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Linear Carbon Chains of Type SiC_nO ($n = 3-8$): Results of Coupled Cluster Calculations[†]

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On the basis of (R)CCSD(T) calculations with the cc-pVQZ basis set, accurate equilibrium bond lengths (ca. 0.0005 Å accuracy) are established for linear carbon chains of type SiC_nO with $n = 3-8$. SiC and CO equilibrium bond lengths are in the range 1.683−1.735 and 1.165−1.167 Å, respectively. A narrow range (1.272−1.287 Å) is obtained for all 25 carbon−carbon equilibrium distances. The equilibrium dipole moments (μ_e) exhibit large correlation effects. The μ_e values for the closed-shell species with even integer n are larger than those for the triplet ground states of SiC_nO chains with odd n values. Various spectroscopic constants such as harmonic vibrational wavenumbers, vibration−rotation coupling, and l-type doubling constants are calculated. The ground-state rotational constants of SiC_3O, SiC_4O, and SiC_5O are predicted with ca. 0.1% accuracy to be 1386.5, 867.0, and 564.4 MHz.

1. Introduction

Linear carbon chains with one or two hetero end atoms dominate the list of interstellar molecules which could be unambiguously identified by means of radio astronomy (see Table 2 of ref 1 for a recent compilation). From a chemical point of view, these species can be crudely classified as systems composed of conjugated triple bonds such as the well-known cyanopolyynes ($HC_{2n+1}N$) and as cumulenic systems. Known interstellar molecules of the latter type involve the small pure carbon chains C_3, C_5 (and possibly C_4), C_3O, C_3S, SiC_4, and carbenes of type H_2C_n with $n = 3$ and 4. However, the variety of interstellar cumulenic systems may well be much larger. To unambiguously identify such molecules in the interstellar or circumstellar medium, one typically has to establish nearly perfect agreement of interstellar radio lines with corresponding precise laboratory measurements or extrapolations thereof. In the search for laboratory spectra of such reactive species and their assignment, results of high-quality ab initio calculations often proved to be of great importance in the past. A good example of this sort is provided by the cumulenic systems SiC_nS which were intensively studied in a joint theoretical/experimental effort, yielding a sound basis for future radioastronomical searches.[2]

Very recently, the first member of the series SiC_nO with $n > 1$ could be detected in the laboratory by means of Fourier transform microwave (FTMW) spectroscopy. Sanz et al.[3] were able to observe four different rotational transitions of SiCCO in the 5−26 GHz frequency range, allowing for the determination of precise values of the ground-state rotational and quartic centrifugal distortion constants. Complementary information on this molecule could be obtained through high-level ab initio calculations as carried out by the author.[4] In particular, an accurate equilibrium structure for SiCCO could be established by suitably combining the results of coupled cluster calculations with experimental rotational constants for SiCCO and different isotopomers of CCCO. Predictions for various spectroscopic constants such as harmonic vibrational wavenumbers, vibration−rotation coupling, and l-type constants were made as well.

The present paper reports the results of a rather extensive theoretical study of the higher member of the series of SiC_nO molecules with $n = 3-8$. These should be of help to experimentalists in the search for high-resolution spectra and their analysis. Comparison will also be made with results obtained earlier for the valence-isoelectronic SiC_nS series[2] and related molecules.

2. Details and Results of Calculations

2.1. Equilibrium Structures. The coupled cluster variant CCSD(T)[5] was used to obtain equilibrium structures for the linear molecules of the SiC_nO series with $n = 3-8$. For the triplet states with odd integer n, the partially restricted version, termed RCCSD(T),[6,7] was employed. Two different basis sets were used in the geometry optimizations, corresponding to Dunning's cc-pVTZ and cc-pVQZ sets.[8,9] Throughout, valence electrons were correlated in the coupled cluster calculations which were carried out with the MOLPRO suite of programs.[6,7,10,11]

Results of the CCSD(T) calculations for the closed-shell species SiC_4O, SiC_6O, and SiC_8O are graphically displayed in Figure 1. The recommended equilibrium bond lengths given below the chemical formula of each molecule are derived from the CCSD(T)/cc-pVQZ results by applying corrections of −0.0076 Å (SiC), −0.0040 Å (CC), and −0.0023 Å (CO). These correction parameters are taken over from SiCCO and C_3O for which accurate equilibrium structures were established recently.[4] The correction parameter used for the CC equilibrium bond lengths of SiC_nO species with $n > 2$ corresponds to the arithmetic means of the two values obtained for C_3O (−0.0035 and −0.0044 Å; see ref 4).

