

## Regular article

# Anharmonic force field and spectroscopic constants of silene: an ab initio study\*

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**Abstract.** High-level ab initio calculations with large basis sets are reported for silene,  $\text{H}_2\text{C}=\text{SiH}_2$ . Correlated harmonic force fields are obtained from coupled cluster CCSD(T) calculations with the cc-pVQZ basis (cc-pVTZ for H) while the anharmonic force fields are computed at the MP2/TZ2Pf level. There is excellent agreement with the available experimental data, in particular the equilibrium geometry and the fundamental vibrational frequencies. Many other spectroscopic constants are predicted for the  $C_{2v}$  isotopomers of silene.

**Key words:** Silene – Ab initio calculations – Anharmonic force field – Fundamental wavenumbers – Spectroscopic constants

## 1 Introduction

Very recently unsubstituted silene (silaethene,  $\text{H}_2\text{C}=\text{SiH}_2$ ) was produced for the first time in the gas phase by pyrolysis of a suitable precursor [1, 2]. The ground-state rotational constants obtained from the millimeter-wave spectra of seven isotopomers were corrected by ab initio rovibrational interaction constants to deduce the equilibrium rotational constants. A least-squares analysis of these data allowed the determination of the equilibrium structure, which was found to be in excellent agreement with theoretical ab initio predictions [1].

It is planned to record the rovibrational spectrum of gaseous silene at high-resolution [3]. Such attempts encounter severe difficulties due to the reactivity and the resulting short lifetime of silene which is only 30 ms in the gas phase at low pressure and room temperature [1, 2].

Some fundamental vibrational bands of silene were previously observed in an argon matrix at 10 K [4, 5]. The infrared spectrum was assigned by comparison with

theoretical calculations available at that time. Since then, the most advanced computation of the harmonic vibrational frequencies of silene employed configuration interaction wavefunctions with single and double excitations in conjunction with a polarized double-zeta basis [6]. In addition, the associated infrared absorption intensities were calculated at the Hartree-Fock self-consistent field (SCF) level of theory [6].

In this article we report accurate ab initio calculations of the harmonic and anharmonic force fields of silene. The theoretical predictions are expected to facilitate and guide the planned experimental work on the high-resolution rovibrational spectrum of silene.

## 2 Computational details

Quantum-chemical calculations were carried out at the correlated levels of second-order Møller-Plesset perturbation theory (MP2) [7] and coupled cluster theory with single and double excitations [8] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [9]. These calculations were performed with GAUSSIAN92 [10], a local version of ACESII [11, 12], and MOLPRO94 [13, 14].

Three different basis sets were employed: TZ2Pf denotes a valence triple-zeta plus double polarization plus *f* function basis set where Si is described by a (12s9p)/[6s5p] basis [15] with two sets of *d* and one set of *f* polarization functions [16]; C is represented by a (10s6p)/[5s3p] basis [17] with two sets of *d* and one set of *f* polarization functions [18]; finally H is described by a (5s)/[3s] basis (scale factor 1.2) [17] with two sets of *p* and one set of *d* polarization functions [18]. The second basis is the correlation-consistent polarized valence triple-zeta set (cc-pVTZ) [16, 18] which is a [5s4p2d1f/4s3p2d1f/3s2p1d] contraction of a (15s9p2d1f/10s5p2d1f/5s2p1d) primitive set for Si/C/H. The largest basis used in the present work and denoted as cc-pV(Q,T)Z is composed of the correlation consistent polarized valence quadruple-zeta basis (cc-pVQZ) [16, 18] at the nonhydrogen atoms and cc-pVTZ at H; cc-pVQZ corresponds to a [6s5p3d2f1g/5s4p3d2f1g] contraction of a (16s11p3d2f1g/12s6p3d2f1g) primitive set for Si/C.

\* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60<sup>th</sup> birthday

Spherical harmonics were used throughout. Unless stated otherwise, all electrons were correlated in the calculations. Additionally, the frozen core (fc) approximation was applied, i.e., the carbon  $1s$ -like and the silicon  $1s2s2p$ -like core molecular orbitals were required to remain doubly occupied in the correlated treatments. Nondynamical electron correlation is not overly important in silene [1]. Therefore, this species is well-described by single reference coupled cluster methods.

The molecular geometry of silene was optimized within the constraint of  $C_{2v}$  point group symmetry. Analytic energy gradients as implemented in the ACESII program [11] were used whenever all electrons were included in the correlation procedure; analytic gradients were also used for the geometry optimization at the MP2/TZ2Pf(fc) level [10]. In the remaining cases [CCSD(T) with the frozen core approximation] numerical gradients as implemented in ACESII [11] were employed. The largest internal gradient components at the stationary points did not exceed  $2 \times 10^{-6}$  a.u.

At the computed equilibrium geometries, harmonic force fields were evaluated either analytically (MP2 [10]; CCSD(T): TZ2Pf and cc-pVTZ [11,12]) or numerically from analytic CCSD(T)/cc-pV(Q,T)Z gradients [11]. Harmonic CCSD(T) force constants without inner-shell correlation contributions were calculated numerically from energies [11]. The normal modes and the harmonic spectroscopic constants were obtained in the usual manner [19, 20]. Electric dipole moments were determined as numerical derivatives of the potential energy with respect to a finite field component (0.003 a.u.) using the MOLPRO94 program [13]. The quadratic Cartesian CCSD(T)/cc-pV(Q,T)Z force constants were transformed to symmetry force constants using the INTDER program [21]. The symmetry-adapted internal coordinates were chosen as follows:

$$\begin{aligned} S_1(a_1) &= 2^{-1/2}(r_{12} + r_{13}) \\ S_2(a_1) &= 2^{-1/2}(r_{45} + r_{46}) \\ S_3(a_1) &= 2^{-1/2}(\alpha_{214} + \alpha_{314}) \\ S_4(a_1) &= r_{14} \\ S_5(a_1) &= 2^{-1/2}(\alpha_{541} + \alpha_{641}) \\ S_6(a_2) &= 2^{-1/2}(\tau_{2145} + \tau_{3146}) \\ S_7(b_1) &= 2^{-1/2}(\gamma_{2145} + \gamma_{3145}) \\ S_8(b_1) &= 2^{-1/2}(\gamma_{5412} + \gamma_{6412}) \\ S_9(b_2) &= 2^{-1/2}(r_{12} - r_{13}) \\ S_{10}(b_2) &= 2^{-1/2}(r_{45} - r_{46}) \\ S_{11}(b_2) &= 2^{-1/2}(\alpha_{214} - \alpha_{314}) \\ S_{12}(b_2) &= 2^{-1/2}(\alpha_{541} - \alpha_{641}), \end{aligned}$$

