rotational lines between 93 and 142 GHz (Thaddeus et al. 1984), diverged by up to three orders of magnitude from those observed (Herbst et al.

1989). This disagreement between the astrochemical models and astronomical observations is based on inaccurate (lacking) laboratory data such as products, an incorrect thermochemistry of the neutral-neutral and ion-molecule reactions of silicon atoms, ions, and molecules, as well as imprecise ionization energies of the organo-silicon-bearing molecules formed. Based on these shortcomings, Ziurys et al. called for a systematic study to determine the formation mechanisms and properties such as ionization energies of (hydrogenated) silicon carbides (Ziurys 2006; Agundez et al. 2008).

Among the inaccurate input data in astrochemical models, the adiabatic ionization energy (AIE) presents a key thermochemical measurement. The ionization energy (IE) dictates the direction of ion-molecule reactions in interstellar environments such as in cold molecular clouds and circumstellar envelopes (Kwok 2007). Further, ionization energies are crucial to predict to what extent newly formed neutral organo-silicon molecules can be ionized (Dalgarno 2006). Finally, ionization energies combined with thermochemical cycles can be exploited to determine enthalpies of formation of organo-silicon molecules (Kwok 2007), which in turn yield information on the outcome of a bimolecular chemical reaction in interstellar space, if the reaction is thermodynamically controlled.

Herein, we present a combined experimental and theoretical study on the adiabatic ionization energies of small organo-silicon molecules  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ). By synthesizing these molecules in situ via laser ablation of a silicon rod and successive reaction of the ablated silicon atoms (Si) with acetylene ( $\text{C}_2\text{H}_2$ ), we produce an intense, supersonic beam containing various  $\text{SiC}_2\text{H}_x$  species. This approach presents a versatile method of forming reactive organo-silicon molecules, which are difficult to synthesize by conventional organic chemistry methods. Subjecting the neutral molecules in this beam to vacuum ultraviolet (VUV) photoionization, we then record the mass spectra of the ionized molecules at various photon energies up to 11 eV. By plotting the ion counts of an ion of a well-defined mass-to-charge ratio versus the photon energy, we extract photoionization efficiency (PIE) curves for species with the

molecular formulae  $\text{SiC}_2$  (52 amu),  $\text{SiC}_2\text{H}$  (53 amu), and  $\text{SiC}_2\text{H}_2$  (54 amu). For distinct structural isomers, i.e., molecules with the same chemical formula but different connectivity of the atoms such as the hydrocarbon methylacetylene ( $\text{CH}_3\text{CCCH}$ ) and allene ( $\text{H}_2\text{CCCH}_2$ ), the AIE and the corresponding PIE curves can differ. Therefore, if multiple structural isomers of, for instance,  $\text{SiC}_2\text{H}_2$  (54 amu) are present in the supersonic beam, the measured PIE curve at  $m/z = 54$  presents the result of a linear combination of the PIE curves of the *individual*  $\text{SiC}_2\text{H}_2$  isomers. Consequently, if the PIE curves of the individual isomers are known, we can identify not only the isomers formed, but can also extract their branching ratios. A comprehensive literature research suggested that only a few theoretical studies on the ionization energies of  $\text{SiC}_2\text{H}_x$  exist. Early electron impact measurements for a few silicon carbides with large error uncertainties exist, but beyond this there is a paucity of information regarding organo-silicon compounds (Linstrom & Mallard 2005). This is particularly true for experimentally determined PIE curves of  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ). Consequently, the PIE curves of the individual  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ) isomers had to be determined computationally in the present study.

## 2. EXPERIMENTAL

Our experiments were conducted with a laser ablation apparatus coupled to a 3 m monochromator of the Chemical Dynamics Beamline at the Advanced Light Source (Heimann et al. 1997; Kaiser et al. 2010a, 2010b). The silicon species are ablated via a frequency doubled (532 nm) Nd:YAG laser operating at 50 Hz and output powers of about 0.8 mJ per pulse and are entrained in acetylene ( $\text{C}_2\text{H}_2$ ; Airgas) carrier gas. Since the acetylene acts as a carrier gas *and* as a reagent medium, the organo-silicon molecules are formed in situ in the supersonic beam via reaction of acetylene with the ablated silicon species. This technique has been utilized recently to produce and to extract the ionization energies of highly reactive organic transient radicals of astrophysical relevance such as the linear and cyclic tricarbon hydride ( $\text{C}_3\text{H}$ ) (Kaiser et al. 2007), the nitrogen-terminated carbon clusters ( $\text{C}_n\text{N}$ ;  $n = 3-14$ ) (Kostko et al. 2010), and also polyacetylenes ( $\text{H}-(\text{C}\equiv\text{C})_n-\text{H}$ ;  $n = 1-9$ ) (Kaiser et al. 2010a, 2010b).

