

Peter Jutzi, Ulrich Schubert (Eds.)

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From the Atom to Extended Systems



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# Silicon Chemistry

From the Atom to Extended Systems



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Part of a polysilane (SiH)<sub>n</sub> nanotube

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## Foreword

In 1995 the *Deutsche Forschungsgemeinschaft* (DFG) started a focussed research program entitled “Specific Phenomena in Silicon Chemistry: New Experimental and Theoretical Approaches for the Controlled Formation and Better Understanding of Multidimensional Systems”. The Austrian *Fonds zur Förderung der wissenschaftlichen Forschung* (FWF) established in 1996 a parallel funding program on silicon chemistry (“Novel Approaches to the Formation and Reactivity of Silicon Compounds”) to improve collaboration between scientists from both countries. Both programs ended in 2002; 33 research groups in Germany and 6 research groups in Austria participated in the focussed programs during the years.

The intention of this book is twofold. First, an overview on the scientific results of the bi-national program is presented. However, the authors of the individual chapters were asked not to go into too much detail, but rather to embed their results in a broader perspective. For the latter reason, two “external” scientists, who had given invited talks at the final bi-national symposium on silicon chemistry in Werfenweng/Austria in 2002, were asked to contribute to this book. Thus, a book on topical developments in silicon chemistry came into being.

More so than for any other element, the development of two- or three-dimensional extended structures from molecular or oligomeric units can be studied (“bottom-up” syntheses) for silicon-based compounds. This aspect of silicon chemistry turned out to be a central topic of both focussed programs during the years. The book is thus organized in three sections. The first section deals with reactive molecular precursors and intermediates in silicon chemistry. Mastering their synthesis, understanding their molecular and electronic structures, and being able to influence their reactivity (including their kinetic stabilization) is essential for using them as building blocks for extended structures. In the second and third sections, the way from molecular building blocks via oligomeric compounds to extended networks is shown for several systems based on Si-O and Si-Si bonds.

The authors of the book thank the *Deutsche Forschungsgemeinschaft* and the *Fonds zur Förderung der wissenschaftlichen Forschung* for funding research in an exciting and topical area for many years.

Peter Jutzi, Ulrich Schubert  
Editors

## Acknowledgement

We gratefully acknowledge the generous financial support from the *Deutsche Forschungsgemeinschaft* (DFG) within the research program entitled "Specific Phenomena in Silicon Chemistry: New Experimental and Theoretical Approaches for the Controlled Formation and Better Understanding of Multidimensional Systems" and from the Austrian *Fonds zur Förderung der Wissenschaftlichen Forschung* (FWF) within the funding program entitled "Novel Approaches to the Formation and Reactivity of Silicon Compounds". We are especially grateful to Dr. A. Mix, University of Bielefeld, for his engagement in formatting and editing the individual contributions.



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## Part I

### Reactive Intermediates in Silicon Chemistry – Synthesis, Characterization, and Kinetic Stabilization

A detailed knowledge about important highly reactive intermediates is the key for a better understanding of fundamental mechanisms and for the optimization of established synthetic procedures; furthermore, it is regarded as a chance to develop synthetic strategies for novel molecules. Part 1 of the present book details recent results concerning the synthesis and characterization of the following short-lived silicon-containing species:

Si (atom)	Si <sub>2</sub>	SiH <sub>2</sub>	SiH <sub>3</sub>
Si <sub>2</sub> H <sub>2</sub>	Si <sub>2</sub> H <sub>4</sub>	Si <sub>4</sub> H <sub>6</sub>	H <sub>2</sub> SiCH <sub>2</sub>
(SiO) <sub>1,2,3</sub>	(SiO <sub>2</sub> ) <sub>1,2</sub>	Si <sub>2</sub> N	SiH <sub>x</sub> O <sub>y</sub>
RR'Si	RR'SiO <sub>2</sub>	F <sub>2</sub> SiS	

For the synthesis and characterization of transient species, rather sophisticated techniques have to be applied. These include high-temperature synthesis by element vaporization, vacuum thermolysis of precursor molecules, photolysis of matrix-entrapped precursor molecules, matrix isolation and spectroscopy (UV/Vis, IR, Raman), dilute gas-phase spectroscopy (including millimeter wave, microwave, high-resolution FTIR, IR spectroscopy), and gas-phase kinetics. The introduction of bulky substituents R instead of hydrogen atoms is the basis for the kinetic stabilization of highly reactive molecules; this strategy has been applied for the stabilization of the species SiH<sub>2</sub>, Si<sub>2</sub>H<sub>2</sub>, Si<sub>2</sub>H<sub>4</sub>, and Si<sub>4</sub>H<sub>6</sub>.