where  $r_{ij}$  is the bond length between atoms  $i$  and  $j$ ,  $\alpha_{ijk}$  is the angle enclosed by the bonds  $r_{ij}$  and  $r_{jk}$  with  $j$  being the apex atom,  $\tau_{ijkl}$  is the torsion angle between the planes formed by the atoms  $i-j-k$  and  $j-k-l$ , and  $\gamma_{ijkl}$  is the out-of-plane angle between the bond  $r_{ij}$  and the plane defined by the atoms  $j-k-l$ . The atoms are numbered as follows: C-1, H-2 and H-3 attached to C, Si-4, H-5 and H-6 attached to Si (with H-5 *cis* to H-2).

The MP2/TZ2Pf cubic and quartic normal coordinate force constants ( $\phi_{ijk}$ ,  $\phi_{ijkk}$ ) were determined with the use of a finite difference procedure [22] involving displacements along reduced 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 equilibrium geometry, the Cartesian gradient components did not exceed  $2 \times 10^{-7}$  a.u. The anharmonic spectroscopic constants were derived from the theoretical normal coordinate force fields applying standard formulas based on second-order rovibrational perturbation theory [23, 24].

### 3 Results and discussion

The results of our calculations are reported in Tables 1–12. Experimental data are included whenever available. Unless noted otherwise, all computed mass-dependent constants refer to the most abundant species  $H_2^{12}C=^{28}SiH_2$ . Other  $C_{2v}$  isotopomers of silene have been considered which are derived from the principal isotopomer by H/D exchange.

The computed equilibrium geometries of silene, both with and without the inner-shell correlation contributions are listed in Table 1. For comparison, the corresponding experimental [1] bond lengths and bond angles are also shown. Except for MP2/TZ2Pf(fc), these data have already been discussed [1]; therefore we only point out that our best predictions [CCSD(T)/cc-pV(Q,T)Z] are in excellent agreement with experiment [1]. At this level the frozen core approximation mainly affects the CSi and SiH bonds which are lengthened by about 0.009 Å and 0.007 Å, respectively. These relatively large changes indicate that the chosen basis sets are not ideal for treating core-valence correlation effects.

The computed harmonic vibrational wavenumbers  $\omega_i$  of silene are shown in Table 2. Qualitative descriptions of each mode derived from the associated potential energy distribution matrices are also given. The  $\omega_i$  values

**Table 1.** Computed and experimental equilibrium geometries (Å, deg) of silene ( $H_2C=SiH_2$ )

Method	Basis	CSi	CH	SiH	HCSi	HSiC
MP2	TZ2Pf(fc)	1.7112	1.0807	1.4702	121.83	122.66
CCSD(T)	TZ2Pf(fc)	1.7192	1.0828	1.4749	122.02	122.51
CCSD(T)	cc-pVTZ(fc)	1.7193	1.0833	1.4759	121.98	122.61
CCSD(T)	cc-pV(Q,T)Z(fc)	1.7130	1.0838	1.4741	122.03	122.49
MP2	TZ2Pf	1.7085	1.0777	1.4680	121.84	122.63
CCSD(T)	TZ2Pf	1.7167	1.0798	1.4727	122.03	122.49
CCSD(T)	cc-pVTZ	1.7126	1.0783	1.4730	121.91	122.88
CCSD(T)	cc-pV(Q,T)Z	1.7042	1.0824	1.4670	122.07	122.51
Experimental [1]		1.7039(18)	1.0819(12)	1.4671(9)	122.00(4)	122.39(3)

from MP2/TZ2Pf are larger than those from CCSD(T)/TZ2Pf, typically by up to 2.5% (exceptions are  $\omega_3$ ,  $\omega_8$ , and  $\omega_{12}$ ). Freezing the core molecular orbitals normally lowers the harmonic wavenumbers by up to  $13\text{ cm}^{-1}$  compared to the correlated all-electron results at a given theoretical level [note some larger changes for CCSD(T)/cc-pVTZ]. The CCSD(T) results show only a moderate basis set dependence, since the corresponding deviations exceed  $15\text{ cm}^{-1}$  only very rarely.

The computed harmonic vibrational wavenumbers  $\omega_i$  for the isotopomers  $\text{H}_2\text{C}=\text{SiD}_2$ ,  $\text{D}_2\text{C}=\text{SiH}_2$ , and  $\text{D}_2\text{C}=\text{SiD}_2$ , along with qualitative descriptions for each individual mode are shown in Table 3. Only the results obtained at the highest theoretical level [CCSD(T)/cc-pV(Q,T)Z] are presented. For each isotopic species the  $\omega_i$  values have been ordered by magnitude within each symmetry block, except for the first two totally symmetric stretches in  $\text{D}_2\text{C}=\text{SiH}_2$  where the order is re-

versed when anharmonicity corrections are included (see below). The corresponding  $\text{CD}_2$  and  $\text{SiH}_2$  stretches in  $\text{D}_2\text{C}=\text{SiH}_2$  are strongly mixed at the CCSD(T)/cc-pV(Q,T)Z level, but not at lower levels (see Table 3, footnotes b and c).

