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Citation: *J. Chem. Phys.* **133**, 184107 (2010); doi: 10.1063/1.3491264

View online: <http://dx.doi.org/10.1063/1.3491264>

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Theoretical characterization of the SiC_3H^- anion

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(Received 9 April 2010; accepted 31 August 2010; published online 11 November 2010)

Highly correlated *ab initio* methods are used to predict the equilibrium structures and spectroscopic parameters of the SiC_3H^- anion. The total energies and physical properties are reported using CASSCF/MRCI, RCCSD(T), and RCCSD(T)-F12 approaches and extended basis sets. The search of stable geometries leads to a total of 12 isomers (4 linear and 8 cyclic), for which electronic ground states have close-shell configurations. The stability of the linear form, $l\text{-SiC}_3\text{H}^-$, is prominent. For the most stable linear isomer, the B_e equilibrium rotational constant has been calculated with RCCSD(T) and a complete basis set. Core-correlation and vibrational effects have been taken into account to predict a B_0 of 2621.68 MHz for $l\text{-SiC}_3\text{H}^-$ and 2460.48 MHz for $l\text{-SiC}_3\text{D}^-$. The dipole moment of $l\text{-SiC}_3\text{H}^-$ was found to be 2.9707 D with CASSCF/aug-cc-pV5Z and the electron affinity to be 2.7 eV with RCCSD(T)-F12A/aug-cc-pVTZ. Anharmonic spectroscopic parameters are derived from a quadratic, cubic, and quartic RCCSD(T)-F12A force field and second order perturbation theory. CASSCF/MRCI vertical excitations supply three metastable electronic states, $^1\Sigma^+$, $^3\Sigma^+$, and $^3\Delta$. Electron affinities calculated for a series of chains type SiC_nH and SiC_n ($n=1-5$) allow us to discuss the anion formation probabilities. © 2010 American Institute of Physics. [doi:10.1063/1.3491264]

I. INTRODUCTION

Silicon-carbon molecules play an important role in the chemistry of chemical vapor deposition and the formation of hydrogenated amorphous silicon carbide films, given their remarkable properties, such as the endurance to high temperature and oxygation.¹

Beyond their fundamental significance to the material sciences, small silicon-carbon species are also of great importance in astrophysics since nearly 10% of the detected molecules in astrophysical objects contain Si.² Although Si is considered a dust-forming element by depletion, many sources such as circumstellar envelopes and carbon rich stars show rich silicon chemistry in the gas phase.³⁻⁵ Actually, many molecules such as SiO ,⁶ SiS ,⁷ SiN , and SiH_2 ,⁸ and several silicon-carbon bearing molecules, SiC ,⁹ SiC_2 ,¹⁰ SiC_4 ,¹¹ SiC_3 ,¹² SiCN , and SiNC ,¹³ are listed as discovered species.

The study of silicon carbon molecules began in the 1980s with the identification of the SiC_2 radical toward IRC+102169,¹⁰ which had already been observed by Merrill¹⁴ and Sanford¹⁵ in carbon-rich stars. McCarthy *et al.*¹⁶ reported many carbon-silicon molecules detected at the laboratory level, some of them contain heteroatoms (H, S, N). They reported various monohydrogenate silicon-carbon chains such as SiC_4H , SiC_5H , and SiC_6H observed by Fourier transform microwave spectroscopy.¹⁶ One of them, SiC_2H , was tentatively detected in IRC+10216.¹⁷ Several

other SiC_nH chains are expected to be discovered in both laboratory and astrophysical sources. They may be precursors to the SiC_n cluster found in stellar atmospheres.

C and Si are isovalent elements. Commonly, carbon compound rates in astrophysical sources are much more significant than those of silicon compounds because cosmic abundances are larger for C than for Si. However, some silicon substituted molecules are more abundant than the pure parent carbon species. This is the case of C_3Si and C_4 . Whereas $c\text{-C}_3\text{Si}$ is a detected molecule,¹² the identification of C_4 remains unclear. We suggested that the linear isomer of C_3Si is responsible for an observed infrared band tentatively assigned to C_4 on the basis of the hyperfine structure of the spectra.^{18,19} For other cases, the substitution of a C by a Si could alter the conventional rates of abundances that also depend on the thermodynamic stabilities and formation processes viability.

On the basis of our previous experience in the study of silicon-carbon and pure carbon chains,¹⁸⁻²² we try, in this paper, to perform a theoretical characterization of the SiC_3H^- anion a new species derived from SiC_3 and comparable to the detected C_4H^- . In the same way that SiC_nH type neutral chains share many chemical properties with the C_nH hydrogen carbon chains, the type SiC_nH^- anions should share properties with the C_nH^- anions. Various molecular parameters of C_4H and C_4H^- were predicted in our recent theoretical study.²¹ Both of these species display preferred linear configurations. The ground state of C_4H^- is a Σ singlet of prominent stability, whereas two adiabatic doublet electronic Σ and Π states, whose energy difference is very small, participate in the electronic ground state of C_4H . C_4H represents one of the first astrophysical molecules to be discovered,²³ whereas the detection of C_4H^- is very recent.²⁴

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The discovery of C_4H^- is a result of the recent interest in the astrophysical search for anions. The presence of negative species in astrophysical sources was first considered by Dalgarno and McCray²⁵ in 1973 and by Herbst²⁶ in 1981, who pointed out their important role in gas phase reactions. Recently, there has been an increasing interest in astrophysical community due to the detection of C_6H^- by McCarthy *et al.*²⁷ in 2006. This has generated the search of C_4H^- ,²⁴ C_8H^- ,²⁸ C_3N^- ,²⁹ and C_5N^- .³⁰ Many other anions are expected to be identified after the release of the new Observatory ALMA. Efforts devoted to their search are reasonable considering that the regular stabilization of linear chains by electron attachment increases their probability of being produced. Anions are now considered as important intermediates of chemical reaction in the astrochemical models.³¹

The relevance of type SiC_nH neutral forms is clear.^{3,4,16,32} Type SiC_nH^+ cations have been considered intermediates of ion-molecule processes involving silicon compounds.^{3,5,32} Whereas neutral short chains have been studied experimentally^{33–35} and theoretically,^{36,37} nothing has been said about the SiC_nH^- anions that we study here. In this paper, we show their viability on the basis of state-of-the-art mono- and multireferential *ab initio* calculations. We report pertinent information concerning their structure and spectroscopic properties which should aid their astrophysical search. Second order perturbation theory is employed to obtain spectroscopic parameters. Significant properties are compared with the corresponding ones of other type SiC_nH , SiC_n , and SiC_n^- chains. The main part of the calculations have been performed with RCCSD(T) theory, although we use RCCSD(T)-F12 to reduce the computational expense of largest calculations. CASSCF/MRCI and CASSCF methods are used for electronic excited state determination and for the search of secondary minima for which static correlation can play an important role.

