First principles electron-correlated calculations of linear optical absorption spectra in silicon hydrides: Si$_2$H$_{2n}$ (n = 1-3)

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Abstract

We have performed the first principles electron-correlated calculations employing large basis sets to optimize the geometries, and to compute linear optical absorption spectra of various low-lying conformers of silicon hydrides: Si$_2$H$_{2n}$, n = 1, 2, 3. The geometry optimization for various isomers was carried out at the coupled-cluster singles-doubles-triples [CCSD(T)] level of theory, while their excited states and absorption spectra were computed using large-scale multi-reference singles-doubles configuration-interaction (MRSDCI) approach, which includes electron-correlation effects at a sophisticated level. Our calculated spectra are the first ones for Si$_2$H$_2$ and Si$_2$H$_4$ conformers, while for Si$_2$H$_6$ we obtain excellent agreement with the experimental measurements, suggesting that our computational approach is reliable. Our calculated absorption spectra exhibit a strong structure-property relationship, suggesting the possibility of identifying various conformers based on their optical absorption fingerprints. We also believe that our results will be useful for optical identification of hydrogenation induced defects in silicon thin films.
I. INTRODUCTION

Silicon is not only one of the most abundant elements on earth, it is also technologically one of the most important ones, with almost entire semiconductor industry based upon it. Being in the same group of periodic table as carbon, it shares many chemical characteristics with it. However, unlike carbon, it is not known to participate in $sp^2$ hybridization, as a result of which it has no planar graphite-like allotrope. However, there are indications that a quasi-planar allotrope of silicon named silicene can be isolated on substrates.[1–4] Silicon and its compounds have fascinated physicists and chemists alike, over the years, both from a fundamental as well as from the applied points of view.[5–8] There has always been a lot of interest in the field of hydrides of various substances, and silicon is no exception.[9–13] Study of hydrides of silicon is important in many ways: (a) during the formation of silicon thin films using plasma-enhanced chemical vapor deposition, various types of hydrides of silicon are produced, which needs to be understood,[14–16] (b) degradation of silicon based electronic devices happens normally through hydrogenation of silicon caused by atmospheric moisture, and (c) hydrogenated amorphous silicon is used extensively in thin film solar cells.[17] Functionalization of silicene films grown on metal substrates by hydrogenation, with the aim of device applications, is an active area of research these days.[18, 19] Furthermore, the process of hydrogenation in silicon is fascinating from a fundamental point of view, given that the study of hydrogenated carbon in form of hydrocarbons is such a mature field.

 Unsaturated silicon hydrides such as SiH, SiH$_2$, and SiH$_3$ etc. have been the subject of a number of experimental investigations because of their importance in astrophysics, due to their presence in space.[20–22] Silicon hydrides of the form Si$_2$H$_{2n}$, n=1-3 have also been extensively studied both experimentally,[23–27] and by means of high-level theory,[25, 26, 28–41] because of their ability to form mono- and dibridged hydrides, as well as multiple bonds of silicon. The carbon analog of Si$_2$H$_2$ is acetylene, which is a triply-bonded system, while that of Si$_2$H$_4$ is ethylene, which contains carbon-carbon double bond. Therefore, the question arises do Si$_2$H$_4$ and Si$_2$H$_2$ similarly have silicon-silicon double, and triple bonds, respectively? And, what similarities, if any, does Si$_2$H$_6$ (disilane) have with C$_2$H$_6$ (ethane)?

 Measurements on Si$_2$H$_2$ have been performed by several groups.[23–25, 27, 42] Bogey et al.[24, 25, 42] performed millimeter- and submillimeter-wave spectroscopy measurements on Si$_2$H$_2$ produced in silane-argon plasma. Ruscic and Berkowitz[23] produced several Si$_2$H$_n$
hydrides, including Si₂H₂, by reacting fluorine with Si₂H₆, and reported photoionization mass spectrometric measurements on it. Recently, Mohapatra et al.[27] synthesized carbene stabilized Si₂H₂, reported measurements of its UV-Vis spectrum. Several first-principles quantum chemical studies of the structure and bonding in Si₂H₂ have been performed by several groups. Lischka and Köhler[36] studied this molecule at the SCF and CEPA-2 level, and were the first ones to predict that in the ground state, the molecule has a *dibridged* structure (Si(H₂)Si) with *C₂ᵥ* symmetry. This prediction was also verified in the experiments of Bogey et al.[24, 25] People also believed that the second most stable isomer of Si₂H₂ is disilavinylidene (H₂SiSI) having *C₂ᵥ* symmetry, while the *trans*-bent structure (H₂SiSiH) with *C₂ₕ* symmetry being the only other minimum.[37] Later on, the structure of Si₂H₂ was re-investigated by Colegrove and Schaefer,[33] and by Grev and Schaefer[37] and they found another higher minimum, corresponding to a monobridged structure (Si(H)SiH) with *C₅* symmetry, confirmed in the experiment of Cordonnier et al.[42] Sax and Kalcher, using a first-principles pseudopotential based multi-configuration-self-consistent field (MC-SCF) approach, computed the enthalpies of formation of a number of hydrides of silicon, including various isomers of Si₂H₂. [29] Sannigrahi and Nandi studied the bonding properties of various isomers of Si₂H₂ using *ab initio* self-consistent-field (SCF) approach.[38] Jursic performed an extensive first principles study of the potential energy surface of Si₂H₂ using density-functional theory (DFT), as well as by employing second-order Möller Plesset perturbation theory combined with Gaussian-1/Gaussian-2/Gaussian-3 approaches. More recently, Schaefer and coworkers[28] computed the electron affinities several hydrides of silicon, including Si₂H₂.

The subject of doubly bonded silicon compounds silenes has been reviewed by Raabe and Michl.[43] In the year 1981, West, Fink and Michl[44] experimentally stabilized the silicon-silicon doubly bonded compound tetramesityldisilene Si₂R₄, by using the bulky 2,4,6-trimethylphenyl (mesityl) group, denoted here as R. These authors, also measured its UV-Vis absorption spectrum.[44] However, the first synthesis of doubly-bonded molecule disilene (Si₂H₄), was reported by Ruscic and Berkowitz[23] in 1991, who also reported the measurements of its ionization potential. Using infrared spectroscopy, supported by first principles DFT calculations, Andrews and Wang concluded that Si₂H₄ has a *C₂ₕ* structure.[22] Sari et al.[26], based upon rotational spectrum measurements of Si₂H₄ by means of Fourier Transform Microwave (FTM) spectroscopy, supported by sophisticated coupled-cluster cal-
culations, concluded that molecule has a monobridged structure. Later on, the same group presented another experiment-theory study dedicated to Si$_2$H$_4$, and concluded that indeed monobridged isomer was most abundant, however, several unidentified spectral lines could imply the presence of a dibridged isomer as well.[41] As far as theoreticians are concerned, there appears to be a general agreement that trans-bent structure of disilene corresponds to the true ground state, while the monobridged structure is believed to be the next higher energy isomer.[22, 26, 28, 30, 34, 35, 40, 41, 45–48] Silysilylene isomer, with the structure H$_3$SiSiH, has been computed to be the third higher energy structure.[26, 30, 34, 35, 41, 47, 48]

Disilane (Si$_2$H$_6$), which is the structural analog of ethane (C$_2$H$_6$), is a stable compound existing in gas phase at room temperature, and has been known for a long time. As a result, a number of experimental and theoretical studies have been performed on it. The infrared spectrum of gas phase disilane was observed by Gutowsky and Stejskal from 350 to 4000 cm$^{-1}$[49], as well as by Andrews and Wang by reacting laser-ablated silicon atoms with molecular hydrogen to form the silicon hydrides[22]. Itoh et al. experimentally studied the vacuum ultraviolet absorption cross sections of disilane.[50] Several authors experimentally studied the photo-electron spectra of silanes (Si$_n$H$_{2n+2}$), and measured their ionization potentials.[51, 52] As far as theoretical calculations on disilane are concerned, in 1976, geometry optimization was performed by Blustin[53], and Pople and coworkers[54]. In the same year, the valence electronic structure and internal rotation barrier of the molecule was computed by Nicolas, Barthelat, and Durand using a pseudo-potential method.[55] In 1981, Ratner and coworkers performed electronic structure calculations employing Hartree-Fock-Slater (HFS) procedure, based upon local-density functional approach.[56] Photolytic fragmentation were studied by Janoschek and coworkers using a pseudo-potential method.[57] In 1986, the geometries and the single point energies of many singly bonded silicon compounds, including disilane, were computed by Schleyer and coworkers using HF and MP4 level of theory.[58] Sax performed local pseudopotential calculations to optimize the ground state geometry of disilane.[30] Using ab initio propagator theory, ionization potentials of various silicon hydrides, including Si$_2$H$_6$, were theoretically computed by Ortiz and Mintmire.[59] Using first-principles configuration interaction (CI) approach, Kawai et al.[60] computed the ultraviolet photoabsorption spectrum of disilane. Rohlfing and Louie computed the optical absorption spectrum of disilane by solving the Bethe-Salpeter equation, within a first-principles formalism based upon density-functional theory (DFT), with quasi-particle
In this work we undertake a comprehensive study of structural stability and optical properties of three hydrides of silicon dimer, namely, Si$_2$H$_2$, Si$_2$H$_4$ and Si$_2$H$_6$ using state-of-the-art correlated-electron first principles electronic structure methodology. Geometry optimization for all the molecules considered was carried out using the coupled-cluster singles-doubles-triples (CCSD(T)) level of theory, using large basis sets including polarization functions. The optical absorption spectra of various clusters were computed using the multi-reference singles-doubles configuration interaction (MRSDCI) approach, which has been used in our group to study the optical properties of a variety of systems such as atomic clusters,[62–65] conjugated polymers,[66–71] and graphene quantum dots.[72, 73] We would like to emphasize that the first-principles electronic structure studies of Si based systems are more computationally expensive as compared to similar studies of clusters made up of smaller atoms, simply because Si has more electrons, thereby requiring larger basis sets, and hence more computer memory and time. For Si$_2$H$_2$ and Si$_2$H$_4$, the linear optical absorption spectra was computed for a number of isomers, with the aim of understanding the influence of geometry on the optical properties of these molecules. The relation between absorption spectra and geometry can be used for the detection and identification of these molecules in optical experiments. So far, optical absorption experiments on Si$_2$H$_2$ and Si$_2$H$_4$ have not been performed. Therefore, our theoretical calculations of their absorption spectra will be useful in guiding future experimental efforts on these systems. For the case of disilane, our calculated optical absorption spectrum is in very good agreement with the experimental measurements of Itoh et al.[50] as well as with the Bethe-Salpeter equation based theoretical calculations of Rohlfing and Louie[61]. This excellent agreement of our calculations with the experiments for disilane gives us confidence that our calculations on Si$_2$H$_2$ and Si$_2$H$_4$ should be equally accurate.