Compared to the recommended SiC equilibrium bond length for SiCCO of 1.644 Å,[4] an elongation by 0.0190 Å is obtained for SiC_4O and subsequent further elongations of 0.0075 and 0.0038 Å are calculated when the chain is increased by one and two more C_2 links, respectively. Considerably smaller elongations were calculated for the corresponding closed-shell SiC_nS species with even integer n, the incremental differences per C_2 unit amounting to 0.0094, 0.0044, and 0.0027 Å. The

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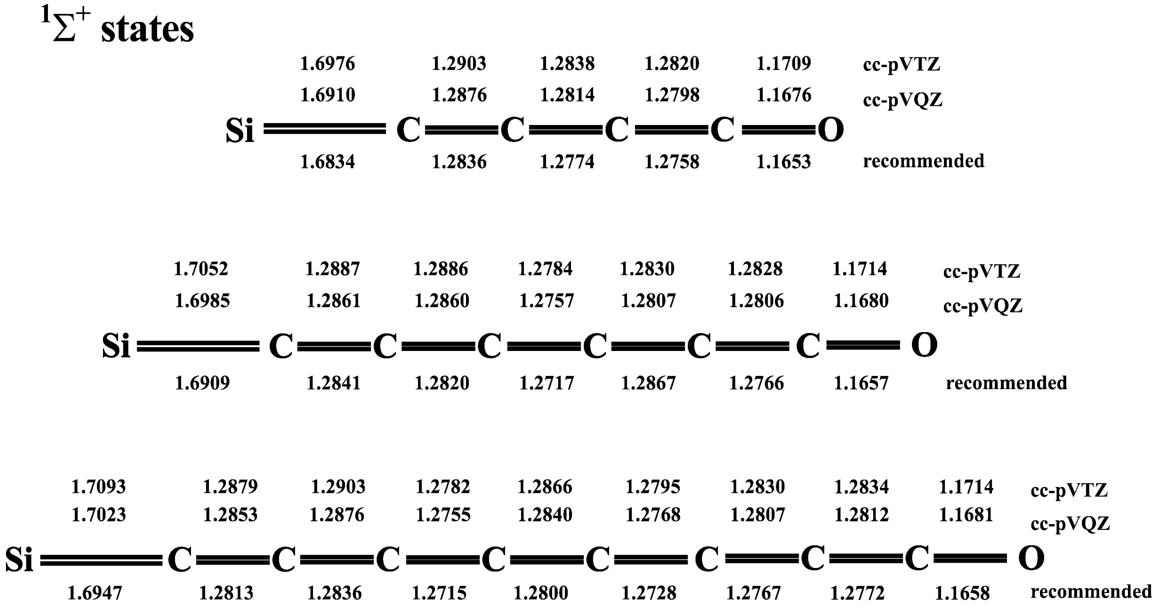

Figure 1. CCSD(T) and recommended equilibrium structures for the electronic ground states of $SiC_{2n}O$ chains with $n = 2-4$.

