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Coupled-cluster calculations of C_2H_2Si and CNHSi structural isomers

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Results of large-scale coupled-cluster calculations of selected C_2H_2Si and CNHSi structural isomers are reported. Equilibrium molecular structures of a total of 12 molecules in their singlet electronic states have been calculated systematically employing the coupled-cluster singles and doubles model augmented by a perturbative correction for triple excitations (CCSD(T)) in combination with Dunning's hierarchy of correlation consistent basis sets. In addition, anharmonic force fields were calculated to yield fundamental vibrational frequencies and rotation-vibration interaction constants $\alpha_i^{A,B,C}$. The latter were used to determine empirical equilibrium structures r_e^{emp} of two molecules — silacyclopropenylidene, c-C_2H_2Si, and silapropadienylidene, H_2CCSi — for which sufficient isotopic data are available from literature. Very good agreement with theoretical equilibrium structures from CCSD(T) calculations employing core-valence basis sets of quadruple and quintuple-zeta quality — i.e., cc-pwCVQZ (337 basis functions), cc-pCV5Z, and cc-pwCV5Z (581 basis functions) is found — to within 0.001 Å for bond lengths and 0.1° for bond angles. Theoretical ground state rotational constants of HSiCN and HSiNC compare very favorably with experimental microwave data from literature, to within 0.15% (HSiCN) and 0.1% (HSiNC) for the B_0 and C_0 rotational constants. In the case of c-C_2H_2Si and H_2CCSi this agreement is even better than 0.1%. For the latter two molecules effects of higher-level electron-correlation and relativity to the equilibrium geometry as well as the electronic contributions to the rotational constants are investigated. For eight molecules not yet studied at high spectral resolution in the gas-phase theoretical molecular parameters are provided to support future laboratory investigations. Theoretical vibrational fundamentals compare well with data of eight species studied previously with infrared matrix isolation spectroscopy. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Silicon belongs to the ten most abundant elements in the cosmos and hence plays a vital role in astrochemistry. As of May 2009, eleven silicon bearing molecules have been detected in space corresponding to almost 10% of the total number of known astronomical molecules.[1] Here, the circumstellar shell of the prototypical late-type star IRC +10 216 has been found to be particularly rich in these molecules.[2,3] Because of their importance for radio astronomy and astrochemistry, several transient silicon bearing molecules have also been studied in the gas phase in the laboratory mainly through rotational spectroscopy.[3] Owing to their similarity to known astronomical molecules, those of the composition C_2H_2Si and CNHSi (see Fig. 1) might be abundant in space as well. Silacyclopropenylidene, c-C_2H_2Si (molecule **1** in Fig. 1), is a dihydrogenated variant of c-SiC_2 which is one of the most abundant molecules in circumstellar shells.[2,4] HSiCN (cyanosilylene, **7**) and HSiNC (isocyanosilylene, **8**) are closed-shell hydrogenated forms of the SiCN and SiNC radicals, both of which are known in IRC +10216.[5,6]

Initial experimental evidence for C_2H_2Si and CNHSi isomers in the laboratory was obtained through infrared matrix isolation spectroscopy performed by the Maier group at Gießen. Their study of C_2H_2Si isomers led to the characterization of silacyclopropenylidene (c-C_2H_2Si, **1**), vinylidenesilanediyl (H_2CCSi, **2**), ethinylsilylene (HSiCCH, **3**), and silacyclopropyne (c-H_2SiC_2, **5**).[7,8] The matrix study of CNHSi isomers[9] revealed evidence for HSiCN (**7**), HSiNC (**8**), azasilacyclopropenylidene (c-CHNSi, **9**), and silaisocyanocarbene, HCNSi (**10**). Subsequently, a total of four C_2H_2Si and CNHSi molecules were also studied by high resolution spectroscopic techniques, i.e., microwave- and millimeter-wave spectroscopy. The millimeter wave spectrum of silacyclopropenylidene (**1**) was reported[10] as was a Fourier transform microwave (FTMW) study of H_2CCSi (**2**).[11] In case of CNHSi structural isomers, HSiCN (**7**) and HSiNC (**8**) were identified in the gas phase through FTMW spectroscopy.[12]

Both molecular systems were also subject of several theoretical investigations. Pioneering quantum-chemical calculations of the C_2H_2Si system were performed by Frenking *et al.*[13] through which silacyclopropenylidene (**1**) was identified as the global minimum on the potential energy surface. A first coupled-cluster study of **1**, **5**, and **6** was then reported by

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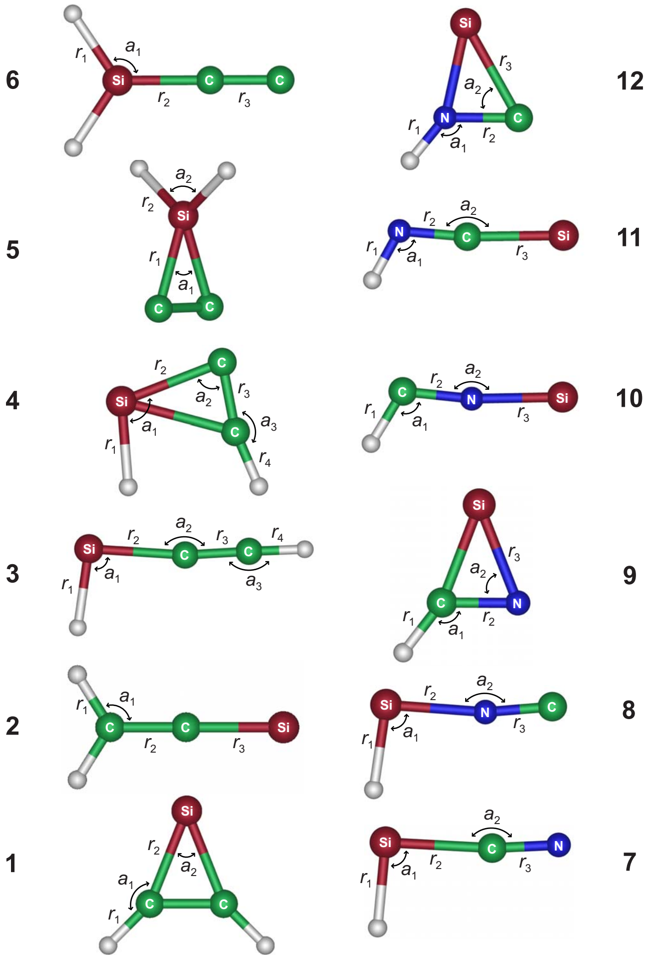

FIG. 1. (Color online) C_2H_2Si (left column) and CNHSi (right column) structural isomers investigated here. c-C_2H_2Si (1) and HSiCN (7) are the global minima on the C_2H_2Si and CNHSi potential energy surfaces, respectively. The isomers are ordered from bottom to top according to their relative stability. All molecules are planar except for 5 where the HSiH and CSiC planes are arranged perpendicularly.

