

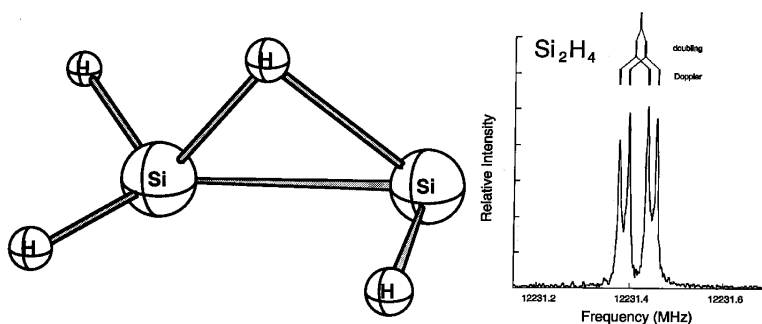
Article

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Mono- and Dibridged Isomers of Si₂H₃ and Si₂H₄: the True Ground State Global Minima. Theory and Experiment in Concert

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Abstract: Highly correlated ab initio coupled-cluster theories (e.g., CCSD(T), CCSDT) were applied on the ground electronic states of Si₂H₃ and Si₂H₄, with substantive basis sets. A total of 10 isomers, which include mono- and dibridged structures, were investigated. Scalar relativistic corrections and zero-point vibrational energy corrections were included to predict reliable energetics. For Si₂H₃, we predict an unanticipated monobridged H₂Si–H–Si-like structure (C_s, ²A'') to be the lowest energy isomer, in contrast to previous studies which concluded that either H₃Si–Si (C_s, ²A'') or near-planar H₂Si–SiH (C₁, ²A) is the global minimum. Our results confirm that the disilene isomer, H₂Si–SiH₂, is the lowest energy isomer for Si₂H₄ and that it has a trans-bent structure (C_{2h}, ¹A_g). In addition to the much studied silylsilylene, H₃Si–SiH, we also find that a new monobridged isomer H₂Si–H–SiH (C₁, ¹A, designated **2c**) is a minimum on the potential energy surface and that it has comparable stability; both isomers are predicted to lie about 7 kcal/mol above disilene. By means of Fourier transform microwave spectroscopy of a supersonic molecular beam, the rotational spectrum of this novel Si₂H₄ isomer has recently been measured in the laboratory, as has that of the planar H₂Si–SiH radical. Harmonic vibrational frequencies as well as infrared intensities of all 10 isomers were determined at the cc-pVTZ CCSD(T) level.

I. Introduction

Small silicon hydrides are of interest because of their potential applications in semiconductors and optoelectronics and in surface growth processes and their likely existence in the circumstellar atmospheres of evolved carbon stars.^{1–9} They play key roles in the plasma-enhanced chemical vapor deposition of thin films and nanomaterials, which is an important but a poorly understood process.^{2,6,10,11} Unsaturated silicon hydrides such as SiH, SiH₂, and Si₂H₂ have been the subject of numerous experimental investigations because silicon molecules are readily observed in space: nearly 10% of the presently identified astronomical molecules contain silicon, and silicon is important in the photochemistry of the carbon rich star IRC+10216.

The ability of silicon to form mono- and dibridged hydrides and existence of Si–Si multiple bonds make the silicon hydrides very attractive molecules for both experimental and theoretical study. This is especially true for unsaturated silicon hydrides, where determinations of ground state geometries and relative isomeric energies are quite challenging. Because potential energy surfaces are often flat, many isomeric arrangements are possible, and accurate predictions of equilibrium geometries require advanced quantum mechanical investigations. In the Si₂H_n series, many theoretical and experimental studies indicate that Si₂H is monobridged and Si₂H₂ is dibridged in their ground states.^{5,12–20} These somewhat surprising findings added a new dimension to the silicon chemistry, which had been widely assumed to be similar to that of carbon.^{16,17,19–21}

The equilibrium geometries for Si₂H₃ and Si₂H₄ are still not fully determined. In 1991, Sax and Kalcher²² reported a study of many silicon hydrides including Si₂H₃ and Si₂H₄. They used

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the MRCI technique with double and triple- ζ quality basis sets and investigated $\text{H}_3\text{Si}-\text{Si}$ ($^2A''$) and the near-planar $\text{H}_2\text{Si}-\text{SiH}$ isomers of Si_2H_3 . They found $\text{H}_3\text{Si}-\text{Si}$ ($^2A''$) to be 1.1 kcal/mol more stable than the near-planar $\text{H}_2\text{Si}-\text{SiH}$. In 1991, Curtiss, Raghavachari, Deutsch, and Pople²³ reported that the lowest energy structure of Si_2H_3 is the $\text{H}_3\text{Si}-\text{Si}$ ($^2A''$) isomer, with near-planar $\text{H}_2\text{Si}-\text{SiH}$ lying 1.3 kcal/mol higher in energy. They also reported that all bridged structures were found to be significantly higher in energy. In 1997, Gong, Guenzburger, and Saitovitch¹¹ studied six different isomers of Si_2H_3 : silylsilylydyne $\text{H}_3\text{Si}-\text{Si}$ (C_s); the near-planar $\text{H}_2\text{Si}-\text{SiH}$ (C_1); two monobridged isomers, $\text{HSi}-\text{H}-\text{SiH}$ (C_2) and $\text{H}_2\text{Si}-\text{H}-\text{Si}$ (C_3); a dibridged; and a tribridged isomer. They concluded that the lowest energy structure is the monobridged structure ($\text{HSi}-\text{H}-\text{SiH}$, C_2), while the other monobridged structure ($\text{H}_2\text{Si}-\text{H}-\text{Si}$, C_3) is only 0.9 kcal/mol (0.04 eV) higher in energy. They also reported that the $\text{H}_3\text{Si}-\text{Si}$ (C_s) like structure, which was predicted to be the lowest energy isomer by both Kalcher²² and Pople,²³ is 9.0 kcal/mol (0.39 eV) higher in energy. The tribridged isomer was found to be significantly higher in energy (0.64 eV). In 2001, Pak, Rienstra-Kiracofe, and one of us⁸ studied the $\text{H}_3\text{Si}-\text{Si}$ (C_s), the near-planar $\text{H}_2\text{Si}-\text{SiH}$ (C_1), and the monobridged ($\text{HSi}-\text{H}-\text{SiH}$, C_2) isomers at the DFT level (B3LYP/DZP+). They reported that the $\text{H}_3\text{Si}-\text{Si}$ (C_s) isomer and the near-planar $\text{H}_2\text{Si}-\text{SiH}$ (C_1) isomer are nearly isoenergetic and that the employed level of theory (B3LYP/DZP+) was not adequate to decide which is the more stable (only a 0.02 kcal/mol energy difference was found between the two structures). The monobridged ($\text{HSi}-\text{H}-\text{SiH}$, C_2) isomer, which was predicted to be the ground state geometry by Saitovitch et al.,¹¹ was predicted to be 4.1 kcal/mol higher in energy.