The computed infrared band intensities  $A_i$  of silene are collected in Table 4. The CCSD(T) results for the chosen basis sets are quite similar to one another. The MP2/TZ2Pf intensities are also qualitatively similar to the CCSD(T) results, except for the two wagging modes  $\omega_7$  and  $\omega_8$ . MP2/TZ2Pf predicts almost equal intensities for these two modes (analogous to a previous SCF study [6]), whereas the CCSD(T) calculations predict the  $\omega_7$  band to be significantly stronger (factor of 2). Experimentally [4, 5],  $\omega_7$  is observed, and  $\omega_8$  is not observed, which is more in line with the CCSD(T) data. Based on the CCSD(T)/cc-pV(Q,T)Z results, there should be two strong infrared bands ( $\omega_{10}$  and  $\omega_{11}$ ), several bands with

**Table 2.** Computed harmonic vibrational wavenumbers  $\omega_i$  ( $\text{cm}^{-1}$ ) of silene ( $\text{H}_2\text{C}=\text{SiH}_2$ )<sup>a</sup>

Mode	Description	MP2/TZ2Pf		CCSD(T)/TZ2Pf		CCSD(T)/cc-pVTZ		CCSD(T)/cc-pV(Q,T)Z	
		ae	fc	ae	fc	ae	fc	ae	fc
$a_1$	1 CH <sub>2</sub> sym stretch	3198	3191	3165	3157	3176	3149	3156	3144
	2 SiH <sub>2</sub> sym stretch	2345	2334	2303	2291	2289	2278	2293	2287
	3 CH <sub>2</sub> scissors	1404	1400	1408	1404	1411	1403	1401	1398
	4 SiC stretch + SiH <sub>2</sub> scissors	1006	1002	983	978	979	975	991	982
	5 SiH <sub>2</sub> scissors + SiC stretch	953	950	935	931	933	928	942	933
$a_2$	6 torsion	743	741	726	724	731	724	728	723
$b_1$	7 CH <sub>2</sub> wagging	757	756	757	755	782	765	767	760
	8 SiH <sub>2</sub> wagging	484	484	424	421	440	418	444	431
$b_2$	9 CH <sub>2</sub> asym stretch	3294	3291	3254	3251	3245	3243	3251	3239
	10 SiH <sub>2</sub> asym stretch	2366	2355	2324	2313	2308	2299	2313	2308
	11 CH <sub>2</sub> + SiH <sub>2</sub> rocking	835	833	833	831	830	830	830	829
	12 SiH <sub>2</sub> + CH <sub>2</sub> rocking	468	468	473	472	458	471	471	471

<sup>a</sup>ae = all electrons correlated; fc = frozen core approximation

**Table 3.** Computed<sup>a</sup> harmonic vibrational wavenumbers  $\omega_i$  ( $\text{cm}^{-1}$ ) of  $\text{H}_2\text{C}=\text{SiD}_2$ ,  $\text{D}_2\text{C}=\text{SiH}_2$ , and  $\text{D}_2\text{C}=\text{SiD}_2$

Mode	$\text{H}_2\text{C}=\text{SiD}_2$		$\text{D}_2\text{C}=\text{SiH}_2$		$\text{D}_2\text{C}=\text{SiD}_2$	
	Description	$\omega_i$	Description	$\omega_i$	Description	$\omega_i$
$a_1$	1 CH <sub>2</sub> sym stretch	3156	CD <sub>2</sub> + SiH <sub>2</sub> sym stretch <sup>b</sup>	2289	CD <sub>2</sub> sym stretch	2292
	2 SiD <sub>2</sub> sym stretch	1642	SiH <sub>2</sub> + CD <sub>2</sub> sym stretch <sup>c</sup>	2296	SiD <sub>2</sub> sym stretch	1641
	3 CH <sub>2</sub> scissors	1399	CD <sub>2</sub> scissors + SiC stretch	1124	CD <sub>2</sub> scissors + SiC stretch	1119
	4 SiC stretch	975	SiH <sub>2</sub> scissors	957	SiC stretch + CD <sub>2</sub> scissors	861
	5 SiD <sub>2</sub> scissors	685	SiC stretch + CD <sub>2</sub> scissors	857	SiD <sub>2</sub> scissors	683
$a_2$	6 torsion	660	torsion	599	torsion	515
$b_1$	7 CH <sub>2</sub> wagging	747	CD <sub>2</sub> wagging	620	CD <sub>2</sub> wagging	586
	8 SiD <sub>2</sub> wagging	346	SiH <sub>2</sub> wagging	430	SiD <sub>2</sub> wagging	344
$b_2$	9 CH <sub>2</sub> asym stretch	3251	CD <sub>2</sub> asym stretch	2417	CD <sub>2</sub> asym stretch	2417
	10 SiD <sub>2</sub> asym stretch	1675	SiH <sub>2</sub> asym stretch	2312	SiD <sub>2</sub> asym stretch	1675
	11 CH <sub>2</sub> rocking	772	SiH <sub>2</sub> + CD <sub>2</sub> rocking	747	CD <sub>2</sub> + SiD <sub>2</sub> rocking	659
	12 SiD <sub>2</sub> + CH <sub>2</sub> rocking	386	CD <sub>2</sub> + SiH <sub>2</sub> rocking	393	SiD <sub>2</sub> + CD <sub>2</sub> rocking	337

<sup>a</sup>CCSD(T)/cc-pV(Q,T)Z. Ordering of  $\omega_i$  by symmetry and magnitude, except for  $\omega_1$  and  $\omega_2$  of  $\text{D}_2\text{C}=\text{SiH}_2$

<sup>b</sup>At the MP2/TZ2Pf and CCSD(T)/cc-pV(Q,T)Z(fc) levels: almost pure and mainly CD<sub>2</sub> sym stretch

<sup>c</sup>At the MP2/TZ2Pf and CCSD(T)/cc-pV(Q,T)Z(fc) levels: almost pure and mainly SiH<sub>2</sub> sym stretch

medium intensity ( $\omega_7$ ,  $\omega_2$ ,  $\omega_5$ ,  $\omega_4$ , and  $\omega_8$ ), two weak bands ( $\omega_3$  and  $\omega_{12}$ ), and two extremely weak absorptions ( $\omega_1$  and  $\omega_9$ , CH<sub>2</sub> stretching modes). Comparisons with experiment [4, 5] will be given later (see below).

