Results of large-scale coupled-cluster calculations of selected $\text{C}_2\text{H}_2\text{Si}$ 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 $\alpha^{\text{A,B,C}}$. The latter were used to determine empirical equilibrium structures $r_{\text{eq}}^{\text{emp}}$ of two molecules — silacyclopropenylidene, $\text{c-C}_2\text{H}_2\text{Si}$, and silapropadienylidene, $\text{H}_2\text{CCSi}$ — 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 $\text{c-C}_2\text{H}_2\text{Si}$ and $\text{H}_2\text{CCSi}$ 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.

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. Here, the circumstellar shell of the prototypical late-type star IRC +10 216 has been found to be particularly rich in these molecules. 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. Owing to their similarity to known astronomical molecules, those of the composition $\text{C}_2\text{H}_2\text{Si}$ and CNHSi (see Fig. 1) might be abundant in space as well. Silacyclopropenylidene, $\text{c-C}_2\text{H}_2\text{Si}$ (molecule 1 in Fig. 1), is a dihydrogenated variant of $\text{c-SiC}_2$ which is one of the most abundant molecules in circumstellar shells. HSiCN (cyanoisilylene, 7) and HSiNC (isocyanosilylene, 8) are closed-shell hydrogenated forms of the SiCN and SiNC radicals, both of which are known in IRC +10216.

Initial experimental evidence for $\text{C}_2\text{H}_2\text{Si}$ and CNHSi isomers in the laboratory was obtained through infrared matrix isolation spectroscopy performed by the Maier group at Gießen. Their study of $\text{C}_2\text{H}_2\text{Si}$ isomers led to the characterization of silacyclopropenylidene ($\text{c-C}_2\text{H}_2\text{Si}$, 1), vinylidensilasilanediyl ($\text{H}_2\text{CCSi}$, 2), ethynylsilylene (HSiCCH, 3), and silacyclopropyne ($\text{c-H}_2\text{SiC}_2$, 5). The matrix study of CNHSi isomers revealed evidence for HSiCN (7), HSiNC (8), azasilacyclopropenylidene ($\text{c-CHNSi}$, 9), and silaisocyanocarbene, HCNSi (10). Subsequently, a total of four $\text{C}_2\text{H}_2\text{Si}$ 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 as was a Fourier transform microwave (FTMW) study of $\text{H}_2\text{CCSi}$ (2). In case of CNHSi structural isomers, HSiCN (7) and HSiNC (8) were identified in the gas phase through FTMW spectroscopy.

Both molecular systems were also subject of several theoretical investigations. Pioneering quantum-chemical calculations of the $\text{C}_2\text{H}_2\text{Si}$ system were performed by Frenking et al. 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...
Recently, frozen-core CCSD(T)/cc-pVTZ calculations of six C$_2$H$_2$Si isomers were reported by Ikuta et al.\textsuperscript{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 iso-electronic CNHSi family, Maier et al.\textsuperscript{16} 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.\textsuperscript{16,17}

The present paper reports results of high-level ab initio calculations of selected molecular properties of singlet C$_2$H$_2$Si and CNHSi structural isomers. In detail the study comprises the determination of molecular equilibrium structures obtained at the CCSD(T) level of theory\textsuperscript{18} using Dunning’s hierarchy of correlation consistent basis sets\textsuperscript{19-24} 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$_2$H$_2$Si (1) and H$_2$CCSi (2), the combination of experimental ground state rotational constants and rotation-vibration interaction constants $a_i^{A,B,C}$ from theory has been used to evaluate empirical equilibrium structures $r_i^{emp}$. Additionally, for energetically higher lying C$_2$H$_2$Si 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 FT MW spectroscopy.

II. THEORETICAL METHODS

Quantum chemical calculations were performed with the 2005 Mainz-Austin-Budapest version of acesh\textsuperscript{23} employing coupled-cluster (CC) theory\textsuperscript{24} in its variant CCSD(T)\textsuperscript{18}.

