Reactions of Silicon Atoms with Methane and Silane in Solid Argon: A Matrix-Spectroscopic Study**

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Abstract: The reaction of silicon atoms with methane (**1**) and silane (**7**) in argon at 10 K has been studied. Methane (**1**) is found to be inert to silicon atoms, but reaction occurs upon photochemical excitation under formation of methylsilylene (**2**). On the contrary, silane (**7**) is spontaneously converted into a mixture of silylsilylene (**10**) and disilene (**12**). Subsequent irradiation generates the butterfly-type disilyne Si_2H_2 (**14**), together with a third photoproduct, which we assume to be the doubly bridged Si_2H_4 isomer **13**. The structural elucidation of the new species is based on the comparison of the experimental IR and UV/Vis spectra with data from density functional theory calculations. The results are supported by isotopic labeling studies.

Keywords: co-condensation • density functional calculations • matrix isolation • photoisomerization

Introduction

During the past five years, we have studied the reactions of thermally generated silicon atoms with low molecular weight reactants in an argon matrix. The reaction products were identified by IR and UV/Vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful.[2] The selected substrates were molecules with isolated, conjugated, or aromatic π bonds, compounds containing π bonds and at the same time free electron pairs, and molecules possessing n electrons only in combination with σ bonds. These reactions can be understood considering the basic features of atomic silicon. First, it has a triplet ground state and thus a diradical type of reaction can be anticipated. According to the law of spin conservation the primary reaction product should be a triplet molecule. Second, the silicon atom has an empty 3p orbital, and as a consequence strong electrophilic behavior can be expected. No wonder that all molecules with π and n electrons are excellent partners.[2] In continuation of our strategy we wanted to learn something about the reactivity of pure σ systems. For instance, which reactions will occur if simple substrate molecules such as methane (**1**) or silane (**7**) come in contact with silicon atoms? The answer is given herein.

Results and Discussion

Reactions of methane: The selection of methane (**1**) has not only an academic aspect but also practical relevance. There are reports that porous silicon can be a dangerous material in the presence of oxygen or nitrogen, depending on the grain size. Lump silicon represents one end of the scale, silicon atoms the other extreme. Silicon powder lies in between.

Applying our standard procedure[2] we condensed methane (**1**) as a gaseous mixture with argon onto a spectroscopic window at 10 K. The concentration varied from pure methane to a methane/argon ratio of 1:1000. The silicon atoms, generated by resistive heating of a silicon rod to a temperature of about 1380 °C, were separately cocondensed at the same time. The relative amount of ^3Si atoms was estimated by using a quartz microbalance. In all cases only the IR spectrum of the starting material could be registered. There was not even an indication for the existence of a complex **4** between methane (**1**) and a silicon atom. This was in our hands the first case that the substrate molecule did not react with silicon atoms.

If one rationalizes how a reaction can be enforced in such a case, one has to keep in mind that the silicon atom in the gas phase shows a weak UV transition at 220 nm and another, strong absorption at 251 nm. This suggests that irradiation with light of wavelength 254 nm can be a way to activate silicon atoms.

Indeed, irradiation of the co-condensate of methane (**1**) and silicon atoms with short wavelengths ($\lambda = 185$ or 254 nm) leads to methylsilylene (**2**). Evidently, photoexcitation enforces the insertion of a silicon atom into the C–H bond of methane (**1**). The intensity of the IR bands of **2** arising during

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[**] Hetero π Systems, Part 32: Part 31 see: ref. [2h]. See also ref. [1]

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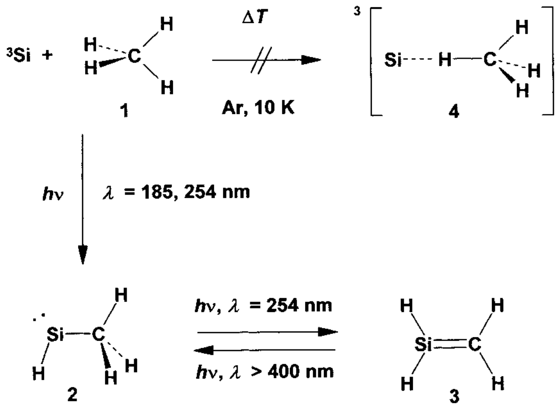
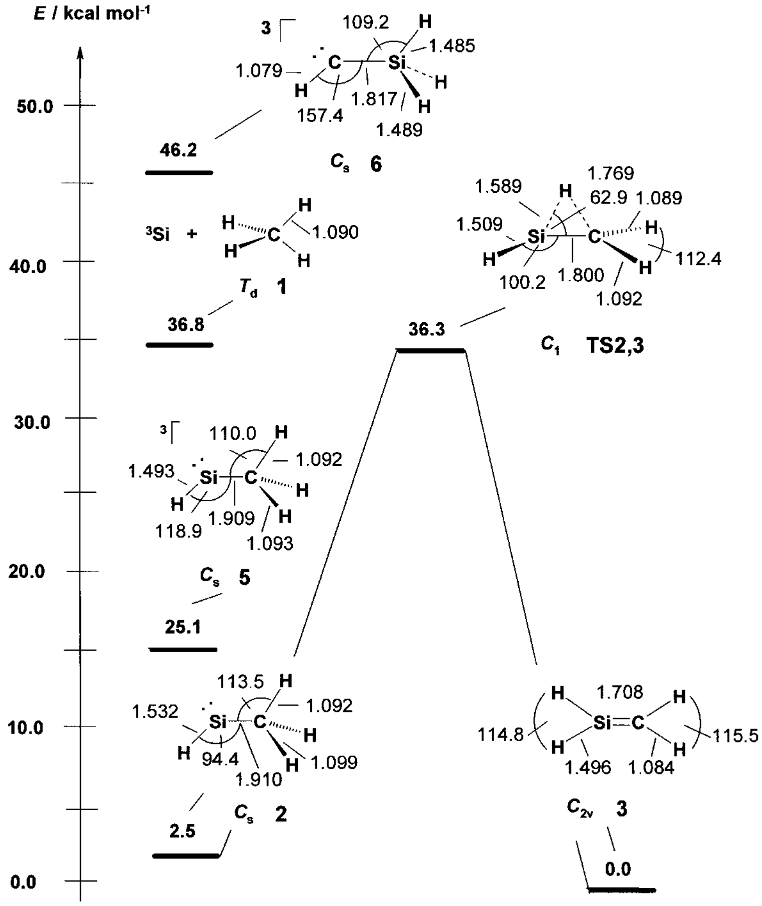


Table 1. Theoretical (B3LYP/6-311++G**) IR absorptions (unscaled; wavenumbers in cm^{-1}) of CH_4Si isomers **2, 3, 5, 6**, and connecting transition state **TS2,3**. Absolute intensities [km mol^{-1}] are given in parentheses.

