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Ab initio characterization of linear C_3Si isomers

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ABSTRACT

Aims. This paper presents an ab initio characterization of linear isomers of C_3Si, which are suitable species for astrophysical detection in carbon-rich sources.

Methods. By the help of multiconfigurational calculations, two linear minima are characterized, namely *l*-SiCCC and *l*-CSiCC, whose relative energy is 3.3 eV, and their electronic ground states have $X^3\Sigma^-$ symmetry, and their electronic spectra present a high density of electronic states at low energy. Anharmonic spectroscopic parameters are predicted for both isomers and for different isotopomers using second order perturbation theory and force fields derived form 6D-potential energy surfaces.

Results. The fundamental frequencies of the IR active bendings are predicted to lie around 434 cm^{-1} and 169 cm^{-1} for *l*-SiCCC. The rotational constants (B_e) are computed to be 2753.16 MHz for *l*-SiCCC and 3205.37 MHz for *l*-CSiCC. For *l*-SiCCC, a relatively large spin-spin constant ($\lambda = -0.605$ cm^{-1}) arises from the interaction between the ground $X^3\Sigma^-$ and the lowest $^1\Sigma^+$ excited state, located at 0.46 eV, resulting in complex vibrational IR-band shapes, at least, when the low- frequency bendings are excited.

Key words. molecular data – catalogs

1. Introduction

In the last decade, we performed a series of systematic studies of odd and even pure carbon chains (C_4, C_5, C_6, and $C_4{}^+$) and some of their mono substituted species (C_3O, C_3S), searching for spectroscopic parameters of the ground electronic states and characterizing their low electronic excited states (Massó et al. 2006; Senent et al. 2007; Massó et al. 2007, 2008; Hochlaf et al. 2007, 2001; Zaidi et al. 2005). The main aim of these computations is to help the assignment of the IR bands observed in astrophysical sources. In the present investigation we are treating a mono Si substituted C_n analog. Eventhough carbon and silicon atoms are isovalent, the substitution of a carbon by a silicon atom alters some of the properties of the carbon chains. Indeed, C_4Si and C_5 are found to be comparable (Massó et al. 2007), where the electronic ground states are linear singlets, as is expected for odd C_n chains. C_4 presents two isomers of similar stabilities: a linear triplet and a D_{2h} rhombic geometry with a singlet ground electronic state (Massó et al. 2006; Senent et al. 2007). However, in C_3Si, the silicon atom breaks the D_{2h} symmetry, strongly stabilizing the cyclic forms with respect to the linear ones (Alberts et al. 1990; Gomei et al. 1997; Rintelman et al. 2001). Moreover, pure carbon chains show zero dipole moment and may only be detected in astrophysical sources with infrared techniques, using the antisymmetric modes (Cernicharo et al. 2002a,b; Goicoechea et al. 2004), whereas the silicon-carbons, type C_nSi, show non-zero permanent dipole moments that make them accessible for radioastronomy. For both types of chains, far infrared techniques are applicable, especially for the IR active bending modes.

Small silicon-carbon molecules type C_nSi play an important role in the chemistry of circumstellar shells, where ten percent of the discovered molecules contain silicon (McCarthy et al. 2003). In addition, they have been found in interstellar dense clouds. Similar to pure carbon chains (C_n), they undergo isomerization processes that convert linear into cyclic structures and vice versa (Massó et al. 2006; Senent et al. 2007; Massó et al. 2007, 2008). The smallest one, SiC, was detected in the outer shell of IRC+10216, existing at low temperatures in spite of the non-volatile nature of Si (Cernicharo et al. 1989). Its presence has been explained as resulting from the gas phase reaction series occurring there (Cernicharo et al. 1989).