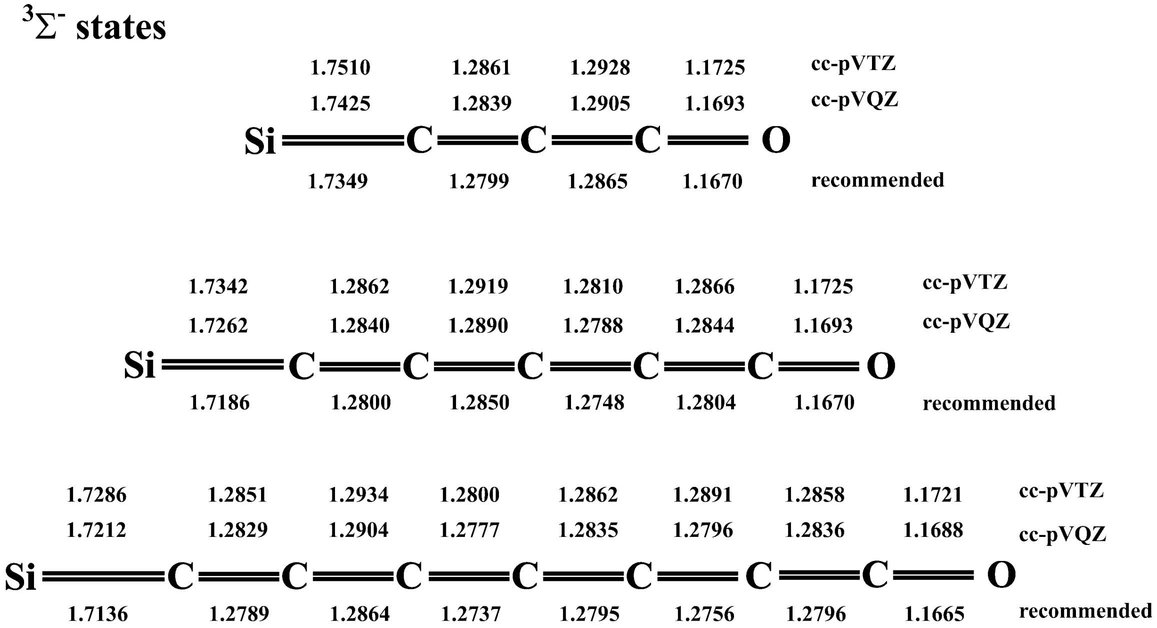

Figure 2. RCCD(T) and recommended equilibrium structures for the electronic ground states of $SiC_{2n-1}O$ chains with $n = 2-4$.

CO equilibrium distance increases only slightly, differences per added C_2 link amounting to 0.0041, 0.0004, and 0.0001 Å.

RCCSD(T) and recommended equilibrium bond lengths for the $^3\Sigma^-$ ground states of SiC_nO species with an odd number of carbon atoms are collected in Figure 2. As was previously found for the linear carbides SiC_n ($n = 3-8$)[12-15] and the SiC_nS species ($n = 1-8$),[2] no great differences exist between bond lengths of singlet and triplet states. The correction parameters used for the singlet states are therefore expected to be appropriate for the triplet states as well. First successful tests of this assumption were possible for linear SiC_3[15] and SiC_3S,[2] for which accurate ground-state rotational constants could be determined experimentally.[2,16] As for the singlet states, recommended equilibrium bond lengths are displayed below the chemical formulas of the three triplet species investigated in the present work.

The variation of the recommended SiC and CO equilibrium bond lengths with the chain length for SiC_nO species ($n = 3-8$) is shown in Figure 3. Oscillatory behavior between the results for singlet and triplet states is observed, but the equilibrium bond lengths of both singlet and triplet states appear to converge to common asymptotic values of ca. 1.701 Å (SiC) and 1.166 Å (CO).

2.2. Electric Dipole Moments. Electric dipole moments are those physical quantities which determine the intensities of rotational transitions. For reactive molecules such as those investigated here, their measurement, for example, by the common technique of measuring the Stark effect on rotational spectra, is difficult. Actually, no experimental data are yet available for any of the cumulenic chains of type SiC_n, SiC_nS, or SiC_nO. Following our earlier work on the former two systems, a rather elaborate theoretical study of the electric dipole moments of SiC_nO species with $n = 3-8$ is given below.

