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Chemical dynamics of the formation of the ethynylsilylidyne radical ($SiCCH(X\ ^2\Pi)$) in the crossed beam reaction of ground state silicon atoms ($Si(^3P)$) with acetylene ($C_2H_2(X\ ^1\Sigma_g^+)$)

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The reaction dynamics of ground state silicon atoms ($Si(^3P)$) with the acetylene molecule ($C_2H_2(X\ ^1\Sigma_g^+)$) were investigated at a collision energy of 101.6 ± 1.6 kJ mol^{-1} under single collision conditions in a crossed molecular beam machine. We found that the reaction dynamics proceeded via an addition of the silicon atom to the π-electrons of the acetylene molecule at a single carbon atom forming a C_s symmetric $SiC_2H_2(X\ ^3A'')$ intermediate. The latter either emitted a hydrogen atom leading to the linear $SiCCH(X\ ^2\Pi)$ product or underwent a hydrogen migration to the $SiCCH_2(X\ ^3A_2)$ isomer prior to the decomposition of the latter to $SiCCH(X\ ^2\Pi)$ plus atomic hydrogen. The overall reaction to form the $SiCCH(X\ ^2\Pi)$ plus atomic hydrogen products was determined to be highly endoergic by 84 ± 6 kJ mol^{-1}. No evidence of a molecular hydrogen elimination channel was found at this collision energy. Our study predicts that this endoergic neutral-neutral reaction can lead to the formation of an organosilicon transient species, i.e., the linear $SiCCH(X\ ^2\Pi)$ radical, in high-temperature environments like in the circumstellar envelope of the carbon star IRC+10 216, where temperatures of a few 1000 K exist close to the central star. *© 2009 American Institute of Physics*. [doi:10.1063/1.3224150]

I. INTRODUCTION

An investigation of the energetics and dynamics of elementary reactions of ground state silicon atoms ($Si(^3P)$) with organic molecules under single collision conditions is of interest to the astrochemistry community to better rationalize the formation of silicon-bearing molecules in the interstellar medium. Molecules such as SiC and c-SiC_2 are thought to play a role in the chemical evolution of the circumstellar envelope of the dying carbon star IRC+10 216.[1,2] Here, temperatures can rise up to a few 1000 K close to the photosphere of the central star.[3,4] Based on chemical intuition, astrochemists proposed that reactions of ground state silicon atoms with hydrocarbon molecules of the generic formula C_nH_m drive the circumstellar silicon chemistry via atomic and/or molecular hydrogen replacement channels [reactions (1) and (2), respectively],

$$Si(^3P) + C_nH_m \rightarrow SiC_nH_{m-1} + H, \tag{1}$$

$$Si(^3P) + C_nH_m \rightarrow SiC_nH_{m-2} + H_2. \tag{2}$$

These considerations have led to the development of astrochemical models of circumstellar envelopes and of the inherent silicon chemistry of the bright carbon star IRC+10 216.[5] It is remarkable that based on reasonable alternative choices for the unknown reaction dynamics and branching ratios, the models show completely inconsistent mechanisms for the principal routes to the buildup of organosilicon molecules. For instance, calculated fractional abundances of SiC and c-SiC_2 diverged by up to three orders of magnitude from those observed.[6,7] This disagreement is based on inaccurate laboratory data on the reaction products and on an incorrect thermochemistry of the neutral-neutral reactions of silicon atoms with hydrocarbon molecules.[8,9]

