12404 J. Phys. Chem. A **2009,** *113,* 12404–12410

Ab Initio Characterization of C_6[†]

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Received: March 8, 2009; Revised Manuscript Received: April 29, 2009

Structural and spectroscopy parameters of C_6 are determined with ab initio calculations confirming the existence of nine isomers. Those geometries with high stability (the linear, where the electronic ground state is a triplet ($X^3\Sigma_g^-$), and the slightly distorted cyclic singlet (X^1A_1')) are determined with CASPT2/CASSCF. The effect of the correlation energy on the isomer stability is discussed. The local potential energy surfaces of the first electronic states of linear-C_6 are determined with CASPT2/CASSCF calculations and the ANO-L C[4s3p2d1f] basis set. We provide minimum energy geometries and excitation energies for 19 electronic states. A new assignment of the electronic spectrum transitions involving high-energy symmetry states is proposed. Electron affinity and ionization potential have been computed to be EA = 3.97 eV and IP = 9.73 eV.

Introduction

The first theoretical studies of C_6 started in 1959 when Pitzer and Clementi[1] found the most stable $^3\Sigma_g^-$ linear structure while searching for the understanding of the heat of sublimation of graphite. Nevertheless, C_6 has not attracted much attention until the 1980s when a huge amount of structural studies were published. In that period, C_n carbon chains were proposed as responsible of the diffuse interstellar bands (DIBs)[2] and started to be considered relevant species for astrophysics research. It is commonly accepted that they play an important role in the reactivity of polycyclic aromatic hydrocarbons (PAHs).[3]

To our knowledge, C_6 has not yet been detected and well characterized in astrophysics research despite the fact that the search for carbon compounds is a common objective of radioastronomical and infrared surveys.[4−6] Far-infrared spectroscopy (FIR) permits the observation of species, such as the linear C_n type chains with zero dipole moment and very low frequency bending modes,[3,7] whose detection is not easy. On the observational difficulties generated by the low abundances, it is necessary to consider the complexity of the assignment derived from the lack of experimental information of chemical and physical properties for the molecular base data. In order to overcome this lack of information, we have initiated systematic theoretical studies of chains starting with C_4 and C_5 using state-of-the-art ab initio calculations.[8−11] They were motivated by previous astrophysical observations performed at our institution.[3,7]

C_4 had been tentatively assigned to a band observed at 174 cm^{-1} considering the chemical properties of the molecule and the astrophysical object.[3] C_5 and C_6 have been selected as possibly responsible of a band observed at very low frequency (102 cm^{-1}) in the carbon-rich young planetary nebula NGC 7027[7] since the band shape could not be reproduced by atomic fine-structure lines, recombination lines, or the rotational emission of abundant molecules.[7] Although, the assignment to the antisymmetric bending mode of C_5 is highly congruent with our previous ab initio results,[11] a final decision implies the characterization of C_6.[7]

In this paper, as starting point for the *linear*-C_6 characterization we discuss its structure and electronic spectrum, using CASPT2/CASSCF ab initio calculations. A further study of the rovibrational spectrum implies the localization of the lowest excited electronic states to predict possible rovibronic interactions. Carbon chains and many cyclic compounds[8−13] depend strongly on static and dynamical correlation, which are well considered in the CASPT2 theory. This method allows us to determine the ground electronic state properties and, also, those of excited electronic states in an efficient way given the molecular size. Our previous study of C_5 was performed at the same level of theory.[11]

The review of Van Order and Saykally[14] provides a detailed report of previous studies performed on the smallest C_n clusters. Small and even pure carbon chains of type C_{2n} are mainly challenging species for a theoretical characterization given the isomerism and the large density of electronic states lying around the ground state configuration.[8] Likewise C_4[8] and C_6 present a typical distribution for even carbon chains showing two favored isomers almost isoenergetic, one of them is cyclic, where the ground electronic state is a singlet, and the other is linear, where the ground electronic state is a triplet. In the same way as C_4, most of the previous experimental works of C_6 have been performed on a linear structure[14−31] although the cyclic isomer has been experimentally detected.[32−36]

All the C_n chains present isomerism with the number of possible isomers increasing fast with the number of carbons.[11] The nature of the minimum energy structure of C_6 has instigated controversy given the important role played by the electronic correlation.[37−51] The first ab initio calculations were those of Raghavachari at al.[37] and Raghavachari and Binkley,[38] who concluded that the slightly distorted D_{3h} cyclic structure presents a higher stability. Few years later, Parasuk and Almlöf[39] showed the $X^3\Sigma_g^-$ linear form to be the favored isomer by correlating a relatively small number of electrons. Hutter et al.,[42] Hutter and Lüthi,[43] and Martin et al.[47] found the D_{3h} form as the most stable structure by using more sophisticated methods. Recently, Schmatz and Botschwina[45] have determined the geometry of the linear form with CCSD(T).

As with C_4, it may be expected that C_6 will show a large density of electric states close to the ground electronic state,

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[†] Part of the "Russell M. Pitzer Festschrift".