Species	Point group	State	IR Absorptions (Intensity), Symmetry
2	C_s	$^1A'$	152.4 (1) a'', 572.5 (5) a'', 628.9 (10) a', 662.5 (57) a', 950.7 (84) a', 1264.3 (27) a', 1434.4 (6) a', 1449.2 (15) a'', 2009.3 (332) a', 2990.5 (4) a', 3042.5 (15) a'', 3103.1 (13) a'
3	C_{2v}	$^1A_1$	454.1 (25) b_1, 485.1 (6) b_2, 729.1 (0) a_2, 780.6 (59) b_1, 841.9 (81) b_2, 941.6 (26) a_1, 994.2 (29) a_1, 1399.1 (10) a_1, 2270.0 (32) a_1, 2293.2 (96) b_2, 3142.1 (0) a_1, 3230.6 (0) b_2
5	C_s	$^3A''$	117.9 (0) a'', 555.8 (8) a', 659.2 (12) a', 791.5 (13) a'', 881.4 (71) a', 1267.9 (0) a', 1449.9 (10) a', 1453.8 (8) a'', 2164.1 (82) a', 3019.8 (10) a', 3091.9 (1) a'', 3108.3 (4) a'
6	C_s	$^3A''$	116.1 (41) a'', 329.5 (32) a', 632.0 (46) a'', 640.3 (48) a', 796.3 (29) a', 943.5 (66) a', 946.1 (52) a'' , 948.2 (210) a' , 2196.2 (118) a'', 2199.4 (79) a', 2224.2 (82) a', 3261.8 (2) a'
TS2,3	C_1	$^1A_1$	– 1101.2 (155) a_1, 593.3 (3) a_1, 788.7 (37) a_1, 808.9 (7) a_1, 892.6 (46) a_1, 994.6 (60) a_1, 1008.6 (94) a_1, 1438.6 (5) a_1, 1891.6 (10) a_1, 2097.4 (208) a_1, 3070.7 (16) a_1, 3164.7 (3) a_1

irradiation was relatively weak. Nevertheless, its structural elucidation has to be taken for granted, since it is possible to establish a photoequilibrium between **2** and the isomeric silaethene (**3**). With $\lambda > 400$ nm the equilibrium is shifted to silaethene (**3**), with $\lambda = 254$ nm to the side of methylsilylene (**2**). The IR spectra of **2** and **3** and the mutual interconversion have been studied by us before.[3]

A thermal equilibrium between **2** and **3** should be on the side of silaethene (**3**). According to calculations (B3LYP/6-311+G**), carried out in comparison to the silane system (see below), methylsilylene (**2**) should be 2.5 kcal mol^{-1} higher in energy (Scheme 1; Table 1). The connecting transition state **TS2,3** is 36.3 kcal mol^{-1} above silaethene (**3**). The starting components ^{3}Si and methane (**1**) lie 36.8 kcal mol^{-1} higher than silaethene (**3**). The singlet/triplet gap of the two silylenes **2** and **5** is calculated to be 22.6 kcal mol^{-1}. Triplet silylcarbene (**6**) is even higher in energy than the starting compounds ^{3}Si atoms plus methane (**1**) and therefore cannot be expected as a product. Attempts to calculate a triplet complex **4** between a silicon atom and methane (**1**) failed.



Scheme 1. Calculated (B3LYP/6-311+G**) relative energies and geometries of some stationary points on the CH_4Si potential energy surface (PES); zero-point vibrational energies included. Distances are given in Å and angles in degrees.

Reactions of silane

Prediction: On the basis of two arguments it is possible to predict that the behavior of silane (**5**) might be completely different from that of methane (**1**). On the one hand Skell and Owen described already in 1967[4] that thermally vaporized silicon atoms insert into the Si–H bond of trimethylsilane, which has been deposited on a liquid nitrogen cooled wall. On the other hand it can be shown by calculation that methane (**1**) and silane (**5**) behave quite differently when attacked by a silicon atom. Gordon et al.[5] calculated in 1989 that the insertion of ^{3}Si atoms into a Si–H bond of silane needs only a small barrier. For the corresponding reaction with methane (**1**) no clear answer could be given. Our own calculations substantiate the big difference in reactivity between silane (**7**) and methane (**1**) (Figure 1).

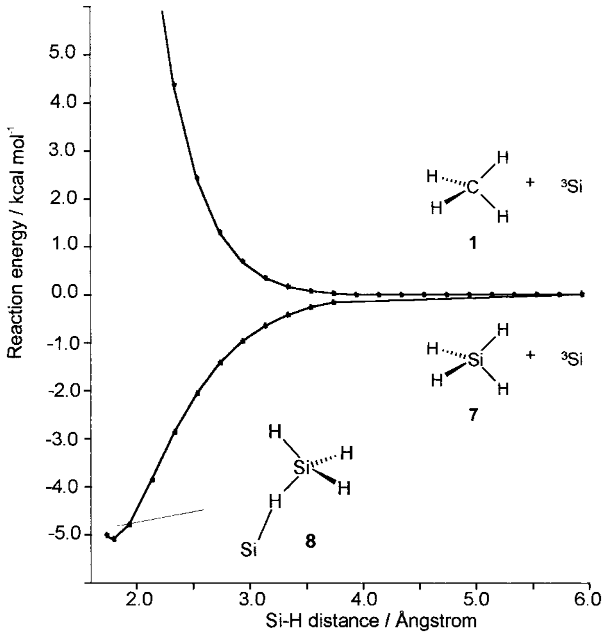


Figure 1. Calculated changes of the potential energy during the approach of a ground state Si atom (triplet) to a methane molecule (**1**; upper curve) or a silane molecule (**7**; lower curve); B3LYP/6–311 + G**; full optimization at each step.

If a silicon atom in its triplet ground state approaches methane (**1**) the energy is continuously raised. There is no indication of any bonding interaction. On the contrary, the reaction coordinate for the approach between a ^{3}Si atom and silane (**7**) descends steadily until complex **8** is reached.

Background: Simple silicon hydrides are of great interest for several reasons. They play an important role in silicon chemical vapor deposition (CVD) processes, which are of significance to the semiconductor industry. A detailed study on the reaction of silicon atoms with silane (**7**) will help to understand the mechanisms of these reactions. Another appeal is that starting with the first isolation of a disilene by West et al.[6] a new chapter in silicon chemistry was opened. But the isolation and identification of the parent disilene is still missing. Last but not least silicon hydrides are excellent target molecules to demonstrate the unique bonding characteristics of silicon compared to carbon, resulting very often in surprising "bridged" structures. These fascinating aspects explain the numerous experimental[7] and theoretical[8] studies covering silicon hydrides SiH_n and Si_2H_n.

