**Crossed molecular beams and ab Initio Investigation of Reaction of Ground State Silicon [Si (*3P*)] with Disilane [Si2H6 (*X1A1)*]: Identification of Intersystem Crossing and Molecular Hydrogen loss Product (Si3H4)**

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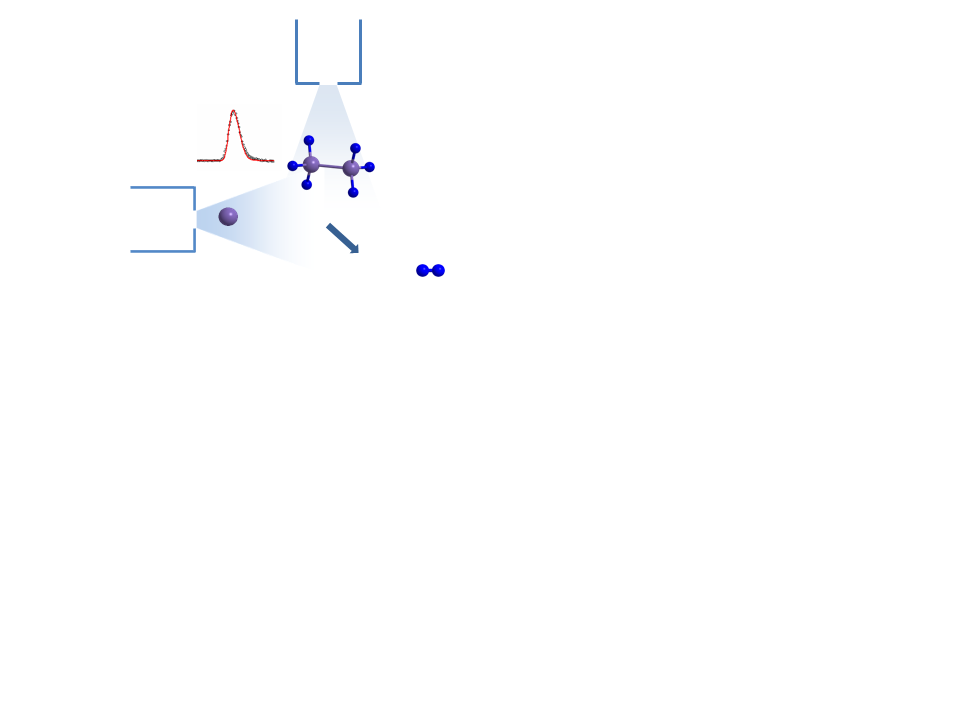
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**Abstract**

**TOC: in progress**



**1. Introduction**

Detection of complex silicon-bearing molecules in the circumstellar shells and interstellar medium[1](#_ENREF_1) demands systematic efforts in laboratory and theoretical investigation not only to understand the formation/destruction processes of such silicon-bearing molecules but also to guide astronomers in identification of potential molecules. Silicon hydrides such as silane (SiH4) and disilane (Si2H6) are routinely used in the chemical vapor deposition (CVD) processes to obtain high quality silicon surface where gas phase chemistry plays a critical role.[2](#_ENREF_2) In the CVD process, gases such as SiH4 or Si2H6 are decomposed by hot filaments or electrons generated within plasmas.[3](#_ENREF_3) During such decomposition processes, in addition to Si and Si2,[4](#_ENREF_4) clusters such as SiHx (x = 1–3), Si2Hx (x = 1–5) and Si3Hx (x = 4, 6, 8) have been identified in the gas phase as major intermediate growth species to produce amorphous, often porous silicon films.[5-7](#_ENREF_5) Understanding of bottom-up reaction sequences in the evolution of these silicon-bearing molecules in astronomical and CVD environments requires investigation of the important reaction parameters such as energetics, dynamics, geometries and electronic configurations. In addition to the astrochemical and CVD, interest in the silicon hydride molecules also arises from the physical-organic chemistry community to compare the structures and reactivity of these molecules with the well-established hydrocarbon counterparts.