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10.1021/jp902083c CCC: $40.75

with many consequences on the infrared and microwave spectra. In addition, the strongest electronic bands for even chains are not excitations to the lowest electronic state for each symmetry. Both problems should be considered for the interpretation of astrophysical observations through IR or electronic transitions as DIBs.[30]

ESR measures in Ar and Ne matrices show that the ground electronic state of the linear form is $^3\Sigma$ and corresponds to a cumulene structure.[15] C_6 presents an electronic affinity of 4.185 eV[18] and an ionization potential of 9.7 ± 0.2 eV.[22] First, theoretical studies of the electronic states are from Parasuk and Almlöf[39] and Liang and Schaefer[40] who analyzed the electronic configuration of two possible linear structures, the most stable *cumulene* ($X^3\Sigma_g^-$) and one *acetylene* ($X^3\Sigma_u^+$). With photoelectron spectroscopy,[27] the first electronic states $^1\Delta_g$, $^1\Sigma_u^+$ and $^3\Pi_u$ have been localized at 0.166, 0.85, and 1.10 eV. Recently, Forney et al.,[25] Freivogel et al.,[26] and Grutter et al.[30] have measured the absorption electronic spectra in neon matrices. In gas phase, first observation of the $2^3\Sigma_g^- \leftarrow X^3\Sigma_g^-$ transition is from Boguslavskiy and Maier.[31] Recent theoretical excitations and oscillator strengths performed by Hanrath et al.[50] and Grein et al.[51] have been employed for the interpretation of the electronic spectra of linear-C_6 and cyclic-C_6.

Theoretical Approach

The determination of the structural parameters of linear-C_6 and cyclic-C_6 and the excitation energies to the first electronic states of linear-C_6 has been performed with the CASPT2/CASSCF method[52,53] implemented in the MOLCAS package,[54] an active space containing 14 valence orbitals with 14 active electrons and the ANO-L C[4s3p2d1f] basis set.[55] Excitation energies were determined from the potential energy surfaces of 19 electronic states mapped around the cumulene and acetylene structures defined in ref 39. Surfaces have been fitted and minimized with the FIT-ESPEC code using polynomial series,[56] for obtaining the geometry parameters of the minima. A preliminary search of C_6 isomers has been performed at the B3LYP/cc-pVTZ level of theory refining the corresponding energies with CCSD(T)/cc-pVTZ.

Results and Discussion

The C_6 Isomers Structure. The search of isomers and stationary points of the 12-dimensional potential energy surface of C_6 has been performed with density functional theory (B3LYP/cc-pVTZ). The corresponding energies have been refined with CCSD(T). The most stable structures have been further refined with CASPT2/CASSCF.

The existence of nine isomers of C_6 is confirmed. Table 1 shows their structural parameters, relative energies, and several first-order spectroscopic properties (harmonic frequencies, rotational constants, and dipole moment), all of them determined with B3LYP/cc-pVTZ. C_6 shows two isomers of prominent stability, one lineal, whose electronic ground state is a triplet ($X^3\Sigma_g^-$), and a slightly distorted cyclic singlet (X^1A_1'). As it is commonly believed, the linear form displays a *cumulene* structure like anticipated the first ESR measures.[15] With B3LYP/cc-pVTZ, the linear form seems to be the favored geometry although the energy difference between both isomers is less than 2100 cm^{-1} (0.27 eV). Single point CCSD(T) calculations on the optimized geometries reverse these stabilities, and the linear form lies 4150 cm^{-1} above the cyclic one, although, for the remaining isomers, the relative order is preserved. In a further paragraph, we discuss the effect of the level of theory on the relative stabilities.

The remaining isomers exist above 10000 cm^{-1}. Five of them, S2, S3, S4, S5, and S6, show singlet ground states, whereas two of them, T2 and T3, are triplets. These structures may be important intermediates of astrophysical and atmospherical reactions involving complex molecules. However, only three structures, S2, S3, and S5, present a nonzero dipole moment which permits their detection by radioastronomy. To be sure of the ground-state spin multiplicity, we searched for the first exited electronic state of each isomer. We determined excitation to the first triplet in the case of the singlet isomers (1.91 eV (*c*-C_6 (cyclic)), 0.06 eV (S2), 1.49 eV (S3), 1.2 eV (S4), 0.35 eV (S5), 1 eV (S6)), and to the first singlet state, in the case of the triplet isomers (0.58 eV (*l*-C_6 (linear)), 3.86 eV (T2), 0.53 eV (T3)).