Calculations: For the structural identification of the expected species it was necessary to obtain the calculated vibrational spectra. In addition to the earlier theoretical treatments[8] we carried out some calculations on our own using the Gaussian package of programs.[9] To get an overview of the Si_2H_4 potential energy surface (PES), several stationary points together with the corresponding vibrational spectra were calculated with the 6–311 + G** basis set and the B3LYP functional. The results are presented in Table 2. Scheme 2 shows the calculated relative energies of some minima and the connecting transition states.

Table 2. Theoretical (B3LYP/6–311 + G**) IR absorptions (unscaled; wavenumbers in cm^{-1}) of Si_2H_4 isomers **8**–**13**, disilyne (**14**), silylene (**15**), and connecting transition states. Absolute intensities [km mol^{-1}] are given in parentheses.

Species	Point group	State	IR Absorptions (Intensity), Symmetry
8	C_1	$^3A_1$	99.2 (1) a_1, 109.8 (0) a_1, 400.1 (16) a_1, 777.6 (27) a_1, 867.4 (497) a_1, 927.6 (69) a_1, 945.2 (60) a_1, 1069.6 (88) a_1, 1827.6 (280) a_1, 2238.3 (79) a_1, 2267.3 (44) a_1, 2282.2 (63) a_1
9	C_s	$^3A''$	108.0 (0) a'', 416.2 (4) a', 428.2 (21) a', 524.4 (8) a'', 648.8 (18) a', 887.6 (358) a', 937.8 (50) a'', 949.4 (63) a', 2162.1 (87) a', 2199.9 (79) a', 2206.1 (91) a'', 2234.6 (90) a'
10	C_s	$^1A'$	67.9 (12) a'', 369.1 (9) a', 389.0 (33) a'', 428.9 (27) a', 717.1 (63) a', 868.1 (224) a', 932.8 (73) a', 957.2 (36) a'', 2031.3 (208) a', 2180.5 (78) a', 2189.5 (112) a'', 2217.5 (119) a'
11	C_1	$^1A_1$	397.4 (7) a_1, 447.4 (3) a_1, 477.7 (27) a_1, 636.2 (7) a_1, 703.1 (37) a_1, 858.5 (94) a_1, 961.4 (40) a_1, 1009.9 (350) a_1, 1625.7 (113) a_1, 2042.7 (182) a_1, 2195.2 (148) a_1, 2220.6 (126) a_1
12	C_{2h}	^1A_g	324.2 (0) a_g, 348.0 (23) a_u, 446.1 (32) b_u, 524.1 (0) a_u, 562.1 (0) a_g, 615.7 (0) b_g, 919.5 (182) b_u, 955.8 (0) a_g, 2224.5 (114) b_u, 2228.9 (0) a_g, 2245.7 (0) b_g, 2257.6 (150) a_u
13	C_{2h}	^1A_g	281.5 (3) b_u , 376.7 (0) a_g, 708.3 (17) a_u, 833.1 (156) b_u, 845.1 (0) a_g, 849.6 (0) b_g, 1287.7 (32) a_u, 1428.6 (0) b_g, 1453.1 (978) b_u, 1633.0 (0) a_g, 2043.6 (0) a_g, 2060.9 (454) b_u
14	C_{2v}	$^1A_1$	522.7 (1) a_1, 961.0 (50) a_1, 1081.8 (0) a_2, 1172.5 (382) b_2, 1535.4 (10) b_1, 1617.2 (5) a_1
15	C_{2v}	$^1A_1$	1024.4 (110) a_1, 2041.8 (303) b_2, 2042.5 (291) a_1
TS8,9	C_1	$^3A_1$	– 1020.8 (33) a_1, 272.3 (0) a_1, 291.7 (28) a_1, 501.9 (11) a_1, 542.0 (4) a_1, 884.2 (356) a_1, 936.9 (53) a_1, 939.7 (107) a_1, 1792.5 (242) a_1, 2183.4 (57) a_1, 2236.1 (73) a_1, 2248.5 (76) a_1
TS10,11	C_1	$^1A_1$	– 320.1 (35) a_1, 406.9 (13) a_1, 457.1 (8) a_1, 521.0 (2) a_1, 703.9 (54) a_1, 832.1 (178) a_1, 877.6 (40) a_1, 959.1 (96) a_1, 1946.1 (72) a_1, 2042.7 (191) a_1, 2211.7 (114) a_1, 2231.0 (118) a_1
TS11,12	C_1	$^1A_1$	– 630.9 (4) a_1, 331.8 (11) a_1, 457.2 (3) a_1, 508.2 (11) a_1, 651.3 (8) a_1, 682.9 (15) a_1, 940.7 (87) a_1, 1001.9 (204) a_1, 1854.3 (94) a_1, 2070.1 (140) a_1, 2153.8 (171) a_1, 2203.1 (128) a_1

The global minimum is disilene (**12**). Already twenty years ago[8o,p] the *trans*-bent geometry was suggested. The stabilization energy compared with the two components triplet silicon atom and silane (**7**) is 43.2 kcal mol^{-1}. Besides **12** three other isomers **10, 11**, and **13**, which should be formed in exothermic reactions from ^{3}Si atoms and **7**, can be expected as reaction products (Scheme 2). In the earlier papers the discussion was concentrated on disilene (**12**) and silylsilylene (**10**). Dibridged isomers of type **13** were for the first time mentioned by Trinquier.[8i] According to our calculations the isomer **11** with a monobridged structure has also to be taken into account. On the triplet energy hypersurface the starting components form without an activation barrier a loose complex **8**. Its stabiliza-

