Infrared spectrum of the disilane cation (Si$_2$H$_6^+$) from Ar-tagging spectroscopy

Marco Savoca, Martin Andreas Robert George, Judith Langer and Otto Dopfer*

The infrared spectrum of the disilane cation, Si$_2$H$_6^+$, in its $^2$A$_{1g}$ ground state is inferred from photodissociation of cold Si$_2$H$_6^+$–Ar$_n$ complexes ($n = 1, 2$). Vibrational analysis is consistent with a D$_{3d}$ symmetric structure of H$_3$SiSiH$_3^+$ generated by ionization from the bonding Si$_{2d}$ orbital. Structural, vibrational, and electronic properties of Si$_2$H$_6$ and Si$_2$H$_6^+$–Ar$_{1,2}$ are determined at the MP2/aug-cc-pVTZ and B3LYP/aug-cc-pVTZ levels. Ar ligands bind weakly at the C$_3$ axis on opposite sides to Si$_2$H$_6^+$ with only a minor impact on the Si$_2$H$_6^+$ properties. The calculations reveal a low-energy H$_2$SiH$_2$SiH$_2^+$ isomer with C$_i$ symmetry and a Si–H–Si bridge, which is only ~15 kJ mol$^{-1}$ above the D$_{3d}$ structure.

1. Introduction

Although Si and C are both group IV elements, their bonding characteristics are substantially different. As a result of the much weaker and less directional Si–Si bonds, Si-containing molecules exhibit a larger variety of binding motifs as compared to the corresponding C-bearing species. For example, Si$_2$H$_y$ molecules often exhibit Si–H–Si bridges,\textsuperscript{1–3} which are quite rare for C$_2$H$_y$. In contrast to the well-characterized C$_2$H$_y$ molecules, considerably less information is available for the more reactive and less stable Si$_2$H$_y$ analogues, because precursors for the latter are less readily available. For example, although IR spectra are available for SiH$_y^+$ with $y = 3, 5$, and 7,\textsuperscript{4–6} no vibrational and electronic spectra are available for Si$_2$H$_y^+$ with $x \geq 2$. Characterization of Si$_2$H$_y$ and their ionic species is not only motivated from fundamental aspects in the theory of chemical bonding but also from understanding of processes in (disilane plasmas\textsuperscript{2,7} and interstellar media.\textsuperscript{3,8} In addition, hydrogen passivation of the highly reactive bare silicon clusters and cages has been suggested as a possible route to generate novel stable silicon nanostructures with potential applications in materials science.\textsuperscript{9,10}\textsuperscript{10} To this end, we set up a program to systematically characterize the geometric and electronic structure of Si$_2$H$_y$ molecules, their ions, and their clusters by spectroscopy and quantum chemical calculations. Herein we report infrared (IR) spectra of Ar clusters of the disilane cation (Si$_2$H$_6^+$) obtained by IR photodissociation (IRPD) spectroscopy of mass selected Si$_2$H$_6^+$–Ar$_n$ clusters, which have been synthesized in a supersonic plasma expansion of SiH$_4$. This tagging approach\textsuperscript{11,12} has previously been employed to investigate a variety of fundamental C$_3$H$_y^+$ ions, including CH$_3^+$,\textsuperscript{13–15} C$_2$H$_2$,\textsuperscript{16,17} C$_3$H$_3^+$,\textsuperscript{18} C$_4$H$_4^+$,\textsuperscript{19–21} C$_5$H$_5$,\textsuperscript{24} C$_6$H$_6^-$,\textsuperscript{25–34} and C$_{10}$H$_{16}^+$,\textsuperscript{35} as well as SiOH$^+$ cluster ions,\textsuperscript{36,37} but seems to be applied for the first time to Si$_2$H$_6^+$ ions.

Neutral Si$_2$H$_6$ is a well-characterized molecule. It has a staggered equilibrium structure with D$_{3d}$ symmetry in its $^1$A$_{1g}$ ground electronic state (Fig. 1). All fundamental vibrational frequencies are accurately known from IR and Raman spectroscopy.\textsuperscript{38–41} The geometric equilibrium structure of Si$_2$H$_6$ has been determined by electron diffraction to be $R = 2.331(3)$ Å, $r = 1.493(3)$ Å, and $\theta = 110.3(4)^\circ$.\textsuperscript{42} The threefold barrier for internal rotation via the transition state (TS) with D$_{3h}$ symmetry has been determined from high-resolution torsional and tunnelling spectroscopy of IR transitions to be $V_3 = 407$ cm$^{-1}$.\textsuperscript{40,41} The 12 vibrational fundamentals of Si$_2$H$_6^+$ have been determined to transform in D$_{3d}$ as $\Gamma_{\text{vib}} = 3a_{1g} + a_{1u} + 2a_{2u} + 3e_u + 3e_g$. We follow the notation of vibrational modes given previously in ref. 38 and 39. The fundamentals with $a_{2u}$ ($v_5, v_6$) and $e_u$ ($v_{12–13}$) symmetry are IR active, whereas those with $a_{1g}$ ($v_{1–4}$) and $e_g$ ($v_{14–15}$) are Raman active.