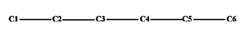
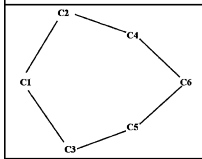
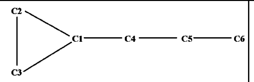
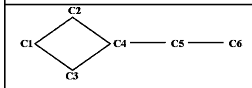
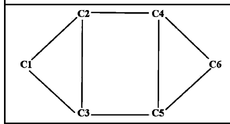
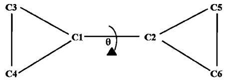
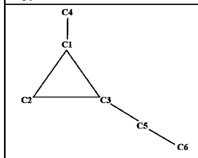
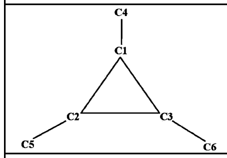
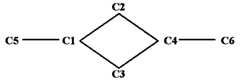
The prominence of *l*-C_6 and *c*-C_6 isomers is really marked. They are the only ones capable of being populated at low temperatures and stable enough for existing as isolated species. Although both structures show a zero dipole moment, they display large amplitude vibrations observable with far-infrared techniques. Their lowest frequencies have been determined at 103 cm^{-1} (π_u) and 436 cm^{-1} (a_2'').

The major stability of *l*-C_6 and *c*-C_6 justifies refinement of the calculated geometry parameters with high correlated ab initio calculations. For this goal and taking into account the molecular size, we performed CASPT2/CASSCF/ANO-L calculations, defining an active space of 14 electrons and 14 orbitals, the largest one allowed by our computational capabilities. In Table 2, the structural parameters of the two isomers are compared with previous calculations performed at different levels of theory. In Table 3, their CASPT2 relative energies are shown and compared with available data. For the linear form, the bond distances have been found to be $R1 = R5 = 1.3127$ Å (outer bonds), $R2 = R4 = 1.2926$ Å, and $R3 = 1.285$ Å (inner bonds). The B_e rotational constant has been found to be 0.047770 cm^{-1}, which is in a good agreement with previous CCSD(T) data ($B_e = 0.047923$ cm^{-1}).[45] It is also congruent with the experimental B_0 determined by infrared diode laser spectroscopy ($B_0 = 0.048479$ cm^{-1}),[21] because the B parameter augments with the vibrational quanta, which can be verified using the second-order perturbation theory implemented in the FIT-ESPEC code.[53]

The *c*-C_6 geometry has always been a matter of controversy since the expected D_{6h} symmetry vanishes. In all the previous papers,[35−39,42,43] the molecule appears slightly distorted showing a D_{3h} structure. With CASPT2 theory, we also obtain a distorted symmetry, since the six bond distances coincide (1.3197 Å), whereas the angles show two alternative values (147.88° and 92.15°). Unfortunately, actual computational facilities do not allow us to define a complete active space for a molecule as C_6, which impedes to assert that the D_{3h} geometry corresponds to a physical reality. As couple cluster theory leads to a distorted structure (see Table 2), the deformation does not seem to be a problem of dynamical correlation. The symmetry break can be a consequence of the lack of static electronic correlation.[12,13]

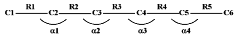
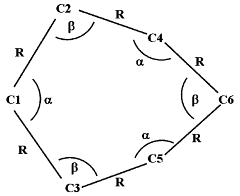
In Table 3, the CASPT2/ANO-L relative energy of *l*-C_6 and *r*-C_6 is compared with previous calculations. They are evidence for how the electronic dynamical correlation plays a basic roll. At the RHF or CASSCF levels, the linear form appears to be the most stable as occurs with our B3LYP calculations. However, high correlated methods (CCSD, MRCI, or CASPT2) lead to the cyclic form as the preferential geometry. Present CASPT2 energy, calculated to be 4063 cm^{-1}, is slightly different than that of ref 43 determined with a different number of correlated electrons (14e^- (this work, cyclic and linear); 10e^- (ref 43, linear), 12e^- (ref 43, cyclic)). The static correlation effect

TABLE 1: B3LYP[a] and CCSD(T)[a] Relative Energies (E_R, in cm^{-1}) of C_6 Isomers: Structural Parameters (in Å, deg), Dipole Moments (μ; in Debyes), Rotational Constants (in, MHz), and Harmonic Frequencies (ω, in cm^{-1}) Calculated with B3LYP[a]