Once the C_{2v} non-rigid structure of the C_2Si ring was characterized (Michalopoulus et al. 1984) and the pure rotational spectrum were measured (Gottlieb et al. 1989), many rotational lines of this molecule were detected in circumstellar shells (Thaddeus et al. 1984). For $\nu = 3$, the rhomboidal SiC_3 form has been astrophysically detected in the expanding envelope of IRC+10216 after being identified in laboratory (Apponi et al. 1999). The less stable rhomboidal structure has been experimentally detected but not in astrophysical sources (McCarthy et al. 1999). Few chains with $n < 8$ are well known (McCarthy et al. 2000), for instance, the linear form of SiC_4, which was accidentally observed in IRC+10216 (Ohishi et al. 1989). Readers are referred

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to the recent review by McCarthy, Gottlieb, and Thaddeus for more details (2003). It is worth noting that the general trends when comparing the C_n and $C_{n-1}Si$ molecular species are better understood by help of theoretical studies, closely compared to highly resolved experimental works.

Previous theoretical treatments established various cyclic and linear isomers for C_3Si when exploring the ab initio potential energy surfaces (Alberts et al. 1990; Gomei et al. 1997; Rintelman et al. 2001; Stanton et al. 2001; Sattelmeyer et al. 2002; Botschwina 2003; Kurashige et al. 2004; Rintelman et al. 2006; Linguerri et al. 2006). The stablest form is the astrophysically detected rhomboidal structure, followed by a second rhomboidal form and a linear isomer, *l*-SiCCC, where Si is at the end of this chain. These two structures are quasi-isoenergetic and are located at CA 1500 cm^{-1} above the global minimum. The linear form is believed to be of triplet spin-multiplicity and the cyclic ones of singlet spin-multiplicity.

Recently, state-of-the-art CCSD(T) ab initio calculations have been used to investigate the spectroscopy of the two rhomboidal forms that are found separated by a large potential barrier of 25 000 cm^{-1} (Linguerri et al. 2006). When examining the literature, little attention has been paid to the spectroscopy of the linear isomer, in spite of its being isovalent to *l*-C_4, a radical of significant astrophysical importance and abundance in interstellar medium (Massó et al. 2006; Senent et al. 2007; Goicoechea et al. 2004). Moreover, recent laboratory measurements allowed estimating quite a large dipole moment (of 4.8 debye) for *l*-SiCCC, which makes it suitable for radioastronomy (McCarthy et al. 2000).

Finally, we would like to emphasize that nothing has been said in the literature concerning the existence of linear SiCCC or its linear isomeric forms, such as CSiCC, in the IRC+10216 eventhough the most stable rhomboidal SiC_3 form is definitely identified there. More generally, the astrophysical catalogues contain a list of well-characterized molecules. However, a lack of information concerning low-frequency modes for many species prevents their identification in these media by far-IR techniques. For instance, several properties of important chains, especially of small sizes, are not understood well. For many cases, large discrepancies between experimental spectroscopic parameters measured using different experimental techniques are noticed. On the other hand, large ab initio computations, similar to the ones done here, represent a good alternative to provide relative values allowing the comparation of properties of different species, and they are often found to be really helpful. For this reason, the main goal of this paper is to give accurate spectroscopic parameters for the linear forms of C_3Si and then to compare them with those of *l*-C_4. For that purpose we use similar methodology to those in our papers treating *l*-C_4 (Massó et al. 2006; Senent et al. 2007). Finally, the present data are discussed in light of eventual astrophysical identification of these molecules in the far-IR domain.

2. Computational details

The electronic computations were performed with the MOLPRO program suite (MOLPRO 2006). For these computations, the Dunning's basis sets were employed (Dunning 1989; Woon et al. 1993). For the molecular species of interest, harmonic frequencies were determined at the coupled cluster including perturbative treatment of triple excitations (RCCSD(T)) (Knowles et al. 1993) and at the complete active space self consistent field (CASSCF) (Knowles et al. 2000) levels using various basis sets and the standard options implemented in the MOLPRO package. The standard algorithms for geometry searches are based on the rational function approach and the geometry DIIS approach (Eckert et al. 1997). Numerical derivatives are employed for the determination of harmonic frequencies (Rauhut et al. 1999). A threshold of 10^{-5} for the gradient is used. The main group of spectroscopic parameters has been calculated with second order perturbation theory applied on the quadratic, cubic and quartic force fields derived from six-dimensional potential energy surfaces (6-D PES) and the code FIT-ESPEC (Senent 2007). These 6D-PESs were mapped close to the respective equilibrium structures of linear C_3Si using both CASSCF and RCCSD(T) approaches and a cc-pVDZ basis set. This allows comparing the multi (CASSCF) and the mono configurational methods (RCCSD(T)) and gave insight into the importance of electron correlation (mainly static) for the C_3Si system (Knowles et al. 1993, 2000). Vertical excitation energies of the lowest electronic excited states of these species were calculated with CASSCF/cc-pVTZ and MRCI+Q/cc-pVTZ (including Davidson correction) techniques (Knowles et al. 1985). For CASSCF calculations, all π electrons were correlated. Finally, spin-orbit calculations were performed using the perturbational algorithm implemented in MOLPRO, where the spin-orbit matrix elements in Cartesian coordinates were evaluated using the CASSCF wavefunctions.