Elemental silicon plays a very important role in solid-state physics (microelectronics, photovoltaic solar cells, etc.) as well as in inorganic and organic silicon chemistry (Müller-Rochow process, etc.). As expected, the reactivity of silicon depends drastically on the particle size (lump silicon < powder < nanoparticles (clusters) < atoms). In this context, fundamental silicon chemistry can be learned from the properties of silicon atoms. In Chapter 1, G. Maier et al. describe studies with thermally generated silicon atoms, which have been reacted in an argon matrix with the reactants SiH<sub>4</sub>, CH<sub>4</sub>, and O<sub>2</sub>. Based on a combination of experimental and theoretical findings, the mechanisms of these reactions are discussed. In the reactions with SiH<sub>4</sub> and CH<sub>4</sub>, the highly reactive double-bond species H<sub>2</sub>Si=SiH<sub>2</sub> (disilene) and H<sub>2</sub>Si=CH<sub>2</sub> (silaethene), respectively, are the final products. The reaction with O<sub>2</sub> mainly leads to SiO (the most abundant silicon oxide in the universe!) and to small amounts of SiO<sub>2</sub>.

More about the matrix chemistry of SiO is reported by H. Schnöckel and R. Köppe in Chapter 2. Condensation of SiO prepared by high-temperature reaction of Si and O<sub>2</sub> gives rise to the formation of oligomers (SiO)<sub>n</sub> with n = 2,3,4. In the reaction of SiO with metal atoms, species of the type MSiO with M = Ag, Au, Pd, Al, Na are formed. Reactions with oxidizing agents yield monomeric species OSiX (X = O,S) and OSiX<sub>2</sub> (X = F, Cl). The synthesis of a dimeric SiO<sub>2</sub> molecule (SiO<sub>2</sub>)<sub>2</sub> allows speculation about a possible formation of fibrous (SiO<sub>2</sub>)<sub>n</sub>. All presented structures have been deduced from spectroscopic data (IR, Raman) and from quantum chemical calculations.

Several highly important technical applications need elemental silicon in the form of thin films (microelectronics, photovoltaic solar cells, digital data storage and display devices, photocopy systems, X-ray mirrors). The preferred fabrication process for such thin films is deposition from the gas phase by physical vapor deposition (PVD) or chemical vapor deposition (CVD). Details of thin-film formation by PVD or CVD on the atomic or molecular scale are still scarce, due to the high reactivity, short lifetime, and low concentration of relevant gas-phase species, but would be very helpful to refine the processes and to regulate the film properties. In Chapter 3, H. Stafast et al. report on diagnostic methods, which allow the in situ characterization of gas-phase species such as Si, Si<sub>2</sub>, SiH<sub>2</sub>, and Si<sub>2</sub>N during a-Si (amorphous silicon) thin-film deposition by PVD (thermal evaporation of Si) and by CVD (SiH<sub>4</sub> pyrolysis) and the measurement of mechanical stress in growing a-Si (during plasma CVD of SiH<sub>4</sub>) thin films. Besides elemental silicon, silicon dioxide also finds many technical applications in the form of thin films due to the dielectric properties of this material. Thin SiO<sub>2</sub> layers are prepared by low-pressure oxidation of SiH<sub>4</sub> or Si<sub>2</sub>H<sub>6</sub> with molecular oxygen in CVD processes. The most important step in the reaction manifold is the oxidation of SiH<sub>3</sub> radicals. This reaction has been investigated in detail by F. Temps et al. and this work is described in Chapter 4. In fast radical-radical reactions, several SiH<sub>x</sub>O<sub>y</sub> intermediates are formed, which show diverse consecutive reaction steps. The experimental results are supported by *ab initio* quantum chemical calculations. Silylene SiH<sub>2</sub> and its derivatives SiR<sub>2</sub> with less bulky substituents R constitute another class of highly reactive silicon compounds. They play an important role as intermediates in several areas of silicon chemistry. In Chapter 5, W. Sander et al. report on the oxidation of silylenes SiRR' (RR' = F, Cl, CH<sub>3</sub> and R = CH<sub>3</sub>, R' = Ph) with molecular oxygen, as studied by matrix-isolation spectroscopy. Dioxasiliranes were obtained as the first isolable products, whereas silanone O-oxides were most likely non-observable intermediates. In combination with DFT or *ab initio* calculations, IR spectroscopy once again proved to be a powerful tool to reliably identify reactive molecules.

Following the classical “double bond rule”, compounds such as H<sub>2</sub>Si=SiH<sub>2</sub>, H<sub>2</sub>Si=CH<sub>2</sub>, and HSi≡SiH (disilyne) with multiple bonding to silicon are too



reactive to be isolated under ordinary conditions and thus are predestined for investigations by more sophisticated methods (matrix experiments, dilute gas-phase studies). Interestingly, such studies have shown that the ground-state structures of these molecules differ to some extent from those found in the analogous carbon compounds. Explanations are given in the contributions of H. Beckers (Chapter 6), N. Wiberg (Chapter 7), and M. Weidenbruch (Chapter 8). The report of H. Beckers deals with the synthesis and characterization of the short-lived species  $F_2Si=S$  and  $H_2Si=CH_2$ , which were obtained by coupling flash vacuum thermolysis (FVT) with matrix IR spectroscopy or with real-time high-resolution gas-phase spectroscopy.