Sherrill *et al.*[14] Recently, frozen-core CCSD(T)/cc-pVTZ calculations of six C_2H_2Si isomers were reported by Ikuta *et al.*[15] to determine equilibrium structures, ionization potentials, and electron affinities. The authors also identified another silacyclopropenylidene **4** as a minimum on the potential energy surface (PES). In case of the isoelectronic CNHSi family, Maier *et al.*[9] found the bent chain HSiCN (**7**) to be the global minimum on the PES followed by the chain molecule HSiNC (**8**) and cyclic azasilacyclopropenylidene (**9**), a result confirmed by more recent theoretical studies.[16,17]

The present paper reports results of high-level *ab initio* calculations of selected molecular properties of singlet C_2H_2Si and CNHSi structural isomers. In detail the study comprises the determination of molecular equilibrium structures obtained at the CCSD(T) level of theory[18] using Dunning's hierarchy of correlation consistent basis sets[19–22] and evaluation of harmonic and anharmonic force fields at selected levels of theory to determine centrifugal distortion constants, vibration-rotation interaction constants, and harmonic as well as fundamental vibrational frequencies. For molecules for which sufficient laboratory isotopic data are available, i.e., c-C_2H_2Si (**1**) and H_2CCSi (**2**), the combination of experimental ground state rotational constants and rotation-vibration interaction constants $\alpha_i^{A,B,C}$ from theory has been used to evaluate empirical equilibrium structures r_e^{emp}. Additionally, for energetically higher lying C_2H_2Si and CNHSi structural isomers the combination of theoretical equilibrium rotational and rotation-vibration interaction constants is used to predict accurate ground-state rotational constants. The determination of fundamental vibrational frequencies permitted a qualitative comparison against infrared data from matrix isolation experiments for more than half a dozen molecules of the sample. Additionally, spectroscopically important parameters such as dipole moments and ^{14}N nitrogen quadrupole coupling constants have been calculated.

The molecules studied here are promising candidates for future laboratory spectroscopic studies in particular by FTMW spectroscopy.

II. THEORETICAL METHODS

Quantum chemical calculations were performed with the 2005 Mainz-Austin-Budapest version of ACESII[23] employing coupled-cluster (CC) theory[24] in its variant CCSD(T).[18] Some calculations were performed using the development version of CFOUR[25] at Mainz with its recent parallel implementation of CC energy and first- and second-derivative algorithms[26] and calculations at the CCSDT(Q)[27,28] level were performed with the string-based many-body code MRCC[29] which has been interfaced to CFOUR. In the frozen-core (fc) approximation, Dunning's d augmented correlation consistent basis sets cc-pV($X+d$)Z[19] with X=T and Q were employed for the silicon atom and standard basis sets cc-pVXZ[20] for hydrogen, carbon, and nitrogen [denoted as CCSD(T)/cc-pV($X+d$)Z in the following]. For calculations correlating all electrons the basis sets cc-pCVXZ[21,22] and their weighted variants cc-pwCVXZ[22] with X=T, Q, and 5 were used, the former type, however, only for the structural optimization of a subsample of molecules — c-C_2H_2Si (**1**), H_2CCSi (**2**), HSiCN (**7**), and HSiNC (**8**) — to study differences in its performance against the weighted basis sets.

Equilibrium geometries were calculated using analytic gradient techniques.[30] Harmonic and anharmonic force fields were calculated using analytic second-derivative techniques[31,32] followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force field.[32,33] While the CCSD(T)/cc-pVQZ level of theory has been found to yield molecular force fields of very high quality and is hence often used as the level of choice in these calculations (e.g., Refs. 34–36), it is computationally (rather) demanding for larger molecules and/or molecules carrying second row elements such as those studied here. At the same time it has been shown on a number of occasions, that accurate empirical equilibrium structures are obtained also with zero-point vibrational corrections computed using smaller basis sets such as cc-pVTZ (see, e.g., Refs. 37–41). As a consequence, the force fields in the present study were calculated at the CCSD(T)/cc-pV(T+d)Z level of theory in the fc approximation for the total sample of 12 molecules. For a subsample of those, the two

TABLE I. CCSD(T) and experimental structural parameters of *c*-C_2H_2Si (**1**, in Å and degrees).

Basis set	r_1	r_2	$r_{C=C}$	a_1	a_2
(fc)cc-pV(T+*d*)Z	1.0825	1.8323	1.3517	156.57	43.29
(fc)cc-pV(Q+*d*)Z	1.0819	1.8255	1.3483	156.60	43.35
cc-pCVTZ	1.0816	1.8279	1.3479	156.53	43.27
cc-pwCVTZ	1.0811	1.8232	1.3467	156.61	43.35
cc-pCVQZ	1.0804	1.8188	1.3448	156.58	43.39
cc-pwCVQZ	1.0803	1.8176	1.3445	156.59	43.41
cc-pCV5Z	1.0801	1.8169	1.3440	156.59	43.42
cc-pwCV5Z	1.0801	1.8165	1.3439	156.58	43.42
r_e^{emp}(ff1)[a]	1.0803	1.8172	1.3441	156.59	43.41
r_e^{emp}(ff2)[b]	1.0803	1.8171	1.3440	156.60	43.41
r_e^{emp}(ff3)[c]	1.0802	1.8172	1.3439	156.58	43.40
r_s[d]	1.0795	1.8200	1.3458	156.54	43.40

[a] From force field calculated at the (fc)CCSD(T)/cc-pV(T+*d*)Z level of theory.

[b] From force field calculated at the CCSD(T)/cc-pwCVTZ level of theory.

[c] From force field calculated at the (fc)CCSD(T)/cc-pV(Q+*d*)Z level of theory.

[d] Reference 10.

energetically lowest structural isomers of either family, harmonic, and anharmonic force fields were also obtained at the CCSD(T)/cc-pwCVTZ and CCSD(T)/cc-pV(Q+*d*)Z levels of theory for comparison. At the former two theoretical levels rotation-vibration interaction constants and fundamental vibrational frequencies were obtained whereas at the CCSD(T)/cc-pV(Q+*d*)Z level only the rotation-vibration interaction constants were calculated according to formulas given in Ref. 42. Transformation of the computed force fields of the main isotopic species to the normal coordinate representation of other isotopic species permits the determination of their corresponding $\alpha_i^{A,B,C}$ values needed for individual correction for zero-point vibrational contribution. Since this is not possible for the semidiagonal quartic force field fundamental vibrational frequencies were calculated only for the parent isotopic species.

