

# Electronic Spectra of SC<sub>n</sub>H Radicals (*n* = 2–4): An ab Initio Study

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The MCSCF and MRCI methods have been used to study the electronic spectra of SC<sub>n</sub>H radicals for *n* = 2–4. Vertical excitation energies and oscillator strengths have been computed for a number of states. The lowest-lying excited doublet states are due to an excitation from the highest inner-valence  $\pi$  orbital to the HOMO, which is of  $\pi$  type. The corresponding vertical excitation energies are compared to the experimental results. We encountered very intense transitions to high-lying  ${}^2\Pi$  terms [ $4^2\Pi \leftarrow X^2\Pi$  (*n* = 2),  $(6,7)^2\Pi \leftarrow X^2\Pi$  (*n* = 3), and  $(7,8,9)^2\Pi \leftarrow X^2\Pi$  (*n* = 4)], as well as moderately intense transitions to lower-lying terms [ $1^2\Pi \leftarrow X^2\Pi$ ,  $1^2\Sigma^+ \leftarrow X^2\Pi$  (*n* = 2),  $(2,3,4)^2\Pi \leftarrow X^2\Pi$  (*n* = 3), and  $1^2\Pi \leftarrow X^2\Pi$  (*n* = 4)]. These intense transitions are frequent in cumulenenic carbon chains but have not been registered so far in the present systems. The  $X^2\Pi$ – $1^4\Pi$  vertical energy gaps are (in electronvolts) 4.94 (*n* = 2), 2.87 (*n* = 3), and 3.71 (*n* = 4); the adiabatic electronic energy gaps should be about 1.95, 0.42, and 0.93 eV smaller, respectively.

## 1. Introduction

The sulfur-bearing carbon chains SC<sub>n</sub>H<sub>m</sub> (*m* = 0, 1) are cumulenes of astrophysical importance<sup>1</sup> that have been the subject of experimental and theoretical studies. The SC<sub>n</sub> chains have been studied by the groups of Lovas,<sup>2</sup> Oshima,<sup>3</sup> Hirahara,<sup>4</sup> and Kasai,<sup>5</sup> who recorded the Fourier transform microwave spectra (FTMW) for *n* = 2, 3, and 5 using Fabry–Perot cavities. Tang and Saito<sup>6</sup> performed a submillimeter-wave study of SC<sub>3</sub>. The infrared absorption spectra of the SC<sub>n</sub> systems (and also of SC<sub>n</sub>S) for *n* = 1–5 have been recorded by Vala and co-workers,<sup>7</sup> who generated these clusters by pulsed laser ablation of carbon/sulfur mixtures. C<sub>3</sub>S has also been studied by infrared absorption spectroscopy in Ar matrixes by Maier and co-workers.<sup>8</sup> Some recent theoretical studies have also focused on the geometries and some spectroscopic properties of SC<sub>n</sub> chains<sup>9,7,10,11</sup> and of the excited states of SC<sub>3</sub>.<sup>12</sup>

SC<sub>n</sub>H radicals have been studied experimentally. In the case of SC<sub>2</sub>H, the electronic and rotational spectra have been the subject of intense experimental and theoretical work. The electronic absorption spectrum was recorded by Krishnamachari and Ramsay in the region between 3770 and 4170 cm<sup>−1</sup> and assigned to a  ${}^2\Pi$ – ${}^2\Pi$  transition.<sup>13</sup> Coquart recorded the emission spectrum in the region of 3900–4500 cm<sup>−1</sup> and also attributed it to a  ${}^2\Pi_i$ – ${}^2\Pi_i$  transition.<sup>14</sup> In addition, laser-induced fluorescence spectra were obtained by Clouthier et al.<sup>15</sup> and by Endo et al.<sup>16</sup> The rotational spectrum was obtained by Vrtilek et al.<sup>17</sup> Tang and Saito performed a study of the Renner–Teller interaction.<sup>18</sup> Yamamoto et al. conducted further spectroscopic studies to determine the hyperfine interaction constants of SC<sub>2</sub>H and SC<sub>2</sub>D.<sup>19</sup> These radicals have also been the subject of recent theoretical studies.<sup>20–25</sup> Szalay studied the  $A^2\Pi_{1/2}$ – $X^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$ – $X^2\Pi_{3/2}$  transitions by means of a equation of motion coupled-cluster method, taking into account the Renner–Teller effect<sup>20</sup> and the spin–orbit splittings. Peyerimhoff and co-workers performed a detailed study of the vibronic levels of the ground state in which they used a variational method to

deal with the Renner–Teller interaction and include also the spin–orbit coupling.<sup>22</sup> Peric et al. studied  $A^2\Pi$ – $X^2\Pi$  transitions by means of extensive ab initio computations including spin–orbit and vibronic structures.<sup>25</sup> Li and Iwata studied the equilibrium geometries and energy profiles for three states ( $X^2\Pi$ ,  $A^2\Pi$ , and  $B^2\Sigma^+$ ).<sup>21</sup> The present author has studied the potential energy surface (PES) of the lowest doublet and quartet states to deal with the dynamics of the S + C<sub>2</sub>H reaction.<sup>23</sup>