Therefore, the fundamental question "How do silicon-bearing molecules form in the interstellar medium?" has not been conclusively resolved. Early kinetic studies by Basu and Husain[10] suggested that at room temperature, ground state silicon atoms react fast, close to gas kinetics values, with unsaturated hydrocarbon molecules. Canosa *et al.*[11] 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} cm^3 s^{-1}. Crossed beam studies of these systems at collision energies between 16 and 50 kJ mol^{-1} did not result in any reactive scattering signal—neither of the atomic nor the molecular hydrogen loss pathway.[12] In those systems, the atomic hydrogen elimination channels are strongly endoergic; for example, the formation of SiC_2H+H was predicted to be endoergic by about 77 kJ mol^{-1}.[12] Based on the energetics alone, Smith *et al.*[13] suggested that the spin-forbidden, yet exoergic molecular hydrogen loss channel to form c-SiC_2+H_2 (-62 kJ mol^{-1}) is open. Smith[14] pointed out that the reaction could proceed via a SiC_2H_2 collision complex, which is formed without entrance barrier. The barrierless addition process was confirmed in a theoretical investigation by Tabi and Talbi.[15] The lifetime of this collision complex with respect to redissociation to the reactants would be very different in the low temperature kinetics and crossed molecular beam studies. In the low temperature kinetics experiments, the addition complex might live long enough for intersystem crossing to occur

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forming eventually c-SiC_2+H_2. On the other hand at the high collision energies in the crossed beam experiment between 16 and 50 kJ mol^{-1}, the complex was suggested to redissociate rapidly; therefore, at these high collision energies, intersystem crossing and consequent formation of c-SiC_2+H_2 were proposed not to compete. Here, we test this hypothesis and conduct a crossed beam data on the reaction of ground state silicon atoms (Si(^{3}P)) with the acetylene molecule ($C_2H_2(X\ ^1\Sigma_g{}^+)$), which serves as the simplest representative of a closed-shell hydrocarbon species holding a carbon-carbon triple bond at a collision energy of 101.6 ± 1.6 kJ mol^{-1}. This collision energy should be high enough to open up the ground state silicon versus atomic hydrogen loss pathway; on the other hand, this high collision energy should not allow intersystem crossing to compete.

II. EXPERIMENTAL

The experiments were carried out under single collision conditions in a crossed molecular beam machine.[16] Pulsed ground state silicon atoms were produced in the primary source by laser ablation of a silicon rod at 266 nm by focusing a few millijoules per pulse on the rotating silicon rod. The ablated species were seeded in neat hydrogen carrier gas (Matheson; 99.9999%) at 3040 torr backing pressure released by a Proch–Trickl pulsed valve operated at pulse widths of 80 μs and −400 V. After passing a skimmer, a four-slot chopper wheel mounted after the ablation zone selected a part out of the seeded ground state silicon atom beam with a peak velocity of 2329 ± 38 m s^{-1} and a speed ratio of 5.5 ± 0.9. Under our experimental conditions, this segment did neither contain electronically excited silicon atoms, nor silicon clusters, nor silicon hydrides. This section of the beam crossed a pulsed acetylene beam (Gaspro; 99.99%); acetylene was seeded in helium at fractions of 5%, and the mixture was expanded via a pulsed valve interfaced to a heated silicon carbide tube. This resulted in peak velocities of the acetylene beam of 3106 ± 10 m s^{-1} and a speed ratio of 10.4 ± 0.6, thus leading to a collision energy of 101.6 ± 1.6 kJ mol^{-1} and a center-of-mass (CM) angle of $51.1°\pm0.5°$. The reactively scattered species are monitored using a triply differentially pumped quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the neutral molecules at 80 eV electron energy. Our detector can be rotated within the plane defined by the primary and the secondary reactant beams to allow recording angular resolved TOF spectra. By taking and integrating the TOF spectra, we obtain the laboratory (LAB) angular distribution which portrays the integrated signal intensity of an ion of distinct m/z versus the laboratory angle. At each angle, we accumulated up to 8×10^6 TOF spectra. To gain information on the chemical dynamics, the laboratory data (TOF and LAB distributions) were transformed into the CM frame and fit using a forward-convolution routine.[17] This procedure initially assumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the CM reference frame. It shall be stressed that based on previous electronic structure calculations as discussed in Sec. I, the reaction is strongly endoergic. Therefore, since the reactions of ground state silicon atoms with acetylene have a characteristic threshold energy E_o, we implemented the energy dependence of the cross section σ within the line-of-center model via Eq. (1) with the translational energy E_T for $E_T\geq E_o$ in the fitting program,[18]