The neutral, supersonic beam is intersected perpendicularly in the ionization region of a reflectron time-of-flight (Re-TOF) mass spectrometer by tunable monochromatic synchrotron radiation in the VUV region of the electromagnetic spectrum. Typically  $10^{13}$  photons  $\text{s}^{-1}$  are available at this synchrotron terminal. Fragment-free VUV photoionization mass spectrometry—a soft ionization method—is unmatched by traditional ionization techniques utilizing electron impact schemes (Hanley & Zimmermann 2009). TOF spectra, i.e., the flight time of the ions versus the intensity of the ion counts, are recorded for the photo IE range between 8.0 eV and 10.5 eV. The typical step size used for these experiments is 50 meV; the signal was collected for up to  $7 \times 10^3$  laser shots. We estimated that typically  $10^8-10^9$  molecules  $\text{cm}^{-3}$  are being ionized in the  $1 \text{ mm}^3$  interaction region. The PIE curves of a well-defined ion of a mass-to-charge ratio ( $m/z$ ) can be obtained by plotting the integrated ion signal at the chosen  $m/z$  value versus the photoionization energy between 8 eV and 11 eV, normalized by the photon flux and the number of laser shots. The synchrotron VUV photon flux is measured by a silicon photodiode (Kaiser et al. 2010a, 2010b). The PIE curves at  $m/z = 52, 53$ , and  $54$  were then fit via a linear combination with calculated PIE curves of various  $\text{SiC}_2$ ,  $\text{SiC}_2\text{H}$ ,

and  $\text{SiC}_2\text{H}_2$  isomers to extract not only the nature of the products formed, but also their adiabatic ionization energies. Recall that the PIE curves of individual  $\text{SiC}_2$ ,  $\text{SiC}_2\text{H}$ , and  $\text{SiC}_2\text{H}_2$  isomers do not exist in the literature, and, therefore, had to be computed theoretically (Section 3).

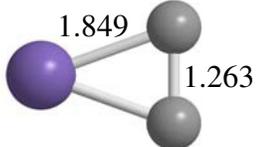
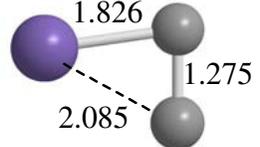
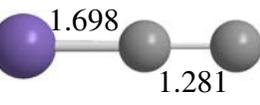
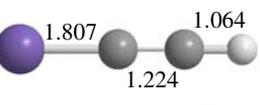
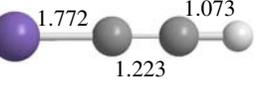
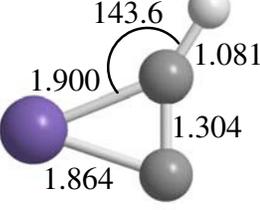
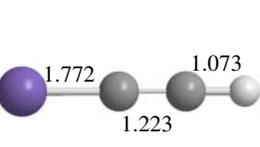
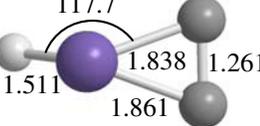
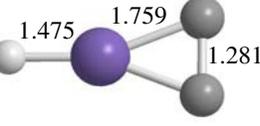
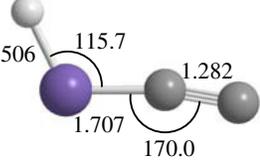
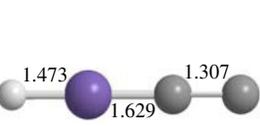
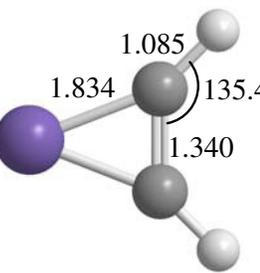
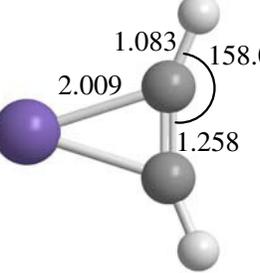
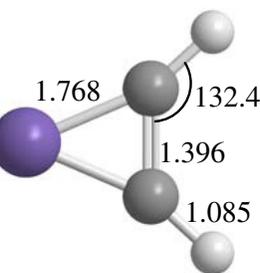
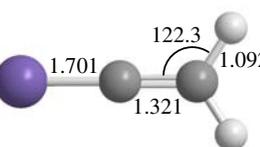
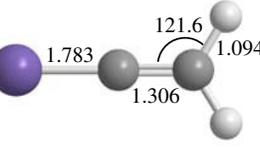
## 3. COMPUTATIONAL METHODS

Geometries of various neutral  $\text{SiC}_2\text{H}_x$  ( $x = 0-2$ ) isomers and their corresponding cations were optimized at the hybrid density functional B3LYP level (Becke 1993; Lee et al. 1988) with the 6-311G\*\* basis set and vibrational frequencies were calculated using the same B3LYP/6-311G\*\* method. The cyclic  $\text{SiC}_2^+$  cation does not exist at a local minimum on the potential energy surface at the B3LYP level, as its optimization converges to a linear  $\text{SiCC}^+$  structure. However, optimization at the quadratic configuration interaction QCISD/6-311G\*\* level of theory (Pople et al. 1987) does produce a cyclic  $\text{SiC}_2^+$  local minimum, for which vibrational frequencies were computed also at QCISD/6-311G\*\*. Relative energies of different neutral isomers as well as their vertical and adiabatic ionization energies were refined employing the coupled cluster CCSD(T) method (Purvis & Bartlett 1982; Scuseria et al. 1988; Scuseria & Schaefer 1989) with Dunning’s correlation-consistent cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets (Dunning 1989). The total CCSD(T) energies were extrapolated to the complete basis set (CBS) limit by fitting the following equation (Peterson & Dunning 1995),  $E_{\text{tot}}(x) = E_{\text{tot}}(\infty) + Be^{-Cx}$ , where  $x$  is the cardinal number of the basis set (2, 3, 4, and 5 for cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z, respectively) and  $E_{\text{tot}}(\infty)$  is the CCSD(T)/CBS total energy. Spin-restricted coupled cluster RCCSD(T) calculations were used for open-shell structures. All ab initio and density functional calculations were performed using the GAUSSIAN-09 (Frisch et al. 2009) and MOLPRO 2010 (Werner et al. 2010) program packages. The CCSD(T)/CBS + ZPE(B3LYP/6-311G\*\*) relative energies and ionization energies are expected to be accurate within  $\pm 0.05$  eV. Ionization Franck–Condon factors used to fit experimental PIE curves were computed with the GAUSSIAN-09 package using the theoretical method developed by Barone and coworkers (Santoro et al. 2007, 2008; Barone et al. 2009).