The rotational spectrum of the SC<sub>3</sub>H radical has been recorded by McCarthy and co-workers<sup>26</sup> and by Endo and co-workers.<sup>27</sup> Both experimental studies concluded that SC<sub>3</sub>H is a linear molecule with a  ${}^2\Pi_{1/2}$  ground electronic level despite the facts that the isovalent HC<sub>3</sub>O radical is nonlinear<sup>28</sup> and that ab initio computations pointed to a bent conformation as the equilibrium structure.<sup>26</sup> Inclusion of basis set extrapolations and spin–orbit corrections in the ab initio computations led to agreement between theory and experiment.<sup>29</sup> A relatively detailed study of the potential energy surfaces of the lowest doublet and quartet states has been performed, as well as trajectory studies of the dynamics of the S + (*l* – *c*)C<sub>3</sub>H reaction.<sup>30,31</sup> The microwave spectrum of SC<sub>4</sub>H has also been obtained in a Fabry–Perot cavity by Hirahara, Oshima, and Endo.<sup>4</sup> It is a linear system with a  ${}^2\Pi_{3/2}$  electronic ground state. Endo and co-workers recently recorded the vibronic bands of a  ${}^2\Pi_{3/2}$ – ${}^2\Pi_{3/2}$  transition in their laser-induced fluorescence spectra of the SC<sub>4</sub>H and SC<sub>4</sub>D radicals in a supersonic jet.<sup>32</sup> On the basis of an ab initio calculation, they concluded that the excited electronic state arises from the first excited  ${}^2\Pi$  term.

Several sulfur polycarbon hydride ions, SC<sub>n</sub>H<sup>+</sup>, have been generated by laser ablation of sulfur–carbon mixtures and studied by crossed-beam tandem time-of-flight mass spectroscopy, together with the corresponding SC<sub>n</sub>H<sup>−</sup> systems.<sup>33</sup> Some SC<sub>n</sub>H<sup>+</sup> and SC<sub>n</sub>H systems (*n* = 2–6) have been identified in the electron impact mass spectrum of benzothiazole.<sup>34</sup>

The aim of the present work is to complete the knowledge of SC<sub>n</sub>H systems (*n* = 2–4) by providing relatively detailed predictions of their electronic spectra. We are not aware of any experimental spectrum for SC<sub>3</sub>H. The electronic spectra of

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carbon-chain cumulenes are receiving considerable attention, as these species might be responsible for the diffuse interstellar bands.<sup>35</sup>

## 2. Computational Methods

The molecular equilibrium geometries used in this paper were determined with the B3LYP<sup>36</sup> method in combination with the 6-311++G\*\* basis set.<sup>37,38</sup> This method has already been used to obtain very good geometrical parameters for sulfur-bearing cumulenes. We computed vertical excitation energies and oscillator strengths by means of the MCSCF (multiconfiguration self-consistent field)<sup>39,40</sup> and MRCI (multireference configuration interaction)<sup>41,42</sup> methods implemented in the MOLPRO package.<sup>43</sup> The MCSCF method was employed to obtain the orbitals for the MRCI computations and, in some cases, to compute transition dipole matrix elements. The MCSCF wave functions were always of the CASSCF type, and the orbitals employed in the MRCI computations were natural orbitals. We employed the aug-cc-pVDZ and aug-cc-pVTZ basis sets.<sup>44,45</sup> In both the MCSCF and MRCI computations, we used the  $C_{2v}$  point group. This choice implies that  $\Pi$  and  $\Phi$  states appear as  $B_1$  or  $B_2$  states, whereas  $\Sigma$  and  $\Delta$  states appear as  $A_1$  or  $A_2$  states. The MCSCF computations were of the state-averaged type; we always gave equal weights to all of the  $C_{2v}$  states included in the average. The MRCI computations included singles and doubles; the energies utilized throughout this work include contributions from higher excitations through the correction of Davidson.

We computed a number of excited doublet states and also some of the lower-lying quartet states for each molecule at the MRCI/aug-cc-pVDZ level. The doublet and quartet states were always computed independently; the energy difference between the *lowest* doublet and quartet states was determined in a separate computation with the aug-cc-pVTZ basis set. The details of the computations of each species are described in the next section.

## 3. Results and Discussion

The  $SC_nH$  species ( $n = 2-4$ ) present  $^2\Pi$  ground states arising from the  $\cdots 9\sigma^2 2\pi^4 3\pi^3$  ( $SC_2H$ ),  $\cdots 11\sigma^2 3\pi^4 4\pi^1$  ( $SC_3H$ ), and  $\cdots 13\sigma^2 3\pi^4 4\pi^3$  ( $SC_4H$ ) electron configurations, respectively. The vertical excitation energies, oscillator strengths, and most important orbital excitations of each transition are reported in Tables 1 ( $SC_2H$ ), 2 ( $SC_3H$ ), and 3 ( $SC_4H$ ). The orbital energies are presented in Figure 1.