$$\sigma\sim[1-E_o/E_T]. \qquad (1')$$

TOF spectra and the laboratory angular distribution were then calculated from these $T(\theta)$ and $P(E_T)$ taking into account the beam spreads and the apparatus functions. Best fits of the TOF and laboratory angular distributions were achieved by refining the $T(\theta)$ parameters and the points of the $P(E_T)$. The crucial output of this fitting routine is the product flux contour map $I(\theta,u)=P(u)T(\theta)$, which plots the intensity of the reactively scattered products (I) as a function of the CM scattering angle (θ) and product velocity (u). This contour map is called the reactive differential cross section and can be seen as the image of the chemical reaction.

III. RESULTS AND DISCUSSION

We monitored reactive scattering signal at mass to charges of $m/z=53$ and 52 corresponding to the ions of the molecular formula SiC_2H^+ and SiC_2^+. It is important to stress that after scaling, the TOF spectra of the SiC_2 ion depict identical patterns when compared to those of $m/z=53$ (SiC_2H^+). This leads us to two conclusions. First, a molecule of the formula SiC_2H is formed in the bimolecular reaction of ground state silicon atoms with acetylene. Second, signal at $m/z=52$ results from dissociative ionization of the SiC_2H parent in the electron impact ionizer. Therefore, the interpretation of the TOF data alone suggests that at a collision energy of 101.6 kJ mol^{-1}, only a molecule of the generic formula SiC_2H is formed via an atomic silicon versus hydrogen atom exchange. Also, the molecular hydrogen loss, which would lead to a SiC_2 molecule, is closed under our experimental conditions. Figures 1 and 2 depict the TOF spectra and laboratory angular distribution. The latter is very narrow and spreads only over 25° within the scattering plane. Nevertheless, this scattering range still allows us to extract information on the underlying dynamics.

As evident from Figs. 1 and 2, the laboratory data recorded at $m/z=53$ (SiC_2H^+) could be fit with a single channel resulting in the formation of reaction products of the molecular masses 53 (SiC_2H) plus 1(H). The corresponding CM functions and flux contour maps are shown in Figs. 3 and 4, respectively. Here, the CM angular distribution $T(\theta)$ depicts flux over the complete angular range from 0° to 180°. This finding suggests indirect scattering dynamics and the existence of (a) SiC_2H_2 reaction intermediate(s). Even within the error limits, which are presented in Fig. 3 as hatched areas, we could not fit the experimental data with a forward-backward symmetric CM angular distribution. Fits could only be achieved with forward-peaked (with respect to the silicon atom beam) distributions holding ratios at the poles $I(0°)/I(180°)$ of $5.0^{-1.0}_{+1.7}$. This in turn indicates that the lifetime of the reaction intermediate is shorter than the rotation period, i.e., a ratio of the lifetime of the intermediate to its rotation period of about 0.3 ± 0.1.[19] We also attempted to