## 4. COMPUTATIONAL RESULTS

The optimized structures of various neutral isomers and their mono cations are collected in Table 1, whereas their computed rotational constants and dipole moments are presented in Table 2. Considering the  $\text{SiC}_2\text{H}_2$  isomers, calculations at the CCSD(T)/CBS//B3LYP/6-311G\*\* level show that the  $\text{C}_{2v}$ -symmetric cyclic structure  $c\text{-SiC}_2\text{H}_2$  with the  $^1A_1$  electronic ground state represents the global minimum. An AIE of 8.96 eV is derived for ionization to a  $\text{C}_{2v}$ -symmetric cation, which has a  $^2B_2$  ground state, whereas the first excited state of the cation,  $^2A_1$  lies only 0.35 eV higher in energy than  $^2B_2$ , so that the AIE to the  $^2A_1$  state of the ion is 9.32 eV. The  $\text{H}_2\text{CCSi}$  structure with  $\text{C}_{2v}$  symmetry and an L shaped planar isomer  $\text{HSiCCH}$ , in which silicon is formally inserted between a carbon and a hydrogen, lie 0.78 and 0.79 eV above the cyclic global minimum, respectively. The calculated AIEs of  $\text{H}_2\text{CCSi}$  and  $\text{HSiCCH}$  are 8.30 and 8.77 eV, respectively. The present theoretical results are in close agreement with those of Ikuta et al. (2004), who reported a comprehensive study on the ionization energies for

**Table 1**  
Relative Energies and Ionization Energies (in eV) of Various SiC<sub>2</sub>H<sub>x</sub> (x = 0–2) Isomers

Neutral/Ion (Symmetry, State)	Neutral Structure	Relative Energy	Ion structure	Adiabatic Ionization Energy
c-SiC <sub>2</sub> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )/c-SiC <sub>2</sub> <sup>+</sup> (C <sub>s</sub> , <sup>2</sup> A')		0.00		9.83
SiCC (C <sub>∞v</sub> , <sup>1</sup> Σ <sup>+</sup> )/SiCC <sup>+</sup> (C <sub>∞v</sub> , <sup>2</sup> Σ <sup>+</sup> )		0.22		9.67
SiCCH (C <sub>∞v</sub> , <sup>2</sup> Π)/SiCCH <sup>+</sup> (C <sub>∞v</sub> , <sup>1</sup> Σ <sup>+</sup> )		0.00		7.27
c-SiC <sub>2</sub> H (C <sub>s</sub> , <sup>2</sup> A')/SiCCH <sup>+</sup> (C <sub>∞v</sub> , <sup>1</sup> Σ <sup>+</sup> )		0.27		7.00 (8.12) <sup>a</sup>
c-HSiC <sub>2</sub> (C <sub>1</sub> , <sup>2</sup> A)/c-HSiC <sub>2</sub> <sup>+</sup> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )		1.77		8.40
HSiCC (C <sub>s</sub> , <sup>2</sup> A')/HSiCC <sup>+</sup> (C <sub>∞v</sub> , <sup>1</sup> Σ <sup>+</sup> )		1.97		9.04
c-SiC <sub>2</sub> H <sub>2</sub> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )/c-SiC <sub>2</sub> H <sub>2</sub> <sup>+</sup> (C <sub>2v</sub> , <sup>2</sup> B <sub>2</sub> )		0.00		8.96
c-SiC <sub>2</sub> H <sub>2</sub> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )/c-SiC <sub>2</sub> H <sub>2</sub> <sup>+</sup> (C <sub>2v</sub> , <sup>2</sup> A <sub>1</sub> )				9.32
H <sub>2</sub> CCSi (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )/H <sub>2</sub> CCSi <sup>+</sup> (C <sub>2v</sub> , <sup>2</sup> B <sub>2</sub> )		0.78		8.30

**Table 1**  
(Continued)

Neutral/Ion (Symmetry, State)	Neutral Structure	Relative Energy	Ion structure	Adiabatic Ionization Energy
HSiCCH ( $C_s$ , $^1A'$ )/HSiCCH $^+$ ( $C_s$ , $^2A'$ )		0.79		8.77
c-HSiCCH ( $C_s$ , $^1A'$ )/HSiCCH $^+$ ( $C_s$ , $^2A'$ )		1.68		7.88 (9.03) <sup>a</sup>
H <sub>2</sub> SiCC ( $C_{2v}$ , $^1A_1$ )/H <sub>2</sub> SiCC $^+$ ( $C_{2v}$ , $^2A_1$ )		2.25		9.29
c-H <sub>2</sub> SiC <sub>2</sub> ( $C_{2v}$ , $^1A_1$ )/H <sub>2</sub> SiCC $^+$ ( $C_{2v}$ , $^2A_1$ )		2.03		9.51 (9.97) <sup>a</sup>

**Notes.** <sup>a</sup> In parentheses: vertical ionization energies—given only for the isomers, for which the corresponding ionic isomer does not exist and the structure of the ion converged to a different isomer after optimization starting from the geometry of the neutral molecule.