The shape of the minimum energy structure of the Si_2H_4 molecule has been studied for almost twenty years. When isolated and characterized in 1981, by Michl, West, and co-workers,²⁴ the first disilene (Si_2R_4) was thought to be planar, like ethylene. The ab initio studies have focused primarily on the two isomers of Si_2H_4 , disilene ($\text{H}_2\text{Si}-\text{SiH}_2$) and silylsilylene ($\text{H}_3\text{Si}-\text{SiH}$). Although all of the theoretical studies found that disilene ($\text{H}_2\text{Si}-\text{SiH}_2$) is the lowest energy isomer, they predict significantly different structures. In 1986, Olbrich²⁵ carried out SCF/TZP calculations and collected the previous estimates of the minimum energy structure of disilene ($\text{H}_2\text{Si}-\text{SiH}_2$). According to Table 1 of his paper, 6 of the 11 previous theoretical studies found it ($\text{H}_2\text{Si}-\text{SiH}_2$) to be planar, like ethylene, and 5 of them found it to be a trans-bent structure. His SCF/TZP calculations predicted the trans-bent structure to be that of minimum energy. Recent theoretical predictions also differ on whether disilene ($\text{H}_2\text{Si}-\text{SiH}_2$) is planar or bent. In 1990, Trinquier²⁶ favored the planar form, in 1991, Pople and co-workers²³ predicted the trans-bent structure, and in 2000, the DFT calculations of Pak et al.⁸ yielded a near-planar trans-bent structure. Very recent (in 2002) infrared spectra taken by Andrews and Wang²⁷ suggested a trans-bent structure for disilene. Predictions for the relative energy of the silylsilylene ($\text{H}_3\text{Si}-\text{SiH}$) isomer vary between 5 and 10 kcal/mol.^{8,14,23,28-31}

Table 1. Dipole Moments (debye), Harmonic Vibrational Frequencies (cm^{-1}), and Associated Infrared Intensities (km/mol, in Parentheses) for the Isomers of Si_2H_3 , Determined at the cc-pVTZ CCSD(T) Level

structure	μ_e	ZPVE	harmonic vibrational frequencies (symmetries, infrared intensities)
1a ($\text{H}_2\text{Si}-\text{SiH}$, $^2A''$)	1.04	13.97	319(a'',2), 385(a'',12), 414(a',4), 470(a',10), 709(a',36), 976(a',85), 2047(a',157), 2214(a',100), 2237(a',106)
1b ($\text{H}_3\text{Si}-\text{Si}$, $^2A''$)	0.30	15.60	396(a'',47), 416(a',11), 486(a',16), 898(a'',291), 964(a',48), 989(a'',33), 2224(a',105), 2266(a',79), 2276(a'',95)
1c ($\text{H}_2\text{Si}-\text{H}-\text{Si}$, $^2A''$)	1.07	14.53	409(a'',7), 472(a',2), 507(a',26), 713(a'',13), 955(a',33), 1016(a',382), 1664(a',94), 2210(a',143), 2221(a'',101)
1d ($\text{H}-\text{Si}-\text{H}-\text{Si}-\text{H}$, 2A)	0.11	14.74	471(a,0), 623(b,108), 658(a,7), 731(a,0), 844(b,591), 1210(b,1049), 1532(a,70), 2109(a,2), 2129(b,331)
1e ($\text{H}-\text{Si}-\text{H}-\text{Si}-\text{H}$, 2A)	0.74	13.73	393(a,13), 423(a,5), 568(a,1), 643(a,47), 889(a,33), 1052(a,210), 1541(a,68), 2010(a,103), 2114(a,164)

No bridged isomer of Si_2H_4 to our knowledge has previously been studied.

The present theoretical studies were motivated in part by recent laboratory measurements, using Fourier transform microwave (FTM) spectroscopy of a supersonic molecular beam, of the rotational spectra of two new silicon hydrides: planar (or nearly planar) Si_2H_3 and an isomer of Si_2H_4 , yielding rotational constants that do not agree with those predicted. Because of the somewhat contradictory theoretical predictions as to the true ground state equilibrium structures and the apparent lack of ab initio studies which adequately explored the stability of bridge structures, we investigated Si_2H_3 and Si_2H_4 using highly correlated coupled-cluster theories [i.e., singles and doubles with a perturbative triples [CCSD(T)] and singles, doubles, and full triples (CCSDT)]. To our knowledge, this is the first time coupled-cluster theory has been used to study the ground electronic states of these two silicon hydrides. Scalar relativistic corrections were also included to determine accurate relative energies. A total of five isomers of Si_2H_3 and five isomers of Si_2H_4 were found to be stable. We conclude on the basis of the close agreement of the theoretical and experimental rotational constants that the new silicon hydride that has been detected in the laboratory is monobridged Si_2H_4 , a low-lying isomer which is calculated to be quite polar ($\mu = 1.14$ D) and to lie only about 7 kcal/mol above disilene.

II. Theoretical Approach

The zeroth-order descriptions of all isomers were obtained using single configuration SCF (restricted open-shell Hartree-Fock for Si_2H_3 and restricted closed-shell Hartree-Fock for Si_2H_4) wave functions. Correlation effects were included using coupled cluster with single and double excitations with perturbative triple excitations [CCSD(T)].³² Correlation consistent

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polarized valence double- ζ (cc-pVDZ) and triple- ζ (cc-pVTZ) basis sets³³ were used for both hydrogen and silicon atoms.

The coupled cluster with single, double, and full-triple excitations (CCSDT) and the newly developed CCSD(2) theory³⁴ which has a new class of correction that involves perturbatively expanding the similarity-transformed Hamiltonian from the coupled-cluster gradient theory have also been employed for single-point energy calculations. The CCSDT calculations are not feasible with the cc-pVTZ basis set due to the extremely high computational costs (a single-point CCSDT/cc-pVTZ calculation for Si₂H₃ would take around 20 days on a 2.4 GHz pentium-4 machine). Therefore, the cc-pVDZ basis set was used for CCSDT calculations, whereas the larger cc-pVTZ basis set was used for CCSD(2) calculations. The effects of full-triple coupled-cluster excitations on relative energies were determined from the differences between the cc-pVDZ CCSDT and cc-pVDZ CCSD(T) results, and these effects were included on top of the cc-pVTZ CCSD(T) values to estimate the cc-pVTZ CCSDT results.

For the determination of the relativistic energy corrections, the one-electron Darwin term, which is always positive, and the mass-velocity term, which is always negative, were evaluated using first-order perturbation theory.^{35,36} The Darwin term corrects the Coulomb attraction, and the mass-velocity term corrects the kinetic energy of the system. This simple relativistic treatment gives satisfactory results for silicon compounds (and all atoms up to $Z = 40$) compared to those from methods such as Dirac-Hartree-Fock (DHF) and the use of relativistic effective core potentials (RECP).^{37,38}

The geometries of the all isomers were optimized via analytic derivative methods^{39,40} at the SCF and CCSD(T) levels. Harmonic vibrational frequencies were determined by means of finite differences of analytic gradients. Cartesian forces at optimized geometries were required to be less than 10^{-6} hartree/bohr in all geometry optimizations. Throughout our study, all computations were carried out using the ACES II package,⁴¹ except for the CCSD(2) calculations which were performed using the Q-Chem package.⁴² IBM RS/6000 workstations, an IBM SP2, and PC machines were used.