Isomers		E_R B3LYP	E_R CCSD(T)	Structural parameters	μ	Rotational constants	ω
	*l*-C_6 ($D_{\infty h}$) $X^3\Sigma g^-$	0.0[b]	4150	$R_{12}=R_{56}=1.2958$ $R_{23}=R_{45}=1.2839$ $R_{34}=1.2715$	0.0000	B=1459.5	103(π_u),216(π_g),382(π_u) 529(π_g);670(σ_g),1229(σ_u) 1733(σ_g) ;2029(σ_u), 2176(σ_g)
	*c*-C_6 (D_{3h}) X^1A_1	2100	0.0[c]	$R_{12}=R_{13}=R_{24}=R_{35}=R_{46}=R_{56}=1.3194$ <213=<246=<356=147.9 <124=<465=<135=92.1	0.0	A=B=8389.2 C=4194.6	436 (a_2”);539(e”); 645(e’) 647(a_1’);1221(a_1’);1230(e’) 1409(a_2’);1759(e’)
	*S2* (C_{2v}) X^1A_1	11737	11478	$R_{12}=R_{13}=1.4323$ $R_{14}=1.3088$ $R_{45}=1.2722$ $R_{56}=1.2961$ <312=56.9	0.0668	A=45174.3 B=1915.6 C=1837.7	98(b_2),121(b_1),271(b_2) 284(b_1),502(b_2),611(b_1) 636(a_1);697(b_2),1163(a_1) 1382(a_1);1733(a_1),2119(a_1)
	*S3* (C_{2v}) X^1A_1	11872	9152	R12=R13=1.4283 R24=R34=1.4298 R45=1.3095;R56=1.2764 <124=115.3;<213=64.7 <243=64.6	1.2821	A=36028.9 B=2476.5 C=2317.2	132(b_1);157(b_2);291(b_1) 448(b_2);623(b_1);667(b_2) 680(a_1);974(b_2);999(a_1) 1365(a_1);1534(a_1);2092(a_1)
	*S4* (D_{2h}) X^1A_g	17035	14207	$R_{12}=R_{13}=R_{46}=R_{56}=1.3748$ $R_{24}=R_{35}=1.3176$ $R_{23}=1.6168$; $R_{16}=3.5402$	0.0	A=16071.2 B=5262.7 C=3964.5	222(b_{3u});427(a_u)489(b_{2g}) 554(b_{3g});689(b_{2u});721(b_{1u}) 879(a_g);1089(b_{3g});1145(a_g) 1224(b_{1u});1363(b_{2u});1841(a_g)
	*T2* (D_{2d}) X^3B_2	18518	19039	$R_{12}=1.3921$ $R_{13}=R_{14}=R_{25}=R_{26}=1.3867$ <413=<625= ; θ=90	0.0	A=23293.2 B=C=2560.4	122(e);170(b_1);346(e) 559(e);613(a_1);1253(a_1) 1259(b_2);1628(b_2);1720(a_1)
	*S5* (C_s) X^1A’	20803	19833	$R_{12}=1.3951$;$R_{13}=1.5740$; $R_{23}=1.3911$;$R_{14}=1.3128$; $R_{35}=1.3021$;$R_{56}=1.2802$; <231=55.5;<213=55.5 <214=174;<135=163.2 <356=176.2	1.6923	A=11670.1 B=2858.5 C=2296.1	142(a”);155(a’);246(a”) 246(a’);435(a”);487(a’) 508(a”);807(a”);994(a”) 1469(a”);1717(a”);2066(a”)
	*S6* (D_{3h}) X^1A_1’	32201	30255	$R_{12}=R_{23}=R_{31}=1.4489$ $R_{14}=R_{25}=R_{36}=1.3060$	0.0	A=B=5307.4 C=2653.7	108(e’), 200(a_2”) 278(a_2’),375(e”),726(e’) 830(a_1’),1629(e’),1938(a_1’)
	*T3* (D_{2h}) X^3B_{1g}	32562	32144	$R_{12}=R_{13}=R_{24}=R_{34}=1.4276$ $R_{23}=1.5460$ $R_{15}=R_{46}=1.3306$	0.0	A=35240.9 B=2684.1 C=2494.2	109(b_{3u});207(b_{2u});342(b_{3g}) 370(b_{2g}); 372(b_{3u});574(b_{2u}) 622(a_g);851(b_{3g});974(a_g) 1081(b_{1u});1483(b_{1u});1689(a_g)

[a] cc-pVTZ basis set; E(B3LYP) = −228.338346 au; E(CCSD(T)) = −227.820265 au.

TABLE 2: Structural Parameters (Distances in Angstromw and Angles in Degrees) and Rotational Constants (in cm^{-1}) of the Two Most Stable Isomers of C_6, Calculated with CASPT2/ANO-L C[4s3p2d1f]

	R1=R5	R2=R4	R3	*Method and Ref.*
 *l*-C_6 ($D_{\infty h}$)	**1.3124**	**1.2926**	**1.285**	*Present work*
	1.293	1.275	1.269	HF/6-31G* [37]
	1.298	1.280	1.265	CAS/ANO C[4s4p2d] [38]
	1.3008	1.2940	1.2812	MBPT(2)/6-31G* [41]
	1.299	1.294	1.280	DFT/P3P86/TZ(d) [42]
	1.308	1.292	1.280	CCSD(T)/TZ2P [43]
	1.30811	1.29314	1.28078	RCCSD(T)/240cGTOs [45]
	1.3257	1.3092	1.2973	CCSD(T)/cc-VDZ [47]
	B_e= 0.047770			*Present work*[a]
	R	α	β	*Method and Ref.*
 *c*-C_6 (D_{3h})	**1.3197**	**147.88**	**92.15**	*Present work*
	1.316	149.6	90.4	HF/6-31G* [37]
	1.330	147.1	92.9	DFT /P2P86/TZ(D)[42]
	1.329	146.8	93.2	CCSD(T)/TZ2P [43]
	1.320	148.1	91.9	B3LYP/cc-pVTZ [36]
	A_e=B_e= 0.279554 C_e= 0.139770			*Present work*