**3.1.  $SC_2H$ .** For the doublet states, we performed an MCSCF computation using as the active space  $[8\sigma-11\sigma, 2\pi-4\pi]$  for 11 electrons. The MCSCF wave function was optimized for a mixture of the lowest  $10^2B_1$  and  $^2B_2$  states, as well as the lowest  $4^2A_1$  and  $3^2A_2$  states. With the resulting orbitals, we performed MRCI computations for  $10^2B_1$ ,  $4^2A_1$ , and  $4^2A_2$  states. These MRCI computations have a common active space:  $[9\sigma-10\sigma, 2\pi-4\pi]$ . In the case of the quartet states, we employed the orbitals of a MCSCF computation with an active space of  $[7\sigma-12\sigma, 2\pi-4\pi]$  for 13 electrons, where the wave function is a mixture of five  $^4B_1$  and  $^4B_2$  states, two  $^4A_1$ , and four  $^4A_2$  states. In the MRCI computations, we used  $[9\sigma-11\sigma, 2\pi-4\pi]$  as the active space. The relative energies of the quartet states with respect to the ground state were determined by means of two MRCI/aug-cc-pVTZ computations for the lowest quartet state ( $1^4\Pi$ ) and the ground state ( $X^2\Pi$ ). These MRCI computations employed  $[9\sigma-11\sigma, 2\pi-4\pi]$  as the active space. The orbitals were obtained by a state-averaged MCSCF computation with the same active space, where both  $C_{2v}$  components of the

**TABLE 1: Vertical Excitation Energies and Oscillator Strengths of  $SC_2H$**

state	excitation energy (eV)	transition(s) <sup>a</sup>	$f^{b,c}$
$X^2\Pi$	0		
$1^2\Pi$	3.31	$2\pi \rightarrow 3\pi$	0.0159
$1^2\Sigma^+$	5.11	$9\sigma \rightarrow 3\pi$	0.2537
$2^2\Pi$	5.32	$3\pi \rightarrow 4\pi$	0.0021
$1^2\Phi$	5.92	$3\pi \rightarrow 4\pi$	0.0000
$3^2\Pi$	6.58	$3\pi \rightarrow 4\pi$	0.0004
$1^2\Sigma^-$	7.05	$3\pi \rightarrow 10\sigma$	0.0537
$1^2\Delta$	7.38	$3\pi \rightarrow 10\sigma, 2\pi \rightarrow 10\sigma$	0.0177
$4^2\Pi$	7.45	$3\pi \rightarrow 4\pi, 2\pi \rightarrow 3\pi, 2\pi \rightarrow 4\pi, 9\sigma \rightarrow 10\sigma$	0.7564
$5^2\Pi$	7.61	$2\pi \rightarrow 4\pi$	0.0014
$2^2\Sigma^+$	7.80	$3\pi \rightarrow 10\sigma, 2\pi \rightarrow 10\sigma$	0.0158
$2^2\Phi$	8.62	$2\pi \rightarrow 4\pi$	0.0000
$6^2\Pi$	8.71	$2\pi \rightarrow 4\pi$	0.0004
$2^2\Sigma^-$	9.39	$2\pi \rightarrow 10\sigma$	0.0047
$7^2\Pi$	9.52	$2\pi \rightarrow 4\pi, 3\pi^2 \rightarrow 4\pi^2$	0.0017
$1^4\Pi$	4.94	$3\pi \rightarrow 4\pi$	
$1^4\Sigma^-$	5.72	$3\pi \rightarrow 10\sigma$	0.0023
$2^4\Sigma^-$	6.39	$3\pi \rightarrow 11\sigma$	0.0003
$2^4\Pi$	6.82	$2\pi \rightarrow 4\pi$	0.0002
$1^4\Phi$	7.67	$2\pi \rightarrow 4\pi$	0.0000
$3^4\Pi$	8.32	$2\pi \rightarrow 4\pi$	0.0000
$1^4\Delta$	8.70	$2\pi \rightarrow 10\sigma$	0.0002
$1^4\Sigma^+$	8.81	$2\pi \rightarrow 10\sigma$	0.0000
$4^4\Pi$	8.81	$2\pi \rightarrow 4\pi, 3\pi^2 \rightarrow 4\pi^2, (2\pi \rightarrow 3\pi, 2\pi \rightarrow 4\pi)$	0.0633

<sup>a</sup> In the case of the quartet states, the transitions refer to the ground state,  $X^2\Pi$ . <sup>b</sup> In the case of the quartet states, the oscillator strengths are computed with respect to the  $1^4\Pi$  state. In all cases, they correspond to one  $C_{2v}$  component of the degenerate states. <sup>c</sup> Computed using MRCISD transition moments and relative energies that include Davidson's corrections.