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Efforts have been made to design, synthesize and isolate trisilaallene compounds by substitution of H atoms with heavy groups on the >Si=Si=Si< skeleton,[8-9](#_ENREF_8) which represents the most stable carbon configuration in C3H4 hydrocarbons. Specific reactivity and isomerization of such compounds were observed, sparking interest into the dynamics and potential energy surface (PES) of the relevant gas phase molecules, such as those shown in Scheme 1. Molecular structures and energies of several Si3H6 and Si3H4 isomers have been investigated in this regard.[10-13](#_ENREF_10) While, in case of Si3H6, trisilacyclopropane (c-(SiH2)3) with D3h symmetry (scheme 1) was found as the minimum energy isomer 41 kJ mol-1 below the carbon analogue silyldisilene (SiH3SiH=SiH2) isomer;[10](#_ENREF_10) a highly bent H2SiSiSiH2 structure with a delocalized π-system over the three silicon atoms with Cs symmetry (scheme 1) was found at the minimum on the PES 85 kJ mol-1 below the carbon analogue trisilaallene (H2Si=Si=SiH2) which exists as a second-order saddle point.[11-12](#_ENREF_11) Substitution of H atoms on the H2SiSiSiH2 molecule by bulky and electropositive groups possessing σ-donor, π-acceptor character, restores the Si=Si=Si bond linearity.[8](#_ENREF_8) These results demonstrate the striking differences in molecular structure and bonding in carbon versus silicon hydrides and emphasize the need of studies that can unravel the fundamental mechanistic processes of silicon hydrides.

Despite their importance in fundamental chemical understanding; virtually no bimolecular experimental studies exist on the formation/decomposition processes of small silicon hydride molecules with the exception of some kinetic studies where identity of the reaction products remains largely unknown.[14-16](#_ENREF_14) Systematic efforts have been initiated in our laboratory to unravel the dynamics of bimolecular reactions of silicon hydrides utilizing crossed molecular beams technique. Recently, we have investigated the Si+SiH4 reaction combined with theoretical calculations accessing the Si2H4 PES.[Ref, Si+SiH4 paper] Some of the key features of this reactions are barrierless insertion of Si (*3P*) in to the Si-H bond of the SiH4 forming HSiSiH3, intersystem crossing of HSiSiH3 intermediate from triplet to singlet, rearrangement of HSiSiH3 to H2SiSiH2 and dissociation into H2SiSi+H2 as a major reaction channel without an exit transition state. Even though this reaction was previously investigated theoretically[17](#_ENREF_17) and experimentally[14](#_ENREF_14), [18](#_ENREF_18) by other methods, only our crossed beams experiments were able to identify the reaction mechanism leading to the isomer specific products distinguishing the kinetically and thermodynamically favorable products and paths. In this paper, we report the bimolecular reaction of silicon ground state, Si(*3P*), with Si2H6, accessing the Si3H6 PES, with mass spectrometric detection of hydrogen molecule loss product Si3H4. Reaction energy and dynamics were measured from the product translational energy distribution and angular distribution, respectively. Experimental data are then combined with the electronic structure calculations to gain insights in to the isomeric reaction product(s), energetics, dynamics and mechanism.

**2. Results**

**2.1 Experimental Results**

Silicon atoms were produced by laser ablation and characterized by Laser Induced Fluorescence (LIF) spectrum as shown in Figure 1, in addition to the mass spectrometric detection. The LIF spectra showed presence of Si atoms only in their ground electronic state, *3P*. No signal was detected for the first electronically excited state, *1D2*. Different *J* states were detected corresponding to the *3P* but these do not play a significant role in our experiments because of small (3 kJ mol-1) energy separation which lies within our experimentally measured translational energy error range. Figure 2 top panel shows the integrated time-of-flight (TOF) peak intensities at various laboratory angles for the Si3H4 product. The intensity was peaked around the center-of-mass (CM) angle of 50.6 ± 1.1 degrees, forward-backward symmetric around the CM, and scattered over 40 degrees over the scattering plane. Figure 2 lower panel shows the experimental TOF data and fits for Si3H4 product (m/z = 88) formed due to H2 loss from collision at various laboratory angles. These findings suggest that the reaction involves indirect, complex forming, scattering dynamics involving the decomposition of Si3H6 complex(es). Therefore, analysis of the lab frame data alone indicates the formation of Si3H4 isomer(s) through an involvement of a silicon ground electronic state atom versus hydrogen molecule exchange channel.

