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Ab initio MR–CI Investigation of Linear HC_5H^+ and HC_7H^+ [#]

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Abstract

Motivation. Linear hydrocarbon clusters with a large ratio of carbon to hydrogen are expected to be widely distributed in the interstellar environments. Positively charged clusters are very reactive and provide difficulties for experimental investigation. On the other hand it is known that theoretical studies of excited states can predict approximate transition energies and oscillator strengths so that such computations are an almost ideal tool to help the experimental search.

Method. Multi–reference configuration interaction (MR–CI) calculations are employed to compute the vertical electronic spectra of HC_5H^+ and HC_7H^+.

Results. The lowest dipole–allowed transitions are computed at 2.56 eV (HC_5H^+) and 2.34 eV (HC_7H^+) in reasonable agreement with experimental work of 499 nm (2.47 eV, HC_5H^+) and 600 nm (2.06 eV, HC_7H^+). Further transitions with relatively large oscillator strength are predicted at 3.85 eV ($3^2\Pi_g$) and 7.03 eV ($4^2\Pi_g$) for HC_5H^+ and at 3.17 eV ($3^2\Pi_u$) and 6.01 eV ($4^2\Pi_u$) for HC_7H^+.

Conclusions. In both molecules the energy difference between SOMO and LUMO is similar to the energy difference between HOMO and SOMO. The description of the two corresponding states shows multi–reference character. The lowering of these transition energies on increase of chain–length is in line with a smaller HOMO–SOMO and SOMO–LUMO gap.

Keywords. MRCI; spectroscopy; excited states; *ab initio*; hydrocarbons; diffuse interstellar bands.

Abbreviations and notations

AO, atomic orbital
cc–pVDZ, correlation consistent valence double zeta
cc–pVTZ, correlation consistent valence triple zeta
CCSD(T), coupled cluster method
CSF, configuration state function
DIESEL, direct intern extern individually selecting MR–CI program package
DFT–B3LYP, density functional method using the functional of Becke, Lee, Young and Par
IRREP, irreducible representation
HOMO, highest occupied molecular orbital
LUMO, lowest unoccupied molecular orbital
MR–CI, multi reference configuration interaction
SOMO, single occupied molecular orbital

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
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1 INTRODUCTION

During the last years carbon clusters and linear hydrocarbon chain molecules HC_nH ($n = 5–18$) with a large ratio of carbon to hydrogen have attracted considerable scientific interest [1–8]. Such molecules are expected to be widely distributed in the interstellar and circumstellar environments.

Besides neutral also the positively charged clusters are believed to play an important role as possible carriers of the diffuse interstellar bands [1,5–7]. Several cationic hydrocarbon clusters like HC_5H^+ and HC_7H^+ have recently been investigated by matrix isolation spectroscopy in neon matrices [1,2].

These unsaturated species are very reactive, which provides difficulties for experimental investigation. On the other hand it is known that theoretical studies of excited states can predict approximate transition energies and oscillator strengths so that such computations are an almost ideal tool to help the experimental search. In prior work we performed several studies on excited states of various pure carbon clusters [9–14]. Recently we could confirm experimental measurements [1,15] of the first dipole–allowed $1^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transition of neutral HC_5H and HC_7H by multi–reference configuration interaction (MR–CI) computations [16,17], but in addition a second $^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transition with considerably large oscillator strength is predicted at higher energy.

The aim of the present study is to extend our prior work of HC_5H [16] and HC_7H [17] to the charged species HC_5H^+ and HC_7H^+, especially to investigate if besides the first dipole–allowed transitions $1^2\Pi_g \leftarrow X^2\Pi_u$ in HC_5H^+ and $1^2\Pi_u \leftarrow X^2\Pi_g$ in HC_7H^+ additional transitions are computed with considerable oscillator strength for these cationic clusters, too.

2 MATERIALS AND METHODS

The equilibrium geometries of linear HC_5H^+ and HC_7H^+ were determined by optimizations using the density functional method (DFT) employing the B3LYP functional. We used the polarized correlation consistent triple–zeta cc–pVTZ basis set from Dunning [18] and the GAUSSIAN 98 [19] program package. The optimized structures were tested for local minima by checking for possible imaginary values in the vibrational analyses. B3LYP/cc–pVTZ optimized geometries are known to be quite reliable. In addition we have explicitly shown in recent work for HC_5H [16] that the DFT–B3LYP/cc–pVTZ results are in reasonable agreement with extensive coupled cluster CCSD(T)/cc–pVTZ optimizations [4].

The computations of the electronically excited states were performed with the multi–reference single and double excitation configuration interaction method MR–CI implemented in the DIESEL program [20]. The MR–CI calculations are performed in abelian subgroups of D_{2h}. Therefore states of Σ_g^+ and Δ_g, Σ_g^- and Δ_g, of Σ_u^+ and Δ_u, and of Σ_u^- and Δ_u, are computed in the same irreducible representation (IRREP). Furthermore Π and Φ states (as well as Δ and Γ states) are found in the same IRREP.