II. COMPUTATIONAL DETAILS

The energies of various electronic states and the geometries and vibrational frequencies of the SiC_3H^- isomers have been calculated with the MOLPRO program suite.³⁸ Extensive treatments of correlation effects were included using RCCSD(T) (restricted coupled cluster theory with a perturbative treatment of triple excitations)³⁹ and the explicitly correlated method RCCSD(T)-F12A.⁴⁰ For the RCCSD(T) method, Dunning's correlation-consistent basis sets augmented by diffuse functions aug-cc-pVXZ ($X=3,4,5$) (Ref. 41) were selected to search for a good description of the anion electronic density. For the explicitly correlated calculations, three basis sets were employed: the orbital aug-cc-pVTZ, an aVTZ-MP2FIT basis set for the density fitting integral evaluation of the F12 integrals, and the VTZ/JKFIT basis set because the many electron integrals are approximated by resolutions of the identity expansions.⁴² To acquire reliable rotational constants for the most stable linear anion, core-correlation consistent basis sets (aug-cc-VCXZ ($X=3,4$)) were also used.⁴³

It is generally accepted that the F12A explicitly correlated correction, recently implemented in MOLPRO, slightly

overestimates the correlation effects.⁴⁰ The capability of both methods RCCSD(T) and RCCSD(T)-F12A for the determination of energies and some significant spectroscopic properties (rotational constants) has been compared. Since results at the RCCSD(T)/aug-cc-pV5Z level are comparable to those at the RCCSD(T)-F12/aug-cc-pVTZ, we have used the explicitly correlated methods to reduce computational expenses in calculations involving large molecules and for the potential energy surfaces. Anharmonic spectroscopic parameters for the electronic ground state are determined from a RCCSD(T)-F12 anharmonic force field using second order perturbation theory and the FIT-ESPEC code.⁴⁴

For linear SiC_3H^- , vertical excitation energies to the low energy excited electronic states were also determined with CASSCF (complete active space self consistent field) and CASSCF/MRCI (multiconfiguration reference internally contracted configuration interaction).^{45,46} CASSCF theory is also employed to search for isomers because static correlation effects can play an important role in carbon-chain isomers of low stability. It was also used for the dipole moment calculations since RCCSD(T) wave methods do not satisfy the Hellmann–Feynman theorem in the usual sense.

For the CASSCF and MRCI calculations, all the π -valence electrons were correlated. The core-orbitals and the σ -valence-orbitals were considered doubly occupied in all the configurations and were optimized.

III. RESULTS AND DISCUSSION

A. Silicon-carbon chain anions

Table I summarizes and compares various properties of various linear silicon carbon-chain types C_nSi and SiC_nH . Electron affinities and dipole moments allow us to discuss their detection probability and anion formation viability. Reported species are the neutral SiC ($X^3\Pi$), SiC_2 (X^1A_1), SiC_3 ($X^3\Sigma^-$), SiC_4 ($X^1\Sigma^+$), and SiC_5 ($X^3\Sigma^-$), and $SiCH$ ($X^2\Pi$), SiC_2H ($X^2\Pi$), SiC_3H ($X^2\Pi$), SiC_4H ($X^2\Pi$), and SiC_4H ($X^2\Pi$) and their respective anions. Almost all present linear geometries with the exceptions of SiC_2 and the favored isomer of SiC_3 which are cyclic.^{49,54} With the exception of SiC_2 , all of them present isomerism.

Spectroscopic parameters for the neutral forms are compared with previous experimental works.^{11,12,34,47–53} Computed parameters of $SiCH$ are compared with the theoretical parameters obtained by Robbe *et al.*⁵³ in their Renner–Teller study, whereas those for anions type SiC_n^- , with the previous theoretical results of Gomei *et al.*⁵² Previous dipole moments are taken from the BASEMOL base data.⁴⁸

Geometry and energy calculations have been performed with RCCSD(T)-F12A/aug-cc-pVTZ. This level of theory, very efficient for large systems such as SiC_5H , provides results which are of the same quality as those obtained with RCCSD(T)/aug-cc-pV5Z. Comparative results of RCCSD(T) and RCCSD(T)-F12A are presented in the next sections.

Hydrogenated compounds display isomerism. Linear forms, where H and Si are outer atoms, are preferred.^{36,37} All of them represent stable structures with positive electron af-

TABLE I. Equilibrium geometries [H–C₁–C₂–...–C_n–Si; R(n–1)=C(n–1)–C(n)] (distances in Å, angles in degrees), total electronic energies (E in a.u.), and electron affinities (Ea, in eV) of various silicon-carbon-chains calculated with RCCSD(T)-F12A/aug-cc-pVTZ. Dipole moments (dipole moments referred to the center of masses) (μ in debyes) calculated with CASSCF/aug-cc-pVTZ.

	Neutral			Anion		
	This work	Previous works		This work		
CSi (X ³ Π)	CSi=1.7237 E=–326.887537	B _e =20 254.5 μ =0.8831	B ₀ =20 297.6 ^a μ =1.7 ^b	I-CSi⁻ (X ² Σ ⁺)	CSi=1.6882 E=–326.976472	B _e =21 115.4 μ =0.6885 Ea= 2.42
c-C₂Si (X ¹ A ₁)	CC=1.2740 CSi=1.8398 CSiC=40.5 E=–364.990318	A _e =51 898.2 B _e =13 131.4 C _e =10 479.8 μ =2.9587	A ₀ =52 473.7 B ₀ =13 158.7 C ₀ =10 441.6 ^c μ =2.393 ^b	I-C₂Si⁻ (X ² Π)	R1=1.2775 CSi=1.7593 E=–365.042265	B _e =6010.7 μ =3.8003 Ea= 1.41
c-C₃Si (X ¹ A ₁)	CC=1.4375; CSi=1.8374 CCC=62.4 CSiC=47.8 E=–402–969684	A _e =37 972.5 B _e =6252.3 C _e =5368.4 μ =3.8671	A ₀ =37 943.8 B ₀ =6 282.9 C ₀ =5 386.9 ^d μ =4.2 ^b	I-C₃Si⁻ (X ² Π)	R1=1.2863 R2=1.3318 CSi=1.7005	B _e =2740.1 μ =4.1481
I-C₃Si (X ³ Σ ⁻)	R1=1.3065; R2=1.2936 CSi=1.7347 E=–402.955065	B _e =2726.7 μ =4.4016	B ₀ =2747.7 ^e μ =4.8 ^b		E=–403.061124	Ea= 2.49
I-C₄Si (X ¹ Σ ⁺)	R1=1.2842; R2=1.3021 R3=1.2766; CSi=1.6984 E=–441.015014	B _e =1520.6 μ =6.2111	B ₀ =1533.8 ^f μ =6.4 ^b	I-C₄Si⁻ (X ² Π)	R1=1.2689; R2=1.3375 R3=1.2638; CSi=1.7491 E=–441.099977	B _e =1484.9 μ =5.9792 Ea= 2.31
I-C₅Si (X ³ Σ ⁻)	R1=1.2983; R2=1.2923 R3=1.2848; R4=1.2837 CSi=1.7257 E=–478.995939	B _e =915.0 μ =6.4927	B ₀ =920.9 ^e	I-C₅Si⁻ (X ² Π)	R1=1.2750; R2=1.2399 R3=1.2621; R4=1.3228 CSi=1.6879 E=–479.117361	B _e =913.7 μ =6.0682 Ea= 3.30
I-SiCH (X ² Π)	HC=1.074; CSi=1.6111 E=–327.515859 HC=1.0658; R1=1.2283	B _e =19 034.1 μ =0.5771	B _e =19 034.1 ^g μ =0.55 ^g μ =0.066 ^h	I-SiCH⁻ (X ¹ Σ ⁺)	HC=1.0820; CSi=1.6577 E=–327.658569 HC=1.0645; R1=1.2371	B _e =18037.1 μ =0.3089 Ea= 3.88 B _e =5179.1
I-SiC₂H (X ² Π)	CSi=1.8122 E=–365.620893 HC=1.0638; R1=1.2332	B _e =5380.8 μ =1.1201	B _e =5436.7 ⁱ μ =1.4 ^b	I-SiC₂H⁻ (X ³ Σ ⁻)	CSi=1.8606 E=–365.669533 HC=1.0617; R1=1.2334	μ =4.2681 Ea= 1.32 B _e =1598.0
I-SiC₃H (X ² Π)	R2=1.3407; CSi=1.7016 E=–403.627363 HC=1.0639; R1=1.2164	B _e =2588.1 μ =1.1074		I-SiC₃H⁻ (X ¹ Σ ⁺)	R2=1.3674; CSi=1.6666 E=–403.726428 HC=1.0617; R1=1.2271	μ =2.9949 Ea= 2.70
I-SiC₄H (X ² Π)	R2=1.3632; R3=1.2400 CSi=1.7941 E=–441.665079	B _e =1401.4 μ =1.3061		I-SiC₄H⁻ (X ³ Σ ⁻)	R2=1.3566; R3=1.2533 CSi=1.8137 E=–441.727130	B _e =1383.6 μ =7.3795 Ea= 1.69
I-SiC₅H (X ² Π)	HC=1.0639; R1=1.2205 R2=1.3501; R3=1.2498 R4=1.3203; CSi=1.7046 E=–479.674515	B _e =245.77 μ =0.5122		I-SiC₅H⁻ (X ¹ Σ ⁺)	HC=1.0616; R1=1.2261 R3=1.3556; R4=1.2456 R5=1.3467; CSi=1.6719 E=–479.784168	B _e =245.61 μ =4.8991 Ea= 2.98