Remainder of this paper is organized as follows. In the next section, we present the details pertaining to our theoretical methodology and computation procedure. In section III, we present and discuss our optimized geometries and optical absorption spectra of various clusters. Finally, in section IV we present our conclusions.
II. THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

A. General Methodology

All the calculations were carried out using a wave-function-based first-principles methodology, employing the molecular Born-Oppenheimer Hamiltonian, in which the orbitals of molecules are expressed as linear combinations of Cartesian-Gaussian-type basis functions. Such a quantum-chemical electronic structure approach has been implemented in a number of program packages, and in this work we used the packages PSI4[74] and MELD.[75]

The geometries of the silicon hydride (Si\textsubscript{2}H\textsubscript{2n}, n = 1-3) molecules studied in this work were optimized using the coupled-cluster single-double-triple (CCSD(T)) approach, as implemented in the program package PSI4,[74] utilizing the correlation-consistent polarized valence-triple-zeta (cc-pVTZ) basis sets. Once the ground state geometries were determined for each isomer, calculations of their optical absorption spectra were performed. For this purpose, calculations of the excited states of the molecules was performed using the multi-reference singles-doubles configuration-interaction (MRSDCI) approach, as implemented in the MELD package.[75] To perform the MRSDCI calculations, first we transform the Hamiltonian from the atomic orbital (AO) representation consisting of Cartesian Gaussian basis functions, to the molecular orbital (MO) representation. This is achieved by obtaining the MOs of the concerned isomer by performing restricted Hartree-Fock (RHF) calculations on its optimized geometry, and then transforming the one- and two-electron integrals from the AO to the MO representation. Next, using the transformed Hamiltonian, a singles-doubles CI (SDCI) calculation is performed using an appropriate single reference wave function, both for the ground state, and the excited states. The many-body wave functions obtained from the SDCI calculation are used for computing its optical absorption spectrum. Next, the wave functions contributing to various peaks are analyzed, and the configuration state functions (CSFs) making significant contributions to the corresponding excited states are included as references for the next set of MRSDCI calculation. This procedure is iterated until the calculated optical absorption spectrum of the isomer converges. At every stage of the calculation, point-group and spin symmetries are fully utilized, thus our ground and excited state wave functions are also eigenfunctions of the corresponding point-group projection operator, and total-spin operator. as well as spin-symmetry operator. The optical
absorption spectrum \( \sigma(\omega) \), is calculated within the electric-dipole approximation, using the formula

\[
\sigma(\omega) = 4\pi\alpha \sum_i \frac{\omega_{i0}|\langle i | \hat{e} \cdot r | 0 \rangle|^2 \gamma^2}{(\omega_{i0} - \omega)^2 + \gamma^2},
\]  

where \( \omega, \hat{e}, r, \) and \( \alpha \), respectively denote the frequency of the incident light, polarization direction of the incident light, the position operator, and the fine structure constant. Furthermore, \( \omega_{i0} \) is the energy difference (in frequency units) between the ground state (0) and the \( i \)th excited state, while \( \gamma \) is the uniform lined width associated with each excited state energy level. The summation over \( i \) in Eq. 1 includes an infinite number of excited states, however, in our calculations we restricted the sum to those excited states which are no more than 10 eV higher than the ground state. For details of the MRSDCI approach adopted in this work, we refer the reader to our earlier works.[62–73]

B. Computational parameters

In this section we discuss our choices of three computational parameters, namely: (a) Gaussian basis functions, (b) orbital basis set, and (c) many-particle configurations.

1. Choice of the Gaussian basis set

A wide variety of Gaussian basis functions are available, depending upon the task at hand. For example, for ground state geometry many workers prefer Pople basis sets of the type 6-311, which are moderately sized, and yield good results for ground state properties. However, we wanted to use a basis set which can be utilized both for ground state geometry optimization, as well as excited state calculations needed for computation of the optical absorption spectra. Therefore, in these calculations we adopted correlation consistent Dunning basis set cc-pVTZ, which, because of the presence of several diffuse exponents, produces good results both for the ground and excited state calculations. Thus, this basis set was used both for Si and H atoms, during geometry optimization performed at the CCSD(T) level,[74] and also for excited state calculations performed using the MRSDCI approach. In an earlier work from our group dealing with the optical absorption of bare Al clusters, we had also used the cc-pVTZ basis set for Al atoms.[65] Given the quality of this basis set, we
expect our calculations to be fairly accurate.

2. **Molecular Orbital basis**

   It is a well-known fact that the computational effort at the CI level scales as $\approx N^6$, where $N$ is the total number of molecular orbitals employed in the CI calculations. Thus, the computation time increases steeply, with the increasing size of the MO set used in the CI calculations. Therefore, to keep the calculations tractable, we employed the frozen-core approximation, thereby not only reducing the orbital basis size, but also the number of electrons employed in the CI calculations to just four per atom, corresponding to the valence electrons of each Si atom. In our earlier works on various clusters, we carefully studied the influence of frozen core approximation on the computed optical absorption spectra, and found that the results were unaffected by it.[62–65] As far as virtual orbitals are concerned, we did not discard any orbital in MRSDCI calculations for all the molecules except for monobridged (Si-H-SiH), disilavinylidene (Si-SiH$_2$), and disilane (H$_3$Si-SiH$_3$), for which we retained all those virtual orbitals whose energies were less than one Hartree. This “one Hartree” cutoff is computationally sound because we are interested in optical excitations whose energy is much smaller. Nevertheless, we would like to emphasize that during geometry optimization performed using the CCSD(T) method,[74] each calculation was performed at the all-electron level, without truncating the available MO set.

3. **Size of the CI expansion.**

   As discussed earlier, we initiate the MRSDCI calculations with a small number of reference configurations, and compute the optical absorption spectrum of the system concerned. By analyzing the excited states contributing to the peaks in the computed spectrum, we increase the number of reference configurations, and perform next level of MRSDCI calculation leading to a new optical absorption spectrum. This procedure is iterated until the calculated absorption spectrum exhibits reasonable convergence. Whether to include a given configuration in the list of reference configurations is based upon the magnitude of its coefficient in the many-particle wave function of an excited state contributing to a significant peak in the calculated absorption spectrum. In Fig. 1 we demonstrate this procedure for
the case of monobridged isomer of Si$_2$H$_4$ molecule. Denoting the total number of reference configurations as $N_{\text{ref}}$, and the total number of CSFs in that CI expansion as $N_{\text{total}}$, the three MRSDCI calculations presented in Fig. 1 were performed using $N_{\text{ref}} = 13$ ($N_{\text{total}} = 851933$), $N_{\text{ref}} = 32$ ($N_{\text{total}} = 1975358$), and $N_{\text{ref}} = 41$ ($N_{\text{total}} = 2506254$), respectively. From the plotted spectra it is obvious that MRSDCI$_3$ calculation has converged to an acceptable level, both qualitatively and quantitatively, when compared to the MRSDCI$_2$ calculation.

![Figure 1: Convergence of the MRSDCI optical absorption spectrum of the monobridged isomer of Si$_2$H$_4$ molecule, with respect to the increasing number of reference configurations ($N_{\text{ref}}$). Calculations labeled MRSDCI$_1$, MRSDCI$_2$, and MRSDCI$_3$ were performed using 13, 32, and 41 reference configurations, respectively.](image)

### III. RESULTS AND ANALYSIS

In Table I we present the results of our geometry optimization calculations on various conformers of the molecules considered in this work. In Table II we present the sizes of the CI matrices involved in the MRSDCI calculations performed on these molecules, for various irreducible representations (irreps) corresponding to their ground, and excited state, wave functions. From the sizes of the CI matrices, it is obvious that our calculations were large scale, and, therefore, account for electron correlation effects in an adequate manner. Next, we discuss the calculated ground state geometries, and the optical absorption spectra, of various isomers of Si$_2$H$_2$, Si$_2$H$_4$, and Si$_2$H$_6$. 