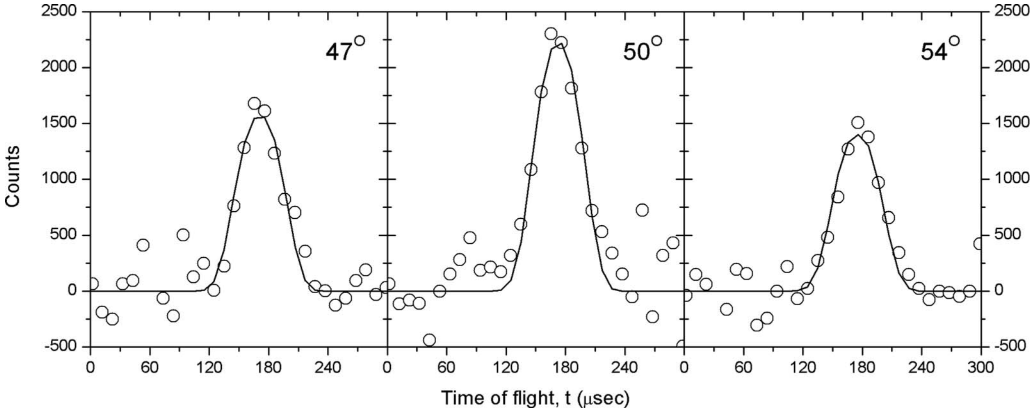

FIG. 1. Selected TOF spectra recorded at a mass-to-charge ratio m/z of 53 (SiC_2H^+) in the crossed beam reaction of ground state silicon atoms ($Si(^3P)$) with acetylene (C_2H_2) at a collision energy of 101.6 kJ mol^{-1}. The circles are the experimental data and the solid lines are the best fits utilizing the CM functions depicted in Fig. 3. Up to 8×10^6 TOF were accumulated per angle.

utilize fits representative of a more direct reaction mechanism. In this case, the fast moving reagents would not "see" the relative shallow well of the HCCHSi collision complex. However, we would like to emphasize that an adequate fit could only be achieved with intensity over the complete angular range from 0° to 180°. Therefore, these findings suggest an indirect reaction mechanism.

The CM translational energy distribution $P(E_T)$ contains further information on the dynamics. Here, best fits could be obtained with $P(E_T)$s extending up to a maximum translational energy of 28 ± 6 kJ mol^{-1}. The fits are extremely sensitive to the position of the maximum translational energy. Recall that the high energy cutoff represents the sum of the reaction energy and the collision energy; therefore, we subtract the collision energy of 101.6 ± 1.6 kJ mol^{-1} from the maximum translational energy. This suggests that the reaction to form the SiC_2H plus a hydrogen atom is endoergic by 84 ± 6 kJ mol^{-1}. Also, the $P(E_T)$ is relatively broad and shows a distribution maximum far away from zero translational energy at 10–15 kJ mol^{-1}. This finding likely indicates the existence of a tight exit barrier when the SiC_2H_2 intermediate decomposes to the final products. Finally, the CM translational energy distribution allows us to estimate the average fraction of the available energy channeling into the translational degrees of freedom of the products to be $39\pm7\%$; if we compare this order of magnitude with previ-

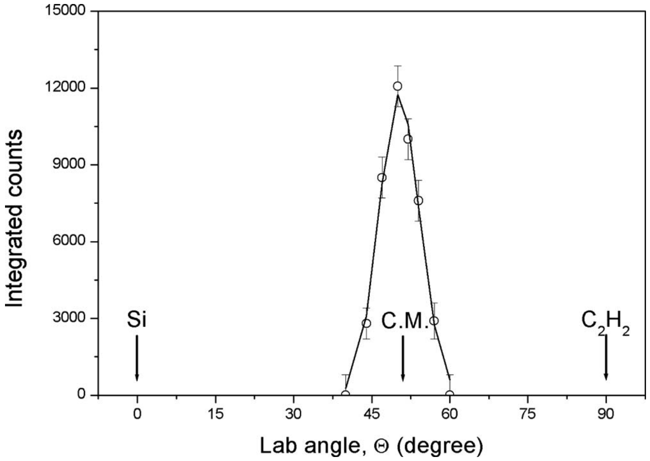

FIG. 2. Laboratory angular distribution of ions extracted from ions at mass-to-charge ratio m/z of 53 (SiC_2H^+) in the crossed beam reaction of ground state silicon atoms ($Si(^3P)$) with acetylene (C_2H_2) at a collision energy of 101.6 kJ mol^{-1}. The circles are the experimental data and the solid lines the best fits utilizing the CM functions depicted in Fig. 3.