The automatic selection of reference configurations was carried out for HC_5H^+ with a summation threshold of 0.85, which means that the sum of the squared coefficients of all reference configurations selected for each state (root) is above 0.85. For HC_7H^+ the active space for the computation of Π and Φ states included the $2\pi_u$ (HOMO), the $2\pi_g$ (SOMO) and the $3\pi_u$ (LUMO) molecular orbitals. The active space for the calculation of Σ, Δ and Γ states of HC_7H^+ is determined by the occupied orbitals $4\sigma_g$, $4\sigma_u$, the SOMO $2\pi_g$ and the virtual $3\pi_u$, $5\sigma_g$ and $5\sigma_u$. In the set of reference configurations all excitations, which are possible within a given active space of occupied and virtual orbitals, are included. These active spaces are the result of careful investigation considering different CI spaces and are considered to be balanced. Enlarging the active spaces is found to change transition energies generally by less than 0.2 eV.

The set of reference configurations per irreducible representation (IRREP) is in the range between 31 and 59 for Σ, Δ and Γ states and 23 to 28 references are selected for the Π and Φ states in the case of HC_5H^+. In the case of HC_7H^+ the set of reference configurations per IRREP is in the range between 40 and 72 for Σ, Δ and Γ states and between 28 and 32 references for the Π and Φ states. An analysis of the molecular orbitals (MO) involved in the selected reference configurations justified the prior choice of treating 21 electrons active in the calculations for both HC_5H^+ and HC_7H^+ while keeping the remaining electrons in doubly occupied orbitals (frozen). From the set of reference configurations (mains) all single and double excitations in the form of configuration state functions (CSFs) are generated and all configurations with an energy contribution ΔE(T) above a given threshold of $T = 5\times10^{-8}$ hartree for HC_5H^+ and $T = 1\times10^{-7}$ hartree for HC_7H^+ are included in the final wavefunction. The effect of those configurations which contribute less than $T = 5\times10^{-8}$ (or 10^{-7}) hartree is accounted for in the energy computation E(MR–CI) by a perturbative λ–extrapolation [21]. The contribution of higher excitations is estimated by applying a generalized Langhoff–Davidson correction formula $E(MR–CI+Q) = E(MR–CI) - (1-c_0^2)\,[E(ref) - E(MR–CI)]/c_0^2$, where c_0^2 is the sum of squared coefficients of the reference species in the total CI wavefunction and E(ref) is the energy of the reference configurations. In order to keep the computation at a manageable size, only up to a maximum of six states per IRREP is computed for Π and Φ states, whereas two states per IRREP are computed for the Σ, Δ and Γ states in both molecules. The number of configuration state functions (CSF) directly included in the energy calculations are as large as 2.0 million (for Σ, Δ and Γ states) and 1.1 million (Π and Φ states) for HC_5H^+ and 420 000 (for Σ, Δ and Γ states) and 710.000 (Π and Φ states) for HC_7H^+ selected from total spaces of 11.7 million (Σ, Δ and Γ states) and 5.4 million (Π and Φ states) in the case of HC_5H^+ and 12.6 million (Σ, Δ and Γ states) and 6.0 million (Π and Φ states) for HC_7H^+ generated configurations.

For carbon we used in the calculations of excited states an AO basis set of Huzinaga–Dunning [22], which consists of 9s5p gaussians in a 5s3p contraction and an additional d polarization function with an exponent of α=0.75. Previous work on C_5 and C_6 [23,24] showed that this basis is flexible with respect to polarization and electron correlation and is considered to be fairly balanced for all states treated so that enlarging this basis set by Rydberg functions or by employing more functions in the polarization and correlation description is expected to change the results for valence transition energies generally by less than 0.2 eV. For hydrogen a correlation consistent AO basis set of double zeta quality (cc–pVDZ) is used for the calculations [18].

3 RESULTS AND DISCUSSION

In figure 1 we present the optimized equilibrium geometries at the DFT–B3LYP/cc–p–VTZ level. All distances are given in Å. The values in brackets for HC_5H^+ are the bond distances for neutral HC_5H obtained by Seburg et al. at the CCSD(T)/cc–pVTZ level [4]. The values given in brackets for HC_7H^+ are the computed distances for neutral HC_7H taken from ref. 17 (B3LYP/cc–pVTZ). The bonding is cumulenic in both molecules as can be expected from similar calculations of the neutral analogous species HC_5H [9] and HC_7H [10].

