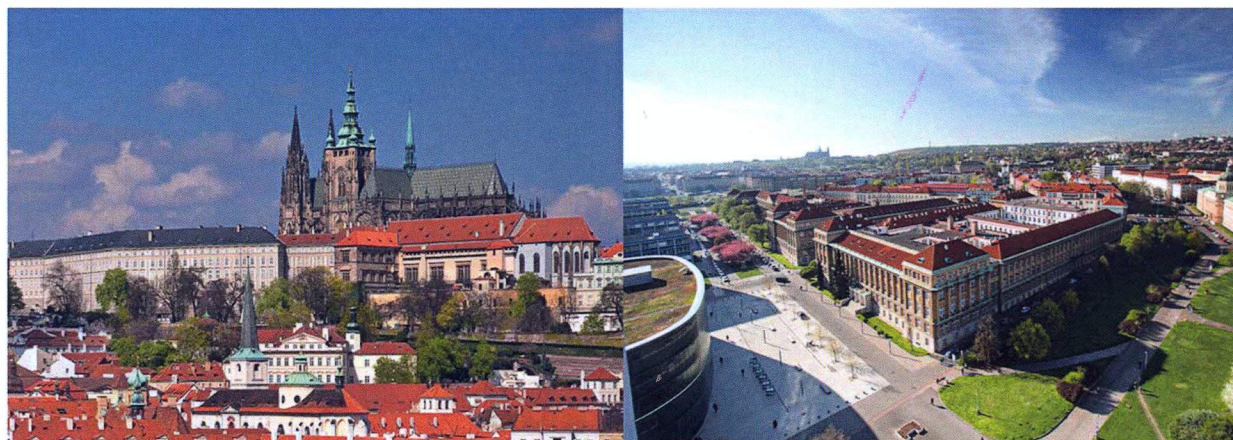




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Small Linear Carbon Chains: Vibrational and Electronic States

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Introduction

The study of carbon chains type C_n and their ions has been attracted a significant effort due to their connection with the astrophysical observations, because pure carbon chains are abundant species in several sources such as the carbon rich circumstellar envelopes. In addition, they can play important roles in the reactivity of large systems containing carbon atoms. Carbon molecules have been considered responsible of the Diffuse Interstellar Bands (DIBs) [1]. Small chains are building blocks of larger species such as the fullerenes and the PAHs.

In spite of their astrophysical relevance, few bare chains have been observed in gas phase extraterrestrial sources. The shortest chain C₂, was the first detected, followed by C₃ and the linear-C₅ [2-3]. Detections were performed through the analysis of Infra-Red active vibrational excitations or through their electronic transitions because they present a zero dipole moment.

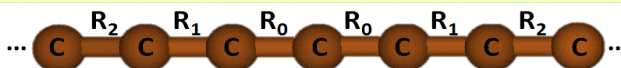
All the C_n chains present a large number of isomers, however, in this work we focus on the linear ones. The large stability of charged linear chains was used as argument to predict the presence of anions in the interstellar medium. Special attention is given to the anions which relevance for reactivity is evident.

Computational Details

For this work, we have employed highly correlated ab initio methods to determined vibrational and electronic energies. The following ab initio methods were used for computations:

- The RCCSD(T)-F12 method implemented in MOLPRO, was employed to determine accurate equilibrium geometries and equilibrium rotational constants as well as harmonic frequencies of the small chains type C_n (n=3,4,5,6,7).

- Multiconfigurational complete active space self-consistent field (CASSCF) calculations were performed to determine vertical energies of the lowest electronic states involved in the molecular reactivity. The energies were refined using multireference configuration interaction (MRCI) theory implemented in MOLPRO. Whereas all the valence electrons were correlated for C₃, and for large systems, the active space was reduced. We used 13 orbitals for C₄, 16 orbitals for C₅, 19 orbitals for C₆ and 22 orbitals for C₇.