In contrast to neutral Si$_2$H$_6$, surprisingly little spectroscopic and quantum chemical data are available for the corresponding Si$_2$H$_6^+$ cation and its clusters, probably due to the experimental challenges involved in preparing sufficient number densities of cold (cluster) ions. The limited number of relatively low-level quantum chemical calculations predicts that adiabatic ionization of Si$_2$H$_6$ occurs from the bonding Si$_{2d}$ orbital with $a_{1g}$ symmetry, leading to a $^2$A$_{1g}$ ground electronic state with staggered configuration (D$_{3d}$).\textsuperscript{14,15} As a consequence of ionization to the ionic ground state, the Si–Si bond contracts substantially and the Si–SiH bond angle strongly decreases, while the Si–H bond length is less affected. The corresponding values obtained at the MP2/6-31G$^*$ level are reported as $\Delta R = +0.32$ Å, $\Delta \theta = -12^\circ$, and $\Delta r = -0.016$ Å, respectively.\textsuperscript{1}
As a result of the large geometry change upon ionization and the induced long Franck–Condon progressions in the totally symmetric SiH$_3$ umbrella and low-frequency Si–Si stretch modes, the He(i) photoelectron spectrum of Si$_2$H$_6$ is broad (>1 eV) and essentially unresolved at the achieved spectral resolution (∼200 cm$^{-1}$), largely preventing vibrational characterization of the cation ground state. 44,45 The only vibrationally resolved feature that has been assigned to the symmetric SiH$_3$ umbrella mode is $\nu_2(a_{1g}) \sim 0.11$ eV (∼900 cm$^{-1}$). 45,46 Photo-ionization mass spectrometry of Si$_2$H$_6$ yields an adiabatic ionization potential of AIE = 9.74(2) eV, and low appearance energies of $\leq$10.04(2) eV and $\leq$10.81(2) eV for H$_2$ elimination generating H$_3$SiSiH$_3^+$ and HSiSiH$_3^+$, respectively. 46

Here we report IRPD spectra and quantum chemical calculations of Si$_2$H$_6^+$–Ar$_n$ clusters with $n = 1$ and 2. The major motivation for this work resulted from the following aspects. (1) The IRPD spectra of cold Si$_2$H$_6^+$–Ar$_n$ clusters provide the first IR vibrational signatures of the fundamental Si$_2$H$_6^+$ cation. (2) Neither spectroscopic nor computational data are available for clusters of Si$_2$H$_6^+$. Hence, this study on Si$_2$H$_6^+$–Ar$_n$ provides a first impression of the intermolecular interaction of the Si$_2$H$_6^+$ cation with neutral ligands. (3) Ab initio and density functional calculations are performed for Si$_2$H$_6^+$–Ar$_n$ at the MP2 and B3LYP levels using the aug-cc-pVTZ basis set. Thus, these calculations employ a much higher theoretical level as compared to previous quantum chemical studies. For example, geometry optimization for Si$_2$H$_6^+$ has only been reported up to the MP2/6-31G* level. The major issues addressed in this work are the effects of ionization and Ar complexation on the geometrical, vibrational, and electronic properties of disilane. We also consider the potential for SiH$_3$ internal rotation because no information appears to exist for the barrier in the ionic ground state. In addition, we explored Si$_2$H$_6^+$ structures with connectivities other than H$_3$SiSiH$_3^+$ and report for the first time a low-energy isomer of the disilane cation with a H$_3$SiHSiH$_3^+$ structure featuring a Si–H–Si bridge.

2. Experimental and computational techniques

IRPD spectra of Si$_2$H$_6^+$–Ar$_n$ with $n = 1$ and 2 are obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap. 47,48 Weakly-bound Si$_2$H$_6^+$–Ar$_n$ clusters are generated in a pulsed supersonic plasma expansion by electron impact and chemical ionization of a suitable gas mixture of SiH$_4$ and Ar close to the nozzle orifice and subsequent clustering reactions in the high pressure regime of the expansion. A typical mass spectrum of the ion source obtained for expanding a SiH$_4$/He/Ar mixture with a ratio of 1/20/200 at 5 bar stagnation pressure is shown in Fig. 2. The major cluster series observed are Ar$_n^+$, Si$_2$H$_6^+$–Ar$_n$, Si$_2$H$_6^+$–(SiH$_4$)$_n$, and Si$_2$H$_6^+$–(SiH$_4$)$_n$–Ar$_m$. Significant polymerization reactions are observed up to Si$_2$H$_6^+$ with $x = 3$. In general, the abundance of Si$_2$H$_6^+$–Ar$_n$ clusters decreases rapidly with increasing cluster size $n$, consistent with the formation of weakly-bound clusters by sequential addition of individual ligands to the molecular Si$_2$H$_6^+$ ion. Although the abundance of Si$_2$H$_6^+$ is at least one order lower compared to the most abundant Si$_2$H$_6^+$ ions (SiH$_3^+$ and SiH$_2^+$), respectable IRPD spectra could be recorded for its weakly-bound Si$_2$H$_6^+$–Ar$_n$ clusters with $n = 1$ and 2, illustrating the high sensitivity of the experimental approach. Si$_2$H$_6^+$–Ar$_n$ ions of interest are mass selected by the first quadrupole and

![Fig. 1](image1.png) Calculated equilibrium structures of Si$_2$H$_6$ and Si$_2$H$_6^+$ with D$_{3d}$ and D$_{3h}$ symmetry in their ground electronic states obtained at the B3LYP/aug-cc-pVTZ level. Minimum structures of Si$_2$H$_6^+$–Ar$_n$ with $n = 1$ and 2 are given as well. Corresponding geometrical, vibrational, and energetic parameters are listed in Tables 1 and 2.