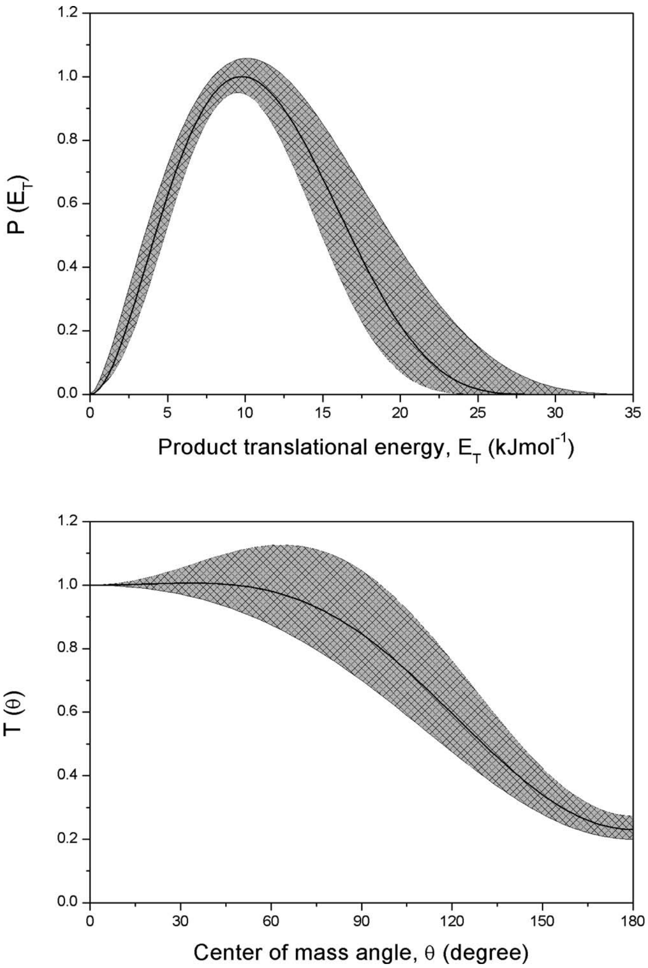

FIG. 3. CM translational energy (top) and angular (bottom) distributions of the linear SiCCH($X\ ^2\Pi$) radical formed in the reaction of ground state silicon atoms with acetylene. The solid lines represent the best fits and the hatched areas represent the allowable fits within the experimental error limits.

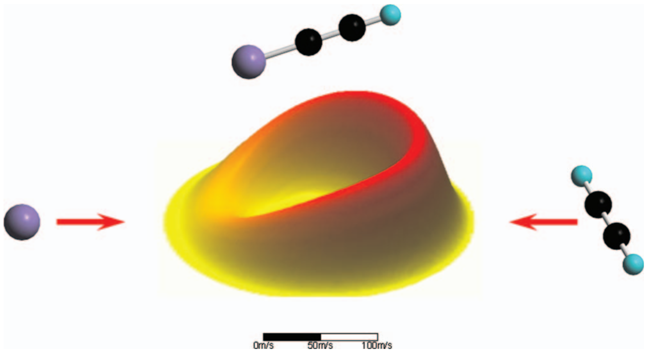

FIG. 4. CM velocity contour flux map for the reaction of ground state silicon atoms (left; 0°) with acetylene (right; 180°) derived from the best fit functions (Fig. 3) at a collision energy of 101.6 $\mathrm{kJ\,mol^{-1}}$ forming atomic hydrogen plus the linear SiCCH($X\,^2\Pi$) radical. The colors in the contour map connect data points with an identical flux and range from red (highest flux) to yellow (lowest flux). The units are given in $\mathrm{m\,s^{-1}}$ (see legend). Silicon, carbon, and hydrogen atoms are shown in purple, black, and blue.