The harmonic symmetry force constants of silene computed at the CCSD(T)/cc-pV(Q,T)Z level of theory, both with and without the frozen core approximation are shown in Table 5. Both force fields are quite similar

**Table 4.** Computed infrared band intensities  $A_i$  (km/mol)<sup>a</sup> of silene (H<sub>2</sub>C=SiH<sub>2</sub>)

Mode		MP2/ TZ2Pf	CCSD(T)/ TZ2Pf	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pV(Q,T)Z
$a_1$	1	0.3	0.5	0.5	0.4
	2	30.6	28.5	31.5	30.8
	3	7.2	5.4	4.8	6.2
	4	32.3	23.7	17.6	21.1
	5	19.7	21.1	28.3	24.2
$a_2$	6	–	–	–	–
$b_1$	7	33.6	35.7	37.8	39.2
	8	32.1	17.3	16.4	16.1
$b_2$	9	0.4	0.0	0.1	0.0
	10	72.7	69.0	81.1	73.6
	11	60.4	56.0	58.5	58.1
	12	5.7	6.4	8.6	7.0

<sup>a</sup>Obtained from the electric dipole moment derivatives in double harmonic approximation

**Table 5.** Computed harmonic symmetry force constants  $F_{ij}$ <sup>a</sup> of silene

$i$	$j$	CCSD(T)/cc-pV(Q,T)Z	
		$F_{ij}$	$F_{ij}$ (fc)
1	1	5.645	5.604
1	2	0.002	0.002
1	3	-0.158	-0.160
1	4	0.022	0.022
1	5	0.025	0.025
2	2	3.060	3.045
2	3	0.032	0.035
2	4	0.076	0.073
2	5	-0.068	-0.070
3	3	1.219	1.219
3	4	0.280	0.276
3	5	0.050	0.049
4	4	5.431	5.306
4	5	0.178	0.175
5	5	1.131	1.123
6	6	0.171	0.170
7	7	0.301	0.296
7	8	-0.127	-0.127
8	8	0.277	0.268
9	9	5.635	5.593
9	10	0.010	0.009
9	11	0.145	0.145
9	12	-0.037	-0.036
10	10	3.026	3.012
10	11	-0.028	-0.027
10	12	0.047	0.046
11	11	0.257	0.261
11	12	-0.121	-0.121
12	12	0.415	0.414

<sup>a</sup>Units are consistent with energy in aJ, bond lengths in Å, and angles in radians

and may therefore be discussed together. Not unexpectedly, the  $a_1$  block is dominated by the diagonal stretching constants  $F_{11}$ ,  $F_{44}$ , and  $F_{22}$ . It is also obvious that many of the nondiagonal constants are rather small in absolute value, i.e., less than 0.1 aJ Å<sup>-2</sup> ( $F_{12}$ ,  $F_{14}$ ,  $F_{24}$ ), 0.1 aJ Å<sup>-1</sup> rad<sup>-1</sup> ( $F_{15}$ ,  $F_{23}$ ,  $F_{25}$ ) or 0.1 aJ rad<sup>-2</sup> ( $F_{35}$ ), respectively. The situation is similar in the  $b_2$  block: again the diagonal stretching force constants  $F_{99}$  and  $F_{10,10}$  are dominant, and there are relatively many small interaction constants ( $F_{9,10}$ ,  $F_{9,12}$ ,  $F_{10,11}$ ,  $F_{10,12}$ ). The current quadratic force constants of silene are believed to be quite accurate, and it is hoped that they may be useful as reference data when constructing general empirical force fields for silaalkenes.

The rotational constants of silene, both for the equilibrium ( $A_e$ ,  $B_e$ ,  $C_e$ ) and for the ground state ( $A_0$ ,  $B_0$ ,  $C_0$ ) are listed in Table 6. Due to the excellent agreement of the CCSD(T)/cc-pV(Q,T)Z equilibrium geometry with the experimentally determined  $r_e$  structure [1] (see Table 1) it is not surprising that the calculated rotational constants have errors as small as 0.24% ( $A_e$ ,  $A_0$ ) and 0.07–0.08% ( $B_e$ ,  $C_e$ ,  $B_0$ ,  $C_0$ ), respectively. Neglecting core correlation effects lengthens the C–Si and Si–H bonds considerably at the CCSD(T)/cc-pV(Q,T)Z(fc) level (see Table 1) which is reflected in an underestimate of the respective rotational constants by 0.55–1.05%.

Table 6 also compares theoretical equilibrium values for the quartic centrifugal distortion constants ( $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ ,  $\delta_K$ ) with the corresponding experimental values for the vibrational ground state [1]. Keeping the limitations of such a comparison in mind, there is reasonable

**Table 6.** Equilibrium ( $A_e$ ,  $B_e$ ,  $C_e$ ) and ground state ( $A_0$ ,  $B_0$ ,  $C_0$ ) rotational constants (cm<sup>-1</sup>), equilibrium quartic centrifugal distortion constants ( $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ ,  $\delta_K$ ) (10<sup>-6</sup> cm<sup>-1</sup>), and equilibrium electric dipole moment  $\mu_e$  (Debye) of silene (H<sub>2</sub>C=SiH<sub>2</sub>)

Constant	CCSD(T) <sup>a</sup>		Experiment <sup>a,b</sup> Ref. [1] <sup>c</sup>
	cc-pV(Q,T)Z	cc-pV(Q,T)Z(fc)	
$A_e$	3.5261	3.4985	3.5178
$B_e$	0.4948	0.4900	0.4952
$C_e$	0.4339	0.4298	0.4342
$A_0$	3.5014	3.4737	3.4930
$B_0$	0.4928	0.4880	0.4932
$C_0$	0.4312	0.4272	0.4315
$\Delta_J$	0.407	0.404	0.422 <sup>d</sup>
$\Delta_{JK}$	5.305	5.218	5.366 <sup>d</sup>
$\Delta_K$	58.626	57.926	63.6 <sup>d</sup>
$\delta_J$	0.0547	0.0543	0.0578 <sup>d</sup>
$\delta_K$	4.005	3.952	4.30 <sup>d</sup>
$\mu_e$	0.693	0.684	<sup>e</sup>
$\mu_e$ (H <sub>2</sub> C=O)	2.339	2.343	2.3321(5) [25]
$\mu_e$ (H <sub>2</sub> C=S)	1.694	1.710	1.6491(4) [25], 1.6483(7) [26]
$\mu_e$ (H <sub>2</sub> C=PH)	0.913	0.930	0.869(3) [27], 0.860(1) [28]

<sup>a</sup>Ground-state corrections  $A_e - A_0$ ,  $B_e - B_0$ ,  $C_e - C_0$  from the MP2/TZ2Pf cubic force field

<sup>b</sup>The experimental data are generally known to more significant digits than reproduced here, except for  $\Delta_K$ ,  $\delta_K$ , and the electric dipole moments. For details see Ref. [1]

<sup>c</sup>For rotational and centrifugal distortion constants

<sup>d</sup>Ground-state values

<sup>e</sup>Unknown

agreement: the theoretical constants are 1–8% (all electrons correlated) and 3–9% (frozen cores) smaller than their experimental counterparts. The average errors amount to 5–6%.