The concept of "kinetic stabilization" has been applied very successfully to the class of compounds incorporating double or even triple bonds to silicon. The last two contributions deal with some recent highlights in this field. In Chapter 7, N. Wiberg reports on the introduction of very bulky silyl substituents R such as  $Si^iBu_3$ ,  $SiH(Si^iBu_3)_2$ , and  $SiMe(Si^iBu_3)_2$ , which allow the synthesis of stable disilenes  $RR'Si=SiRR'$ . Elimination reactions possibly lead to the novel triply-bonded species  $RSi\equiv SiR$ , the final goal in the field of kinetic stabilization. In Chapter 8, M. Weidenbruch reports on the synthesis and characterization of a tetrasilabuta-1,3-diene containing two neighboring  $Si=Si$  double bonds (and also on the first tetragermabuta-1,3-dienes). Kinetic stabilization could be realized with the help of bulky 2,4,6-(triisopropyl)phenyl substituents. Several types of addition reactions are described, some of which lead to compounds with isolated  $Si=Si$  double bonds. Finally, novel types of conjugated compounds are presented, formed by the reaction of hexa-*tert*-butyl-cyclotrisilane with di- and polyynes.

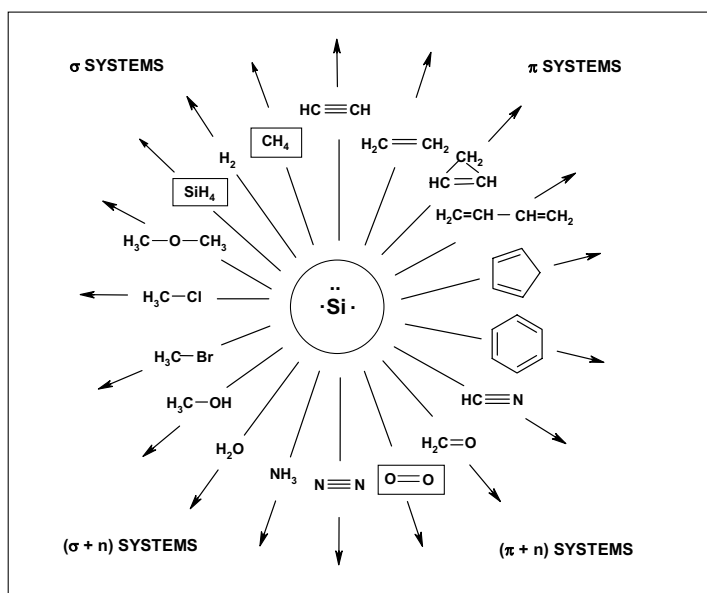
Peter Jutzi, Ulrich Schubert

# 1 Investigations on the Reactivity of Atomic Silicon: A Playground for Matrix Isolation Spectroscopy

G. Maier, H. P. Reisenauer, H. Egenolf, and J. Glatthaar\*

## 1.1 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 means of IR and UV/Vis spectroscopy, aided by comparison with calculated spectra. The method turned out to be very versatile and successful. The reactions that we have carried out to date cover a wide range of substrate molecules (Scheme 1.1).<sup>[1]</sup>



**Scheme 1.1.** Reactions of silicon atoms with different substrate molecules.

In order to get an idea about the potential of silicon atoms, we selected examples which belong to four different groups, namely ( $\pi$ ) systems, ( $\pi + n$ ) systems, ( $\sigma + n$ ) systems, and pure ( $\sigma$ ) systems. These reactions can be

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understood considering the basic features of atomic silicon. First, it has a triplet ground state. A diradical type of reaction can thus 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. As a consequence, a strong electrophilic behavior can be expected.

The matrix study of silicon atoms is not merely an academic exercise, but also has practical relevance. This will be demonstrated by the selection of oxygen, silane, and methane as reaction partners (enframed in Scheme 1.1).

There are reports that porous silicon can be a dangerous material in the presence of oxygen<sup>[2]</sup> or even nitrogen,<sup>[3]</sup> depending on the grain size. Lump silicon is at one end of the scale, silicon atoms represent the other extreme. Silicon powder lies in between. Thus, the properties of silicon atoms can tell us something about the chemical behavior of “activated” silicon. Another example concerns simple silicon hydrides, which play an important role in silicon chemical deposition (CVD) processes, which are of significance to the semiconductor industry. Again, detailed study on the reaction of silicon atoms with silane will help to understand the mechanisms of these reactions. Last but not least, knowledge about the reaction pattern of atomic silicon in the presence of compounds such as chloromethane, methanol, or dimethyl ether can help us to understand the detailed features of the “direct process” (Müller–Rochow synthesis).

