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The equilibrium structure of silene $\text{H}_2\text{C}=\text{SiH}_2$ from millimeter wave spectra and from *ab initio* calculations

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Silene, H_2CSiH_2 , has been efficiently produced by pyrolysis of 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene (SBO). Seven isotopomers have been observed by millimeter- and submillimeter-wave spectroscopy. From the different sets of experimental molecular parameters and from *ab initio* calculations of the rovibrational interaction parameters, the equilibrium structure has been obtained by a least squares analysis of the rotational constants. The results are: $r_e(\text{Si}=\text{C}) = 1.7039(18) \text{ \AA}$, $r_e(\text{C}-\text{H}) = 1.0819(12) \text{ \AA}$, $r_e(\text{Si}-\text{H}) = 1.4671(9) \text{ \AA}$, $\angle \text{HCSi} = 122.00(4)^\circ$, and $\angle \text{HSiC} = 122.39(3)^\circ$. This experimental structure is in excellent agreement with the equilibrium geometry calculated at the CCSD(T) level of theory with a cc-pV(Q,T)Z basis set. This is the first experimental determination without any constraint of the $\text{Si}=\text{C}$ double bond length in the parent compound of the silaalkene family. A lifetime of 30 ms has been observed for this molecule in the gas phase at low pressure. © 1997 American Institute of Physics. [S0021-9606(97)02124-7]

I. INTRODUCTION

Silene (silaethene, $\text{H}_2\text{C}=\text{SiH}_2$, **I**) is the parent molecule of the silaalkene family which has in common a $\text{Si}=\text{C}$ double bond. Silaalkenes have long been sought but in spite of former reports they could not be characterized unambiguously before the early 80's. Owing to the high reactivity of the $\text{Si}=\text{C}$ bond^{1,2} bulky ligands both at Si and C are required to stabilize silaalkenes so that they can be studied at ambient temperature. Indeed $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{1-adamantyl}$, $\text{Me}=\text{CH}_3$, was the first silaalkene to be amenable to a single crystal x-ray study.³ The $\text{Si}=\text{C}$ bond length, $1.764(3) \text{ \AA}$,³ is significantly shorter than that of a $\text{Si}-\text{C}$ single bond which ranges typically from 1.86 to 1.94 \AA . Numerous examples of chemical characterization of silaalkenes by trapping reactions have been reported which however do not necessarily involve the free silaalkenes as intermediates and are therefore not further discussed here.

Matrix isolation at low temperature is a different method to kinetically stabilize thermodynamically unstable transients to enable observation. By this method Maier *et al.*^{4,5} were able to unambiguously characterize in Ar at 10 K for the first time **I** which was obtained by vacuum flash pyrolysis of 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene (SBO) at 650 °C and 1.4×10^{-5} mbar. The assignment of the IR spectrum to **I** was made by comparison with theoret-

ical calculations and confirmed by Si-deuteration experiments.

In a related study Rosmus *et al.*⁶ investigated the He(I) photoelectron spectrum of the pyrolysis products of SBO and other potential precursors of **I**. They observed a band as predicted at 8.95 eV with a vibrational fine structure consistent with the expected vibrational energy pattern. In both studies^{5,6} it was attempted in vain to generate **I** also from other precursors, in particular from silacyclobutane (SCB) and 1,3-disilacyclobutane (DSB), under comparable conditions.

Numerous *ab initio* calculations have been published on silene.⁷⁻¹⁸ In 1980, Goddard *et al.*⁸ calculated the structures and the energy separation for methylsilylene, CH_3SiH , **I** and silylmethylene, H_3SiCH , at the SCF/DZ(+*d*) level of theory. They found that methylsilylene was the most stable form by few kcal/mol. Yoshioka and Schaefer⁹ obtained a barrier height for the migration of an H atom from silene to methylsilylene of the order of 40 kcal. In 1981, Hanamura *et al.*¹⁰ found for the first time that 1,1-dimethylsilene, $\text{Me}_2\text{Si}=\text{CH}_2$, was more stable than $\text{MeSi}-\text{CH}_2\text{Me}$. In 1982, Schaefer¹¹ details the silicon-carbon double bond compounds. Colvin *et al.*¹² determined the optimized geometry and harmonic frequencies at the SCF and CISD level of theory with a DZ+*P* basis set. Shin and co-workers¹³ found that silene was more stable than methylsilylene by 11.6 kcal/mol at the CC-CI/VDZ+*P* level with MP2/6-31G** geometries. More recently, Grev *et al.*¹⁴ using large basis sets and a variety of methods for the inclusion of electron correlation

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effects predicted an energy difference of 3.6 kcal/mol (CISD/TZ2P geometries) while Boatz and Gordon¹⁵ arrived at a value of 4.1 kcal/mol by calculating the enthalpies of formation. Allendorf and Melius¹⁶ obtained the heats of formation for molecules in the series H_nSiCH_m through *ab initio* calculations coupled with semiempirical corrections. The dimerization of silene to form disilacyclobutane (DSCB) was studied by Seidl *et al.*¹⁷ with *ab initio* quantum mechanical techniques. They found that dimerization occurs through a small barrier of 5.2 kcal/mol and that the dimer is more stable by 80 kcal/mol. Jacobsen and Ziegler¹⁸ used density functional theory (local density approximation augmented by nonlocal exchange and correlation corrections) to calculate properties of ethylene analogues including silene.

Gutowski *et al.*¹⁹ observed in 1991 six rotational transitions between 8 and 9.2 GHz for the transient silaalkene 1,1-dimethylsilaethylene (DMSE) within a supersonic jet expansion using a microwave Fourier transform spectrometer.

The full characterization of free **I** in the gas phase being still an unsolved and challenging problem, we have taken up again the search for **I** by millimeter wave (mmw) spectroscopy accompanied by high level *ab initio* calculations. We have observed a clean mmw spectrum of **I** when SBO seeded in Ar was pyrolyzed at 600 °C. Lower yields of **I** were also obtained from SCB at 1000 °C, and very weak signals of **I** were seen when DSCB was pyrolyzed at further raised temperatures and pressure. Pulsed 193 nm ArF laser irradiation of SBO also furnished **I** and enabled us to determine the $1/e$ lifetime of the exponential decay at room temperature to be 30 ± 2 ms.²⁰

We have been able to measure 142 rotational lines of the most abundant isotopic species of $\text{H}_2\text{C}=\text{SiH}_2$. From the smallness of the inertial defect, planarity of **I** was concluded, and nuclear spin statistics suggested C_{2v} symmetry.

Since for any isotopic variety of **I** only two rotational constants can be obtained that are not correlated by the planarity condition, any experimental determination of the five structural parameters of **I** has to employ data on several isotopic species, the accuracy of the structure improving the larger the body of isotopic data is. Very accurate structural data for **I** are most desirable because they will have a reference character for the whole family of silaalkenes. The sensitivity of the mmw experiment being such that only the ^{29}Si isotopic varieties could be detected in natural abundance (4.7%), we were tempted to synthesize isotopically labeled precursors in order to collect the required inertial data. We have prepared precursors either deuterated at Si, or at C, and thereof generated the following seven isotopic varieties of **I** and measured their mmw spectra (throughout ^{12}C): $\text{H}_2\text{C}^{28}\text{SiH}_2$ (**Ia**), $\text{H}_2\text{C}^{29}\text{SiH}_2$ (**Ib**), $\text{H}_2\text{C}^{28}\text{SiHD}$ (**Ic**), $\text{H}_2\text{C}^{28}\text{SiD}_2$ (**Id**), $\text{H}_2\text{C}^{29}\text{SiD}_2$ (**Ie**), $\text{D}_2\text{C}^{28}\text{SiH}_2$ (**If**), and $\text{D}_2\text{C}^{29}\text{SiH}_2$ (**Ig**).