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Table I: Ground state (GS) energies (in Hartree), point group, symmetry of the ground state, relative energies (in eV), correlation energy (in eV) of hydrogenated silicon conformers associated in CCSD[T] calculations using cc-pVTZ basis set.

| Molecule | Conformer       | Point group | Symmetry of the GS | Total energy (Ha) | Relative energy (eV) | Correlation energy (eV) |
|----------|-----------------|-------------|--------------------|-------------------|----------------------|------------------------|
| Si$_2$H$_2$ | Dibridged disilyne | C$_{2v}$    | $^1A_1$             | -579.33918        | 0.0                  | 6.75                   |
| Si$_2$H$_2$ | Monobridged     | C$_s$       | $^1A'$              | -579.32320        | 0.4348               | 5.81                   |
| Si$_2$H$_2$ | Disilavinylidene | C$_{2v}$    | $^1A_1$             | -579.31788        | 0.5796               | 5.49                   |
| Si$_2$H$_2$ | Trans-bent      | C$_{2h}$    | $^1A_g$             | -579.30975        | 0.8008               | 7.04                   |
| Si$_2$H$_4$ | Disilene        | C$_{2h}$    | $^1A_g$             | -580.55905        | 0.0                  | 5.78                   |
| Si$_2$H$_4$ | Monobridged     | C$_1$       | $^1A$               | -580.54854        | 0.2859               | 5.98                   |
| Si$_2$H$_4$ | Silylsilylene   | C$_s$       | $^1A'$              | -580.54823        | 0.2944               | 5.51                   |
| Si$_2$H$_6$ | Disilane        | D$_{3d}$    | $^1A_{1g}$          | -581.81644        | -                    | 5.86                   |
Table II: Point group symmetry employed in the calculations, along with the total number of configurations ($N_{total}$) in the MRSDCI expansion, aimed at computing the optical absorption spectra of various hydrogenated silicon conformers. In all the calculations, cc-pVTZ basis sets were used both for Si and H atoms.

| Molecule | Conformer           | Point group used | Symmetry | $N_{total}$  |
|----------|---------------------|------------------|----------|-------------|
| Si$_2$H$_2$ | Dibridged disilyne | C$_{2v}$         | $^1$A$_1$ | 1458235     |
|          |                     |                  | $^1$B$_1$ | 1951202     |
|          |                     |                  | $^1$B$_2$ | 1105180     |
| Si$_2$H$_2$ | Monobridged        | C$_1$            | $^1$A       | 1681403     |
| Si$_2$H$_2$ | Disilavinylidene   | C$_1$            | $^1$A       | 2526917     |
| Si$_2$H$_2$ | Trans-bent         | C$_{2h}$         | $^1$A$_g$   | 221709      |
|          |                     |                  | $^1$A$_u$   | 2818861     |
|          |                     |                  | $^1$B$_u$   | 2643120     |
| Si$_2$H$_4$ | disilene           | C$_{2h}$         | $^1$A$_g$   | 42206       |
|          |                     |                  | $^1$A$_u$   | 359342      |
|          |                     |                  | $^1$B$_u$   | 501900      |
| Si$_2$H$_4$ | monobridged        | C$_1$            | $^1$A       | 2506254     |
| Si$_2$H$_4$ | silylsilylene      | C$_1$            | $^1$A       | 3404169     |
| Si$_2$H$_6$ | Disilane           | C$_{2h}$         | $^1$A$_g$   | 20621       |
|          |                     |                  | $^1$A$_u$   | 1634632     |
|          |                     |                  | $^1$B$_u$   | 2038895     |
A. \( \text{Si}_2\text{H}_2 \)

\( \text{Si}_2\text{H}_2 \) is the smallest member of the \( \text{Si}_2\text{H}_{2n} \) class of molecules, several of whose conformers have been studied in the past.[33, 36–38] The five most studied conformers are dibridged disilyne, mono-bridged structure, disilavinyldene, trans-bent structure, and the planar dibridged disilyne isomer. The stability analysis of these conformers revealed that all of them are stable, except for the planar dibridged disilyne structure, which corresponds to a saddle point, or a transition state, on the potential energy surface.[33, 36–38] As a result, we restricted the present study to the four stable structures, and we optimized their geometries using the the \( \text{cc-pVTZ} \) basis set, and the coupled-cluster singles-doubles-triples [CCSD(T)] method, as implemented in the PSI4 computer program.[74] The optimized geometries are presented in Fig. 2, while Table I contains their total and relative energies. From the table it is obvious that the dibridged disilyne is the lowest energy isomer, followed by the mono-bridged structure which is 0.44 eV higher. Next are two conformers disilavinyldene and trans-bent structure, which are higher in energy by 0.58 eV, and 0.80 eV, respectively, as compared to the lowest-energy dibridged disilyne conformer. It is obvious that all the higher energy conformers are within 1 eV of the lowest-energy structure, and even closer to each other. Therefore, it will be interesting to see if their optical absorption spectra, which were computed using the MRSDCI approach using these geometries, are different enough to facilitate their optical detection. In the following sections we discuss the optimized geometries and optical absorption spectra of individual conformers.

Figure 2: Ground state geometries of various isomers of \( \text{Si}_2\text{H}_2 \) molecule, optimized using the CCSD(T) method, and the \( \text{cc-pVTZ} \) basis set. All the bond lengths are in Å unit.
1. *Dibridged disilyne (Si-H₂-Si)*

Our optimized structure of dibridged disilyne conformer, as shown in Fig. 2(a), consists of two three-center Si-H-Si bonds with identical Si-H bond lengths of 1.67 Å, which are non-planar leading to the $C_{2v}$ point-group symmetry, instead of $D_{2h}$, had they been planar. Furthermore, we obtained the optimized Si-Si distance to be 2.20 Å, along with Si-H-Si, H-Si-H and H-Si-Si bond angles as 82.5°, 72.3° and 48.8°, respectively. Our optimized geometry parameters are in good agreement with the experimental results of Bogey *et al.*[25] obtained using millimeter- and submillimeter-wave spectroscopy, as also with their *ab initio* theoretical results. Our results are also in good agreement with the theoretical calculations reported by Gerv and Schaefer[37], Adamczyk and Broadbelt[76], Jursic,[39] and Sannigrahi and Nandi.[38] Atomic coordinates corresponding to the optimized geometry are presented in Table S9 of the Supporting Information.

![Optical absorption spectrum of non-planar disilyne (Si-H₂-Si) conformer](image)

**Figure 3:** Optical absorption spectrum of non-planar disilyne (Si-H₂-Si) conformer, computed using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, 0.1 eV uniform line-width was used.

The calculated photoabsorption spectrum of this conformer is presented in Fig. 3, and it starts with a relatively weak peak near 3.36 eV, followed by an even weaker peak at 4.60 eV. The first of these peaks (peak I) is due to an excited state whose wave function is dominated by the singly-excited configuration $|H \rightarrow L\rangle$, while that corresponding to the second peak (peak II) consists mainly of the configuration $|H \rightarrow L + 2\rangle$. These weak peaks are followed by the two of the most intense peaks (peaks III and IV) of the spectrum,
located near 5.74 eV, and 6.99 eV. Peak III is due to two excited states, whose wave functions exhibit significant configuration mixing. The first state at 5.73 eV contributes the dominant intensity to the peak, and its wave function consists mainly of configurations $|H - 1 \rightarrow L\rangle$ and $|H \rightarrow L + 4\rangle$. The wave function of the second state around 5.77 eV is dominated by doubly-excited configurations $|H \rightarrow L + 3; H \rightarrow L + 3\rangle$ and $|H \rightarrow L; H \rightarrow L\rangle$. The final peak of the spectrum (peak V) located close to 7.93 eV, is weaker compared to these two, and is due to two excited states located at 7.91 eV and 7.94 eV. The wave function of the first of these is dominated by the double excitation $|H - 1 \rightarrow L + 3; H - 1 \rightarrow L + 3\rangle$, while that of the second one derives main contributions from single excitations $|H - 1 \rightarrow L + 2\rangle$ and $|H - 2 \rightarrow L + 1\rangle$. Detailed information about all the excited states contributing to the peaks in the spectra is presented in Table S1 of the Supporting Information, while its Fig. 1 contains the plots of frontier MOs participating in the optical absorption.

2. Monobridged (Si-H-SiH)

The monobridged conformer of Si$_2$H$_2$ molecule is energetically next in order as compared to the lowest-energy conformer non-planar dibridged disilyene discussed in the previous section. This structure, denoted as Si-H-SiH, contains one tricenter Si-H-Si bond, while the other hydrogen atom is attached to a Si atom to form a conventional Si-H single bond, with $C_3$ point group symmetry of the conformer, and a closed-shell electronic ground state of symmetry $^1A'$. Our optimized geometry parameters are (see Fig. 2(b)): (a) two Si-H bond distances in the tricenter Si-H-Si bond are 1.72 Å, and 1.63 Å, (b) the bond length for the single Si-H bond is 1.48 Å, and (c) the distance between two silicon atoms is 2.10 Å. Inside the Si-H-Si triangle, Si-H-Si bond angle is 77.7°, while the two H-Si-Si bond angles are, 49.2° and 53.1°. The external H-Si-H bond angle is computed to be 109°. Our optimized geometry parameters are in good agreement with the experimental and theoretical results of Cordonnier et al.,[42] and with the theoretical results reported by Colegrove and Schaefer,[33] Adamczyk and Broadbelt,[76] Grev and Schaefer,[37] Sannigrahi and Nandi,[38] Curtiss et al.[45] and Koseki and Gordon.[77] Atomic coordinates corresponding to our optimized geometry of this conformer are presented in Table S10 of the Supporting Information.