Finally, CCSD(T)/cc-pV(Q,T)Z results for the electric dipole moment of silene and structurally related molecules, i.e., formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ), thioformaldehyde ( $\text{H}_2\text{C}=\text{S}$ ), and phosphoethene ( $\text{H}_2\text{C}=\text{PH}$ ), are also shown in Table 6. All dipole moments have been calculated at the corresponding theoretical equilibrium geometries. The computed values for silene (with and without core correlation contributions) agree within 0.01 D and are very close to 0.70 D (see Table 6). This is a predicted value, since an experimentally derived electric dipole moment value is not yet available for silene. In the case of formaldehyde, thioformaldehyde, and phosphoethene, accurate dipole moments have been measured in the ground states of these molecules [25–28], and the corresponding data are also shown in Table 6. For these three species the largest deviation between theory and experiment occurs for phosphoethene and amounts to 0.070 D. The error in the predicted dipole moment of silene may be of similar magnitude.

Theoretical (MP2/TZ2Pf) results for the vibration-rotation coupling constants  $\alpha_i^X$  ( $X = A, B, C$ ;  $i = 1-12$ ) of silene are listed in Table 7. These constants have been used to obtain the differences between the equilibrium and the ground state rotational constants ( $A_e - A_0$ ,  $B_e - B_0$ ,  $C_e - C_0$ ) given in Table 6. In several cases complications due to Coriolis interactions [23, 24] arise. We have removed Coriolis contributions from the perturbational expressions of the  $\alpha_i^X$  constants [24] if the interacting vibrational levels are closer than  $200 \text{ cm}^{-1}$  and if the associated Coriolis coupling constants  $\zeta_{ij}^x$  ( $x = a, b, c$ ) are greater than 0.1. Corresponding effective (starred) values

$\alpha_i^{X*}$  are also given in Table 7 (for further details see footnotes c–i). So far no experimental information about the vibrational dependence of the rotational constants in silene is available. The errors in the predicted  $\alpha_i^X$  constants should usually be smaller than 20%, but larger errors cannot be excluded in special cases (e.g., Coriolis resonances).

The anharmonicity constants  $x_{ij}$  of silene calculated at the MP2/TZ2Pf level are shown in Table 8. These constants depend on the quadratic, cubic, and quartic force fields [23, 24]. Strong anharmonic interactions between fundamentals and overtones or combination states may lead to a breakdown of the corresponding perturbational formulas [23, 24]. It is then necessary to define effective (starred) constants by excluding the respective contributions from the perturbational summations [24]. Such effective anharmonicity constants are introduced here to account for the Fermi interactions  $v_3/2v_7$ ,  $v_4/2v_8$ , and  $v_5/2v_8$  in silene. In these three cases, the perturbational and variational MP2/TZ2Pf values for the anharmonic shifts of  $v_3$ ,  $v_4$ , and  $v_5$  differ by more than the  $2 \text{ cm}^{-1}$  (up to  $4 \text{ cm}^{-1}$ ) which has been adopted as our criterion for an explicit treatment of cubic interactions [29]. All computed anharmonicity constants of silene serve as predictions. They are used to derive the anharmonicity corrections  $\omega_i - v_i$  [24] for the vibrational wavenumbers of silene.

Our best theoretical estimates of the fundamental vibrational wavenumbers  $v_i$  of silene are presented in Table 9. The theoretical values are obtained from CCSD(T)/cc-pV(Q,T)Z harmonic wavenumbers  $\omega_i$  (see Table 2) and MP2/TZ2Pf anharmonicity corrections  $\omega_i - v_i$  which are also included in Table 9. In the case of explicitly treated Fermi interactions which affect the fundamentals  $v_3$ ,  $v_4$ , and  $v_5$  (see above) the corre-

**Table 7.** Computed<sup>a</sup> vibration-rotation interaction constants ( $\text{cm}^{-1}$ ) of silene ( $\text{H}_2\text{C}=\text{SiH}_2$ )

$i$	$\alpha_i^A \cdot 10^2$	$\alpha_i^B \cdot 10^4$	$\alpha_i^C \cdot 10^4$	Effective values <sup>b</sup>		
				$\alpha_i^{A*} \cdot 10^2$	$\alpha_i^{B*} \cdot 10^4$	$\alpha_i^{C*} \cdot 10^4$
1	2.070	6.588	8.300			
2	2.648	3.554	6.591			
3	-2.262	-9.140	5.678			
4	-1.441	5.579	12.574			
5	-1.807	-3.284	5.792		0.010 <sup>d</sup>	16.033 <sup>c</sup>
6	4.539	-15.895	-0.834		-19.486 <sup>f</sup>	10.031 <sup>e</sup>
7	0.789	13.683	-5.671	-2.097 <sup>g</sup>	10.389 <sup>d</sup>	
8	-9.759	19.977	-1.197	6.624 <sup>h</sup>		
9	1.438	8.645	7.891			
10	2.003	4.568	5.458			
11	-9.782	-13.800	9.720	-6.896 <sup>g</sup>	-10.209 <sup>f</sup>	6.261 <sup>c</sup> , 5.480 <sup>e</sup> , 2.021 <sup>i</sup>
12	16.519	19.676	-1.313	0.136 <sup>h</sup>		

<sup>a</sup> MP2/TZ2Pf

<sup>b</sup> Calculated without the contributions from the Coriolis interactions specified in footnotes c–i

<sup>c</sup>  $|\zeta_{4,11}^c| = 0.2804$ ,  $\omega_4 - \omega_{11} = 171.6 \text{ cm}^{-1}$

<sup>d</sup>  $|\zeta_{5,7}^b| = 0.2560$ ,  $\omega_5 - \omega_7 = 196.0 \text{ cm}^{-1}$

<sup>e</sup>  $|\zeta_{5,11}^c| = 0.2589$ ,  $\omega_5 - \omega_{11} = 118.9 \text{ cm}^{-1}$