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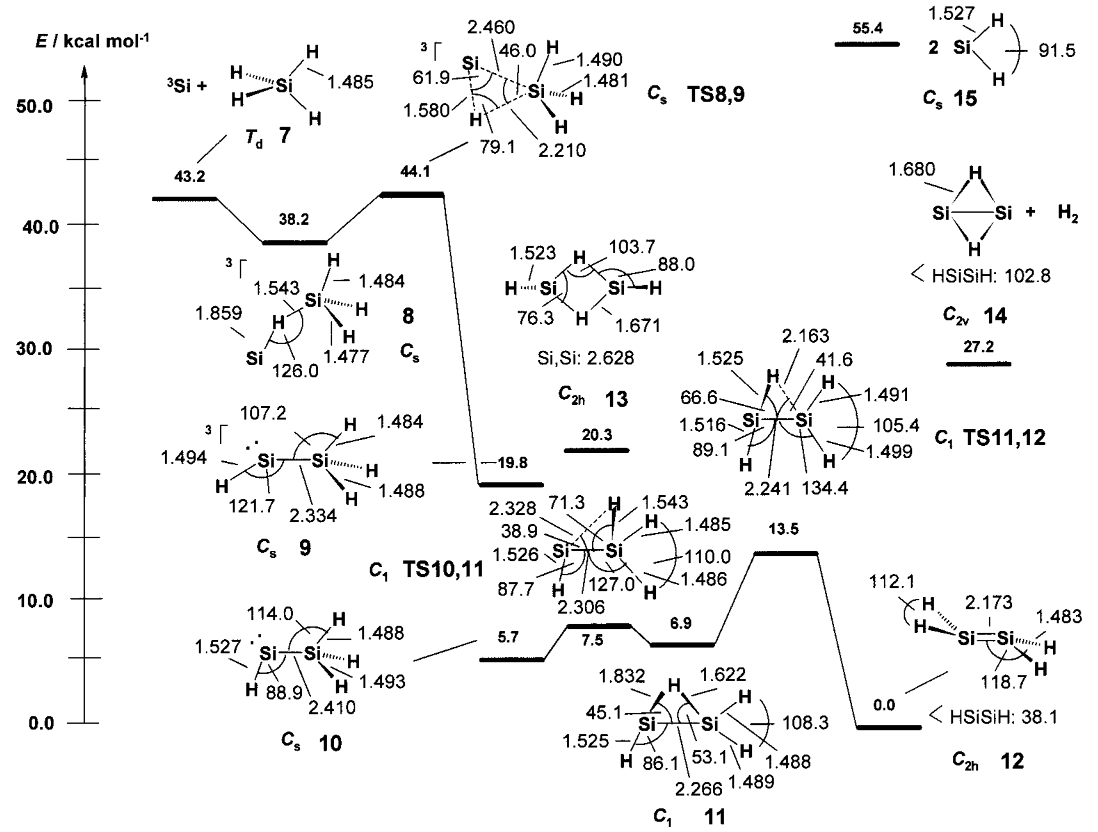
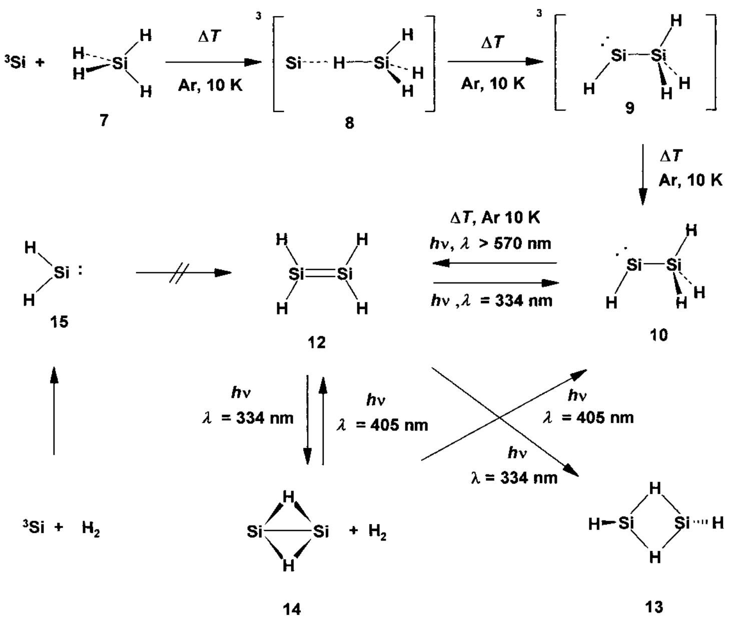


Scheme 2. Calculated (B3LYP/6–311 + G**) relative energies and geometries of some stationary points on the H_4Si_2 PES; zero-point vibrational energies included. Distances are given in Å and angles in degrees.

tion energy amounts to 5 kcal mol^{-1}. In a subsequent step the primary complex **8** is transformed (activation energy of 5.9 kcal mol^{-1}) into triplet silylsilylene (**9**), followed by intersystem crossing to singlet silylsilylene (**10**) (T/S gap 14.1 kcal mol^{-1}). On the singlet energy hypersurface now isomerization of **10** to the thermodynamically more stable ($\Delta E = 5.7$ kcal mol^{-1}) **12** takes place. The monobridged isomer **11** is only 1.2 kcal mol^{-1} higher in energy than **10** and 13.4 kcal mol^{-1} more stable than the dibridged species **13**. Two calculated transition structures **TS10,11** and **TS11,12** are found on the isomerization of **10** to **12**. The barriers leading from **10** to the monobridged species **11** (1.8 kcal mol^{-1}) and from **11** to **12** (6.6 kcal mol^{-1}) are remarkably low. For comparison: In case of the transformation of **2** to **3** the calculated barrier amounts to 33.8 kcal mol^{-1}.



Matrix experiments: A gaseous mixture of silane (**7**) and argon was deposited together with silicon atoms, generated by resistive heating of a silicon rod to a temperature of about 1380 °C, onto a CsI window at 10 K. FTIR and UV/Vis spectra were taken of the matrices. Besides the very intense absorptions of unreacted SiH_4 and small bands of unavoidable side products (SiN_2,[2h] SiH_2 (**15**), Si_2H_2 (**14**),[2a] Si_2H_6) additional absorptions in the spectral range around 900 and 1950–2200 cm^{-1} were registered. Some of these bands overlapped with the strong absorptions of the starting material SiH_4. The additional new bands could be revealed by producing difference spectra during subsequent irradiation of the matrices with different wavelengths (Figures 2 and 3). The analysis of the spectra (see below) shows that the reaction of silicon atoms with silane (**7**) leads to a mixture of silylsilylene (**10**) and disilene (**12**). Upon irradiation of the matrix with long wavelengths ($\lambda > 570$ nm) **10** is isomerized to **12**. The back-reaction can be enforced by using shorter wavelengths. With $\lambda = 334$ nm **12** regenerates **10**. Parallel to this isomerization partial dehydrogenation of **12** is initiated and one observes the bands of disilyne (**14**)[2a] with its typical butterfly-type geometry.[10] In addition a single band at 1355.4 cm^{-1} appears, which we tentatively attribute to the dibridged isomer **13**. If wavelengths longer than 310 nm (especially 505 nm) are used the hydrogen attached to disilyne (**14**) in the same matrix cage is recaptured again (as products could be identified **12** (UV spectroscopy) and **10** (IR spectroscopy)).

Based on the experimental and theoretical findings the mechanism of the reaction of ^{3}Si atoms with silane (**7**) can be summarized as follows: Via the triplet complex **8** triplet silylsilylene (**9**) is formed. Both are too short-lived to be detected. Intersystem crossing gives singlet silylsilylene (**10**). The reaction leading to **10** delivers enough energy to surpass the two barriers on the pathway from **10** to **12** even at 10 K. Dependent on the wavelength mutual interconversions with the third Si_2H_4 isomer **13** and disilyne (**14**) can be photoinitiated.