(A color version of this table is available in the online journal.)

**Table 2**

Rotational Constants and Dipole Moments of Various SiC<sub>2</sub>H<sub>x</sub> ( $x = 0-2$ ) Neutral Molecules and Monocations Calculated at the B3LYP/6-311G\*\* Level of Theory

Molecule	Rotational Constants (GHz)			Dipole Moment (D)
c-SiC <sub>2</sub>	52.78542	12.95003	10.39885	2.44
c-SiC <sub>2</sub> $^+$	54.99378	11.24570	9.33648	1.74
SiCC	6.27578	6.27578	4.58	4.58
SiCC $^+$	6.08883	6.08883	1.44	1.44
SiCCH	5.41085	5.41085	1.09	1.09
SiCCH $^+$	5.55262	5.55262	0.28	0.28
c-SiC <sub>2</sub> H	40.98771	11.77043	9.14443	1.67
c-HSiC <sub>2</sub>	45.76879	11.69982	9.85972	2.98
c-HSiC <sub>2</sub> $^+$	51.36394	12.77805	10.23247	4.34
HSiCC	291.53458	6.02556	5.90355	4.79
HSiCC $^+$	6.02555	6.02555	6.34	6.34
c-SiC <sub>2</sub> H <sub>2</sub>	33.77199	11.71309	8.69679	1.01
c-SiC <sub>2</sub> H <sub>2</sub> $^+$ ( $^2B_2$ )	34.00295	9.90218	7.66888	0.08
c-SiC <sub>2</sub> H <sub>2</sub> $^+$ ( $^2A_1$ )	31.93572	12.78497	9.12994	0.70
H <sub>2</sub> CCSi	294.72388	5.33123	5.23651	1.12
H <sub>2</sub> CCSi $^+$	288.90949	5.08381	4.99590	0.29
HSiCCH	220.32413	5.23400	5.11255	0.96
HSiCCH $^+$	313.55144	5.45531	5.36202	0.99
c-HSiCCH	36.13872	9.70740	7.65196	2.32
H <sub>2</sub> SiC	165.84689	5.83310	5.63491	5.73
H <sub>2</sub> SiC $^+$	152.16547	5.79110	5.57878	2.04
c-H <sub>2</sub> SiC <sub>2</sub>	40.86162	10.89831	9.55262	3.34

various isomers of SiC<sub>2</sub>H<sub>2</sub> at the similar CCSD(T)/cc-pVQZ level of theory, suggesting that the global minima for the neutral and the cation, ( $C_{2v}$ ,  $^1A_1$ ) and ( $C_{2v}$ ,  $^2B_2$ ), are silacyclopropenylidene structures with AIE of 8.97 eV, and also with Kertvirtis et al. (1995), who obtained an AIE of 9.00 eV for the silacyclopropenylidene isomer at the QCISD (T, full) level of theory. The SiC<sub>2</sub>H<sub>2</sub> molecule has numerous other isomers in singlet and triplet electronic states which lie much higher in energy. For instance, a cyclic c-HSiCCH ( $C_s$ ,  $^1A'$ ) structure is 1.68 eV less favorable than the global minimum and, upon ionization, opens up to the L shaped HSiCCH $^+$  cation. The vertical ionization energy (VIE) of c-HSiCCH is 9.03 eV but, owing to the large geometry relaxation in the cation, the AIE drops to 7.88 eV. Another cyclic isomer, c-H<sub>2</sub>SiC<sub>2</sub> ( $C_{2v}$ ,  $^1A_1$ ), in which both hydrogen atoms are connected to the silicon atom, resides 2.03 eV above silacyclopropenylidene and also does not survive ionization, after which geometry relaxation leads to the linear H<sub>2</sub>SiCC $^+$  ( $C_{2v}$ ,  $^2A_1$ ) structure. The VIE and AIE of c-H<sub>2</sub>SiC<sub>2</sub> are 9.97 and 9.51 eV, respectively. The neutral linear H<sub>2</sub>SiCC ( $C_{2v}$ ,  $^1A_1$ ) isomer is 0.22 and 2.25 eV less stable than c-H<sub>2</sub>SiC<sub>2</sub> and the global minimum, respectively, and has AIE of 9.29 eV. All other SiC<sub>2</sub>H<sub>2</sub> singlet and triplet structures reside even higher in energy and have ionization energies below 7.6 eV.