III. Experimental Details

Rotational lines of Si₂H₃ and Si₂H₄ were detected at centimeter wavelengths with a sensitive FTM spectrometer that has been used to detect over 100 reactive carbon and silicon chains and rings during

the past seven years. This instrument operates between 5 and 43 GHz and possesses a very sensitive microwave receiver that can be cooled together with the large confocal mirrors of the spectrometer to the temperature of liquid nitrogen.⁴³ It is automated to the point that rotational spectra can be rapidly acquired either in a search mode, where individual spectra, each limited in spectral range by the confocal cavity to about 0.5 MHz, are stitched together, or in a single-scan mode, where individual spectra are recorded at many different preselected frequencies. Data acquisition is under computer control in either mode. A rotational line of a known molecule was routinely monitored for calibration. Reactive molecules are produced in a small electric discharge in the throat of a nozzle through a stream of precursor gases heavily diluted in a buffer gas, just prior to supersonic expansion to about Mach 2 in a large vacuum chamber.

The strongest lines of the two new silicon hydrides were observed with source conditions similar to those used to detect a variety of silicon carbides and other silicon-bearing molecules:⁴⁴ silane (0.1–0.2%) heavily diluted in neon (99.8%), a stagnation pressure behind the pulsed valve of 3.5 atm, a discharge potential of 900–1000 V, and a gas pulse 200 μ s long (i.e., a gas flow of 10–15 sccm). As Figures 4 and 5 illustrate, under these conditions, rotational lines of both silicon hydrides can be observed with a high signal-to-noise ratio in only a few minutes of integration. Lines of the normal isotopic species are so strong for both silicon hydrides that the two ²⁹Si and the two ³⁰Si isotopic species were also detected, despite their low fractional abundances (4.7% and 3.1%, respectively).

The fundamental ($1_{0,1} \rightarrow 0_{0,0}$) rotational transitions of both Si₂H₃ and Si₂H₄ were first detected in a large frequency survey between 11 and 16 GHz using source conditions which optimized the production of monobridged Si(H)SiH.⁴⁵ Although the unidentified line density is fairly high in this region, with a line roughly every 20 MHz, both molecules have a distinctive spectroscopic pattern: each rotational transition of Si₂H₃ consists of many features closely spaced in frequency, while each transition of Si₂H₄ is a closely spaced doublet of equal intensity. Once these transitions were identified, subsequent searches for the $2_{0,2} \rightarrow 1_{0,1}$ transition, as well as other transitions, quickly yielded an additional series of lines of comparable intensity and multiplicity.

The present identifications are subject to very little doubt. Our new molecules are almost certainly silicon hydrides because the lines are only found in the presence of an electrical discharge through gas containing SiH₄, as expected for a silicon-bearing molecule, and the lines vanish when silane is replaced with SiD₄, indicating a hydrogen-bearing molecule. Impurities from contaminants in the gas samples and van der Waals complexes with the buffer gas can also be ruled out, because the silane gas is of high purity (99.9%), and the lines were also produced with nearly equal intensity with disilane (Si₂H₆) as the precursor gas and when Ar replaced Ne as the buffer gas. As expected for the paramagnetic doublet electronic ground state of Si₂H₃, the assigned lines exhibit a pronounced Zeeman effect when a strong permanent magnet is brought near the molecular beam of our FTM spectrometer; for the closed-shell, singlet electronic state of Si₂H₄, the lines are unchanged in intensity and width when the same magnetic test is performed. Crucial conformation of the Si₂H₃ and Si₂H₄ assignments is finally provided by isotopic substitution: as explained in the next section, lines of the ²⁹Si and the ³⁰Si isotopic species and

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those of the doubly deuterated isotopic species of both molecules were observed to be in perfect agreements with those calculated from the theoretical structures.

IV. Results and Discussion

The optimized equilibrium geometries at the cc-pVTZ CCSD(T) level of theory are presented in Figure 1 for isomers of Si_2H_3 and in Figure 2 for isomers of Si_2H_4 . The determined rotational constants for each isomer are also given there. Figure 3 shows the structure of the transition state between two equivalent monobridged isomers of Si_2H_4 . The experimentally obtained rotational spectrum of the planar Si_2H_3 isomer is given in Figure 4, and that of monobridged isomer of Si_2H_4 is shown in Figure 5. The predicted dipole moments, harmonic vibrational frequencies, infrared intensities, and zero-point vibrational energies (ZPVE) are given in Table 1 for Si_2H_3 and in Table 5 for Si_2H_4 . Tables 2–4 give the relative energies of the different isomers of Si_2H_3 , and Tables 6–8 give the corresponding energies for the isomers of Si_2H_4 . Tables 9 and 10 show the experimental and theoretical rotational constants of the planar $\text{H}_2\text{Si-SiH}$ isomer (structure **1a**) and the monobridged $\text{H}_2\text{Si-H-SiH}$ isomer (structure **2c**), respectively.

A. Structures. 1. Si_2H_3 . We have located five distinct minima on the doublet ground electronic state of Si_2H_3 . The corresponding structure for each minimum is presented in Figure 1. The much studied planar form (structure **1a**, C_s , ${}^2A''$) and the $\text{H}_3\text{Si-Si}$ isomer (structure **1b**, C_s , ${}^2A''$) were correctly located as well as three different monobridged structures; the $\text{H}_2\text{Si-H-Si}$ -like isomer (Structure **1c**, C_s , ${}^2A''$), the trans-like H-Si-H-Si-H monobridged isomer (structure **1d**, C_2 , 2A), and the cis-like H-Si-H-Si-H monobridged isomer (structure **1e**, C_1 , 2A). The shortest Si-Si bond, 2.244 Å, was found for the $\text{H}_2\text{Si-H-Si}$ monobridged isomer (structure **1c**); the longest Si-Si bond, 2.379 Å, was found for the $\text{H}_3\text{Si-Si}$ isomer (structure **1b**).

The geometrical parameters of the planar (structure **1a**) and the $\text{H}_3\text{Si-Si}$ isomer (structure **1b**) are very consistent with previous theoretical predictions,^{8,15,23} except that all the previous studies found a near-planar (or quasi-planar) form for the $\text{H}_2\text{Si-SiH}$ isomer. We did optimizations in both C_1 and C_s symmetries, and both of them gave the same perfectly planar structure with exactly the same energy. However, the geometrical parameters are very consistent with what were given for a near-planar structure. Two of the three monobridged isomers that we found, the $\text{H}_2\text{Si-H-Si}$ -like isomer (Structure **1c**) and trans-like H-Si-H-Si-H monobridged isomer (structure **1d**) were also predicted by Gong et al.¹¹ However, although they mentioned the relative energies, Gong did not report geometrical parameters. Therefore, no literature data about these two monobridged isomers of Si_2H_3 have been found to compare with our structures. In addition, a third monobridged isomer (structure **1e**) has been successfully optimized at all levels of theory employed here. This newly predicted monobridged isomer (structure **1e**) has no symmetry (C_1), and the distances of the bridged hydrogen to the two Si atoms are not equivalent. The two nonbridged hydrogen atoms are slightly out of the plane that contains the Si atoms (around 8° and in the opposite directions). We have searched for a possible dibridged or a tribridged isomer of Si_2H_3 without success.

