Geometrical structure of monobridged disilyene Si(H)SiH

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Abstract

By means of Fourier transform microwave spectroscopy of a supersonic molecular beam, we have detected the more abundant rare isotopic species of monobridged Si(H)SiH, and determined of its geometrical structure by isotopic substitution. Unexpected abundance anomalies of the singly deuterated isotopic species with respect to normal and Si(D)SiD were observed with equal mixtures of SiH4 and SiD4. This nonstatistical distribution is consistent with Si(H)SiH formation which is dominated by the reaction of a bare Si atom or ion with either SiH2 or SiH4. Dedicated laboratory searches were also undertaken for the remaining singlet isomer, H2SiSi, so far without success. From the absence of lines at the expected frequencies we conclude that H2SiSi is at least 50 times less abundant than Si(H)SiH. Because it is only slightly less stable than Si(H)SiH and because the barrier to isomerization is calculated to be quite low, H2SiSi may rearrange on the timescale of the supersonic expansion to Si(H)SiH.

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1. Introduction

Disilyene, Si2H2, is one of only a few silicon hydrides with more than one Si atom which have been the subject of both high-level theoretical calculations and high-resolution spectroscopy. Rotational spectra of the dibridged singlet Si(H2)Si (I in Fig. 1; [1]), the most stable isomer, and a low-lying monobridged isomer Si(H)SiH (II; [2]), calculated at the coupled cluster level of theory to be 8.7 kcal/mol higher in energy [3], were first measured by millimeter-wave absorption spectroscopy in the early 1990s. A precise experimental structure derived from isotopic substitution for the dibridged isomer was subsequently reported [4], but owing to poor signal to noise, only a partial structure was derived for the monobridged isomer [2]. A third singlet isomer III with a vinylidene-like structure, H2SiSi, is predicted to lie only 2.9 kcal/mol above the monobridged isomer, but its rotational spectrum has never been measured, possibly owing to a small dipole moment calculated to be ~0.1 D, and a low barrier (2.4 kcal/mol) to rearrangement [3].

Very strong lines of Si(H)SiH have now been detected in a silane discharge in the centimeter band by means of Fourier transform microwave (FTM) spectroscopy of a supersonic molecular beam. The lines of the normal isotopic species of this isomer are so strong that all of the most abundant rare Si isotopic species have been detected in natural abundance. In combination with the rotational constants of Si(D)SiH and Si(H)SiD, which have also been measured here for the first time, a precise geometric structure for Si(H)SiH has been derived. Well-resolved nuclear quadrupole hyperfine structure (hfs) has been observed in the rotational lines of each deuterated isotopic species, and is analyzed here to yield precise D coupling constants; the rotational spectra of 29Si(H)SiH and Si(H)29SiH also exhibit hfs from nuclear spin–rotation.

In the course of the isotopic investigations, large differences between the abundance of the two singly deuterated isotopic species relative to Si(H)SiH and Si(D)SiD were observed with equal mixtures of SiH4 and SiD4. The preferential production by a factor of 10

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or more of Si(H)SiH and Si(D)SiD relative to Si(D)SiH and Si(H)SiD suggests that Si(H)SiH is formed primarily via the reaction of a bare Si atom or ion with either SiH$_2$ or SiH$_4$, both of which are probably present in high abundance in our supersonic beam.

Because rotational line intensities in FTM spectroscopy are proportional to the first power of $\mu$, not $\mu^2$ as in conventional spectroscopy, and because Si(H)SiH is abundantly produced in our discharge source, deliberate searches for the rotational lines of disilylenide H$_2$SiSi, the remaining singlet Si$_2$H$_2$ isomer, have also been undertaken. No lines have been detected at the predicted frequencies, implying that H$_2$SiSi is at least 50 times less abundant than Si(H)SiH. Because it is calculated to be only slightly less stable than Si(H)SiH, and therefore should be produced with comparable abundance [5], the anomalously low-abundance limit for H$_2$SiSi in our discharge may indicate that it rearranges on the timescale of the supersonic expansion to the more stable monobridged form [3].