3. Results and discussion

3.1. Molecular structures of linear C_3Si species

By analogy to *l*-C_4 $X^3\Sigma_g^-$, we started our investigations by looking for eventual stationary points on the lowest triplet potential energy surface. Two structures corresponding to the outer and inner positions of the silicon atom (i.e. *l*-SiCCC and *l*-CSiCC), are found. *l*-SiCCC has been already identified by ab initio computations (Alberts et al. 1990; Gomei et al. 1997; Rintelman et al. 2001; Sattelmeyer et al. 2002; Botschwina 2003; Kurashige et al. 2004; Rintelman et al. 2006) and by muw (McCarthy et al. 2000). As is evident, *l*-SiCCC represents a minimum energy geometry. In addition, all the ab initio methods as used above produce positive harmonic frequencies (see Table 1). *l*-CSiCC is never characterized either theoretically or experimentally. It is located at 25 488 cm^{-1} (=3.16 eV) and 26 682 cm^{-1} (=3.31 eV) above the *l*-SiCCC minimum at the RCCSD(T)/cc-pVTZ and CASSCF/cc-pVQZ levels of theory, respectively. However, the situation is not quite clear whether *l*-CSiCC corresponds to a minimum or a maximum in the lowest triplet PES. Indeed, coupled cluster methods give one imaginary frequency (i.e. a transition state), whereas multi-configurational approaches lead to all positive harmonic wavenumbers (i.e. a minimum) (cf. Table 1 for more details). Futhermore, UCCSD(T) results are qualitatively identical to the ones obtained with the restricted theory. Strictly speaking, this makes difficult to define it as an isomer or a transition state, nevertheless, we believe that *l*-CSiCC corresponds to a minimum in the lowest triplet SiC_3 PES, since it has to be taken into consideration that multi-configurational approaches are better suited to the study of linear C_n and $C_{n-1}Si$ molecular systems because of the multiconfigurational nature of their electronic wavefunctions. Thus, we will be treating its spectroscopy (see below). Finally, the dipole moment of *l*-SiCCC was calculated to be 4.4064 debye (CASSCF/cc-pVQZ), whereas it is distinctly lower for *l*-CSiCC (1.8326 debye). Then, our computed dipole moment of 4.0–4.4 debye for *l*-SiCCC accords well with the value of 4.8 debye estimated with RHF calculations (Alberts et al. 1990). Hence, *l*-SiCCC and *l*-CSiCC may be detected by

Table 1. Equilibrium geometry (in Å) dipole moment (μ, in Debyes), rotational constants (B_e, D_e and B_0, in MHz), harmonic wavenumbers (ω_i, in cm^{-1}), and intensities (I, in Debyes^2/Å^2 amu) of *l*-SiCCC.