To estimate relativistic effects and the electron contribution to the moments of inertia, test calculations were performed for two C_2H_2Si isomers, **1** and **2**. Relativistic effects were calculated at the MP2/cc-pCVQZ level of theory using an analytic scheme for the computation of scalar-relativistic corrections to nuclear forces (denoted as MVD1)[43] and via a direct perturbation theory (DPT2) scheme.[44] Electronic contributions ΔB_{el} to the rotational constants are related to the rotational g tensor via $\Delta B_{el}=(m_e/m_p)gB_e$,[45] with m_e and m_p being the masses of the electron and the proton. Rotational g tensors for **1** and **2** were calculated at the respective CCSD(T)/cc-pwCVQZ equilibrium structures using the CCSD(T) approach and the aug-cc-pCVTZ basis set.[21,22,46,47] The rotational g tensors are obtained as second derivatives of the energy with respect to the external magnetic field and rotational angular momentum, while gauge-origin independence and fast basis set convergence are ensured by using gauge-including atomic orbitals (London atomic orbitals) as well as their extension to treat rotational perturbations (rotational London atomic orbitals).[48,49]

III. MOLECULAR STRUCTURE

Over the years, several approaches have been developed to determine approximate molecular equilibrium structures from rotational constants obtained through high resolution spectroscopic investigations (see, e.g., Ref. 50, and references therein). The experimental determination of equilibrium structures through microwave spectroscopy requires measurement of molecular rotational constants from a sufficient sample of isotopic species and all their rotation-vibration interaction constants making this approach practical only for small molecules. Probably the most convenient way to determine accurate equilibrium structures for molecules exceeding three atoms lies in the combination of experimental rotational constants and zero-point vibrational corrections from *ab initio* theory according to

$$B_e^{emp} = B_0^{exp} + \frac{1}{2}\sum_i \alpha_i^{B,calc}, \tag{3.1}$$

where similar equations also hold for the A and C rotational constants. In Eq. (3.1), B_0^{exp} is the experimental rotational constant in the ground vibrational state. The zero-point vibrational corrections $\frac{1}{2}\Sigma_i\alpha_i^{A,B,C,calc}$ $(=\Delta A_0,\Delta B_0,\Delta C_0)$ are obtained from theoretical anharmonic force fields and second-order rovibrational perturbation theory (VPT2).[42] The sum over vibration-rotation interactions constants is taken over each of the normal vibrational modes. With this approach, empirical (also dubbed semiexperimental) rotational constants A_e^{emp}, B_e^{emp}, and C_e^{emp} are obtained that are subjected to a least-squares fitting procedure to finally yield the empirical equilibrium structural (r_e^{emp}) parameters.

Some statistical studies on the determination of empirical equilibrium structures have been described in the literature for sets of molecules containing first-row atoms[34,35] and it was found that the approach outlined above yields equilibrium structures of generally high quality. Additionally, from a comparison of (empirical) equilibrium structures against CCSD(T) calculations in combination with different basis sets it was concluded that equilibrium structures obtained *ab initio* at the CCSD(T)/cc-pCVQZ level of theory are very accurate. This was basically confirmed in a more recent statistical theoretical study of molecules harboring second row elements[51] in which it was pointed out that usage of the

TABLE II. CCSD(T) and experimental structural parameters of H_2CCSi (**2**, in Å and degrees).

Basis set	r_1	r_2	r_3	a_1
(fc)cc-pV(T+*d*)Z	1.0885	1.3333	1.7083	121.90
(fc)cc-pV(Q+*d*)Z	1.0877	1.3304	1.7039	121.87
cc-pCVTZ	1.0875	1.3298	1.7045	121.93
cc-pwCVTZ	1.0871	1.3286	1.6999	121.94
cc-pCVQZ	1.0863	1.3271	1.6978	121.88
cc-pwCVQZ	1.0862	1.3269	1.6967	121.88
cc-pCV5Z	1.0860	1.3266	1.6963	121.85
cc-pwCV5Z	1.0860	1.3265	1.6959	121.85
r_e^{emp}(ff1)[a]	1.0861	1.3268	1.6969	121.81
r_e^{emp}(ff2)[b]	1.0859	1.3267	1.6969	121.83
r_e^{emp}(ff3)[c]	1.0862	1.3270	1.6970	121.81
r_0[d]	1.099	1.321	1.703	121.35

[a] From force field calculated at the (fc)CCSD(T)/cc-pV(T+*d*)Z level of theory.
[b] From force field calculated at the CCSD(T)/cc-pwCVTZ level of theory.
[c] From force field calculated at the (fc)CCSD(T)/cc-pV(Q+*d*)Z level of theory.
[d] Reference 11.

weighted basis cc-pwCVQZ yielded yet another slight improvement. In the same study also the better performance of the cc-pV(X+d)Z basis sets over the cc-pVXZ basis sets for second row atoms was stressed. In the present study, calculations were carried out generally following these findings.

IV. RESULTS AND DISCUSSION

A. *c*-C_2H_2Si (1) and H_2CCSi (2)

To date, a total of four isotopologues were reported for **1**[10] and five for **2**[11] which were used in these studies to evaluate corresponding r_s or r_0 structures (see Tables I and II). In the present investigation empirical equilibrium structures are evaluated corresponding to minima on the C_2H_2Si potential energy surface. The required zero-point vibrational corrections were determined from three *ab initio* force fields (ff1 to ff3) and the corresponding results are collected in Tables III and IV. As can be seen, the values are found to be consistent and to vary only very little to within about 1 MHz for the B and C rotational constants. Prior to the derivation of an empirical equilibrium structure of **1**, as a check, the data of Izuha *et al.*[10] were refitted using a Watson-type Hamiltonian in the A reduction and representation III^l.[52] Essentially, the same rotational constants and centrifugal distortion (cd) terms were obtained. It should be recalled that these rotational constants are effective rotational constants and slightly dependent on whether A or S reduction is used in the line fitting procedure. Reduction independent rotational constants were calculated for each isotopic species with corrections obtained from the corresponding cd terms using equations given in Ref. 52. However, the magnitude of this correction is very small (of order 100 kHz for A and 20 kHz only for B and C) and negligible here in the determination of the empirical equilibrium structure of **1**. Subsequently, empirical equilibrium rotational constants of **1** were calculated from Eq. (3.1) and are compiled in Table III. The inertial defect $\Delta = I_c^v - I_b^v - I_a^v$ may serve as an indicator for the effectiveness with which the zero-point vibrational effects are removed through this procedure. Table III gives $\Delta_0 = I_c^0 - I_b^0 - I_a^0$ and $\Delta_e = I_c^e - I_b^e - I_a^e$ values obtained from the ground state rotational constants and the empirical equilibrium rotational constants, respectively. While Δ_0 is small and positive (of order +0.1 amu Å^2), as expected for small and planar molecules such as **1**, Δ_e drops to consistent values close to zero—an indication of efficient removal of zero-point vibrational contributions to the inertial defect. Owing to the relation $\Delta_0 - \Delta_{\mathrm{vib}} = \Delta_{\mathrm{cent}} + \Delta_{\mathrm{elec}}$ (e.g., Ref. 52) the remainder of −0.006 amu Å^2 (from ff1) and −0.007 amu Å^2 (ff2 and ff3) may be considered a (semi)empirical measure of the sum of the much smaller contributions from centrifugal distortion and electron-rotation interaction to the inertial defect.