\[ \begin{align*}
&\text{I} \quad \text{Si} \quad \text{Si} \\
&\text{H} \quad \text{Si}_a \quad \text{Si}_b \\
&\angle \text{Si}_a \text{Si}_b \text{Si} = 103.2^\circ \\
&\text{H} \quad 1.684 \\
&\text{Si} \quad 2.208
\end{align*} \]

\[ \begin{align*}
&\text{II} \quad \text{Si} \quad \text{H} \quad \text{Si} \\
&\text{Si}_a \quad 2.119(1) \\
&\text{Si}_b \quad 1.506(4) \\
&\angle \text{Si}_a \text{H} \text{Si}_b = 52.2(8)^\circ \\
&\angle \text{Si}_b \text{H} \text{Si}_a = 153.9(4)^\circ \\
&\angle \text{Si}_a \text{H} \text{Si} = 1.586(19)
\end{align*} \]

\[ \begin{align*}
&\text{III} \quad \text{Si} \quad \text{Si} \\
&\text{H} \quad (1.485) \\
&\angle \text{Si} \text{H} \text{Si} = 112.6^\circ \\
&\text{H} \quad (2.218)
\end{align*} \]

Fig. 1. Structures of three low-lying singlet isomers of Si$_2$H$_2$. The bond lengths (in Å) and angles (in degrees) for SiH$_2$/Si [4] and Si(H)SiH were obtained by isotopic substitution, but for H$_2$SiSi they are (in parentheses) from the ab initio geometry of [3].

\[ \begin{align*}
\text{Relative Intensity} \\
\text{Frequency (MHz)}
\end{align*} \]

Fig. 2. The $^1_{0,1}$ transition of $^{30}$Si(H)$^{30}$SiH, the result of 3 min integration. The double-peaked lineshape is instrumental, the result of the Doppler shift of the Mach 2 molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Perot.

2. Experimental

The FTM spectrometer used for the present work operates between 5 and 43 GHz and possesses a very sensitive microwave receiver which can be cooled together with the large confocal mirrors of the spectrometer to the temperature of liquid nitrogen [6]. The small discharge which produces reactive molecules is struck in the throat of the supersonic nozzle through a stream of precursor gases heavily diluted in an inert buffer, just prior to adiabatic expansion to about Mach 2 in a large vacuum chamber. The strongest lines of Si(H)SiH were observed with source conditions similar to those used to detect a variety of silicon carbides and other silicon-bearing molecules: 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 μs long, yielding a gas flow of 10–15 sccm. Under these conditions, Si(H)SiH is produced in such high abundance that, as the sample spectrum in Fig. 2 illustrates, its double silicon-30 species can be observed with a signal-to-noise ratio of better than 10 in a few minutes of integration, in spite of its low-fractional abundance: 0.11%. By comparing line intensities with those of the rare isotopic species of OCS in a supersonic molecular beam of 1% OCS in Ar in the absence of a discharge, we estimate that more than $3 \times 10^{12}$ Si(H)SiH molecules are produced per gas pulse.

With such strong lines, it has been possible to detect transitions in the $K_a = \pm 1$ rotational ladders of Si(H)-SiH, which are about 13 K above the corresponding transitions in the $K_a = 0$ ladder. From the intensities of
lines with $K_a = \pm 1$ relative to those with $K_a = 0$, a rotational temperature of $T_{rot} = 2.5 \pm 0.2\,\text{K}$ has been derived, in good agreement with previous measurements. For Si(D)SiD, $T_{rot} = 2.0 \pm 0.2\,\text{K}$.

Rotational constants for the rare isotopic species of Si(H)SiH were well predicted by the molecule structure of Cordonnier et al. [2]. Transitions of the $^{29}\text{Si}$ and $^{30}\text{Si}$ isotopic species were observed in natural abundance, but for the two singly deuterated isotopic species, equal mixtures of SiH$_4$ and SiD$_4$ in the discharge were required for detection.

### 3. Data and analysis

The measured rotational lines of isotopic Si(H)SiH are given in Table 1 and derived spectroscopic constants in Table 2. The effective rotational constant $(B + C)/2$ was determined instead of $B$ and $C$ individually, because only transitions in the $K_a = 0$ ladder were measured for several isotopic species. For those, $A$ and $B - C$ were constrained to the theoretical values [3]; for the remaining species, $B - C$ was varied and $A$ was fixed at the value derived from the millimeter-wave measurements [2]. Where comparison is possible, the spectroscopic constants determined here are in good agreement with previously reported values [2].