		RCCSD(T)	RCCSD(T)	UCCSD(T)	CASSCF	CASSCF	CASSCF	MCSCF	CCSD(T)	MP2	CISD	*mω*[g]
		cc − pVDZ[a]	*cc − pVTZ*[b]	*cc − pVTZ*[b]	*cc − pVDZ*[a]	*cc − pVTZ*[b]	*cc − pVQZ*[b]	6-31G(*d*)[c]	cc-pVQZ[d]	6-31G(*d*)[e]	DZ*P*[f]	
R_1	(Si-CCC str)	1.7662	1.7447	1.7427	1.7531	1.7410	1.7197	1.74	1.7249	1.732	1.722	
R_2	(SiC-CC str)	1.3299	1.2959	1.2954	1.2966	1.2841	1.2956	1.29	1.2899	1.297	1.298	
R_3	(SiCC-C str)	1.3120	1.3108	1.3133	1.3111	1.3003	1.2987	1.31	1.3062	1.3111	1.3070	
μ						4.0293	4.4064					
B_e		2636.4	2705.49	2706.86	2691.68	2736.88	2753.16					2747.7085
B_0		2637.8			2690.45							
$D_e \times 10^{-6}$		221.529			218.844							255.23
$\omega_1(\sigma)$	(C-C-C stretching)	2016.2	2040	1971	2070.0	2060	2005 (I = 152)	2055		2003		
$\omega_2(\sigma)$	(Si-C stretching)	1368.8	1391	1318	1357.1	1365	1366 (I = 11)	1342		1332		
$\omega_3(\sigma)$	(C-C-C stretching)	593.8	612	606	611.3	621	639 (I = 4)	613		629		
$\omega_4(\pi)$	(trans-bending)	379.8	384	381	443.1	455	463 (I = 9)	382		380		
$\omega_5(\pi)$	(cis-bending)	147.2	147	147	166.9	175	166 (I = 3)	150		151		

[a] This work. Values derived from our 6D PES; [b] this work. Values obtained using standard approaches implemented in MOLPRO. Refs. (Eckert et al. 1997) (Rauhut et al. 1999); [c] Ref. (Rintelman et al. 2001); [d] Ref. (Sattelmeyer et al. 2002); [e] Ref. (Gomei et al. 1997); [f] Ref. (Alberts et al. 1990); [g] Ref. (McCarthy et al. 2000).

submillimeter techniques in contrast to *l*-C_4, which is opaque for radioastronomy.

Table 1 lists the equilibrium distances, the dipole moment, the rotational constants, and the harmonic wevernumbers of *l*-SiCCC $X^3\Sigma^-$ computed at the coupled cluster and CASSCF levels of theory using the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, together with their comparison with previous theoretical and experimental determinations. Briefly, our computed SiC distance is shortened by increasing the size of the basis set. However, the CC distances are described well even with small basis sets. This can be rationalized by the better description of the Si atom by the more diffuse functions of the larger basis sets because of its large polarizability. For the rotational B_e constant, our computed values with CASSCF/cc-pVTZ (B_e = 2736.88 MHz) and CASSCF/cc-pVTZ (B_e = 2753.16 MHz), compare quite well with the B_e value of 2747.7085 MHz deduced from the muw spectrum of *l*-SiCCC by McCarthy et al. (McCarthy et al. 2000). Finally, the CASSCF calculated harmonic wavenumbers for *l*-SiCCC are in the ranges 2005–2070 cm^{-1} for ω_1 (CCC stretching), 1357–1366 for ω_2 (SiC stretching), 611–639 cm^{-1} for ω_3 (CCC stretching), 443–463 cm^{-1} for ω_4 (*trans* bending), and 166–175 cm^{-1} for ω_5 (*cis* bending), depending on the basis set used for these computations. For ω_1 a relatively large energy domain is given here because of numerical problems encountered when computing the harmonic frequencies of this molecular species using standard approaches, especially when using the cc-pVQZ basis set. From Table 1, one can clearly see that the Coupled cluster approaches underestimate both bending wavenumbers, compared to the CASSCF ones. The highest intensity is calculated for the high-frequency stretching (ω_1) and appreciable intensities are computed for all other modes.

Table 2 gives our computed data for the *l*-CSiCC isomer. These data represent predictions for this species. The CASSCF/cc-pVQZ equilibrium structure is R_1(CSi) = 1.7886 Å, R_2 (SiC) = 1.6640 Å and R_3(CC) = 1.2789 Å. The rotational constant at the minimum is calculated to be 3205.37 MHz and should have similar accuracy as for *l*-SiCCC (see above). Concerning the harmonic frequencies, we suggest that, with the exception of the SiC-stretch, the whole of the spectrum of CSiCC is displaced to lower frequencies with respect to the one of *l*-SiCCC. The absolute intensities are higher for the CSiCC bands. Readers are referred to Table 2 for more details.