^aReference 47.^bReference 55.^cReference 49.^dReference 50.^eReference 51.^fReference 11.^gReference 52.^hReference 34.ⁱReference 53.

finities (E_A). Complex spectra showing Renner–Teller and spin-orbit features are expected for the SiC_nH neutral forms and the C_nSi⁻ anions whose electronic ground states are doublets.³³ However, linear structure types C_nSi and SiC_nH⁻ show singlet or triplet ground states depending on the parity

of n (for even n, C_nSi are singlets and SiC_nH⁻ are triplets). This propensity rule for spin multiplicities is distinctive for C_n carbon chains.^{18,20}

With the exception of the C₅Si chain (comparable to C₆), large electron affinities and stabilities correspond to the com-

pounds type $\text{SiC}_{2m+1}\text{H}^-$ of closed-shell configuration. In general, E_A increases with the molecular sizes, as was first described by Nakajima *et al.*⁵⁵ As is the case of pure carbon chains, linear silicon-carbon bearing chains stabilize drastically by electron attachment.

For anions, dipole moment increases with the molecular size, although type SiC_nH^- anions show unexpectedly large dipoles, if the electronic ground states are triplets. Electric properties have been determined with CASSCF/aug-cc-pVTZ. For species with 1, 2, 3, 4, and 5 carbon atoms, the active space was defined considering, respectively, 8, 10, 12, 14, and 19 orbitals doubly occupied in all the configurations and optimizing them during the CASSCF procedure. As was first observed for C_4H^- ,²¹ the determination of one-electron properties using expectation values and multiconfigurational methods is “safer” than monoreferential methods in the case of systems such as carbon chains with high densities of electronic states near the ground state region. In addition, in our codes, the CCSD dipole moment determination implies the use of numerical methods that can introduce inaccuracies.

Anions with singlet electronic ground states (SiCH^- , SiC_3H^- , and SiC_5H^-) display significant values for E_A . However, their dipole moments, which augment with the molecular size, are lower for singlets than for triplets. In addition, μ is lower for SiCH^- than for SiCH , whereas, for SiC_3H^- and SiC_5H^- , μ is larger for the anions. The order of magnitude of the SiC_3H^- dipole moment corresponds to chains with three carbon atoms ($l\text{-SiC}_3$, $l\text{-SiC}_3^-$, and the detected $c\text{-SiC}_3$).

E_A determines the photodetachment rate and μ makes the detection feasible. Whereas anions with $n=3,5$ carbon atoms are isovalent with the first astrophysically detected (type C_{2m}H^-) chains, the C_2H^- molecule,^{56,57} isoelectronic with SiCH^- , remains undiscovered. Its low abundance with respect to the neutral C_2H and other anions such as C_6H^- has been justified by the low electron attachment rate which depends on the density of vibrational states.⁵⁶ It may persist undetected given its low dipole moment. These two arguments are also valid for SiCH^- . The pentatomic SiC_3H^- , isovalent with the detected C_4H^- [$E_A=3.558 \pm 0.0015$ eV (Ref. 58)], and SiC_5H^- , isovalent with the detected C_6H^- , could be the most abundant hydrogenated compounds.

B. The isomers of SiC_3H^-

Although neutral SiC_3H is an important building block of polycarbosilanes,⁴⁷ little attention has been offered to their ionic forms. Sun *et al.*,⁵⁹ have characterized 18 isomers for the neutral molecule.

The starting point of the SiC_3H^- characterization has been the search of stable geometries by taking into consideration previous results concerning the neutral SiC_3H and C_3Si species as well as our first calculations on the astrophysically detected C_4H^- anion. In this case, the hydrogen attachment doubles the number of stable structures of C_4 . On the other hand, C_3Si possesses at least five minima; two of them are linear and two are cyclic, while the other is a $d\text{-C}_3\text{Si}$ structure of C_{2v} symmetry, with Si at the molecular center. In principle, for C_3Si , there are many active centers

for the hydrogen attachment although they do not always correspond to stable geometries. Table II summarizes results for located isomers in which all the calculated harmonic frequencies are positive.

For SiC_3H^- , 12 minimum energy structures were found, which is less than that for the neutral SiC_3H ,⁵⁹ but more than those for longer carbon chains that are building blocks of graphenes.⁶⁰ Four isomers are linear and eight are cyclic (see Table II). All of them show singlet electronic ground states. For their labeling, we use the l -(linear) and c -(cyclic) symbols. Even though most of the stable forms of C_3Si are cyclic, the preferred geometry, $l\text{-SiC}_3\text{H}^-$, is linear as occurs with C_4H^- and neutral SiC_3H .⁵⁹ The remaining isomers lie above 1 eV. The hydrogen and electron attachments reverse the relative order of stabilities of C_3Si , confirming the prominent stability of linear carbon chains anions with respect to other possible structures. In the most stable $\text{C}_{\infty v}$ linear isomer $l\text{-SiC}_3\text{H}^-$, the Si and H atoms attach to opposite outer carbon atoms (see figure in Table II). The parent neutral isomer (C-C-C-Si) represents the most stable linear form of C_3Si for which the cyclic structures are preferred. Remaining linear isomers are C-C-C-Si-H , C-C-Si-C-H , and C-Si-C-H , following the order of stabilities.

The calculations have been performed with two different *ab initio* methods, RCCSD(T) and CASSCF,²¹ as is our custom with carbon chains. Their comparison allows us to evaluate the role of static correlation, which can produce important effects due to the unsaturated character, and the high density of electronic states near the ground state and sometimes, orbital near-degeneracy. The effect of static correlation can be important for secondary minimum and specially for low stability isomers.

In general (with a few exceptions), the relative orders of stabilities derived with RCCSD(T) and CASSCF, are coincident. All the isomers in Table II yield real harmonic frequencies with both methods. We did not find significant changes for the structural parameters. However, as was expected, the multiconfigurational character of the wave functions decreases with the isomer relative stability. The weight of the RHF configuration varies from 0.94 in $c1\text{-SiC}_3\text{H}^-$ to 0.86 in $c6\text{-SiC}_3\text{H}^-$. The $c1$ -cyclic isomers exhibiting four corner rings are the “more monoconfigurational” structures as was first observed in C_4 where the rhombic isomer displays a singlet electronic ground state whereas the stablest linear form is a triplet.¹⁸ For the last isomers of Table II, RCCSD(T) energy does not converge when starting geometries are far away from the equilibrium. In these cases, CASSCF calculations are safer and their results may be used as starting point for the CCSD calculations.

The zero order spectroscopic parameters are given in third column of Table II. The equilibrium rotational constant B_e as well as the fundamental frequencies have been calculated with RCCSD(T)/aug-cc-pVTZ, even though we used CASSCF/aug-cc-pVTZ for dipole moments. All the isomers show very low frequency bending modes ($\omega < 200$ cm^{-1}).