Throughout, electric dipole moments were calculated at the recommended equilibrium structures from the present work (cf. Figures 1 and 2). Three different flexible basis sets, all including diffuse functions of s, p, d, and f types, were employed. They correspond to the full aug-cc-pVTZ (or avtz) and aug-cc-pVQZ

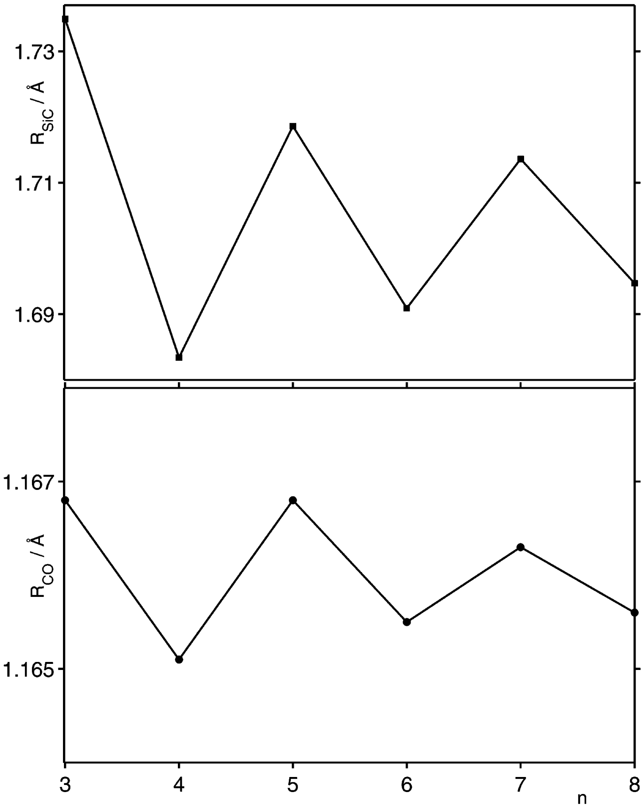

Figure 3. Variation of the recommended SiC and CO equilibrium bond lengths of SiC_nO chains with the chain length.

(or avqz) basis sets of Dunning and co-workers[8,9,16] plus the latter basis set exclusive of g functions, abbreviated by spdf (avqz). Results for the closed-shell species SiC_4O, SiC_6O, and SiC_8O as obtained by five different methods are listed in Table 1. Like in the author's previous calculations for SiC_4, SiC_6, and $SiC_{2n}S$ ($n = 1-4$),[2,14] electron correlation plays a decisive role. Already for SiC_4O, the Hartree−Fock approximation overestimates the equilibrium dipole moment by 79% (with respect to the CCSD(T)/avqz result) and correlation effects are further increasing with increasing chain length. Throughout, second-order perturbation theory according to Møller and Plesset (MP2) overestimates the electron correlation effects on the dipole moment, but the differences from the CCSD(T) results do not exceed 18%. Differences between the two coupled cluster variants accounting for connected triple substitutions in a perturbative manner, CCSD-T[7] and CCSD(T),[5] are of the order of 1−2%. Like for the SiC_{2n} and $SiC_{2n}S$ species, connected triples make a large contribution to the dipole moment which strongly increases with the chain length.

A graphical representation of the calculated dipole moments for the whole series of SiC_nO species with $n = 1-8$ is given in Figure 4. Throughout, the spdf (avqz) basis is employed. The recommended equilibrium structure for SiCO is R_{1e} (SiC) = 1.8173 Å and R_{2e} (CO) = 1.1543 Å, that used for SiCCO has been published earlier.[4] The small RCCSD(T) value of $\mu_e = -0.357$ D obtained for SiCO may explain why no microwave (MW) or millimeter (MM) wave spectrum has yet been observed for this molecule. The situation is significantly better for SiC_3O, for which $\mu_e = -0.950$ D is calculated at the RCCSD(T)/avqz level (cf. Table 2). Note that a FTMW spectrum could be observed for SiC_3S[2] despite the fact that the predicted μ_e value (RCCSD(T)/avqz) is only −0.559 D. Because of the significant increase in the μ_e values with increasing chain length, the larger SiC_nO species may well be suitable candidates for forthcoming studies in the MW or MM region of the spectrum.