4. Anharmonic vibrational analysis

For linear tetratomic molecules, six internal coordinates permit generating the potential energy surfaces (PESs): the three bond lengths, R_1, R_2, and R_3, two planar angles, θ_1 and θ_2, and a dihedral torsion angle, τ. For the definition of these internal coordinates, please see Fig. 1. The 6D PESs was mapped around the corresponding equilibrium geometries of *l*-SiCCC $X^3\Sigma^-$ at the CASSCF/cc-pVDZ level of theory. The grid contained 4982 selected geometries defined for the following values of the coordinates: R^{ref}+0.1 Å $\geq R \geq R^{\text{ref}}$–0.1 Å, $\theta^{\text{ref}}+10^{\circ} \geq \theta \geq \theta^{\text{ref}}-10^{\circ}$ and $\tau = 0, 5, 10, 170, 175, 180^{\circ}$, where R^{ref}, θ^{ref}, and $\tau = 0^{\circ}$ are the equilibrium geometries. The initial force field depends on seven coordinates after transforming the angular coordinates following the definition of Hoy et al. (1972). Then, anharmonic force field containing quadratic, cubic, quartic, and four-coupling terms was derived from the 6-dimensional potential energy surfaces for the stablest form of tricarbon-silicon. Table 3 shows the anharmonic wavenubers determined using perturbation theory and the code FIT-ESPEC (Senent 2007). FIT-ESPEC performs a linear fit of the energies and geometries to a polynomial series. Thus, a force field expressed in curvilinear internal coordinates is obtained for the local minima. The transformation from curvilinear to normal coordinates of (Hoy et al. 1972) allowed us to determine anharmonic constants. Although a modest basis set has been employed here to generate these 6D-PESs, computations may be powerful enough as preliminary determination of the band position displacements caused by anharmonicities, since the cubic, and quartic forces responsible for anharmonic effects are not dependent on the level of calculations (Császár et al. 1997) as the quadratic terms. Indeed, the main aim of these computations is to estimate the anharmonicity effects and then to use these corrections, together with the data depicted in Tables 1 and 2, to evaluate their anharmonic wavenumbers at higher levels, since the corresponding computations are extremely demanding (cf. Senent et al. 2007, for more details). Presently, we will be using the harmonic wavenumbers derived from CASSCF/cc-pVTZ rather than the ones from CASSCF/cc-pVQZ because of numerical problems encountered using the later basis set (see above). Table 3 lists the corresponding results for *l*-SiCCC , where the ν_1 is evaluated 2024, ν_2 = 1352, ν_3 = 611, ν_4 = 434, and ν_5 = 169. All values are in cm^{-1}. Finally, Table 4 gives data deduced from calculations achieved for various isotopomers containing ^{13}C, the second

Table 2. Equilibrium geometry (in Å), dipole moment (μ, in Debyes), rotational constants (B_e, D_e and B_0 in MHz), harmonic wavenumbers (ω_i, in cm^{-1}), and intensities (I, in $Debyes^2/Å^2$ amu) of *l* -CSiCC.

		RCCSD(T) cc-pVTZ[a]	UCCSD(T) cc-pVTZ[a] cc-pVDZ[b]	CASSCF cc-pVTZ[a]	CASSCF cc-pVQZ[a]	CASSCF
R_1	(C-SiCC str)	1.8330	1.8320	1.8096	1.7931	1.7886
R_2	(CSi-CC str)	1.6898	1.6911	1.6897	1.6676	1.6640
R_3	(CSiC-C str)	1.2886	1.2891	1.2868	1.2814	1.2789
μ					1.7700	1.8326
B_e		3101.54	3099.96	3129.07	3191.06	3205.37
B_0				3162.50		
$D_e \times 10^{-6}$				353.484		
$\omega_1(\sigma)$	(C-C-C stretching)	1890	1886	1961.2	1940	1941 (I = 900)
$\omega_2(\sigma)$	(Si-C stretching)	915	909	934.8	976	979 (I = 32)
$\omega_3(\sigma)$	(C-C-C stretching)	619	619	604.5	655	660 (I = 2)
$\omega_4(\pi)$	(trans-bending)	i118	i127	211.5	166	164 (I = 47)
$\omega_5(\pi)$	(cis-bending)	28	27	91.6	91	86 (I = 0)