Using these geometry parameters, the calculated photoabsorption spectrum of the monobridged conformer is presented in Fig. 4, while detailed information about the excited states
contributing to the peaks in the spectrum are presented in Table S2 of the Supporting Information. The calculated photoabsorption spectrum of this conformer is spread over a wide energy range starting from 2.8 eV to about 9.5 eV. The absorption begins with a very feeble peak near 2.81 eV, due to an excited state whose wave function largely consists of the $|H \rightarrow L\rangle$ configuration. It is followed by three comparatively stronger peaks near 4.08 eV, 5.16 eV, and 5.75 eV, all due to excited states whose wave functions are dominated by the singly-excited configurations. The first of these peaks (peak II) derives almost equal intensity from two closely located states exhibiting significant mixing of configurations $|H \rightarrow L+1\rangle$, $|H-1 \rightarrow L\rangle$, and $|H \rightarrow L+2\rangle$, $|H \rightarrow L+4\rangle$, respectively. The most intense peaks of the spectrum are peaks VIII and IX, located at 7.91 eV and 8.86 eV, respectively. Wave functions of the excited states giving rise to these peaks exhibit strong mixing of singly excited configurations. The wave function corresponding to peak VIII is a mixture of characterized by the singly-excited configurations $|H-1 \rightarrow L+4\rangle$ and $|H-2 \rightarrow L+2\rangle$, while that corresponding to peak IX is largely composed of $|H-1 \rightarrow L+4\rangle$ and $|H-3 \rightarrow L\rangle$. The spectrum terminates with peak X, which appears to be a shoulder of the preceding peak, and is due to an excited state located at 9.16 eV, whose wave function derives dominant contributions from the double-excitations $|H \rightarrow L+1; H-1 \rightarrow L+2\rangle$ and $|H \rightarrow L+2; H \rightarrow L+2\rangle$. When we compare the absorption spectrum of this conformer to that of the lowest-energy structure, we find significant differences. Therefore, it should be possible to distinguish between the two conformers using absorption spectroscopy.

Fig. 2 of the Supporting Information presents the plots of the orbitals which participate in the photobsorption in the monobridged conformer.
Figure 4: Optical absorption spectrum of the monobridged conformer (Si-H-SiH), computed using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, 0.1 eV uniform line-width was assumed.

3. Disilavinylidene (Si-SiH$_2$)

This conformer is 0.58 eV higher in energy as compared to the lowest Si$_2$H$_2$ dibridged disilyne structure, but just 0.14 eV above the mono-bridged isomer. Its geometrical configuration is denoted as Si-SiH$_2$, and has one Si atom attached to two H atoms through normal Si-H single bonds, while no H atoms are attached to the other Si atom, leading to a C$_{2v}$ symmetric structure (see Fig. 2(c)), and a ground state of symmetry $^1A_1$. Our optimized geometry parameters with the distance between two Si atoms as 2.20 Å, both the Si-H bonds lengths of 1.48 Å, and the Si-Si-H and H-Si-H bond angles as 124°, and 112°, respectively, are in very good agreement with the theoretically reported values by several other groups.[33, 37, 38, 45, 76, 77] The atomic coordinates corresponding to our optimized geometry are presented in Table S11 of Supporting information.

The calculated photoabsorption spectrum of the disilavinylidene conformer, corresponding to the optimized geometry, is presented in Fig. 5, while the information related to its peaks such as the oscillator strengths, dominant many particle wave functions of the contributing excited states, their excitation energies etc., are detailed in Table S3 of the Supporting Information.

The optical absorption spectra of this isomer starts with a tiny peak at 2.48 eV, followed by four small peaks near 3.13 eV, 4.29 eV, 5.79 eV and 6.43 eV, most of which are dominated
by the singly-excited configurations, with double excitations also making important contributions in a couple of cases. Wave function of the excited state contributing to peak I is dominated by single excitation $|H - 1 \rightarrow L \rangle$, while peak II corresponds to a state dominated by the double excitation $|H \rightarrow L; H \rightarrow L \rangle$. Wave function of the state corresponding to peak III is dominated by singly-excited configuration $|H \rightarrow L + 1 \rangle$, while the one corresponding to peak IV exhibits significant mixing of the single excitation $|H - 2 \rightarrow L \rangle$ and the double excitation $|H \rightarrow L; H - 2 \rightarrow L + 1 \rangle$. The most intense peak of the spectrum (peak VII) occurs at 7.57 eV, and is due to a state whose wave function exhibits strong mixing of singly-excited configurations $|H - 1 \rightarrow L + 2 \rangle$ and $|H - 1 \rightarrow L + 4 \rangle$. The last peak of the calculated spectrum (peak IX) is located at 8.51 eV, and is due to a state whose wave function consists predominantly of the double excitation $|H \rightarrow L; H - 2 \rightarrow L + 1 \rangle$. If we compare the absorption spectrum of disilavinylidene conformer to those of the two previously discussed structures, including close-lying monobridged structure, we find significant differences both in terms of peak locations, and relative intensities, thus making their optical detection feasible.

The plots of the orbitals contributing to the absorption spectrum are presented in Fig. 3 of Supporting Information.

Figure 5: Optical absorption spectrum of disilavinylidene (Si-SiH$_2$) conformer, calculated using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, 0.1 eV uniform line-width was used.
4. Trans-bent (HSi-SiH)

The trans-bent conformer, which has the highest energy as compared to rest of the three conformers considered in this work, has the geometrical configuration denoted as HSi-SiH. This structure is just 0.22 eV higher in energy as compared to the disilavinylidene conformer, and with two Si-H single bonds has the point group symmetry \( C_{2h} \), as shown in Fig. 2(d). Our optimized geometry parameters with Si-H and Si-Si bond distances of 1.49 Å, and 2.10 Å, respectively, and the Si-Si-H bond angle of 125.6°, are in good agreement with those reported by Adamczyk and Broadbelt[76] computed using the G3//B3LYP approach, and by Sannigrahi and Nandi[38] based on \textit{ab initio} SCF calculations. Using a DFT based approach, employing various basis sets, and exchange-correlation functionals, Jursic obtained the optimized bond lengths of the trans-bent structure, which are also in good agreement with our results.[39] The atomic coordinates corresponding to our optimized geometry of this structure are presented in Table S12 of Supporting Information.

Using our optimized geometry, the photoabsorption spectrum of the trans-bent conformer computed using the MRSDCI approach, from its \(^1 A_g\) ground state, is presented in Fig. 6, while the detailed information pertaining to the excited states contributing to various peaks is given in Table S4 of Supporting Information. Absorption in the trans-bent conformer starts with a feeble peak at 1.16 eV, due to a state whose wave function is dominated by the singly-excited configuration \(|H \rightarrow L\rangle\). This is followed by the most intense peak of the spectrum at 2.96 eV, due to a state whose wave function exhibits strong mixing of singly-excited configurations \(|H - 1 \rightarrow L\rangle\) and \(|H \rightarrow L + 1\rangle\). We note that the location of the most intense peak at a much lower energy, as compared to the other three conformers, is enough of a distinguishing feature of this conformer to allow its detection through optical spectroscopy. It is followed by two relatively weaker features III and IV at 4.56 eV, and 5.05 eV, respectively. The wave functions of the state corresponding to peak III is dominated by the single excitation \(|H - 1 \rightarrow L + 1\rangle\), while that of peak IV exhibits strong mixing of singly-excited configurations \(|H \rightarrow L + 1\rangle\) and \(|H - 1 \rightarrow L\rangle\). Next three features V, VI, and VII located at 6.00 eV, 6.28 eV, and 6.59 eV, respectively, are due to states whose wave functions derive strong contributions from doubly-excited configurations. Feature V, which is a shoulder to peak VI is due to a state whose wave function is largely composed of the double excitation \(|H \rightarrow L; H \rightarrow L + 2\rangle\), while VI and VII exhibit strong mixing of double
and single excitations $|H - 1 \rightarrow L; H \rightarrow L + 2\rangle$, and $|H \rightarrow L + 3\rangle$. The computed spectrum has its last peak at 7.35 eV due to two close lying states at 7.32 eV and 7.42 eV, which exhibit strong mixing of double excitations $|H - 2 \rightarrow L; H \rightarrow L\rangle$, $|H \rightarrow L + 2; H \rightarrow L + 1\rangle$, and $|H - 2 \rightarrow L; H - 1 \rightarrow L\rangle$, $|H - 2 \rightarrow L + 1; H \rightarrow L\rangle$, respectively. In Fig. 4 of Supporting Information, the plots of the frontier orbitals participating in the optical absorption in this conformer are presented.

Figure 6: Optical absorption spectrum of trans-bent (HSi-SiH) conformer, calculated using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, a uniform line-width of 0.1 eV was used.

B. $\text{Si}_2\text{H}_4$

Figure 7: Ground state geometries of $\text{Si}_2\text{H}_4$ isomers, optimized using the CCSD(T) method, and the cc-pVTZ basis set. All the bond lengths are in Å unit.
Geometries and relative stabilities of the isomers of Si$_2$H$_4$ have been studied extensively over the years using electronic-structure methods by several authors.[26, 28–30, 34, 35, 38, 40, 45–48] Earlier, two main isomers of Si$_2$H$_4$ were investigated, namely, disilene containing of a Si-Si double bond, and silylsilylene, a completely singly-bonded structure.[34, 35] For disilene as well several structures are possible, but two main structures have been investigated, namely: (a) planar ethylene like structure consisting of a true Si-Si double bond, with $D_{2h}$ symmetry, and (b) a trans-bent structure with a nominal Si-Si double bond, with $C_{2h}$ symmetry.[30, 34, 38, 46, 47] However, it was soon revealed by calculations of vibrational frequencies, that planar disilene was not stable, and actually corresponded to a transition state on the potential energy surface.[34, 46, 47] Later on a new low-lying isomer with a monobridged structure was discovered computationally, and found to be stable.[26, 41, 48] The present-day consensus is that the trans-bent disilene structure is energetically the lowest, followed by mono-bridged, and silylsilylene isomers, lying slightly above it.[26, 40, 41, 48]. We performed our own geometry optimization for these three structures using the CCSD(T) method, coupled with the cc-pVTZ basis, and the optimized geometries are shown in Fig. 7. Energetically speaking, we found the ordering trans-bent $<$ mono-bridged $<$ silylsilylene, with mono-bridged and silylsilylene structures being almost degenerate and just 0.286 eV and 0.294 eV above the trans-bent structure (see Table I). Thus, our results on the geometries and energies of these isomers are in excellent agreement with the results of recent calculations.[26, 40, 41, 48] Next, we discuss the geometries and optical absorption spectra of the individual isomers in the following sections.