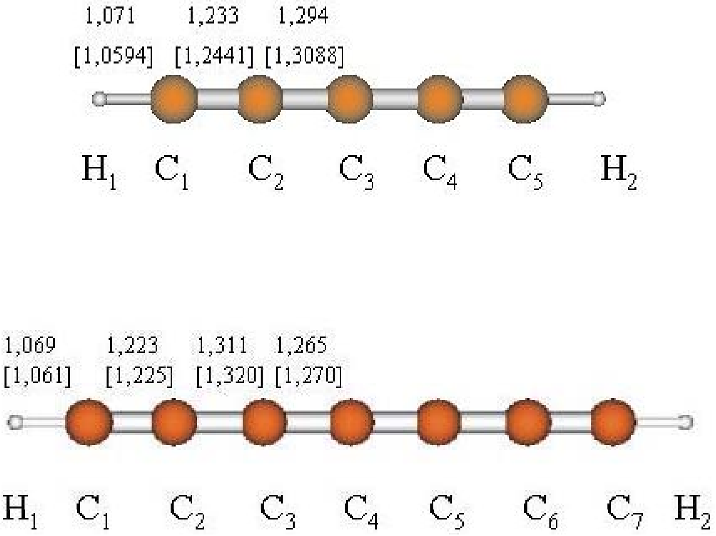

Figure 1. Equilibrium geometry of linear HC_5H and HC_7H (at the DFT–B3LYP/cc–p–VTZ level).

In HC_5H^+ the CC bond–lengths are shortened by about 0.006 to 0.015 Å compared to neutral HC_5H [4, 16] optimized by Seburg *et al*. at the CCSD(T)/cc–pVTZ level (fig. 1). The HC bonds of the cationic structure are about 0.012 Å longer than in HC_5H. The optimized structure of HC_7H^+ also shows slightly longer HC bonds (0.008 Å) and little shortened CC bonding distances (0.002 Å to 0.015 Å) compared to the neutral structure previously optimized at the DFT–B3LYP/cc–pVTZ [17].

3.1 HC_5H^+

Linear HC_5H^+ possesses a doublet $X^2\Pi_u$ ground state with the electronic configuration $...3\sigma_g^{\ 2}\ 3\sigma_u^{\ 2}\ 1\pi_u^{\ 4}\ 1\pi_g^{\ 4}\ 2\pi_u^{\ 1}\ /\ 2\pi_g^{\ 0}$. The corresponding orbital energies of the prior SCF calculation can be seen from figure 2.

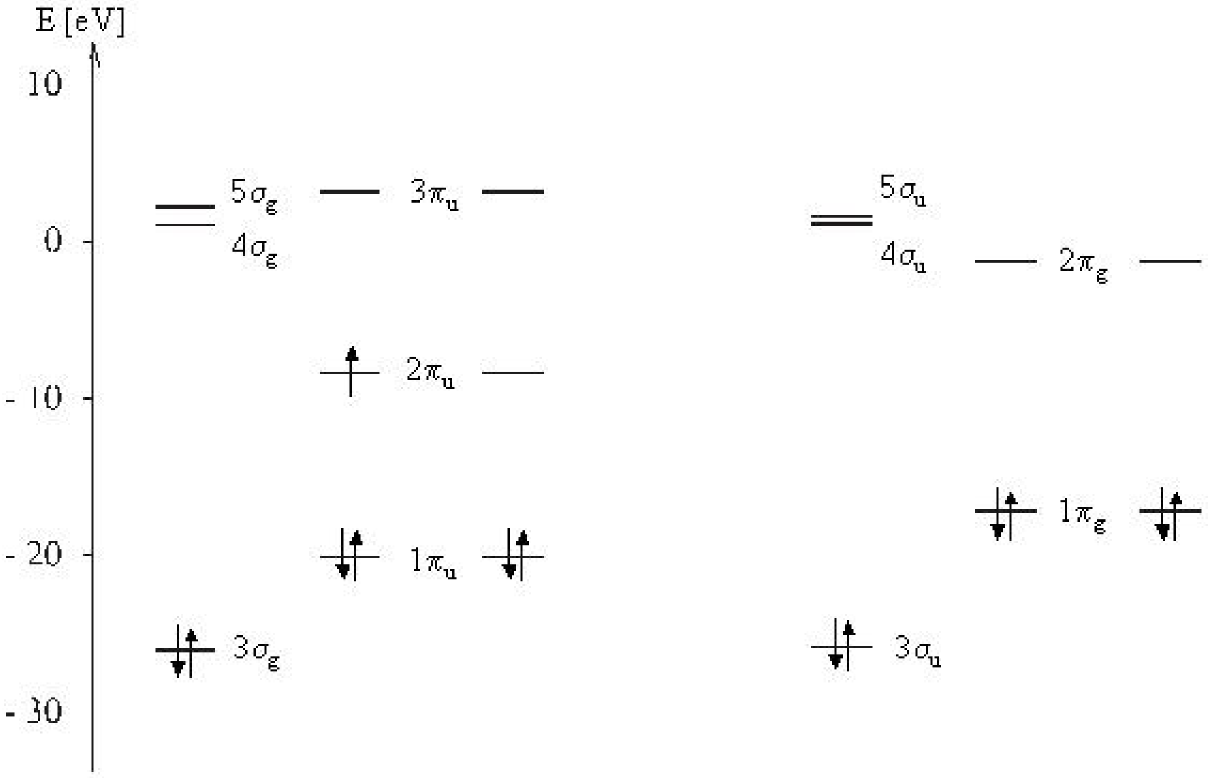

Figure 2. Schematic diagram of the molecular orbital (MO) energy spectrum of the ground state configuration of linear HC_5H^+. The values are obtained at the SCF level. Occupied MOs are marked with arrows.