The experimental effort directed towards the determination of an accurate structure of **I** was accompanied by new advanced *ab initio* calculations.

II. EXPERIMENT

The different isotopic species **Ia–Ig** were mostly generated from SBO, deuteration at Si being easily achieved using LiAlD_4 (**Id**, **Ie**), or mixtures of LiAlH_4 and LiAlD_4 (**Ic**), for the reduction of the intermediate 1,1-dichloro-1-silacyclohexa-2,4-diene.

The different SBO varieties were synthesized as described,⁵ the only change being the use of a glass ampoule allowing a maximum pressure of 10 bar for the addition of hexafluorobutyne to 1-silacyclohexa-2,4-diene. After 14 h at 90 °C the yield of SBO was $\sim 40\%$.

The CD_2 -species **If** was generated in first experiments from 2,2,3,4,4-pentadeutero-1-silacyclobutane. This was obtained by the propynoic acid/allyl alcohol/allyl bromide route according to Ref. 21; deuterium being introduced by treatment of propynoic acid first with $\text{D}_2\text{O}/\text{Na}_2\text{CO}_3$ and then D_2SO_4 . Bromination of allyl alcohol- d_6 with HBr yielded allyl bromide- d_5 , to which HSiCl_3 was added in the presence of H_2PtCl_6 as a catalyst.²² Ring closure to 2,2,3,4,4-pentadeutero-1,1-dichloro-1-silacyclobutane was achieved with Mg,²² from which SCB- d_5 was obtained in the usual way with LiAlH_4 at $-5-0$ °C in di-*n*-butyl ether.

Since SCB is a poor source for **I** that did not permit to detect the ^{29}Si isotopomer in natural abundance we decided to synthesize SBO- d_6 as a precursor for **If** and **Ig**. The deuterium atoms have to be introduced prior to the very first step of the synthesis that starts from cyclopentadiene.⁵ We have employed a procedure described in Ref. 23 using a large excess of D_2O in hexamethyl phosphorus acid triamide under catalysis of NaOD. Heating of cyclopentadiene- d_6 to 60 °C for several hours yielded dicyclopentadiene- d_{12} that was utilized in the synthesis of SBO- d_6 as described above. Multi-nuclear NMR data of the deuterated precursors are given in Ref. 24.

The mmw spectrometer used in this study has been described extensively²⁵ as have been several modifications and improvements.²⁶ As previously, up to 300 GHz the mmw power was obtained by harmonic generation from klystrons or Gunn oscillators emitting in the 50–80 GHz frequency range. The harmonic generators were commercial Custom Microwave multipliers equipped with Schottky barrier diodes. In the submillimeter-wave range (340–475 GHz), two phase-locked backward-wave-oscillators (BWO) provided by Thomson CSF were used. Their high output level allowed an improved sensitivity in this frequency range, typically 10^{-8} cm^{-1} for a 10 Hz bandwidth detection, and some isotopomers of silene **I** were only studied in this domain.

The detection was achieved by an helium cooled InSb detector from QMC Instruments. The mmw emission was frequency modulated at 40 kHz, while the signal was demodulated at twice this frequency providing a second derivative line shape. Frequency scanning, data acquisition, signal processing and frequency measurement were controlled by an HP-microcomputer. Under these conditions, the estimated experimental error of the frequency measurement was less than 50 kHz.

The observation cell consisted of a 1 m long, 5 cm in-

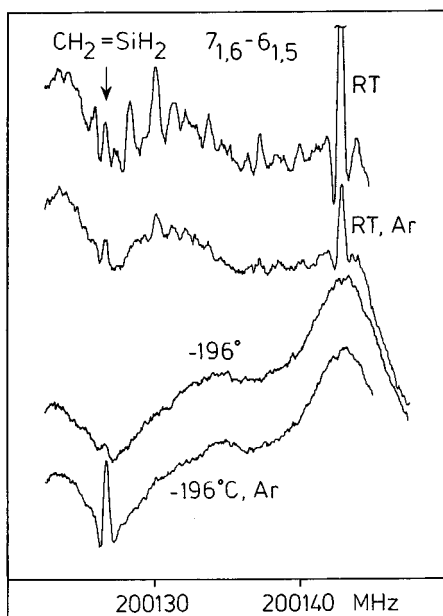


FIG. 1. Comparison between the different signals detected when the SBO precursor is flowed alone or with argon through the oven, the cell being at room temperature (RT) or cooled to liquid nitrogen temperature (-196°C).

ternal diameter pyrex tube connected on one side to the vacuum pump and on the other side to a cross-shaped glass part (50 cm long and 10 cm i.d.). Both ends of the cell were closed by two Teflon windows at Brewster incidence in order to improve transmission and to reduce standing waves. A quartz tube heated by a tungsten coil was used as an oven and introduced in a side-arm of the cross-shaped part. In a first negative experiment, a 10 cm long and 1.4 cm i.d. oven was used, and it was finally replaced by a smaller one, 2 cm long and 0.8 cm i.d. which gave better results. In order to trap condensable by-products such as unreacted SBO or other various thermolysis products, the cross-shaped part of the cell was cooled by flowing liquid nitrogen through a rubber tube wound round it. This system allowed the production of reactive species by flash-vacuum thermolysis directly inside the observation cell. Argon was used as a buffer and carrier gas and was flowed with SBO through the oven heated to 600°C . The best experimental conditions were $P(\text{SBO}) = 7 \times 10^{-3}$ mbar and $P(\text{Ar}) = 1.5 \times 10^{-2}$ mbar. The advantage of using argon as buffer and carrier gas and of cooling the cell is illustrated in Fig. 1: At room temperature and without argon, the spectrum was that complicated by the presence of numerous by-products that it was impossible to identify any silene line; with argon, the intensity of the lines due to by-products was reduced; cooling the cell completely cleared the spectrum and addition of argon drastically increased the signal due to silene. Under these experimental conditions, the spectrum was very clean and only the spectrum of methylsilane was observed simultaneously with that of silene **I**.

Silene was also produced, but in a lower yield, by UV photolysis at $\lambda = 193$ nm of SBO with an ArF excimer laser

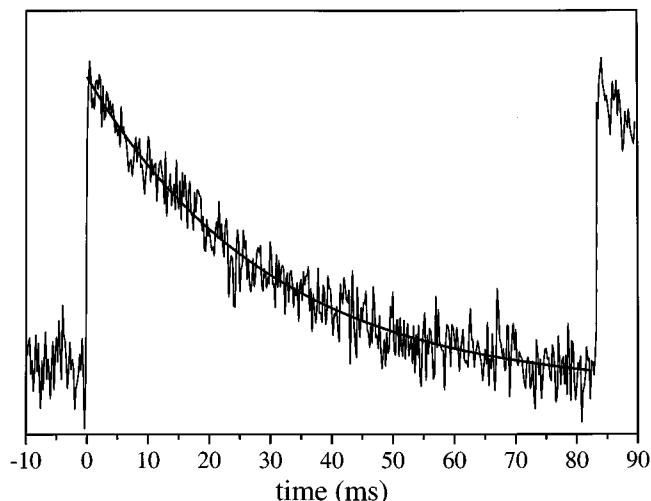


FIG. 2. Time variation of the $7_{1,6} - 6_{1,5}$ rotational absorption line following a laser pulse at 193 nm in pure SBO. The fitted exponential decay ($\tau = 30$ ms) is superimposed on the signal.