<sup>f</sup>  $|\zeta_{6,11}^b| = 0.1841$ ,  $\omega_6 - \omega_{11} = -92.0 \text{ cm}^{-1}$

<sup>g</sup>  $|\zeta_{7,11}^a| = 0.2109$ ,  $\omega_7 - \omega_{11} = -77.1 \text{ cm}^{-1}$

<sup>h</sup>  $|\zeta_{8,12}^a| = 0.2271$ ,  $\omega_8 - \omega_{12} = 15.7 \text{ cm}^{-1}$

<sup>i</sup> Without the contributions from both  $\zeta_{4,11}^c$  and  $\zeta_{5,11}^c$  (see footnotes c and e)

**Table 8.** Computed<sup>a</sup> anharmonicity constants  $x_{ij}$  ( $\text{cm}^{-1}$ ) of silene ( $\text{H}_2\text{C}=\text{SiH}_2$ )<sup>b</sup>

1	2	3	4	5	6	7	8	9	10	11	12	$j/i$
-27.11	-0.06	-5.93	-1.47	-0.52	-4.41	-6.51	-3.78	-113.25	-0.06	-6.14	-2.07	1
	-16.35	-1.30	-2.10	-6.11	-3.06	-1.79	-5.72	+0.21	-64.15	-2.83	-2.15	2
		-9.13	-1.60	-1.12	-4.94	-4.75*	+6.79	-17.89	-1.01	-1.45	+3.18	3
			-2.24	-4.60	-1.67	-4.21	-7.74*	-1.23	-3.09	-2.29	+1.05	4
				-0.70	-0.54	-1.89	-3.56*	-0.09	-7.03	-0.53	+1.80	5
					+0.21	-5.96	-3.78	-3.51	-3.06	+0.33	+3.37	6
						+1.97*	-0.30	-10.92	-2.02	+3.31	+2.41	7
							<sup>c</sup>	-5.38	-6.42	+3.65	+1.82	8
								-31.32	+0.31	-6.96	-2.65	9
									-16.37	-2.47	-2.01	10
										+0.08	-7.06	11
											+2.46	12

<sup>a</sup>MP2/TZ2Pf<sup>b</sup>The right upper triangle of the symmetric matrix formed by the  $x_{ij}$  values is given. Values which are affected by Fermi interactions are marked by an asterisk. The corresponding data are effective values without the contribution from the relevant cubic interaction. To be more specific:  $x_{37}$  and  $x_{77}$  without the contributions from  $\nu_3/2\nu_7$ ,  $x_{48}$  without the contribution from  $\nu_4/2\nu_8$ , and  $x_{58}$  without the contribution from  $\nu_5/2\nu_8$ . For  $x_{88}$  see footnote c<sup>c</sup> $x_{88}$  is affected by the Fermi interactions  $\nu_4/2\nu_8$  and  $\nu_5/2\nu_8$ ; specific effective values for  $x_{88}$  depend on which contribution is excluded:  $x_{88}^* = +9.68 \text{ cm}^{-1}$  without the contribution from  $\nu_4/2\nu_8$ ,  $x_{88}^{\#} = -3.48 \text{ cm}^{-1}$  without the contribution from  $\nu_5/2\nu_8$ ,  $x_{88}^{\dagger} = +4.73 \text{ cm}^{-1}$  without the contributions from  $\nu_4/2\nu_8$  and  $\nu_5/2\nu_8$ 

sponding Fermi shifts have been computed by matrix diagonalization using CCSD(T)/cc-pV(Q,T)Z harmonic wavenumbers and cubic force constants from MP2/TZ2Pf. We have generated two theoretical data sets for the fundamentals, using harmonic wavenumbers calculated either by correlating all electrons (ae) or only the valence electrons (fc). The root-mean-square deviation between these two data sets is  $8 \text{ cm}^{-1}$ ; the individual deviations lie in the range  $0\text{--}12 \text{ cm}^{-1}$ . For convenience, the associated theoretical infrared band intensities  $A_i$  in silene have been added to Table 9 (taken from Table 4). In matrix isolation studies (argon, 10 K) [4, 5] 7 out of 12 fundamental wavenumbers of silene have been observed. These experimental data

are also listed in Table 9 to allow comparison with the corresponding theoretical values: the deviations lie between  $1\text{--}14 \text{ cm}^{-1}$  (ae) and  $0\text{--}17 \text{ cm}^{-1}$  (fc), respectively. Except for two cases [ $\nu_7$ (ae),  $\nu_4$ (fc)], the errors do not exceed  $10 \text{ cm}^{-1}$ . This agreement is remarkable and very satisfying, especially when taking into account that at the chosen level of theory errors of about  $10 \text{ cm}^{-1}$  have to be expected on average [30] and that the argon matrix may induce shifts in the observed fundamental wavenumbers. These shifts may be of the order of 0.5% compared with the gas phase [31] which means about  $5\text{--}10 \text{ cm}^{-1}$  on an absolute scale (shifts that are twice as large are not excluded [31]). Five fundamentals have not been observed experimentally [4, 5], i.e.,  $\nu_1$ ,  $\nu_6$

**Table 9.** Computed anharmonicity corrections  $\omega_i - \nu_i$  ( $\text{cm}^{-1}$ ), fundamental vibrational wavenumbers  $\nu_i$  ( $\text{cm}^{-1}$ ), and infrared band intensities  $A_i$  ( $\text{km/mol}$ ) of silene ( $\text{H}_2\text{C}=\text{SiH}_2$ ). The observed [5] fundamentals ( $\text{cm}^{-1}$ ) are also given

Mode	MP2 <sup>a</sup>		CCSD(T) <sup>b</sup>		Exp.	
	TZ2Pf		cc-pV(Q,T)Z	cc-pV(Q,T)Z(fc)		
	$\omega_i - \nu_i$		$\nu_i$	$A_i$		$\nu_i$
$a_1$	1	126.4	3030	0.4	3018	not observed
	2	77.2	2216	30.8	2210	2219 (m)
	3	33.3*	1353 (14.5)	6.2	1350 (15.5)	1350
	4	18.9*	978 (-5.8)	21.1	968 (-5.1)	985 (w)
	5	13.5*	931 (-2.5)	24.2	921 (-1.9)	927 (w)
$a_2$	6	13.2	714	–	710	IR-inactive
$b_1$	7	12.4	755	39.2	748	741 (s)
	8	2.8	441	16.1	429	not observed
$b_2$	9	143.3	3108	0.0	3096	not observed
	10	78.2	2234	73.6	2229	2239 (m)
	11	11.1	818	58.1	818	817 (s)
	12	-3.8	474	7.0	475	not observed