Hyperfine structure has been observed in the lowest rotational transitions of the two $^{29}\text{Si}$ and all of the deuterated isotopic species, owing to the high-spectral resolution (i.e., 0.2 ppm) of the FTM technique when used in combination with an axial molecular beam. For the two $^{29}\text{Si}$ species, hfs of order 10 kHz arises from the interaction of the $I = 1/2$ nuclear spin of $^{29}\text{Si}$ with the small magnetic field produced by molecular rotation. The effective spin–rotation constants ($C_{bb} + C_{cc}$; see Table 2) are comparable in magnitude to those for $^{29}\text{SiC}_3$ [7] and $^{29}\text{Si}_3$ [8]. From well-resolved quadrupole hfs in the $1_{0,1} - 0_{0,0}$ transitions of the singly substituted D isotopic species, the coupling constant $\lambda_{aa}$ has been determined to an accuracy of a few percent or better. An example of the agreement between theory and experiment is shown for Si(D)SiD in Fig. 3.

The deuterium coupling constant along the terminal Si–D bond is calculated to be $\lambda_{zz} = 105\,\text{kHz}$, on the assumption of cylindrical symmetry and an angle of $\theta = 24^\circ$ between the Si–D bond and the $a$-axis. This value is about 50% smaller than those for C–D bonds which are typically in the $160$–$220\,\text{kHz}$ range [9,10]. The D coupling constant for a Si–D bond has to our knowledge not been determined previously; it is smaller than that for a C–D bond, plausibly as a result of the lower electronegativity of Si [11] and the longer bond (1.50 Å vs. 1.05 Å).

<table>
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<tr>
<th>$J_a$</th>
<th>$K_a$</th>
<th>$J_b$</th>
<th>$K_b$</th>
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**Table 1**

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<td>2607.267</td>
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<tr>
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<td>3</td>
<td>1</td>
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<td>4</td>
<td>1</td>
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<td>0</td>
<td>5</td>
<td>1</td>
<td>2697.771</td>
<td>2679.771</td>
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</table>

**Table 2**

- **Note:** Units of MHz. Estimated measurement uncertainty: 2 kHz.
- **b** Centroid of hyperfine-split line.
3.1. Geometrical structure of Si(H)SiH

The structure of Si(H)SiH was obtained by a least squares adjustment of the three bonds and two angles in Fig. 1 to reproduce by means of the Hamiltonian for rigid body rotation, the measured transitions of the eight isotopic species on the assumption that Si(H)SiH is planar. Uncertainties in the bond lengths and angles were derived on the basis of three assumptions: (i) the largest unknown source of error is zero-point vibration, (ii) all of the measurements have the same standard deviation, and (iii) the minimized \( \chi^2 \) equals 5, the most probable value for five degrees of freedom [12]. The calculated moments of inertia from the best-fit structure reproduce those measured to within \( 0.005 \text{ amu}	ext{-A}^2 \) for all eight isotopic species, yielding rotational constants which are accurate to about \( 0.5 \text{ MHz} \).

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The derived \( r_0 \) structure is compared in Table 3 with ab initio \( r_c \) structures at three different levels of theory. The length of the Si–Si bond is within the range predicted from theory (2.115–2.133 \( \text{A} \)), but the length of the Si–H bond for the bridged H atom and the \( \angle \text{SiSiH} \) angle for the terminal H atom differ considerably (by at least 0.04 \( \text{A} \) and 5°, respectively) from those predicted at all three levels of theory here. There is a strong correlation \( (r = -0.98) \) between the Si–H bond and Si–Si–H angle for both H atoms, but when either one of the two structural parameters is constrained to one of the...
ab initio values, the quality of the fit decreases by a factor of 10 or more.

As pointed out by Cordonnier et al. [2], the Si–Si bond length (2.119 Å) is one of the shortest silicon–silicon bonds known: it is more than 0.05 Å shorter than in disilene (2.174 Å; [13]) and its derivatives [14], about 0.1 Å shorter than in Si2 (2.246 Å; [15]), dibridged Si(H)Si (2.208 Å; [4]), and monobridged H2Si(H)SiH (2.248 Å; [13]), and more than 0.2 Å shorter than in disilane (2.327 Å; [16]). The terminal Si–H bond length is close to that found in saturated compounds such as Si2H4 and Si3H4 where Si–H bonds are typically 1.48–1.52 Å [17]. Owing the three-center, two-electron nature of the monobridged Si–H bond, its length (1.59 Å) is intermediate between that in Si(H)Si (1.684 Å) and a single Si–H bond.