(Lumonics PM848).²⁷ The pulsed emission of the laser allowed the measurement of the lifetime of **I** in the gas phase and at room temperature as in our experimental conditions (pure SBO, $P = 8.10^{-3}$ mbar). Figure 2 shows the decrease of the intensity of the $7_{1,6} - 6_{1,5}$ rotational line at 200 126.595 MHz. This decrease fits perfectly well (coefficient of determination $r^2 = 0.938$) to an exponential curve with a time constant of 30 ± 2 ms. This lifetime is relatively long compared to that of silanone, H_2SiO , measured under analogous experimental conditions: 1.2 ms.²⁸ As for DMSE which had been produced by pyrolysis of 1,1-dimethylsilacyclobutane (DMSCB),¹⁹ silene was also generated by pyrolysis of SCB. In this condition, the spectrum of **I** was only half as intense even employing a higher partial pressure of the precursor and a temperature of the oven as high as $\sim 1000^\circ\text{C}$. Only a very weak signal was observed when DSCB was used as precursor, even if pressure and temperature were further increased.

III. AB INITIO CALCULATIONS

A. Computational details

The molecular geometry of silene **I** was optimized under the constraint of C_{2v} point group symmetry at the Hartree–Fock self-consistent field (SCF) level of theory²⁹ and at the correlated levels of second-order Møller–Plesset perturbation theory (MP2),³⁰ coupled cluster theory with single and double excitations (CCSD),³¹ and CCSD augmented by a perturbational treatment of connected triple excitations [CCSD(T)].³² For the purpose of comparison, the molecular structures of thioformaldehyde ($\text{CH}_2=\text{S}$) and silane (SiH_4) were also optimized in C_{2v} and T_d point group symmetry, respectively.

The quantum chemical calculations were performed using four different basis sets: TZ2P denotes a valence triple-zeta plus double polarization plus f function basis set where Si and S are described by a $(12s9p)/[6s5p]$ basis³³ with

TABLE I. Computed equilibrium geometries (\AA , $^\circ$) of silene ($\text{H}_2\text{C}=\text{SiH}_2$).

Method	Basis	CSi	CH	SiH	HCSi	HSiC
SCF	TZ2Pf	1.6922	1.0739	1.4684	122.31	123.01
MP2	TZ2Pf	1.7085	1.0777	1.4680	121.84	122.63
CCSD	TZ2Pf	1.7084	1.0781	1.4713	122.12	122.64
CCSD(T)	TZ2Pf	1.7167	1.0799	1.4728	122.04	122.50
CCSD(T)	cc-pVTZ	1.7126	1.0784	1.4730	121.90	122.87
CCSD(T)	cc-pV(Q,T)Z	1.7043	1.0824	1.4670	122.06	122.49
CCSD(T)	cc-pVQZ	1.7031	1.0800	1.4606	122.13	122.55
Frozen core approximation:						
CCSD(T)	TZ2Pf	1.7193	1.0829	1.4749	122.02	122.51
CCSD(T)	cc-pVTZ	1.7193	1.0834	1.4759	121.97	122.61
CCSD(T)	cc-pV(Q,T)Z	1.7130	1.0839	1.4742	122.03	122.48
CCSD(T)	cc-pVQZ	1.7130	1.0828	1.4731	122.02	122.46

two sets of d and one set of f polarization functions;³⁴ C is represented by a $(10s6p)/[5s3p]$ basis³⁵ with two sets of d and one set of f polarization functions;³⁶ finally H is described by a $(5s)/[3s]$ basis (scale factor 1.2)³⁵ with two sets of p and one set of d polarization functions.³⁶ The correlation consistent polarized basis sets (cc-pVnZ) of Dunning and co-workers^{34,36} were also employed: The valence triple-zeta basis (cc-pVTZ) is a $[5s4p2d1f/4s3p2d1f/3s2p1d]$ contraction of a $(15s9p2d1f/10s5p2d1f/5s2p1d)$ primitive set for Si,S/C/H, whereas the quadruple-zeta basis (cc-pVQZ) corresponds to a $[6s5p3d2f1g/5s4p3d2f1g/4s3p2d1f]$ contraction of a $(16s11p3d2f1g/12s6p3d2f1g/6s3p2d1f)$ primitive set. We also checked the performance of a basis set composed of cc-pVQZ at all nonhydrogen atoms and cc-pVTZ at H which is denoted as cc-pV(Q,T)Z. Such a mixed basis set has been shown to lead to little loss in accuracy compared to the full cc-pVQZ set at all atoms^{37,38} while reducing the computation times significantly.

Spherical harmonics were used in all calculations, except that the SCF/TZ2Pf wave functions were represented by Cartesian Gaussian-type orbitals. Unless stated otherwise, all electrons were correlated in the MP2, CCSD, and CCSD(T) treatments. Whenever the frozen core approximation was applied, the core molecular orbitals were defined as $(1s)$ for carbon and $(1s2s2p)$ for silicon and sulfur. Nondynamical electron correlation is not overly important in silene, as judged from the coupled cluster T_1 diagnostic^{39,40} which is 0.015 for all four basis sets at the corresponding CCSD(T) stationary points in the frozen core approximation (the analogous value for thioformaldehyde is 0.017). Therefore, silene is expected to be well described by single reference coupled cluster methods.

Geometry optimizations employing the TZ2Pf basis were performed using analytical energy gradients as implemented in the GRADSCF,⁴¹ GAUSSIAN92,⁴² and ACESII⁴³ program systems, whereas the corresponding computations employing the correlation-consistent basis sets and/or the frozen core approximation were carried out with the use of numerical gradients (typical stepsizes: 0.01 Bohr for bond distances and 1° for the angles) as implemented in the MOLPRO94 program system.^{44,45} The largest internal gradient components at

the stationary points were always less than 2×10^{-4} a.u.

For comparison with the present experimental data, the quadratic and cubic force fields of silene are required to provide theoretical values for the centrifugal distortion constants, for the differences between the equilibrium and ground-state rotational constants, and for the inertial defects. Harmonic force fields were evaluated in Cartesian coordinates either analytically at the MP2/TZ2Pf level of theory or numerically from CCSD(T)/TZ2Pf energies (stepsize 0.01 \AA) using the GAUSSIAN92 program⁴².

The MP2/TZ2Pf cubic normal coordinate force constants which are not reported explicitly were determined with the use of a finite difference procedure⁴⁶ involving displacements along dimensionless normal coordinates (stepsize $\Delta q = 0.05$) and the calculation of analytic second derivatives (relative precision $\epsilon < 10^{-7}$) at these displaced geometries. At the MP2/TZ2Pf stationary point of silene, the Cartesian gradient components did not exceed 2×10^{-7} a.u. The ground-state corrections to the rotational constants were computed from the theoretical vibration-rotation coupling constants using standard formulas based on second-order rovibrational perturbation theory.^{47,48} The cubic normal coordinate force constants of the less abundant isotopomers of silene containing deuterium and/or ^{29}Si were obtained from those for $^{12}\text{CH}_2=^{28}\text{SiH}_2$ by appropriate nonlinear transformations^{49,50} via an intermediate representation of the cubic force field in terms of symmetry-adapted internal coordinates.

B. Results and discussion

Table I contains the equilibrium geometry of silene computed at various theoretical levels. For the sake of comparison, Table II lists the corresponding theoretical equilibrium structures of thioformaldehyde and silane together with the available experimental data.^{51,52}

Considering the dependence of the results with the TZ2Pf basis on the chosen correlation treatment, MP2 and CCSD yield very similar geometries for each of the three molecules. Taking into account the effects of connected triple excitations at the CCSD(T) level leaves most of the structural parameters nearly unchanged, except for the

TABLE II. Computed and experimental equilibrium geometries ($\text{\AA},^\circ$) of thioformaldehyde ($\text{H}_2\text{C}=\text{S}$) and silane (SiH_4).