Preliminary Results

1- Structural Parameters, Rotational Constants and Harmonic Frequencies :

Table 1: RCCSD(T)-F12/aug-cc-pVTZ Energies, Structural Parameters, Rotational Constants and Frequencies of C_n

chains	c3	c4	c5	c6	C7 [8]	
E (a.u.)	-113.871334	-151.841888	-189.902731	-227.881957	-265.915226	
Structure (A°)	R ₀ R ₁ R ₂	1.2973 1.3127	1.2934 1.2928	1.2854 1.2901 1.3040	1.2756 1.2900 1.2925	
B ₀ (MHz)	12511.437	4945.984	2537.225	1444.290	911.792	
B ₀ exp (MHz)	12908.712[4]	4979.882[5]	2557.628[6]	1453.364[7]	917.755[9]	
Frequencies (in cm ⁻¹)	ω(σ _g) ω(σ _u) ω(π _g) ω(π _u)	1200.2 2098.0 365.3 169.8	2106.9; 939.7 1922.9 198.1 169.8	1986.8; 778.2 2215.7; 1453.2 198.1 525.6; 115.4	2140.7; 1705.1; 656.9 2201.9; 1254.2 461.9; 461.8; 203.1; 203.0 358.4; 97.5; 97.3	2166.5; 1564.4; 574.9 2200.1; 1931.6; 1088.1 468.6; 147.2 460.5; 227.7; 63.9

Table 2: RCCSD(T)-F12/aug-cc-pVTZ Energies, Structural Parameters, Rotational Constants and Frequencies of C_n⁻

Anions	C3 ⁻	c4 ⁻	c5 ⁻	c6 ⁻	c7 [8]	
E (a.u.)	-113.944512	-151.986434	-190.006614	-227.921074	-266.037098	
Structure (A°)	R ₀ R ₁ R ₂	1.3100 1.3399 1.2805	1.2886 1.3037	1.3291 1.2807 1.3284	1.2801 1.3111 1.223	
B ₀ (MHz)	12271.011	4951.093	2501.059	1409.174	901.579	
Frequencies (in cm ⁻¹)	ω(σ _g) ω(σ _u) ω(π _g) ω(π _u)	1849.7 3477.5 397.2; 249.4	3136.6; 2518.2 4115.2 464.7; 418.2 228.8; 211.2	1887.1; 755.0 978.9; 1430.6 354.6; 258.7 554.2; 352.7; 142.4; 131.0	2171; 1857; 654 2021; 1215 560; 498; 261; 248 449; 408; 120; 115	3148.6; 2027.5; 840.8 4896.1; 2568.9; 647.9 488.9; 486.5; 180.5; 174.1 359.7; 345.3; 263.7; 260.9; 76.8; 70

2- Harmonic Stretching Frequencies:

Table 3: RCCSD(T)-F12/aug-cc-pVTZ Harmonic Stretching Frequencies and MP2/aug-cc-pVTZ Intensities of C_n

	ω	Calc.	Exp.	Intensity (km/Mole)
C3	ω(σ _g)	1200.2	1224.49[10]	0
	ω(σ _u)	2098.0	2040.0192[6][11]	521.6
C4	ω(σ _g)	2106.89	2032[50][12]; 2057[50][13]	0
	ω(σ _u)	939.70		0
C5	ω(σ _g)	1922.90	1548.6128[4][5]	638.9
	ω(σ _u)	1986.76		0
C6	ω(σ _g)	778.18	798[45][14]; 775.8[12]	0
	ω(σ _u)	2215.74	2169.4410[2][6]	1534.2
C7 [8]	ω(σ _g)	1453.17	1446.6[15]	82.9
	ω(σ _u)	2140.67	2061[10] [16]	0
C6	ω(σ _g)	1705.10	1694[50] [13]	0
	ω(σ _u)	656.94	637[50] [13]	0
C7 [8]	ω(σ _g)	2201.88	1959.85852[18] [7]	1804.0
	ω(σ _u)	1254.18	1197.3 [17]	475.5
C7 [8]	ω(σ _g)	2166.5		0
	ω(σ _u)	1564.4		0
C7 [8]	ω(σ _g)	574.9	548[90][12]	0
	ω(σ _u)	2200.1	2138.3152[9]; 2127.8[18]	2436.8
C7 [8]	ω(σ _g)	1931.6	1898.3758[9][19,20]	596.2
	ω(σ _u)	1088.1		11.7