[a] $B_0^{(exp)} = 0.048479$ cm^{-1};[21] $B_e^{(RCCSDT)} = 0.047923$ cm^{-1}.[45]

TABLE 3: Relative Energies[a] (E_R in cm^{-1}) of the Two Most Stable Isomers of C_6

	$E_R = E_{lineal} - E_{cyclic}$	ref
CASPT2/ANO-L C[4s3p2d1f]	**4063**[b]	this work
Previous calculations		
HF/6-31G*	−12007	37
MP2/6-31G*	10454	37
MP4/6-31G*	7140	37
MP4/6-31G*+ZPVE	6706	37
CASSCF (10/10)	−5177	39
MRCI/CASSCF (10/10)	−12925	39
DFT/B3P86/TZ(D)	25225	42
MP2/ANO 4s3p2d1f	4447	43
CCSD/ANO 4s3p2d1f	2988	43
CCSD(T)/ANO 4s3p2d1f	3718	43
CASSCF/ANO 4s3p2d1f	−1841	43
CASPT2/ANO 4s3p2d1f	5142[c]	43
MRCI/ANO 4s3p2d	1042	44
MRCI+Q/ANO 4s3p2d	1737	44
CCSD(T)/cc-pVTZ	3822	47
CCSD(T)/cc-pVTZ+cor	5212	47

[a] ER < 0 if $E_{lineal} < E_{cyclic}$. [b] CAS preformed correlating 14 electrons. [c] CAS performed correlating 12 (cyclic) and 10 (linear) electrons.

does not appear to be crucial, although employed active spaces always neglect part of the valence orbitals.

The Electronic Spectrum of *l*-C_6. Even chain electronic structure is not straightforward. They mostly present a large density of electronic states nearby the ground-state region. Thus, nonadiabatic, rovibronic, Renner−Teller, and spin−orbit effects can supply complex band shapes. Furthermore, ab initio calculations are very sensitive to effects arising from the proximity of states, which can originate instabilities of the wave functions and makes hard the determination of force fields, spectroscopic properties, and adiabatic potential energy surfaces. This behavior was clearly shown for *l*-C_4[8,9] and can be expected for *l*-C_6.

Ab initio calculations are really suitable for a prediction of adiabatic excitations energies. For accurate vibrational structures, the localization of the lowest electronic states for geometries around the ground electronic state minimum is crucial. In the best case, the region of populated vibrational levels will be free of rovibronic interactions allowing detailed analysis to be performed. In Table 4, the minimum energy geometries and the excitation energies of 19 electronic states calculated with CASPT2/ANO-L are shown. For each symmetry of the D_{2h} abelian group, the CASSCF average energy of two roots has been optimized. The geometries have been determined by fitting, with the code FIT-ESPEC,[56] the vertical excitations energies of 66 linear structures to polynomial series with further minimization. Geometries were selected around the cumulene and acetylene forms of ref 39 covering the intermediate configurational space. In Figure 1, we show cuts of the fitted potential energy surfaces mapped from the *cumulene* to the *acetylene* form. The potential energy surfaces of the lowest states show a unique minimum. The interconversion of structures implies an excitation to high electronic states.

The excitation energies of Table 4 were calculated from the minimum of the ground electronic state surface to the excited-state minima. Then, values are always lower than the corresponding vertical excitation energies of Hanrath et al.[50] determined with MR-CI and the Huzinaga−Dunning 9s5p/5s3p basis set. We obtain, with CASPT2 and a larger basis set, a good correlation between their results and our calculations for energies and relative order of states. The geometry optimization effect is relatively small especially for cumulene states.

TABLE 4: Excitation Energies (in eV) Calculated from the Ground Electronic State of *l*-C_6 ($E = -227.740031$ a.u.) to the Minimum of the Lowest Excited Electronic States[a]