## 1.2 Matrix Isolation Spectroscopy

Matrix isolation is a very suitable technique for the synthesis and detection of highly reactive molecules. This method allows spectroscopic studies of the target species with routine spectroscopic instrumentation (IR, UV, ESR) without having to use fast, time-resolved methods. The reactive species are prevented from undergoing any chemical reaction by embedding them in a solid, provided that three conditions are fulfilled: (a) the solid has to be chemically inert, (b) isolation of the single molecules must be achieved by choosing concentrations which are sufficiently low, and (c) diffusion in the solid has to be suppressed by applying low temperatures during the experiments. In this way the kinetic instability inherent to the isolated molecules is counteracted.

In general, there are two possible means of creating a solid with the desired properties, the so-called *matrix*. The molecules of interest can be generated from suitable precursors by reactions in the gas phase. The routine method is the high-vacuum flash pyrolysis of thermally labile compounds followed by direct condensation of the reaction products and co-deposition with an excess of host material on the cold matrix holder. The second way is to produce the

reactive species in situ by photolysis of the entrapped precursor molecules in the matrix material. Other procedures are also known. One such special case is presented in this article (see below).

For full information on the development of matrix isolation methods and their application, the reader is referred to several monographs.<sup>[4]</sup>

The properties of the matrix material determine the spectroscopic methods that can be applied. The use of solid rare gases like argon and xenon or solid nitrogen is well established, since they are optically transparent in the commonly observed spectral ranges. The fact that there is nearly no interaction between the host lattice and the enclosed guest species and that the rotational movements are frozen has an important effect on the IR spectra; under ideal conditions the recorded infrared spectra are reduced to spectra consisting of very narrow lines ( $< 1 \text{ cm}^{-1}$ ). Each of them originates from the respective vibrational transition. UV/Vis spectra are also obtained easily and are likewise useful for the structural elucidation of unknown species. What is even more important is the fact that the UV absorptions allow the selection of the appropriate wavelengths for the induction of photochemical reactions, which under matrix conditions are often reversible.

### **1.3 Computational Methods**

An important breakthrough in the development of matrix isolation was the construction of suitable cryostats, which goes back to the 1970s. A similar push, which, during the last few years, has opened a new dimension for the structure determination of matrix-isolated species, has come from theory. Quantum chemical computations of energies, molecular structure, and molecular spectra are nowadays no longer a task reserved to few specialists. The available programs, for instance the Gaussian package of programs,<sup>[5]</sup> have reached the degree of convenience and ease of application that nearly anyone can formulate the needed input data to obtain reliable information about the energy, electronic structure, geometry, and spectroscopic properties of the species of interest.

In our own experience, density functional calculations (B3LYP-DFT functional) are very well suited for a reliable prediction of vibrational spectra. TD (time dependent) calculations even give surprisingly good results for electronic transitions.

## 1.4 Identification of Matrix-Isolated Species

Comparison of the calculated and experimental vibrational spectra is in most cases (at least for molecules of moderate size) sufficient to identify an unknown molecule unequivocally. Examples are given below.

Special techniques can be applied if additional information is needed for the structural elucidation of the entrapped molecules (our study of the reactions of silicon atoms with nitrogen<sup>[1h]</sup> sets some shining examples in this respect). Since the matrix-isolated species are too reactive to be handled under standard conditions and therefore cannot be identified by routine methods, the structure determination has to rely exclusively on the matrix spectra. Sometimes, if a species can be reversibly photoisomerized upon matrix irradiation, the unchanged elemental composition provides valuable information. The advantages of IR compared with UV/Vis spectra are obvious: a) Calculated IR spectra are of high accuracy. b) FT-IR instruments allow the generation of difference spectra by subtraction of the measured spectra. In other words, if one of the matrix-isolated components is specifically isomerized to a new compound upon irradiation, one can eliminate all the bands of the photostable molecules. By these means it is possible to extract exclusively and separately the absorptions of the diminishing photolabile educt molecule and the newly formed photoproduct. c) If a compound has only a few (sometimes only one) observable IR bands, it may be dangerous to depend solely on the comparison of experimental and calculated spectra. In these cases isotopic labeling will help. Isotopic shifts of the IR absorptions are dependent on the structure, and on the other hand can be calculated with utmost precision.