<sup>a</sup>In the case of important cubic interactions, deperturbed values are given and are marked by an asterisk. The relevant interactions are:  $\nu_3/2\nu_7$ ,  $\nu_4/2\nu_8$ ,  $\nu_5/2\nu_8$ <sup>b</sup>Anharmonicity corrections from MP2/TZ2Pf. Values in parentheses: shifts ( $\text{cm}^{-1}$ ) due to cubic interactions (see footnote a) which must be added to the deperturbed  $\omega_i - \nu_i$  values to arrive at the total anharmonic shift of the corresponding vibrational wavenumber. These shifts have been calculated variationally using harmonic wavenumbers from the indicated level of theory and cubic force constants from MP2/TZ2Pf. The intensities  $A_i$  have been taken from Table 4<sup>c</sup>In parentheses: qualitative infrared absorption intensities according to Ref. [4]

(infrared inactive),  $\nu_8$ ,  $\nu_9$ , and  $\nu_{12}$ . In view of the almost vanishing infrared intensities for  $\nu_1$  and  $\nu_9$ , it is not surprising that the bands for the symmetric ( $\nu_1$ ) and antisymmetric ( $\nu_9$ )  $\text{CH}_2$  stretching modes have not been identified [4, 5]. On the other hand,  $\nu_8$  and also  $\nu_{12}$  are predicted with sufficient intensity so their bands should be observable as infrared absorptions.

In complete analogy to Table 9, our best theoretical estimates of the fundamental vibrational wavenumbers  $\nu_i$  of  $\text{H}_2\text{C}=\text{SiD}_2$  are listed in Table 10. Three anharmonic interactions affecting the fundamentals  $\nu_2$ ,  $\nu_3$ , and  $\nu_5$  of this isotopomer have been treated explicitly (see Table 10, footnote a). Again two theoretical data sets are included (ae and fc). The root-mean-square deviation between these two sets is  $9\text{ cm}^{-1}$ ; the individual deviations cover  $0\text{--}17\text{ cm}^{-1}$ . The largest individual deviation appears in  $\nu_5$  where the sign of the  $\nu_5/2\nu_8$  Fermi shift depends on the details of the correlation procedure (ae versus fc) (see Table 10). With the exception of  $\nu_5$ , the individual deviations lie in the range  $0\text{--}12\text{ cm}^{-1}$ , as in the case of the main isotopomer (see above). For  $\text{H}_2\text{C}=\text{SiD}_2$  seven fundamentals have been identified experimentally [4, 5] under analogous conditions as for  $\text{H}_2\text{C}=\text{SiH}_2$  (argon matrix, 10 K). The experimental results are also shown in Table 10. Theoretical [CCSD(T)/cc-pV(Q,T)Z] and experimental  $\nu_i$  values differ by  $1\text{--}17\text{ cm}^{-1}$  (ae) and  $1\text{--}9\text{ cm}^{-1}$  (fc), respectively. Except for  $\nu_7$ (ae), the errors are below  $10\text{ cm}^{-1}$ , i.e., the overall agreement between theory and experiment is as good as can be expected (see above). Five fundamentals of  $\text{H}_2\text{C}=\text{SiD}_2$  have not been detected [4, 5]:  $\nu_1$ ,  $\nu_5$ ,  $\nu_6$  (infrared inactive),  $\nu_8$ , and  $\nu_9$ . As in  $\text{H}_2\text{C}=\text{SiH}_2$ , the absence of the  $\text{CH}_2$  stretching bands  $\nu_1$  and  $\nu_9$  from the spectra is immediately explained by intensity arguments (see Table 10). However, according to the computed infrared intensities,  $\nu_5$  and  $\nu_8$  should be observable as medium and weak infrared absorption bands, respectively.

An earlier study [32] has claimed the preparation of silene by gas phase pyrolysis at low pressure using silacyclobutane and 1,3-disilacyclobutane as precursors.

The infrared spectra of the reaction products have been attributed to  $\text{H}_2\text{C}=\text{SiH}_2$  and  $\text{H}_2\text{C}=\text{SiD}_2$ , respectively [32]. These spectra are different from those observed in the argon matrix [4, 5], and there is no agreement between the assignment of the frequencies attributed to silene in Ref. [32] and the corresponding theoretical data in Tables 9 and 10. This confirms that silene was not seen in the early work [32].

Finally, our best theoretical estimates for the fundamentals in  $\text{D}_2\text{C}=\text{SiH}_2$  and  $\text{D}_2\text{C}=\text{SiD}_2$  are presented in Tables 11 and 12. The fundamental wavenumbers for these isotopomers have not yet been measured so the theoretical  $\nu_i$  values are predictions. Their accuracy should be similar as in the case of  $\text{H}_2\text{C}=\text{SiH}_2$  and

**Table 11.** Computed anharmonicity corrections  $\omega_i - \nu_i$  ( $\text{cm}^{-1}$ ), fundamental vibrational wavenumbers  $\nu_i$  ( $\text{cm}^{-1}$ ), and infrared band intensities  $A_i$  ( $\text{km/mol}$ ) of  $\text{D}_2\text{C}=\text{SiH}_2$ .