![Fig. 2](image2.png) Typical mass spectrum of the electron impact cluster ion source for an SiH$_4$/He/Ar expansion (1/20/200) at 5 bar stagnation pressure. Major cluster series observed are Ar$_n^+$, Si$_2$H$_6^+$–Ar$_n$, Si$_2$H$_6^+$–(SiH$_4$)$_n$, and Si$_2$H$_6^+$–(SiH$_4$)$_n$–Ar$_m$. Part of the spectrum is vertically expanded by a factor of 5.
irradiated in an adjacent octopole with tuneable IR laser radiation generated by an IR optical parametric oscillator pumped by a Q-switched nanosecond Nd:YAG laser. The IR laser is characterized by a pulse energy of \( \sim 0.1-0.5 \) mJ in the 650–2200 cm\(^{-1}\) range, a repetition rate of 10 Hz, and a bandwidth of 1 cm\(^{-1}\). Calibration of the IR laser frequency is accomplished by a wavemeter. Resonant vibrational excitation of \( \text{Si}_2\text{H}_6^-\text{Ar}_n \) induces evaporation of a single Ar ligand (Ar-tagging), according to:

\[
\text{Si}_2\text{H}_6^-\text{Ar}_n + h\nu_{\text{IR}} \rightarrow \text{Si}_2\text{H}_6^-\text{Ar}_m + (n - m)\text{Ar} \quad (m = n - 1)
\]  

(1)

The resulting \( \text{Si}_2\text{H}_6^-\text{Ar}_{n-1} \) fragment ions are selected by the second quadrupole and monitored as a function of the laser frequency to obtain the IR photodissociation spectrum of \( \text{Si}_2\text{H}_6^-\text{Ar}_n \). To separate the fragment ions arising from metastable decay and laser-induced dissociation, the ion source is triggered at twice the laser frequency, and signals from alternating triggers are subtracted. Although the IR spectra have been normalized for laser intensity fluctuations, the relative intensities of widely spaced bands are believed to be accurate to within a factor of two, mainly due to the changes in the spatial overlap between the ion and IR laser beams. As the mass spectrum of the ion source is rather complex, collision-induced dissociation (CID) experiments are performed to verify the composition of the mass-selected parent ions. To this end, the octopole is filled with \( N_2 \) collision gas up to 10 \(^{-5}\) mbar, facilitating single collision conditions with a collision energy of 10 eV in the laboratory frame. The CID spectrum of mass-selected \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \) in Fig. 3 demonstrates Ar loss as only fragment channels, indicating that the composition of the \( m/z \) 142 ion is indeed \( 102^-\text{Ar} \) or \( 62^-\text{Ar}_2 \), consistent with the \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \) parent ion.

\( \text{Si}_2\text{H}_6, \text{Si}_2\text{H}_6^+, \) and \( \text{Si}_2\text{H}_6^-\text{Ar}_n \) clusters are characterized in their ground electronic states by quantum chemical calculations at the B3LYP and MP2 levels using the cc-pVDZ and aug-cc-pVTZ basis sets,\(^{49}\) to investigate the effects of ionization and Ar complexation on the geometric, vibrational, and electronic structure as well as the SiH\(_3\) internal rotation potential. As the results using the two different basis sets are similar for the monomer species, only the data for the larger aug-cc-pVTZ basis set are reported here. All coordinates are relaxed for the search of stationary points on the potential, and their nature as minimum or transition state (TS) is established by harmonic frequency analysis. Energies are corrected for harmonic zero-point vibrational energy. Harmonic frequencies are scaled by factors of 0.9780 (0.9518) and 0.9942 (0.9742) for B3LYP (MP2) frequencies above and below 1500 cm\(^{-1}\), respectively, to optimize the agreement between the calculated and the measured frequencies of \( \text{Si}_2\text{H}_6 \). Such a dual scaling factor procedure accounts for the rather different anharmonicity of the Si–H hydride stretch modes and the other vibrations.\(^{50}\)

Application of these scaling factors to the B3LYP (MP2) harmonic frequencies could reproduce the measured frequencies of the fundamentals to better than 13 \((18)\) cm\(^{-1}\), with an average deviation of 5 \((5)\) cm\(^{-1}\). Spin contamination for the radical cation species is negligible, with values of \(<0.006\) and \(<10^{-4}\) for \( \langle S^2 \rangle \) \(-0.75\) before and after annihilation, respectively. The charge distribution is calculated using the natural bond orbital (NBO) population analysis.