Method	Basis	CS	CH	HCS	SiH
SCF	TZ2Pf	1.5929	1.0771	122.12	1.4774
MP2	TZ2Pf	1.6115	1.0821	121.93	1.4741
CCSD	TZ2Pf	1.6109	1.0816	122.03	1.4782
CCSD(T)	TZ2Pf	1.6202	1.0835	121.95	1.4792
CCSD(T)	cc-pVTZ	1.6182	1.0826	121.81	1.4785
CCSD(T)	cc-pV(Q,T)Z	1.6136	1.0864	121.83	1.4736
CCSD(T)	cc-pVQZ	1.6136	1.0841	121.82	1.4684
Frozen core approximation:					
CCSD(T)	TZ2Pf	1.6223	1.0867	121.92	1.4818
CCSD(T)	cc-pVTZ	1.6223	1.0875	121.87	1.4825
CCSD(T)	cc-pV(Q,T)Z	1.6165	1.0880	121.82	1.4807
CCSD(T)	cc-pVQZ	1.6163	1.0867	121.81	1.4798
Experimental					
		1.6110(8) ^a	1.0856(21) ^a	122.1(6) ^a	1.4732(2) ^b

^aReference 51.

^bReference 52.

double bonds which are lengthened significantly ($\text{C}=\text{Si}$ by 0.0083 \AA , $\text{C}=\text{S}$ by 0.0093 \AA). In the case of thioformaldehyde, the $\text{C}=\text{S}$ bond lengths from MP2/TZ2Pf and CCSD/TZ2Pf are in close agreement with experiment⁵¹ while CCSD(T)/TZ2Pf overestimates this bond length by 0.0092 \AA due to basis set incompleteness. Therefore we expect, by analogy, that the structural predictions for silene from MP2/TZ2Pf and CCSD/TZ2Pf will be more accurate than those from CCSD(T)/TZ2Pf.

The convergence of the theoretical results with basis set improvement can be judged from the CCSD(T) data in Tables I and II. When using the frozen core approximation, all structural parameters exhibit the expected smooth convergence. As is well known, the bond lengths are slightly overestimated at this level due to the neglect of core-valence correlation. For accurate predictions, all electrons need to be correlated. The corresponding CCSD(T) results again show reasonable convergence with basis set extension, except for the SiH bond length in silene and silane (see Tables I and II) which decreases by about 0.006 \AA when going from the cc-pV(Q,T)Z to the cc-pVQZ basis. Based on previous experience, we would expect a much smaller decrease (cf. the frozen core results). We believe that the cc-pVQZ basis

exaggerates core-valence correlation effects in this particular case, also causing an untypical underestimation of the equilibrium SiH bond length in silane (see Table II). Therefore we prefer the cc-pV(Q,T)Z basis for structural predictions in silene. It should be noted in this connection that the cc-pVnZ basis sets have not been designed to cover core-valence correlation and that the more appropriate cc-pCVnZ sets⁵³ are not yet available for second-row elements.

Based on these observations we adopt the CCSD(T)/cc-pV(Q,T)Z geometry of silene as our best theoretical prediction. We expect an accuracy of 0.003 \AA for the bond lengths and of 0.3° for the bond angles. The CCSD(T)/cc-pVQZ results for all structural parameters except SiH lie within these error estimates.

Table III reports theoretical equilibrium and ground state rotational constants and inertial defects for the principal isotopomer of silene and for eight less abundant isotopomers, six of which have been measured presently (see experimental section). The equilibrium rotational constants have been computed at the CCSD(T)/cc-pV(Q,T)Z level (see above). They have been corrected for the effects of zero-point nuclear motions (MP2/TZ2Pf) to arrive at the corresponding ground-state values. The inertial defects have been obtained

TABLE III. Computed^a equilibrium (A_e, B_e, C_e) and ground state (A_0, B_0, C_0) rotational constants (MHz) and inertial defects Δ_0 (u \AA^2) for several silene ($\text{H}_2\text{H Si}=\text{C H}_2$) isotopomers.

Isotopomer	A_e	B_e	C_e	A_0	B_0	C_0	Δ_0
1,1 28=12 1,1	105 688	14 833	13 007	104 945	14 773	12 928	0.0660
1,1 29=12 1,1	105 688	14 713	12 915	104 945	14 653	12 836	0.0661
2,1 28=12 1,1	81 506	14 087	12 011	81 046	14 036	11 941	0.0812
2,2 28=12 1,1	64 274	13 502	11 158	63 984	13 456	11 095	0.0928
2,2 29=12 1,1	64 274	13 423	11 104	63 984	13 377	11 042	0.0928
1,1 28=12 2,2	78 049	12 654	10 889	77 552	12 610	10 829	0.0762
1,1 29=12 2,2	78 049	12 540	10 804	77 552	12 497	10 745	0.0763
2,2 28=12 2,2	52 885	11 564	9489	52 630	11 529	9441	0.0917
2,2 29=12 2,2	52 885	11 486	9436	52 630	11 451	9389	0.0917

^a A_e, B_e, C_e from CCSD(T)/cc-pV(Q,T)Z; ground-state corrections $A_e - A_0, B_e - B_0, C_e - C_0$ from the MP2/TZ2Pf cubic force field.

TABLE IV. Computed^a quartic centrifugal distortion constants^b (kHz) for several silene (H,H Si=C H,H) isotopomers.

Isotopomer	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
1,1 28=12 1,1	12.035	161.98	1737.8	1.603	120.84
1,1 29=12 1,1	11.865	160.89	1739.1	1.566	119.47
2,1 28=12 1,1	10.898	133.23	1493.5	1.892	113.70
2,2 28=12 1,1	9.499	148.96	718.62	1.889	108.05
2,2 29=12 1,1	9.380	148.98	718.71	1.852	107.42
1,1 28=12 2,2	8.579	90.36	835.18	1.343	77.08
1,1 29=12 2,2	8.444	89.34	836.33	1.310	76.04
2,2 28=12 2,2	6.827	63.90	407.94	1.415	56.50
2,2 29=12 2,2	6.732	63.94	408.00	1.385	56.09

^aCCSD(T)/TZ2Pf.^bEquilibrium values (A reduction, I' representation).

by converting the *ab initio* ground-state rotational constants to inertial moments and forming the appropriate differences.

Table IV lists our most reliable [i.e., CCSD(T)/TZ2Pf] predictions for the equilibrium centrifugal distortion constants of silene and the relevant isotopomers. As in the case of the rotational constants and inertial defects, these data will be compared in a later section with the observed ground-state constants.

IV. SPECTROSCOPIC RESULTS

The first search of the spectrum of silene **I** was guided by the *ab initio* values of the rotational constants (Table III) and of the centrifugal distortion parameters (Table IV). Silene belongs to the C_{2v} point group of symmetry, the C_2 axis being the axis of the least moment of inertia. The rotational spectrum should then display the characteristic a type pattern of a slightly asymmetric top, $\kappa \approx -0.9599$, with the spin statistics corresponding to two pairs of equivalent hydrogen nuclei; this leads to a weight of 10 for $K_a K_c = oo$ and oe , and 6 for ee and eo rotational levels.

In the experimental conditions described previously, a very clean spectrum of silene was observed and 142 rotational lines were measured, corresponding to $6 \leq J \leq 16$ and $K_a \leq 11$ in the 180–473 GHz frequency range. Their frequencies are reported in Table V. These data were fitted to a standard Watson-type A -reduced Hamiltonian in the I' representation⁵⁴ with a standard deviation of 16.9 kHz, which corresponds to residuals well below the expected experimental accuracy of 50 kHz. As mentioned in Table V, two unresolved K_a -doublets were excluded from the fit. The residuals are given in Table V and the adjusted rotational and centrifugal distortion constants are reported in Table VI. Only two of the sextic centrifugal distortion parameters, Φ_{KJ} and Φ_K , were determined with significance, and they must be considered as fitting terms. The others sextic terms were fixed to zero. The inertial defect $\Delta_0 = 0.061\,158\,\text{u}\text{\AA}^2$ is small and characteristic of a planar molecule.