Table 4: RCCSD(T)-F12/aug-cc-pVTZ Harmonic Stretching Frequencies and MP2/aug-cc-pVTZ Intensities of C_n⁻

anion	ω	calculated	Intensity (km/Mole)
C3 ⁻	ω(σ _g)	1849.69	0
	ω(σ _u)	3477.47	7183.4
C4 ⁻	ω(σ _g)	3136.63	0
	ω(σ _u)	2518.24	0
C5 ⁻	ω(σ _g)	4115.24	7322.3
	ω(σ _u)	1887.11	-0
C6 ⁻	ω(σ _g)	754.97	0
	ω(σ _u)	1978.89	2402.7
C7 ⁻ [8]	ω(σ _g)	1430.63	7302.9650
	ω(σ _u)	2171.0	0
C6 ⁻	ω(σ _g)	1857.0	0
	ω(σ _u)	654.0	0
C7 ⁻ [8]	ω(σ _g)	2021	**
	ω(σ _u)	1215	1338.3
C7 ⁻ [8]	ω(σ _g)	3148.6	0
	ω(σ _u)	2027.5	0
C7 ⁻ [8]	ω(σ _g)	840.8	0
	ω(σ _u)	4896.1	1206.2
C7 ⁻ [8]	ω(σ _g)	2568.9	3058.7
	ω(σ _u)	647.9	71.8

3- Electronic Excited States

MRCI/aug-cc-pVTZ Relative Vertical Excitation Energies (E in eV) to the First Electronic States of Neutral and Charged C _n for n=3,4,5,6,7									
C3	C4	C4	C5	C6	C6	C7[8]	C7[8]	C7[8]	C7[8]
symmetry	E	symmetry	E	symmetry	E	symmetry	E	symmetry	E
X ¹ Σ _g ⁺	0	x ³ Σ _g ⁻	0	X ¹ Σ _g ⁺	0	X ³ Σ _g ⁻	0	X ¹ Σ _g ⁺	0
¹ Π _u	2.14	¹ Δ _g	0.40	³ Σ _g ⁻	1.56	¹ Π _g	2.37	¹ Δ _g	0.32
		¹ Σ _g ⁺	0.59	³ Σ _u ⁻	1.61	³ Σ _g ⁻	2.39	³ Σ _g ⁻	0.47
		³ Π _u	1.06	³ Π _u	2.44	³ Π _u	1.35	³ Π _u	1.38
		³ Π _g	1.32			³ Π _g	1.38	³ Π _g	1.38
		² Σ _g ⁺	1.75			¹ Π _u	1.96	³ Σ _u ⁻	2.21
		¹ Π _u	1.86			¹ Π _g	1.98	¹ Δ _u	2.36
		¹ Π _g	2.12			X ³ Σ _g ⁻	0	¹ Σ _g ⁺	2.43
		³ Σ _g ⁻	1.98			⁴ Π _u	2.36		
						⁴ Π _g	2.41		
						⁴ Σ _g ⁻	2.49		

* E(C₃) = -113.813032 a.u. / E(C₄) = -113.875302 a.u. / E(C₄) = -151.745625 a.u. / E(C₅) = -151.874858 a.u. / E(C₆) = -189.735415 a.u. / E(C₆) = -189.821795 a.u. / E(C₇) = -227.666058 a.u. / E(C₇) = -227.804974 a.u. / E(C₇) = -265.624595 a.u. / E(C₇) = -265.724890 a.u.

Conclusions

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Acknowledgments

We acknowledge support from the Agence Nationale de la Recherche (Anion Cos Chem ANR-14-CE33-0013), the COST Actions CM1405 "MOLIM" and CM1401 "Our Astrochemical History". We also acknowledge the CTI (CSIC) and CESGA for computing facilities.

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Small linear carbon chains: vibrational and electronic states

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In spite of their astrophysical relevance, few bare chains have been observed in gas phase extraterrestrial sources. The shortest chain C_2 , was the first detected, followed by C_3 and the linear- C_5 [2-3]. Detections were performed through the analysis of Infra-Red active vibrational excitations or through their electronic transitions because they present a zero dipole moment.

All the C_n chains present a large number of isomers, however, in this work we focus on the linear ones. The large stability of charged linear chains was used as argument to predict the presence of anions in the interstellar medium. We present computed molecular properties calculated using highly correlated ab initio methods (CCSD(T)-F12, MRCI/CASSCF). We determine structures, infrared frequencies and excitations energies to the lowest electronic states and electron affinities of the small chains type C_n ($n=3,4,5,6,7$). Special attention is given to the anions which relevance for reactivity is evident. Non-adiabatic effects and spin-orbit effects will be predicted.

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