	CSPT2/ANO-L C[4s3p2d1f]			excitation energies		
symmetry	R1 = R5 (outer)	R2 = R4	R3 (inner)		exp	electronic configuration
X $^3\Sigma_g^-$	1.312	1.293	1.285	0.00	0.0	$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^2$
$^1\Delta_g$	1.310	1.299	1.280	0.18	0.166 [27]	$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^2$
$^1\Sigma_g^+$	1.316	1.299	1.279	0.26		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^2$
$^3\Pi_u$	1.268	1.324	1.256	0.85	1.10 [27]	$6(\sigma_u)^2\ 7(\sigma_g)^1\ 1(\pi_g)^4\ 2(\pi_u)^3$
$^3\Pi_g$	1.268	1.322	1.258	0.88	**0.85** [27][b]	$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^3$
$^1\Pi_u$	1.262	1.360	1.231	1.29		$6(\sigma_u)^2\ 7(\sigma_g)^1\ 1(\pi_g)^4\ 2(\pi_u)^3$
$^1\Pi_g$	1.263	1.346	1.239	1.28		$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^3$
$^1\Sigma_u^-$	1.302	1.336	1.247	1.60		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$^3\Sigma_u^+$	1.299	1.334	1.249	1.85		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$^3\Delta_u$	1.297	1.332	1.249	1.71		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$^3\Sigma_u^-$	1.343	1.297	1.299	2.49	2.42 [25]	$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$^5\Pi_g$				2.94[c]		$6(\sigma_u)^2\ 7(\sigma_g)^1\ 1(\pi_g)^4\ 2(\pi_u)^2\ 2(\pi_g)^1$
$^5\Pi_u$				2.98[c]		$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^2\ 2(\pi_g)^1$
$2^3\Pi_g$	1.287	1.332	1.264	3.12		$6(\sigma_u)^2\ 7(\sigma_g)^1\ 1(\pi_g)^4\ 2(\pi_u)^2\ 2(\pi_g)^1$
$2^3\Pi_u$	1.185	1.331	1.200	3.72		$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^4$
$^1\Delta_u$	1.328	1.298	1.300	3.24		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$^1\Sigma_u^+$	1.320	1.378	1.271	3.78		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^3$
$2^1\Pi_u$	1.267	1.335	1.283	3.85		$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^3\ 2(\pi_u)^4$
$2^1\Pi_g$	1.267	1.334	1.286	3.83		$6(\sigma_u)^2\ 7(\sigma_g)^1\ 1(\pi_g)^3\ 2(\pi_u)^4$
$2^3\Sigma_u^-$				3.86[c]		$6(\sigma_u)^2\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^1\ 2(\pi_g)^1$
$3^3\Sigma_u^-$				4.31[c]		$6(\sigma_u)^2\ 7(\sigma_g)^0\ 1(\pi_g)^4\ 2(\pi_u)^3\ 2(\pi_g)^1$
$3^3\Pi_u$				4.81[c]	**4.97** [28][b]	$6(\sigma_u)^1\ 7(\sigma_g)^2\ 1(\pi_g)^4\ 2(\pi_u)^2\ 2(\pi_g)^1$

[a] To compare with recent previous calculations of vertical excitations, see ref 50. [b] New assignment based on present CASPT2 calculations. [c] Vertical excitations.

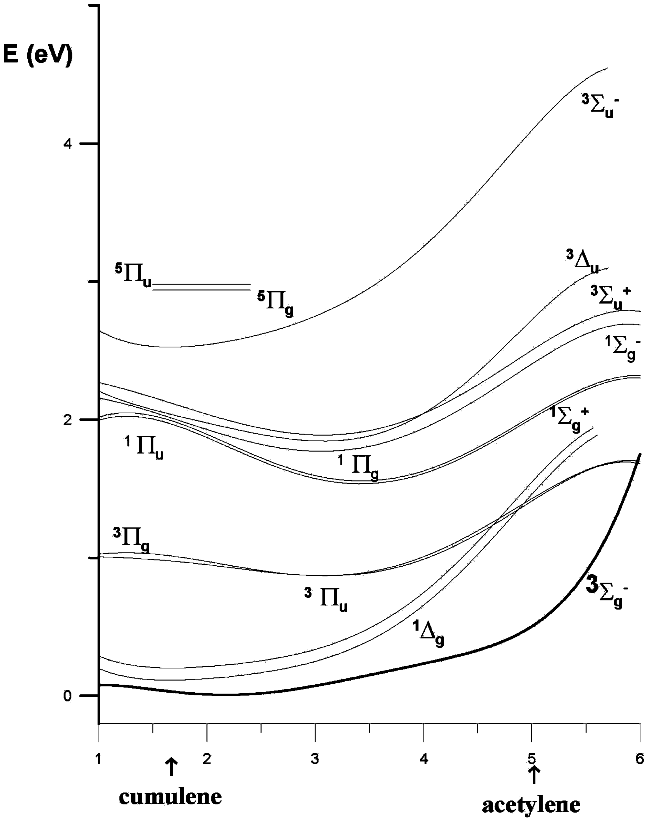


Figure 1. Cuts of the fitted potential energy surfaces mapped from the cumulene to the acetylene form.

l-C_6 low-energy electronic state distribution is similar to those O_2 and of *l*-C_4.[8] With CASPT2/ANO-L theory, several states (i.e., the ground electronic state; see Tables 3 and 4) present *cumulene* minimum energy geometries. Other states ($1\Sigma_u^+$, $1^3\Pi_u$, $1^3\Pi_g$, etc.) present *near-acetylene* structures, far away from the acetylene one of ref 39 obtained at the RHF level. The excitations from the cumulene triplet $X^3\Sigma_g^-$ ground state to the two first electronic states have been determined to be 0.18 eV ($^1\Delta_g$) and 0.26 eV ($^1\Sigma_g^+$), which agree with available experimental data. For example, the first $^1\Delta_g$ excited state was assigned to a band observed at 0.166 eV with photoelectron spectroscopy.[27] The small difference between calculated and experimental data (0.18−0.166 eV) is of an order of magnitude comparable to the vibrational energies. It can be related to the zero vibrational energy neglected in our model.