1. Disilene ($H_2Si-SiH_2$)

The trans-bent structure of disilene, with $C_{2h}$ point group symmetry, has the lowest energy among all the Si$_2$H$_4$ clusters. The optimized geometry of this conformer has equal bond lengths of 1.48 Å for the two Si-H bonds. Additionally, Si-Si bond length was computed to be 2.16 Å, along with the H-Si-H, and H-Si-Si bond angles of 113°, and 119°, respectively (see Fig. 7(a)). These values are in good agreement with the geometry parameters reported in the literature.[26, 28, 30, 40, 41] The atomic coordinates corresponding to our optimized geometry of this conformer are presented in Table S13 of Supporting information.

The calculated photoabsorption spectrum of the trans-bent disilene ($H_2Si-SiH_2$) con-
former is presented in Fig. 8, and the corresponding dominant many particle wave functions contributing to the peaks of the optical spectra are given in Table S5 of the Supporting Information.

![Optical absorption spectrum of disilene](image)

**Figure 8:** Optical absorption spectrum of disilene (H$_2$Si-SiH$_2$) conformer, computed using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, a uniform line-width of 0.1 eV was assumed.

The optical absorption spectrum of this disilene conformer starts with a intense peak at 4.13 eV, corresponding to an excited state whose wave function is dominated by singly-excited configuration $|H \rightarrow L\rangle$. It is followed by a weak peak at 6.05 eV, due to an excited state with wave function deriving dominant contributions from the singly-excited configurations $|H \rightarrow L + 3\rangle$ and $|H \rightarrow L + 4\rangle$. The most intense peak, with a very large oscillator strength, is located at 7.31 eV, with many-particle wave function dominated again by same set of single excitations $|H \rightarrow L + 3\rangle$ and $|H \rightarrow L + 4\rangle$. In Fig. 5 of Supporting Information, the plots of the frontier orbitals participating in the optical absorption in disilene are presented.

2. **Monobridged (H$_2$Si-H-SiH)**

The ground state of monobridged conformer has C$_1$ symmetry, and is predicted to be only 0.286 eV (see Table I) higher than the ground state of disilene conformer of Si$_2$H$_4$. Because of this close energetic proximity of the monobridged isomer to disilene, their optical absorption spectra become important because they offer the possibility of optical identification of these
close-lying isomers. Schaefer and co-workers[26], by means of highly-correlated ab initio calculations, were the first ones to predict this isomer. Later on, the same group[41] detected this isomer experimentally using Fourier transform microwave spectroscopy technique. Our optimized geometry obtained using the CCSD(T) method, and the ccpVTZ basis set, is shown in Fig. 7(b). The optimized lengths were found to be 2.24 Å for Si-Si bond, 1.48 Å for the two Si-H bonds on the left, and 1.52 Å for the Si-H bond on the right. On the left side, the three H-Si-H bond angles are 103.1°, 106.8° and 108.3°, while on the right, the H-Si-Si bond angle is 85.4°. For the bridged hydrogen atom, our optimized Si-H bond lengths are 1.62 Å, and 1.82 Å. Inside the Si-H-Si triangle, the Si-H-Si bond angle is 81.4°, while the two H-Si-Si bond angles are 53.2°, and 45.4°, respectively, from left to right. Additionally, H-Si-H bond angle on the right is optimized to be 84.3°. These results are in good agreement with the values reported by Schaefer and coworkers.[26, 41] The atomic coordinates corresponding to our optimized geometry of the monobridged conformer are presented in Table S14 of Supporting information.

The calculated photoabsorption spectrum of the monobridged (H₂Si-H-SiH) conformer, using our optimized geometry, is presented in Fig. 9, while the detailed information about the excited states contributing to various peaks, including their many particle wave functions are presented in Table S6 of the Supporting Information.

![Optical absorption spectrum of the monobridged (H₂Si-H-SiH) conformer](image)

**Figure 9:** Optical absorption spectrum of the monobridged (H₂Si-H-SiH) conformer, computed using the MRSDCI method and the cc-pVTZ basis set. For plotting the spectrum, a uniform line-width of 0.1 eV was assumed.

As compared to the disilene conformer, optical photoabsorption spectrum of the mono-
bridged isomer consists of several well-separated peaks over the same energy range. It starts with a small peak at 3.83 eV, due to a state whose many-particle wave function is dominated by the singly-excited configuration $|H \rightarrow L\rangle$. This is followed by an even weaker peak at 4.84 eV, due to a state whose wave function derives its main contribution from the configuration $|H - 1 \rightarrow L\rangle$. A comparatively intense peak appears at 5.44 eV, with the wave function of the excited state dominated by the singly-excited configuration $|H \rightarrow L + 1\rangle$. This is followed by a series of five well-separated peaks ranging from 6.58 eV to the most intense peak (peak VIII) of the spectrum located at 7.80 eV. Various properties of the excited states, along with their wave functions for this conformer are presented in Table S6 of the Supporting Information, from where it is obvious that the wave functions of all the states are dominated by singly-excited configurations, except for peak VII whose wave function is dominated by a configuration consisting of HOMO-LUMO double excitation $|H \rightarrow L; H \rightarrow L\rangle$. The wave function of the excited state giving rise to the most intense peak VIII, is dominated by single excitations $|H \rightarrow L + 4\rangle$, and $|H - 3 \rightarrow L\rangle$. If we compare the absorption spectrum of the monobridged isomer with that of disilene, we note that they are sufficiently different both in terms of the number of peaks, and their locations, such that the optical spectroscopy can be used for their identification. The frontier MOs participating in various optical excitations of this conformer are presented in Fig. 6 of the Supporting Information.

3. Silylsilylene ($H_3Si-SiH$)

Similar to the case of disilene, over the years extensive research has been done on the electronic structure and geometry of silylsilylene ($H_3Si-SiH$) conformer of $Si_2H_4$.[41, 76] Our optimized geometrical parameters of its ground state of $C_s$ symmetry, obtained using the CCSD(T) approach, and cc-pVTZ basis set are: (a) Si-Si bond length 2.39 Å, and (b) Si-H bond lengths of 1.49 Å, 1.49 Å, and 1.48 Å on the right side, with H-Si-H bond angles 109.5°, 109.5° and 113.9°. On the left side optimized Si-H bond length is 1.52 Å, along with the H-Si-Si bond angle 89.2° (see Fig. 7(c)). These values are in good agreement with those reported by McCarthy et al.[41] and Adamczyk et al.[76] The atomic coordinates corresponding to our optimized geometry of this conformer are presented in Table S15 of Supporting information.

Energetically speaking, silylsilylene is just 0.294 eV higher than disilene, and a negligible
0.008 eV higher than the monobridged isomer. Again, the question arises, whether their optical absorption spectra are sufficiently different so as to allow their identification using this spectroscopy.

Using our optimized geometry, we present the calculated photoabsorption spectrum of silylsilylene in Fig. 10, and the most noteworthy point is that this conformer, except for a couple of very feeble peaks, does not exhibit any significant absorption till about 6 eV, beyond which the intensity of the absorption rises. This aspect of its absorption spectrum distinguishes it from those of the two previous conformers, and can be used as a fingerprint for its optical detection.

The absorption spectrum of silylsilene conformer starts with very weak peaks located at 1.93 eV, and 3.79 eV, due to excited states whose many-particle wave functions are dominated by the singly-excited configurations $|H \rightarrow L\rangle$, and $|H - 1 \rightarrow L\rangle$, respectively. The most intense peak (peak V) appears at 6.97 eV, due to a state whose wave functions are dominated by single excitations $|H \rightarrow L + 1\rangle$, and $|H \rightarrow L + 2\rangle$. The last peak of our calculated spectrum (peak VI) is located at 7.35 eV, and is due to a state with wave function deriving main contribution from $|H \rightarrow L + 3\rangle$ configuration, with a smaller contribution from the single excitation $|H - 1 \rightarrow L + 1\rangle$. Detailed information about all the excited states contributing to various peaks in the absorption spectrum of silylsilylene is presented in Table S7 of the Supporting Information, whose Fig. 7 contains plots of MOs participating in the absorption.

Figure 10: Optical absorption spectrum of silylsilylene (H$_3$Si-SiH) conformer, computed using the MRSDCI method, and cc-pVTZ basis set. For plotting the spectrum, a uniform line-width of 0.1 eV was used.
C. Disilane $\text{Si}_2\text{H}_6$

As far as disilane ($\text{Si}_2\text{H}_6$) is concerned, it has only one stable conformer with a three-dimensional $sp^3$-hybridized structure, and the configuration $\text{H}_3\text{Si-SiH}_3$, similar to the case of ethane ($\text{C}_2\text{H}_6$). In this structure, again similar to the case of ethane, the hydrogen atoms are arranged in a staggered configuration, instead of an eclipsed one, leading to the ground state point-group symmetry $D_{3d}$. Our optimized geometry obtained using the CCSD(T) method, and cc-pVTZ basis set, depicted in Fig. 11, has only two unique bond lengths: (a) Si-Si bond length of 2.34 Å, and (b) Si-H bond length 1.48 Å, along with the H-Si-H and H-Si-Si bond angles of 108.6° and 110.3°. Our calculated geometry parameters are in good agreement with the experimental,[78, 79] as well as theoretical values computed by other authors.[30, 55, 59] The atomic coordinates corresponding to our optimized geometries are presented in Table S16 of the Supporting Information.