The search of the spectra of the different isotopomers of silene (**Ib**→**Ig**) required a prediction of their rotational constants. The *ab initio* parameters given in Table III were sub-

TABLE V. Rotational frequencies of CH₂SiH₂ (in MHz).

$J_{K_a K_c}$	\leftarrow	$J_{K_a K_c}$	ν_{obs}	$\Delta\nu^a$
7 _{1,7}	\leftarrow	6 _{1,6}	187 215.875	0.001
7 _{0,7}	\leftarrow	6 _{0,6}	192 484.327	0.001
7 _{2,6}	\leftarrow	6 _{2,5}	193 816.055	0.003
7 _{6,2}	\leftarrow	6 _{6,1}	194 040.530	−0.001
7 _{6,1}	\leftarrow	6 _{6,0}	194 040.530	−0.001
7 _{5,3}	\leftarrow	6 _{5,2}	194 087.035	0.014
7 _{5,2}	\leftarrow	6 _{5,1}	194 087.035	0.013
7 _{4,4}	\leftarrow	6 _{4,3}	194 148.122 ^b	0.123
7 _{4,3}	\leftarrow	6 _{4,2}	194 148.122 ^b	−0.131
7 _{3,5}	\leftarrow	6 _{3,4}	194 241.720	0.030
7 _{3,4}	\leftarrow	6 _{3,3}	194 275.481	−0.035
7 _{2,5}	\leftarrow	6 _{2,4}	195 375.042	0.000
7 _{1,6}	\leftarrow	6 _{1,5}	200 126.595	−0.002
8 _{2,7}	\leftarrow	7 _{2,6}	221 404.516	−0.002
8 _{7,2}	\leftarrow	7 _{7,1}	221 718.100	0.027
8 _{6,3}	\leftarrow	7 _{6,2}	221 770.963	−0.002
8 _{5,4}	\leftarrow	7 _{5,3}	221 831.488	0.001
8 _{4,5}	\leftarrow	7 _{4,4}	221 915.119	0.013
8 _{4,4}	\leftarrow	7 _{4,3}	221 915.794	−0.012
8 _{3,6}	\leftarrow	7 _{3,5}	222 041.144	−0.004
8 _{3,5}	\leftarrow	7 _{3,4}	222 108.683	−0.008
8 _{2,6}	\leftarrow	7 _{2,5}	223 720.766	0.002
8 _{1,7}	\leftarrow	7 _{1,6}	228 553.620	−0.003
9 _{2,8}	\leftarrow	8 _{2,7}	248 953.356	0.001
9 _{7,3}	\leftarrow	8 _{7,2}	249 440.464	−0.005
9 _{6,4}	\leftarrow	8 _{6,3}	249 505.535	−0.002
9 _{5,5}	\leftarrow	8 _{5,4}	249 583.055	0.007
9 _{5,4}	\leftarrow	8 _{5,3}	249 583.055	−0.003
9 _{4,6}	\leftarrow	8 _{4,5}	249 694.718	0.004
9 _{4,5}	\leftarrow	8 _{4,4}	249 696.394	0.001
9 _{3,7}	\leftarrow	8 _{3,6}	249 855.728	−0.002
9 _{3,6}	\leftarrow	8 _{3,5}	249 979.273	−0.003
9 _{2,7}	\leftarrow	8 _{2,6}	252 217.843	0.003
9 _{1,8}	\leftarrow	8 _{1,7}	256 910.073	0.001
10 _{1,10}	\leftarrow	9 _{1,9}	266 909.664	−0.001
10 _{0,10}	\leftarrow	9 _{0,9}	272 768.018	−0.007
10 _{2,9}	\leftarrow	9 _{2,8}	276 457.788	0.000
10 _{8,3}	\leftarrow	9 _{8,2}	277 092.798	−0.016
10 _{7,4}	\leftarrow	9 _{7,3}	277 165.559	0.004
10 _{6,4}	\leftarrow	9 _{6,3}	277 244.764	0.001
10 _{5,6}	\leftarrow	9 _{5,5}	277 342.599	0.012
10 _{5,5}	\leftarrow	9 _{5,4}	277 342.599	−0.018
10 _{4,7}	\leftarrow	9 _{4,6}	277 488.221	0.003
10 _{4,6}	\leftarrow	9 _{4,5}	277 491.850	−0.001
10 _{3,8}	\leftarrow	9 _{3,7}	277 684.334	0.034
10 _{3,7}	\leftarrow	9 _{3,6}	277 895.430	0.004
11 _{0,11}	\leftarrow	10 _{0,10}	299 137.991	0.003
11 _{2,10}	\leftarrow	10 _{2,9}	303 913.153	−0.001
11 _{8,4}	\leftarrow	10 _{8,3}	304 808.250	0.017
11 _{7,5}	\leftarrow	10 _{7,4}	304 893.620	−0.008
11 _{6,6}	\leftarrow	10 _{6,5}	304 989.150	−0.008
11 _{5,7}	\leftarrow	10 _{5,6}	305 111.017	0.029
11 _{5,6}	\leftarrow	10 _{5,5}	305 111.017	−0.047
11 _{4,8}	\leftarrow	10 _{4,7}	305 296.902	−0.003
11 _{4,7}	\leftarrow	10 _{4,6}	305 304.158	−0.003
11 _{3,9}	\leftarrow	10 _{3,8}	305 524.813	−0.001
11 _{3,8}	\leftarrow	10 _{3,7}	305 866.445	0.002
11 _{2,9}	\leftarrow	10 _{2,8}	309 653.473	−0.004
11 _{1,10}	\leftarrow	10 _{1,9}	313 360.908	−0.005
12 _{2,10}	\leftarrow	11 _{2,9}	338 562.424	−0.001
12 _{1,11}	\leftarrow	11 _{1,10}	341 427.245	−0.002
13 _{1,13}	\leftarrow	12 _{1,12}	346 136.097	0.000
13 _{0,13}	\leftarrow	12 _{0,12}	351 357.926	−0.008
13 _{2,12}	\leftarrow	12 _{2,11}	358 658.812	0.002
13 _{11,3}	\leftarrow	12 _{11,2}	359 922.317	−0.042

TABLE V. (*Continued.*)