Strong rotational lines of planar Si_2H_3 (structure **1a**) have now been detected in the laboratory by means of FTM

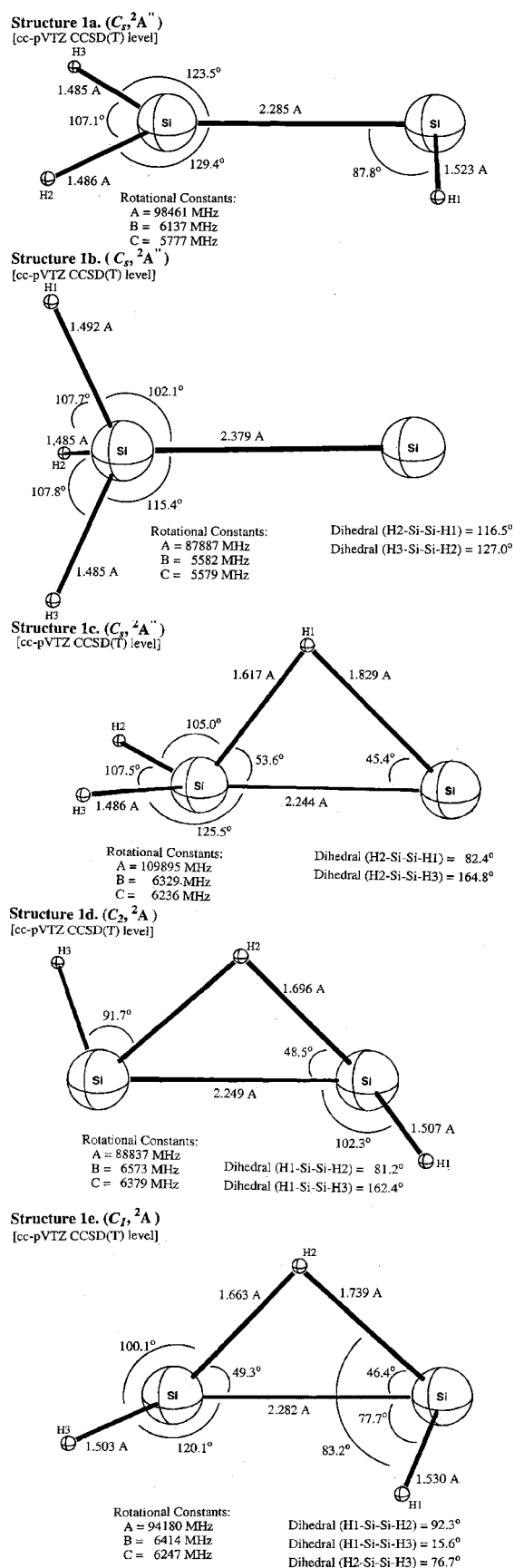


Figure 1. Isomers of Si_2H_3 , optimized at the cc-pVTZ CCSD(T) level of theory.

spectroscopy. As shown in Figure 4, owing to the hyperfine structure from the three unequivalent hydrogen atoms and

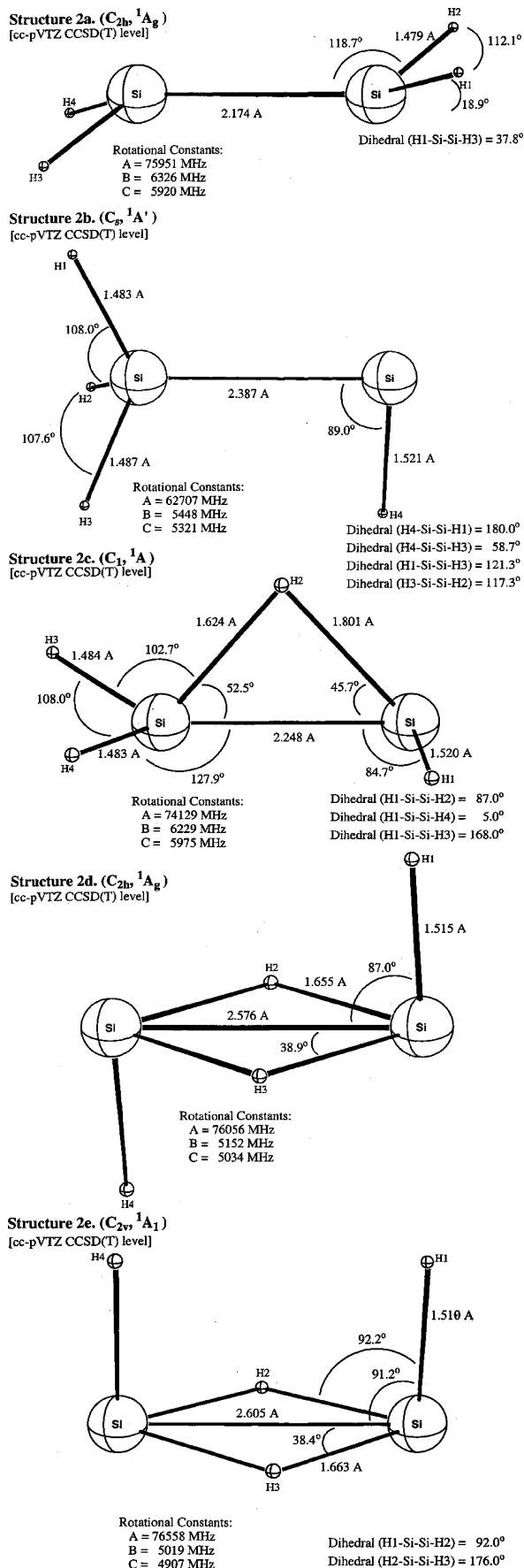


Figure 2. Isomers of Si_2H_4 , optimized at the cc-pVTZ CCSD(T) level of theory.

Structure of the transition state ($C_{1s}, ^1A_1$)

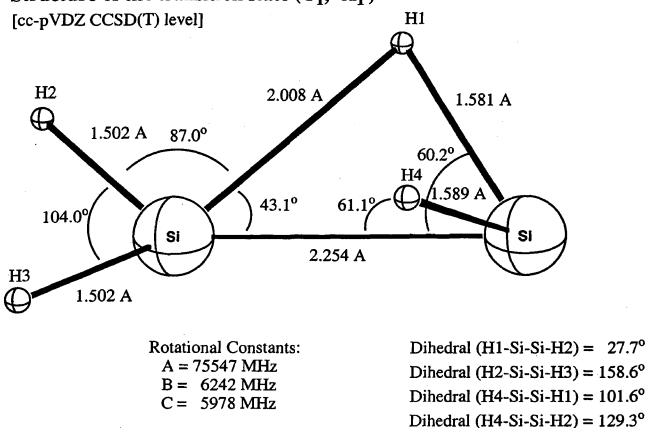


Figure 3. Structure of the transition state between two equivalent monobridged isomers (structure 2c) of Si_2H_4 .