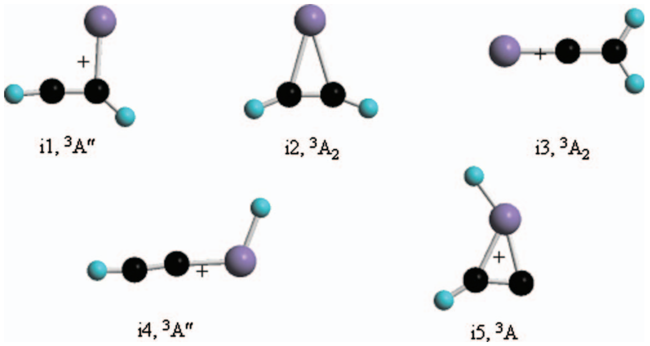

FIG. 5. Structures of various triplet SiC_2H_2 reaction intermediates potentially formed in the reaction of ground state silicon atoms with acetylene as extracted from Ref. 15. The location of the rotational axis located perpendicular to the paper plane, which would lead to *B*-like rotations in the linear SiCCH($X\,^2\Pi$) radical, is defined as + and was derived from the geometries of the intermediates as calculated by Talbi.

ous reactions following indirect scattering dynamics, we find that this fraction is indicative of a complex-forming reaction mechanism involving a relatively short lived reaction intermediate.[20] Our findings are compiled in the flux contour plot (Fig. 4).

To extract the underlying reaction dynamics, we compare now our experimental findings with previous computational studies of this reaction. Unfortunately, comprehensive triplet and singlet SiC_2H_2 potential energy surfaces incorporating all SiC_2H_2 isomers, their inherent isomerization barriers, and exit transition states leading via atomic and molecular hydrogen loss pathways to SiC_2H and SiC_2 molecules do not exist so far. Therefore, we are focusing first on the experimentally extracted reaction endoergicity of $84 \pm 6\ \mathrm{kJ\,mol^{-1}}$ and compare these data with theoretically computed ones. Here, only limited theoretical data exist as well. Bohme and co-workers[21] suggested enthalpies of formation of the linear SiCCH($X\,^2\Pi$) molecule to be between 527 and 537 $\mathrm{kJ\,mol^{-1}}$ with errors of about 17 $\mathrm{kJ\,mol^{-1}}$. Combining this value with NIST data on the enthalpies of formation of the reactants and of the hydrogen atom, the formation of the SiCCH($X\,^2\Pi$) molecules is endoergic by $73 \pm 17\ \mathrm{kJ\,mol^{-1}}$. This correlates nicely with our experimentally derived value of $84 \pm 6\ \mathrm{kJ\,mol^{-1}}$. Largo-Cabrerizo and Flores[22] identified a thermodynamically less stable (by 19 $\mathrm{kJ\,mol^{-1}}$) cyclic SiC_2H($X\,^2A'$) structure. However, an incorporation of a reaction energy of $+65 \pm 6\ \mathrm{kJ\,mol^{-1}}$ in our fitting routine did not yield a reasonable fit of the experimental data; here, the resulting TOF spectra were well too narrow and also too slow. Therefore, we can conclude that at least the linear SiCCH($X\,^2\Pi$) molecule is formed in the crossed beam reaction of ground state silicon atoms with acetylene under our experimental conditions.