TABLE II. Electronic energies (E in a.u.), relative energies (E_r in eV), structural parameters (distances in angstroms; angles in degrees), equilibrium rotational constants (in megahertz), harmonic fundamentals (ω in cm^{-1}), and dipole moments (μ in debyes) of SiC_3H^- isomers.

SiC ₃ H ⁻ isomers		CASSCF aug-cc-pVTZ	RCCSD(T) aug-cc-pVTZ	Spectroscopic parameters
I-SiC₃H⁻ $X^1\Sigma^+$ (C _{∞v})	R=1.6783, R ₂ =1.3751, R ₁ =1.2225, r=1.0501 E=-403.205988 E_r=0.0	R=1.6761, R ₂ =1.3708, R ₁ =1.2372, r=1.0624 E=-403.674994 E_r=0.0	$B_e=2578.13 \mu=3.3237$ $\omega=174(\pi), 322(\pi), 502(\pi) 632(\sigma), 1325(\sigma), 1986(\sigma), 3450(\sigma)$
c-SiC₃H⁻ X^1A' (C _s)	R=1.7548, R ₁ =1.4419, R ₂ =1.2638, R ₃ =2.1557, r=1.0697, $\theta_1=41.7, \theta_2=105.1,$ $\theta_3=84.2, \theta_4=125.9$ E=-403.152960 E_r=1.44	R=1.7490, R ₁ =1.4610, R ₂ =1.2776, R ₃ =2.0747, r=1.0796, $\theta_1=43.9,$ $\theta_2=99.4, \theta_3=80, \theta_4=127.1$ E=-403.632743 E_r=1.15	$A_e=14694.1 B_e=7237.73$ $C_e=4849.20 \mu=5.5184$ $\omega=131(a'), 363(a''), 466(a'), 498(a''), 791(a'), 964(a'), 1040(a'), 1816(a'), 3218(a')$
II-SiC₃H⁻ X^1A' (C _s)	R=1.7683, R ₁ =1.3172 R ₂ =1.2922, r=1.5314 $\theta_1=96.8, \theta_2=168.7, \theta_3=177.1$ E=-403.147833 E_r=1.58	R=1.7455, R ₁ =1.3263, R ₂ =1.2868, r=1.5267, $\theta_1=94.4, \theta_2=170.2,$ $\theta_3=177.2$ E=-403.612338 E_r=1.70	$A_e=216458 B_e=2646.23$ $C_e=2614.28 \mu=2.9114$ $\omega=158(a''), 187(a'), 330(a''), 459(a''), 587(a'), 675(a'), 1335(a'), 1899(a'), 2001(a')$
cI-SiC₃H⁻ X^1A' (C _s)	R=1.9093, R ₁ =1.4188, R ₂ =1.5004, r=1.5334, $\theta_1=99.2, \theta_2=63.8$ $\theta_3=46.3, \text{SiC2C3C4}=177.6$ E=-403.151836 E_r=1.47	R=1.9231, R ₁ =1.4216, R ₂ =1.4835, r=1.5400, $\theta_1=97.3, \theta_2=62.9,$ $\theta_3=45.4, \text{SiC2C3C4}=176.5$ E=-403.606744 E_r=1.86	$A_e=32667.2 B_e=5571.28$ $C_e=4971.78 \mu=2.4399$ $\omega=344(a''), 344(a'), 602(a'), 629(a''), 803(a''), 966(a'), 984(a'), 1448(a'), 1921.0(a')$
c2-SiC₃H⁻ X^1A' (C _s)	R=1.8677, R ₁ =1.4094 R ₂ =1.4855, r=1.0729 d=2.9075, $\theta=143.5, \text{SiC2C3C4}=174$ E=-403.134698 E_r=1.94	R=1.8607, R ₁ =1.4402, R ₂ =1.4856, r=1.0867, d=2.9353, $\theta=137.98,$ $\text{SiC2C3C4}=174$ E=-403.604560 E_r=1.92	$A_e=36790.4 B_e=5642.83$ $C_e=4939.70 \mu=2.3239$ $\omega=355(a'), 407(a''), 583(a'), 591(a''), 663(a'), 986(a'), 1004(a''), 1353(a'), 3112(a')$
c3-SiC₃H⁻ X^1A' (C _s)	r=1.0755, R=1.6825, R ₁ =1.4326, R ₂ =2.0949, R ₃ =1.3172, $\theta_1=174.4,$ $\theta_2=136.0, \theta_3=128.7, \theta_4=132.2$ E=-403.137555 E_r=1.86	r=1.0797, R=1.7189, R ₁ =1.4415, R ₂ =1.6325, R ₃ =1.3303, $\theta_1=160.2$ $\theta_2=148.9, \theta_3=137.8, \theta_4=150.27$ E=-403.604438 E_r=1.92	$A_e=38309.1 B_e=3911.21$ $C_e=3548.89 \mu=2.9297$ $\omega=105(a'), 341(a''), 425(a'), 661(a''), 677(a'), 980(a'), 1087(a'), 1581(a'), 3208(a')$
I2-SiC₃H⁻ X^1A' (C _s)	R=1.6758, R ₁ =1.7490 R ₂ =1.2663, r=1.0733 $\theta_1=135.3, \theta_2=166.13, \beta=144$ E=-403.146517 E_r=1.62	R=1.6629, R ₁ =1.7535, R ₂ =1.2675, r=1.0808, $\theta_1=140.8, \theta_2=165.9,$ $\beta=150.9$ E=-403.600104 E_r=2.04	$A_e=194922.3 B_e=3147.45$ $C_e=3097.43 \mu=5.2353$ $\omega=124(a''), 140(a'), 244(a'), 451(a''), 550(a''), 656(a'), 1113(a'), 1913(a'), 3244(a')$
c4-SiC₃H⁻ X^1A' (C ₁)	R=1.5806, R ₁ =1.7881, R ₂ =1.9535 R ₃ =1.3616, r=1.0741, $\theta=140.2$ $\tau_1=92.8, \tau_2=93.2$ E=-403.134643 E_r=1.94	R=1.5324, R ₁ =1.7995, R ₂ =1.9568, R ₃ =1.3738, r=1.0875, $\theta=138.6,$ $\tau_1=93.6, \tau_2=92.3$ E=-403.599173 E_r=2.06	$A_e=17112.8 B_e=7638.69$ $C_e=5966.13 \mu=3.0360$ $\omega=376, 424, 480, 676, 807, 866, 1046, 1310, 3111$
c5-SiC₃H⁻ X^1A' (C _s)	R=1.9100, R ₁ =2.1344 R ₂ =1.4109, r=1.0805 $\theta_1=141.5, \theta_2=78.4,$ $\beta=100.4$ E=-403.121092 E_r=2.31	R=1.9019, R ₁ =2.1260 R ₂ =1.4270, r=1.0926 $\theta_1=140.4, \theta_2=77.9,$ $\beta=99.5$ E=-403.596199 E_r=2.14	$A_e=14753.3 B_e=8711.90$ $C_e=6265.35 \mu=2.2381$ $\omega=481(a'), 485(a'), 510(a''), 743(a'), 895(a'), 967(a''), 1193(a'), 1234(a''), 3039(a')$
c6-SiC₃H⁻ X^1A' (C _s)	R=1.7900, R ₁ =1.4598, R ₂ =1.3762, r=1.5275, $\theta_1=95.4, \theta_2=56.2,$ $\text{H5Si1C2C3}=95.6,$ $\text{H5Si1C2C4}=95.6$ E=-403.140801 E_r=1.77	R=1.8004, R ₁ =1.4531, R ₂ =1.3776, r=1.5359, $\theta_1=93.13, \theta_2=56.60,$ $\text{H5Si1C2C3}=98.4$ $\text{H5Si1C2C4}=98.4$ E=-403.585653 E_r=2.43	$A_e=36968.44 B_e=3927.17$ $C_e=3667.69 \mu=5.0582$ $\omega=175(a''), 333(a'), 460(a''), 615(a'), 1027(a''), 1048(a''), 1105(a'), 1605(a''), 2609(a')$
c7-SiC₃H⁻ X^1A' (C _s)	R=2.1663, R ₁ =2.0421, R ₂ =1.3259, r=1.5381, $\tau=96.3, \theta_1=96.9, \theta_2=153.5,$ $\text{C2SiC4C3}=177.3$ E=-403.120509 E_r=2.33	R=2.1589, R ₁ =2.0294, R ₂ =1.3345, r=1.5490, $\tau=96.7, \theta_1=95.4, \theta_2=152.4$ $\text{C2SiC4C3}=171.8$ E=-403.578488 E_r=2.63	$A_e=11841.41 B_e=8836.23$ $C_e=5313.16 \mu=0.5328$ $\omega=125(a''), 187(a'), 421(a'), 599(a'), 702(a''), 803(a'), 1158(a'), 1585(a''), 1871(a')$
I3-SiC₃H⁻ X^1A' (C _s)	R=1.7437, R ₁ =1.8613 R ₂ =1.2181, r=1.0529 $\theta_1=135.2$ E=-403.114917 E_r=2.49	R=1.7372, R ₁ =1.8555 R ₂ =1.2292, r=1.0645 $\theta_1=140.63$ E=-403.572246 E_r=2.80	$A_e=75697.3 B_e=3054.93 C_e=2936.43 \mu=7.5704$ $\omega=87(a'), 268(a''), 280(a'), 534(a'') 555(a'), 558(a'') 966(a'), 1980(a'), 3435(a')$