3. Results and discussion

3.1 Experimental IR spectra

The IRPD spectra of \( \text{Si}_2\text{H}_6^-\text{Ar} \) and \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \) recorded in the Ar loss channel are shown in Fig. 4. They exhibit only three transitions (A–C) in the investigated frequency range \((650–2230\) cm\(^{-1}\)), consistent with the high symmetry of the \( \text{Si}_2\text{H}_6^+ \) ion and the weak perturbation by the Ar ligands. The transitions A at 725 and 719 cm\(^{-1}\) for \( n = 1 \) and 2 are assigned to the antisymmetric linear combination of the umbrella inversion motions, \( \nu_6 \). The bands B at 926 and 925 cm\(^{-1}\) for \( n = 1 \) and 2 are attributed to the asymmetric SiH\(_3\) deformation mode, \( \nu_3 \). While the assignments of A and B to fundamentals of \( \text{Si}_2\text{H}_6^+ \) are fully supported

![Fig. 3](cid_spectrum.png)

**Fig. 3** CID spectrum obtained by mass-selecting \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \) \((m/z\) 142) with the first quadrupole and scanning the second quadrupole. The only fragments observed are \( \text{Si}_2\text{H}_6^-\text{Ar}_n \) with \( n = 0 \) and 1 \((m/z\) 62 and 102) indicating that the composition of the \( m/z\) 142 ion is indeed \( 102^-\text{Ar} \) or \( 62^-\text{Ar}_2 \), consistent with \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \). All peaks are saturated in order to detect possible weak fragment signals.

![Fig. 4](irpd_spectra.png)

**Fig. 4** Experimental IRPD spectra of \( \text{Si}_2\text{H}_6^-\text{Ar} \) and \( \text{Si}_2\text{H}_6^-\text{Ar}_2 \) compared to linear IR absorption spectra of \( \text{Si}_2\text{H}_6^-\text{Ar} \) \((C_3^v), \text{Si}_2\text{H}_6^-\text{Ar}_1 \) \((D_{3d}), \text{Si}_2\text{H}_6^+ \) \((D_{3d},D_{3h}), \text{Si}_2\text{H}_6^-\text{Ar}_2 \), and \( \text{Si}_2\text{H}_6^-\text{Ar}_3 \) calculated at the B3LYP/aug-cc-pVTZ level (Fig. 1 and Table 2). The calculated spectra are drawn to the same scale.
by the calculations presented below, the interpretation of bands C at
1500 and 1505 cm$^{-1}$ for $n = 1$ and 2 is less clear, because Si$_2$H$_6^+$ does not
have any fundamental mode in this frequency range. Currently,
the tentative assignment is to the $\nu_6 + \nu_2$ combination band.
The Si$_2$H$_6^+$–Ar$_2$ spectrum could only be obtained in the Si$_2$H$_6^+$–Ar
fragment channel. The fact that no laser-induced dissociation signal
was detected in the Si$_2$H$_6^+$ channel indicates that the IR photon
energy of the observed IR resonances is insufficient to evaporate
both Ar ligands. The widths of the vibrational transitions
(50–25 cm$^{-1}$) result mainly from unresolved rotational fine
structure.

Efforts in recording the IR(M)PD spectrum of Si$_2$H$_6^+$ monitored in
the Si$_2$H$_6^+$ fragment channel failed despite the relatively low
reported dissociation energy of $<0.3$ eV ($\sim 2400$ cm$^{-1}$). The lack of
observation of resonant laser-induced dissociation is ascribed to the
single-photon absorption conditions in connection of observation of resonant laser-induced dissociation is ascribed to the
single-photon absorption conditions in connection

3.2 Computational results

The computational results obtained for Si$_2$H$_6$, Si$_2$H$_6^+$, and
Si$_2$H$_6^+$–Ar$_n$ relevant for the present work are summarized in
Fig. 1, 4, and 5 and Tables 1 and 2, respectively.

In agreement with experiment and previous computations, the
global minimum of Si$_2$H$_6$ in its $^3A_1g$ ground electronic state
obtained in the present B3LYP and MP2 calculations has a
staggered equilibrium structure with $D_{sd}$ symmetry (Fig. 1).
The structural parameters of $R_e = 2.35$ Å, $r_e = 1.48$ Å, and $\theta_e = 110^\circ$
agree well with the values derived from electron scattering, $R =
2.331(3)$ Å, $r = 1.493(3)$ Å, and $\theta = 110.3(4)^\circ$. The rotational
constants of $A_0 = 43.104$ and $B_0 = 5017$ MHz (B3LYP) are also close to
the measured values of $A_0 = 43.208(23)$ and $B_0 = 5120.095(45)$ MHz.
Similarly, the scaled fundamental frequencies can reproduce the
measured fundamentals well, with a maximum uncertainty of less
than 20 cm$^{-1}$. Since the B3LYP values are more accurate, we refer to
these frequencies in the text and in Fig. 4, although Table 2 offers
also the only slightly less accurate MP2 values. The simulated IR
spectrum of Si$_2$H$_6$ in Fig. 4 shows all five IR active fundamentals
with $\nu_{42}$ ($\nu_{5b}$) and $\nu_{34}$ ($\nu_{23}$) symmetry. These include the two
asymmetric Si–H stretch modes $\nu_{57}$, the asymmetric umbrella
inversion mode $\nu_{6}$, an asymmetric SiH$_3$ deformation mode $\nu_{8}$,
and an asymmetric SiH$_3$ rocking mode $\nu_{9}$. The NBO charges of
$\rho_{\text{Si}} = 0.6$ e and $\rho_{\text{H}} = -0.2$ e (MP2) are in line with the higher
electron negativity of H. The potential for internal SiH$_3$ rotation
of Si$_2$H$_6$ is shown in Fig. 5. The HSiSiH dihedral angle has been
varied in steps of $1^\circ$, and for each angle all other coordinates
have been relaxed. The threefold barrier occurs at the transition
state with eclipsed configuration ($0^\circ$, Fig. 1, $D_{3h}$) and amounts
to $V_3 = 377$ and $336$ cm$^{-1}$ at the MP2 and B3LYP levels,
respectively, in good agreement with the experimental value of
$V_3 = 407$ cm$^{-1}$. The geometrical and vibrational parameters
of the $D_{3h}$ transition state are quite similar to those of the $D_{sd}$ minimum.