Another observation is of importance in relation to the standard procedure to prepare highly hindered disilenes, that is the dimerization of the corresponding silylenes.[6] We found no indication that the parent silylene (**13**), which is present in the matrix—or can be generated independently in high yield by cocondensation of silicon atoms with hydrogen—dimerizes upon annealing of the matrix (30–35 K) to disilene (**12**).

Spectroscopic identification: Recent efforts in the experimental search for Si_2H_4 species resulted in the observation that compounds of this elemental composition can exist. Neutral Si_2H_4 was first detected as a transient species in photoionization mass spectrometric studies.[7d] Quite recently Stafast et al.[7b] showed that Si_2H_4 compounds are intermediates in the laser chemical vapor deposition of silane. Koshi et al.[7a] were able to observe Si_2H_4 species produced in the thermal decomposition of silanes by using time-of-flight mass spectrometry coupled with VUV laser photoionization.

In our opinion the structural elucidation of disilene **12** and/or its isomers was still missing. Matrix isolation spectroscopy is the method of choice to fill this gap.

Tables 3–8—together with Figures 2 and 3—summarize the calculated and experimental IR spectra of the isomers **10, 12**, and **13**.

Because of the C_{2h} symmetry of disilene **12** only three IR bands with a sufficient intensity can be expected (Table 3) to be detectable, two SiH stretching vibrations and one SiH_2 wagging vibration. All three can be detected in the difference spectrum (Figure 2). The agreement between the calculated and experimental spectra is acceptable. The two SiH stretches are additionally split by matrix effects. There are at least two different matrix sites. Similar phenomena have been observed by us before for the SiH stretching vibrations of **3**.[3c] Additional structural proof for **12** stems from the measured isotopic shifts in the tetradeuterated isotopomer [D_4]**12** (Table 4, Figure 3). An even better help in the elucidation of disilene (**12**) can be expected from a study of the less symmetrical trideuterated isotopomer [D_3]**12**, in which even the band for the Si–Si stretching vibration should be IR-active (Table 5). Effectively, this band was too low in intensity to be identified in the complex experimental spectrum.

Table 3. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of disilene (**12**).

	Symmetry	Mode	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_4	a_g	δ_s bend	324.2	(0.0)	–	–
ν_7	a_u	δ_{as} rock	348.0	(22.9)	–	–
ν_{12}	b_u	δ_{as} bend	446.1	(31.6)	–	–
ν_6	a_u	δ_{as} twist	524.1	(0.2)	–	–
ν_3	a_g	ν_s Si-Si str.	562.1	(0.0)	–	–
ν_9	b_g	δ_{as} rock	615.7	(0.0)	–	–
ν_{11}	b_u	δ_{as} scissor	919.5	(182.2)	904.3	(s)
ν_2	a_g	δ_s scissor	955.8	(0.0)	–	–
ν_{10}	b_u	ν_{as} SiH str.	2224.5	(113.5)	2180.2	(w)[a]
ν_1	a_g	ν_s SiH str.	2228.9	(0.0)	–	–
ν_8	b_g	ν_{as} SiH str.	2245.7	(0.0)	–	–
ν_5	a_u	ν_{as} SiH str.	2257.6	(150.0)	2207.8	(w)[a]

[a] Additional IR absorptions at 2163.2, 2191.0, and 2212.3 cm^{-1} of a second matrix site were also observed.

Table 4. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of [D_4]disilene ([D_4]**12**).

	Symmetry	Mode	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_7	a_u	δ_{as} rock	248.5	(11.6)	–	–
ν_4	a_g	δ_s bend	255.8	(0.0)	–	–
ν_{12}	b_u	δ_{as} bend	326.9	(16.7)	–	–
ν_6	a_u	δ_{as} twist	371.5	(0.1)	–	–
ν_9	b_g	δ_{as} rock	468.9	(0.0)	–	–
ν_3	a_g	ν_s Si-Si str.	513.4	(0.0)	–	–
ν_{11}	b_u	δ_{as} scissor	665.0	(94.6)	658.3	(s)
ν_2	a_g	δ_s scisssor	713.2	(0.0)	–	–
ν_{10}	b_u	ν_{as} SiD str.	1594.3	(63.3)	1573.4	(m)
ν_1	a_g	ν_s SiD str.	1600.2	(0.0)	–	–
ν_8	b_g	ν_{as} SiD str.	1629.2	(0.0)	–	–
ν_5	a_u	ν_{as} SiD str.	1638.4	(80.5)	1614.7	(m)

In the spectrum of silylsilylene (**10**) all vibrations are IR-active (Table 6). A characteristic feature of silylenes with a hydrogen atom at the divalent silicon is the low frequency (1900–2010 cm^{-1}) of the SiH stretching vibration.[3a] The sensitivity of these species to matrix effects is notorious. For instance, methylsilylene (**2**) shows remarkable splittings in the SiH stretching range. Analogously, silylsilylene (**10**) reveals three SiH stretches at 1963, 1974, and 2013 cm^{-1}(Table 6, Figure 2), originating from different matrix sites. The normal SiH valence stretch vibrations of the SiH_3 group could not be registered as nicely, since they overlapped with the strong absorptions of unreacted silane (**7**). A very good correlation between the calculated and experimental value exists for the second dominant band, which has to be assigned to the SiH_3 deformation vibration (calcd 868.1, exp 860.6 cm^{-1}). An