Some calculations were performed using the development version of CFOUR\textsuperscript{25} at Mainz with its recent parallel implementation of CC energy and first- and second-derivative algorithms\textsuperscript{26} and calculations at the CCSDT(Q)\textsuperscript{27,28} level were performed with the string-based many-body code MRCC\textsuperscript{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\textsuperscript{19} with $X=$T and Q were employed for the silicon atom and standard basis sets cc-pVXZ\textsuperscript{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\textsuperscript{21,22} and their weighted variants cc-pwCVXZ\textsuperscript{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$_2$H$_2$Si (1), H$_2$CCSi (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.\textsuperscript{30} Harmonic and anharmonic force fields were calculated using analytic second-derivative techniques\textsuperscript{31,32} followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force field\textsuperscript{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
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 \( \alpha_{1}A_{1}^{B}C \) 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\(_2\)H\(_2\)Si 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 MVD)\(^{33} \) and via a direct perturbation theory (DPT2) scheme.\(^{44} \) Electronic contributions \( \Delta B_{0} \) to the rotational constants are related to the rotational \( g \) tensor via \( \Delta B_{0} = (m_{e}/m_{p})g B_{e} \)\(^{45} \) 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 \textit{ab initio} theory according to

\[ B_{r}^{\text{emp}} = B_{r}^{\text{exp}} + \frac{1}{2} \sum_{i} g_{i}^{B}B_{r}^{\text{calc}}, \]  

(3.1)

where similar equations also hold for the \( A \) and \( C \) rotational constants. In Eq. (3.1), \( B_{r}^{\text{exp}} \) is the experimental rotational constant in the ground vibrational state. The zero-point vibrational corrections \( \sum_{i} g_{i}^{A,C}A_{i}^{B,C,\text{calc}} = \Delta A_{0}, \Delta B_{0}, \Delta C_{0} \) are obtained from theoretical anharmonic force fields and second-order rovibrational perturbation theory (VPT2).\(^{52} \) 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 \( A_{i}^{\text{emp}}, B_{i}^{\text{emp}}, \) and \( C_{i}^{\text{emp}} \) are obtained that are subjected to a least-squares fitting procedure to finally yield the empirical equilibrium structural \( (r_{i}^{\text{emp}}) \) 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 \textit{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 H2CCSi (2 Å in degrees).

<table>
<thead>
<tr>
<th>Basis set</th>
<th>r1</th>
<th>r2</th>
<th>r3</th>
<th>a1</th>
</tr>
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<tr>
<td>(fc)cc-pV(T+d)Z</td>
<td>1.0885</td>
<td>1.3333</td>
<td>1.7083</td>
<td>121.90</td>
</tr>
<tr>
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<td>1.3304</td>
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<td>1.3298</td>
<td>1.7045</td>
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<td>1.3271</td>
<td>1.6978</td>
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<td>1.3269</td>
<td>1.6967</td>
<td>121.88</td>
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<td>cc-pCVSZ</td>
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<td>1.3266</td>
<td>1.6963</td>
<td>121.85</td>
</tr>
<tr>
<td>cc-pwCVSZ</td>
<td>1.0860</td>
<td>1.3265</td>
<td>1.6959</td>
<td>121.85</td>
</tr>
</tbody>
</table>

| r<sub>c</sub>emp(ff1)<sup>a</sup> | 1.0861 | 1.3268 | 1.6969 | 121.81 |
| r<sub>c</sub>emp(ff2)<sup>b</sup> | 1.0859 | 1.3267 | 1.6969 | 121.83 |
| r<sub>c</sub>emp(ff3)<sup>c</sup> | 1.0862 | 1.3270 | 1.6970 | 121.81 |
| r<sub>d</sub><sup>d</sup> | 1.099  | 1.321  | 1.703  | 121.35 |

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

TABLE III. Experimental ground state rotational constants, theoretical zero-point vibrational corrections, and equilibrium rotational constants of isotopic species of silacyclopropenylidene, C<sub>2</sub>H<sub>2</sub>Si (in MHz).