Table 1. Low–lying triplet electronic states of linear HC_5H^+ (fig.1) as expected from qualitative MO–theory. The $X^2\Pi_u$ ground state configuration is $...3\sigma_g^{\ 2}\ 3\sigma_u^{\ 2}\ 1\pi_u^{\ 4}\ 1\pi_g^{\ 4}\ 2\pi_u^{\ 1}\ /2\pi_g^{\ 0}$ (valence electrons only).

Excitation	Configuration	Doublet States
–	$2\pi_u^{\ 1}$	$^2\Pi_u$
$2\pi_u \rightarrow 2\pi_g$	$2\pi_g^{\ 1}$	$^2\Pi_g$
$1\pi_g \rightarrow 2\pi_u$	$1\pi_g^{\ 3}\ 2\pi_u^{\ 2}$	$^2\Pi_g(3)$, $^2\phi_g$
$1\pi_u \rightarrow 2\pi_u$	$1\pi_u^{\ 3}\ 2\pi_u^{\ 2}$	$^2\Pi_u(3)$, $^2\phi_u$
$3\sigma_g \rightarrow 2\pi_u$	$3\sigma_g^{\ 1}\ 2\pi_u^{\ 2}$	$^2\Sigma_g^{\ +}$, $^2\Sigma_g^{\ -}$, $^2\Delta_g$
$3\sigma_u \rightarrow 2\pi_u$	$3\sigma_u^{\ 1}\ 2\pi_u^{\ 2}$	$^2\Sigma_u^{\ +}$, $^2\Sigma_u^{\ -}$, $^2\Delta_u$
$2\pi_u \rightarrow 3\pi_u$	$3\pi_u^{\ 1}$	$^2\Pi_u$
$2\pi_u \rightarrow 4\sigma_g$	$4\sigma_g^{\ 1}$	$^2\Sigma_g^{\ +}$
$2\pi_u \rightarrow 4\sigma_u$	$4\sigma_u^{\ 1}$	$^2\Sigma_u^{\ +}$
$1\pi_g \rightarrow 2\pi_g$	$1\pi_g^{\ 3}\ 2\pi_u^{\ 1}\ 2\pi_g^{\ 1}$	$^2\Pi_u(3)$, $^2\phi_u$
$1\pi_u \rightarrow 2\pi_g$	$1\pi_u^{\ 3}\ 2\pi_u^{\ 1}2\pi_g^{\ 1}$	$^2\Pi_g(3)$, $^2\phi_g$

Possible low–energy doublet electronic states are listed in Table 1 and in Table 2 we present the results for the states we actually calculated. Low–lying transitions are expected to correspond to single excitation from the occupied levels $1\pi_u$ and $1\pi_g$ (HOMO) to the singly occupied molecular orbital (SOMO) $2\pi_u$. Excitations from this $2\pi_u$ SOMO to the lowest lying virtual orbital $3\pi_u$ (LUMO) are also expected low lying. The lowest states of Σ, Δ and Γ symmetry are expected to result from $3\sigma_g \rightarrow 2\pi_u$, $2\pi_u \rightarrow 4\sigma_g$, $3\sigma_u \rightarrow 2\pi_u$ and $2\pi_u \rightarrow 4\sigma_u$ excitations. Contrary to the pure carbon clusters [9–14] double excitations are less important at low energies in HC_5H^+ and HC_7H^+.

Table 2. Calculated transition energies ΔE(eV) and oscillator strengths f from the $X^2\Pi_u$ ground state of linear HC_5H^+ (fig.1) to its low–lying electronic states and comparison with values derived from measurements. All f–values are only for one of the degenerate components. The ground state configuration of linear HC_5H^+ is $...3\sigma_g^2\ 3\sigma_u^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^1\ /2\pi_g^0$ (valence electrons only). The experimental value ΔE(exptl.) is taken from Ref. [1].