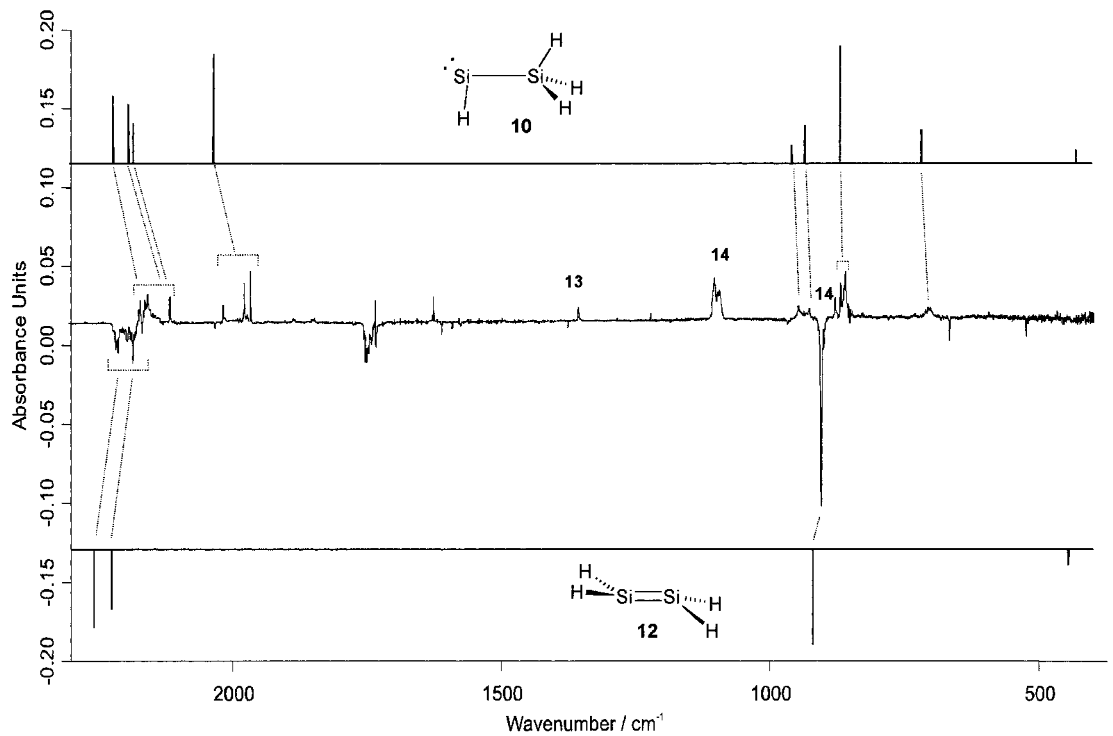


Figure 2. IR spectra of disilene (**12**) and silylsilylene (**10**): Top and bottom: Calculated at the B3LYP/6–311 + G** level of theory. Middle: Difference spectrum of the photoisomerization **12** → **10** in argon at 10 K. Positive bands increase, negative decrease during the irradiation with light of wavelength $\lambda = 334$ nm.

analogous analysis is also possible for the isotopomer [D$_4$]**10** (Table 7, Figure 3). In case of [D$_3$]**10** with its C$_s$ symmetry three different positional isomers can be anticipated. Accordingly, the experimental spectrum of [D$_3$]**10** was very complicated and gave no additional information.

According to calculation (Table 8) the dibridged isomer **13** should show an intense asymmetric Si$_2$H stretching vibration at 1453.1 cm^{-1}. In the experiment a corresponding band can be observed at 1355.4 cm^{-1} (Figure 2). We are aware of the fact that it is dangerous to argue on the basis of a single band.

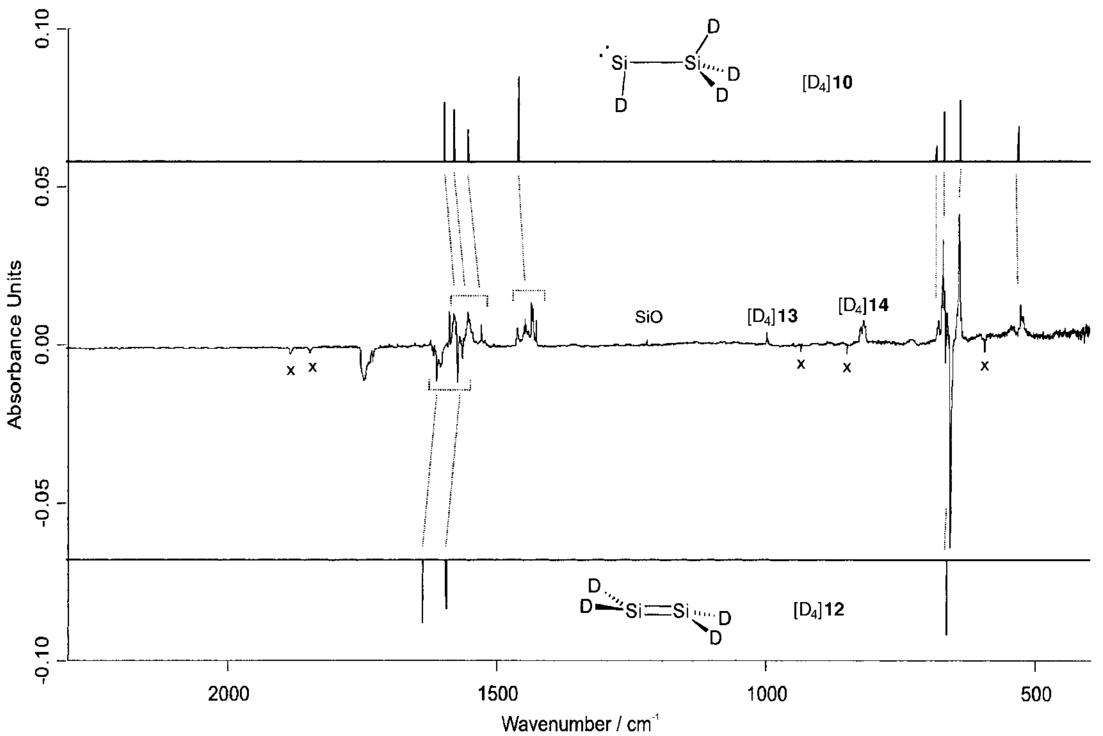


Figure 3. IR spectra of [D$_4$]disilene [D$_4$]**12** and [D$_4$]silylsilylene [D$_4$]**10**: Top and bottom: Calculated at the B3LYP/6–311 + G** level of theory. Middle: Difference spectrum of the photoisomerization [D$_4$]**12** → [D$_4$]**10** in argon at 10 K. Positive bands increase, negative decrease during the irradiation with light of wavelength $\lambda = 334$ nm. x: Hydroxysilylene.

Table 5. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of [D$_3$]disilene ([D$_3$]**12**).

	Symmetry	Mode	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_{12}	a_1	δ_s rock	262.8	(8.0)	–	–
ν_{11}	a_1	δ_s bend	267.5	(5.3)	–	–
ν_{10}	a_1	δ_{as} bend	341.0	(14.5)	–	–
ν_9	a_1	δ_s twist	425.1	(2.5)	–	–
ν_8	a_1	δ_{as} rock	490.4	(1.0)	–	–
ν_7	a_1	ν_s Si-Si str.	545.2	(5.5)	–	–
ν_6	a_1	δ_{as} scissor	688.9	(64.2)	681.8	(s)
ν_5	a_1	δ_s scisssor	833.3	(50.4)	827.5	(m)
ν_4	a_1	ν_{as} SiD str.	1597.0	(36.8)	1575.5	(w)
ν_3	a_1	ν_s SiD str.	1615.0	(21.1)	1591.5	(w)
ν_2	a_1	ν_{as} SiD str.	1634.3	(48.4)	1609.9	(w)
ν_1	a_1	ν_s SiH str.	2245.8	(67.3)	2191.9	(m)

Table 6. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of silylsilylene (**10**).