<table>
<thead>
<tr>
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<th>A&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Σ&lt;sub&gt;A&lt;/sub&gt;/2</th>
<th>B&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Σ&lt;sub&gt;B&lt;/sub&gt;/2</th>
<th>C&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Σ&lt;sub&gt;C&lt;/sub&gt;/2</th>
<th>Δ&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Δ&lt;sub&gt;v&lt;/sub&gt;</th>
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<td>+168.985</td>
<td>33 673.752</td>
<td>11 899.420</td>
<td>+64.087</td>
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<tr>
<td></td>
<td>ff2</td>
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<td>+170.966</td>
<td>33 675.733</td>
<td>⋯</td>
<td>+65.196</td>
<td>11 964.616</td>
<td>⋯</td>
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<tr>
<td></td>
<td>ff3</td>
<td>⋯</td>
<td>+168.190</td>
<td>33 672.957</td>
<td>⋯</td>
<td>+64.280</td>
<td>11 963.700</td>
<td>⋯</td>
<td>+63.577</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;Si&lt;sup&gt;13&lt;/sup&gt;</td>
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<td>+169.217</td>
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<td>⋯</td>
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<td>+155.110</td>
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<td>+61.083</td>
<td>11 583.688</td>
<td>⋯</td>
<td>+60.000</td>
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<sup>e</sup>Force field calculated in the derivation 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 H₂CCSi (2). The three sets of B₂ and C₂ 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 α₁ varies only within 0.1° [from 156.53° (cc-pCVTZ) to 156.61° (cc-pwCVTZ)]. Little variation is also found for α₂ which varies within less than 0.15°, from 43.27° (cc-pCVTZ) to 43.42° (cc-pwCVTZ) and the unique angle α₃ in H₂CCSi (2) which varies well within 0.1°. In either case, the different sets of bond angles—ab initio versus rₑemp—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 rᵢ−rₑemp are shown as a function of the basis sets (Fig. 2). Very good agreement Δ(rᵢ−rₑemp) ≤ 1 × 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-pCVXZ is superior to that of the cc-pCVXZ family, as displayed through the corresponding bond length shortening and in accord with the finding of Coriani et al.¹ 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 rᵢ−rₑemp 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 material³³ (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 ΔBₑ to the ground state rotational constants has been found to be very

<table>
<thead>
<tr>
<th>Isotopic species</th>
<th>ff²</th>
<th>B₀</th>
<th>Σ(αᵢ₋₀/ᵢ)²/2</th>
<th>Bₑ</th>
<th>C₀</th>
<th>Σ(αᵢ₋₀/ᵢ)²/2</th>
<th>Cₑ</th>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>3.536</td>
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<td>7.010</td>
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<tr>
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<tr>
<td>H₂²CSi</td>
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<tr>
<td>ff1</td>
<td>5317.009</td>
<td>3.892</td>
<td>5320.901</td>
<td>5219.128</td>
<td>7.286</td>
<td>5226.414</td>
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<tr>
<td>ff2</td>
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</tr>
<tr>
<td>ff3</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>H₂²²CSi</td>
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<tr>
<td>ff1</td>
<td>5255.722</td>
<td>3.453</td>
<td>5259.175</td>
<td>5160.011</td>
<td>6.833</td>
<td>5166.844</td>
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<td>ff2</td>
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<tr>
<td>ff3</td>
<td></td>
<td></td>
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<tr>
<td>D₂CSi</td>
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</tr>
<tr>
<td>ff1</td>
<td>4764.555</td>
<td>2.438</td>
<td>4766.993</td>
<td>4610.808</td>
<td>7.641</td>
<td>4617.549</td>
<td></td>
</tr>
<tr>
<td>ff2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ff3</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

¹Ground state rotational constants for given isotopic species taken from Ref. 11.
²Force 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-pCV(Q+d)Z.

The zero-point vibrational corrections for isotopic species 2, in MHz. 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 material³³ (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 ΔBₑ to the ground state rotational constants has been found to be very
been calculated at the CCSD/H20849 level of theory employing the CCSD/Be\textsubscript{20850} basis set in the frozen-core approximation.\textsuperscript{54} For molecules 1 and 2, $\Delta B_{el}$ has been calculated at the CCSD(T)/aug-cc-pCVTZ level of theory employing the CCSD(T)/cc-pCVQZ equilibrium structures and the results are given in Table II of the SEM. As expected, $\Delta B_{el} \ll \Delta B_0$ and the magnitude of $\Delta B_{el}$ is comparable to the variation of $\Delta B_0$ 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 equilibrium 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 $B_0 = B_0 + \Delta B_0 + \Delta B_{el}$) reveals that the changes are practically negligible. For 1, changes do not exceed $10^{-3}$ 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 $3 \times 10^{-4}$ Å is observed. The change in angle $\alpha_4$ does not exceed 0.02°.

Finally, it is concluded that very accurate theoretical equilibrium structures for the molecules 1 and 2 are obtained.
TABLE VI. Theoretical equilibrium rotational constants (CCSD(T)/cc-pwCVQZ), zero-point vibrational corrections (\(\Sigma c\))/CCSD(T)/cc-pV(T+dZ) \(\Sigma c\)/2 and ground state rotational constants for energetically higher lying C\(_2\)H\(_2\)Si structural isomers (in MHz).