Our calculations show that for the neutral SiC<sub>2</sub>H isomers, the lowest lying isomer is the linear SiCCH radical ( $C_{\infty v}$ ,  $^2\Pi$ ) with an AIE of 7.27 eV. The corresponding SiCCH $^+$  ion is also linear and has a  $^1\Sigma^+$  electronic state. Note that Kertvirtis

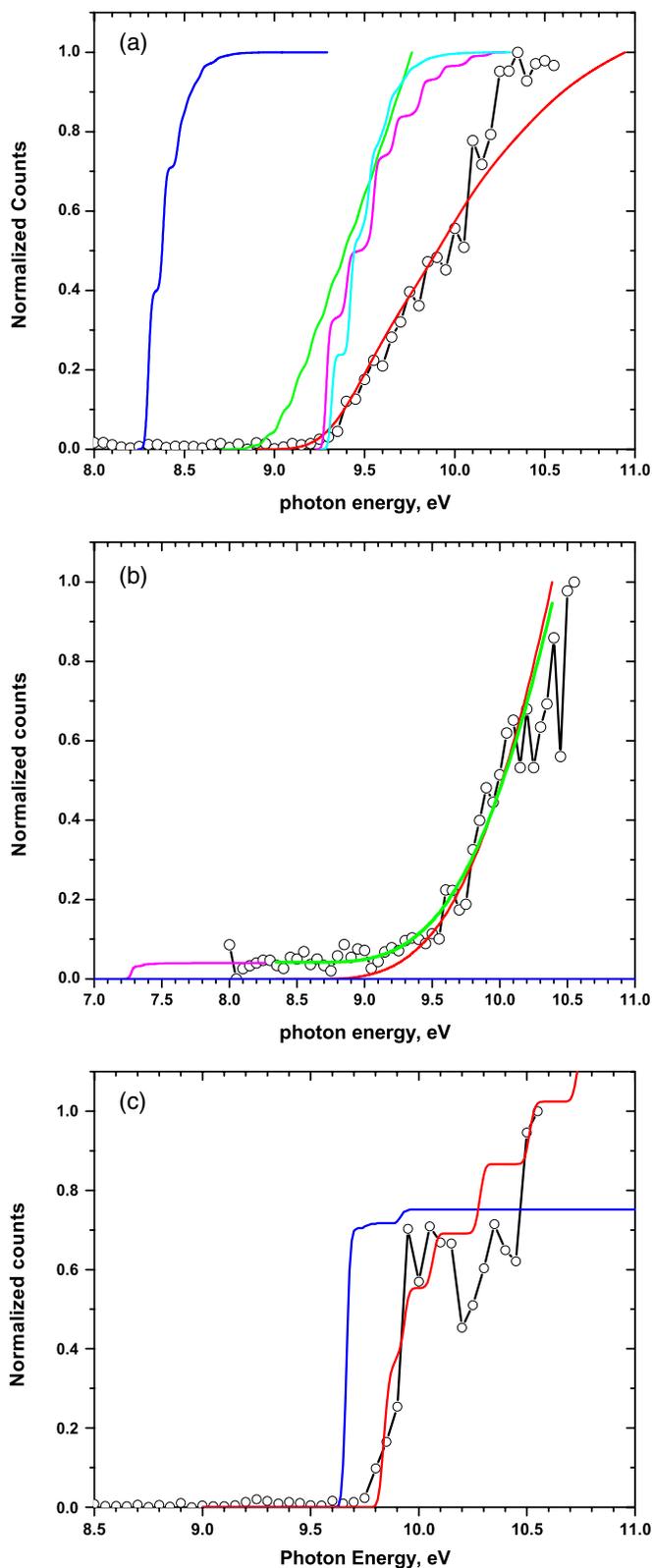
et al. (1995) calculated the AIE of 7.06 eV for this isomer at the QCISD (T, full) level. A cyclic isomer  $c\text{-SiC}_2\text{H}$  ( $C_s, ^2A'$ ) is computed to be 0.27 eV above the linear global minimum. Upon ionization, this isomer relaxes to the linear  $\text{SiCC}^+$  cation ( $C_{\infty v}, ^1\Sigma^+$ ) with a VIE and an AIE of 8.12 eV and 7.00 eV, respectively. A second cyclic isomer,  $c\text{-HSiC}_2$  ( $C_1, ^2A$ ), is asymmetric and has the hydrogen atom linked to silicon. This structure is 1.77 eV higher in energy than the global minimum. When ionized, the geometry becomes planar and  $C_{2v}$ -symmetric with the  $^1A_1$  electronic state and the AIE is 8.40 eV. Finally, an acyclic  $\text{HSiCC}$  ( $C_s, ^2A'$ ) isomer, which can be produced directly from the L shaped isomer of  $\text{SiC}_2\text{H}_2$  by the carbon–hydrogen bond cleavage, resides 1.97 eV above the linear  $\text{SiCC}$  radical and have the calculated AIE of 9.04 eV. Interestingly, in the ionized state, the structure of  $\text{HSiCC}^+$  ( $C_{\infty v}, ^1\Sigma^+$ ) is linear.

It is believed that  $\text{SiC}_2$  exists in the cyclic form and our computational results support this hypothesis, with  $c\text{-SiC}_2$  ( $C_{2v}, ^1A_1$ ) as the global minimum. B3LYP/6-311G\*\* geometry optimization of the  $C_{2v}$ -symmetric  $c\text{-SiC}_2^+$  cation generates a structure with one imaginary frequency and, after the molecular symmetry is relaxed, the optimization converges to the linear  $\text{SiCC}^+$  ( $C_{\infty v}, ^2\Sigma^+$ ) isomer. However, QCISD/6-311G\*\* geometry optimization converges to a semi-open cyclic structure with  $C_s$  symmetry and  $a^2A'$  electronic state. The corresponding calculated AIE is 9.83 eV. The linear  $\text{SiCC}$  ( $C_{\infty v}, ^1\Sigma^+$ ) isomer is only 0.22 eV less favorable than the cyclic global minimum and is ionized to the linear  $\text{SiCC}^+$  ( $C_{\infty v}, ^2\Sigma^+$ ) structure with AIE of 9.67 eV. Our present results are in agreement with earlier theoretical calculations (Yadav et al. 2006) at the B3LYP/6-311G(3df) level generating ionization energies of 9.69 and 9.79 eV for linear  $\text{SiCC}$  and cyclic  $\text{SiC}_2$ , respectively. However, LDA-DFT calculations by Pradhan & Ray (2006) report AIEs of 10.38–10.78 eV ( $\text{SiC}_2$ ), that are systematically above our values, suggesting that the local density approximation adopted by these authors is inaccurate.