3.2. Formation of Si(H)SiH

Although rotational lines of Si(D)SiH and Si(H)SiD were detected using equal mixtures of SiH4 and SiD4, their intensities are anomalously weak with respect to either Si(H)SiH and Si(D)SiD. Table 4 summarizes the relative abundances of the four isotopic species. These have been derived from intensity measurements which in the present work are reliable to within 10%. Predicted abundances assuming two different formation reactions are given in the adjacent columns in Table 4: the first, a well-shuffled reaction [e.g., 2SiH2 → (H2SiSiH2)+ → Si(H)SiH + H2] in which the H/D is statistically distributed in the molecule; and the second, an addition reaction in which Si reacts with either SiH2 or SiH4 (the latter followed by loss of H2).

The low abundance of the partially deuterated isotopic species is probably best explained if nearly 90% of Si(H)SiH is produced by an addition reaction in which all of the hydrogen (or deuterium) originates from a single monosilicon hydride, most plausibly from SiH2 or SiH4. This formation mechanism implicates the same species which are abundantly produced in the thermal decomposition of silane [21]: SiH2 and then Si via sequential elimination of H2. Although with our FTM spectrometer we cannot detect SiH2 (its lines are too high in frequency), there is strong circumstantial evidence that Si atoms are copiously produced in our discharge source: strong rotational lines of more than 25 silicon carbides (SiCn)+, silicon-bearing carbon-chain radicals (SiCnH), and silacumulenes (SiCnH2) have been detected through a discharge of dilute silane and diacetylene in neon [20]. Si3 has also recently been detected using silane gas alone in the discharge, at an abundance calculated to be in excess of 10^13 molecules per gas pulse [8].

Boo and Armentrout [22] demonstrated that the reaction of silicon ions with silane forms Si2H2+, which then dissociates with high efficiency (>90%) to Si2H2+ and H2. At thermal energies, only Si2H2+ is observed, but at slightly higher kinetic energies (>1 eV), Si2H+, Si2+, and Si2H+ were detected as well. Because the energy barriers to H migration are thought to be small, various isomers may be readily formed prior to dehydrogenation. The monosilicon hydrides, SiH+ and SiH2+, may simply arise from Si–Si bond cleavage from the disilicon hydride isomer H3SiSiH+.

It may not be difficult to undertake additional experiments to pin down the formation of Si(H)SiH in our discharge source. Isotopically enriched 29SiH4 in combination with SiD4 would preferentially produce specific isotopic species, if Si(H)SiH is made via a simple addition reaction. Similar isotopic experiments employing 30Si+ or SiD4 as the reactant, for example, allowed Boo and Armentrout to infer the formation mechanism and thermochemical properties of neutral and ionized disilicon hydrides.

Table 3

<table>
<thead>
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<tbody>
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<td>Si–Si (Å)</td>
<td>2.119(1)</td>
<td>2.120</td>
<td>2.115</td>
<td>2.133</td>
</tr>
<tr>
<td>Si–H (Å)</td>
<td>1.586(19)</td>
<td>1.638</td>
<td>1.626</td>
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<tr>
<td>Si–H (Å)</td>
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<td>1.483</td>
<td>1.476</td>
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<td>153.9(4)</td>
<td>159.0</td>
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<td>158.9</td>
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</table>

* Structure that best reproduces the observed rotational transitions of the eight isotopic species. See Fig. 1 for the labeling of the atoms. Estimated uncertainties (see text) in the last significant digit are given in parentheses.

Table 4

Relative abundances of normal and deuterated Si(H)SiH with equal mixtures of SiH4 and SiD4

<table>
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<tr>
<th>Isotopic species</th>
<th>Observed</th>
<th>Statistical</th>
<th>Si + SiH2 (or SiH3)</th>
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<tr>
<td>Si(H)SiH</td>
<td>0.43(4)</td>
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<td>0.50</td>
</tr>
<tr>
<td>Si(D)SiH</td>
<td>0.02(1)</td>
<td>0.25</td>
<td>...</td>
</tr>
<tr>
<td>Si(H)SiD</td>
<td>0.04(1)</td>
<td>0.25</td>
<td>...</td>
</tr>
<tr>
<td>Si(D)SiD</td>
<td>0.50(5)</td>
<td>0.25</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Note. Abundances, derived from intensity measurements, are normalized to unity; estimated (1σ) uncertainties in parentheses.
3.3. A laboratory search for H2SiSi

Laboratory searches were also undertaken for H2SiSi (isomer III), using a gas mixture and experimental conditions that optimized the production of Si(H)SiH. Searches for the 10-1 transition were based on a high-level coupled cluster calculation of Grev and Schaefer [3], and covered a frequency range that corresponds to ±1% of the predicted rotational constants, which were scaled by 1.014 since those of Si(H)Si and Si(H)SiH were systematically off by this factor.