Similar to neutral Si$_2$H$_6$, the global minimum of Si$_2$H$_6^+$ in its
$^2A_1g$ ground electronic state also has a staggered equilibrium
structure with $D_{sd}$ symmetry. The adiabatic ionization energies
of AIE = 9.49 (9.56) eV calculated at the B3LYP (MP2) level are consistent with the experimental value of AIE = 9.74(2) eV, indicating that the chosen computational approaches describe
the electronic structure of Si$_2$H$_6$ well in both charge states.

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**Table 1** Geometrical parameters (in Å and degree), relative energies and
binding energies (in cm$^{-1}$), and NBO charge distribution (in e) of the equilibrium
structures of Si$_2$H$_6$, Si$_2$H$_6^+$, and Si$_2$H$_6^+$–Ar$_n$, with $n = 1$ and 2 evaluated at the MP2
and B3LYP levels using the aug-cc-pVTZ basis set (Fig. 1)

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<th>Si$_2$H$_6$</th>
<th>Si$_2$H$_6^+$</th>
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<tr>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>232 (227)</td>
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* Experimental values are $R = 2.331(3)$ Å, $r = 1.493(3)$ Å, and $\theta =
110.3(4)^\circ$. $^b$ MP2/6-31G* values are $R = 2.659$ Å, $r = 1.487$ Å, and $\theta =
110.4^\circ$. $^c$ Values of the parameters related to the SiH$_3$ moiety binding
to Ar are indicated by asterisks. $^d$ Numbers in parentheses include zero-
point energy.

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**Fig. 5** Potential for internal SiH$_3$ rotation of Si$_2$H$_6$ and Si$_2$H$_6^+$ as a function of the
HSiSiH dihedral angle evaluated at the MP2 and B3LYP levels using the aug-cc-pVTZ
basis set. The staggered $D_{sd}$ structure ($60^\circ$) is more stable than the eclipsed $D_{3h}$
geometry ($0^\circ$) for both charge states.
Removal of one electron from the bonding $\sigma_{\text{Si-Si}}$ orbital causes the Si–Si bond to drastically elongate by $\Delta R = +0.4$ Å and the Si-SiH bond angle to shrink by $\Delta \theta = -12^\circ$, while the Si–H bonds slightly contract by $\Delta r = -0.014$ Å. These massive structural changes are similar to those predicted at the MP2/6-31G* level and translate directly into the vibrational frequencies and the corresponding IR spectrum. For example, the Si–H stretch frequency $\nu_3$ is reduced by a factor of 2 from 419 to 212 cm$^{-1}$. The Si–H stretch fundamentals $\nu_1$, $\nu_2$, and $\nu_3$ increase by 40–94 cm$^{-1}$, with an average value of 76 cm$^{-1}$. The SiH$_3$ rocking frequencies $\nu_9$ and $\nu_{12}$ are also reduced by a factor of 1.5 and 2, respectively, and the SiH$_3$ torsional frequency drops by 40%. The symmetric and antisymmetric SiH$_3$ umbrella frequencies $\nu_{12}$ and $\nu_{13}$ decrease both by about 15%, while the SiH$_3$ deformation frequencies $\nu_8$ and $\nu_{11}$ decrease merely by $\sim 4\%$. Thus, with the exception of the Si–H stretch modes, all frequencies are substantially reduced upon removal of the bonding $\sigma_{\text{Si-Si}}$ electron, indicating that the force constants for SiH$_3$ rocking, deformation, and torsion as well as Si–Si stretching decrease drastically due to a softer potential in the cation ground state. The potential for internal SiH$_3$ rotation of SiH$_3$, similar to that for neutral SiH$_3$, with the major difference that the barrier at the $D_{3h}$ transition state is lower in the ionic state, $V_3 = 285$ (233) versus $377$ (336) cm$^{-1}$ at the MP2 (B3LYP) level. Significantly, the barrier in the ionic state is still far too large for tunnelling splittings to be resolved at the current spectral resolution. As the IR spectrum of the $D_{3h}$ transition state is rather similar to that of the $D_{3d}$ global minimum (Fig. 4), the two configurations cannot be distinguished by the current IR spectroscopic experiment. Most frequencies differ by less than 5 cm$^{-1}$, and as expected the largest differences are predicted for the two SiH$_3$ rocking frequencies $\nu_9$ and $\nu_{12}$ with 53 and 19 cm$^{-1}$, respectively. The NBO charge distribution of SiH$_3$ and SiH$_3$ is detailed in Table 1 suggests that the excess charge arising from ionization from the $\sigma_{\text{Si-Si}}$ orbital is indeed fully localized on the Si–Si bond. The resulting charge distribution in the cation ground state at the MP2 (B3LYP) level assigns high positive partial charge to the Si atoms, $q_{12} = +0.99$ (+0.82) e, and much smaller negative charges to the H atoms, $q_{12} = -0.16$ (0.11) e.