Our CASPT2 excitation energy for the $^3\Sigma_u^- \leftarrow X^3\Sigma_g$ transition is 2.49 eV, in very good agreement of the experimental value of 2.42 eV, obtained by electronic absorption spectroscopy in Ne matrices.[24,25] The corresponding vertical excitation calculated by Hanrath et al.[50] is 2.66 eV.

Large nonadiabatic interactions can be expected since the gap among states is three times shorter for C_6 than for C_4. For example, the two first electronic states of *l*-C_4[8] were calculated to lie 0.44 eV ($^1\Delta_g$) and 0.61 eV ($^1\Sigma_g^+$) over the ground electronic state (with MRCI/CASSCF). In ref 9, we discussed the spin−orbit interaction between the $^1\Sigma_g^+$ and $X^3\Sigma_g^-$ in C_4, for predicting their effect on the ground-state vibrational band shapes. For comparison, we use the isoelectronic molecule C_3Si, which Si atom multiplies A_{SO} by a factor of 7.6.[10] With the same technique, we found a spin−spin splitting for the X-state of *l*-C_6 in the 0.17−0.2 cm^{-1} range, which is lower than that for C_3Si and of the same order of magnitude as the corresponding C_4, although, the small gap among states of C_6 favors interactions.

Parts a and b of Figure 2 show one-dimensional cuts of the first electronic state PESs as functions of internal coordinates. In Figure 2a, the θ independent variable is the lowest π_u bending normal coordinate defined as a linear combination of two planar angles (∠C2C3C4 and ∠C5C4C3). The curves follow the process

$$l\text{-}C_6 \rightarrow c\text{-}C_6$$

As is expected (since l-C_6 is a singlet), at ~145°, one of the Δ_g state components passes through the $^3\Sigma_g^-$ ground-state surface of the linear form. In Figure 2b, the R_3 independent coordinate is the central bond stretching. The curves follow the process

$$l\text{-}C_6 \rightarrow l\text{-}C_3 + l\text{-}C_3$$

The electron affinity and the ionization potential have been computed to be EA = 3.97 eV and IP = 9.73 eV close to the experimental values of EA = 4.185 eV[18] and IP = 9.7 ± 0.2 eV.[22] For their evaluation, we have compared the energies of the $X^2\Pi_u$ states of l-C_6^- and l-C_6^+ calculated defining an active space of 14 orbitals, with the corresponding energy of the neutral species. In general, our CASPT2/ANO-L calculations reproduce well the available experimental data. There are few exceptions.

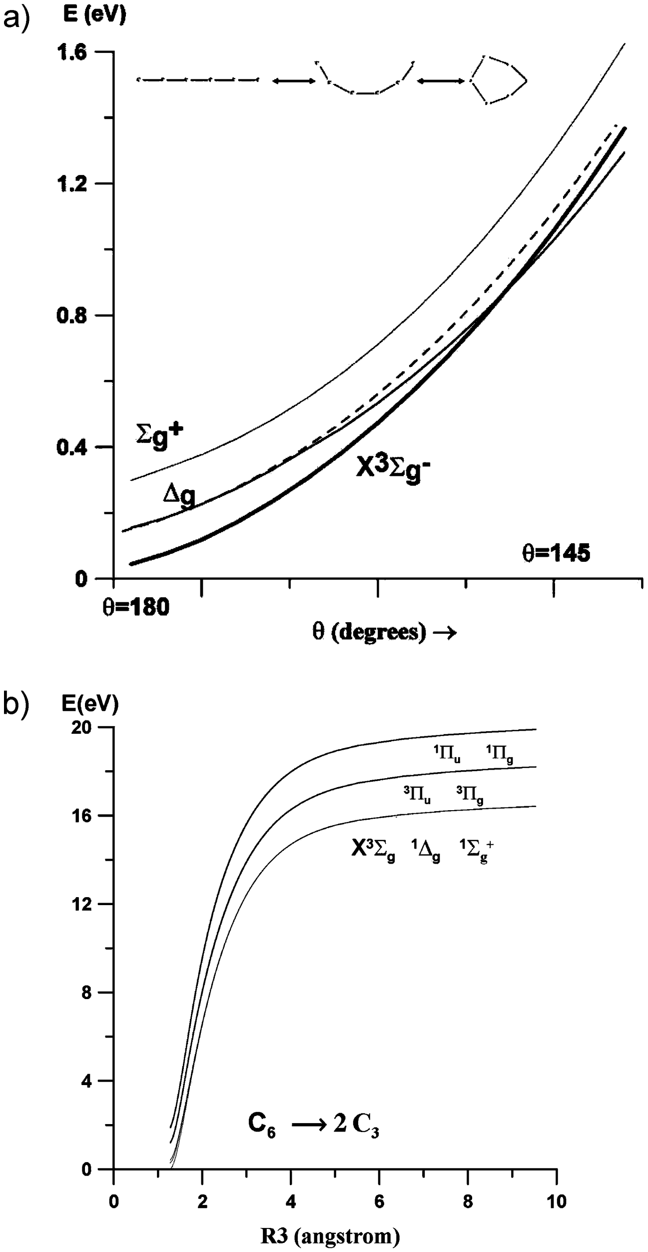


Figure 2. One-dimensional cuts of the fitted potential energy surfaces for the lowest electronic states depending on the following: (a) the θ independent variable is the lowest π_u bending normal coordinate defined as a linear combination of two planar angles (∠C2C3C4 and ∠C5C4C3); (b) the R_3 independent coordinate is the central bond stretching.