Our photoabsorption spectrum of disilane is presented in Fig. 12, and it is obvious that it consists of six well-separated peaks of fairly strong intensities, except for the last one, which is comparatively weaker.
The optical absorption in disilane starts at fairly high energies, as compared to previously discussed molecules, with a moderately intense peak near 7.80 eV. This peak is due to two close-lying excited states, both whose wave function are dominated by the singly-excited configuration $|H \rightarrow (L + 2)\rangle$, where the orbital $L + 2$ is doubly degenerate. The first absorption is followed by the most intense peak (peak II) of the spectrum located at 8.45 eV, due to a state whose wave function mainly consists of the single excitation $|H \rightarrow L\rangle$. The next peak in the spectrum (peak III) occurs at 9.21 eV, and is due to a state whose wave function is dominated by almost equal contributions from the two degenerate excitations $|H - 1 \rightarrow L + 2\rangle$, where orbital $H - 1$ is also doubly degenerate, just like orbital $L + 2$. Next we have two peaks in the spectrum located at 9.41 eV and 9.84 eV, both of which are due to two closely-lying states each. The first of these peaks (peak IV) derives its main intensity from a state located at 9.40 eV, with a small contribution from a state at 9.47 eV. The main contribution to oscillator strength of peak V comes from a state located at 9.82 eV, with a much smaller intensity derived from a state located 9.92 eV. The wave functions of all the four excited states contributing to peaks IV and V exhibit strong configuration mixing, and are composed of various degenerate combinations of singly-excited configurations $|H - 1 \rightarrow L + 2\rangle$, $|H - 1 \rightarrow L\rangle$, and $|H - 2 \rightarrow L\rangle$ (see Table S8 of Supporting Information). Final peak of the computed spectrum (peak VI) located at 10.16 eV is a relatively weaker one, and is due to a state whose wave function consists mainly of the configuration $|H \rightarrow L + 4\rangle$, with a smaller contribution from the excitation $|H - 1 \rightarrow L + 2\rangle$. 

Figure 12: Optical absorption spectrum of disilane computed using the MRSDCI method, and the cc-pVTZ basis set. For plotting the spectrum, we assumed a uniform line-width of 0.1 eV.
In Table III we compare our calculated peak locations to the experimentally measured values of Itoh et al.[50], and the Bethe-Salpeter equation based calculations of Rohlfing et al.[61] and find that our results are in very good agreement with the experiments. This level of agreement between our calculations and the experiments for the case of disilane, the largest studied molecule in this work, suggests that our computational methodology is sound and trustworthy.

Table III: Comparison of the peak locations (in eV) in the calculated optical absorption spectrum of disilane, with the experimental values reported by Itoh et al.,[50] and the theoretical values reported by Louie et al.,[61] obtained from their Bethe-Salpeter equation based calculations.

| This work | Expt. (Ref. [50]) | Theory (Ref. [61]) |
|-----------|------------------|------------------|
| 7.80      | 7.6              | 7.6              |
| 8.45      | 8.4              | 9.0              |
| 9.41      | 9.5              | 9.6              |
| 9.84      | 9.9              | 9.8              |

IV. CONCLUSIONS

In this work we presented state of the art quantum chemical calculations, utilizing large basis sets, aimed at obtaining electronic structure, geometrical, and optical properties of hydrides of silicon dimer of the class $\text{Si}_2\text{H}_{2n}$, $n = 1, 2, 3$. Geometry optimization was carried out using the CCSD(T) approach, while the optical absorption spectra was computed by means of large-scale MRSDCI calculations. For $\text{Si}_2\text{H}_2$ and $\text{Si}_2\text{H}_4$ several stable, energetically low-lying, and very closely spaced, conformers were considered, and it was discovered that each conformer has a distinct optical absorption spectrum, suggesting their possible detection and identification using absorption spectroscopy. Although, no experimental results exist on the absorption spectra of $\text{Si}_2\text{H}_2$ and $\text{Si}_2\text{H}_4$ conformers, but for disilane ($\text{Si}_2\text{H}_6$) excellent agreement with experimental measurement was found. This suggests that our computational methodology based on the MRSDCI method is sound, and, therefore, our calculated spectra for $\text{Si}_2\text{H}_2$ and $\text{Si}_2\text{H}_4$ conformers must be trustworthy. We hope that there will be
future experimental efforts to measure the absorption spectra of conformers of Si$_2$H$_2$ and Si$_2$H$_4$, against which our results could be benchmarked. It is well known that during the synthesis of silicon thin films, hydrides of various of its molecules are formed as undesirable defects. Therefore, as suggested by our calculations, defect identification could be done by using optical absorption spectroscopy.

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Supporting Information for
First principles electron-correlated calculations of linear optical absorption spectra in hydrogenated silicon clusters: Si$_2$H$_{2n}$, $n = 1$-3

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In this supporting information we present the plots of the frontier orbitals, and the wave functions of important excited states contributing to the calculated optical absorption spectra of various conformers of Si$_2$H$_2$, Si$_2$H$_4$, and Si$_2$H$_6$.

![Figure 1. Various frontier molecular orbitals of dibridged disilyne isomer [main article, Fig. 2(a)] of Si$_2$H$_2$ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote HOMO and LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).](image)

Table S1. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of dibridged disilyne (Si-H$_2$-Si) isomer [main article, Fig. 2(a)] of Si$_2$H$_2$ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and $f$ denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S9.

| Peak | E (eV) | f | Polarization | Wave function |
|------|--------|---|--------------|---------------|
| GS   |        |   |              | $|HF\rangle(0.9190)$ |
|      |        |   |              | $|H \rightarrow L; H \rightarrow L\rangle(0.0685)$ |
| I    | 3.360  | 1.37| $y$          | $|H \rightarrow L\rangle(0.8945)$ |
|      |        |   |              | $|H \rightarrow L + 12\rangle(0.1101)$ |
| II   | 4.604  | 0.23| $x$          | $|H \rightarrow L + 2\rangle(0.8769)$ |
|      |        |   |              | $|H - 1 \rightarrow L; H \rightarrow L + 1\rangle(0.1450)$ |
| III  | 5.734  | 13.049| $y$        | $|H - 1 \rightarrow L\rangle(0.7791)$ |
|      | 5.768  | 0.352| $z$          | $|H \rightarrow L + 4\rangle(0.3966)$ |
|      |        |   |              | $|H \rightarrow L + 3; H \rightarrow L + 3\rangle(0.6692)$ |
|      |        |   |              | $|H \rightarrow L; H \rightarrow L\rangle(0.5101)$ |
| IV   | 6.986  | 13.818| $y$       | $|H \rightarrow L + 4\rangle(0.7267)$ |
|      |        |   |              | $|H - 3 \rightarrow L + 1\rangle(0.4110)$ |
| V    | 7.914  | 1.018| $z$          | $|H - 1 \rightarrow L + 3; H - 1 \rightarrow L + 3\rangle(0.7953)$ |
|      | 7.942  | 3.719| $x$          | $|H \rightarrow L + 5; H \rightarrow L + 5\rangle(0.2791)$ |
|      |        |   |              | $|H - 1 \rightarrow L + 2\rangle(0.5350)$ |
|      |        |   |              | $|H - 2 \rightarrow L + 1\rangle(0.4774)$ |
Figure 2. Various frontier molecular orbitals of mono-bridged isomer [main article, Fig. 2(b)] of Si$_2$H$_2$ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S2. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of mono-bridged disilyne (Si-H-SiH) isomer [main article, Fig. 2(b)] of Si$_2$H$_2$ molecule. ‘E’ corresponds to excitation energy (in eV) of an excited state, and $f$ denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. ‘HF’ corresponds to Hartree-Fock configuration. ‘H’ and ‘L’ stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S10.

| Peak | E (eV) | $f$  | Polarization | Wave function |
|------|--------|------|--------------|---------------|
|      |        |      |              | $|HF⟩(0.9044)$ |
|      |        |      |              | $|H \rightarrow L⟩(0.8984)$ |
|      |        |      |              | $|H \rightarrow L + 1; H \rightarrow L + 1⟩(0.1311)$ |
| I    | 2.81   | 0.082| y            | $|H - 1 \rightarrow L⟩(0.6557)$ |
|      |        |      |              | $|H \rightarrow L + 1⟩(0.3348)$ |
| II   | 4.01   | 0.755| x/z          | $|H - 1 \rightarrow L + 1⟩(0.7516)$ |
|      | 4.14   | 0.655| y            | $|H \rightarrow L + 1⟩(0.8654)$ |
|      |        |      |              | $|H \rightarrow L + 2⟩(0.1240)$ |
| III  | 5.16   | 3.462| x/z          | $|H - 1 \rightarrow L⟩(0.6557)$ |
|      |        |      |              | $|H \rightarrow L + 1⟩(0.3348)$ |
| IV   | 5.75   | 0.939| x/z          | $|H - 1 \rightarrow L + 2⟩(0.6559)$ |
|      |        |      |              | $|H - 2 \rightarrow L⟩(0.5002)$ |
| V    | 6.80   | 4.753| x/z          | $|H - 2 \rightarrow L⟩(0.4030)$ |
|      |        |      |              | $|H - 1 \rightarrow L + 2⟩(0.3875)$ |
| VI   | 7.22   | 6.728| y            | $|H \rightarrow L + 1⟩(0.6325)$ |
|      |        |      |              | $|H \rightarrow L + 1; H \rightarrow L + 2⟩(0.3402)$ |
| VII  | 7.66   | 5.660| x/z          | $|H \rightarrow L; H - 1 \rightarrow L + 1⟩(0.4170)$ |
|      |        |      |              | $|H \rightarrow L; H \rightarrow L + 2⟩(0.3670)$ |
| VIII | 7.91   | 12.025|x/z         | $|H - 1 \rightarrow L + 4⟩(0.3523)$ |
|      |        |      |              | $|H - 2 \rightarrow L + 2⟩(0.3201)$ |
| IX   | 8.86   | 11.742|x/z         | $|H - 1 \rightarrow L + 4⟩(0.4106)$ |
|      |        |      |              | $|H - 3 \rightarrow L⟩(0.3441)$ |
| X    | 9.16   | 5.864| x/z          | $|H \rightarrow L + 1; H - 1 \rightarrow L + 2⟩(0.4375)$ |
|      |        |      |              | $|H \rightarrow L + 2; H \rightarrow L + 2⟩(0.2899)$ |
Figure 3. Various frontier molecular orbitals of disilavinylidene isomer [main article, Fig. 2(c)] of Si$_2$H$_2$ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S3. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of disilavinylidene (Si-SiH$_2$) isomer [main article, Fig. 2(c)] of Si$_2$H$_2$ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and $f$ denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak.