Empirical equilibrium structures of **1** were finally obtained through least-squares fitting of the structural parameters to the empirical equilibrium moments of inertia I_b^e and I_c^e (calculated from the B_e and C_e constants in Table III and using the same weight for all isotopic species) assuming C_{2v} symmetry of the molecule. The three empirical equilibrium structures are given in Table I. As can be seen, there is virtually no influence of the force field used in the derivation of

TABLE III. Experimental ground state rotational constants, theoretical zero-point vibrational corrections $\Sigma_i \alpha_i/2$, and derived equilibrium rotational constants of isotopic species of silacyclopropenylidene, C_2H_2Si (**1**, in MHz).

Isotopic species	ff[a]	A_0	$\Sigma_i \alpha_i^A/2$	A_e	B_0	$\Sigma_i \alpha_i^B/2$	B_e	C_0	$\Sigma_i \alpha_i^C/2$	C_e	Δ_0	Δ_e
C_2H_2Si	ff1	33 504.767	+168.985	33 673.752	11 899.420	+64.087	11 963.507	8764.856	+63.393	8828.249	+0.105	−0.006
	ff2	⋯	+170.966	33 675.733	⋯	+65.196	11 964.616	⋯	+64.349	8829.205	⋯	−0.007
	ff3	⋯	+168.190	33 672.957	⋯	+64.280	11 963.700	⋯	+63.577	8828.433	⋯	−0.007
$C_2H_2^{29}Si$	ff1	33 504.573	+169.217	33 673.790	11 706.836	+62.859	11 769.695	8659.868	+62.387	8722.255	+0.105	−0.006
	ff2	⋯	+171.199	33 675.772	⋯	+63.948	11 770.784	⋯	+63.330	8723.198	⋯	−0.007
	ff3	⋯	+168.422	33 672.995	⋯	+63.045	11 769.881	⋯	+62.566	8722.434	⋯	−0.007
C_2D_2Si	ff1	26 256.853	+111.874	26 368.727	10 641.620	+50.874	10 692.494	7559.133	+49.111	7608.244	+0.118	−0.006
	ff2	⋯	+113.716	26 370.569	⋯	+51.657	10 693.277	⋯	+49.836	7608.969	⋯	−0.007
	ff3	⋯	+110.615	26 367.468	⋯	+51.241	10 692.861	⋯	+49.310	7608.443	⋯	−0.007
$^{13}C_2H_2Si$	ff1	31 601.136	+155.110	31 756.246	11 522.605	+60.923	11 583.528	8428.560	+59.835	8488.395	+0.108	−0.006
	ff2	⋯	+156.851	31 757.987	⋯	+61.987	11 584.592	⋯	+60.735	8489.295	⋯	−0.007
	ff3	⋯	+154.480	31 755.616	⋯	+61.083	11 583.688	⋯	+60.000	8488.560	⋯	−0.007

[a] Force field used in the calculation of zero-point vibrational contributions. ff1: (fc)CCSD(T)/cc-pV(T+*d*)Z, ff2: CCSD(T)/cc-pwCVTZ, ff3: (fc)CCSD(T)/cc-pV(Q+*d*)Z.

TABLE IV. Theoretical zero-point vibrational corrections $\Sigma_i \alpha_i^{B,C}/2$ for isotopic species of H_2CCSi (**2**, in MHz).

Isotopic species[a]	ff[b]	B_0	$\Sigma_i \alpha_i^B/2$	B_e	C_0	$\Sigma_i \alpha_i^C/2$	C_e
H_2CCSi	ff1	5331.953	+3.536	5335.489	5233.472	+7.010	5240.482
	ff2	⋯	+3.719	5335.672	⋯	+7.266	5240.738
	ff3	⋯	+2.683	5334.636	⋯	+6.161	5239.633
$H_2{}^{13}CCSi$	ff1	5150.877	+3.096	5153.973	5058.932	+6.335	5065.267
	ff2	⋯	+3.273	5154.150	⋯	+6.580	5065.512
	ff3	⋯	+2.275	5153.152	⋯	+5.518	5064.450
$H_2C^{13}CSi$	ff1	5317.009	+3.892	5320.901	5219.128	+7.286	5226.414
	ff2	⋯	+4.067	5321.076	⋯	+7.535	5226.663
	ff3	⋯	+3.066	5320.075	⋯	+6.462	5225.590
$H_2CC^{29}Si$	ff1	5255.722	+3.453	5259.175	5160.011	+6.833	5166.844
	ff2	⋯	+3.634	5259.356	⋯	+7.085	5167.096
	ff3	⋯	+2.613	5258.335	⋯	+5.997	5166.008
D_2CCSi	ff1	4764.555	+2.438	4766.993	4610.808	+6.741	4617.549
	ff2	⋯	+2.600	4767.155	⋯	+6.975	4617.783
	ff3	⋯	+1.692	4766.247	⋯	+6.038	4616.846

[a] Ground state rotational constants for given isotopic species taken from Ref. 11.

[b] Force field used in the calculation of zero-point vibrational contributions. ff1: (fc)CCSD(T)/cc-pV(T+*d*)Z, ff2: CCSD(T)/cc-pwCVTZ, ff3: (fc)CCSD(T)/cc-pV(Q+*d*)Z.

the zero-point vibrational corrections since the equilibrium structural parameters obtained are practically identical. The same approach was followed in the derivation of the empirical equilibrium structures of H_2CCSi (**2**). The three sets of B_e and C_e rotational constants obtained from Eq. (3.1) and the zero-point vibrational corrections from force fields ff1 to ff3 are given in Table IV and the resulting empirical equilibrium rotational constants are collected in Table II. Again the three equilibrium structures are practically identical. Statistical uncertainties of structural parameters in the fits are generally very small, not exceeding 2×10^{-4} Å for bond lengths and 0.01° for angles.