C. The rotational constant of I-SiC₃H⁻

Although many of the isomers are of low stability, they can play important roles as reaction intermediates or building blocks of larger silicon-carbon molecules. However,

I-SiC₃H⁻ ($X^1\Sigma^+$) is roundly stable. Due to the high probability of the existence, we have made an effort in accurately determining its spectroscopic properties, especially the B_0 rotational constant and the dipole moment, which are the two

TABLE III. Structural parameters and equilibrium rotational constants of l -SiC₃H[−] and l -SiC₃D[−] calculated with RCCSD(T) theory and different basis sets and sets of frozen core orbitals.

Basis set	n ^a	R (C1–Si)	R2 (C2–C1)	R3 (C3–C2)	R (H–C3)	E	l -SiC ₃ H [−] B _e	l -SiC ₃ D [−] B _e
RCCSD(T)-F12A	8	1.6666	1.3674	1.2333	1.0617	−403.726 428	2598.33	2438.24
aug-cc-pVTZ								
aug-cc-pVTZ	8	1.6762	1.3707	1.2372	1.0625	−403.674 994	2578.13	2419.55
aug-cc-pVQZ	8	1.6686	1.3683	1.2339	1.0617	−403.709 931	2594.03	2434.29
aug-cc-pV5Z	8	1.6654	1.3681	1.2329	1.0613	−403.720 679	2599.57	2439.36
CBS ^b	8					−403.729 061	2605.16	2444.36
aug-cc-pCVQZ	4	1.6618	1.3686	1.2335	1.0617	−404.032 806	2603.00	2442.46
aug-cc-pCVQZ	1	1.6604	1.3665	1.2308	1.0603	−404.195 880	2611.51	2450.45

^an=number of frozen core orbitals.^bCBS=complete basis set (aug-cc-pV ∞ Z); B_e^{CBS} determined using Eq. (1).

basic properties used for molecular detection by radioastronomy. To aid future ALMA astronomical observations or laboratory experiments, very accurate parameters are necessary.

The dipole moment has been evaluated to be $\mu = 2.9707$ D with CASSCF/aug-cc-pV5Z. To increase accuracy, the B_e parameter given in Table II that was calculated with RCCSD(T)/aug-cc-pVTZ has been refined following the most significant stages of the Puzzarini *et al.*⁶¹ procedure. Thus, the equilibrium rotational constants of Table III, obtained with RCCSD(T) and different basis sets type aug-cc-pVXZ (X=T, Q, 5), are used to determine the B_e^{CBS} extrapolated parameters of l -SiC₃H[−] and l -SiC₃D[−]. We used the following equation:

$$B_e = B_e^{\text{CBS}} + B_e^1(Y+1)^{-3} + B_e^2(Y+1)^{-5} + \dots \quad (1)$$

$$(Y = 3(X=T), Y = 4(X=Q), Y = 5(X=5)).$$

In Fig. 1(a) we compare the B_e parameter calculated with different basis sets, and in Fig. 1(b) we show the evolution of the rotational parameters with the selected core. We obtained B_e^{CBS} to be 2605.16 MHz for l -SiC₃H[−] and 2444.36 MHz for l -SiC₃D[−]. Afterward, B_e^{CBS} was corrected adding up the ΔB_e^{core} core-correlation ($\Delta B_e^{\text{core}} = B_e(\text{aug-cc-pVCQZ}, n=1) - B_e(\text{aug-cc-pVQZ}, n=8)$). In this last equation, n represents the number of frozen core orbitals.

The observable parameter B₀ is connected to B_e by the equation

$$B_0 = B_e + \Delta B_{\text{vib}} + \Delta B_{\text{el}},$$

where ΔB_{vib} is the vibrational correction calculated (as we describe below) using an anharmonic force field and second order perturbation theory. ΔB_{el} is the electronic contribution which is usually negligible. Thus, $B_0 = B_e^{\text{CBS}} + \Delta B_e^{\text{core}} + \Delta B_{\text{vib}}$.

For both isomers, $\Delta B_e^{\text{core}} \sim 17$ MHz and $\Delta B_{\text{vib}} < 2$ MHz. Finally, B₀ was determined to be 2621.68 MHz (l -SiC₃H[−]) and to be 2460.48 MHz (l -SiC₃D[−]).

Bond distances and energies are also shown in Table III where we compare the RCCSD(T)-F12A/aug-cc-pVTZ and the RCCSD(T) results obtained with different basis sets. It should be remarked that the RCCSD(T)-F12A parameters do not rise above the RCCSD(T)/CBS value, although the F12A correction overestimates the correlation. The very efficient F12 procedure, recently implemented in MOLPRO, provides results as accurate as those of RCCSD(T)/aug-cc-pV5Z, while the computational expenses decrease significantly.

D. Electronic transitions of l -SiC₃H[−]

The l -SiC₃H[−] electron affinity has been evaluated to be 2.70 eV with RCCSD(T)-F12A (see Table I). The CASSCF and CASSCF/MRCI vertical excitation energies to the excited electronic states are shown in Table IV and compared with the corresponding ones for the neutral parent species. Although, CASSCF/MRCI and CASSCF provide similar relative order of energies for the states, we accept that CASSCF/MRCI results should be the most accurate since they consider dynamical correlation corrections. Anionic states lying below the electron affinity (2.70 eV) are pointed out (in black). They can correspond to metastable states.

One proof of existence is that an anion should show positive electron affinity with respect to its parent state. For l -SiC₃H[−] all possible singlet excited states are located above the ground state of the neutral l -SiC₃H, which make them implausible. On the other hand, the region between 2.48 and 2.70 eV shows a large density of triplet electronic states. However, on the basis of relative energies, the stability of $^3\Sigma^+$ (2.48 eV), $^3\Delta$ (2.66), and $^3\Sigma^-$ (2.85 eV) is not certain. It may be inferred that a unique state, the electronic ground state, is metastable. Nothing new can be expected to be derived from more sophisticated calculations considering

FIG. 1. (a) Evolution of the calculated rotational constants with basis set enlargement. (b) Evolution of the calculated rotational constants with the number of core orbitals.