## 5. EXPERIMENTAL RESULTS

A mass spectrum of the products formed from the ablation of a silicon rod in acetylene carrier gas was recorded at a photon energy of 10.5 eV. This mass spectrum demonstrates the presence of ion signal at  $m/z = 52$  ( $\text{SiC}_2^+$ ), 53 ( $\text{SiC}_2\text{H}^+$ ), and 54 ( $\text{SiC}_2\text{H}_2^+$ ). Consecutively, the mass spectra were recorded at photon energies between 8 eV and 11 eV allowing extraction of the PIEs of  $m/z = 52, 53,$  and 54 shown in Figure 1.

The PIE for the ion counts of the  $\text{SiC}_2\text{H}_2^+$  cation was recorded at  $m/z = 54$  and is depicted in Figure 1(a). In the absence of complications caused by, for instance, auto ionization, the basic PIE curve arises from direct ionization appearing as a series of step-like features, which are proportional to the Franck–Condon factor. A similar geometry of the neutral molecule and of the cation is expected to result in a narrow spectrum, whereas a significant change in geometry is reflected in a broader, less abrupt slope. Based on the raw data, the first step onset can be observed between 9.0 eV and 9.1 eV suggesting an AIE of  $9.05 \pm 0.05$  eV. These data correlate well with our computed IE of  $8.96 \pm 0.05$  eV for the ionization of the cyclic  $\text{SiC}_2\text{H}_2$  isomer to the  $^2B_2$  state of the cation (Table 1). Up to 10.1 eV, the PIE graph has a relatively moderate slope suggesting a modest geometry change from the neutral to the cation. This is also reflected in the calculations. Both the neutral and the cation belong to the  $C_{2v}$  point group; however, the



**Figure 1.** Experimentally (open symbol and black line) recorded photoionization efficiency (PIE) curves and computed PIE curves (solid colored lines) of the low-lying individual isomers for (a) ( $\text{SiC}_2\text{H}_2^+$ ), blue line  $\text{H}_2\text{CCSi}$ ; green line  $\text{HSiCCH}$ , gray line  $\text{SiC}_2\text{H}_2$  cyclic ( $2A_1$ ); magenta line  $\text{H}_2\text{SiCC}$  linear; red line  $\text{SiC}_2\text{H}_2$  cyclic ( $2B_2$ ), (b) ( $\text{SiC}_2\text{H}^+$ ), blue line:  $\text{HSiCC}$  linear; red line  $\text{HSiCC}$  cyclic; magenta line,  $\text{SiCCH}$  linear, green line is a best fit of combined PIE curves and is discussed in the text, and (c) ( $\text{SiC}_2^+$ ) red line  $\text{SiC}_2$  cyclic; blue line  $\text{SiC}_2$  linear.

(A color version of this figure is available in the online journal.)

silicon–carbon bond extends from 1.834 Å to 2.009 Å. On the other hand, the carbon–carbon bond contracts from 1.340 Å to 1.258 Å upon ionization of the neutral. Considering the higher energy isomers, the presence of H<sub>2</sub>CCSi and HSiCCH in the molecular beam would lead to onsets of the ion counts at about 8.30 eV and 8.77 eV. This is clearly not observed as the PIE curve between 8.00 eV and 9.0 eV is flat. This suggests that neither H<sub>2</sub>CCSi nor HSiCCH, which are higher in energy by 0.78 eV and 0.79 eV compared to the global cyclic minimum, are formed in our experiment. All remaining SiC<sub>2</sub>H<sub>2</sub> isomers are even higher in energy and will not be populated in our molecular beam. Therefore, we suggest that the cyclic isomer of SiC<sub>2</sub>H<sub>2</sub> is exclusively produced. These conclusions are also supported by comparing the experimental PIE curve with the theoretically simulated ones for the three lowest SiC<sub>2</sub>H<sub>2</sub> isomers. Here, the simulated curve for c-SiC<sub>2</sub>H<sub>2</sub> depicts a perfect match to the experimental PIE curve from 9.00 eV to 10.10 eV, whereas the simulations for H<sub>2</sub>CCSi and HSiCCH do not reproduce the experimental PIE curve at  $m/z = 54$  at all. Consequently, both the onset of the ion counts and a comparison of the experimental and theoretically simulated PIE curves strongly indicate that the cyclic SiC<sub>2</sub>H<sub>2</sub> isomer is present.