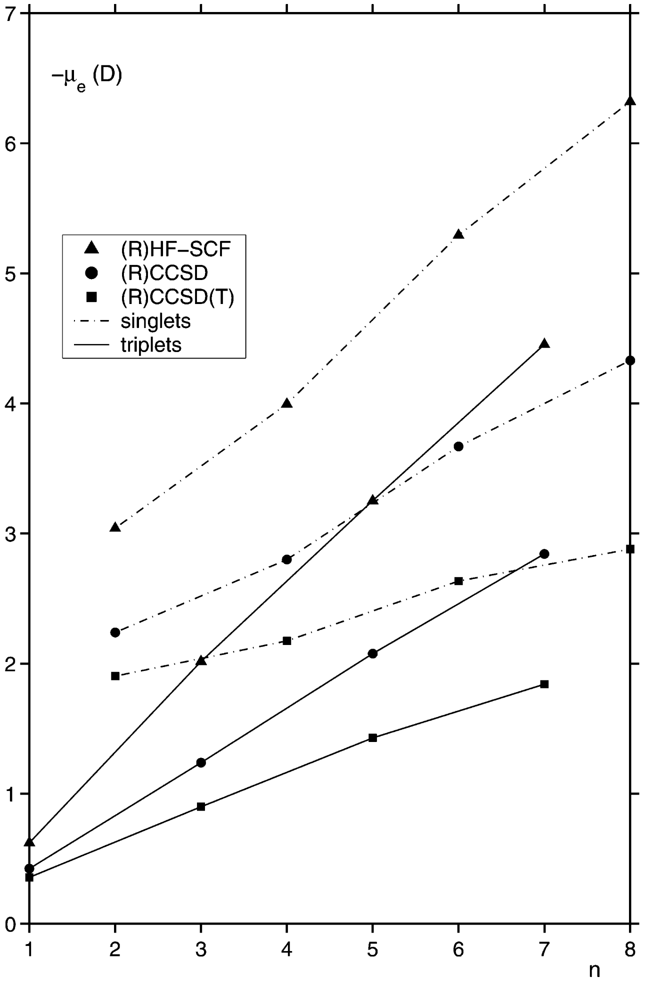

Figure 4. Calculated equilibrium dipole moments for SiC_nO chains ($n = 1-8$): basis, spdf(avqz).

2.3. (R)CCSD(T) Spectroscopic Constants for SiC_nO ($n = 3-6$). By the use of least-squares fitting of (R)CCSD(T)/vqz energies, complete cubic force fields have been calculated for linear SiC_3O, SiC_4O, and SiC_5O. Since this material is

TABLE 1: Calculated Equilibrium Dipole Moments (in D) for Closed-Shell Species $SiC_{2n}O$ ($n = 2-4$)[a]

	SiC_4O			SiC_6O			SiC_8O	
method	avtz	spdf(avqz)	avqz	avtz	spdf(avqz)	avqz	avtz	spdf(avqz)
HF−SCF	−3.985	−3.996	−3.996	−5.278	−5.294	−5.294	−6.303	−6.321
MP2	−1.904	−1.945	−1.966	−2.225	−2.279	−2.308	−2.312	−2.377
CCSD	−2.754	−2.800	−2.852	−3.608	−3.669	−3.738	−4.255	−4.331
CCSD-T	−2.173	−2.211	−2.259	−2.632	−2.682	−2.748	−2.871	−2.933
CCSD(T)	−2.135	−2.175	−2.227	−2.582	−2.635	−2.705	−2.815	−2.881

[a] An obvious shorthand notation is employed to denote the basis sets. The dipole moment evaluations are carried out at the recommended equilibrium geometries from this work (cf. Figure 1): polarity, $^{+}SiC_{2n}O^{-}$.