**TABLE 2: Vertical Excitation Energies and Oscillator Strengths of  $SC_3H$**

state	excitation energy (eV)	transition(s) <sup>a</sup>	$f^{b,c}$
$X^2\Pi$	0.00		
$1^2\Pi$	1.42	$3\pi \rightarrow 4\pi$	0.0004
$1^2\Phi$	1.97	$3\pi \rightarrow 4\pi$	0.0000
$2^2\Pi$	2.49	$3\pi \rightarrow 4\pi$	0.0029
$3^2\Pi$	2.92	$4\pi \rightarrow 5\pi, 3\pi \rightarrow 4\pi, 2\pi \rightarrow 4\pi$	0.0348
$4^2\Pi$	3.62	$2\pi \rightarrow 4\pi, 4\pi \rightarrow 5\pi$	0.0288
$2^2\Phi$	4.08	$2\pi \rightarrow 4\pi$	0.0000
$1^2\Sigma^+$	4.10	$4\pi \rightarrow 12\sigma$	0.0024
$5^2\Pi$	4.60	$2\pi \rightarrow 4\pi$	0.0030
$6^2\Pi$	4.70	$2\pi \rightarrow 4\pi, 3\pi^2 \rightarrow 4\pi^2$	0.0956
$7^2\Pi$	5.78	$3\pi^2 \rightarrow 4\pi^2, 3\pi \rightarrow 5\pi, (2\pi \rightarrow 4\pi, 3\pi \rightarrow 4\pi)$	0.0225
$2^2\Sigma^+$	6.92	$3\pi \rightarrow 12\sigma$	0.0013
$1^2\Delta$	7.43	$3\pi \rightarrow 12\sigma$	0.0006
$1^4\Pi$	2.87	$3\pi \rightarrow 4\pi$	
$2^4\Pi$	5.07	$2\pi \rightarrow 4\pi$	0.0109
$1^4\Sigma^+$	6.83	$3\pi \rightarrow 12\sigma$	0.0014
$3^4\Pi$	7.06	$3\pi^2 \rightarrow 4\pi^2, 3\pi \rightarrow 5\pi$	0.0216
$1^4\Delta$	7.40	$3\pi \rightarrow 12\sigma$	0.0015
$1^4\Sigma^-$	7.72	$3\pi \rightarrow 12\sigma$	0.0015
$1^4\Phi$	8.30	$(3\pi \rightarrow 4\pi, 2\pi \rightarrow 4\pi), 3\pi \rightarrow 5\pi$	0.0000
$2^4\Delta$	9.50	$2\pi \rightarrow 12\sigma, (3\pi \rightarrow 12\sigma, 3\pi \rightarrow 4\pi)$	0.0000
$2^4\Sigma^-$	9.76	$2\pi \rightarrow 12\sigma, (3\pi \rightarrow 12\sigma, 3\pi \rightarrow 4\pi)$	0.0000

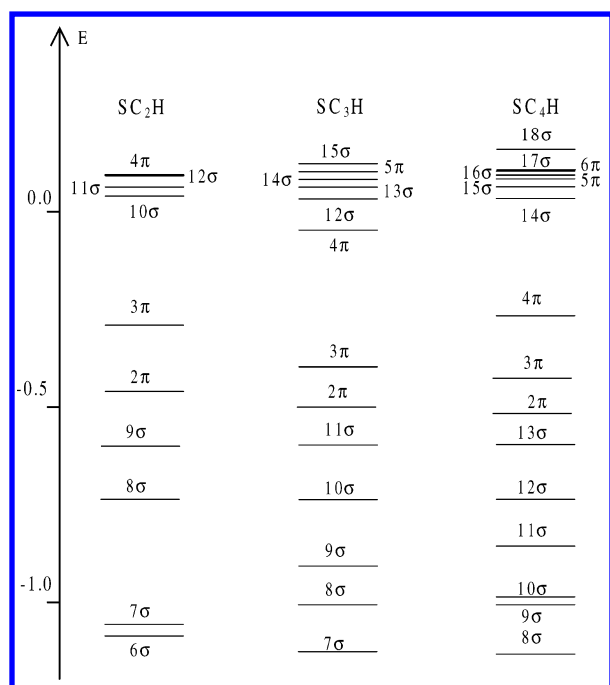
<sup>a</sup> In the case of the quartet states, the transitions also refer to the ground state,  $X^2\Pi$ . <sup>b</sup> In the case of the quartet states, the oscillator strengths are computed with respect to the  $1^4\Pi$  state. In all cases, they correspond to one  $C_{2v}$  component of the degenerate states. <sup>c</sup> In the case of the  $\Pi$  and  $\sigma$  states, the oscillator strengths are computed at the MRCISD level, whereas in the case of the  $\Sigma$  and  $\Delta$  states, MRCISD energy and MCSCF transition dipole matrix elements are employed. The energy differences include Davidson's corrections.

$1^4\Pi$  and  $X^2\Pi$  terms were included in the average. The energies of the rest of the quartet states were computed by adding their

**TABLE 3: Vertical Excitation Energies and Oscillator Strengths of SC<sub>4</sub>H**

state	excitation energy (eV)	transition(s) <sup>a</sup>	<i>f</i> <sup>b,c</sup>
X <sup>2</sup> Π	0		
1 <sup>2</sup> Π	2.72	3π → 4π	0.0298
2 <sup>2</sup> Π	3.94	4π → 5π	0.0024
1 <sup>2</sup> Φ	4.34	4π → 5π	0.0000
3 <sup>2</sup> Π	4.54	2π → 4π	0.0000
4 <sup>2</sup> Π	4.83	4π → 5π	0.0012
5 <sup>2</sup> Π	5.95	3π → 5π	0.0000
1 <sup>2</sup> Σ <sup>+</sup>	6.06	13σ → 4π	0.0194
1 <sup>2</sup> Σ <sup>-</sup>	6.21	4π → 14σ, 4π → 15σ	0.0032
1 <sup>2</sup> Δ	6.57	4π → 14σ, 4π → 15σ	0.0893
2 <sup>2</sup> Φ	6.67	3π → 5π	0.0000
2 <sup>2</sup> Σ <sup>+</sup>	6.87	4π → 14σ, 4π → 15σ	0.0883
2 <sup>2</sup> Δ	7.22	4π → 15σ, 4π → 14σ	0.0003
3 <sup>2</sup> Σ <sup>+</sup>	7.49	4π → 15σ, 4π → 14σ	0.0000
3 <sup>2</sup> Δ	8.70	3π → 14σ	0.0050
1 <sup>4</sup> Π	3.71	4π → 5π	0.0000
2 <sup>4</sup> Π	5.39	3π → 5π	0.0001
1 <sup>2</sup> Φ	6.01	3π → 5π	0.0000
1 <sup>4</sup> Σ <sup>-</sup>	6.23	4π → 14σ	0.0001
3 <sup>4</sup> Π	6.49	3π → 5π	0.0000
2 <sup>4</sup> Σ <sup>-</sup>	7.75	4π → 15σ	0.0025
1 <sup>4</sup> Δ	8.86	3π → 14σ	0.0001