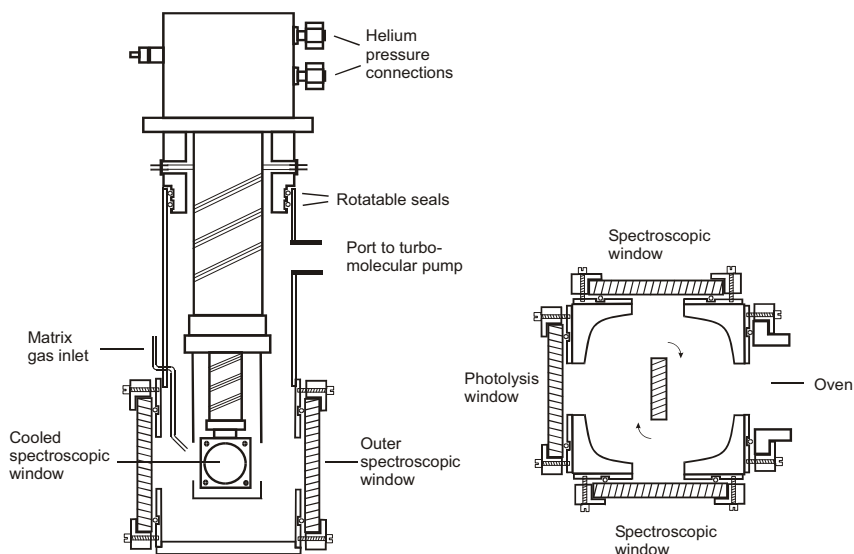
## 1.5 Experimental Procedure

For matrix-isolation studies there is a minimum of necessary equipment. The essentials include: a) a refrigeration system (cryostat), b) a sample holder, c) a vacuum chamber (shroud) to enclose the sample, d) means of measuring and controlling the sample temperature, e) a vacuum-pumping system, f) a gas-handling system, g) devices for generating the species of interest, h) spectrometers for analysis of the matrices.

The generation of the species discussed in this article is different from the two classical methods mentioned above: Solid silicon is vaporized and the extremely reactive silicon atoms create the envisaged molecules in the moment of co-deposition by reaction with the selected partner (such as oxygen, silane, or methane) on the surface of the cold matrix holder. The products remain

isolated in the argon matrix and can then be studied spectroscopically or transformed into other species upon irradiation.

Nowadays, the standard cryostats are closed-cycle helium refrigerators. They are commercially available. We use either the “Displex Closed-Cycle System CSA” from Air Products or the “Closed-Cycle Compressor Unit RW 2 with Coldhead Base Unit 210 and Extension Module ROK” from Leybold. These systems can run for thousands of hours with minimal maintenance. The sample holder can be cooled to temperatures from room temperature to about 10 K. A typical example of a closed-cycle helium matrix apparatus is shown in Figure 1.1.

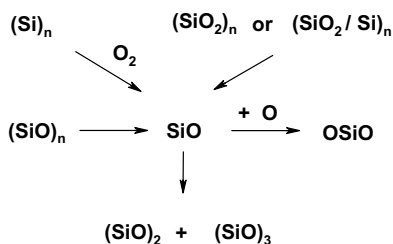


**Figure 1.1.** Closed-cycle helium cryostat.

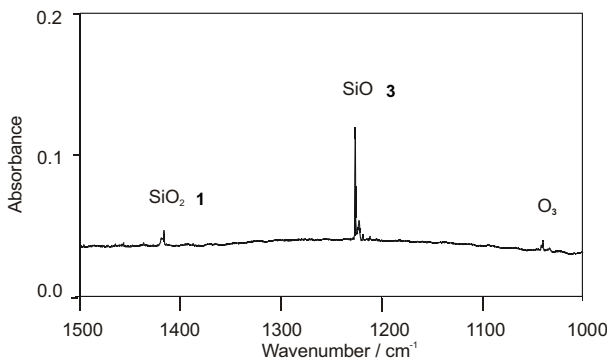
## 1.6 Generation of Silicon Atoms

A critical point in the work presented in this communication was the generation of a steady stream of silicon atoms which have to be condensed together with the substrate molecule and an excess of matrix material onto the cooled window. In our early experiments, silicon was vaporized from a tantalum Knudsen cell (Figure 1.2, Type A) or a boron nitride crucible which was surrounded by an aluminum oxide tube. The oven was resistively heated to temperatures of 1490–1550 °C by means of a tungsten wire wound around the alumina tube (Figure 1.2, Type B). In later runs, a rod of dimensions 0.7·2·22





Schnöckel<sup>[6]</sup> has shown that co-condensation of gaseous SiO, which can be prepared by thermal depolymerization of solid  $(\text{SiO})_n$ , and oxygen atoms, generated by a microwave discharge, yields molecular  $\text{SiO}_2$ . Not only molecular SiO, but also its oligomers  $(\text{SiO})_2$  and  $(\text{SiO})_3$  are well-known species.<sup>[7]</sup> They can be obtained upon heating solid quartz or a mixture of quartz and bulk silicon,<sup>[7]</sup> or when molecular oxygen is passed over heated silicon.<sup>[8]</sup>