The CM frame data, presented in Figure 3, provide additional information on the reaction dynamics. The top panel in the Figure 3 shows the translational energy distribution, *ET*, while the bottom panel shows the angular distribution, *θ,* for the Si3H4 + H2 product channel. The *P*(*ET*) value peaks away from the zero translational energy at around 8-15 kJ mol-1 suggesting a loose exit transition state with energy barrier of such magnitude for the reverse reaction. The maximum of the *ET* gives the sum of the collision energy and reaction energy in the limit that total available energy transfers to the translational degree of freedom. Therefore, *ET* maxima can be utilized to extract the reaction energy. For the maximum translational energy of 50 ± 15 kJ mol-1, the reaction is determined to be exothermic by 24 ± 17 kJ mol-1 after subtracting the nominal collision energy. The *θ* distribution is forward-backward symmetric with respect to the reactant beams and is distributed over the complete angular range of 00 – 1800 with maximum flux *T(θ)* around 900. Detection of the reaction product over complete angular range and the symmetry of the peak suggests that this system follows indirect scattering dynamics via the formation of Si3H6 reaction intermediate(s).[19](#_ENREF_19) Furthermore, no optimal flux at any CMangle *θ* within the experimental error limit indicates no preferential direction for the leaving H2 group or a low symmetry for the exit transition state. This result can also be interpreted by the existence of multiple exit transition states with different angles of preference with respect to the molecular plane for the leaving group.

**2.2 Theoretical Results**

Figure 4 presents the PES for the Si+Si2H6 reaction which includes reactants, selected intermediates, transition states and products relevant to the experiment.

**3. Discussion**

**4. Methods**

**4.1 Experimental Methods**

The crossed molecular beams study of silicon (Si; *3P*) with disilane (Si2H6) was investigated in a universal crossed molecular beams machine at the University of Hawaii at Manoa which has been described previously[20-21](#_ENREF_20) and hence only the relevant details are given here. In the primary chamber, pulsed silicon atoms were produced *in situ* by ablating a rotating silicon rod by the output of a Spectra-Physics Quanta-Ray Pro 270 Nd:YAG laser operating at 30 Hz and 266 nm with a power of 260 ± 20 mW. The ablated species were then seeded in neon (Ne; 99.999 %; Specialty Gases of America) carrier gas at a backing pressure of 4 atmospheres ejected from a pulsed piezoelectric valve (Piezo Disk Translator P-286.23; Physik Instrumente) at a repetition rate of 60 Hz, pulse width of 80 μs and a peak voltage of -400 V. The pulsed beam of the silicon atoms seeded in neon then passed through a skimmer and a four-slit chopper wheel rotating at 120 Hz, resulting into a section of beam with a well-defined peak velocity (vp) and speed ratio (S) of 1510 ± 14 ms-1 and 2.8 ± 0.2, respectively. In the secondary chamber, pulsed beam of disilane (99.998%, Voltaix) was prepared by the secondary piezoelectric valve with a repetition rate of 60 Hz, pulse width of 80 μs and a peak voltage of -400 V with backing pressure of 550 torr resulting in peak velocity and speed ratio of 775 ± 15 ms-1 and 7.8 ± 0.4, respectively. Due to the extreme flammability of disilane, we utilized a nitrogen cold trap (Nor-Cal products) in the foreline between the turbo and roughing pumps in order to capture the disilane molecules. After passing through the secondary skimmer, the pulsed disilane beam crossed perpendicularly with the silicon atoms seeded in neon, resulting into collision energy of 24.3 ± 0.8 kJ mol-1 and center-of-mass (CM) angle of 50.6 ± 1.1°. Note that the primary pulsed valve was triggered after 1872 µs with respect to the time zero defined by the infrared diode mounted at the top of the chopper wheel, while the flash lamp of the ablation laser was fired 155 µs after the primary pulse valve with Q-switch fired 186 µs after the flash lamp, in order to create the maximum overlap of the pulsed laser beam and the neon beam. The secondary pulsed valve was triggered 65 µs prior to the primary pulsed valve due to relatively slower velocity of disilane. The 60 Hz repetition rate of pulsed valves and 30 Hz repetition rate of the ablation laser enable a “laser-on” minus “laser-off” subtraction to eliminate the background from non-ablated species.

The reactively scattered products were mass filtered after ionization utilizing a quadrupole mass spectro­meter (QMS) and detected by a Daly-type TOF detector housed in a rotatable, triply-differentially pumped ultrahigh vacuum chamber (210-11 Torr) after electron-impact ionization of the neutral products at an electron energy of 80 eV and an emission current of 2 mA. This detector can be rotated within the plane defined by the primary and the secondary reactant beams allowing recording of angular-resolved TOF spectra. At each angle, up to 6105 TOF spectra were accumulated to obtain good signal-to-noise ratios. The recorded TOF spectra were then integrated and normalized to the intensity of the TOF at the center of mass angle to extract the product angular distribution in the laboratory frame. In order to acquire information on the scattering dynamics, the laboratory data were then transformed from the laboratory into the center-of-mass reference frame utilizing a forward-convolution routine.[22-24](#_ENREF_22) This iterative method employs a para­me­trized or point-form angular flux distribution, *T(θ)*, and translational energy flux distribution, *P(ET)*, in the CM system. Laboratory TOF spectra and the laboratory angular distributions are cal­cu­la­ted from the *T(θ)* and *P(ET)* function and are averaged over a grid of Newton diagrams accounting for the apparatus functions, beam divergences, and velocity spreads. For the fitting, we considered a reactive scattering cross section of an *ET*-1/3 energy dependence, where *ET* stands for the translational energy. This method is usually adopted within the line-of-center model for exoergic and entrance barrierless reactions dominated by long-range attractive forces.[25](#_ENREF_25)