	Symmetry	Mode	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_{12}	a″	δ_{as} twist	67.9	(12.0)	–	–
ν_8	a′	ν_s Si-Si str.	369.1	(8.5)	–	–
ν_{11}	a″	δ_{as} SiH def.	389.0	(33.1)	–	–
ν_7	a′	δ_s SiH def.	428.9	(27.1)	–	–
ν_6	a′	δ_s SiH def.	717.1	(63.4)	707.3	(w)
ν_5	a′	δ_s SiH_3 def.	868.1	(224.1)	860.6	(s)[a]
ν_4	a′	δ_s SiH_3 def.	932.8	(73.3)	927.2	(w)
ν_{10}	a″	δ_{as} SiH_3 def.	957.2	(36.2)	947.5	(w)
ν_3	a′	ν_s SiH str.	2031.3	(208.3)	1963.3	(s)[b]
ν_2	a′	ν_s SiH str.	2180.5	(77.6)	2111.9	(m)
ν_9	a″	ν_{as} SiH str.	2189.5	(112.4)	2153.2	(m)
ν_1	a′	ν_s SiH str.	2217.5	(219.4)	2166.7	(m)

[a] Additional IR absorptions (other matrix sites) were observed at 868.8 (m) and 879.5 (m) cm^{-1}. [b] Additional IR absorptions (other matrix sites) were observed at 1974.5 (m) and 2013.2 (w) cm^{-1}.

Table 7. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of [D$_4$]silylsilylene ([D$_4$]**10**).

	Symmetry	Mode	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_{12}	a″	δ_{as} twist	49.5	(6.2)	–	–
ν_{11}	a″	δ_{as} SiD def.	282.7	(17.8)	–	–
ν_8	a′	δ_s SiD def.	290.4	(10.0)	–	–
ν_7	a′	ν_s Si-Si str.	378.3	(16.4)	–	–
ν_6	a′	δ_s SiD def.	533.3	(43.3)	526.7	(w)
ν_5	a′	δ_s SiD_3 def.	641.7	(76.9)	642.4	(s)
ν_4	a′	δ_s SiD_3 def.	671.3	(62.7)	–[a]	–
ν_{10}	a″	δ_{as} SiD_3 def.	686.2	(20.1)	681.3	(w)
ν_3	a′	ν_s SiD str.	1461.2	(106.9)	1427.7	(s)[b]
ν_2	a′	ν_s SiD str.	1554.6	(40.3)	1529.5	(w)
ν_9	a″	ν_{as} SiD str.	1581.2	(65.5)	1552.1	(w)[c]
ν_1	a′	ν_s SiD str.	1599.1	(75.6)	1581.2	(w)[c]

[a] Hidden underneath SiD_4 def. absorptions. [b] Additional absorptions (matrix effect) were observed at 1434.0, 1436.0, 1448.0, and 1462.3 cm^{-1}. [c] Broad signal.

However, for [D$_4$]**13** the same kind of band with the expected isotopic shift (calcd 1041.9, exp 999.9 cm^{-1}) is observed (Table 8, Figure 3). This observation can be taken as an indication that the structural assignment might be correct. For [D$_3$]**13** both types of absorption should occur. But owing to the small intensities of these bands an experimental verification was not possible.

Table 8. Theoretical (B3LYP/6–311 + G**) and experimental (Ar, 10 K) IR absorptions of dibridged isomer **13** and [D$_4$]**13**.

	Symmetry	Mode	Isotop-omer	ν_{calcd} [cm^{-1}]	I_{calcd} [km mol^{-1}]	ν_{exp} [cm^{-1}]	
ν_{12}	b_u	δ_{as} SiH		281.5	(3.4)	–	–
			D_4	202.0	(1.7)	–	–
ν_4	a_g	ν_s Si-Si str.		376.7	(0.0)	–	–
			D_4	367.0	(0.0)	–	–
ν_6	a_u	$\delta_s$oop SiH		708.3	(16.8)	–	–
			D_4	508.6	(8.3)	–	–
ν_{11}	b_u	δ_{as} SiH		833.1	(155.5)	–	–
			D_4	601.5	(77.1)	–	–
ν_3	a_g	δ_s SiH		845.1	(0.0)	–	–
			D_4	623.9	(0.0)	–	–
ν_8	b_g	$\delta_s$oop Si_2H		849.6	(0.0)	–	–
			D_4	605.8	(0.0)	–	–
ν_5	a_u	ν_s Si_2H str.		1287.7	(32.3)	–	–
			D_4	926.9	(17.9)	–	–
ν_7	b_g	ν_s Si_2H str.		1428.6	(0.0)	–	–
			D_4	1018.2	(0.0)	–	–
ν_{10}	b_u	ν_{as} Si_2H str.		1453.1	(987.2)	1355.4	(vw)
			D_4	1041.9	(513.7)	999.9	(vw)
ν_2	a_g	ν_s Si_2H str.		1633.0	(0.0)	–	–
			D_4	1157.8	(0.0)	–	–
ν_1	a_g	ν_s SiH str.		2043.6	(0.0)	–	–
			D_4	1470.3	(0.0)	–	–
ν_9	b_u	ν_{as} SiH str.		2060.9	(453.7)	–	–
			D_4	1482.3	(239.5)	–	–

Additional support for the structural identification of **10** and **12** comes from the UV-spectroscopic measurements. Calculations predict for **12** a very strong UV transition ($^1B_u \leftarrow {}^1A_g$) at 322 nm. The experimental value is 329 nm and fits very well to that of other disilenes substituted by four small alkyl groups (Me or Et: 345 nm[6b]). As expected, the characteristic feature for **10** is a long wavelength absorption of low intensity. The difference spectrum taken during the photoisomerization [D$_4$]**10** → [D$_4$]**12** with light of wavelenth $\lambda > 570$ nm (Figure 4) is in accordance (($^1A'' \leftarrow {}^1A'$); $\lambda = 582$ nm) with theory ($\lambda = 669$ nm). In a similar manner the difference spectrum of the photoisomerization **14** + **H$_2$** → **12** + **10** with light of the wavelength $\lambda = 405$ nm (Figure 5) can be regarded as a strong hint for the postulated reaction. The agreement between the calculated (408 nm) and experimental (409 nm) absorption of disilyne (**14**) is remarkable.

Conclusion

The reactions of silicon atoms in an argon matrix at 10 K with methane (**1**) and silane (**7**) belong to two completely different worlds. With methane (**1**) no thermal reaction occurs and the insertion of the ^{3}Si atoms into the C–H bond needs photoactivation. In contrast, insertion into the Si–H bond of silane (**7**) takes place without an activation barrier and a mixture of silylsilylene (**10**) and disilene (**12**) can be detected.