We discuss now the PIE collected at  $m/z = 53$  (SiC<sub>2</sub>H<sup>+</sup>). The experimental PIE curve shows a low-intensity plateau of the ion counts from about 8.00 eV to 9.20 eV. The ion counts increase steadily from 9.20 eV to 10.50 eV. Our calculations predict that the two lowest SiC<sub>2</sub>H isomers, HCCSi and c-SiC<sub>2</sub>H, have adiabatic ionization energies of 7.27 eV and 7.00 eV, respectively. Considering the cyclic isomer, our calculations show that the cyclic cation does not present a local minimum; upon ionization, c-SiC<sub>2</sub>H rather rearranges to the linear SiCCH cation with C<sub>∞v</sub> symmetry with a VIE and an AIE of 8.10 eV and 6.96 eV, respectively. It is reasonable to expect that these states do not exhibit much intensity in the ionized cationic states because of poor Franck–Condon factors. Our simulated PIE curve of the c-SiC<sub>2</sub>H isomer supports this conclusion. As shown in Figure 1(b), low intensities of the ion counts are predicted for photon energies up to ~9.10 eV; from here on, the ion counts rise sharply. A visual comparison of the experimental and theoretically derived PIE curve for the c-SiC<sub>2</sub>H isomer depicts striking similarities. A quantitative fit of the experimental PIE curve with a linear combination of the theoretically calculated PIE curves of the individual SiC<sub>2</sub>H isomers suggests that 90% of the c-SiC<sub>2</sub>H isomer is present, with the remaining signal originating from the linear HCCSi structure. We should note that these percentages do not reflect the actual branching ratios of these isomers in the molecular beam since their photoionization cross sections are not known. However, we provided compelling evidence for the two lowest SiC<sub>2</sub>H isomers, the linear HCCSi and the cyclic SiC<sub>2</sub>H isomer, being present in the molecular beam.

Finally, we analyze the PIE curve obtained at  $m/z = 52$  (SiC<sub>2</sub><sup>+</sup>). A qualitative inspection of the PIE suggests an onset of ion counts at a photon energy of ~9.75 ± 0.10 eV. This energy falls between the theoretically predicted ionization energies of the c-SiC<sub>2</sub> and of the energetically less stable SiCC isomers with IEs of 9.83 eV and 9.67 eV, respectively. Furthermore, a comparison of the geometries of the cyclic neutral SiC<sub>2</sub> and of the ionized species predicts a significant change upon ionization. This can be seen from the elongation of the silicon–carbon bond from 1.849 Å to 2.085 Å and the reduction of symmetry from C<sub>2v</sub> to C<sub>s</sub>. Therefore, this is expected to lead to poor Franck–Condon factors. Similar to the SiC<sub>2</sub>H isomers, in order to extract the

nature of the SiC<sub>2</sub> isomer(s) formed, we have to simulate the experimental PIE curve at  $m/z = 52$  (Figure 1(c)). Here, an excellent correspondence of the experimental and theoretical PIE curves is reached from 9.70 eV to 10.20 eV by rationalizing that only the cyclic SiC<sub>2</sub> isomer is present in the molecular beam.

## 6. ASTROPHYSICAL IMPLICATIONS

Our studies suggest the existence of four distinct organo-silicon bearing species in the molecular beam: the cyclic SiC<sub>2</sub> molecule (c-SiC<sub>2</sub>), both the linear and cyclic SiC<sub>2</sub>H isomers (HCCSi, c-SiC<sub>2</sub>H), and the cyclic SiC<sub>2</sub>H<sub>2</sub> isomer (c-SiC<sub>2</sub>H<sub>2</sub>). Among these neutral molecules, only c-SiC<sub>2</sub> has been observed in the interstellar medium toward the infrared carbon star IRC + 10216 (Thaddeus et al. 1984) and later toward the carbon star IRAS12311–3509 (Evans et al. 2000). A recent high-resolution line survey of IRC + 10216 with *Herschel*/HIFI covering a spectral range from 488 to 1901 GHz confirmed this detection (Cernicharo et al. 2010). Here, 55 transitions of the cyclic SiC<sub>2</sub> molecule were detected involving energy levels between 300 K and 900 K. The authors suggest that c-SiC<sub>2</sub> is produced in the inner dust formation zone with high fractional abundances of about  $2 \times 10^{-7}$  relative to molecular hydrogen and column densities of typically  $6 \times 10^{15}$  cm<sup>-2</sup>. Recent chemical models propose an involvement of periodic shocks induced by the stellar pulsation on the coupled gas. These shocks induce a distinct non-equilibrium chemistry of the shocked gas layers even allowing collisional dissociation of carbon monoxide with a bond energy of about 11.2 eV. In these shocked regions, c-SiC<sub>2</sub> is proposed to be formed as a by-product of silicon carbide dust synthesis. Therefore, the non-equilibrium nature of the shocks can destroy and reform even exotic molecules such as c-SiC<sub>2</sub> over a pulsation period in the shocked gas of the dust formation zone. Similar processes could also lead to dust formation in carbon-rich Wolf–Rayet (WC) stars (Cherchneff et al. 2000). Since WC stars have lost all hydrogen, the chemical processes leading to organo silicon molecules in these environments resemble those in graphite or metal vaporization experiments eventually classifying high density regions in form of clumps or disks as the birth place of dust formation in WC stars.