State	Excitation		ΔE	f	ΔE(exptl.)
$X^2\Pi_u$	$1\pi_g^4\ 2\pi_u^1$		0.0	–	
$1^2\Pi_g$	$1\pi_g \rightarrow 2\pi_u$		2.56	0.004	499 nm (2.47 eV) [a]
$1^2\Phi_g$	$1\pi_g \rightarrow 2\pi_u$		3.19	–	
$2^2\Pi_g$	$1\pi_g \rightarrow 2\pi_u$		3.75	0.0004	
$3^2\Pi_g$	$1\pi_g \rightarrow 2\pi_u$	$c^2 = 0.47$	3.85	0.1	
	$(2\pi_u \rightarrow 2\pi_g$	$c^2 = 0.28)$			
$1^2\Pi_u$	$1\pi_u \rightarrow 2\pi_u$		4.48	–	
$1^2\Phi_u$	$1\pi_u \rightarrow 2\pi_u$		5.09	–	
$2^2\Pi_u$	$1\pi_u \rightarrow 2\pi_u$	$c^2 = 0.36$	5.23	–	
	$(1\pi_g^2 \rightarrow 2\pi_u^2$	$c^2 = 0.17)$			
$3^2\Pi_u$	$1\pi_u \rightarrow 2\pi_u$		5.47	–	
$4^2\Pi_u$	$1\pi_g^2 \rightarrow 2\pi_u^2$		$c^2=0.31$	6.16	–
	$(1\pi_u \rightarrow 2\pi_u$	$c^2 = 0.10)$			
$4^2\Pi_g$	$1\pi_u\ 1\pi_g \rightarrow 2\pi_u^2$		7.02	0.0002	
$5^2\Pi_g$	$2\pi_u \rightarrow 2\pi_g$	$c^2 = 0.36$	7.03	2.3	
	$(1\pi_g \rightarrow 2\pi_u$	$c^2 = 0.33)$			
$1^2\Sigma_g^+$	$2\pi_u \rightarrow 4\sigma_g$		9.05	0.0002	
$1^2\Sigma_u^+$	$2\pi_u \rightarrow 4\sigma_u$		9.53	–	
$1^2\Sigma_u^-$	$3\sigma_u \rightarrow 2\pi_u$		9.70	–	
$1^2\Sigma_g^-$	$3\sigma_g \rightarrow 2\pi_u$		10.27	0.01	

[a] E[eV] = 1239,824 [nm x eV] / λ [nm].

The first dipole–allowed transition $1^2\Pi_g \leftarrow X^2\Pi_u$, which corresponds to $1\pi_g \rightarrow 2\pi_u$ excitation is calculated at 2.56 eV with an oscillator strength of f = 0.004. It is in reasonable agreement to the experimentally measured 499 nm (2.47 eV) [1]. The two dominating transitions in the electronic spectrum of linear HC_5H^+ from the $X^2\Pi_u$ ground state to $^2\Pi_g$ states show multi–reference character. Two leading configurations are found to be almost equally important judged on the basis of the squared coefficients c^2 of the wavefunction: $1\pi_g \rightarrow 2\pi_u$ (HOMO–>SOMO) and $2\pi_u \rightarrow 2\pi_g$ (SOMO–>LUMO). Both excitations result in states with $^2\Pi_g$ symmetry so that a mixing of configurations is found. These states are calculated at 3.85 eV (f = 0.1) and 7.03 eV (f = 2.3) with considerably large f–values. Furthermore a $^2\Phi_g$ and a $^2\Pi_g$ state resulting from the $1\pi_g \rightarrow 2\pi_u$ promotion are obtained at 3.19 and 3.75 eV respectively.

The excitation $1\pi_u \rightarrow 2\pi_u$ gives rise to the dipole–forbidden states computed at 4.48 eV ($^2\Pi_u$), 5.09 eV ($^2\Pi_u$), 5.23 eV ($^2\Pi_u$) and 5.65 eV ($^2\Pi_u$). The $2^2\Pi_u$ state at 5.23 eV also shows a significant multi–reference character. It is constituted from a linear combination of the $1\pi_u \rightarrow 2\pi_u$ and $1\pi_g^2 \rightarrow 2\pi_u^2$ excitations. The corresponding $4^2\Pi_u$ state to this linear–combination is found at 6.16 eV. The $4^2\Pi_g$ state is computed at a much higher transition energy around 7.02 eV. It results from the excitation $1\pi_u\ 1\pi_g \rightarrow 2\pi_u^2$ and shows an f value of 0.0004. The lowest $^2\Sigma$ states are computed above 8.4 eV. The excitations $2\pi_u \rightarrow 4\sigma_g$ and $2\pi_u \rightarrow 4\sigma_u$ result in the states $^2\Sigma_g^+$ computed at 9.1 eV and $^2\Sigma_u^+$ at 9.4 eV. The states $^2\Sigma_u^-$ and $^2\Sigma_g^-$ obtained at 9.7 and 10.3 eV respectively correspond to promotions from $3\sigma_u$ and $3\sigma_g$ to $2\pi_u$.