[a] This work. Values obtained using standard approaches implemented in MOLPRO. Refs. (Eckert et al. 1997; Rauhut et al. 1999); [b] This work. Values derived from our 6D PES; [c] Ref. (Rintelman et al. 2001).

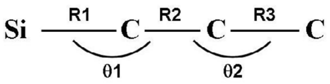

Fig. 1. Internal coordinates of *l*-SiCCC.

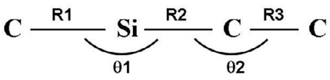

Fig. 2. Internal coordinates of *l*-CSiCC.

Table 3. Perturbatively computed fundamentals of *l*-SiCCC. All values are in cm^{-1}.

	CASSCF/cc-pVDZ[a]	CASSCF/cc-pVTZ[b]
$\nu_1(\sigma)$	2034	2024
$\nu_2(\sigma)$	1344	1352
$\nu_3(\sigma)$	601	611
$\nu_4(\pi)$	422	434
$\nu_5(\pi)$	160	169

[a] Derived from our 6D-PESs; [b] Estimations. See text for more details.

most abundant carbon isotope existing in the ISM (abundance ratio $^{13}C/^{12}C = 1/45$), ^{29}Si, and ^{30}Si. This table shows the rotational constants, including the vibrational corrections for the zero point vibrational energy (B_0) and the isotopic shifts on the anharmonic wavenumbers. Isotopic substitutions produce stronger effects on the three stretching and the *trans* bending modes, whereas the isotopic shifts of the *cis* bending mode are less significant. It is worth noting that a single carbon substitution displaces the bands significantly whereas the substitution of ^{29}Si by ^{30}Si weakly affects the fundamentals, but exception should be made for the ν_3 band. The data in Table 4 for the other isotopomers and those of the unknown fundamentals should be helpful in their identification in laboratory and in interstellar media.

5. Electronic transitions and spin-spin calculations

Tables 5 and 6 list the dominant electron configuration and the vertical excitation energies of the *l*-SiCCC and *l*-CSiCC lowest excited electronic states calculated for each symmetry. These tables show transitions to singlets, triplets, and quintets states determined at the CASSCF and MRCI+Q levels of theory and the cc-pVTZ basis set. These calculations were done at the corresponding equilibrium geometries of *l*-SiCCC and *l*-CSiCCC. For both species, the data computed using either CASSCF or MRCI+Q are close in energy, showing that CASSCF accounts for electron correlation. For *l*-SiCCC, the excitations to the two first excited states, $^1\Delta$ and $^1\Sigma^+$, were calculated to be 0.29 eV and 0.46 eV, which compares well with the MCQDPT data of Rintelman and Gordon (Rintelman et al. 2001). For *l*-CSiCC, the lowest $^1\Delta$ and $^1\Sigma^+$ are located at 0.69 eV and 0.98 eV. In our previous paper (Massó et al. 2006) the corresponding values for *l*-C_4 0.44 eV ($^1\Delta_g$) and 0.61 eV ($^1\Sigma_g{}^+$) were found using the same level of calculations as in the current work. When comparing the electronic spectra of the linear C_3Si species to the isovalent *l*-C_4 molecule (Massó et al. 2006), one can easily see that these three molecular species present similar electronic states in the 0–4 eV energy range, except for the $^3\Pi$ and $^1\Pi$ electronic states of *l*-SiCCC, which are located distinctly higher in energy. For instance, *l*-SiCCC($^3\Pi$) is computed to be above 2.5 eV, whereas it is lying at 1–1.3 eV for *l*-C_4($^3\Pi$) and for *l*-CSiCC($^3\Pi$).