<sup>a</sup> In the case of the quartet states, the transitions also refer to the ground state, X<sup>2</sup>Π. <sup>b</sup> In the case of the quartet states, the oscillator strengths are computed with respect to the 1<sup>4</sup>Π state. In all cases, they correspond to one C<sub>2v</sub> component of the degenerate states. <sup>c</sup> In the case of the Π and σ states, the oscillator strengths are computed at the MRCISD level, whereas in the case of the Σ and Δ states, MRCISD energy differences and MCSCF transition dipole matrix elements are employed. The energy differences include Davidson's corrections.



**Figure 1.** Energies of the valence orbitals of the SC<sub>n</sub>H radicals (au) computed at the SCF/aug-cc-pVDZ level for the ground state, X<sup>2</sup>Π. The electronic configurations of the ground state are ...9σ<sup>2</sup>2π<sup>4</sup>3π<sup>3</sup> (*n* = 2), ...11σ<sup>2</sup>2π<sup>4</sup>3π<sup>4</sup>4π<sup>1</sup> (*n* = 3), and ...13σ<sup>2</sup>2π<sup>4</sup>3π<sup>4</sup>4π<sup>3</sup> (*n* = 4).

MRCI/aug-cc-pVDZ energy differences with respect to the 1<sup>4</sup>Π state to the MRCI/aug-cc-pVTZ 1<sup>4</sup>Π–X<sup>2</sup>Π energy difference.

The first excited state is 1<sup>2</sup>Π, which corresponds not to a HOMO–LUMO excitation (3π → 10σ) but to a 2π → 3π excitation (note that 2π is the inner-valence π orbital). This transition also has the largest oscillator strength among the low-

energy transitions. It is the state studied by Krishnamachari and Ramsay<sup>13</sup> and Coquart.<sup>14</sup> It is noteworthy that our vertical energy is about 0.3 eV higher than the experimental values of the 0–0 transition, 3.01 eV (A<sup>2</sup>Π<sub>3/2</sub> ← X<sup>2</sup>Π<sub>3/2</sub>) and 2.99 eV (A<sup>2</sup>Π<sub>1/2</sub> ← X<sup>2</sup>Π<sub>1/2</sub>).<sup>14</sup> The origin of this discrepancy is not the vibrational energy difference, which would decrease the electronic energy gap by less than 0.03 eV.<sup>25</sup> The present value is clearly higher than the MRCI/cc-pVTZ result of Li and Iwata (2.67 eV) for Te,<sup>21</sup> whereas it is much lower than Szalay's equation of motion coupled-cluster results for the vertical energy; the value computed with the PVQZ basis set is 3.54 eV.<sup>20</sup> We performed specific MRCI computations for these two states using the equilibrium geometries given by Peric et al.<sup>22,25</sup> for each state and the active space described above. The resulting Te values are 3.02 eV with the aug-cc-pVTZ basis and 3.06 eV with the cc-pVTZ basis set; both values are in good agreement with the experimental 0–0 values and the Te value determined by Peric et al. (3.09 eV).<sup>25</sup>

The 2<sup>2</sup>Π ← X<sup>2</sup>Π transition (5.32 eV) arises from a 3π → 4π excitation; the electron configuration of 2<sup>2</sup>Π is ...9σ<sup>2</sup>3π<sup>2</sup>4π<sup>1</sup>. There are two more transitions that arise neatly from the 3π → 4π excitation, which lead to the 1<sup>2</sup>Φ and 3<sup>2</sup>Π states. The 9σ → 3π excitation leads to the 1<sup>2</sup>Σ<sup>+</sup> state, which lies even lower than the 2<sup>2</sup>Π state; the corresponding transition should be very intense. The HOMO–LUMO excitation (3π → 10σ) is the most important in the case of the 1<sup>2</sup>Σ<sup>-</sup>, 1<sup>2</sup>Δ, and 2<sup>2</sup>Σ<sup>+</sup> states. The 2π → 4π excitation leads to the 5<sup>2</sup>Π state and to the next states of the doublet Φ–Π systems. The very high oscillator strength of the 4<sup>2</sup>Π ← X<sup>2</sup>Π transition is noteworthy. It is essentially an N–V transition that arises from multiple orbital excitations, including 9σ → 10σ. It is not unusual for N–V transitions to have large intensities.<sup>46</sup> The 2π → 10σ excitation leads to the very high-lying 2<sup>2</sup>Σ<sup>-</sup> state.