3.2 HC_7H^+

The electronic $X^2\Pi_g$ ground state of linear HC_7H^+ possesses the electronic configuration $...4\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^4\ 2\pi_g^1/\ 3\pi_u^0$. The corresponding orbital energy diagram from the prior SCF calculation is given in Figure 3 and possible low–energy doublet electronic states are listed in Table 3.

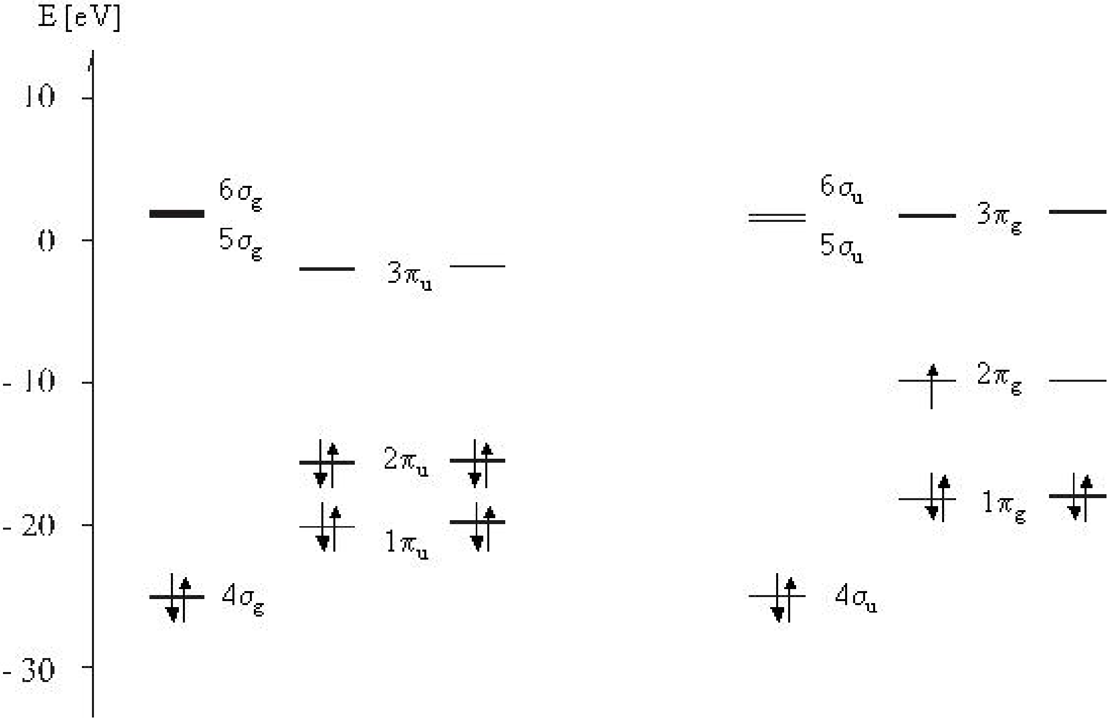

Figure 3. Schematic energy diagram of the molecular orbitals (MO) of the ground state configuration of linear HC_7H^+. The values were obtained at the SCF level. Occupied MOs are marked with arrows.

Single excitation from the occupied levels $1\pi_g$ and $2\pi_u$ (HOMO) to the singly occupied molecular orbital $2\pi_g$ (SOMO) and excitations from this $2\pi_g$ to the lowest lying virtual orbital $3\pi_u$

(LUMO) can be expected to be low lying in energy. The lowest states with Σ_g symmetry are expected to result from $4\sigma_g$ –> $2\pi_g$ and $2\pi_g$ –> $5\sigma_g$ excitations. Similarly the lowest states with $^2\Sigma_u$ symmetry can be expected to result from $4\sigma_u$ –> $2\pi_g$ and $2\pi_g$ –> $5\sigma_u$.

Table 3. Low–lying doublet electronic states of linear HC_7H^+ (Figure 1) as expected from qualitative MO–theory. The $X^2\Pi_g$ ground state configuration is $...4\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^4\ 2\pi_g^1/\ 3\pi_u^0$ (valence electrons only).