$J_{K_a K_c}$	←	$J_{K_a K_c}$	ν_{obs}	$\Delta\nu^a$
13 _{10,4}	←	12 _{10,3}	360 030.631	−0.012
13 _{9,5}	←	12 _{9,4}	360 136.846	0.019
13 _{8,6}	←	12 _{8,5}	360 244.471	0.004
13 _{7,7}	←	12 _{7,6}	360 359.916	−0.002
13 _{6,8}	←	12 _{6,7}	360 495.523	0.004
13 _{5,9}	←	12 _{5,8}	360 678.068 ^b	0.176
13 _{5,8}	←	12 _{5,7}	360 678.068 ^b	−0.190
13 _{4,10}	←	12 _{4,9}	360 964.197	−0.007
13 _{4,9}	←	12 _{4,8}	360 988.288	−0.002
13 _{3,11}	←	12 _{3,10}	361 228.987	−0.003
13 _{3,10}	←	12 _{3,9}	362 016.022	0.003
13 _{2,11}	←	12 _{2,10}	367 564.544	−0.002
13 _{1,12}	←	12 _{1,11}	369 366.943	−0.001
14 _{1,14}	←	13 _{1,13}	372 437.951	0.000
14 _{0,14}	←	13 _{0,13}	377 256.754	0.001
14 _{2,13}	←	13 _{2,12}	385 940.702	0.003
14 _{10,5}	←	13 _{10,4}	387 725.076	−0.026
14 _{9,6}	←	13 _{9,5}	387 843.698	0.000
14 _{8,7}	←	13 _{8,6}	387 965.597	0.003
14 _{7,8}	←	13 _{7,7}	388 098.726	−0.001
14 _{6,9}	←	13 _{6,8}	388 258.513	−0.003
14 _{5,10}	←	13 _{5,9}	388 478.190	0.051
14 _{5,9}	←	13 _{5,8}	388 478.807	−0.063
14 _{4,11}	←	13 _{4,10}	388 824.477	0.000
14 _{4,10}	←	13 _{4,9}	388 865.301	−0.004
14 _{3,12}	←	13 _{3,11}	389 084.169	−0.006
14 _{3,11}	←	13 _{3,10}	390 218.538	0.002
14 _{2,12}	←	13 _{2,11}	396 626.205	0.003
14 _{1,13}	←	13 _{1,12}	397 163.421	0.004
15 _{1,15}	←	14 _{1,14}	398 687.980	0.003
15 _{0,15}	←	14 _{0,14}	403 053.529	0.004
15 _{11,5}	←	14 _{11,4}	415 287.700	0.073
15 _{10,6}	←	14 _{10,5}	415 419.512	0.006
15 _{9,7}	←	14 _{9,6}	415 551.464	0.008
15 _{8,8}	←	14 _{8,7}	415 688.942	0.008
15 _{7,9}	←	14 _{7,8}	415 841.704	−0.002
15 _{6,10}	←	14 _{6,9}	416 028.751	0.004
15 _{5,11}	←	14 _{5,10}	416 290.767	0.038
15 _{5,10}	←	14 _{5,9}	416 292.061	−0.055
15 _{4,12}	←	14 _{4,11}	416 703.148	−0.003
15 _{4,11}	←	14 _{4,10}	416 769.720	−0.003
15 _{3,13}	←	14 _{3,12}	416 934.499	−0.003
15 _{3,12}	←	14 _{3,11}	418 523.212	0.006
15 _{2,13}	←	14 _{2,12}	425 710.887	0.001
15 _{1,14}	←	14 _{1,13}	424 799.595	0.002
16 _{1,16}	←	15 _{1,15}	424 888.185	0.004
16 _{0,16}	←	15 _{0,15}	428 777.249	−0.006
16 _{2,15}	←	15 _{2,14}	440 303.761	0.004
16 _{11,6}	←	15 _{11,5}	442 969.072	−0.011
16 _{10,7}	←	15 _{10,6}	443 113.854	0.006
16 _{9,8}	←	15 _{9,7}	443 260.152	−0.008
16 _{8,9}	←	15 _{8,8}	443 414.652	0.010
16 _{7,10}	←	15 _{7,9}	443 589.142	−0.008
16 _{6,11}	←	15 _{6,10}	443 806.745	0.012
16 _{5,12}	←	15 _{5,11}	444 116.497	−0.002
16 _{5,11}	←	15 _{5,10}	444 118.996	−0.020
16 _{4,13}	←	15 _{4,12}	444 600.275	−0.008
16 _{4,12}	←	15 _{4,11}	444 705.231	−0.002
16 _{3,14}	←	15 _{3,13}	444 773.969	−0.010
16 _{3,13}	←	15 _{3,12}	446 942.708	0.003
16 _{2,14}	←	15 _{2,13}	454 782.248	0.019
16 _{1,15}	←	15 _{1,14}	452 258.556	0.007
17 _{1,17}	←	16 _{1,16}	451 041.093	0.005
17 _{0,17}	←	16 _{0,16}	454 453.819	0.000
17 _{2,16}	←	16 _{2,15}	467 378.516	0.013

TABLE V. (*Continued.*)

$J_{K_a K_c}$	←	$J_{K_a K_c}$	ν_{obs}	$\Delta\nu^a$
17 _{11,7}	←	16 _{11,6}	470 649.645	−0.034
17 _{10,8}	←	16 _{10,7}	470 808.139	0.018
17 _{9,9}	←	16 _{9,8}	470 969.874	0.004
17 _{8,10}	←	16 _{8,9}	471 142.881	0.008
17 _{7,11}	←	16 _{7,10}	471 341.355	−0.001
17 _{6,12}	←	16 _{6,11}	471 593.024	0.030
17 _{6,11}	←	16 _{6,10}	471 593.024	−0.041
17 _{5,13}	←	16 _{5,12}	471 956.265	0.007
17 _{5,12}	←	16 _{5,11}	471 960.639	−0.013
17 _{4,14}	←	16 _{4,13}	472 515.508	−0.005
17 _{4,13}	←	16 _{4,12}	472 676.143	0.004
17 _{3,15}	←	16 _{3,14}	472 596.131	−0.004

^a $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$.^bFor these unresolved K_a -doublets, the frequencies were not included in the fit.

sequently corrected⁵⁵ by scaling them with factors obtained by comparing the *ab initio* constants of the parent silene with the experimental values:

$$X_{\text{scal}}^i = X_{\text{ab in}}^i \times (X_{\text{exp}}^p / X_{\text{ab in}}^p). \quad (1)$$

In this formula, X represents any rotational constant; the indices i and p refer to an isotopic substitution and to the parent molecule respectively; *scal*, *exp*, and *ab in* denote the scaled, experimental, and *ab initio* values. Without having any real theoretical basis, this method has often provided good estimates of the rotational constants, the accuracy being always better for the substitution of the heaviest atoms. The spectra were predicted by using the values of the centrifugal distortion constants obtained for the parent molecule.

All isotopic measurements were carried out with the two BWOs in the 340–475 GHz frequency range where the spectrometer was the most sensitive. Small scans of few hundred MHz were large enough to find and identify the most intense lines. They were used in a preliminary least-squares fit in order to refine the scaled molecular constants and to get better predictions. The agreement between these experimental constants and the scaled values confirms, if necessary, the identification of silene.

Except H₂CSiHD, all the observed isotopomers belong to the C_{2v} point group of symmetry. Those with two equivalent deuterium atoms display nuclear spin statistics different from that of the parent compound: The statistical weights are 15 for the *ee* and *eo* levels, and 21 for the *oo* and *oe* levels.

The three ²⁹Si substitutions were observed in natural abundance in the corresponding ²⁸Si parent species. Under our experimental conditions, only the most intense lines were detected: 27 transitions for H₂C²⁹SiH₂, 32 for H₂C²⁹SiD₂ and 20 for D₂C²⁹SiH₂ corresponding respectively to $K_a \leq 4$, $K_a \leq 6$ and $K_a \leq 5$. Concerning the three remaining observed isotopomers, 73 lines with $K_a \leq 10$ were measured for H₂CSiD₂, 70 with $K_a \leq 11$ for H₂CSiHD, and 48 with $K_a \leq 10$ for D₂CSiH₂. All these data were fitted to a standard Watson A -reduced Hamiltonian in the I' representation⁵⁴ with standard deviations varying from 8.5 to 20 kHz.

TABLE VI. Experimental molecular constants in MHz of seven isotopomers of silene in the ground vibrational state.