Present CASPT2 calculations do not confirm the existence of an *acetylene* form with a $X^3\Sigma_u^+$ ground electronic state, as previous ab initio calculations predicted.[39,40] In those papers, the assumed ground state was determined to lie ~1 eV over the *cumulene* form ground state.[39,40] On the basis of those calculations, two states observed at 0.85 and 1.10 eV with photoelectron spectroscopy[27] were assigned to the $^3\Sigma_u^+$ ground state of the *acetylene* form and to the first degenerate $^3\Pi_u$ state. Although, we obtain for $^3\Sigma_u^+$ a near-*acetylene* minimum geometry (1.299, 1.334, 1.249 Å) (see Figure 1), it cannot be considered the *acetylene* ground electronic state since two degenerate states, $^3\Pi_u$ and $^3\Pi_g$, lying below at 0.85 and 0.88 eV, present also near-*acetylene* structures (see Figure 1).

Furthermore, for $^3\Pi_u$, there is a reasonable correspondence between present calculations (0.85 eV) and photoelectron spectroscopy assignments (1.10 eV),[27] whereas for $^3\Sigma_u^+$, there is a huge divergence. Our CASPT2 adiabatic excitations place the first $^3\Sigma_u^+$ state at 1.85 eV, which is in a good agreement with the recent vertical excitation of 2.12 eV calculated with MR-CI in ref 50, but far away from the band observed at 0.85 eV. As the observed band is very strong, it should correspond to an excited state origin,[27] instead of to the vibrational structure of a low energy state. Therefore, we suggest the origin band of the $^3\Pi_g$ near-*acetylene* state that has not yet assigned, on the fact that there is a good agreement between experiments and calculations for many properties, confirming the quality of CASPT2 calculations. Furthermore, $^3\Pi_g \leftarrow X^3\Sigma_g$ transitions are visible using the employed technique and justify the polarization dependence of the observed M peak, connected to electronic configuration change by Xu et al.[27] It may be a $\sigma \rightarrow \pi$ transition.

In many cases, the lowest energy band system of a particular symmetry does not have the large intensity.[30,50] For even carbon chains the first $^3\Sigma_u^- \leftarrow X^3\Sigma_g$ transition usually has small oscillator strength.[30] More significant oscillator strengths are those of the transitions connecting the ground state and high-energy symmetry states, as confirms ab initio calculations.[50] For $2^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ and $3^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$, the CASPT2 excitation energies have been determined to be 3.86 and 4.31 eV. The transition to $2^3\Sigma_u$ was first measured by Boguslavskiy and Maier in gas phase,[31] and, on the basis of their own CI calculations, Grutter et al.,[28] assigned it to a band observed at 5.22 eV with electronic absorption spectroscopy in Ne matrices, ~1 eV over our present calculation. Thus, CASPT2 calculations predict an assignment of the band a 5.22 eV to a transition $N^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$, where $N > 3$.

Grutter et al.[28] have also measured an excitation at 4.97 eV involving a higher state of the Π_u ($N^3\Pi_u \leftarrow X^3\Sigma_g^-$).[28] Our corresponding predicted excitation energies for $2^3\Pi_u \leftarrow X^3\Sigma_g^-$ and $3^3\Pi_u \leftarrow X^3\Sigma_g^-$ are 3.72 and 4.81 eV. They support the assignment of the observed transitions to $N = 3\Pi_u$ state. Grutter et al.[28] assigned it to $N = 5$.

Conclusions

Preliminary results show that C_6 presents at least nine isomers (six triplets and three singlets). Among them, the lowest in energy is linear, whose electronic ground state is a triplet ($X^3\Sigma_g^-$), and a slightly distorted cyclic singlet (X^1A_1'). Both present prominent stabilities.

With high correlated ab initio calculations including dynamic corrections to the correlation energy, the cyclic isomer is the most stable, although differences of energy are very small. We confirm the cumulene character of the ground electronic state of the linear form, although no barriers of energy impede the process to become the acetylene form. For this one, the ground electronic state is ${}^3\Pi_u$. On the basis of the calculated excitation energy, we propose a new assignment for the band observed at 0.85 eV with photoelectron spectroscopy. In addition, new assignments for the high-energy symmetry states are proposed.

Acknowledgment. Massó and Senent want to acknowledge the Ministerio de Ciencia e Innovación of Spain, for grants AYA2005-00702 and AYA2008-00446 and to CESGA and LUNARC for computing facilities.

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JP902083C