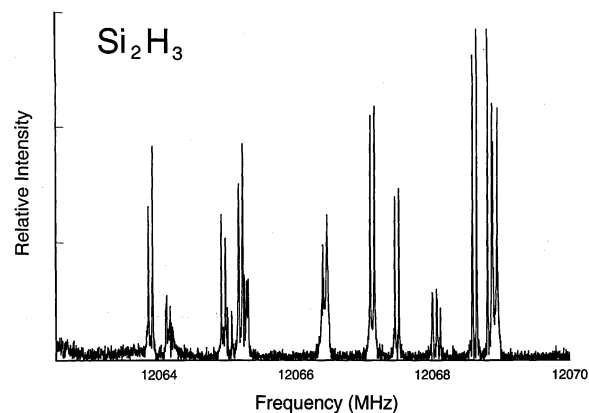


Figure 4. Transition ($1_{0,1} \rightarrow 0_{0,0}$) of planar Si_2H_3 showing the complex spectral pattern which arises from spin rotation of the unpaired electron and hyperfine structure from the three inequivalent hydrogen atoms. The integration time was approximately 5 h.

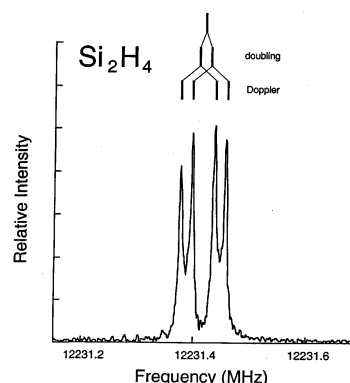


Figure 5. Transition ($1_{0,1} \rightarrow 0_{0,0}$) of monobridged $\text{H}_2\text{Si}-\text{H}-\text{SiH}$ showing the characteristic doubling of each rotational line which arises from inversion. Each feature possesses a double-peaked line shape owing to an instrumental artifact: the Doppler splitting which results from the interaction of the supersonic axial molecular beam with the standing wave of the confocal Fabry-Perot microwave cavity. The integration time was approximately 2 min.

electron spin rotation (the two effects are comparable in magnitude), each rotational transition of this radical consists of many closely spaced features. Lines of the normal isotopic species are so strong that all of the most abundant rare Si isotopic species have also been detected in natural abundance, as has Si_2D_3 using SiD_4 instead of SiH_4 as a precursor gas. The

Table 2. Relative Energies (kcal/mol) for the Isomers of the Si₂H₃ at Different Levels of Theory (with the cc-pVTZ Basis Set)

structure	SCF	CCSD(2)	CCSD(T)
1a (H ₂ Si–SiH, ² A'')	5.48	0.29	0.98
1b (H ₃ Si–Si, ² A'')	0.00	1.15	0.00
1c (H ₂ Si–H–Si, ² A'')	not a minimum	0.00	0.10
1d (H–Si–H–Si–H, ² A)	20.20	4.57	4.27
1e (H–Si–H–Si–H, ² A)	21.89	12.05	12.04

Table 3. Effects of Full-Triple Coupled-Cluster Excitations on the Relative Energies of the Isomers of Si₂H₃, Determined with the cc-pVDZ Basis Set [kcal/mol, Values Are with Respect to the Monobridged (**1c**) Isomer]

structure	CCSD(T)	CCSDT	change
1a (H ₂ Si–SiH, ² A'')	0.15	0.03	–0.12
1b (H ₃ Si–Si, ² A'')	–1.80	0.31	+2.11
1c (H ₂ Si–H–Si, ² A'')	0.00	0.00	0.00
1d (H–Si–H–Si–H, ² A)	4.46	4.36	–0.10
1e (H–Si–H–Si–H, ² A)	12.03	11.99	–0.04

Table 4. Effects of Full-Triple Coupled-Cluster Excitations, Relativistic (MVD) Corrections, and Zero-Point Vibrational Energy Corrections on the Relative Energies of the Isomers of Si₂H₃^a

structure	cc-pVTZ CCSD(T)	full-triples corrections	relativistic corrections	ZPVE corrections	best estimates
1a (H ₂ Si–SiH, ² A'')	0.88	–0.12	+0.03	–0.56	0.23
1b (H ₃ Si–Si, ² A'')	–0.10	+2.11	+0.07	+1.07	3.15
1c (H ₂ Si–H–Si, ² A'')	0.00	0.00	0.00	0.00	0.00
1d (H–Si–H–Si–H, ² A)	4.17	–0.10	–0.08	+0.21	4.20
1e (H–Si–H–Si–H, ² A)	11.94	–0.04	–0.10	–0.80	11.00

^a The best estimates for the relative energies include all corrections on top of the cc-pVTZ CCSD(T) results [kcal/mol, all values are with respect to the monobridged (**1c**) isomer].

experimentally determined effective rotational constants (*B* + *C*) of normal Si₂H₃ (structure **1a**), its rare ²⁹Si and ³⁰Si isotopic species, and Si₂D₃ are summarized in Table 9. Conclusive evidence that the carrier of the observed lines is planar H₂SiSiH and no other molecule is provided by the close agreement between theory and experiment of *B* + *C* for the normal and isotopic species. Laboratory searches are now underway for monobridged H₂SiHSi whose fundamental 1_{0,1} → 0_{0,0} rotational transition is predicted to lie near 12.6 GHz.

2. Si₂H₄. The disilene (structure **2a**, C_{2h}, ¹A_g) and the silylsilylene (structure **2b**, C_s, ¹A') have been extensively studied.^{8,14,15,23,25,46,47} In 1990, Trinquier²⁶ carried out DZP/CI calculations and found that two more dibridged isomers, the trans dibridged (structure **2d**, C_{2h}, ¹A_g) and cis dibridged (structure **2e**, C_{2v}, ¹A₁), should be minima. To our knowledge, there has been no report of a monobridged form of Si₂H₄. We have now located a monobridged isomer (structure **2c**, C₁, ¹A) which is comparable energetically to silylsilylene (structure **2b**) [see the energetics section], and it is the only structure which has no symmetry. The high computational cost of optimizations in C₁ symmetry may be the reason it could not be located on the potential energy surface in previous theoretical studies.