TABLE 2: Calculated Equilibrium Dipole Moments (in D) for Open-Shell Species SiC$_{2n-1}$O (n = 2−4)[a]

	SiC$_3$O			SiC$_5$O			SiC$_7$O	
method	avtz	spdf(avqz)	avqz	avtz	spdf(avqz)	avqz	avtz	spdf(avqz)
RHF−SCF	−1.997	−2.017	−2.016	−3.232	−3.253	−3.252	−4.432	−4.454
RCCSD	−1.192	−1.239	−1.293	−2.017	−2.077	−2.150	−2.769	−2.843
RCCSD-T	−0.878	−0.919	−0.969	−1.400	−1.451	−1.519	−1.805	−1.867
RCCSD(T)	−0.856	−0.900	−0.950	−1.378	−1.429	−1.499	−1.779	−1.842

[a] An obvious shorthand notation is employed to denote the basis sets. The dipole moment evaluations are carried out at the recommended equilibrium geometries from this work (cf. Figure 2): polarity, $^{+}SiC_{2n-1}O^{-}$.

TABLE 3: (R)CCSD(T)/vqz Harmonic Vibrational Wavenumbers for SiC$_n$O Chains (n = 3−6)

n	symmetry	wavenumbers/cm^{-1}
3	σ	2257, 1854, 1108, 525
	π	502, 326, 104
4	σ	2286, 2085, 1630, 1023, 499
	π	547, 514, 153, 58
5	σ	2280, 2069, 1846, 1370, 848, 438
	π	514, 476, 325, 146, 59
6	σ	2291, 2172, 2001, 1687, 1236, 793, 407
	π	539, 514, 464, 197, 101, 41

TABLE 4: (R)CCSD(T)/vqz Vibration−Rotation Coupling Constants for SiC$_3$O, SiC$_4$O, and SiC$_5$O[a]

n	symmetry	vibration−rotation coupling constants/MHz
3	σ	5.185, 4.748, 3.803, 1.857
	π	−1.627, −3.181, −3.909
4	σ	2.645, 2.936, 2.154, 1.452, 0.560
	π	−0.618, −0.997, −2.786, −2.830
5	σ	1.370, 1.772, 1.380, 1.065, 0.789, 0.283
	π	−0.344, −0.563, −0.817, −1.079, −1.070

[a] Numbering of vibrational modes according to Table 3 which obeys common spectroscopic convention (see, e.g., ref 18).

TABLE 5: Recommended Rotational and (R)CCSD(T) Equilibrium Centrifugal Distortion Constants for SiC$_n$O Chains (n = 3−8)

n	B_e/MHz	B_0/MHz	D_e^J/Hz
3	1385.6	1386.5	40.0
4	864.7	867.0	11.1
5	563.8	564.4	3.97
6	394.9		1.62
7	285.9		
8	215.4		

probably of interest to a smaller number of readers, it is made available only as Supporting Information. For economical reasons, only the complete harmonic force field was calculated for SiC$_6$O. On the basis of these force fields, various spectroscopic constants (harmonic vibrational wavenumbers ω_r, vibration−rotation coupling constants α_r, l-type doubling constants q_t^e and q_t^J as well as equilibrium quartic centrifugal distortion constants D_e^J) have been calculated. Conventional second-order perturbation theory in normal coordinate space is employed. The results, given in a compact representation, are given in Tables 3−6. More detailed information, including many data for less abundant isotopomers, is provided as Supporting Information.

(R)CCSD(T)/vqz harmonic vibrational wavenumbers for SiC$_n$O (n = 3−6) are listed in Table 3. The largest wavenumber (ω_1) lies in the range 2257−2291 cm^{-1} and exhibits some oscillatory behavior between singlet states with the larger and triplet states with the smaller values, with a common asymptotic value around 2293 cm^{-1}. Anharmonicity effects may reduce the (R)CCSD(T) values for ω_1 by about 1.8%, which corresponds to the relative difference between ω_1 (CCSD(T)/vqz) and the experimental anharmonic value for C$_3$O.[4,19]

TABLE 6: (R)CCSD(T)/vqz l-type Doubling Constants for SiC$_n$O Chains (n = 3−6)[a]

n	type	l-type doubling constant
3	q_t^e/MHz	0.320, 0.448, 1.263
	q_t^J/Hz	0.015, −0.139, −1.604
4	q_t^e/MHz	0.113, 0.120, 0.335, 0.858
	q_t^J/Hz	−0.005, −0.007, −0.204, −1.405
5	q_t^e/MHz	0.050, 0.053, 0.073, 0.151, 0.364
	q_t^J/Hz	−0.002, −0.002, −0.006, −0.037, −0.224
6	q_t^e/MHz	0.024, 0.025, 0.027, 0.056, 0.105, 0.256

[a] Numbering of vibrational modes according to Table 3 which obeys common spectroscopic convention (see, e.g., ref 18).