<table>
<thead>
<tr>
<th>Species</th>
<th>(A_x)</th>
<th>(\Sigma c)/2</th>
<th>(A_0)</th>
<th>(B_x)</th>
<th>(\Sigma c)/2</th>
<th>(B_0)</th>
<th>(C_x)</th>
<th>(\Sigma c)/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSiCC (3)</td>
<td>227 080.268</td>
<td>1540.742</td>
<td>225 539.526</td>
<td>5 241.918</td>
<td>-0.863</td>
<td>5 242.781</td>
<td>5123.644</td>
<td>4.446</td>
</tr>
<tr>
<td>c-HSiCC (4)</td>
<td>35 891.312</td>
<td>-106.124</td>
<td>35 997.436</td>
<td>9 986.378</td>
<td>+138.892</td>
<td>9 847.486</td>
<td>7812.604</td>
<td>+98.641</td>
</tr>
<tr>
<td>c-H(_2)SiC(_2) (5)</td>
<td>40 594.554</td>
<td>+117.188</td>
<td>40 477.366</td>
<td>11 164.717</td>
<td>+96.402</td>
<td>11 068.315</td>
<td>9727.549</td>
<td>+98.786</td>
</tr>
<tr>
<td>l-H(_2)SICC (6)</td>
<td>167 735.360</td>
<td>+3530.960</td>
<td>164 204.400</td>
<td>5 861.542</td>
<td>-62.858</td>
<td>5 924.400</td>
<td>5663.626</td>
<td>-58.359</td>
</tr>
</tbody>
</table>

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 \(\mu_c^i = I^i_c + I^i_e\) 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 \(\mu_1\) to \(\mu_3\) 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 electric dipole moment component equilibrium values of the six C\(_2\)H\(_2\)Si species. They are found from range about one up to several debyes making all molecules intrinsically well suited for microwave spectroscopic detection.

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+dZ) level of theory for comparison.

<table>
<thead>
<tr>
<th>DC</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu_x)</td>
<td>1.04</td>
<td>0.94</td>
<td>0.86</td>
<td>0.03</td>
<td>3.12</td>
<td>6.01</td>
</tr>
<tr>
<td>(\mu_y)</td>
<td>...</td>
<td>...</td>
<td>0.14</td>
<td>2.40</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>DC/nqcc</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>(\mu_x)</td>
<td>3.17</td>
<td>2.75</td>
<td>0.51</td>
<td>1.24</td>
<td>0.11</td>
<td>0.62</td>
</tr>
<tr>
<td>(\mu_y)</td>
<td>0.26</td>
<td>0.27</td>
<td>1.55</td>
<td>1.15</td>
<td>1.27</td>
<td>2.50</td>
</tr>
<tr>
<td>(\chi_{xx})</td>
<td>-5.07(-5.08)(^a)</td>
<td>-1.31(-1.30)(^b)</td>
<td>-2.64</td>
<td>-1.27</td>
<td>-1.08</td>
<td>-1.05</td>
</tr>
<tr>
<td>(\chi_{yy})</td>
<td>+1.53(+1.56)(^b)</td>
<td>+0.48(+0.47)(^b)</td>
<td>-2.66</td>
<td>+0.42</td>
<td>-2.13</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

\(^a\)Experimental values are \(\chi_{xx} = -5.07\) MHz and \(\chi_{yy} = +1.52\) MHz (Ref. 12).

\(^b\)Experimental values are \(\chi_{xx} = -1.31\) MHz and \(\chi_{yy} = +0.48\) MHz (Ref. 12).
four molecules are given in Tables IX–XIII in the SEM. Equilibrium dipole moment components of all six structural CNHSi isomers from the CCSD(T)/cc-pwCVQZ calculations are collected in Table VII. All molecules have two dipole moment components $\mu_a$ and $\mu_b$ 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$_2$H$_2$Si (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 probable character of 2, 6, and 7 and $a$-type spectra observed only two out of five cd terms—$D_{ij}$ 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 $\chi_{aa}$ and $\chi_{bb}$ 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.

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

$^a$CCSD(T)/cc-pwCVQZ.

$^b$(fc)CCSD(T)/cc-pV(T + d/Z) including the $G_0$ term (see text).
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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29 M. C. McCarthy (unpublished).