The geometrical parameters for the much-studied silylsilylene (structure **2b**) are in very good agreement with the literature values.^{8,14,15,23,25,46,47} For the disilene isomer (structure **2a**), both planar and trans-bent structures were reported. As

Table 5. Dipole Moments (debye), Harmonic Vibrational Frequencies (cm^{–1}), and Associated Infrared Intensities (km/mol, in Parentheses) for the Isomers of Si₂H₄, Determined at the cc-pVTZ CCSD(T) Level

structure	μ _e	ZPVE	harmonic vibrational frequencies (symmetries, infrared intensities)
2a (H ₂ Si–SiH ₂ , ¹ A _g)	0.00	19.58	317(a _g ,177408n), 334(a _u ,18), 441(b _u ,21), 514(a _u ,O), 566(a _g ,0), 604(b _g ,O), 922(b _u ,182), 955(a _g ,0), 2247(b _u ,110), 2251(a _g ,0), 2267(b _g ,0), 2277(a _u ,128)
2b (H ₃ Si–SiH, ¹ A')	0.23	19.34	99(a'',10), 381(a',9), 386(a'',25), 434(a',17), 716(a',53), 879(a',230), 947(a',56), 970(a'',36), 2058(a',161), 2204(a',67), 2217(a'',96), 2239(a',117)
2c (H ₂ Si–H–SiH, ¹ A)	1.14	19.76	389(a,7), 475(a,2), 518(a,13), 645(a,6), 694(a,35), 878(a,69), 972(a,68), 1074(a,328), 1645(a,96), 2060(a,140), 2228(a,131), 2247(a,109)
2d (H–Si–H ₂ –Si–H, ¹ A _g)	0.00	20.31	264(b _u ,2), 394(a _g ,0), 733(a _u ,14), 858(b _u ,135), 859(a _g ,O), 871(b _g ,0), 1360(a _u ,21), 1517(b _g ,0), 1527(b _u ,917), 1665(a _g ,0), 2074(a _g ,0), 2089(b _u ,340)
2e (H–Si–H ₂ –Si–H, ¹ A ₁)	0.50	20.03	363(a ₁ ,0), 396(a ₁ ,0), 645(a ₂ ,0), 749(b ₁ ,88), 866(b ₂ ,14), 889(a ₁ ,24), 1334(b ₂ ,26), 1440(a ₂ ,0), 1465(b ₁ ,1214), 1656(a ₁ ,0), 2092(b ₁ ,20), 2115(a ₁ ,300)

Table 6. Relative Energies (kcal/mol) for the Isomers of the Si₂H₄ at Different Levels of Theory (with the cc-pVTZ Basis Set)

structure	SCF	CCSD(2)	CCSD(T)
2a (H ₂ Si–SiH ₂ , ¹ A _g)	0.00	0.00	0.00
2b (H ₃ Si–SiH, ¹ A')	0.07	6.28	6.86
2c (H ₂ Si–H–SiH, ¹ A)	not a minimum	7.01	6.64
2d (H–Si–H ₂ –Si–H, ¹ A _g)	22.34	19.54	19.20
2e (H–Si–H ₂ –Si–H, ¹ A ₁)	24.65	22.23	22.13

Table 7. Effects of Full-Triple Coupled-Cluster Excitations on the Relative Energies of the Isomers of the Si₂H₄ (kcal/mol, with the cc-pVDZ Basis Set)

structure	CCSD(T)	CCSDT	change
2a (H ₂ Si–SiH ₂ , ¹ A _g)	0.00	0.00	0.00
2b (H ₃ Si–SiH, ¹ A')	6.44	6.60	+0.16
2c (H ₂ Si–H–SiH, ¹ A)	7.93	8.15	+0.22
2d (H–Si–H ₂ –Si–H, ¹ A _g)	19.42	20.12	+0.70
2e (H–Si–H ₂ –Si–H, ¹ A ₁)	21.96	22.13	+0.17

explained in the Introduction, Olbrich²⁵ reported that 6 of the 11 previous theoretical studies found disilene (H₂Si–SiH₂) to be planar, like ethylene, and 5 of them found it to be a trans-bent structure. Recently, the DFT calculations of Pak et al.⁸ found a near-planar structure. Very recently (in 2002), infrared spectra taken by Andrews and Wang²⁷ suggested a trans-bent structure for the disilene. The reported deviations from the planarity predicted by previous theoretical studies do not in agree with each other. Many different values within the range 0°–40° were reported.^{8,14,15,23,25,46,47} Our best level of theory, cc-pVTZ CCSD(T), gave a trans-bent disilene with a 18.9°

(46) Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140.(47) Somosundram, K.; Amos, R. D.; Handy, N. C. *Theor. Chim. Acta* **1988**, *70*, 393.

Table 8. Effects of Full-Triple Coupled-Cluster Excitations, Relativistic (MVD) Corrections, and Zero-Point Vibrational Energy Corrections on the Relative Energies of the Isomers of Si₂H₄^a

structure	cc-pVTZ CCSD(T)	full-triple corrections	relativistic corrections	ZPVE corrections	best estimates
2a (H ₂ Si–SiH ₂ , ¹ A _g)	0.00	0.00	0.00	0.00	0.00
2b (H ₃ Si–SiH, ¹ A′)	6.86	+0.16	−0.27	−0.24	6.51
2c (H ₂ Si–H–SiH, ¹ A)	6.64	+0.22	+0.12	+0.18	7.16
2d (H–Si–H ₂ –Si–H, ¹ A _g)	19.20	+0.70	−0.12	+0.73	20.51
2e (H–Si–H ₂ –Si–H, ¹ A ₁)	22.13	+0.17	−0.11	+0.45	22.64

^a The best estimates for the relative energies include all corrections on top of the cc-pVTZ CCSD(T) results [kcal/mol, all values are with respect to the disilene (**2a**) isomer].

Table 9. Experimental and Theoretical Rotational Constants of Isotopic Planar H₂SiSiH (in MHz)

isotopic species	B + C		difference (%)
	experiment ^a	theory	
H ₂ SiSiH	12 067	11 914	−1.3
H ₂ ²⁹ SiSiH	11 902	11 748	−1.3
H ₂ ³⁰ SiSiH	11 748	11 588	−1.4
H ₂ Si ²⁹ SiH	11 872	11 717	−1.3
H ₂ Si ³⁰ SiH	11 689	11 527	−1.4
D ₂ SiSiD	10 632	10 484	−1.4

^a Derived from preliminary spectral analysis. Estimated uncertainty is 1–2 MHz.

Table 10. Experimental and Theoretical Rotational Constants of Isotopic Monobridged H₂SiHSiH (in MHz)

isotopic species	rotational constant	B + C		difference (%)
		experiment ^a	theory	
H ₂ SiHSiH	A	73012(187)	74129	1.5
	B	6243.731(1)	6229	−0.2
	C	5987.703(1)	5976	−0.2
H ₂ ²⁹ SiHSiH	A	73012 ^b	74113	
	B	6156(1)	6142	−0.2
	C	5911(1)	5895	−0.3
H ₂ ³⁰ SiHSiH	A	73012 ^b	74097	
	B	6077(1)	6058	−0.3
	C	5836(1)	5818	−0.3
H ₂ SiH ²⁹ SiH	A	73012 ^b	74100	
	B	6140(1)	6125	−0.2
	C	5894(1)	5879	−0.3
H ₂ SiH ³⁰ SiH	A	73012 ^b	74072	
	B	6045(1)	6024	−0.3
	C	5804(1)	5786	−0.3
D ₂ SiDSiD	A	37518 ^c	37518	
	B	5561.0(5)	5529	−0.6
	C	5171.9(5)	5144	−0.5

^a Note: 1σ uncertainties (in parentheses) are in units of the last significant digit. ^b Constrained to the value of the normal isotopic species. ^c Constrained to the theoretical value of the fully deuterated isotopic species.

deviation from the planarity. The predicted shapes of the trans and cis dibridged isomers reported by Trinquier²⁶ are quite similar to what we determined (structures **2d** and **2e**). The largest discrepancy between our dibridged structures and those given by Trinquier²⁶ is seen to be in the angles between the nonbridged hydrogens and the plane of two Si atoms. Angles of 89.1° and 94.2° were reported by Trinquier²⁶ for trans- and cis-like isomers, respectively; we determined the same angles to be 87.0° for structure **2d** and 91.2° for structure **2e**. The reported Si–Si bond distances are in agreement with ours to within 0.01 Å for both trans- and cis-like structures.