	H ₂ C ²⁸ SiH ₂	H ₂ C ²⁹ SiH ₂	H ₂ C ²⁸ SiHD	H ₂ C ²⁸ SiD ₂	H ₂ C ²⁹ SiD ₂	D ₂ C ²⁸ SiH ₂	D ₂ C ²⁹ SiH ₂
<i>A</i>	104 716.60(18)	104 716.54(24)	80 865.836(79)	63 852.718(38)	63 852.88(12)	77 446.61(09)	77 446.17(21)
<i>B</i>	14 786.7020(12)	14 667.2364(21)	14 051.0443(11)	13 471.860 83(94)	13 392.8447(38)	12 623.7769(18)	12 510.013(51)
<i>C</i>	12 936.2854(12)	12 844.7439(20)	11 949.052 47(85)	11 103.152 24(53)	11 049.4255(16)	10 837.6546(14)	10 753.696(39)
Δ_J	0.012 639 5(11)	0.012 461 5(19)	0.011 440 08(98)	0.009 999 60(84)	0.009 875 7(38)	0.009 033 7(98)	0.008 885 3(30)
Δ_{JK}	0.160 858 1(94)	0.159 750(35)	0.129 101(13)	0.142 982(15)	0.142 956(19)	0.094 832(15)	0.093 783(18)
Δ_K	1.908(70)	1.917(77)	1.607(15)	0.8069(46)	0.829(18)	0.952(11)	0.951(31)
δ_J	0.001 733 6(10)	0.001 695 6(19)	0.002 026 84(73)	0.002 027 68(54)	0.001 987 2(22)	0.001 451 77(92)	0.001 413 1(27)
δ_K	0.128 91(44)	0.127 77(49)	0.119 86(15)	0.111 951(61)	0.111 78(26)	0.084 795(94)	0.083 52(31)
Φ_{KJ}	−0.000 000 741(67)	−0.000 000 741 ^a	−0.000 007 49(10)	−0.000 001 30(12)	−0.000 001 30 ^a	0.000 001 54(9)	0.000 001 54 ^a
Φ_K	0.007 04(15)	0.007 04 ^a	0.003 538(85)	0.001 442(50)	0.001 442 ^a	0.002 83(11)	0.002 83 ^a
σ (kHz)	16.9	15.1	12.2	9.3	20.2	8.5	16.0
Number of lines	142	27	70	73	32	48	20

^aConstrained.

All the measured and calculated frequencies for the different isotopic substitutions are available as a supplementary publication for this paper.⁵⁶ The rotational constants and the centrifugal distortion parameters are reported in Table VI together with those of the parent molecule. For the ²⁹Si substitutions, the two determinable sextic centrifugal distortion constants were fixed to the values obtained for the corresponding ²⁸Si species.

The experimentally determined rotational constants are in very good agreement with the values calculated *ab initio*: The relative discrepancies vary between − 0.14% and − 0.22% for *A*, between 0.09% and 0.12% for *B* and between 0.06% and 0.08% for *C*.

Concerning the centrifugal distortion constants the agreement with the *ab initio* values is generally of the order of 5% or better, except for Δ_K for which it is 10%. This illustrates *inter alia* the high quality of the theoretical quadratic force field.

V. MOLECULAR STRUCTURE

Due to the high reactivity of the unsubstituted silaalkene **I**, its structure, particularly the length of the Si=C double bond, could not be determined experimentally. The present

spectroscopic study of seven isotopomers of silene provides their accurate rotational constants and thereby enables a determination of the molecular structure.

To eliminate the most important part of the residual centrifugal distortion effects in the rotational constants, they were first transformed to the so-called Watson's determinable parameters *A*₀, *B*₀, and *C*₀^{54,57} which are given in Table VII. The theoretical rotation–vibration interaction constants which were deduced from the *ab initio* cubic force field (Table III) were combined with the experimental ground state rotational constants to yield the semiexperimental equilibrium rotational constants *A*_{*e*}, *B*_{*e*}, and *C*_{*e*} reported in Table VII. In this table, the corresponding equilibrium moments of inertia (conversion factor from Ref. 58) are also given together with the inertial defects Δ_0 and Δ_e . The equilibrium inertial defect should be zero for a planar molecule. The Δ_e values in Table VII are not exactly zero, but vary between − 0.003 80 and − 0.006 85 uÅ² for the different isotopic substitutions. This is due to the fact that the equilibrium rotational constants are not purely experimental, but contain corrections from theoretical calculations. Nevertheless, the Δ_e values are very small, which proves the high quality of the theoretical rotation–vibration interaction constants derived from the *ab initio* cubic force field.

TABLE VII. Experimental rotational constants,^a equilibrium rotational constants, equilibrium moments of inertia and inertial defects (Δ_0 and Δ_e) for the seven observed isotopomers of silene.

	H ₂ C ²⁸ SiH ₂	H ₂ C ²⁹ SiH ₂	H ₂ C ²⁸ SiHD	H ₂ C ²⁸ SiD ₂	H ₂ C ²⁹ SiD ₂	D ₂ C ²⁸ SiH ₂	D ₂ C ²⁹ SiH ₂
<i>A</i> ₀ (MHz)	104 716.63	104 716.56	80 865.859	63 852.738	63 852.90	77 446.63	77 446.19
<i>B</i> ₀ (MHz)	14 786.6268	14 667.1621	14 050.9525	13 471.795 85	13 392.7799	12 623.7173	12 509.955
<i>C</i> ₀ (MHz)	12 936.7328	12 845.1875	11 949.448 22	11 103.543 18	11 049.8157	10 837.9400	10 753.977
<i>A</i> _{<i>e</i>} (MHz)	105 459.63	105 459.56	81 325.859	64 142.738	64 142.90	77 943.63	77 943.19
<i>B</i> _{<i>e</i>} (MHz)	14 846.6268	14 727.1621	14 101.9525	13 517.795 85	13 438.7799	12 667.7173	12 552.955
<i>C</i> _{<i>e</i>} (MHz)	13 015.7328	12 924.1875	12 019.448 22	11 166.543 18	11 111.8157	10 887.9400	10 812.977
<i>I</i> _{<i>e</i>} ^a (uÅ ²)	4.826 16	4.792 16	6.214 25	7.878 98	7.878 96	6.483 90	6.483 94
<i>I</i> _{<i>e</i>} ^b (uÅ ²)	34.178 12	34.316 12	35.837 52	37.386 20	37.606 02	39.895 04	40.259 77
<i>I</i> _{<i>e</i>} ^c (uÅ ²)	39.065 43	39.103 35	42.046 78	45.258 33	45.481 23	46.373 82	46.738 20
Δ_0 (uÅ ²)	0.061 158	0.061 18	0.075 89	0.086 50	0.086 49	0.070 94	0.070 92
Δ_e (uÅ ²)	−0.003 83	−0.004 93	−0.004 99	−0.006 85	−0.003 75	−0.005 13	−0.005 51

^aAfter centrifugal distortion corrections leading to the so-called Watson's determinable constants.

TABLE VIII. Experimental equilibrium structure of silene, H_2CSiH_2 , and comparison with the *ab initio* geometry at the CCSD(T)/cc-pV(Q,T)Z level of theory.^a

	Experiment	<i>Ab initio</i>
Si=C	1.7039 (18) ^b	1.7043
C-H	1.0819 (12)	1.0824
Si-H	1.4671 (9)	1.4670
HCSi	122.00 (4)	122.06
HSiC	122.39 (3)	122.49

^aDistances are in Å and angles in degrees.

^bThe quoted accuracy corresponds to 15 standard deviations.

The equilibrium structure was deduced from a least-squares fit of the equilibrium rotational constants. These constants were weighted according to an estimate of the accuracy of the theoretical $X_e - X_0$ values where X denotes A , B , or C . This gave an extremely well-behaved fit with a very low condition number ($x = 16$) and low standard deviations (typically less than 0.0002 Å for the distances and less than 0.015° for the angles) indicating that the derived structure is likely to be very reliable. To check the sensitivity of the results to the weighting scheme, the iteratively reweighted least-squares method was used with the Tukey's biweight estimate.⁵⁹ The objective of this method is to find suitable weights to compensate for the deficiencies of the model (i.e., inaccuracy of the calculated rovibrational corrections). The derived structure was identical to that obtained with the standard weighted least-squares method but with still smaller standard deviations. The assignment of error limits to the refined parameters is a difficult task because the least-squares fit gives small standard deviations which are certainly too optimistic. The final results are still affected by small systematic errors (on rovibrational corrections) which are not properly taken into account in the least-squares procedure. The experimental equilibrium bond lengths and angles are given in Table VIII with an uncertainty corresponding to 15 standard deviations which seems to be a reasonable estimate of the possible error. These values are in exceptionally good agreement with the CCSD(T)/cc-pV(Q,T)Z theoretical results. Such a high-level correlated *ab initio* calculation with a very large basis set is expected to provide reliable geometries that are accurate to a few thousandths of an angstrom in bond length and to a few tenths of a degree in bond angles.^{40,60,61} Here, the agreement with experiment is even better than expected, i.e., about 0.0005 Å in bond lengths and 0.1° in bond angles.