How can the SiCCH($X\,^2\Pi$) molecule be formed? For this, we compare the structures of the initial reactants with those of the product molecule. First, the silicon atom is connected to a single acetylenic carbon atom. In the entrance channel, the ground state silicon atom could either add to one or to two carbon atoms of the acetylene molecule yielding either the C_s symmetric SiC_2H_2($X\,^3A''$) [i1] or the C_{2v} symmetric SiC_2H_2($X\,^3A_2$) intermediate [i2] (Fig. 5). However, computational studies by Tabi and Talbi[15] and Ikuta *et al.*[23] agree that the C_{2v} symmetric SiC_2H_2($X\,^3A_2$) structure [i2] presents a transition state; only the C_s symmetric SiC_2H_2($X\,^3A''$) molecule [i1], formed via a barrierless addition of the silicon atom under C_s symmetry, presents a local minimum which is stabilized by 47 $\mathrm{kJ\,mol^{-1}}$ with respect to the separated reactants. This intermediate could undergo hydrogen migration from the central carbon to the terminal carbon or to the silicon atom yielding the vinylidenesilene ($SiCCH_2$; $^3A_2$) [i3] and silylenylacetylene (HSiCCH; $^3A''$) [i4] intermediates, respectively; within the computational error limits both structures [i3] and [i4] are isoenergetic. Unfortunately, Talbi's surface is incomplete, and a reaction path from SiC_2H_2($X\,^3A''$) [i1] to HSiCCH($X\,^3A''$) [i4] was not considered. In addition, a simultaneous hydrogen shift-ring closure in [i1] to form a cyclic $SiHC_2H$($X\,^3A$) intermediate [i5], which can isomerize to silylenylacetylene [i4], was located. However, Talbi's computation does not consider a unimolecular decomposition of these reaction intermediates via atomic or molecular hydrogen elimination. Based on the energetics and fits of our reaction, we could exclude the existence of the cyclic SiC_2H($X\,^2A'$) isomer as the main reaction product. Therefore, the decomposition of the cyclic $SiHC_2H$($X\,^3A$) intermediate [i5], which correlates with the formation of the cyclic SiC_2H($X\,^2A'$) product, can be likely ruled out. This leaves us with the SiC_2H_2($X\,^3A_2$) [i1], $SiCCH_2$($X\,^3A_2$) [i3], and HSiCCH($X\,^3A''$) [i4] intermediates as candidates of the decomposing complex(es). In principle, all three intermediates can eject a hydrogen atom to form the linear SiCCH($X\,^2\Pi$) molecule. However, we have to recall that the CM angular distribution was found to be forward scattered. To account for this, the incorporated silicon atom and the leaving hydrogen atom must be located on opposite sides of the rotation axis of the decomposing intermediate.[24] Considering that the linear SiCCH($X\,^2\Pi$) product can be only excited to *B*-like rotations, the intermediates and hence the three heavy atoms in SiC_2H_2($X\,^3A_2$) [i1], $SiCCH_2$($X\,^3A_2$) [i3], and HSiCCH($X\,^3A''$) [i4] likely rotate within one plane. Considering the rotational axis perpendicular to the rotation plane, which contains the heavy atoms as shown in Fig. 5, intermediates $SiC_2H_2(X\,^3A_2)$ [i1] and $SiCCH_2(X\,^3A_2)$ [i3] guarantee that the incorporated silicon and leaving hydrogen atoms are located on opposite sides of the rotational axis. We would like to stress that this system presents a textbook example in which the initial orbital angular momentum is transformed mainly into the rotational excitation of linear SiCCH($X\,^2\Pi$) product. Here, the total angular momentum $\mathbf{J}$ is given as $\mathbf{J}=\mathbf{L}+\mathbf{j}=\mathbf{L}'+\mathbf{j}'$ with $\mathbf{j}$ and $\mathbf{j}'$ being the initial and final rotational angular momenta of the reactants and products and $\mathbf{L}$ and $\mathbf{L}'$. Since the reactant beams are prepared in a supersonic expansion, the rotational excitation of the reactant molecules is expected to be small so that $j \ll L$ and $\mathbf{J} \approx \mathbf{L} \approx \mathbf{L}'+\mathbf{j}'$. Due to the emission of a light hydrogen atom, a significant fraction of the total angular momentum is channeled into rotational excitation of the linear SiCCH($X\,^2\Pi$) product.[18]