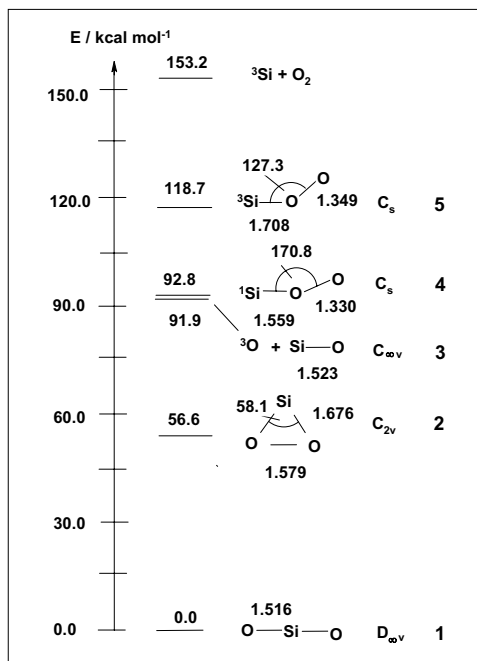


**Figure 1.3.** IR spectrum after co-condensation of silicon atoms and oxygen in argon (1:500).

Surprisingly, there was no known study of the reactions of silicon atoms with oxygen when we began an experimental and theoretical investigation of the  $\text{SiO}_2$  energy hypersurface. In the meantime Roy et al.<sup>[9]</sup> carried out such experiments in connection with a search for silicon trioxide  $\text{SiO}_3$ .

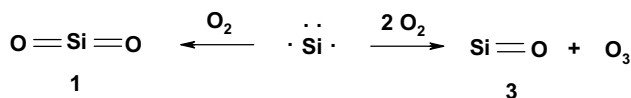
As expected, the global minimum within the series of  $\text{SiO}_2$  isomers is the linear OSiO molecule. The reaction of the components  $^3\text{Si}$  and  $\text{O}_2$  to give OSiO **1** is highly exothermic ( $\Delta E = 153.2 \text{ kcal mol}^{-1}$ ). Astonishingly, even the splitting of molecular oxygen into two atoms and recombination of one of them with a silicon atom under formation of SiO **3** is exothermic ( $\Delta E = 61.3 \text{ kcal mol}^{-1}$ ). So one can expect not only OSiO but also SiO upon reaction of silicon atoms with oxygen.





**Scheme 1.2.** Calculated energies and geometries of SiO<sub>2</sub> species (B3LYP/6-311+G\*\*, zero-point energies included).

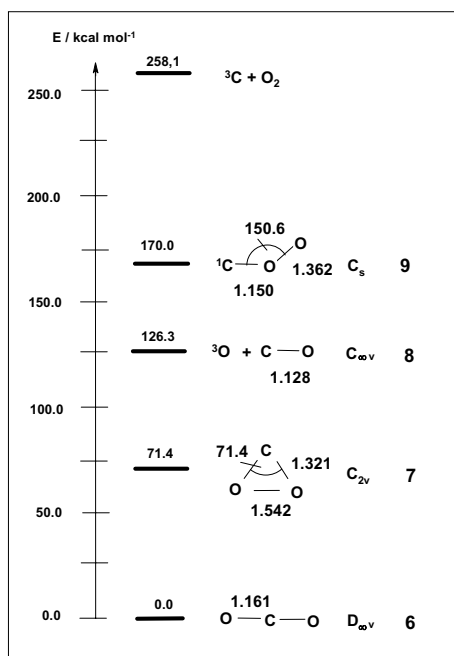
The calculations are in agreement with experiment (Figure 1.3). Co-deposition of silicon atoms and molecular oxygen in argon at 10 K mainly leads to SiO **3**. In addition, a small amount of SiO<sub>2</sub> **1** is formed. Traces of O<sub>3</sub> can be explained as the result of the capture of O atoms by O<sub>2</sub>. The higher aggregates of SiO, namely Si<sub>2</sub>O<sub>2</sub> and Si<sub>3</sub>O<sub>3</sub>, can also be detected (beyond the scale of Figure 3), especially after annealing of the matrix. The main products after warm-up to 30 K are OSiO **1** and O<sub>3</sub>.



As far as the mechanism of the oxidation of silicon (yielding SiO **3** and OSiO **1**) is concerned it can be assumed that the first reaction product is triplet peroxide **5**, which either splits off an oxygen atom – even at 10 K – under formation of SiO **3** or forms singlet peroxide **4**. Silicon dioxide OSiO **1** can

result from **4** via the cyclic peroxide **2**, in which the O,O bond should be broken very easily, but it is also possible that SiO **3** recaptures an oxygen atom.

For comparison, we also calculated the CO<sub>2</sub> energy hypersurface. The replacement of a silicon by a carbon atom leads to a very similar situation, although the energy differences are much greater in the case of carbon. The reaction of a carbon atom with molecular oxygen forming OCO **6**, the global minimum, is strongly exothermic ( $\Delta E = 258.1 \text{ kcal mol}^{-1}$ ). Again, the formal splitting of molecular oxygen into two O atoms and addition of one of them to a C atom is also exothermic ( $\Delta E = 131.8 \text{ kcal mol}^{-1}$ ).