In addition to the mass spectrometric detection, quantum states of silicon atoms were also characterized utilizing laser-induced fluorescence (LIF) spectroscopic method.[26-27](#_ENREF_26) Si atoms in the ground (triplet) and first excited (singlet) spin states were probed via 3p2 3P → 3p4s 3P and 3p2 1D → 3p4s 1P transitions around 251 nm and 288 nm, respectively. 3P ground states were detected for several *J* states which lie within 3 kJ mol-1 which is too small to be resolved in our scattering results. No signal was detected for the 3p2 1D → 3p4s 1P transition implying the absence of excited electronic states in the silicon atomic beam.

**4.2 Theoretical Methods**

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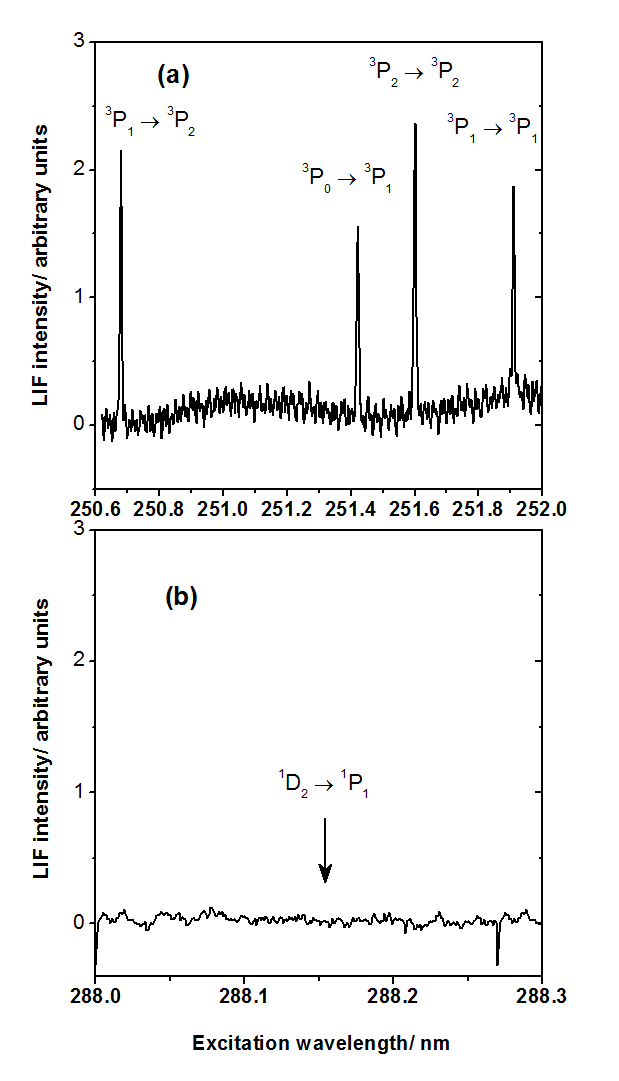
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**Figure 1:** Laser Induced Fluorescence (LIF) spectra of **(a)** ground (*3P*), and **(b)** excited (*1D*) states of atomic silicon recorded in a laser ablation source. Arrow in the panel **(b)** indicates expected position for noted transition.

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**Figure 2:** Laboratory angular distribution (top) and time-of-flight spectra (bottom) recorded at a mass-to-charge ratio m/z = 88 (Si3H4+) in the reaction of ground state atomic silicon with disilane. The circles define the experi­men­tal data and the red lines the calculated distribution with the best fit center-of-mass functions as depicted in Figure 2. C.M. designates the center of mass angle.

C:\My Documents\Beni Dangi\UH\silicon\Si_Si2H6\graphs\Product translational energy and COM angle distribution.tif

**Figure 3:** Center-of-mass angular (top) and translational energy flux distributions (bottom) lead­ing to the formation of the Si3H4 product in the reac­ti­on of ground state atomic silicon with disilane. Hatched areas indicate the ac­cept­able upper and lower error limits of the fits. The solid lines define the best fit functions.