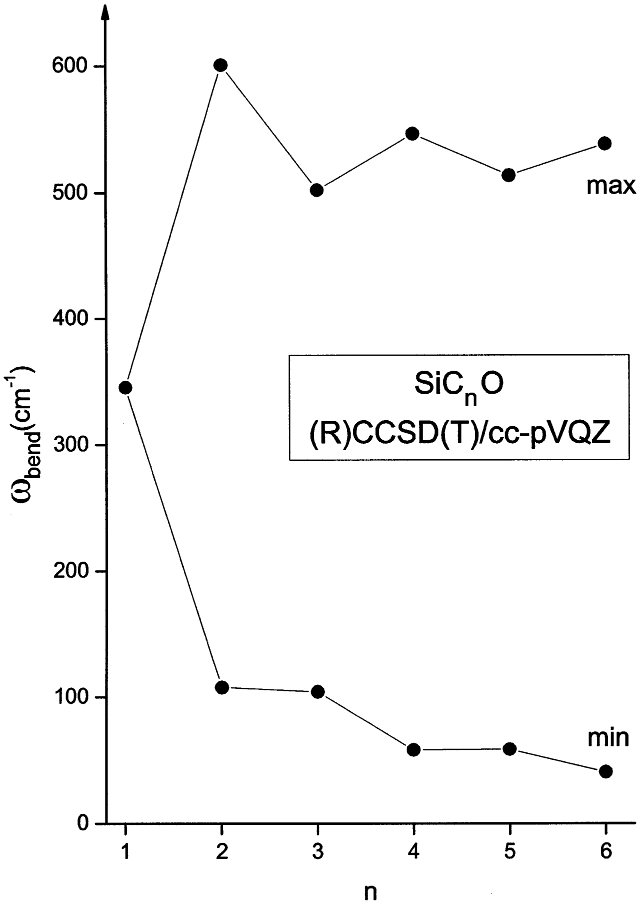

Figure 5. Maximum and minimum harmonic bending vibrational wavenumbers for SiC$_n$O chains (n = 1−8).

The harmonic bending vibrational wavenumbers with highest (ω_{bend}^{max}) and lowest (ω_{bend}^{min}) values are graphically displayed in Figure 5, which also includes data for SiCO ($X^3\Sigma^-$) and SiCCO ($X^1\Sigma^+$). The latter are taken from ref 4 while the harmonic bending vibrational wavenumber of SiCO was newly calculated to be ω_2 = 345.2 cm^{-1} (RCCSD(T)/vqz). With increasing chain lengths, $\omega_{\mathrm{bend}}^{\max}$ tends to converge to a common value of ca. 530 cm^{-1}, with the singlet data converging from above and the triplet data from below. The asymptotic value for SiC$_n$O chains is larger than the corresponding value recently estimated for pure carbon chains ($\approx$500 cm^{-1})[20] by ca. 6%.

Vibration−rotation coupling constants α_r, which approximately describe the change in rotational constants with single-quantum vibrational excitation, are listed in Table 4. As is common for linear molecules, the α_r values for stretching vibrations have a positive sign while those for the doubly degenerate bending vibrations are negative. For essentially unperturbed singly excited states, (R)CCSD(T)/vqz calculations usually yield α_r values in close agreement with experiment. Among the cumulenic systems with a silicon end atom, some comparison between theory and experiment is possible for SiC$_4$[14] and SiCCS.[2] In the former case, an experimental value of $\alpha_6 = -5.119$ MHz is obtained as the difference of the measured rotational constants in the vibrational ground state and the $\nu_6 = 1$ excited vibrational state (cf. Tables 3 and 5 of ref 14), to be compared with a CCSD(T) value of −4.953 MHz. Experimental and theoretical values (the latter in parentheses) for SiCCS[2] are $\alpha_1 = 8.198$ (8.397) MHz and $\alpha_4 = -2.628$ (−2.520) MHz.