Excitation	Configuration	Dublet States
—	$2\pi_g^1$	$^2\Pi_g$
$2\pi_u \rightarrow 2\pi_g$	$2\pi_u^3\ 2\pi_g^2$	$^2\Pi_u(3)$, $^2\phi_u$
$1\pi_g \rightarrow 2\pi_g$	$1\pi_g^3\ 2\pi_g^2$	$^2\Pi_g(3)$, $^2\phi_g$
$1\pi_u \rightarrow 2\pi_g$	$1\pi_u^3\ 2\pi_g^2$	$^2\Pi_u(3)$, $^2\phi_u$
$4\sigma_g \rightarrow 2\pi_g$	$4\sigma_g^1\ 2\pi_g^2$	$^2\Sigma_g^+$, $^2\Sigma_g^-$, $^2\Delta_g$,
$4\sigma_u \rightarrow 2\pi_g$	$4\sigma_u^1\ 2\pi_g^2$	$^2\Sigma_u^+$, $^2\Sigma_u^-$, $^2\Delta_u$,
$2\pi_g \rightarrow 3\pi_u$	$3\pi_u^1$	$^2\Pi_u$
$2\pi_u \rightarrow 3\pi_u$	$2\pi_u^3\ 3\pi_u^1\ 2\pi_g^1$	$^2\Pi_g(3)$, $^2\phi_g$
$1\pi_g \rightarrow 3\pi_u$	$1\pi_g^3\ 2\pi_g^1 3\pi_u^1$	$^2\Pi_u(3)$, $^2\phi_u$
$1\pi_u \rightarrow 3\pi_u$	$1\pi_u^3\ 2\pi_g^1 3\pi_u^1$	$^2\Pi_g(3)$, $^2\phi_g$
$2\pi_g \rightarrow 5\sigma_g$	$2\pi_u^4\ 5\sigma_g^1$	$^2\Sigma_g^+$
$2\pi_g \rightarrow 5\sigma_u$	$2\pi_u^4\ 5\sigma_u^1$	$^2\Sigma_u^+$
$2\pi_u^2 \rightarrow 2\pi_g^2$	$2\pi_u^2\ 2\pi_g^2$	$^2\Pi_g(3)$, $^2\phi_g$
$2\pi_u^2 \rightarrow 2\pi_g\ 3\pi_u$	$2\pi_u^2\ 3\pi_u^1\ 2\pi_g^2$	$^2\Pi_u(12)$, $^2\phi_u(4)$

As can be seen from table 4 in conjunction with table 3 the first dipole allowed transition $1^2\Pi_u \leftarrow X^2\Pi_g$ of linear HC_7H^+ is computed at 2.34 eV (f = 0.002) in reasonable agreement to the experimentally measured wavelength of 600 nm (2.47 eV) [1]. Compared to the first dipole–allowed transition of HC_5H^+ (computed at 2.56 eV) this transition is obtained at somewhat lower energy. Given the decrease of the HOMO–LUMO gap, which was already observed for the neutral molecules [16,17], this shift is in line with our expectations. The corresponding $2\pi_u \rightarrow 2\pi_g$ excitation gives also rise to the states obtained at 2.82 eV ($1^2\Phi_u$), 3.14 eV ($2^2\Pi_u$) and at 3.17 eV ($3^2\Pi_u$).

The latter $2^2\Pi_u$ state shows multi–reference character similarly to $3^2\Pi_g$ state of HC_5H^+. Again two leading configurations resulting from $2\pi_u \rightarrow 2\pi_g$ (HOMO → SOMO) and $2\pi_g \rightarrow 3\pi_u$ (SOMO → LUMO) excitations are nearly equally important for this $3^2\Pi_u$ state and the corresponding $4^2\Pi_u$ state computed at 6.01 eV. These $^2\Pi_u$ states dominate the lower energy range of the electronic absorption spectrum of HC_7H^+. They are also obtained at lower energies compared to the corresponding transitions $3^2\Pi_g \leftarrow X^2\Pi_u$ and $5^2\Pi_g \leftarrow X^2\Pi_u$ of HC_5H^+ calculated at 3.85 eV and 7.03 eV respectively. This time in addition to the smaller HOMO–SOMO gap also the decrease of the SOMO–LUMO gap is necessary to rationalize the larger shift computed here. Both changes effectively result in a lowering of the energy difference between the HOMO and LUMO levels.

Table 4. Calculated transition energies ΔE(eV) and oscillator strengths f from the $X^2\Pi_g$ ground state of linear HC_7H^+ (fig.1) to its low–lying electronic states and comparison with values derived from measurements. All f–values are only for one of the degenerate components. The $X^2\Pi_g$ ground state configuration is $...4\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^4\ 2\pi_g^1/\ 3\pi_u^0$ (valence electrons only). The experimental value ΔE(exptl.) is adopted from Ref. [1].