Our studies provide accurate adiabatic ionization energies of (hydrogenated) silicon–carbon clusters of c-SiC<sub>2</sub> [9.75 ± 0.10 eV; 9.83 ± 0.05 eV], l-HCCSi [7.00 ± 0.05 eV], c-SiC<sub>2</sub>H [7.27 ± 0.05 eV], and c-SiC<sub>2</sub>H<sub>2</sub> [9.05 ± 0.05 eV; 8.96 ± 0.05 eV]; numbers in italics depict computed data. These data should provide more accurate values for future astrochemical models. The molecular inventory of discrete interstellar environments such as cold molecular clouds, diffuse clouds, and planetary nebulae provides a clock to probe the physical conditions such as the temperature and the radiation field. The UV and VUV with flux maxima in the Ly $\alpha$  region close to central stars have the capability not only to photodissociate, but also to photoionize molecules. Consequently, the “inventory” of neutral interstellar molecules and radicals can be influenced significantly by photoionization processes, yielding, for instance, singly ionized, (hydrogenated) carbon silicon molecules. This is in particular true for the c-SiC<sub>2</sub>H isomer, where photoionization changes the structure from a cyclic to a linear singly ionized molecule. This contributes to potential complications since linear HCCSi<sup>+</sup> could arise from photoionization of c-SiC<sub>2</sub>H and HCCSi.

Finally, we discuss potential formation mechanisms of the detected  $\text{SiC}_2\text{H}_x$  ( $x = 0, 1, 2$ ) isomers so that future astrochemical models simulating the formation and growth of organo-silicon molecules together with dust can incorporate our findings. Early kinetics studies by Husain et al. suggested that at room temperature, ground-state silicon atoms react fast, close to gas kinetic values, with acetylene ( $\text{C}_2\text{H}_2$ ) (Basu & Husain 1988). Later, Canosa et al. (2001) examined the kinetics down to 15 K using acetylene and ethylene as prototype reaction systems. At 15 K, this translated to rate constants of a few  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Based on the energetics, Smith et al. (2006) suggested that the spin forbidden, yet exoergic molecular hydrogen loss channels to form  $c\text{-SiC}_2$  plus  $\text{H}_2$  are open. This interpretation was challenged by Talbi (2006). These studies confirmed Canosa's finding that the initial addition of atomic silicon to acetylene has no entrance barrier. However, electronic structure calculations proposed that intersystem crossing and radiative emissions are not important, suggesting that the large rate constants may originate from a stabilization of the intermediates by the carrier gas. On the other hand, Smith (2006) proposed that intersystem crossing operates efficiently at lower collision energies. A recent crossed molecular beam experiment by Kaiser & Gu (2009) of ground-state silicon atoms ( $\text{Si}(^3P)$ ) with acetylene at a collision energy of  $101.6 \pm 1.6 \text{ kJ mol}^{-1}$  provided experimental evidence that the reaction proceeded via an addition of the silicon atom to the  $\pi$ -electrons of the acetylene molecule at a single carbon atom forming a  $\text{C}_s$  symmetric  $\text{SiC}_2\text{H}_2(\text{X}^3\text{A}')$  intermediate. The latter either emitted a hydrogen atom leading to the linear  $\text{HCCSi}$  isomer or underwent a hydrogen migration to the  $\text{H}_2\text{CCSi}$  isomer prior to the decomposition to linear  $\text{HCCSi}$  plus atomic hydrogen; minor contributions of the energetically less stable, cyclic  $\text{SiC}_2\text{H}$  isomer could not be ruled out. At this elevated collision energy, no evidence of a molecular hydrogen elimination channel leading to  $c\text{-SiC}_2$  was found. Combining these results with our data from the present investigations implies the following reaction pathways. Silicon atoms react with the acetylene molecule to form a cyclic  $\text{SiC}_2\text{H}_2$  molecule. The latter can stabilize with a third body collision, undergo unimolecular decomposition, or isomerize ultimately to the  $\text{HCCSiH}$  isomer. Based on our experimental findings,  $c\text{-SiC}_2\text{H}_2$  can lose a hydrogen atom forming the  $c\text{-SiC}_2\text{H}$  molecule. Likewise, the  $\text{HCCSiH}$  isomer can fragment by atomic hydrogen emission to form the  $\text{HCCSi}$  product. Two formation routes could account for the  $c\text{-SiC}_2$  molecule: hydrogen loss from the  $c\text{-SiC}_2\text{H}$  isomer or a molecular hydrogen emission from  $c\text{-SiC}_2\text{H}_2$ .

Our experimental conditions are related to shocks in the circumstellar envelopes of carbon stars when we consider that shocks and the current laser ablation experiments are conducted under non-chemical equilibrium conditions, where ablated silicon atoms can be injected into the gas phase, where they might react with acetylene molecules to form the cyclic  $\text{SiC}_2$  molecule ( $c\text{-SiC}_2$ ), both the linear and cyclic  $\text{SiC}_2\text{H}$  isomers, and the cyclic  $\text{SiC}_2\text{H}_2$  isomer ( $c\text{-SiC}_2\text{H}_2$ ). Since only  $c\text{-SiC}_2$  has been detected so far toward IRC + 10216, further surveys should also probe the rotational transitions of the hydrogenated species: linear and cyclic  $\text{SiC}_2\text{H}$  and the cyclic  $\text{SiC}_2\text{H}_2$  isomer ( $c\text{-SiC}_2\text{H}_2$ ). Once observed, an incorporation of distinct structural isomers into chemical models of the circumstellar envelope of IRC + 10216 could be utilized to constrain the chemical and physical conditions of shocked regions and might even help to better understand dust formation processes in these environments.

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