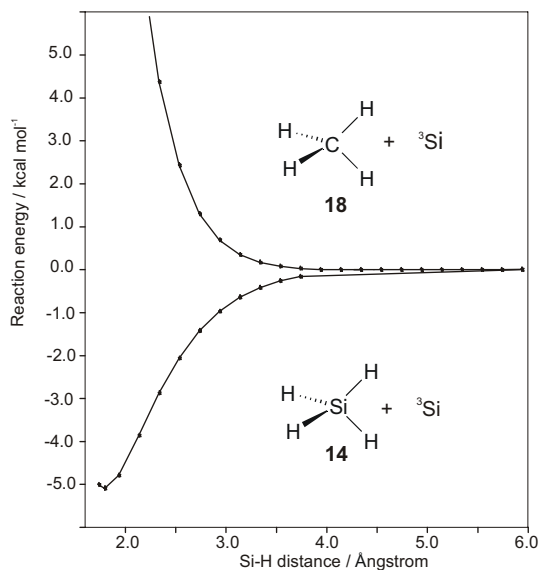
**Scheme 1.3.** Calculated energies and geometries of CO<sub>2</sub> species (B3LYP/6-311+G\*\*, zero-point energies included).

It is trivial that CO<sub>2</sub> **6** and CO **8** are the combustion products of carbon. Nevertheless, there is a chance that other isomers of **6**, namely the cyclic form **7** and the singlet peroxide **9** might be detected in the reaction of atomic carbon with oxygen. Like the silicon analogues **2** and **4**, both are still unknown. Perhaps they are intermediates in the addition of oxygen to the carbon atom under formation of OCO **6**. The mechanistic implication would be similar to the silicon series. According to calculations the triplet peroxide <sup>3</sup>COO is not a minimum on the energy hypersurface.

## 1.8 Reactions of Silicon Atoms with Silane and Methane

A detailed study on the reaction of silicon atoms with silane will not only give us more insight into silicon CVD processes. Another appeal stems from the fact that starting with the first isolation of a disilene by West et al.<sup>[10]</sup> a new chapter in silicon chemistry was opened, yet the isolation and identification of the parent disilene was 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 and theoretical studies covering silicon hydrides  $\text{SiH}_n$  and  $\text{Si}_2\text{H}_n$ .

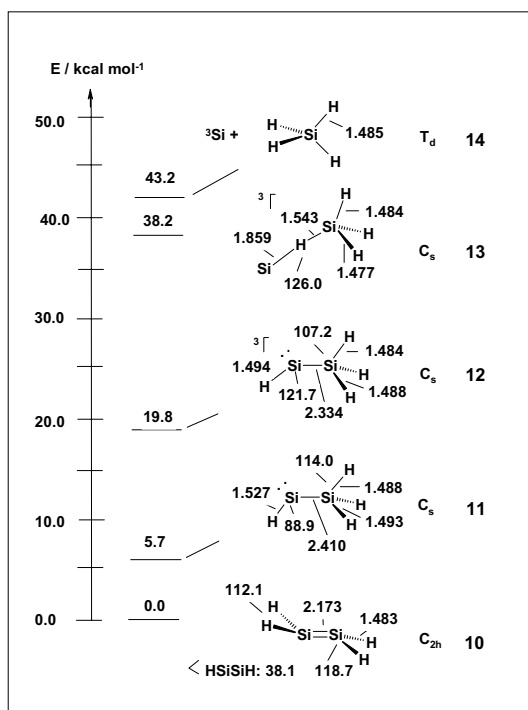
On the other hand, a study of methane would also have scientific and practical relevance. It can be shown by calculation that methane **18** and silane **14** behave quite differently when attacked by a silicon atom (Figure 1.4). If a silicon atom in its triplet ground state approaches methane, the energy is continuously raised. There is no indication of any bonding interaction. On the contrary, the reaction coordinate for the approach between a  $^3\text{Si}$  atom and silane descends steadily until the formation of a complex between the two partners is reached.



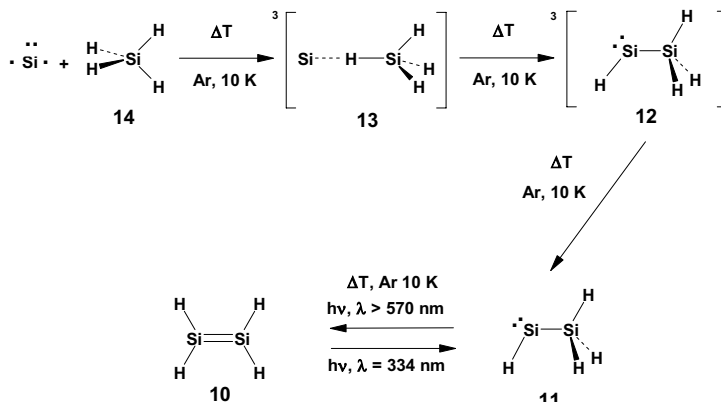
**Figure 1.4.** Calculated changes of the potential energy during the approach of a  $^3\text{Si}$  atom to a methane (upper curve) or a silane molecule (lower curve); UB3LYP/6-311+G\*\*<sub>2</sub>; full optimization at each step.