To estimate the influence of Ar complexation on the properties of SiH$_3$, minima have been searched for on the SiH$_3$–Ar potential using a variety of starting geometries for energy optimization. The only minimum located at both the MP2 and the B3LYP level is the $C_{2v}$ symmetric structure shown in Fig. 1, in which the Ar ligand binds to one of the SiH$_3$ groups of the $D_{3d}$ conformation of SiH$_3$ on the $C_3$ symmetry axis (Table 1). In this configuration, the Ar atom can interact optimally with the positively charged Si atom collinear with the partially filled and thus electrophilic $\sigma_{\text{Si-Si}}$ orbital. Other starting geometries, in particular those involving H-bonding to

### Table 2

<table>
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<tr>
<th>Mode</th>
<th>Description</th>
<th>$\nu_{1}(a_1\bar{g})$</th>
<th>$\nu_{2}(a_2\bar{g})$</th>
<th>$\nu_{3}(a_1\bar{g})$</th>
<th>$\nu_{4}(a_1u)$</th>
<th>$\nu_{5}(a_1l)$</th>
<th>$\nu_{6}(a_1u)$</th>
<th>$\nu_{7}(e_g)$</th>
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<th>$\nu_{9}(e_u)$</th>
<th>$\nu_{10}(e_u)$</th>
<th>$\nu_{11}(e_u)$</th>
<th>$\nu_{12}(e_u)$</th>
<th>$\nu_{13}(e_u)$</th>
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<tbody>
<tr>
<td>$\nu_{2}(a_g)$</td>
<td>$\sigma_{\text{Si-Si}}$</td>
<td>2021</td>
<td>2020</td>
<td>2019</td>
<td>2018</td>
<td>2017</td>
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<tr>
<td>$\nu_{3}(a_1g)$</td>
<td>$\sigma_{\text{SiH}}$</td>
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<td>2021</td>
<td>2020</td>
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<td>2018</td>
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</tr>
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</table>

* IR intensities (in km mol$^{-1}$) of allowed transitions are listed in parentheses. Top (bottom) numbers refer to the MP2 (B3LYP) level. Experimental frequencies are listed in italics. 

$\sigma_{\text{Si-Si}}$ Symmetry given in the $D_{3d}$ point group. $\sigma_{\text{Si-Si}}$ Stretch ($\sigma$), rock ($\gamma$), torsion ($\tau$), deformation ($\beta$). 

$\sigma_{\text{Si-Si}}$ From IR and Raman spectra in the gas phase.
the Si–H protons, did not yield minima. This observation is attributed to the high positive partial charge on the Si atoms, which are the main attractors for the Ar ligands. In addition, no minimum was obtained with a D_{3h} symmetric Si_{2}H_{6}^{+} ion core, indicating that the weak interaction with Ar does not invert the torsional potential. At the MP2 level, the intermolecular bond in Si_{2}H_{6}^{+}–Ar is characterized by a Si–Ar bond separation of R_{Si–Ar} = 2.99 Å, a dissociation energy of D_{0} = 881 cm^{-1}, and intermolecular bend and stretch frequencies of β = 57 and σ = 74 cm^{-1}, respectively. Ar complexation at this binding site breaks the symmetry between the two SiH_{3} groups. The Si–Si bond becomes a bit weaker, and there are minor changes in the SiSiH bond angles and Si–H bond lengths of the two non-equivalent SiH_{3} groups. As expected, the weak interaction with Ar has only little impact on the intramolecular frequencies of Si_{2}H_{6}^{+}. Most frequencies change by less than 5 cm^{-1}, and as expected – the largest differences are predicted for the two SiH_{3} rocking frequencies ν_{6} and ν_{12} with +47 and +68 cm^{-1}, respectively. Although symmetry reduction from D_{3d} to C_{3v} upon Ar complexation has the interesting effect that many more modes of Si_{2}H_{6}^{+} become IR active for Si_{2}H_{6}^{+}–Ar, namely the a_{1g} (ν_{1–3}) and e_{g} (ν_{19–12}) modes, their activation is minor in all cases (I < 20 km mol^{-1}) due to the weak perturbation and could not be exploited in the present work to detect more vibrational transitions. However, in principle this tagging technique may be used in the future to detect the IR forbidden transitions of Si_{2}H_{6}^{+}, such as the interesting Si–Si stretch mode (ν_{3}) via tagging spectroscopy. The attractive part of the intermolecular Si_{2}H_{6}^{+}–Ar interaction is mainly based upon charge-induced dipole and dispersion forces. The charge on the Ar ligand is predicted to be less than 0.05 e. As dispersion provides a large contribution to the interaction, the B3LYP level predicts much weaker and longer bonds than the MP2 level (428 vs. 881 cm^{-1}, 3.12 vs. 2.99 Å).