Based on our findings, we can propose the following dynamics: the silicon atom adds without barrier to the acetylene molecule forming the $SiC_2H_2(X\,^3A_2)$ intermediate [i1]. The latter either decomposed via hydrogen atom emission to the linear SiCCH($X\,^2\Pi$) product or underwent a hydrogen migration to $SiCCH_2(X\,^3A_2)$ [i3]. Intermediate [i3] can also emit a hydrogen atom to synthesize the linear SiCCH($X\,^2\Pi$) product via a tight exit transition state. The latter is rotationally excited to *B*-like rotations. Note that the experimental finding of a tight exit transition state also accounts for the proposed reaction mechanism. In the reversed reaction, the hydrogen atom must add to either the C1 or C2 carbon atom of the carbon-carbon triple bond of the SiCCH($X\,^2\Pi$) molecule to form [i1] and [i3], respectively. The addition of a hydrogen atom to a closed shell olefinic or acetylenic bond is always connected with an entrance barrier in the order of 20 kJ mol^{-1}. Therefore, the order of magnitude of 10–15 kJ mol^{-1} as derived experimentally presents a reasonable exit barrier height.

IV. CONCLUSIONS AND SUMMARY

We have investigated the reaction dynamics of ground state silicon atoms with the acetylene molecule at a collision energy of 101.6 ± 1.6 kJ mol^{-1} under single collision conditions in a crossed molecular beam experiment. We found that the reaction dynamics were indirect and proceeded via an addition of the silicon atom to the π-electrons of the acetylene molecule at a single carbon atom forming a C_s symmetric $SiC_2H_2(X\,^3A'')$ intermediate [i1]. The latter either emitted a hydrogen atom leading to the linear SiCCH($X\,^2\Pi$) product or underwent a hydrogen migration to the $SiCCH_2(X\,^3A_2)$ isomer [i3] prior to the decomposition of the latter to SiCCH($X\,^2\Pi$) plus atomic hydrogen. At this high collision energy and at previous crossed beam experiments conducted at collision energies as low as 16 kJ mol^{-1}, no evidence for a molecular hydrogen elimination channel was found. The SiCCH($X\,^2\Pi$) product was found preferentially forward scattered with respect to the silicon beam; the overall reaction was derived to be endoergic by 84 ± 6 kJ mol^{-1}; these data agree well with a computational estimate predicting the reaction to be endoergic by 80 ± 5 kJ mol^{-1}. How do these findings compare with previous investigations? Recall that Smith[14] suggested that the lifetime of the SiC_2H_2 collision complex with respect to redissociation to the reactants is likely to be very different in the low temperature kinetics and crossed molecular beam studies. Whereas in the CRESU experiments, the complex could live long enough for intersystem crossing to happen, Smith proposed that the lifetime at the crossed beam experiments is too low so that intersystem crossing is effective. Our present experiments clearly show that at a collision energy of 101.6 ± 1.6 kJ mol^{-1}, no molecular hydrogen loss channel is observable. These findings are entirely consistent with Smith[14] interpretation.

Our data present evidence that endoergic neutral-neutral reactions involving silicon atoms can lead to the formation of organosilicon transient species such as the linear SiCCH($X\,^2\Pi$) radical in high-temperature environments as in circumstellar envelopes of carbon stars like IRC+10 216, where temperatures of a few 1000 K exist close to the central star. Since crossed beam experiment can mimic and hence predict the chemical evolution of interstellar environments,[25] subsequent searches of the linear SiCCH($X\,^2\Pi$) molecule in the circumstellar envelope of IRC+10 216 could help to better understand the role of a high-temperature chemistry in this circumstellar envelope. The radio spectrum of the SiCCH($X\,^2\Pi$) species—a crucial requirement to search for this molecule in the interstellar medium—was observed recently in the laboratory via Fourier transform microwave and millimeter-wave absorption spectroscopy.[26] We hope that this first "directed" synthesis under single collision conditions of the SiCCH($X\,^2\Pi$) molecule—after an identification of this species via neutralization-reionization mass spectrometry[27]—leads to the investigation of further reactions of ground state silicon atoms under single collision conditions not only with closed shell hydrocarbon molecules, but also with their corresponding radical species to better understand the organosilicon chemistry of the circumstellar envelope surrounding the carbon star IRC+10 216.

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