VI. DISCUSSION

The goal of this work was not only the characterization of silene in the gas phase but also the determination of the equilibrium structure without any additional constraints. The agreement between experiment and theory is remarkable and demonstrates the quality of the CCSD(T)/cc-pV(Q,T)Z theoretical treatment for this type of molecule.

An early CISD calculation in 1986 by Colvin *et al.*¹² with a standard DZP basis set already gave accurate Si=C and C-H bond lengths of 1.703 and 1.083 Å, respectively,

but the Si-H bond length (1.459 Å) was too short by 0.008 Å. The current CCSD(T) calculations with a TZ2Pf basis set overestimate the Si=C double bond length, but predict the correct value when using the larger cc-pV(Q,T)Z or cc-pVQZ basis. Concerning the C-H and Si-H bond lengths, the theoretical results for silene are similar to those obtained for $\text{H}_2\text{C}=\text{S}$ and SiH_4 : the C-H bond length is slightly underestimated at the CCSD(T)/TZ2Pf level, while the Si-H bond length is overestimated. Both in silene and in silane, CCSD(T)/cc-pVQZ gives Si-H bond lengths that are too short by about 0.005 Å whereas the CCSD(T)/cc-pV(Q,T)Z predictions are essentially correct. In general, for bond lengths, the best theoretical values compared to experiment are obtained at the CCSD(T)/cc-pV(Q,T)Z level of theory. The same holds for the bond angles, even though they are well calculated also at lower levels of theory (see Table I).

The experimental determination of the Si=C double bond length in the parent molecule of the silaalkene family is important for reference purposes. The obtained value is in good agreement with the Si=C bond length measured by x-ray crystallography in $\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)_1(\text{SiMe}_2\text{Bu}_2)$: 1.702 Å.^{62,63} Larger differences are found in the tetrahydrofuran adduct where the Si=C bond is longer, 1.747 Å,⁶⁴ and in $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)_1\text{-adamantyl}$ where it is still longer, 1.764 Å.³ In this last case, the variation is probably due to the bulky 1-adamantyl substituent which twists the double bond by 14.6° and thereby lengthens it.^{11,65} Two measurements of the Si=C double bond length have been made on DMSE (1,1-dimethylsilaethylene), one by microwave spectroscopy which led to a value of $1.692(3)$ Å,¹⁹ which is 0.012 Å less than our value in silene, and another one obtained by electron diffraction yielding a surprisingly large value of $r_g(\text{Si}=\text{C}) = 1.83(4)$ Å.⁶⁶ This difference cannot be explained only by the fact that electron diffraction does not lead to the true r_e structure but to the r_g one, which corresponds to bond lengths and angles at thermal equilibrium; the r_e bond length should be smaller than r_g by only $0.01\text{--}0.02$ Å.⁶⁶ The two CH_3 substituents could increase the Si=C bond length, but certainly by much less than 0.1 Å. The early electron diffraction measurement⁶⁶ has been strongly criticized by Schaefer.¹¹ We agree with this criticism. The microwave-based structure of DMSE cannot be used as a reference for the Si=C double bond length because only the parameters of the planar C_2SiC skeleton were determined from the three rotational constants while all other structural parameters were constrained to their *ab initio* predictions.

In a recent paper, Izuha *et al.*⁶⁷ reported the first measurement of the millimeter-wave spectrum of silylidene, H_2CSi , and they estimated the C=Si bond length, $1.695(9)$ Å, which is in good agreement with our result for silene.

As expected, the Si=C double bond in silene, $r_e(\text{Si}=\text{C}) = 1.704(1)$ Å, is longer than the C=C double bond in ethylene, $r(\text{C}=\text{C}) = 1.3307(3)$ Å,⁶⁸ but shorter than the Si=Si bond in dibridged disilyne, $r(\text{Si}=\text{Si}) = 2.215$ Å,⁶⁹ or in monobridged disilyne, $r(\text{Si}=\text{Si}) = 2.119$ Å.⁷⁰ Even though these bridged molecules belong to the class of non-classical electron deficient compounds where the lines con-

necting neighboring atoms do not represent electron-pair bonds, the $\text{Si}=\text{Si}$ bond lengths are comparable to that calculated in the lowest-energy C_{2h} isomer of $\text{H}_2\text{Si}=\text{SiH}_2$ (2.16 Å)⁷¹ and look like double bonds.

The $\text{Si}=\text{C}$ double bond, $r(\text{Si}=\text{C}) = 1.704(1)$ Å is significantly shorter than the $\text{Si}-\text{C}$ single bond: in methylsilane, Wong *et al.*⁷² measured a $\text{Si}-\text{C}$ bond length of $1.864(1)$ Å. However, this shortening is less pronounced than the shortening of the $\text{C}-\text{C}$ bond: Harmony⁷³ has determined the length of the $\text{C}-\text{C}$ single bond in ethane, $1.522(2)$ Å, and the $\text{C}=\text{C}$ double bond length in ethylene is $1.331(1)$ Å.⁶⁸ This difference between the CC and the SiC bonds may be explained by the following argument:⁷⁴ the s and p orbitals of carbon have a comparable extension and can easily form hybrid orbitals; on the contrary, in silicon, the p orbitals are substantially more diffuse than the s orbitals and hybridization is not so efficient; therefore, the shortening of the double bond is not so pronounced.

For the $\text{C}-\text{H}$ bond length (1.0819 Å) and the $\angle\text{HCSi}$ angle (122.00°) in silene, there are significant but very small differences from ethylene, $r(\text{CH}) = 1.0809(3)$ Å and $\angle\text{CCH} = 121.44(3)^\circ$.⁶⁸ The $\text{Si}-\text{H}$ bond length (1.4671 Å) in silene is significantly shorter than in SiH_4 where it is $1.4732(2)$ Å.⁵² This shortening is quite similar to the behaviour of the $\text{C}-\text{H}$ bond length (1.0819 Å) which is 1.086 Å in CH_4 .⁷⁵

The short lifetime measured for silene confirms the results of Maier, Mihm, and Reisenauer.^{4,5} The IR absorptions due to silene in an Ar-matrix at 10 K disappeared when the temperature was increased up to 35 K, and they also disappeared when the matrix was irradiated in the UV at 254 nm. The observed lifetime definitively rules out the possibility of trapping and storing silene for several months at -196°C as reported by Auner and Grobe.⁷⁶

Maier *et al.*⁵ suggested that through the irradiation at 254 nm, silene was transformed into methylsilylene CH_3SiH . This can explain the weakness of the signal observed when silene was produced by photolysis of SBO at 193 nm. We plan to study in the near future the conversion of silene to methylsilylene in the gas phase and to measure the millimeter-wave spectrum of this compound.

VII. CONCLUSION

Unsubstituted silene was produced for the first time in the gas phase by pyrolysis of SBO. The observation of the millimeter-wave spectra of seven isotopomers and the theoretical calculation of the rovibrational interaction parameters led to the determination of the equilibrium structure of this molecule. The geometry parameters obtained are in exceptionally good agreement with their *ab initio* counterparts determined at the CCSD(T)/cc-pV(Q,T)Z level of theory. The yield of silene was lower when SCB was pyrolyzed, and much lower when DSCB was used. A photolysis experiment allowed the measurement of the lifetime of silene in the gas phase at low pressure.

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