TABLE IV. Symmetry, vertical excitation energies (E in eV), and dominant electronic configurations corresponding to the ground and lowest excited states of the neutral *l*-SiC₃H. Vertical excitation energies for *l*-SiC₃H⁻, calculated with CASSCF/aug-cc-pVTZ and MRCI/aug-cc-pVTZ.

<i>l</i> -SiC ₃ H				<i>l</i> -SiC ₃ H ⁻			
Sym	ECASSCF	ErMRCI	Dominant configuration	Sym	ECASSCF	EMRCI	Dominant configuration
X ² Π	0.0 ^a	0.0 ^b	(11σ) ² (2π) ⁴ (3π) ³	X ¹ Σ ⁺	0.0 ^c	0.0^d	(11σ) ² (2π) ⁴ (3π) ⁴
² Σ ⁺	2.45	2.01	(11σ) ¹ (2π) ⁴ (3π) ⁴	¹ Π	3.03	3.09	(11σ) ² (12σ) ¹ (2π) ⁴ (3π) ³
² Δ	5.99	5.66	(11σ) ² (12σ) ¹ (2π) ⁴ (3π) ²	¹ Δ	4.11	3.29	(11σ) ² (2π) ⁴ (3π) ³ (4π) ¹
² Σ ⁻	5.42	5.43	(11σ) ² (12σ) ¹ (2π) ⁴ (3π) ²	¹ Σ ⁻	3.47	3.22	(11σ) ² (2π) ⁴ (3π) ³ (4π) ¹
⁴ Σ ⁺	3.82	3.43	(11σ) ¹ (2π) ⁴ (3π) ³ (4π) ¹	³ Σ ⁺	2.57	2.48	(11σ) ² (2π) ⁴ (3π) ³ (4π) ¹
⁴ Δ	4.78	3.82	(11σ) ¹ (2π) ⁴ (3π) ³ (4π) ¹	³ Π	2.65	3.10	(11σ) ² (12σ) ¹ (2π) ⁴ (3π) ³
⁴ Σ ⁻	5.34	4.19	(11σ) ¹ (2π) ⁴ (3π) ³ (4π) ¹	³ Δ	2.98	2.66	(11σ) ² (2π) ⁴ (3π) ³ (4π) ¹
⁴ Π	2.77	2.21	(11σ) ² (2π) ⁴ (3π) ² (4π) ¹	³ Σ ⁻	3.43	2.85	(11σ) ² (2π) ⁴ (3π) ³ (4π) ¹

^aEa=-403.139215^bEa=-403.509450^cEa=-493.205588 a.u.^dEa=-403.597248 a.u.

modifications of the geometry with electronic excitations. However, it could be that electron depletion can have other causes (spin-forbidden autodetachment, etc.)

Carbon chains usually display a large density of electronic states in the electronic ground state region. Linear C₄H shows two doublet states, X ²Σ⁺ and ²Π, which are very close in energy. However, the substitution of a C atom by a Si atom reverses the relative order of the states. The electronic ground state of *l*-SiC₃H is a X ²Π, and the relative energy of Σ⁺ and Π has been estimated to be 2.45 eV. Significant changes are also predicted for dipole moments 1.1074 (*l*-SiC₃H, X ²Π), 0.8924 (C₄H, X ²Σ⁺), and 3.3336 (C₄H, X ²Π) (in debyes).

E. The infrared spectra of *l*-SiC₃H⁻ (X ¹Σ⁺)

For *l*-SiC₃H⁻, excited electronic states lay far away from the spectral region of fundamental vibrational frequencies. Thus, nonadiabatic rovibronic effects are not expected at low temperatures.

Rovibrational spectroscopic parameters for two isotopic varieties, *l*-SiC₃H⁻ and *l*-SiC₃D⁻, determined following previous procedures,^{19–21} are shown in Table V. They have been calculated using second order perturbation theory from a full-dimensional RCCSD(T)-F12/aug-cc-pVTZ quadratic, cubic, and quartic force fields. This last force field was determined by fitting 1874 relative energies up to 5000 cm⁻¹ to a Taylor series containing 334 basis functions. The analytical form of the potential energy surface is

$$V(q_1, q_2, \dots, q_n) = \sum_{i=1}^n \sum_{j=1}^n \frac{1}{2} f_{ij} q_i q_j + \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \frac{1}{6} f_{ijk} q_i q_j q_k + \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \sum_{l=1}^n \frac{1}{24} f_{ijkl} q_i q_j q_k q_l.$$

The 1874 geometries have been selected around the local minimum (see Table III) by taking increments of 0.03 Å, 3.0°, and 5.0° for the stretching, bending angles, and torsional coordinates, respectively. The final fitting parameters are R²=1.0, σ=1.9 cm⁻¹. The fitted force field defined in curvilinear internal coordinates **q_i** is provided as supplement

tary material.⁶² For the linear angles, responsible for the π-vibrational coordinates, the Hoy, Mills, and Strey definitions of the coordinates were used.⁶³

In Table V, harmonic and anharmonic fundamentals, the α-rovibrational parameters, rotational constants, q_i *l*-doubling constants and the diagonal x_{ii}, and the most significant nondiagonal anharmonic constants (x_{ij}>10 cm⁻¹) are provided. Tabulated infrared intensities were determined with the standard algorithms of MOLPRO.³⁸ Anharmonic effects are very strong for the vibrational modes ν₁ and ν₆ with an important participation of the H atom coordinates. The vibrational contribution to the rotational parameters ΔB_{vib} has been determined to be very small: -1.0 and -0.04 MHz for *l*-SiC₃H⁻ and *l*-SiC₃D⁻, respectively.

Small Fermi displacements are observed for both varieties (the maximum displacement are 7.8 cm⁻¹ for the hydrogenates species and 5.2 cm⁻¹ for the deuterated one). Combination stretching bands interact with the stretching fundamentals (i.e., the ν₁ with ν₃+ν₄ and ν₂ with ν₂+ν₃). The bending ν₅+ν₇ also interacts with the ν₄ stretching.

The three bending modes interact strongly, much more than in *l*-C₄H⁻. The internal coordinates are strongly combined for producing the π vibrational coordinates although ν₆ may be identified with the H-C-C bending, whereas ν₅ and ν₇ with C-C-C and C-C-Si linear angles. The enlargement of the bond lengths, derived from the substitution of a C by a heavier atom such as Si, has many consequences for large amplitude vibrations and their interactions.^{64,65} For this reason, the effect of the deuteration is visible on the low frequency modes of *l*-SiC₃H⁻, whereas for C₄H⁻, this effect is concentrated on the ν₆ mode. The three fundamentals have been calculated to be ν₅=514, ν₆=227, and ν₇=149 cm⁻¹ for *l*-SiC₃H⁻ and ν₅=489, ν₆=176, and ν₇=152 cm⁻¹ for *l*-SiC₃D⁻.

One of the bending modes, related to the silicon-carbon chain deformation, lies at very low energies (149 cm⁻¹ for *l*-SiC₃H⁻ and 152 cm⁻¹ for *l*-SiC₃D⁻). This order of magnitude allows the astrophysical detection using far infrared techniques, although the spectral region is shared with many other chains such as C₄, C₅, and C₃Si.^{18–20} This fact prevents the IR identification. Many carbon chains and silicon-carbon chains and their isotopomers display bands in the same spec-

TABLE V. Spectroscopic parameters (in black: strong Fermi displacements; nondiagonal anharmonic constants $> 10 \text{ cm}^{-1}$) for the most stable isomer of the $l\text{-SiC}_3\text{H}^-$ anion calculated with second order perturbation theory and a RCCSD(T)-F12/cc-pVTZ-F12 anharmonic force field.