The empirical equilibrium structures of **1** and **2** may now be compared against the corresponding theoretical equilibrium structures obtained. The structural parameters of **1** and **2** obtained *ab initio* at the CCSD(T) level of theory and using six different basis sets are also given in Tables I and II. From there it is found that bond angles show very little sensitivity to the basis set employed. In **1**, the angle a_1 varies only within 0.1° [from 156.53° (cc-pCVTZ) to 156.61° (cc-pwCVTZ)]. Little variation is also found for a_2 which varies within less than 0.15°, from 43.27° (cc-pCVTZ) to 43.42° (cc-p(w)CV5Z) and the unique angle a_1 in H_2CCSi (**2**) which varies well within 0.1°. In either case, the different sets of bond angles—*ab initio* versus r_e^{emp}—show very good agreement. The theoretical bond lengths exhibit the expected shortening upon expansion of the basis set. To illustrate and evaluate their dependence on the basis sets and to estimate the quality of the *ab initio* structural calculations performed here (and ultimately the predictive power for related molecules), plots were produced in which the bond length differences $r_i - r_{e,i}^{\text{emp}}$ are shown as a function of the basis sets (Fig. 2). Very good agreement $\Delta(r_i - r_{e,i}^{\text{emp}}) \ll 1\times 10^{-3}$ Å is found at the CCSD(T)/cc-pwCVQZ level for both molecules. It is apparent, that the performance of the weighted core-valence basis sets cc-pwCV*XZ* is superior to that of the cc-pCV*XZ* family, as displayed through the corresponding bond length shortening and in accord with the finding of Coriani *et al.*[51] This behavior is observed for any bond length but most significantly for those involving the second row element silicon and in particular when using the core-valence basis set of triple-zeta quality. Upon further expansion of the core-valence basis sets from quadruple to quintuple-zeta quality the theoretical bond lengths involving hydrogen and/or carbon exhibit only a minor decrease indicating that their basis set limit has almost been reached. In contrast, bonds involving silicon still show a significant shortening resulting in significantly negative values of $r_i - r_{e,i}^{\text{emp}}$ of up to -1×10^{-3} Å for **2**. The shortening is so large, that even further shortening of a few 10^{-4} Å is expected upon expansion to a hypothetical cc-p(w)CV6Z basis.

To investigate the intrinsic shortcoming of the CCSD(T) method, comparative calculations have been performed using the coupled-cluster variants CCSD(T), CCSDT, and CCSDT(Q), i.e., including a full treatment of triple excitations and with an additional perturbative treatment of quadruple excitations, respectively, in combination with the cc-pVDZ basis set. The results of these calculations are shown in Table V. As can be seen, the structural changes between CCSD(T) and CCSDT are practically negligible. However, with the CCSDT(Q) method a significant lengthening of about 1.5×10^{-3} Å is found for the carbon-silicon bond distances in both molecules which rather well matches the shortening observed at the CCSD(T)/cc-p(w)CV5Z level of theory.

For the sake of completeness, two more possible (but significantly smaller) influences on the molecular structures of **1** and **2** were investigated, relativistic effects and the electronic contribution to the moment of inertia. Relativistic effects obtained at the MP2/cc-pCVQZ level of theory are tabulated in Table I in the supplementary electronic material[53] (SEM) where they are compared against structural parameters obtained at the same level of theory without taking relativistic effects into consideration. As can be seen, their influence is found to be practically negligible for both molecules studied. The electronic contribution ΔB_{el} to the ground state rotational constants has been found to be very