Since the spin-orbit constant of atomic Si (148.9 cm^{-1}) is greater than its value for atomic C (29 cm^{-1}) (Lefebvre-Brion et al. 2004), we expect that the spin-orbit interaction effect of C_3Si (see Table 7) is greater than its in *l*-C_4. At the CASSCF/cc-pVTZ level of theory and using the formula developed in Lefebvre et al. (2004), the spin-spin λ constant of C_3Si, originating from two Σ states interaction, is –0.605 cm^{-1} for *l*-SiCCC and 0.08 cm^{-1} for *l*-CSiCC. Our computed value for *l*-SiCCC accords with the one deduced by McCarthy et al. (2000) from the analysis of their muw spectra. The computed value for *l*-CSiCC $X^3\Sigma^-$ is of the same order of magnitude as for *l*-C_4, however, λ(*l*-SiCCC $X^3\Sigma^-$) is distinctly larger than λ(*l*-C_4 $X^3\Sigma_g^-$). We do believe that the λ(*l*-SiCCC $X^3\Sigma^-$) constant is large enough to split the ro-vibrational levels in a experimentally quantifiable way. Therefore, IR bands of *l*-SiCCC should be complex. In Senent et al. (2007), we discussed the assignment of a complex band observed at 174 cm^{-1} in IRC+10216 (Cernicharo et al. 2002a), tentatively assigned to *l*-C_4. This assignment is not supported by our calculations of C_4 spin-spin interaction, eventhough the range of calculated frequency sustains it. An interpretation of far infrared bands implies completing the astrophysical catalog that show a lack of spectroscopic data for carbon chains, especially for the large-amplitude vibrations. Only with a large

Table 4. Isotopic substitution displacements of the band centers (in cm^{-1}) and the B_0 rotational constant (in MHz) for *l*-SiCCC.

	^{13}C-C-C-Si	C-^{13}C-C-Si	C-C-^{13}C-Si	C-C-C-^{29}Si	C-C-C-^{30}Si
$\nu_1(\sigma)$	–10.2	–45.1	–19.2	–0.3	–0.6
$\nu_2(\sigma)$	–22.2	–2.3	–26.6	–0.7	–1.3
$\nu_3(\sigma)$	–6.5	–4.3	–0.9	–5.4	–10.6
$\nu_4(\pi)$	–1.1	–8.8	–5.4	0.0	0.0
$\nu_5(\pi)$	–1.8	–0.9	–2.9	–0.4	–0.7
B_0	–95	–24.8	0.0	–40.9	–79.5

Table 5. Vertical excitation energies (in eV) and dominant electron configuration of the lowest electronic states of *l*-SiCCC. These energies are given with respect to the $X^3\ \Sigma^-$ ground state.

State	CASSCF/cc-pVTZ[a]	MRCI+Q/cc-pVTZ[b]	MCQDPT[c]	Electron configuration
$X^3\Sigma^-$	0.0	0.0	0.0	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^1\Delta$	0.30	0.29	0.40	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^1\Sigma^+$	0.44	0.46	0.46	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^1\Sigma^-$	2.10	2.20		$(11\sigma)^2(2\pi)^4(3\pi)^1(4\pi)^1$
$^3\Delta$	2.16	2.29		$(11\sigma)^2(2\pi)^4(3\pi)^1(4\pi)^1$
$^3\Sigma^+$	2.17	2.35		$(11\sigma)^2(2\pi)^4(3\pi)^1(4\pi)^1$
$^3\Pi$	2.42	2.50		$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^1\Pi$	3.61	3.22		$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^5\Pi$	3.44	3.80		$(11\sigma)^1(2\pi)^4(3\pi)^2(4\pi)^1$
$^3\Pi$	4.70	4.53		$(11\sigma)^1(2\pi)^4(3\pi)^2(4\pi)^1$
$^5\Sigma^-$	4.54	4.78		$(11\sigma)^2(2\pi)^3(3\pi)^2(4\pi)^1$
$^5\Delta$	4.67	4.92		$(11\sigma)^2(2\pi)^3(3\pi)^2(4\pi)^1$
$^5\Sigma^+$	4.77	5.02		$(11\sigma)^2(2\pi)^3(3\pi)^2(4\pi)^1$
$^1\Pi$	5.77	5.63		$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^5\Pi$	6.01	6.34		$(11\sigma)^1(2\pi)^3(3\pi)^3(4\pi)^1$

[a] E(CASSCF/cc-pVTZ) = –402.4642666 E_h; [b] E(MRCI+Q/cc-pVTZ) = –402.896849 E_h; [c] (MCQDPT/aug-cc-pVDZ) (Rintelman et al. 2001).