For the structural identification of the expected species it was again necessary to obtain the calculated vibrational spectra. To get an overview of the  $\text{Si}_2\text{H}_4$  potential energy surface, several stationary points, together with the corresponding vibrational spectra, were calculated. Scheme 1.4 shows the calculated relative energies of some relevant minima.

The global minimum is disilene **10**. The *trans*-bent geometry was suggested some twenty years ago.<sup>[11]</sup> The stabilization energy compared with the two components triplet silicon atom and silane **14** is  $43.2 \text{ kcal mol}^{-1}$ . Besides **10**, silylsilylene **11** should also be formed in an exothermic reaction from  $^3\text{Si}$  atoms and **14**. On the triplet energy hypersurface, the starting components form, without an activation barrier, a loose complex **13**. Its stabilization energy amounts to  $5 \text{ kcal mol}^{-1}$ . In a subsequent step the primary complex **13** can be transformed into triplet silylsilylene **12**, followed by intersystem crossing to singlet silylsilylene **11** (T/S gap  $14.1 \text{ kcal mol}^{-1}$ ). On the singlet energy hypersurface, isomerization of silylsilylene **11** to the thermodynamically more stable ( $\Delta E = 5.7 \text{ kcal mol}^{-1}$ ) disilene **10** then takes place.



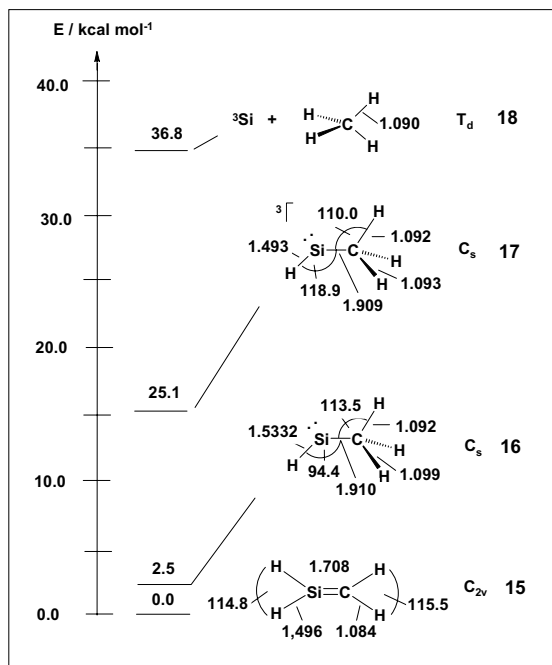
**Scheme 1.4.** Calculated energies and geometries of some  $\text{Si}_2\text{H}_4$  species (B3LYP/6-311+G\*\*, zero-point energies included).



The analysis of the spectra shows that the reaction of silicon atoms with silane **14** leads to a mixture of silylsilylene **11** and disilene **10**. Upon irradiation of the matrix at long wavelengths ( $\lambda > 570$  nm), **11** is isomerized to **10**. The backreaction can be induced by using shorter wavelengths. With  $\lambda = 334$  nm, disilene **10** regenerates silylsilylene **11**.

Through a combination of the experimental and theoretical findings the mechanism of the reaction of  $^3\text{Si}$  atoms with silane **14** can be summarized as follows. Via the triplet complex **13** triplet silylsilylene **12** is formed. Both are too short-lived to be detected. Intersystem crossing gives singlet silylsilylene **11**. The reaction leading to **11** releases enough energy to surpass the barriers on the pathway from **11** to **10**, even at 10 K.

Applying our standard procedure, we condensed methane **18** as a gaseous mixture with argon onto a spectroscopic window at 10 K. 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 **19** between methane **18** and a silicon atom. This was the first time that a substrate molecule had not reacted with silicon atoms in our experiments. This observation suggests that mineral oil may be a suitable medium to protect “activated” silicon from unforeseeable reactions with oxygen or nitrogen.



**Scheme 1.5.** Calculated energies and geometries of some CSiH<sub>4</sub> species (B3LYP/6-311+G\*\*, zero-point energies included).

If one considers 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 might be a way to activate silicon atoms. Indeed, irradiation of the co-condensate of methane **18** and silicon atoms at short wavelengths ( $\lambda = 185$  or 254 nm) leads to methylsilylene **16**. Obviously, photoexcitation leads to the insertion of a silicon atom into the C,H bond of methane **18**. The intensity of the IR bands of **16** arising during irradiation was relatively weak. Nevertheless, its structural elucidation has to be taken for granted, since it is possible to establish a photoequilibrium between **16** and the isomeric silaethene **15**. At  $\lambda > 400$  nm the equilibrium is shifted to silaethene **15**; at  $\lambda = 254$  nm it lies on the side of methylsilylene **16**.