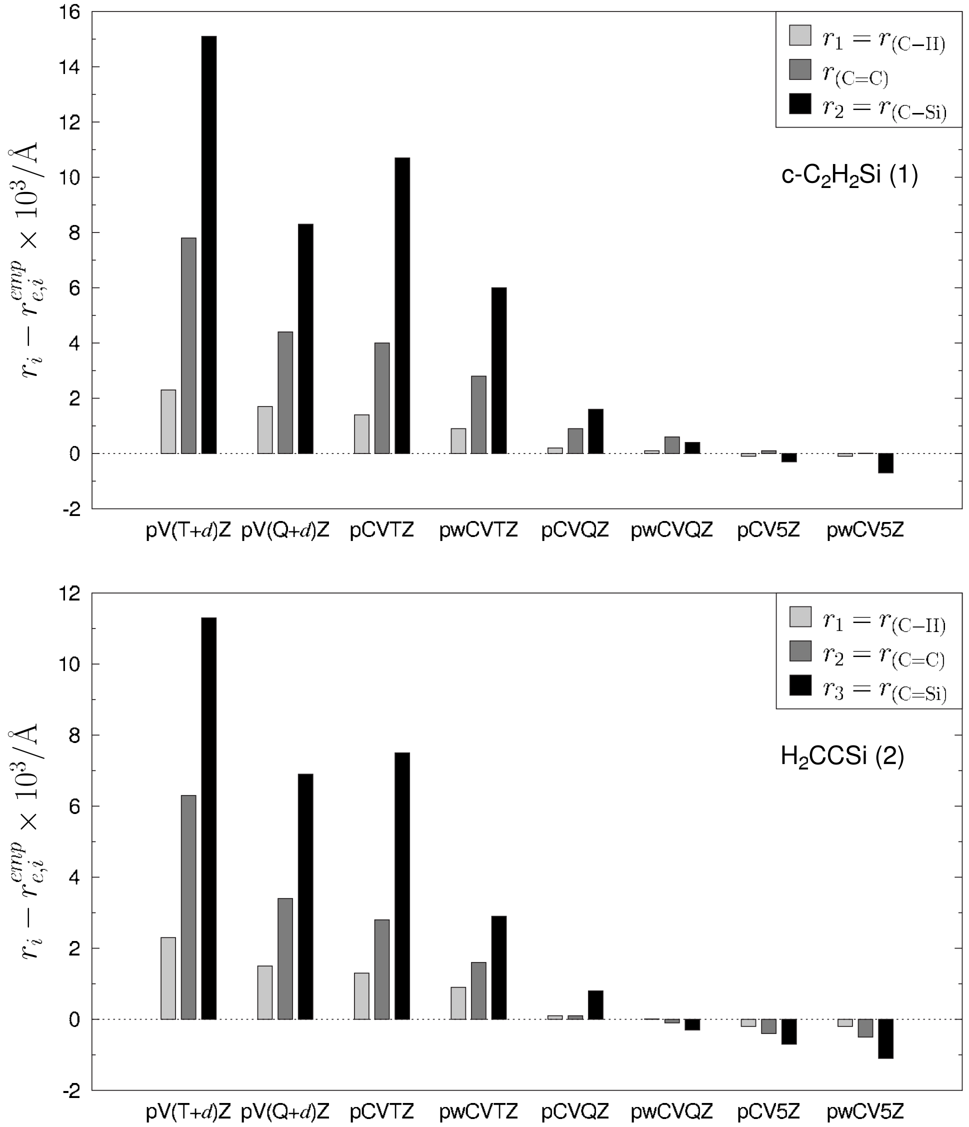

FIG. 2. Bond length differences $r_i - r_{e,i}^{\text{emp}}$(ff3) for c-C_2H_2Si (**1**, top) and H_2CCSi (**2**, bottom) as a function of the basis set used in the CCSD(t) structural optimization (see text). The cc-pV(X+d)Z basis sets were used in frozen-core calculations whereas the cc-pCVXZ and cc-pwCVXZ basis sets were used when correlating all electrons. The parameter definitions r_i refer to the ones introduced in Fig. 1 and are also given in the inserts in the upper right.

small for a statistical sample of molecules harboring first-row elements exclusively.[54] For molecules **1** and **2** ΔB_{el} has been calculated at the CCSD(T)/aug-cc-pCVTZ level of theory employing the CCSD(T)/cc-pwCVQZ equilibrium structures and the results are given in Table II of the SEM. As expected, $\Delta B_{\text{el}} \ll \Delta B_0$ and the magnitude of ΔB_e is comparable to the variation of ΔB_0 observed for the three different force fields ff1 to ff3 which has already been shown to affect the empirical equilibrium structures only very little. A comparison of empirical equilibriums structures of **1** and **2** in Tables I and II against structures additionally taking into account the electronic contribution to the moment of inertia (using the relation $B_e = B_0 + \Delta B_0 + \Delta B_{\text{el}}$) reveals that the changes are practically negligible. For **1**, changes do not exceed 10^{-4} Å for any bond length and 0.02° for the angles. In **2**, changes do not exceed 10^{-4} Å for the C–C and Si–C bond lengths; for C–H, a lengthening of 3×10^{-4} Å is observed. The change in angle a_1 does not exceed 0.02°.

Finally, it is concluded that very accurate theoretical equilibrium structures for the molecules **1** and **2** are obtained

TABLE V. Effect of higher order excitations in the CC expansion on the structural parameters of **1** and **2** using the cc-pVDZ basis set in the frozen-core approximation (in Å and degrees). CCSDT and CCSDT(Q) values quote changes relative to the CCSD(T) results.

	c-C_2H_2Si (**1**)			H_2CCSi (**2**)		
Parameter	CCSD(T)	CCSDT	CCSDT(Q)	CCSD(T)	CCSDT	CCSDT(Q)
$r_{\text{C–H}}$	1.0986	0.0000	+0.0002	1.1038	0.0000	+0.0001
$r_{\text{C–Si}}$	1.8622	0.0000	+0.0014	1.7328	+0.0003	+0.0017
$r_{\text{C–C}}$	1.3659	0.0000	+0.0008	1.3489	−0.0003	+0.0009
a_1	156.45	−0.04	+0.01	121.97	+0.01	+0.01
a_2	43.03	0.00	−0.01	⋯	⋯	⋯

TABLE VI. Theoretical equilibrium rotational constants (CCSD(T)/cc-pwCVQZ), zero-point vibrational corrections ((fc)CCSD(T)/cc-pV(T+*d*Z) $\Sigma_i\alpha_i^{A,B,C}/2$ and ground state rotational constants for energetically higher lying C_2H_2Si structural isomers (in MHz).

Species	A_e	$\Sigma_i\alpha_i^A/2$	A_0	B_e	$\Sigma_i\alpha_i^B/2$	B_0	C_e	$\Sigma_i\alpha_i^C/2$	C_0
HSiCCH (**3**)	227 080.268	+1540.742	225 539.526	5 241.918	−0.863	5 242.781	5123.644	+4.446	5119.198
c-HSiCCH (**4**)	35 891.312	−106.124	35 997.436	9 986.378	+138.892	9 847.486	7812.604	+98.641	7713.963
c-H_2SiC_2 (**5**)	40 594.554	+117.188	40 477.366	11 164.717	+96.402	11 068.315	9727.549	+98.786	9628.763
l-H_2SiCC (**6**)	167 735.360	+3530.960	164 204.400	5 861.542	−62.858	5 924.400	5663.626	−58.359	5721.985

at the CCSD(T)/cc-pwCVQZ level of theory and in addition an adequate description of the molecular force field is obtained at the CCSD(T)/cc-pV(T+*d*) level of theory. In the following, this approach will be used to make predictions for rotational constants of structural isomers not yet studied through rotational spectroscopy.

B. HSiCCH, *c*-HSiCCH, *c*-H_2SiC_2, and H_2SiCC

Molecular equilibrium structures of the higher energy isomers **3** to **6** were calculated using CCSD(T) and the cc-pV(T+*d*)Z, cc-pV(Q+*d*)Z, cc-pwCVTZ, and cc-pwCVQZ basis sets. Individual tables for each molecule summarizing the structural data obtained at the four levels of theory are given in Tables III–VI of the SEM. Predictions for the ground state rotational constants A_0, B_0, and C_0 of the four molecules are given here in Table VI. The A_e, B_e, and C_e rotational constants in Table VI are based on the molecular equilibrium structures obtained at the CCSD(T)/cc-pwCVQZ level of theory given in Table XIII of the SEM. There a larger number of decimal places is provided to allow for reproduction of equilibrium rotational constants as obtained with the ACESII program (for all 12 molecules studied here). The zero-point vibrational contributions $\frac{1}{2}\Sigma_i\alpha_i^{A,B,C}$ are obtained from the CCSD(T)/cc-pV(T+*d*)Z force fields. Table VII gives the CCSD(T)/cc-pwCVQZ electric dipole moment component equilibrium values of the six C_2H_2Si species. They are found to range from about one up to several debyes making all molecules intrinsically well suited for microwave spectroscopic detection.