Further complexation with a second Ar ligand on the opposite side of Si_{2}H_{6}^{+}–Ar on the C_{3} axis restores the original D_{3d} symmetry of the monomer cation. The intermolecular bonds in the n = 2 complex are slightly weaker than that for n = 1 (D_{0} = 815 vs. 881 cm^{-1}), consistent with the noncooperative three-body induction forces typically observed for solvation of a molecular core ion with neutral nonpolar and inert solvent molecules. These binding energies are compatible with the observed photo-fragmentation behaviour. Transitions A and B at around 720 and 925 cm^{-1} are observed only in the single Ar loss channel in both IRPD spectra in Fig. 4.

Finally, we reconsider the spectroscopic assignments of the experimental spectra of Si_{2}H_{6}^{+}–Ar with n = 1 and 2 given in Section 3.1 in the light of the computational results. Clearly, the transitions A at 725 and 719 cm^{-1} for n = 1 and 2 are assigned to the ν_{6} fundamental of the Si_{2}H_{6}^{+} moiety in the Si_{2}H_{6}^{+}–Ar_{n} clusters, which are predicted at 715 and 709 cm^{-1}, respectively. The B3LYP calculations predict small incremental redshifts for this transition of ~3 and ~6 cm^{-1}, and the latter agrees with the measured shift of ~6 cm^{-1}. The extrapolated value for the bare Si_{2}H_{6}^{+} ion is thus ν_{6} = 728 cm^{-1}, and the derived ionization-induced redshift of Δν_{6} = −115.5 cm^{-1} matches the predicted value, Δν_{6} = −116 cm^{-1}. The ν_{6} fundamentals in Si_{2}H_{6}^{+}–Ar_{n} with n = 1 and 2 give rise to parallel transitions, which are consistent with the narrow rotational band contours observed (12 and 6 cm^{-1}).

The bands B at 926 and 925 cm^{-1} for n = 1 and 2 are attributed to the ν_{9} fundamental of Si_{2}H_{6}^{+}–Ar_{n} with predicted values of 912 and 910 cm^{-1}, respectively. The B3LYP calculations yield incremental redshifts of ~1 and ~2 cm^{-1}, and the latter agrees with the observed shift of ~1 cm^{-1}. The extrapolated experimental value of ν_{9} = 927 cm^{-1} for the isolated Si_{2}H_{6}^{+} ion implies an ionization-induced redshift of Δν_{9} = −13 cm^{-1}, which is somewhat smaller than the predicted value of Δν_{9} = −37 cm^{-1}. The ν_{9} fundamentals in Si_{2}H_{6}^{+}–Ar_{n} with n = 1 and 2 give rise to perpendicular transitions, and indeed the observed ν_{9} rotational band contours are much broader (25 and 20 cm^{-1} for n = 1 and 2) than those of the corresponding parallel ν_{6} bands.

The interpretation of bands C at 1500 and 1505 cm^{-1} for n = 1 and 2 is less certain, as there is no fundamental of the Si_{2}H_{6}^{+} ion with D_{3d} symmetry in this frequency range. Thus, the first option is an assignment to a combination or overtone band. The only possible candidate involving two vibrational quanta is the symmetry-allowed ν_{6} + ν_{9} combination (a_{2u}) with predicted frequencies of 1502 and 1493 cm^{-1} for n = 1 and 2 neglecting cross anharmonicities. A second option is an assignment to a Si_{2}H_{6}^{+} isomer with a connectivity different from the D_{3d} structure. It is possible that higher energy isomers of Si_{2}H_{6}^{+} are also formed in the supersonic plasma expansion, which then could be stabilized and cooled in the adiabatic expansion by collisions and subsequent aggregation with Ar. Indeed, we could identify such a low-energy isomer, namely H_{2}SiHSiH_{3}^{+} with C_{3v} symmetry, which is only 15 (16) kJ mol^{-1} less stable than the D_{3d} structure at the MP2 (B3LYP) level. However, as its predicted IR spectrum is quite different from the observed one (Fig. 6), we exclude at the present stage an assignment to higher energy isomers. The calculated H_{2}SiHSiH_{3}^{+} isomer is characterized by a Si–H–Si bridge with a very long Si–Si contact (R = 3.04 Å) and very long Si–H bonds (r = 1.62 and 1.66 Å). Thus, the Si–Si stretch frequency is only 135 cm^{-1} and the asymmetric Si–H–Si