The first quartet state 1<sup>4</sup>Π is due to a 3π → 4π promotion from the ground state (...9σ<sup>2</sup>2π<sup>4</sup>3π<sup>2</sup>4π<sup>1</sup>) and lies close to the second excited doublet state, 2<sup>2</sup>Π, which also arises from this excitation. The next quartet states come from the 4π → 10σ and 4π → 11σ excitations from the 1<sup>4</sup>Π state; note that promotion to the 11σ orbital is not a relevant excitation in the case of the doublet states. The 2π → 3π excitation from the 1<sup>4</sup>Π state gives rise to the 2<sup>4</sup>Π, 1<sup>4</sup>Φ, and 3<sup>4</sup>Π terms. The high-lying 1<sup>4</sup>Δ and 1<sup>4</sup>Σ<sup>+</sup> states, which are very close in energy, arise from the 2π → 10σ promotion from the ground state or from a two-electron excitation from 1<sup>4</sup>Π (4π → 10σ, 2π → 3π). The 4<sup>4</sup>Π ← 1<sup>4</sup>Π transition arises mostly from a 2π → 3π excitation from the 1<sup>4</sup>Π state, even though many electron configurations contribute significantly to the 4<sup>4</sup>Π state. It must be noted that the optimized geometry of the lowest quartet state of the SC<sub>2</sub>H chain is far from linear (∠SC<sub>1</sub>C<sub>2</sub> = 118.1°, ∠C<sub>1</sub>C<sub>2</sub>H = 133.2° at the B3LYP/6-311G\*\* level). This effect should bring the energy gap between the lowest quartet and doublet states to a value about 1.95 eV lower than the vertical energy gap. The oscillator strengths of the quartet states given in Table 1 should be viewed as a very gross approximation in this case; they are provided for completeness.

**3.2. SC<sub>3</sub>H.** In this case, the orbitals employed in the MRCI computations of the doublet states were obtained in a MCSCF computation with [11σ–13σ, 2π–5π] as the active space for 11 electrons. The wave function of this MCSCF computation is an average of 10 <sup>2</sup>B<sub>1</sub> and <sup>2</sup>B<sub>2</sub> terms, 3 <sup>2</sup>A<sub>1</sub> terms, and 1 <sup>2</sup>A<sub>2</sub> term. The MRCI computations of the doublet states feature the [11σ–13σ, 3π–4π] active space for the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>A<sub>2</sub> terms (which give <sup>2</sup>Σ<sup>(+)</sup> and <sup>2</sup>Δ states) and the [2π–5π] active space for the <sup>2</sup>B<sub>1</sub> terms (<sup>2</sup>Π and <sup>2</sup>Φ states). The relative energies of



the  ${}^2A_1$  and  ${}^2A_2$  terms with respect to the ground state ( $X^2\Pi$ ) were determined with the help of independent MRCI/aug-cc-pVTZ computations of the lowest states of the  ${}^2A_1$  and  ${}^2A_2$  symmetries, as well as the ground state. In these MRCI/aug-cc-pVTZ computations, the orbitals of an MCSCF calculation with the  $[12\sigma, 2\pi-4\pi]$  active space were used. The wave function of this MCSCF/aug-cc-pVTZ computation is an average over the lowest doublet and quartet terms of each symmetry species of the  $C_{2v}$  point group.

In the case of the quartet states, the MCSCF/aug-cc-pVDZ computation was performed with  $[11\sigma-14\sigma, 2\pi-5\pi]$  as the active space, the wave function being an average of six  ${}^4B_1$  and  ${}^4B_2$  states and four  ${}^4A_1$  and  ${}^4A_2$  states. The MRCI computations of the quartet terms used  $[12\sigma, 2\pi-5\pi]$  as the active space. The relative energies of the quartets were determined with the help of independent MRCI/aug-cc-pVTZ computations for the lowest state of each  $C_{2v}$  symmetry species. The active space and orbitals were the same as for the  ${}^2A_1$  and  ${}^2A_2$  computations described above.

The ground state of  $SC_3H$  is  $X^2\Pi$ , in which  $\cdots 11\sigma^2 3\pi^4 4\pi^1$  is the dominant electron configuration. As in the case of  $SC_2H$ , the lowest-energy transition,  $1^2\Pi \leftarrow X^2\Pi$ , corresponds to an excitation from the highest fully occupied  $\pi$  orbital to the HOMO ( $3\pi \rightarrow 4\pi$  in  $SC_3H$ ), which is of  $\pi$  type in both cases. There is a difference, however, because in  $SC_3H$ , there are three low-lying states arising neatly from the  $3\pi \rightarrow 4\pi$  promotion. It is noteworthy that only the third transition,  $2^2\Pi \leftarrow X^2\Pi$ , has a relatively large oscillator strength with a vertical excitation energy (2.49 eV) that is not far from that of the  $1^2\Pi \leftarrow X^2\Pi$  transition of  $SC_2H$  (3.31 eV). The transitions to the  $3^2\Pi$  and  $4^2\Pi$  states should have large intensities. They cannot be attributed to a single electron promotion, but the  $4\pi \rightarrow 5\pi$  ( $3^2\Pi$ ) and  $2\pi \rightarrow 4\pi$  ( $4^2\Pi$ ) excitations carry the largest weights. The first transition due to the HOMO–LUMO excitation ( $4\pi \rightarrow 12\sigma$ ) leads to the  $1^2\Sigma^+$  state, which lies at 4.10 eV. This value is much lower than that of the  $1^2\Sigma^-$  state of  $SC_2H$ , which also arises from the HOMO–LUMO excitation. The  $5^2\Pi$  and  $6^2\Pi$  states arise from a  $2\pi \rightarrow 4\pi$  excitation, but it is the latter, which carries a significant weight of other promotions such as  $3\pi^2 \rightarrow 4\pi^2$ , that is the one with largest oscillator strength. The  $7^2\Pi$  state also arises from multiple excitations; the corresponding transition should also be quite intense. The high-lying  $2^2\Sigma^+$  and  $1^2\Delta$  states originate in an electron promotion from the inner-valence  $3\pi$  orbital to the LUMO ( $12\sigma$ ).