C. HSiCN and HSiNC

HSiCN (**7**) and HSiNC (**8**) are the two CNHSi structural isomers characterized experimentally in the gas-phase so far, identified by means of FTMW spectroscopy.[12] Not only the parent isotopic species but also the deuterated variants DSiCN and DSiNC were characterized. However, since $I_c^e = I_b^e + I_a^e$ in planar molecules, the rotational constants from two isotopic sets are not sufficient to determine the five unique parameters in an experimental structural determination of neither HSiCN nor HSiNC without imposing any constraints so no empirical equilibrium structures were determined here. Tables VII and VIII, and XIII in the SEM summarize the *ab initio* structural parameters of HSiCN and HSiNC obtained at the six different levels of theory in the present investigation. Zero-point vibrational corrections from ff1 to ff3 as well as resultant theoretical ground state rotational constants A_0, B_0, and C_0 using the equilibrium rotational constants at the CCSD(T)/cc-pwCVQZ level of theory are given here in Table VIII. A comparison of the theoretical $(B_0+C_0)/2$ against the precisely determined experimental values from Ref. 12 reveals agreement to better than 0.15% for both molecules irrespective of the force field used.

D. *c*-CHSiN, HCNSi, HNCSi, and *c*-NHSiC

Table VIII gives theoretical ground state rotational constants for four additional energetically higher lying CNHSi structural isomers **9** to **12** obtained from the CCSD(T)/cc-pwCVQZ equilibrium rotational constants and the zero-point vibrational corrections evaluated at the CCSD(T)/cc-pV(T+*d*)Z level of theory. Theoretical equilibrium structures from CCSD(T) calculations using four different basis sets for all

TABLE VII. CCSD(T)/cc-pwCVQZ dipole moment components (DC, in D) and ^{14}N nuclear quadrupole coupling constants (nqcc, in MHz) of the twelve molecules studied here. Numbers in parentheses give nqcc values at the (fc)CCSD(T)/cc-pV(T+*d*)Z level of theory for comparison.

DC	**1**	**2**	**3**	**4**	**5**	**6**
μ_a	1.04	0.94	0.86	0.03	3.12	6.01
μ_b	⋯	⋯	0.14	2.40	⋯	⋯
DC/nqcc	**7**	**8**	**9**	**10**	**11**	**12**
μ_a	3.17	2.75	0.51	1.24	0.11	0.62
μ_b	0.26	0.27	1.55	1.15	1.27	2.50
χ_{aa}	$-5.07(-5.08)^a$	$-1.31(-1.30)^b$	−2.64	−1.27	−1.08	−1.05
χ_{bb}	$+1.53(+1.56)^a$	$+0.48(+0.47)^b$	−2.66	+0.42	−2.13	−0.10

[a] Experimental values are $\chi_{aa}=-5.07$ MHz and $\chi_{bb}=+1.52$ MHz (Ref. 12).

[b] Experimental values are $\chi_{aa}=-1.31$ MHz and $\chi_{bb}=+0.48$ MHz (Ref. 12).

TABLE VIII. Theoretical equilibrium rotational constants (CCSD(T)/cc-pwCVQZ) and zero-point vibrational corrections $\Sigma_i \alpha_i^{A,B,C}/2$ ((fc)CCSD(T)/cc-pV(T+d)Z) for six CNHSi structural isomers (in MHz).

Species	ff[a]	A_e	$\Sigma_i \alpha_i^A/2$	A_0	B_e	$\Sigma_i \alpha_i^B/2$	B_0	C_e	$\Sigma_i \alpha_i^C/2$	C_0
HSiCN (**7**)	ff1	228 149.442	+1487.309	226 662.133	5359.884	−2.923	5 362.807	5236.856	+2.628	5234.228
	ff2	⋯	+1574.159	226 575.283	⋯	−2.408	5 362.292	⋯	+3.236	5233.620
	ff3	⋯	+1514.248	226 635.194	⋯	−3.501	5 363.385	⋯	+2.066	5234.790
HSiNC (**8**)	ff1	224 704.116	+1210.306	223 493.810	6197.532	−6.232	6 203.764	6031.187	−0.032	6031.219
	ff2	⋯	+1309.262	223 394.854	⋯	−5.950	6 203.482	⋯	+0.378	6030.809
	ff3	⋯	+1201.909	223 502.207	⋯	−6.753	6 204.285	⋯	−0.675	6031.862
c-CHSiN (**9**)	ff1	40 210.531	+138.236	40 072.295	12346.008	+67.298	12 278.710	9445.819	+66.763	9379.056
HCNSi (**10**)	ff1	598 039.557	−569.744	598 609.301	6188.397	+12.501	61 75.896	6125.016	+15.774	6109.242
HNCSi (**11**)	ff1	668 938.017	−6991.236	675 929.253	5393.312	+10.061	5 383.251	5350.176	+12.596	5337.580
c-NHSiC (**12**)	ff1	39 411.136	+177.865	39 233.271	12039.195	+64.662	11 974.533	9222.066	+67.741	9154.325

[a] Force field used in the calculation of zero point vibrational contributions. ff1: (fc)CCSD(T)/cc-pV(T+d)Z, ff2: CCSD(T)/cc-pwCVTZ, ff3: (fc)CCSD(T)/cc-pV(Q+d)Z.

four molecules are given in Tables IX–XIII in the SEM. Equilibrium dipole moment components of all six structural CNHSi isomers from the CCSDT(T)/cc-pwCVQZ calculations are collected in Table VII. All molecules have two dipole moment components μ_a and μ_b of which at least one in each molecule is found to be greater than 1 D making them intrinsically good candidates for detection with microwave spectroscopy.

E. Relative energies

The molecular numbering scheme employed here (Fig. 1) is based on the relative energy ordering evaluated at different levels of theory in earlier studies of both molecular systems.[9,15–17] For the sake of completeness, relative energies have also been computed here using absolute energies evaluated at the CCSD(T)/cc-pwCVQZ level of theory and zero-point vibrational energies at the CCSD(T)/cc-pV(T+d)Z level of theory (Table IX). To avoid resonance denominators in the anharmonicity constants used to calculate the zero-point vibrational energy (ZPVE) contribution, the so-called G_0 term was included (see Refs. 55–57,and references therein).

F. Centrifugal distortion terms

Theoretical equilibrium centrifugal distortion constants of all 12 molecules are given in Table XIV in the SEM. In case of *c*-C_2H_2Si (**1**), the full set of quartic cd constants is known from experiment obtained from a least-squares analysis employing a Watson type asymmetric rotor Hamiltonian in the *A* reduction.[10] The agreement between experimental and the different sets of calculated equilibrium cd terms is found to be generally very good. Owing to the highly prolate character of **2**, **6**, and **7** and *a*-type spectra observed only two out of five cd terms—D_J and D_{JK}—were obtained in the experimental investigations[11,12] which are in good agreement with the theoretical data obtained here. Discrepancies are attributed to the lack of vibrational contributions to the cd terms which were not calculated here. For the remaining species theoretical values were calculated from ff1 and are given either in *A* reduction (**4**, **5**, **9**, **12**) or *S* reduction (**3**, **6**, **10**, **11**).