| Peak | E (eV) | $f$ | Polarization | Wave function |
|------|-------|----|--------------|---------------|
| GS   |       |    | H          | $|HF\rangle(0.9027)$ |
|      |       |    |            | $|H \rightarrow L + 1; H \rightarrow L + 1\rangle(0.1626)$ |
| I    | 2.48  | 0.120 | x | $|H - 1 \rightarrow L\rangle(0.8898)$ |
|      |       |    |            | $|H - 1 \rightarrow L; H \rightarrow L + 1; H \rightarrow L + 1\rangle(0.1306)$ |
| II   | 3.13  | 0.213 | y | $|H \rightarrow L; H \rightarrow L\rangle(0.8578)$ |
|      |       |    |            | $|H \rightarrow L + 1\rangle(0.1760)$ |
| III  | 4.29  | 3.820 | y | $|H \rightarrow L + 1\rangle(0.8258)$ |
|      |       |    |            | $|H - 1 \rightarrow L + 2\rangle(0.2004)$ |
| IV   | 5.79  | 1.064 | y | $|H - 2 \rightarrow L\rangle(0.7332)$ |
|      |       |    |            | $|H \rightarrow L; H - 2 \rightarrow L + 1\rangle(0.3659)$ |
| V    | 6.43  | 1.783 | z | $|H \rightarrow L + 3\rangle(0.6899)$ |
|      |       |    |            | $|H \rightarrow L + 4\rangle(0.4886)$ |
| VI   | 7.10  | 8.653 | z | $|H \rightarrow L + 4\rangle(0.5807)$ |
|      |       |    |            | $|H \rightarrow L + 3\rangle(0.5414)$ |
| VII  | 7.57  | 19.917 | y | $|H - 1 \rightarrow L + 2\rangle(0.6371)$ |
|      |       |    |            | $|H - 1 \rightarrow L + 4\rangle(0.4699)$ |
| VIII | 7.89  | 6.977 | y | $|H - 1 \rightarrow L + 3\rangle(0.8021)$ |
|      |       |    |            | $|H - 1 \rightarrow L + 2\rangle(0.2299)$ |
| IX   | 8.51  | 1.821 | y | $|H \rightarrow L; H - 2 \rightarrow L + 1\rangle(0.7731)$ |
|      |       |    |            | $|H - 1 \rightarrow L + 4\rangle(0.2011)$ |
Figure 4. Various frontier molecular orbitals of trans-bent isomer [main article, Fig. 2(d)] of Si₂H₂ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S4. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of trans-bent (HSi-SiH) isomer [main article, Fig. 2(d)] of Si₂H₂ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and f denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S12.

| Peak | E (eV) | f  | Polarization | Wave function |
|------|-------|----|--------------|---------------|
| GS   |       |    |              | |HF⟩(0.8889) |
|      |       |    |              | |H → L+1⟩(0.1945) |
| I    | 1.161 | 0.210 | ⊥            | |H → L⟩(0.9045) |
|      |       |    |              | |H → L+1⟩(0.0871) |
| II   | 2.965 | 10.079 | ||         | |H → L+1⟩(0.5865) |
|      |       |    |              | |H → L+1)⟩(0.6892) |
| III  | 4.561 | 0.873 | ⊥            | |H → L+1⟩(0.8919) |
|      |       |    |              | |H → L+14)⟩(0.1047) |
| IV   | 5.047 | 1.363 | ||         | |H → L+1⟩(0.6117) |
|      |       |    |              | |H → L+1)⟩(0.5007) |
| V    | 6.004 | 0.411 | ||         | |H → L+2)⟩(0.8233) |
|      |       |    |              | |H → L+4)⟩(0.1640) |
| VI   | 6.276 | 3.976 | ⊥            | |H → L+2)⟩(0.5882) |
|      |       |    |              | |H → L+3)⟩(0.4964) |
| VII  | 6.585 | 3.905 | ⊥            | |H → L+3)⟩(0.6696) |
|      |       |    |              | |H → L+2)⟩(0.5031) |
| VIII | 7.087 | 0.474 | ⊥            | |H → L+2)⟩(0.6953) |
|      |       |    |              | |H → L+2)⟩(0.3095) |
| IX   | 7.323 | 1.140 | ⊥            | |H → L+2)⟩(0.4417) |
|      |       |    |              | |H → L+2)⟩(0.4411) |
|     | 7.419 | 0.466 | ||         | |H → L+2)⟩(0.6161) |
|      |       |    |              | |H → L+1)⟩(0.4922) |
Figure 5. Various frontier molecular orbitals of disilene isomer [main article, Fig. 7(a)] of Si₂H₄ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S5. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of disilene (H₂Si-SiH₂) isomer [main article, Fig. 7(a)] of Si₂H₄ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and \( f \) denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S13.

| Peak | E (eV) | \( f \) | Polarization | Wave function |
|------|--------|--------|--------------|--------------|
| GS   |        |        |              | \( |H \rangle (0.9179) \) |
|      |        |        |              | \( |H \rightarrow L; H \rightarrow L \rangle (0.1926) \) |
| I    | 4.132  | 7.816  | x/y          | \( |H \rightarrow L \rangle (0.8879) \) |
|      |        |        |              | \( |H - 1 \rightarrow L + 2 \rangle (0.1258) \) |
| II   | 6.05   | 0.635  | x/y          | \( |H \rightarrow L + 3 \rangle (0.7787) \) |
|      |        |        |              | \( |H \rightarrow L + 4 \rangle (0.4370) \) |
| III  | 7.091  | 0.511  | z            | \( |H \rightarrow L; H \rightarrow L + 1 \rangle (0.6929) \) |
|      | 7.309  | 14.375 | x/y          | \( |H \rightarrow L + 6 \rangle (0.3992) \) |
|      |        |        |              | \( |H \rightarrow L + 4 \rangle (0.7321) \) |
|      |        |        |              | \( |H \rightarrow L + 3 \rangle (0.4620) \) |
Figure 6. Various frontier molecular orbitals of mono-bridged isomer [main article, Fig. 7(b)] of Si$_2$H$_4$ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S6. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of mono-bridged (H$_2$Si-H-SiH) isomer [main article, Fig. 7(b)] of Si$_2$H$_4$ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and $f$ denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S14.

| Peak | E (eV) | f  | Polarization | Wave function                        |
|------|-------|----|--------------|--------------------------------------|
| GS   |       |    |              | $|HF⟩(0.9248)$                       |
|      |       |    |              | $|H → L; H → L⟩(0.0647)$             |
| I    | 3.831 | 0.815 | x/z         | $|H → L⟩(0.8789)$    |
|      |       |    |              | $|H → L + 1⟩(0.1414)$               |
| II   | 4.845 | 0.309 | x/z         | $|H − 1 → L⟩(0.7965)$           |
|      |       |    |              | $|H → L + 1⟩(0.3411)$               |
| III  | 5.439 | 4.036 | x            | $|H → L + 1⟩(0.7770)$           |
|      |       |    |              | $|H − 1 → L⟩(0.3132)$               |
| IV   | 6.576 | 0.696 | y/z         | $|H − 1 → L + 1⟩(0.6786)$         |
|      |       |    |              | $|H → L + 2⟩(0.4134)$              |
| V    | 6.862 | 1.260 | y/z         | $|H → L + 2⟩(0.5174)$           |
|      |       |    |              | $|H − 1 → L + 1⟩(0.4870)$         |
|      | 6.976 | 2.346 | x            | $|H → L + 3⟩(0.5177)$           |
|      |       |    |              | $|H − 2 → L⟩(0.5144)$              |
| VI   | 7.249 | 3.596 | x/z         | $|H − 2 → L⟩(0.6016)$           |
|      |       |    |              | $|H → L + 4⟩(0.3915)$              |
| VII  | 7.430 | 2.481 | x/y/z       | $|H → L; H → L⟩(0.5338)$         |
|      |       |    |              | $|H − 3 → L⟩(0.3569)$              |
| VIII | 7.801 | 6.823 | x/y/z       | $|H → L + 4⟩(0.5845)$           |
|      |       |    |              | $|H − 3 → L⟩(0.4178)$              |
Figure 7. Various frontier molecular orbitals of silylsilylene isomer [main article, Fig. 7(c)] of Si₂H₄ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO).

Table S7. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of silylsilylene (H₃Si-SiH) isomer [main article, Fig. 7(c)] of Si₂H₄ molecule. ‘E’ corresponds to excitation energy (in eV) of an excited state, and \( f \) denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. ‘HF’ corresponds to Hartree-Fock configuration. ‘H’ and ‘L’ stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak.