	<i>l</i> -C ₃ SiH ⁻				<i>l</i> -C ₃ SiH ⁻	<i>l</i> -C ₃ SiD ⁻
	ω	I ^a				
$\omega_1(\sigma)$ (cm ⁻¹)	3457	73	2633	α_1 (x10 ⁻⁴) (cm ⁻¹)	0.9386	1.4749
$\omega_2(\sigma)$ (cm ⁻¹)	1995	323	1913	α_2 (x10 ⁻⁴) (cm ⁻¹)	3.2710	2.9908
$\omega_3(\sigma)$ (cm ⁻¹)	1406	6	1393	α_3 (x10 ⁻⁴) (cm ⁻¹)	4.3512	3.8129
$\omega_4(\sigma)$ (cm ⁻¹)	640	0.2	632	α_4 (x10 ⁻⁴) (cm ⁻¹)	1.4862	1.3341
$\omega_5(\pi)$ (cm ⁻¹)	527	4	521	α_5 (x10 ⁻⁴) (cm ⁻¹)	-1.1518	-1.1106
$\omega_6(\pi)$ (cm ⁻¹)	380	64	290	α_6 (x10 ⁻⁴) (cm ⁻¹)	-0.9238	-1.3475
$\omega_7(\pi)$ (cm ⁻¹)	168	11	164	α_7 (x10 ⁻⁴) (cm ⁻¹)	-2.6281	-2.2610
$\nu_1(\sigma)$ (cm ⁻¹)	3273		2535	B(ν_1) (MHz)	2594.87	2434.53
$\nu_2(\sigma)$ (cm ⁻¹)	1919		1857	B(ν_2) (MHz)	2587.88	2429.56
$\nu_3(\sigma)$ (cm ⁻¹)	1377		1365	B(ν_3) (MHz)	2584.64	2427.10
$\nu_4(\sigma)$ (cm ⁻¹)	626		622	B(ν_4) (MHz)	2593.23	2434.52
$\nu_5(\pi)$ (cm ⁻¹)	514		489	B(ν_5) (MHz)	2601.14	2441.86
$\nu_6(\pi)$ (cm ⁻¹)	227		176	B(ν_6) (MHz)	2600.46	2442.57
$\nu_7(\pi)$ (cm ⁻¹)	149		152	B(ν_7) (MHz)	2605.56	2445.61
B _e (MHz)	2598.65		2438.49	q ₅ (x10 ⁻⁵) (cm ⁻¹)	4.087	3.621
B ₀ (MHz)	2597.69		2438.53	q ₆ (x10 ⁻⁵) (cm ⁻¹)	4.163	4.808
D _e (x10 ⁻³) (MHz)	0.184 817		0.156 597	q ₇ (x10 ⁻⁵) (cm ⁻¹)	9.488	8.562
x ₁₁ (cm ⁻¹)	-55.364		-24.043	x ₁₂ (cm ⁻¹)		-16.837
				x ₁₆ (cm ⁻¹)	-60.369	-39.415
x ₂₂ (cm ⁻¹)	-9.232		-7.117	x ₂₃ (cm ⁻¹)	-22.013	-13.264
x ₃₃ (cm ⁻¹)	-4.922		-4.555	x ₂₄ (cm ⁻¹)	-15.174	-10.330
x ₄₄ (cm ⁻¹)	-1.153		-1.114	x ₄₆ (cm ⁻¹)		
				x ₂₆ (cm ⁻¹)	-22.381	-14.024
x ₅₅ (cm ⁻¹)	-1.884		-1.574	x ₅₆ (cm ⁻¹)	10.225	-12.618
x ₆₆ (cm ⁻¹)	-45.088		-29.869	x ₅₇ (cm ⁻¹)	-11.935	-7.307
x ₇₇ (cm ⁻¹)	-1.361		-1.243			
g ₅₅ (cm ⁻¹)	0.569		0.420			
g ₆₆ (cm ⁻¹)	19.244		13.570			
g ₇₇ (cm ⁻¹)	0.939		0.862			

^aIR intensities in km/mol.

tral region. In addition, theoretical and experimental technical problems difficult the determination of very accurate rovibrational band positions.

For $l\text{-SiC}_3\text{H}^-$ (and $l\text{-SiC}_3\text{D}^-$), the absence of previous studies does not allow us rigorous conclusions about the accuracy of our results. For pure C_n and C_nH carbon chains, we have obtained error bars of 10 cm^{-1} .^{20,21} It is important to stand up that the very anharmonic modes (ν_1 and ν_6) are really difficult to be described with our techniques. In these cases, frequencies are very sensitive to the potential fitting and also they are displaced by interactions, for example, Fermi interactions. Quartic force field plays an important role. Accurate band center determination implies to perform variational calculations.

IV. CONCLUSIONS

Highly correlated *ab initio* methods have been used to predict the equilibrium structures and spectroscopic parameters of the SiC_3H^- anion whose electron affinity is 2.7 eV. The molecule was found to stabilize strongly with electron attachment. On the basis of E_A and μ determination, it is inferred that the probability of the observation of SiC_3H^- is larger than for other anion chains type SiC_nH^- or type SiC_n^- .

SiC_3H^- was found to have 12 isomers. For the preferred linear isomer, whose stability is prominent, the B_e equilibrium rotational constant has been calculated using RCCSD(T) and a complete basis set. Core-correlation and vibrational effects have been taken into account to predict a B_0 of 2621.68 MHz for $l\text{-SiC}_3\text{H}^-$ and 2460.48 MHz for $l\text{-SiC}_3\text{D}^-$. The dipole moment was found to be 2.9707 D. CASSCF/MRCI vertical excitations to the lowest excited electronic states allow the prediction of three metastable electronic states, $^1\Sigma^+$, $^3\Sigma^+$ and $^3\Delta$. Large amplitude bending modes lie in the same region of C_n bending modes, at very low energies. Its astrophysical identification by infrared techniques is thus difficult.

ACKNOWLEDGMENTS

The authors acknowledge the Ministerio de Ciencia e Innovación of Spain for the Grant Nos. AYA2008-00446 and AYA2009-05801-E/AYA and to CESGA for computing facilities.

N.P.I. acknowledges the AECID-MAEC postdoctoral grant.

¹T. Taki, *J. Inorg. Organomet. Polym.* **2**, 269 (1992).

²L. Colangeli, Th. Henning, J. R. Brucato, D. Clément, D. Fabian, O.