The lowest quartet state is  $1^4\Pi$ , as in the case of  $SC_2H$ ; its electron configuration is  $\cdots 11\sigma^2 3\pi^3 4\pi^2$ , so it results from a  $3\pi \rightarrow 4\pi$  promotion from the ground state. It is much lower in energy than the lowest quartet of  $SC_2H$  (4.94 eV), which involves a promotion from the HOMO ( $3\pi$ ) to the virtual  $4\pi$  orbital. The next quartet state ( $2^4\Pi$ ) can be reached by means of a  $2\pi \rightarrow 3\pi$  excitation from the  $1^4\Pi$  state; this transition probably has a large intensity. The first quartet state arising from a  $\pi \rightarrow \sigma$  excitation is  $1^4\Sigma^+$ , which involves a  $4\pi \rightarrow 12\sigma$  promotion from the  $1^4\Pi$  state. The  $1^4\Delta$  and  $1^4\Sigma^-$  states also come from this excitation, and the corresponding transitions from the lowest quartet state have oscillator strengths that are very similar to that of the  $1^4\Sigma^+ \leftarrow 1^4\Pi$  transition. The  $2^4\Delta$  and  $2^4\Sigma^-$  terms lie very high in energy and are due mostly to ( $2\pi \rightarrow 3\pi$ ,  $4\pi \rightarrow 12\sigma$ ) excitations from the  $1^4\Pi$  state. The higher  ${}^4\Pi$  and  ${}^4\Phi$  states arise, respectively, from  $3\pi^2 \rightarrow 4\pi^2$  and ( $3\pi \rightarrow 4\pi$ ,  $2\pi \rightarrow 4\pi$ ) promotions from the ground state (i.e.,  $3\pi \rightarrow 4\pi$  and  $2\pi \rightarrow 4\pi$  excitations from  $1^4\Pi$ ), but with some contamination from the  $3\pi \rightarrow 5\pi$  promotion. The equilibrium geometry of the lowest quartet state of the  $SC_3H$  chain is

moderately nonlinear (only  $\angle CCH = 148.6^\circ$  differs significantly from  $180^\circ$  in our B3LYP/6-311G\*\* computations). Taking into account the geometry variation would reduce the relative energy of the lowest quartet by about 0.42 eV.

**3.3.  $SC_4H$ .** In this case, the orbitals employed in the MRCI computations of the doublet states were obtained in an MCSCF computation with  $[13\sigma-15\sigma, 2\pi-6\pi]$  as the active space for 13 electrons. The MCSCF wave function is an average of eight  ${}^2B_1$  and  ${}^2B_2$  terms, five  ${}^2A_1$  terms, and four  ${}^2A_2$  terms. In the MRCI computations of the  ${}^2\Phi$  and  ${}^2\Pi$  terms, we used  $[2\pi-5\pi]$  as the active space; the occupation numbers of the  $C_{2v}$  components of the  $2\pi$  orbital were limited to either 1 or 2. In the MRCI computations of the  ${}^2\Sigma$  and  ${}^2\Delta$  states, we used  $[13\sigma-15\sigma, 2\pi-5\pi]$  as the active space; the occupation numbers of the  $14\sigma$ ,  $15\sigma$ , and  $C_{2v}$  components of the  $5\pi$  orbitals were restricted to a maximum of 1. The orbitals of this MRCI computation were obtained in an MCSCF computation with  $[13\sigma-16\sigma, 3\pi-6\pi]$  as the active space where five  ${}^2A_1$  and five  ${}^2A_2$  states were included.

In the case of the quartet states, we first performed an MCSCF computation with  $[12\sigma-15\sigma, 2\pi-6\pi]$  as the active space for a state that is the average of four  ${}^2B_1$  and  ${}^2B_2$  terms as well as one  ${}^2A_1$  and three  ${}^2A_2$  terms. In the MRCI computation of the  ${}^4\Phi$  and  ${}^4\Pi$  states, the  $[2\pi-6\pi]$  active space was used, whereas in the MRCI computation of the  ${}^4\Delta$  and  ${}^4\Sigma$  states,  $[13\sigma-15\sigma, 2\pi-5\pi]$  was used. The relative energies of the doublet and quartet  $\Delta$  and  $\Sigma$  states, as well as those of the quartet  $\Phi$  and  $\Pi$  terms, were calculated with the help of MRCI/aug-cc-pVTZ computations of the lowest-lying states of each spin and symmetry as well as the ground state,  $X^2\Pi$ . These MRCI/aug-cc-pVTZ computations used a common set of orbitals obtained in an MCSCF computation with  $[12\sigma-15\sigma, 3\pi-6\pi]$  as the active space for nine electrons. In this MCSCF computation, the wave function was optimized for an average of the lowest doublet and quartet terms of all symmetry species of the  $C_{2v}$  point group. The energy gaps between the lowest terms of the  ${}^4\Delta$ ,  ${}^2\Sigma^-$ , and  ${}^4\Pi$  symmetries and the ground state ( $X^2\Pi$ ) were obtained by means of the MRCI/aug-cc-pVTZ energies. The relative energies of the rest of the excited states were determined by adding MRCI/aug-cc-pVTZ energy differences to the  $1^2\Sigma^- - X^2\Pi$  energy gap in the case of  ${}^2\Sigma^{(-,+)}$  and  ${}^2\Delta$  states, to the  $1^4\Delta - X^2\Pi$  gap in the case of  ${}^4\Sigma^{(-,+)}$  and  ${}^4\Delta$  states, and to the  $1^4\Pi - X^2\Pi$  gap in the case of  ${}^4\Pi$  and  ${}^4\Phi$  states.