Experimental Section

The cryostat for matrix isolation was a closed-cycle compressor unit RW2 with coldhead base unit 210 and extension module ROK from Leybold. The matrix window was CsI and the spectrometer was an IFS85 FTIR

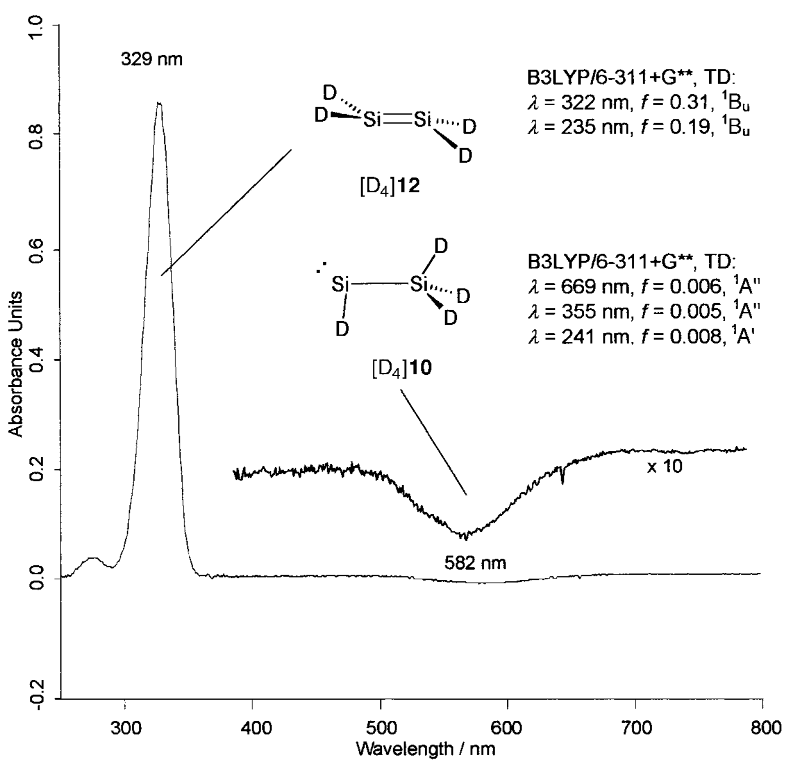


Figure 4. UV/Vis spectra of [D$_4$]disilene ([D$_4$]**12**) and [D$_4$]silylsilylene ([D$_4$]**10**): Difference spectrum of the photoisomerization [D$_4$]**10** → [D$_4$]**12** in argon at 10 K. Positive bands increase, negative bands decrease during the irradiation with light of wavelength $\lambda > 570$ nm.

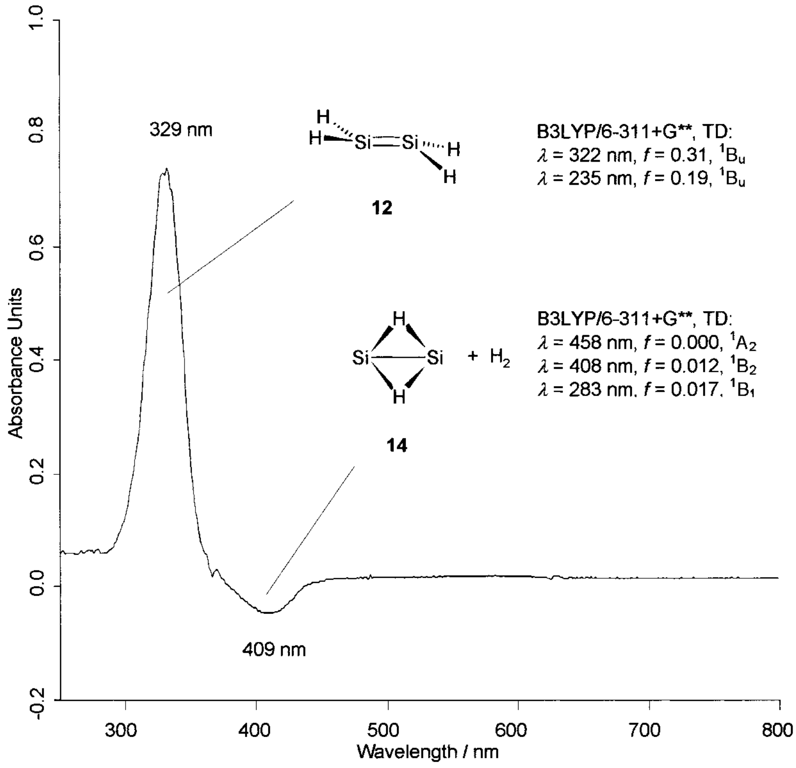


Figure 5. UV/Vis spectra of disilene (**12**) and disilyne (**14**): Difference spectrum of the photoisomerization **14** + $\mathbf{H_2}$ → **12** + **10** in argon at 10 K. Positive bands increase, negative bands decrease during the irradiation with light of wavelength $\lambda = 405$ nm.

instrument from Bruker. The light sources used were a mercury high-pressure lamp (HBO200 from Osram) with a monochromator (Bausch and Lomb) and a mercury low-pressure spiral lamp with a Vycor filter (Gräntzel).

For the production of silicon atoms a rod with the dimensions 0.7 × 2 × 22 mm was cut out from a highly doped silicon wafer and heated resistively by using a current of 10 A at 10 V. Under these conditions the surface temperature amounted to 1350–1380 °C.

Silane (**7**) was purchased from Aldrich (puriss. 99.99%) and was used without further purification.

[D$_4$]Silane ([D$_4$]**7**) was prepared by treatment of tetrachlorosilane with lithium aluminum tetradeuteride by using a slightly modified version of the procedure described in literature[11]: A Schlenk tube, filled with a solution of $LiAlD_4$ (210 mg, 5.00 mmol; Aldrich 98%-D) in dry methyl *tert*-butyl ether (25 mL) was connected to a vacuum line and degassed by four freeze–pump–thaw cycles. The degassed solution was frozen (−196 °C) again, and freshly distilled and degassed $SiCl_4$ (850 mg 5.00 mmol) was condensed onto it. The reaction mixture was allowed to warm up slowly. At about 0 °C a lively evolution of gas was observed. The reaction products were condensed into a second trap (−196 °C). The trap, containing the crude [D$_4$]silane, was then warmed up to −120 °C, and the silane was condensed into a third trap at −196 °C to remove small traces of the solvent. By repeating this procedure two times, pure SiD_4 ([D$_4$]**7**) (110 mL, 180 mg, 4.98 mmol) was isolated (99% yield).

In the same manner [D$_3$]silane ([D$_3$]**7**) was prepared by treatment of trichlorosilane with lithium aluminum tetradeuteride: $HSiD_3$ (175 mg, 4.98 mmol, 99% yield) was isolated from the reaction of $HSiCl_3$ (670 mg, 5.00 mmol) with $LiAlD_4$ (210 mg) in methyl *tert*-butyl ether (25 mL).

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