- Guillois, F. Huisken, C. Jäger, E. K. Jessberger, A. Jones, G. Ledoux, G. Manicó, V. Mennella, F. J. Molster, H. Mutschke, V. Pirronello, C. Reynaud, J. Roser, G. Vidal, and L. B. F. M. Waters, *Astron. Astrophys. Rev.* **11**, 97 (2003).
- ³E. Herbst, T. J. Millar, S. Wlobeck and D.-K.-Bohme, *Astron. Astrophys.* **222**, 205 (1989).
- ⁴D. D. S. MacKay and S. B. Charnley, *Mon. Not. R. Astron. Soc.* **793**, 302 (1999).
- ⁵C. M. Walmley, G. Pineau des Forêts, and D. R. Flower, *Astron. Astrophys.* **342**, 542 (1999).
- ⁶R. W. Wilson, A. A. Penzias, K. B. Jeefferts, M. Kutner, and P. Thaddeus, *Astrophys. J. Lett.* **167**, L97 (1971).
- ⁷M. Morris, W. Gilmore, P. Palmer, B. E. Turner, and B. Zuckerman, *Astrophys. J. Lett.* **199**, L47 (1975).
- ⁸B. E. Turner, *Astrophys. J.* **388**, L35 (1992).
- ⁹J. Cernicharo, C. A. Gottlieb, M. Guélin, P. Thaddeus, and J. M. Virtilek, *Astrophys. J.* **341**, L25 (1989).
- ¹⁰P. Thaddeus, S. E. Cummins, and R. A. linke, *Astrophys. J. Lett.* **283**, L45 (1984).
- ¹¹M. Ohishi, N. Kaifu, K. Kawaguchi, A. Murakami, S. Saito, S. Yamamoto, S.-I. Ishikawa, Y. Fujita, Y. Shiratori, and W. M. Irvine, *Astrophys. J.* **345**, L83 (1989).
- ¹²A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, *J. Chem. Phys.* **111**, 3911 (1999).
- ¹³M. Guélin, M. Muller, J. Cernicharo, A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, *Astron. Astrophys.* **163**, L9 (2000).
- ¹⁴P. W. Merrill, *Publ. Astron. Soc. Pac.* **38**, 175 (1926).
- ¹⁵R. F. Sanford, *Publ. Astron. Soc. Pac.* **38**, 177 (1926).
- ¹⁶M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, *Mol. Phys.* **101**, 697 (2003).
- ¹⁷M. Guélin, J. Cernicharo, C. Kahane, and J. Gómez-González, *Astron. Astrophys.* **157**, L17 (1986).
- ¹⁸H. Massó, M. L. Senent, P. Rosmus, and M. Hochlaf, *J. Chem. Phys.* **124**, 234304 (2006).
- ¹⁹N. Inostroza, M. Hochlaf, M. L. Senent, and R. Letelier, *Astron. Astrophys.* **486**, 1047 (2008).
- ²⁰H. Massó, V. Veryazov, P.-Å. Malmqvist, B. O. Roos, and M. L. Senent, *J. Chem. Phys.* **127**, 154318 (2007).
- ²¹M. L. Senent and M. Hochlaf, *Astrophys. J.* **708**, 1452 (2010).
- ²²M. Hochlaf, G. Chambaud, and M. L. Senent, *Mol. Phys.* **108**, 1277 (2010).
- ²³M. Guélin, S. Green, and P. Thaddeus, *Astrophys. J.* **224**, L27 (1978).
- ²⁴J. Cernicharo, M. Guélin, M. Agúndez, K. Kawaguchi, M. C. McCarthy, and P. Thaddeus, *Astron. Astrophys.* **467**, L37 (2007).
- ²⁵A. Dalgarno and R. A. McCray, *Astrophys. J.* **181**, 95 (1973).
- ²⁶E. Herbst, *Nature (London)* **289**, 656 (1981).
- ²⁷M. C. McCarthy, C. A. Gottlieb, H. Gupta, and P. Thaddeus, *Astrophys. J.* **652**, L141 (2006).
- ²⁸S. Brünken, H. Gupta, C. A. Gottlieb, M. C. McCarthy, and P. Thaddeus, *Astrophys. J.* **644**, L143 (2007).
- ²⁹P. Thaddeus, C. A. Gottlieb, H. Gupta, S. Brünken S., M. C. McCarthy, M. Agúndez, M. Guélin, and J. Cernicharo, *Astrophys. J.* **677**, 1132 (2008).
- ³⁰J. Cernicharo, M. Guélin, M. Agúndez, M. C. McCarthy, and P. Thaddeus, *Astrophys. J.* **688**, L83 (2008).
- ³¹C. Walsh, N. Harada, E. Herbst, and T. J. Millar, *Astrophys. J.* **700**, 752 (2009).
- ³²<http://www.udfa.net/>.
- ³³L. Sari, J. M. Gonzales, and Y. Yamaguchi, *J. Phys. Chem.* **114**, 4472 (2001).
- ³⁴T. C. Smith, D. J. Clouthier, and T. C. Steimie, *J. Phys. Chem.* **115**, 817 (2001).
- ³⁵R. I. Kaiser and Y. Osamura, *Astrophys. J.* **630**, 1217 (2005).
- ³⁶H. Sun, N. Tan, H. Q. He, X. M. Pan, Z. M. Su, and R. S. Wang, *Theor. Chem. Acc.* **119**, 501 (2008).
- ³⁷A. Largo-Cabrerizo and J. R. Flores, *Chem. Phys. Lett.* **147**, 90 (1988).
- ³⁸H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, MOLPRO, version 2009.1, a package of *ab initio* programs, see <http://www.molpro.net>.
- ³⁹P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993); **112**, 3106 (2000).
- ⁴⁰G. Knizia, T. B. Adler, and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009); H.-J. Werner, T. B. Adler, and F. R. Manby, *ibid.* **126**, 164102 (2007).
- ⁴¹D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- ⁴²F. Weigend, *PCCP* **4**, 4285 (2002); F. Weigend, A. Köhn, and C. Hättig, *J. Chem. Phys.* **116**, 3175 (2002).
- ⁴³D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **103**, 4572 (1995); K. A. Peterson and T. H. Dunning, Jr., *ibid.* **117**, 10548 (2002).
- ⁴⁴M. L. Senent, 2001; FIT-ESPEC, "A FORTRAN code for calculating spectroscopic parameters from a force field in internal coordinates."
- ⁴⁵H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ⁴⁶H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).
- ⁴⁷M. Bogey, C. Demuyne, and J. L. Destombes, *Astron. Astrophys.* **232**, L19 (1990).
- ⁴⁸*Constants for molecules of astrophysical interest in the gas phase: Photodissociation, microwave and infrared spectra*, J. Crovisier (2002); <http://www.lesia.obspm.fr/perso/jacques-crovisier/basemole/>.
- ⁴⁹C. A. Gottlieb, J. M. Vertilek, and P. Thaddeus, *Astrophys. J.* **343**, L29 (1989).
- ⁵⁰M. C. McCarthy, A. J. Apponi, C. A. Gottlieb, and P. Thaddeus, *Astrophys. J.* **538**, 766 (2000).
- ⁵¹A. J. Apponi, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, *Astrophys. J.* **536**, L55 (2000).
- ⁵²M. Gomei, R. Kishi, A. Nakajima, S. Iwata, and K. Kaya, *J. Chem. Phys.* **107**, 10051 (1997).
- ⁵³J. M. Robbe, H. Lavendy, J. P. Flament, and G. Chambaud, *Chem. Phys. Lett.* **267**, 91 (1997).
- ⁵⁴R. Linguerr, P. Rosmus, and S. Carter, *J. Chem. Phys.* **125**, 034305 (2006).
- ⁵⁵A. Nakajima, T. Taguwa, K. Nakao, M. Gomei, R. Kishi, S. Iwata, and K. Kaya, *J. Chem. Phys.* **103**, 2050 (1995).
- ⁵⁶S. Brünken, C. A. Gottlieb, H. Gupta, M. C. McCarthy, and P. Thaddeus, *Astron. Astrophys.* **464**, L33 (2007).
- ⁵⁷X. Huang and T. J. Lee, *J. Chem. Phys.* **131**, 104301 (2009).
- ⁵⁸T. R. Taylor, C. Xu, and D. M. Neumark, *J. Chem. Phys.* **108**, 10018 (1998).
- ⁵⁹X. Cheng, Z. Xie, Y. Song, J. Xiao, and Y. Wang, *J. Appl. Polym. Sci.* **99**, 1188 (2006).
- ⁶⁰H. Massó and M. L. Senent, *J. Phys. Chem. A* **113**, 12404 (2009).
- ⁶¹C. Puzzarini, M. Heckert, and J. Gauss, *J. Chem. Phys.* **128**, 194108 (2008).
- ⁶²See supplementary material at <http://dx.doi.org/10.1063/1.3491264> for a complete set of the quadratic, cubic, and quartic force fields (in aJ) of *l*-C₃SiH⁻.
- ⁶³A. R. Hoy, I. M. Mills, and G. Strey, *Mol. Phys.* **24**, 1265 (1972).
- ⁶⁴D. C. Moule, Y. G. Smeyers, M. L. Senent, D. J. Clouthier, J. Karolczak, and R. Judge, *J. Chem. Phys.* **95**, 3137 (1991).
- ⁶⁵M. L. Senent and Y. G. Smeyers, *J. Chem. Phys.* **105**, 2789 (1996).