G. ^{14}N quadrupole coupling

At centimeter wavelengths rotational spectra of CNHSi isomers exhibit hyperfine structure from the presence of the ^{14}N nucleus ($I=1$) resolvable with high resolution techniques such as FTMW spectroscopy. ^{14}N nuclear quadrupole coupling constants χ_{aa} and χ_{bb} were calculated from the corresponding electric field gradients obtained at the CCSD(T)/cc-pwCVQZ level of theory (Table VII). Almost perfect agreement is found against the experimental values for HSiCN (**7**) and HSiNC (**8**).[12] For comparison, values obtained at the lowest level employed here (CCSD(T)/cc-pV(T+d)Z) are also given for those two molecules which are of comparable quality suggesting that this theoretical level is adequate to evaluate electric field gradients in the molecules studied here.

TABLE IX. Total energies (in hartrees), zero-point vibrational energies (ZPVE, in kcal/mol), and relative energies (in kcal/mol) of structural isomers studied here.

Molecule	Total energy[a]	ZPVE[b]	Relative energy	Molecule	Total energy[a]	ZPVE[b]	Relative energy
6	−366.642 275	13.83	53.3	**12**	−382.743 609	11.32	33.7
5	−366.653 635	14.56	46.9	**11**	−382.747 130	10.48	30.7
4	−366.666 065	14.96	39.5	**10**	−382.747 232	9.57	29.1
3	−366.698 854	15.18	19.1	**9**	−382.790 237	11.30	4.4
2	−366.704 815	17.73	17.9	**8**	−382.789 688	8.52	2.0
1	−366.734 353	18.36	0.0	**7**	−382.793 140	8.70	0.0

[a] CCSD(T)/cc-pwCVQZ.

[b] (fc)CCSD(T)/cc-pV(T+d)Z including the G_0 term (see text).

H. Vibrational fundamentals

Harmonic and fundamental vibrational frequencies were calculated from quadratic, cubic, and semidiagonal quartic force fields at the (fc)CCSD(T)/cc-pV(T+*d*)Z level of theory for all twelve molecules studied here (ff1) and additionally at the CCSD(T)/cc-pwCVTZ (ff2) level for molecules **1**, **2**, **5**, **7**, and **8**. No indications for (third-rank) Fermi resonances were found for molecules **1**, **8**, and **9**. From our calculations the following resonances are identified: molecule **2**: ff1: $\nu_3 \sim 2\nu_4$ and $\nu_1 \sim \nu_2 + \nu_3$; ff2: $\nu_1 \sim \nu_2 + \nu_3$; **3**: $\nu_1 \sim 2\nu_8$; **4**: $\nu_1 \sim 2\nu_8$; **5**: ff1 and ff2: $\nu_7 \sim \nu_5 + \nu_9$ and $\nu_4 \sim 2\nu_9$; **6**: $\nu_2 \sim 2\nu_6$ and $\nu_4 \sim \nu_9 + \nu_5$; **7**: ff1 and ff2: $\nu_4 \sim 2\nu_5$; **10**: $\nu_4 \sim 2\nu_5$; **11**: $\nu_4 \sim 2\nu_5$; **12**: $\nu_1 \sim 2\nu_6$ and $\nu_2 \sim \nu_4 + \nu_5$.

In the case of resonances the vibrational fundamentals in Tables XV–XXVI of the SEM were obtained by diagonalization of a dressed Hamiltonian (for details see, e.g., Ref. 58). In the absence of any gas-phase high resolution spectroscopic studies of any of the molecules no quantitative comparison of the theoretical vibrational fundamentals against experiment is feasible. Qualitatively, our results may be compared against data from matrix isolation spectroscopy of selected C_2H_2Si (**1**, **2**, **3**, **5**) and HCNSi (**7**, **8**, **9**, **10**) structural isomers[7–9] which reveals good agreement.

V. CONCLUSIONS

The present paper reports results from high-level coupled-cluster calculations of twelve small silicon bearing molecules of the C_2H_2Si and CNHSi families. The sets of semiexperimental structural parameters obtained for c-C_2H_2Si (**1**) and H_2CCSi (**2**) agree to within 3×10^{-4} Å and 0.02° and are in excellent agreement with results from high-level coupled-cluster calculations performed here, in particular, with those obtained at the CCSD(T)/cc-p(w)CV*XZ* (X $=$Q,5) levels of theory. Usage of basis sets of quintuple-zeta quality, however, yields equilibrium bond lengths between carbon and silicon that appear too short by an amount up to or even exceeding 10^{-3} Å, a finding which we identify as being due to a lack of quadruple excitations in the CCSD(T) treatment. It is concluded that the CCSD(T)/cc-pwCVQZ level of theory offers the best computational cost-benefit ratio of all theoretical levels used here in determining accurate molecular equilibrium structures. A systematic study of a larger sample of molecules is clearly indicated. Properties such as zero-point vibrational contributions to the rotational constants, quartic centrifugal distortion constants, and ^{14}N quadrupole coupling constants are obtained reliably at moderate computational cost. In addition, theoretical fundamental frequencies obtained show good agreement with experimental values obtained from matrix isolation spectroscopy of several species.

Very recently, HSiCCH (**3**) was characterized by FTMW spectroscopy and a detailed description of this study will be given elsewhere.[59] This structural isomer is calculated here to lie 20 kcal/mol above the global minimum **1**. The ring species **4** lies about 40 kcal/mol above ground followed by **5** located at 48 kcal/mol. Given the fact that, for example, HC_3N structural isomers up to 51 kcal/mol above the global minimum were already detected by FTMW spectroscopy[60,61] isomers **4**, **5**, and probably even **6** might be detectable with this sensitive technique. The same holds for the CNHSi structural isomers for which the energetically highest lying species studied here is found at about 34 kcal/mol above the global minimum. As found out already in previous studies, isomer **9** is located only slightly higher than the global minimum (calculated here at 4 kcal/mol) and hence is a prime candidate for future microwave detection.

Provided sufficient isotopic data is available from experiment, the present study suggests that accurate empirical equilibrium structures of polyatomic molecules carrying second row elements may be obtained with zero-point vibrational contributions calculated at a moderate level of computational cost, such as CCSD(T) with basis sets of triple-zeta quality. Systematic studies of larger samples of molecules are desirable for future quantitative analysis.

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