State	Excitation		ΔE	f	ΔE(exptl.)
$X^2\Pi_g$	$2\pi_u^4\ 2\pi_g^1$		0.0	–	
$1^2\Pi_u$	$2\pi_u \rightarrow 2\pi_g$		2.34	0.002	600 nm (2.06 eV) [a]
$1^2\Phi_u$	$2\pi_u \rightarrow 2\pi_g$		2.82	0.00004	
$2^2\Pi_u$	$2\pi_u \rightarrow 2\pi_g$		3.14	0.001	
$3^2\Pi_u$	$2\pi_u \rightarrow 2\pi_g$	$c^2 = 0.38$	3.17	0.09	
	$(2\pi_g \rightarrow 3\pi_u$	$c^2 = 0.34)$			
$1^2\Pi_g$	$2\pi_u \rightarrow 3\pi_u$		5.13	–	
$1^2\Phi_g$	$2\pi_u \rightarrow 3\pi_u$	$c^2 = 0.34$	5.17	–	
	$(2\pi_u^2 \rightarrow 2\pi_g^2$	$c^2 = 0.23)$			
$2^2\Pi_g$	$2\pi_u^2 \rightarrow 2\pi_g^2$	$c^2 = 0.42$	5.49	–	
	$(2\pi_u \rightarrow 3\pi_u$	$c^2 = 0.11)$			
$4^2\Pi_u$	$2\pi_g \rightarrow 3\pi_u$	$c^2 = 0.32$	6.01	3.4	
	$(2\pi_u \rightarrow 2\pi_g$	$c^2 = 0.16)$			
$3^2\Pi_g$	$2\pi_u \rightarrow 3\pi_u$		6.13	–	
$4^2\Pi_g$	$2\pi_u \rightarrow 3\pi_u$		6.16	–	
$5^2\Pi_u$	$2\pi_u^2 \rightarrow 2\pi_g\ 3\pi_u$		8.07	0.005	
	$2\pi_g \rightarrow 3\pi_u$				
$1^2\Sigma_u^+$	$2\pi_g \rightarrow 5\sigma_u$		9.48	0.0004	
$1^2\Sigma_g^+$	$2\pi_g \rightarrow 5\sigma_g$		9.54	–	
$1^2\Sigma_g^-$	$4\sigma_g \rightarrow 2\pi_g$		10.08	–	
$1^2\Sigma_u^-$	$4\sigma_u \rightarrow 2\pi_g$		10.10	0.009	

[a] E[eV] = 1239,824 [nm x eV] / λ [nm].

Transitions to states originating from the excitation $2\pi_u \rightarrow 3\pi_u$ are dipole–forbidden. They are computed at 5.13 eV ($1^2\Pi_g$), 5.17 eV ($1^2\Phi_g$), 6.13 eV ($3^2\Pi_g$) and around 6.16 eV ($4^2\Pi_g$). The $2^2\Phi_g$ state obtained at 5.17 eV corresponds to a linear–combination of the $2\pi_u \rightarrow 3\pi_u$ and $2\pi_u^2 \rightarrow 2\pi_g^2$ excitations, to which the corresponding $4^2\Pi_g$ state is calculated at 5.49 eV. The transition $5^2\Pi_u \leftarrow X^2\Pi_g$ obtained at 8.07 eV belongs to the excitation $1\pi_u\ 1\pi_g \rightarrow 2\pi_u^2$. It is calculated with a sizeable oscillator strength of f = 0.005 probably caused by a contribution from $2\pi_g \rightarrow 3\pi_u$ excitation. The lowest $^2\Sigma$ states are computed around 9.5 eV ($^2\Sigma_u^+$ and $^2\Sigma_g^+$) and at 10.1 eV ($^2\Sigma_g^-$ and $^2\Sigma_u^-$).

4 CONCLUSIONS

Multi–reference configuration interaction calculations (MR–CI) are performed to obtain low–lying excited states and transition probabilities for HC_5H^+ and HC_7H^+. Both clusters possess a ground state of Π symmetry, so that low lying transitions are of Π or Φ symmetry, whereas Σ, Δ and Γ states are computed at higher energies (above 9 eV). The lowest dipole–allowed transitions are computed at 2.56 eV (f = 0.004, HC_5H^+) and 2.34 eV (f = 0.002, HC_7H^+) in reasonable agreement with experimental work [1] of 499 nm (2.47 eV, HC_5H^+) and 600 nm (2.06 eV, HC_7H^+).

Several transitions to higher $^2\Pi$ states are computed with relatively large oscillator strength. The electronic spectrum of HC_5H^+ is dominated by transitions calculated at 3.85 eV ($3^2\Pi_g \leftarrow X^2\Pi_u$) and

7.03 eV ($4^2\Pi_g \leftarrow X^2\Pi_u$) with f values of 0.1 and 2.3 respectively. The corresponding states of HC_7H^+ are predicted at 3.17 eV ($3^2\Pi_u \leftarrow X^2\Pi_g$, f = 0.09) and 6.01 eV ($4^2\Pi_u \leftarrow X^2\Pi_g$, f = 3.4). In both molecules the energy difference between SOMO and LUMO is similar to the energy difference between HOMO and SOMO. The two electronic configurations resulting from these excitations are found to be almost equally important for the description of the two corresponding states, which therefore show multi–reference character. The lowering of these transition energies on increase of chain–length is in line with a smaller HOMO–SOMO and SOMO–LUMO gap. These results are also in line with our previous studies on the neutral molecules HC_5H and HC_7H [16,17] and with what was expected from the experiment [1].

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