The experimental rotational constants of the new silicon hydride are in extremely close agreement with those predicted here for monobridged Si₂H₄ (structure **2c**). As shown in Table

10, the rotational constants of the normal isotopic species are within 2% of those predicted at the best level of theory, and this agreement alone makes it unlikely that we have discovered some other molecule. By comparison, B + C = 12.25 GHz for disilene (**2a**), 10.77 GHz for silylsilylene (**2b**), 12.21 GHz for the monobridged structure (**2c**), 10.19 GHz for the trans-like dibridged structure (**2d**), and 9.93 GHz for cis-like dibridged structure (**2e**). On this basis, all but disilene and the monobridged isomer can be eliminated from further consideration. Since disilene is nonpolar by symmetry, it too can be eliminated as a candidate, leaving only H₂Si–H–SiH, which is calculated to possess a dipole moment of 1.14 D at the cc-pVTZ CCSD(T) level of theory. Finally, conclusive evidence for this identification is provided by the detection of the ²⁹Si and ³⁰Si isotopic species and D₂SiDSiD at precisely the expected isotopic shifts (see Table 10). A detailed account of the Si₂H₄ laboratory measurements and data analysis will be given elsewhere.

There is evidence for inversion doubling in the rotational spectrum of monobridged (**2c**) Si₂H₄. Each rotational line consists of a tight doublet of equal intensity (Figure 5), with a splitting so small, typically several tens of kHz, that it is resolved in the present experiments only by virtue of the high spectral resolution of the FTM technique. The line doubling implies that the molecule is interconverting between two equivalent structures, the magnitude of the splitting indicating that there is a fairly high barrier to inversion. To see whether this explanation is correct, we searched for a possible transition state (at the cc-pVDZ CCSD(T) level) that might lead to such motion and found the transition state shown in Figure 3. As shown there, the structure has one imaginary harmonic vibrational frequency of 657i cm^{−1}, which corresponds to the replacement of the terminal hydrogen of the monobridged isomer (structure **2c**) with the bridged hydrogen, producing the equivalent monobridged isomer. The barrier height for this motion is determined to be 10.9 kcal/mol at the cc-pVDZ CCSD(T) level. A single-point computation at the cc-pVTZ CCSD(T) level was carried out on the optimized transition state structure, and an energy barrier of 10.0 kcal/mol was found.

B. Dipole Moments. Dipole moments were determined as first derivatives of the total energies with respect to external electric fields. The cc-pVTZ CCSD(T) values are given in Table 1 for Si₂H₃ and in Table 5 for Si₂H₄. The calculated dipole moments for the planar (structure **1a**) and newly predicted monobridged (structure **1c**) isomers of Si₂H₃ are very close to each other (1.04 and 1.07 D, respectively). The trans-like monobridged isomer (structure **1d**) has a small dipole moment of 0.30 D, and the cis-like monobridged isomer (structure **1e**) has a somewhat larger moment of 0.70 D. The most polar isomer of Si₂H₄ is the newly predicted monobridged isomer (structure **2c**). It has a permanent dipole moment of 1.14 D, which is close to that of monobridged isomer of Si₂H₃ (structure **1c**). The Si₂H₄ disilene (structure **2a**) and the trans dibridged (structure **2d**) isomers are nonpolar by symmetry.

C. Harmonic Vibrational Frequencies. Although there are many theoretical studies of the structure and energetics of Si₂H₃ and Si₂H₄, there are only two reported studies of the harmonic vibrational frequencies, both for Si₂H₄. To the best of our knowledge, the present work therefore represents the first prediction of the harmonic vibrational frequencies and infrared intensities of the isomers of Si₂H₃. The results are given in Table

1. All of the harmonic vibrational frequencies (varying from 319 cm^{-1} to 2276 cm^{-1}) are real, which confirms that the optimized structures are true minima on the potential energy surface. For the monobridged isomer of Si_2H_3 (structure **1c**), predicted to be the lowest energy isomer, an active mode with a infrared intensity of 382 km/mol is found. This mode corresponds to the bending of two terminal hydrogens, along with the motion of bridged hydrogen in the perpendicular plane. It has a' symmetry with a 1016 cm^{-1} harmonic vibrational frequency. This mode can be used to characterize our predicted monobridged isomer if the infrared spectrum of Si_2H_3 is obtained.

Trinquier²⁶ predicted harmonic vibrational frequencies for three different isomers of Si_2H_4 ; the disilene (structure **2a**), the trans-like (structure **2d**), and cis-like dibridged (structure **2e**) isomers. However, he found a planar disilene at his level of computation (SCF/DZP). Therefore, his results for disilene are quite different from our predictions. His predictions concerning the dibridged structures are generally $60\text{--}90\text{ cm}^{-1}$ larger than our results. This is expected because correlated levels usually produce smaller harmonic vibrational frequencies. Another study of Si_2H_4 was reported by Andrews et al.²⁷ in 2002. They experimentally obtained an infrared spectrum and also carried out B3LYP/6-31++G(d,p) calculations. They resolved an 858.5 cm^{-1} SiH_2 bending mode and a 2154.0 cm^{-1} Si-H stretching mode from their spectrum. Based on their B3LYP/6-31++G(d,p) predictions, they concluded that the observed peaks are associated with a trans-bent disilene. Their B3LYP/6-31++G(d,p) results showed three harmonic vibrational frequencies with large intensities. These are the two Si-H stretches, at 2264.0 cm^{-1} and 2231.1 cm^{-1} , and an SiH_2 bending mode. Our results showed that disilene has a b_u Si-H stretching at 2247 cm^{-1} with a 110 km/mol intensity, an a_u Si-H stretching at 2277 cm^{-1} with a 128 km/mol intensity, and a b_u SiH_2 bending at 922 cm^{-1} with a 182 km/mol intensity. The experimentally observed values of 858.5 cm^{-1} and a 2154.0 cm^{-1} are close to our active modes of b_u Si-H stretching (2247 cm^{-1}) and b_u SiH_2 bending (922 cm^{-1}) symmetry.