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**Fig. 6** Experimental IRPD spectra of Si_{2}H_{6}^{+}–Ar compared to linear IR absorption spectra of H_{2}SiHSiH_{3}^{+} (D_{3d}) and H_{2}SiHSiH_{3}^{+} (C_{3}) isomers calculated at the B3LYP/aug-cc-pVTZ level.
stretch has also an unusually low frequency (1785 cm\(^{-1}\)) and an enormous IR oscillator strength (882 km mol\(^{-1}\)). The latter mode is the vibrational IR fingerprint of the Si–H–Si bridge and not observed in the experimental spectra. The third option considered is an assignment to different X–Ar\(_{n}\) species, which are isobaric to Si\(_2\)H\(_{6}\)–Ar\(_{n}\) with \(n = 1\) and 2. The CID spectra of the ions with \(m/z\) 102 and 142 clearly establish that their composition is of the type 62\(^{2}\)-Ar\(_{1}\) and 102\(^{2}\)-Ar\(_{2}\) (Fig. 3). Possible impurities X with \(m/z\) 62 are isotopologues of Si\(_2\)H\(_{6}\)\(^{+}\) involving \(^{28}\)Si or \(^{30}\)Si isotopes which occur with natural abundances of 5 and 3%, respectively. Possible candidates for \(m/z\) 62 are then \(^{28}\)Si\(^{29}\)SiH\(_5\)\(^{+}\), \(^{29}\)Si\(^{29}\)SiH\(_5\)\(^{+}\), \(^{30}\)Si\(^{28}\)SiH\(_5\)\(^{+}\), etc. However, we have failed so far to record the IRPD spectra of \(^{28}\)Si\(_2\)H\(_{5}\)–Ar\(_{n}\) and \(^{29}\)Si\(_2\)H\(_{5}\)–Ar, and the IRPD spectrum of \(^{28}\)Si\(_2\)H\(_{6}\)–Ar also looks different from that of Si\(_2\)H\(_{6}\)–Ar shown in Fig. 4. Other conceivable impurities X with \(m/z\) 62 involve species with O atoms such as [SiO\(_2\)H\(_2\)]\(^{+}\) due to the presence of H\(_2\)O impurity in the gas inlet system, as evidenced from the weak (H\(_2\)O)\(_2\)\(^{+}\) peak at \(m/z\) 36. However, in the presence of oxygen the SiH\(_{4}\) plasma mass spectrum usually exhibits strong signals for SiO\(^{+}\), SiOH\(^{+}\), and SiH\(_{2}\)OH\(^{+}\) at \(m/z\) 44, 45, and 49, 36, 37. As these ions are completely absent in the mass spectrum in Fig. 2, we also exclude this scenario. In summary, we currently favour the first option with an assignment of bands C to \(\nu_6 + \nu_2\) of Si\(_2\)H\(_{6}\)–Ar\(_{n}\).

Inspection of Fig. 4 and Table 2 reveals that, although the Si\(_2\)H\(_{6}\)\(^{+}\) cation has five IR active transitions, only two of them have high IR oscillator strength (\(\nu_6\) and \(\nu_5\)) and are detected in the present experiment. The three other IR active modes have very low IR oscillator strengths (<20 km mol\(^{-1}\)) and are also outside the investigated frequency range (650-2200 cm\(^{-1}\)). Unfortunately, the high IR oscillator strengths of the Si–H–Si stretch fundamentals \(\nu_5\) and \(\nu_7\) of neutral Si\(_2\)H\(_{6}\) (120 and 400 km mol\(^{-1}\)) are largely quenched upon ionization (1 and 20 km mol\(^{-1}\)).

The low-resolution photoelectron spectrum exhibits a progression in the symmetric SiH\(_4\) umbrella mode measured to be \(\nu_2(\text{a}\text{$_{1g}$})\sim 0.11\text{ eV}, which corresponds to \sim 900\text{ cm}^{-1}$. The current calculations predict for this mode a significantly lower frequency of only \sim 800 cm\(^{-1}\) (817 and 787 cm\(^{-1}\) at the MP2 and B3LYP level, respectively). As the vibrational assignment is probably correct and the calculations are accurate to better than \pm 20 cm\(^{-1}\), the discrepancy is probably due to the large uncertainty in the photoelectron measurement arising from the low spectral resolution.

4. Conclusions

The IR spectrum of the disilane cation, Si\(_2\)H\(_{6}\)\(^{+}\), has been inferred from IRPD spectra of cold Si\(_2\)H\(_{6}\)–Ar\(_{n}\) complexes (\(n = 1\) and 2). Vibrational analysis guided by MP2 and B3LYP calculations with the aug-cc-pVTZ basis set is consistent with a D\(_{3d}\) symmetric structure of H\(_2\)SiSiH\(_{5}\)\(^{+}\) in its \(\text{A}\text{$_{1g}$}\) electronic ground state generated by removal of one electron from the highest occupied bonding \(\sigma_{\text{Si-Si}}\) orbital. The only intense IR active fundamentals are the \(\nu_6\) and \(\nu_2\) modes with frequencies of 728 and 927 cm\(^{-1}\), respectively. The Ar ligands in Si\(_2\)H\(_{6}\)–Ar and Si\(_2\)H\(_{6}\)–Ar\(_{2}\) bond weakly by induction and dispersion forces at the C\(_3\) rotational axis on opposite sides to the Si\(_2\)H\(_{6}\)\(^{+}\) core ion and cause only little perturbation of its geometric, vibrational, and electronic structure. The calculations reveal a low-energy H\(_2\)SiSiH\(_{5}\)\(^{+}\) isomer of Si\(_2\)H\(_{6}\)\(^{+}\) with C\(_{2v}\) symmetry and a Si–H–Si bridge. Although it is predicted to be only \sim 15 kJ mol\(^{-1}\) less stable than the D\(_{3d}\) structure, it is not observed in the experimental spectra. Future efforts are directed toward the vibrational and electronic characterization of related Si\(_2\)H\(_{6}\)\(^{+}\) ions and their complexes to further investigate their intramolecular chemical bonding characteristics and their interaction with solvent molecules.

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References