Mode	MP2 <sup>a</sup>		CCSD(T) <sup>b</sup>		
	TZ2Pf	cc-pV(Q,T)Z		cc-pV(Q,T)Z(fc)	
		$\omega_i - \nu_i$	$\nu_i$	$A_i^c$	$\nu_i$
$a_1$	1	71.4*	2238 (-21.1)	15.2	2229 (-20.1)
	2	75.7	2221	15.4	2214
	3	22.9*	1089 (11.4)	9.8	1084 (10.1)
	4	23.0	934	39.8	926
	5	15.7	842	0.6	835
$a_2$	6	9.4	589	–	586
$b_1$	7	9.5	611	15.8	605
	8	3.1	427	19.8	415
$b_2$	9	80.6	2337	0.1	2328
	10	78.0	2234	74.4	2229
	11	6.9	740	57.5	738
	12	-2.0	395	2.0	396

<sup>a</sup> See footnote a in Table 9. The relevant interactions are:  $\nu_1/2\nu_3$ ,  $\nu_3/\nu_{11} + \nu_{12}$

<sup>b</sup> See footnote b in Table 9

<sup>c</sup> At the MP2/TZ2Pf level where the modes 1 and 2 are almost pure  $\text{CD}_2$  and  $\text{SiH}_2$  stretches, respectively, the  $A_i$  ( $i = 1\text{--}12$ ) values are:  $a_1$ , 0.1, 30.9, 14.6, 43.1, 0.1;  $a_2$ , -;  $b_1$ , 8.2, 39.1;  $b_2$ , 0.6, 74.1, 59.3, 1.1

**Table 10.** Computed anharmonicity corrections  $\omega_i - \nu_i$  ( $\text{cm}^{-1}$ ), fundamental vibrational wavenumbers  $\nu_i$  ( $\text{cm}^{-1}$ ), and infrared band intensities  $A_i$  ( $\text{km/mol}$ ) of  $\text{H}_2\text{C}=\text{SiD}_2$ . The observed [5] fundamentals ( $\text{cm}^{-1}$ ) are also given

Mode	MP2 <sup>a</sup>		CCSD(T) <sup>b</sup>			Exp. Refs. [4, 5]
	TZ2Pf	cc-pV(Q,T)Z		cc-pV(Q,T)Z(fc)		
		$\omega_i - \nu_i$	$\nu_i$	$A_i$	$\nu_i$	Ar-matrix (10 K) <sup>c</sup>
$a_1$	1	125.9	3030	0.4	3018	not observed
	2	40.3*	1598 (3.1)	19.1	1592 (5.6)	1600 (m)
	3	34.5*	1341 (24.2)	4.3	1336 (26.4)	1335
	4	16.3	959	2.5	948	952 (w)
	5	6.9*	667 (11.8)	21.6	684 (-11.4)	not observed
$a_2$	6	11.0	649	–	645	IR-inactive
$b_1$	7	11.5	736	46.9	728	719 (s)
	8	1.3	344	7.7	335	not observed
$b_2$	9	143.3	3108	0.0	3096	not observed
	10	42.3	1633	44.6	1629	1635 (m)
	11	11.3	760	37.5	762	759 (s)
	12	-2.4	388	7.6	388	396 (w)

<sup>a</sup> See footnote a in Table 9. The relevant interactions are:  $\nu_2/\nu_4 + \nu_5$ ,  $\nu_3/2\nu_7$ ,  $\nu_5/2\nu_8$

<sup>b</sup> See footnote b in Table 9

<sup>c</sup> See footnote c in Table 9

**Table 12.** Computed anharmonicity corrections  $\omega_i - \nu_i$  ( $\text{cm}^{-1}$ ), fundamental vibrational wavenumbers  $\nu_i$  ( $\text{cm}^{-1}$ ), and infrared band intensities  $A_i$  ( $\text{km/mol}$ ) of  $\text{D}_2\text{C}=\text{SiD}_2$

Mode	MP2 <sup>a</sup>		CCSD(T) <sup>b</sup>		cc-pV(Q,T)Z(fc)
	TZ2Pf	cc-pV(Q,T)Z	cc-pV(Q,T)Z	cc-pV(Q,T)Z(fc)	
	$\omega_i - \nu_i$	$\nu_i$	$A_i$	$\nu_i$	
$a_1$	1	72.2*	2241 (-20.6)	0.0	2231 (-20.0)
	2	39.9	1601	18.3	1597
	3	19.3*	1094 (5.6)	5.4	1088 (6.1)
	4	17.4	844	0.9	837
	5	7.0*	666 (10.4)	21.2	680 (-9.4)
$a_2$	6	6.8	508	–	505
$b_1$	7	7.8	578	26.5	572
	8	1.9	343	8.4	333
$b_2$	9	80.6	2336	0.5	2328
	10	41.4	1633	44.6	1630
	11	6.6	652	36.3	652
	12	-1.4	338	3.4	339

<sup>a</sup> See footnote a in Table 9. The relevant interactions are:  $\nu_1/2\nu_3$ ,  $\nu_3/2\nu_7$ ,  $\nu_5/2\nu_8$

<sup>b</sup> See footnote b in Table 9

$\text{H}_2\text{C}=\text{SiD}_2$ , i.e., typically about  $10 \text{ cm}^{-1}$  with individual errors that may range up to about  $20 \text{ cm}^{-1}$ . Concerning the theoretical infrared intensities,  $A_1$  is close to zero for all isotopomers except  $\text{D}_2\text{C}=\text{SiH}_2$  (Table 11) where the totally symmetric  $\text{CD}_2$  and  $\text{SiH}_2$  stretching modes are energetically close and thus mix strongly. At the CCSD(T)/cc-pV(Q,T)Z level, this leads to significant intensity borrowing so the two bands  $\nu_1$  and  $\nu_2$  are predicted to have almost the same intensity (Table 11). The amount of mixing is quite sensitive to the theoretical level applied [e.g., much less mixing for MP2/TZ2Pf, see Table 11 footnote c, and also for CCSD(T)/cc-pVTZ].

## 4 Conclusions

Correlated harmonic [CCSD(T)/cc-pV(Q,T)Z] and anharmonic (MP2/TZ2Pf) force fields provide theoretical predictions for the fundamental vibrational wavenumbers and many other spectroscopic constants of silene and its deuterated isotopomers with  $C_{2v}$  symmetry. The present theoretical data compare very well with available experimental data [1, 2, 4, 5], but do not support the claim that silene has been detected during gas-phase pyrolysis of silacyclobutane and 1,3-disilacyclobutane [32]. The predictions for experimentally unknown spectroscopic constants are expected to be reliable enough to guide the planned high-resolution experimental work on silene.

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*Supporting information available.* Computed (MP2/TZ2Pf) vibration-rotation interaction and anharmonicity constants for  $\text{H}_2\text{CSiD}_2$ ,  $\text{D}_2\text{CSiH}_2$ , and  $\text{D}_2\text{CSiD}_2$  can be obtained upon request from the authors. Analogous data for  $\text{H}_2\text{CSiHD}$  are also available.

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