From the recommended equilibrium structures displayed in Figures 1 and 2, equilibrium rotational constants (B_e) have been calculated. They are listed in Table 5. The table also includes ground-state rotational constants (B_0) for chains up to SiC$_5$O, which were obtained by means of the formula

$$B_0 \approx B_e - \frac{1}{2}\sum_r \alpha_r d_r \qquad (1)$$

In eq 1, d_r are degeneracy factors (1 for stretching and 2 for bending vibrational modes). The B_0 predictions from the present work are expected to be accurate to ca. 0.1%. The last column of Table 5 lists (R)CCSD(T)/vqz values for the equilibrium centrifugal distortion constants D_e^J, which are readily available from the equilibrium structures, nuclidic masses, and harmonic stretching force constants. Compared to the corresponding ground-state values, the equilibrium values are underestimates. For example, the ratios D_0^J (exp.)/D_e^J (theor.) for SiC$_n$S species with $n = 2$, 3, and 4 are 1.17, 1.21, and 1.29, respectively.[2] A somewhat larger value of 1.33 may be calculated for SiCCO from the data of Table 2 of ref 4.

Further spectroscopic constants which characterize the bending vibrations of linear molecules are the l-type doubling constants q_t^e and q_t^J. The latter describe the rotational dependence; for their sign, the definition of Watson[21] is adopted. Theoretical q_t^e values for linear molecules, which are derived from high-level ab initio calculations by means of second-order perturbation theory in normal coordinate space, are typically smaller than the corresponding experimental values by a few percent. For the two bending states of SiC$_4$ and SiCCS which could be investigated spectroscopically,[14,2] the author's previous CCSD(T) calculations underestimated q_6 (SiC$_4$) and q_4 (SiCCS) by 4.4 and 5.6%, respectively. Results for the SiC$_n$O species ($n = 3-6$), expected to be of comparable quality, are given in Table 6.

3. Conclusions

Among the ca. 130 molecules which could be detected in the interstellar or circumstellar medium so far,[1] cumulenic systems provide a characteristic motif. Besides smaller members of the series SiC$_n$, C$_n$O, and C$_n$S, which could already be unambiguously identified by radio astronomy, the SiC$_n$O species might be suitable interstellar candidates, as well. Following recent experimental and theoretical work on SiCCO,[3,4] the present paper reports predictions of various spectroscopic properties for the molecules SiC$_n$O with $n = 3-8$. Quantities of particular importance to radio astronomy and MW or MM spectroscopy are ground-state rotational constants (B_0) and electric dipole moments. Predictions of the former with ca. 0.1% accuracy were obtained for SiC$_3$O, SiC$_4$O, and SiC$_5$O from empirically corrected (R)CCSD(T)/vqz equilibrium structures and differences $\Delta B_0 = B_e - B_0$ computed ab initio. The calculated equilibrium dipole moments exhibit large effects of electron correlation. Since they increase with chain length, the prospects to observe rotational spectra of chains larger than SiCCO appear to be reasonably good. Harmonic vibrational wavenumbers were calculated for SiC$_n$O chains up to SiC$_6$O. The isotopic data provided as Supporting Information may be of interest to forthcoming investigations by means of matrix-isolation IR spectroscopy.

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Supporting Information Available: Tables S1−S8 reporting complete cubic (R)CCSD(T)/vqz force fields for SiC$_3$O, SiC$_4$O, and SiC$_5$O, the complete harmonic force field for SiC$_6$O, and various spectroscopic constants (harmonic vibrational wavenumbers, vibration−rotation coupling constants, l-type doubling constants, and equilibrium quartic centrifugal distortion constants) for isotopomers of all four molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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