Table 6. Vertical excitation energies (in eV) and dominant electron configuration of the lowest electronic states of *l*-CSiCC. These energies are given with respect to the $X^3\ \Sigma^-$ ground state.

State	CASSCF/cc-pVTZ[a]	MRCI+Q/cc-pVTZ[b]	Electron configuration
$X^3\Sigma^-$	0.0	0.0	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^1\Delta$	0.43	0.69	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^1\Sigma^+$	0.79	0.98	$(11\sigma)^2(2\pi)^4(3\pi)^2$
$^3\Pi$	1.17	1.11	$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^1\Sigma^-$	1.62	2.19	$(11\sigma)^2(2\pi)^3(3\pi)^3$
$^1\Pi$	2.73	2.27	$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^3\Delta$	1.97	2.32	$(11\sigma)^2(2\pi)^3(3\pi)^3$
$^3\Sigma^+$	1.71	2.38	$(11\sigma)^2(2\pi)^3(3\pi)^3$
$^5\Pi$	3.20	3.31	$(11\sigma)^1(2\pi)^4(3\pi)^2(4\pi)^1$
$^1\Pi$	3.87	3.48	$(11\sigma)^1(2\pi)^4(3\pi)^3$
$^3\Pi$	3.44	3.55	$(11\sigma)^1(2\pi)^3(3\pi)^4$
$^5\Sigma^-$	3.02	3.69	$(11\sigma)^2(2\pi)^3(3\pi)^2(4\pi)^1$
$^5\Sigma^+$	3.98	4.37	$(11\sigma)^2(2\pi)^4(3\pi)^2(4\pi)^1$
$^5\Pi$	4.08	4.67	$(11\sigma)^2(12\sigma)^1(2\pi)^3(3\pi)^2$

[a] E(CASSCF/cc-pVTZ) = –402.347488 E_h; [b] E(MRCI+Q/cc-pVTZ) = –402.781500 E_h.

list of data of many molecules, the assignment will be assured. By taking the stability, electronic structure, the λ spin-spin constants, and the band positions into consideration, *l*-SiCCC has to be taken into consideration as candidate for understanding the FIR observations. However, because *l*-SiCCC shows a large dipole moment, this existence in astrophysical sources should be confirmed by radioastronomy.

6. Conclusion

In the present contribution, we characterized the linear C_3Si isomers and determined the effect of substituting of a carbon by a silicon atom on the molecular properties, suggesting the bending modes of *l*-SiCCC responsible of astrophysically observed far infrared bands. This study may help future inquires since

Table 7. Spin-spin constant in the ground electronic state of *l*-SiCCC and *l*-CSiCC. All values are in cm^{-1}.

	l-SiCCC	*l*-CSiCC
$\Delta E\ (X^3\Sigma^- \rightarrow {}^1\Sigma^+)$	4077	8379
λ^a	–0.605	0.08
	-0.547186^b	

[a] Ref. (Lefebvre-Brion et al. 2004); [b] deduced from μw measurements, Ref. (McCarthy et al. 2000).

astrophysical carbon rich sources always contain silicon, and the coexistence of *l*-C_3Si and *l*-C_4 can be expected. Future accurate instruments for radioastronomy will be able to identify both species. In addition, computations performed using different ab initio methods permit discussion of the adequacy of monoconfigurational methods for tetratomic Si mono substituted carbon chain studies. Standard methods show qualitative differences between frequencies calculated using these two kinds of methods. As for pure carbon chains, it is believed that only multiconfigurational approaches lead to equivocal data.

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