The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S15.

| Peak | E (eV) | \( f \) | Polarization | Wave function |
|------|-------|-------|--------------|--------------|
| GS   |       |       |              | \(|HF\rangle(0.9250)\) |
|      |       |       |              | \(|H \rightarrow L; H \rightarrow L\rangle(0.0978)\) |
| I    | 1.935 | 0.131 | z            | \(|H \rightarrow L\rangle(0.9163)\) |
|      |       |       |              | \(|H \rightarrow L + 15\rangle(0.0960)\) |
| II   | 3.795 | 0.136 | z            | \(|H - 1 \rightarrow L\rangle(0.8985)\) |
|      |       |       |              | \(|H - 1 \rightarrow L + 15\rangle(0.1136)\) |
| III  | 6.105 | 0.505 | x            | \(|H - 1 \rightarrow L; H \rightarrow L\rangle(0.8374)\) |
|      | 6.257 | 0.216 | z            | \(|H \rightarrow L + 1\rangle(0.2040)\) |
|      |       |       |              | \(|H - 2 \rightarrow L\rangle(0.8484)\) |
|      |       |       |              | \(|H - 2 \rightarrow L; H \rightarrow L + 1\rangle(0.1526)\) |
| IV   | 6.639 | 1.186 | x/y          | \(|H \rightarrow L + 2\rangle(0.6048)\) |
|      |       |       |              | \(|H \rightarrow L + 1\rangle(0.5465)\) |
| V    | 6.971 | 15.375| x            | \(|H \rightarrow L + 1\rangle(0.5637)\) |
|      |       |       |              | \(|H \rightarrow L + 2\rangle(0.5528)\) |
| VI   | 7.354 | 4.986 | x/y          | \(|H \rightarrow L + 3\rangle(0.7725)\) |
|      |       |       |              | \(|H - 1 \rightarrow L + 1\rangle(0.2561)\) |
Figure 8. Various frontier molecular orbitals of disilane isomer [main article, Fig. 11] of Si$_2$H$_6$ molecule, contributing to optical transitions of comparatively high oscillator strength. Symbols H and L denote the HOMO and the LUMO orbitals, while H-n (L+n) represents n-th orbital below (above) HOMO (LUMO). Subscripts are used to index the degenerate orbitals.

Table S8. Many-particle wave functions of the excited states contributing to the peaks in the optical absorption spectrum of disilane (H$_3$Si-SiH$_3$) isomer [main article, Fig. 11] of Si$_2$H$_6$ molecule. 'E' corresponds to excitation energy (in eV) of an excited state, and $f$ denotes the oscillator strength for a particular electric dipole transition to that excited state, from the ground state. In the “Polarization” column, x, y and z denote the absorption of light polarized along x, y, and z directions, respectively. 'HF' corresponds to Hartree-Fock configuration. 'H' and 'L' stand for HOMO and LUMO orbitals. In the “Wave function” column, each number inside the parentheses denotes the coefficient of the corresponding configuration in the CI wave function. GS indicates the ground states wave function of the isomer, and not that of an excited state corresponding to a peak. The atomic coordinates corresponding to the optimized geometry of this isomer are presented in Table S16.

| Peak | E (eV) | $f$ | Polarization | Wave function |
|------|--------|-----|--------------|---------------|
| GS   |        |     |              | $|HF\rangle$(0.9409) |
| I    | 7.767  | 2.976 | x/y          | $|H\rightarrow(L+2)_{2}\rangle$(0.8791) |
|      |        |      |              | $|(H-1)_{1}\rightarrow L\rangle$(0.1246) |
|      | 7.812  | 5.984 | z            | $|H\rightarrow(L+2)_{1}\rangle$(0.8809) |
|      |        |      |              | $|(H-2)_{1}\rightarrow L\rangle$(0.1257) |
| II   | 8.445  | 20.638 | x/y         | $|H\rightarrow L\rangle$(0.8486) |
|      |        |      |              | $|(H-1)_{1}\rightarrow(L+2)_{2}\rangle$(0.1901) |
| III  | 9.208  | 6.959 | z            | $|(H-1)_{1}\rightarrow(L+2)_{1}\rangle$(0.6114) |
|      |        |      |              | $|(H-1)_{2}\rightarrow(L+2)_{2}\rangle$(0.5962) |
| IV   | 9.404  | 8.843 | x/y          | $|(H-1)_{1}\rightarrow L\rangle$(0.5695) |
|      |        |      |              | $|(H-1)_{1}\rightarrow(L+2)_{2}\rangle$(0.4532) |
|      | 9.471  | 0.800 | z            | $|(H-2)_{1}\rightarrow L\rangle$(0.5852) |
|      |        |      |              | $|(H-1)_{2}\rightarrow(L+2)_{2}\rangle$(0.4249) |
| V    | 9.816  | 8.668 | x/y          | $|(H-1)_{1}\rightarrow(L+2)_{2}\rangle$(0.6397) |
|      |        |      |              | $|(H-1)_{1}\rightarrow L\rangle$(0.3825) |
|      | 9.924  | 1.031 | z            | $|(H-2)_{1}\rightarrow L\rangle$(0.6167) |
|      |        |      |              | $|(H-1)_{2}\rightarrow(L+2)_{2}\rangle$(0.4176) |
| VI   | 10.161 | 2.259 | x/y          | $|H\rightarrow L+4\rangle$(0.7547) |
|      |        |      |              | $|(H-1)_{2}\rightarrow(L+2)_{1}\rangle$(0.3177) |
Table S9. Atomic coordinates (in Å units) corresponding to the optimized geometry of dibridged disilyne (Si-H$_2$-Si)

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| Si| 0.000000000000| 1.100740944342 | -0.027074095829 |
| Si| 0.000000000000| -1.100740944342 | -0.027074095829 |
| H | -0.985364830979| 0.000000000000| 0.751568938885 |
| H | 0.985364830979 | 0.000000000000 | 0.751568938885 |

Table S10. Atomic coordinates (in Å units) corresponding to the optimized geometry of monobridged structure (Si-H-SiH)

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| Si| -0.836958729655| 0.017059638406| -0.709155735004 |
| Si| 0.806304271215| -0.014312279108| 0.606308390319 |
| H | -0.772104895994| -0.038038610383| 1.012668921759 |
| H | 1.6230063648110| -0.04202025198 | 1.842343123724 |

Table S11. Atomic coordinates (in Å units) corresponding to the optimized geometry of disilavinylidene isomer (Si-SiH$_2$)

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| Si| 0.000038658677| 1.165679188613| 0.000000000000 |
| Si| -0.000024520199| -1.031699608620| 0.000000000000 |
| H | 1.227406465634| -1.859865255861| 0.000000000000 |
| H | -1.227798936833| -1.859368487152| 0.000000000000 |

Table S12. Atomic coordinates (in Å units) corresponding to the optimized geometry of trans-bent isomer (HSi-SiH)

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| Si| 1.049560638794| -0.012108929052| 0.000000000000 |
| Si| -1.049560638794| 0.012108929052| 0.000000000000 |
| H | 1.901548085640| -1.229661195450| 0.000000000000 |
| H | -1.901548085640| 1.229661195450| 0.000000000000 |

Table S13. Atomic coordinates (in Å units) corresponding to the optimized geometry of disilene isomer (H$_2$Si-SiH$_2$)

|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| Si| -0.014527084989| 1.078610931417| 0.000000000000 |
| Si| 0.014527084989| -1.078610931417| 0.000000000000 |
| H | -0.388083856897| 1.807751814186| 1.227693520012 |
| H | -0.388083856897| 1.807751814186| -1.227693520012 |
| H | 0.388083856897 | -1.807751814186| 1.227693520012 |
| H | 0.388083856897 | -1.807751814186| -1.227693520012 |
Table S14. Atomic coordinates (in Å units) corresponding to the optimized geometry of mono-bridged isomer (H$_2$Si-H-SiH)

|   | x           | y           | z            |
|---|-------------|-------------|--------------|
| Si| 1.172682525006 | 0.047991888154 | -0.052395704519 |
| Si| -1.070659956950 | 0.004587875388 | -0.004943355672 |
| H | 1.079592180677 | -1.466417217376 | -0.026756050259 |
| H | -0.073757438423 | -0.034913083199 | 1.266626592692 |
| H | -1.881741837422 | 1.218385602498 | 0.242557859563 |
| H | -1.956209393611 | -1.76924076404 | 0.109287047982 |

Table S15. Atomic coordinates (in Å units) corresponding to the optimized geometry of silylsilylene isomer (H$_3$Si-SiH)

|   | x           | y           | z            |
|---|-------------|-------------|--------------|
| Si| 1.126462143734 | 0.027035432078 | -0.000006113340 |
| Si| -1.258201977707 | -0.087127476208 | -0.00000612313 |
| H | -1.308985044826 | 1.431034864085 | -0.00001211523 |
| H | 1.587300210721 | -0.767155781338 | 1.203027047658 |
| H | 1.791407763335 | -1.297349115623 | -0.000057042453 |
| H | 1.587336122859 | 0.76729544767 | 1.202914086260 |

Table S16. Atomic coordinates (in Å units) corresponding to the optimized geometry of disilane (H$_3$Si-SiH$_3$)

|   | x           | y           | z            |
|---|-------------|-------------|--------------|
| Si| 0.000000000915 | -1.169370238817 | 0.000000000000 |
| Si| -0.000000000915 | 1.169370238817 | 0.000000000000 |
| H | -1.388422645000 | -1.684057891419 | 0.000000000000 |
| H | 0.694211326479 | -1.684057901803 | -1.202409278566 |
| H | 0.694211326479 | -1.684057901803 | 1.202409278566 |
| H | 1.388422645000 | 1.684057891419 | 0.000000000000 |
| H | -0.694211326479 | 1.684057901803 | -1.202409278566 |
| H | -0.694211326479 | 1.684057901803 | 1.202409278566 |