The absence of rotational lines that can be attributed to H2SiSi might be the result of the limited search range, but at the predicted frequencies implies that the product of the dipole moment times the abundance (μ·N) may be at least 1500 times smaller for H2SiSi than for Si(H)SiH. Owing to the 10-fold lower dipole moment of this C2v structure, its 5-fold higher rotational partition function, and its 3-fold poorer nuclear spin statistics, we estimate that H2SiSi is at least 50 times less abundant than Si(H)SiH. Because the two are calculated to be comparably stable, and because the relative abundances of isomers approximately correlate with their relative rotational constants in our discharge, we might expect a priori similar abundances for the two isomers.

Because the isomerization barrier between H2SiSi and Si(H)SiH is calculated to be only 2.4 kcal/mol [3], our failure to detect H2SiSi may indicate that it rearranges on the timescale of the expansion to the slightly more stable monobridged isomer. If the dipole moment of H2SiSi is much smaller than 0.1 D; however, the applied microwave power might have been insufficient to achieve the π/2 pulse condition and the rotational lines of H2SiSi might be significantly fainter than expected. Detection of H2SiSi may still be possible: with further improvements in instrumentation and production efficiency a factor of three or more in sensitivity may be within reach.

4. Discussion

The high abundance of Si(H)SiH in our molecular beam suggests that low-lying triplet isomers of Si2H2 and other polar disilicon hydrides of the form Si2Hm may be found with dedicated laboratory searches using silane as a precursor gas. The most stable triplet isomer, H2SiSi, is calculated to be lie only 10 kcal/mol above singlet Si(H)SiH and to possess a much larger dipole moment (1.04 D vs. 0.10 D) than the singlet form with the same structure [23,24]. In addition to probing the potential energy surface of Si2H2 at higher energies, laboratory detection of triplet H2SiSi would provide spectroscopic information on the spin-spin and spin–rotation coupling constants in a pure silicon hydride.

Owing to the heavy mass of Si relative to H and the large separation between the two Si atoms (typically 2.1–2.4 Å), the fundamental 10–10 transition of most disilicon hydrides with a nonzero component of the dipole moment along the a-inertial axis is expected to lie in the 10–15 GHz range. For Si(H)SiH, for example, this transition lies fairly high in frequency (at 14.5 GHz; see Table 1) because of the extremely short Si–Si bond length and because one of the H atoms lies near the center of mass. For other silicon hydrides, the frequency of the same transition will depend sensitively on the length of the Si–Si bond, the number of H atoms, and their position relative to the center of mass.

An initial search for rotational transitions of new disilicon hydrides has already been undertaken between 10 and 15 GHz using a gas mixture and experimental conditions which optimize the production of Si(H)SiH. The unidentified line density is about 1 line per 40 MHz (i.e., for a total of ~125 lines), and chemical and other assays establish that the carriers of many of the lines are silicon hydrides. On the basis of ab initio calculations, the nearly planar Si2H3 radical and a novel monobridged isomer of Si2H4 have recently been detected [13]. The large number of remaining unidentified lines suggests that other exotic silicon molecules of chemical and astronomical interest await laboratory detection.

It may also be possible to detect the SiH and SiH3 radicals in the same molecular beam. Fairly precise frequencies for the A-doubling transitions of SiH [25] and the inversion transitions of SiH3 [26] are available from infrared observations; at a rotational temperature of a few Kelvin, the strong lines are calculated to lie near 3 GHz. Although this frequency is below the diffractive cut-off of our present FTM spectrometer, detection may be possible with a recently constructed circular waveguide cavity which operates in the 2–6 GHz frequency range. These lines would improve the spectroscopic constants of two fundamental silicon hydrides and allow fairly precise estimates of their abundance in our discharge source.

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References