D. Relative Energies. 1. Si_2H_3 . Sax and Kalcher²² used the MRCI technique with double and triple- ζ quality basis sets and investigated $\text{H}_3\text{Si-Si}$ ($^2A''$) and the near-planar $\text{H}_2\text{Si-SiH}$ isomers of the Si_2H_3 molecule. They predicted the $\text{H}_3\text{Si-Si}$ ($^2A''$) isomer to be 1.1 kcal/mol more stable than the near-planar $\text{H}_2\text{Si-SiH}$ isomer. In the same year, Curtiss et al.²³ did G2 calculations, and they reported that the lowest energy isomer is the $\text{H}_3\text{Si-Si}$ ($^2A''$) structure, in agreement with the results obtained by Sax and Kalcher. They also stated that “mono-, di-, and tri-bridged structures were also investigated, but all bridged structures were found to be significantly higher in energy”. However, in 1997, Gong et al.¹¹ predicted a monobridged structure (HSi-H-SiH , C_2) to be the lowest energy isomer, after investigating six different structures: silylsilylydine $\text{H}_3\text{Si-Si}$ (C_s); the near-planar $\text{H}_2\text{Si-SiH}$ (C_1); two monobridged isomers, HSi-H-SiH (C_2) and $\text{H}_2\text{Si-H-Si}$ (C_s); a dibridged; and a tribridged isomer. They also reported that the $\text{H}_3\text{Si-Si}$ (C_s) like structure, which was predicted to be the lowest energy isomer by both Kalcher²² and Pople,²³ is 9.0 kcal/mol (0.39 eV) higher in energy. The tribridged isomer was found to be significantly higher in energy (0.64 eV). In 2001, Pak et al.⁸ reported B3LYP/DZP+ calculations and studied the $\text{H}_3\text{Si-Si}$

(C_s), the near-planar $\text{H}_2\text{Si-SiH}$ (C_1), and the monobridge (HSi-H-SiH , C_2) isomers. They reported that the $\text{H}_3\text{Si-Si}$ (C_s) isomer and the near-planar $\text{H}_2\text{Si-SiH}$ (C_1) isomer are almost equivalent in energy. Therefore, they pointed out that high level quantum chemical methods should be employed in order to tell which isomer is the lowest in energy.

As seen in Table 2, the $\text{H}_3\text{Si-Si}$ (structure **1b**) is the lowest isomer at the SCF (Hartree-Fock) level, as predicted previously. At the same level of theory, the monobridged isomer (structure **1c**) could not be located. However, when the correlated levels [cc-pVDZ CCSD(T) and cc-pVTZ CCSD(T)] were employed, the monobridged isomer (structure **1c**) was found (with all real harmonic vibrational frequencies, see Table 1). The monobridged isomer (structure **1c**) is stabilized by both electron correlations and basis set expansion, as seen in Table 2 and 3. At the cc-pVDZ CCSD(T) level, the relative energy of the monobridged form (structure **1c**) with respect to the $\text{H}_3\text{Si-Si}$ (structure **1b**) is $+1.80\text{ kcal/mol}$, whereas, at the cc-pVDZ CCSDT level, it is -0.31 kcal/mol . The CCSD(T) level of theory predicts the same energy difference as $+0.10\text{ kcal/mol}$ with the cc-pVTZ basis set. When we add the effect of full-triple corrections [cc-pVDZ CCSDT-cc-pVDZ CCSD(T)] to the estimated value at the cc-pVTZ CCSD(T) level (to predict cc-pVTZ CCSDT), as well as with the zero-point vibrational energy (ZPVE) and relativistic corrections, we found that the monobridged isomer (structure **1c**) is 3.15 kcal/mol below the $\text{H}_3\text{Si-Si}$ isomer (structure **1b**), as given in Table 4.

The planar Si_2H_3 isomer (structure **1a**), previously predicted^{8,11,22,23} to be higher in energy than the $\text{H}_3\text{Si-Si}$ (structure **1b**), is found to be stabilized by both correlation effects and basis set expansion. Although it is 5.48 kcal/mol higher in energy than the $\text{H}_3\text{Si-Si}$ (structure **1b**) at the SCF level, it is only 0.98 kcal/mol higher in energy at the cc-pVTZ CCSD(T) level. Including all effects (ZPVE, full-triples, and scalar relativity) to the cc-pVTZ CCSD(T) results, we predict that the planar form (structure **1a**) is lower in energy than the $\text{H}_3\text{Si-Si}$ isomer by 2.92 kcal/mol . The monobridged isomer in C_2 symmetry (structure **1d**), which was predicted to be the lowest energy form by Gong et al, is found to be 4.20 kcal/mol higher than the monobridged structure in C_s symmetry (structure **1c**).

2. Si_2H_4 . All previous Si_2H_4 theoretical studies found that disilene (structure **2a**) lies lower in energy than silylsilylene (structure **2b**).^{8,22,23,25,27} We similarly predict that disilene is 6.51 kcal/mol more stable than silylsilylene. However, the competition here is found to be between the newly predicted monobridged isomer (structure **2c**) and silylsilylene (structure **2b**). As we mentioned earlier, the newly predicted monobridged isomer is not found at the SCF level. At the cc-pVDZ CCSD(T) level, the silylsilylene (structure **2b**) is 1.49 kcal/mol more stable than the monobridged form. However, at the cc-pVTZ CCSD(T) level, the monobridged isomer was found to lie 0.22 kcal/mol lower than the silylsilylene (structure **2b**; see Table 6 and 7). In other words, basis set expansion favors the monobridged form with respect to the silylsilylene. Both relativistic corrections and ZPVE corrections favor the silylsilylene. As seen in Table 8, the relativistic corrections (MVD) lower the relative energy of silylsilylene by 0.27 kcal/mol and increase the relative energy of the monobridged structure by 0.12 kcal/mol with respect to the disilene. The ZPVE for the monobridged form is estimated to be 0.42 kcal/mol larger than that for the silylsilylene (see

Table 5). As a result, when we collected all of the corrections, the silylsilylene (structure **2b**) is found to be 0.65 kcal/mol *below* the monobridged form. As seen in Table 6, the cc-pVTZ CCSD(2) level of theory also predicts the silylsilylene to be more stable than the monobridged form by 0.73 kcal/mol.

Both the trans (structure **2d**) and cis (structure **2e**) dibridged forms of Si_2H_4 are estimated to be about 20 kcal/mol higher in energy than the disilene, the lowest energy form. As expected, the trans-like dibridged form is found to be more stable than the cis-like dibridged form. As a best value, 2.13 kcal/mol energy is estimated for the energy gap between the latter two isomers.

V. Concluding Remarks

A total of 10 stable isomers of the Si_2H_3 and Si_2H_4 molecules have been located on the ground electronic state potential energy hypersurfaces. Scalar relativistic corrections and zero-point vibrational energy corrections were included in order to predict accurate energetic properties. For the first time, the monobridged

$\text{H}_2\text{Si}-\text{H}-\text{Si}$ isomer (C_s , $^2A''$) is predicted to be the lowest energy structure on the ground potential energy surface of Si_2H_3 . One monobridged and two dibridged isomers are also found for the Si_2H_4 . In addition to the much studied silylsilylene, $\text{H}_3\text{Si}-\text{SiH}$, we find that an unexpected monobridged isomer $\text{H}_2\text{Si}-\text{H}-\text{SiH}$ (C_1 , 1A) is a minimum on the potential energy surface. By means of Fourier transform microwave spectroscopy of a supersonic molecular beam, the rotational spectrum of this novel monobridged Si_2H_4 , as well as the for the planar ($\text{H}_2\text{Si}-\text{SiH}$) isomer of Si_2H_3 , has been measured. Excellent agreement with theory has been observed. Harmonic vibrational frequencies as well as infrared intensities for all isomers are predicted at the cc-pVTZ CCSD(T) level of theory.

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