The lowest-lying excited state of  $SC_4H$  is  $1^2\Pi$ , as in the other two molecules. It arises from a  $3\pi \rightarrow 4\pi$  excitation, i.e., a promotion from the highest inner  $\pi$  orbital to the HOMO. The corresponding transition appears to be quite intense ( $f = 0.0298$ ) and is predicted to be at 2.72 eV; i.e., it is somewhat higher in energy than in  $SC_3H$  (2.49 eV), but it is clearly lower than in  $SC_2H$  (3.31 eV). The  $1^2\Pi - X^2\Pi$  transition is the one recorded by Endo and co-workers in their LIF spectra;<sup>32</sup> they obtained a value of  $T_0 = 19\,980.687\text{ cm}^{-1}$  (2.48 eV). Our vertical excitation energy agrees with this experimental result; note that it lacks zero-point and spin–orbit corrections and that the difference between vertical and  $T_e$  values is 0.29 eV in the case of the same transition in  $SC_2H$ . The next two states of the doublet  $\Pi - \Phi$  system arise from a transition from the HOMO ( $4\pi$ ) to the lowest virtual  $\pi$  orbital ( $4\pi \rightarrow 5\pi$ ), as in the case of  $SC_2H$ . The next state ( $3^2\Pi$ ) is due to a promotion from the innermost valence  $\pi$  orbital to the HOMO ( $2\pi \rightarrow 4\pi$ ). The corresponding transition has a very low oscillator strength, just as the other transitions between nonconsecutive  $\pi$  orbitals; see, for instance,  $3\pi \rightarrow 5\pi$ , which gives rise to the  $5^2\Pi$  term. There is a  $2^2\Phi$  term at 6.67 eV, which also arises from the  $3\pi \rightarrow 5\pi$

**TABLE 4: MCSCF/aug-cc-pVTZ Vertical Energies and Oscillator Strengths of 13 Components of the  ${}^2\Pi-{}^2\Phi$  System of SC<sub>4</sub>H**

state	excitation energy (eV)	$f^a$
X <sup>2</sup> Π	0	
1 <sup>2</sup> Π	2.79	0.0152
2 <sup>2</sup> Π	4.16	0.0022
1 <sup>2</sup> Φ	4.53	0.0000
3 <sup>2</sup> Π	4.66	0.0004
4 <sup>2</sup> Π	5.15	0.0012
5 <sup>2</sup> Π	6.04	0.0000
1 <sup>2</sup> Φ	6.92	0.0000
6 <sup>2</sup> Π	6.96	0.0004
7 <sup>2</sup> Π	7.11	0.0225
8 <sup>2</sup> Π	7.72	0.1306
1 <sup>2</sup> Φ	7.74	0.0000
9 <sup>2</sup> Π	8.05	0.6736

<sup>a</sup> In all cases, the oscillator strengths correspond to one  $C_{2v}$  component of the degenerate states.

transition. None of the five  ${}^2\Pi \leftarrow X^2\Pi$  transitions appears to have the kind of large oscillator strengths that were found in the other two radicals ( $4^2\Pi \leftarrow X^2\Pi$  in SC<sub>2</sub>H, (6,7) ${}^2\Pi \leftarrow X^2\Pi$  in SC<sub>3</sub>H). The likely reason is that the corresponding states appear at much higher energies. Given that we could not compute these states at the MRCI level, we performed an MCSCF/aug-cc-pVTZ computation using  $[13\sigma-14\sigma, 2\pi-6\pi]$  as the active space for 13 electrons, where we included 13  ${}^2B_1$  and  ${}^2B_2$  states. The results are presented in Table 4. The first eight states correspond to the same terms as appear in the MRCI computation; their relative energies are 0.07–0.32 eV higher than the MRCI values, whereas the oscillator strengths of their transitions from the ground state are, in general, quite similar to the MRCI results. Among the additional five states, there are three states with transitions of large oscillator strengths. In particular, the  $9^2\Pi \leftarrow X^2\Pi$  transition has an oscillator strength close to that of the  $4^2\Pi \leftarrow X^2\Pi$  transition of SC<sub>2</sub>H (0.7564) and much larger than that of the  $6^2\Pi \leftarrow X^2\Pi$  transition of SC<sub>3</sub>H (0.0956). Note that the  $9^2\Pi$  term of SC<sub>4</sub>H is slightly higher in energy than the  $4^2\Pi$  term of SC<sub>2</sub>H (7.45 eV) and much higher than the  $6^2\Pi$  term of SC<sub>3</sub>H (4.70 eV). The wave functions of these three high-lying states of SC<sub>4</sub>H incorporate many electron promotions. The  $7^2\Pi$  term arises mainly from the  $3\pi \rightarrow 4\pi$  and  $4\pi \rightarrow 5\pi$  excitations, but the other two terms are much more mixed. The  $8^2\Pi$  state has significant contributions from the  $2\pi \rightarrow 5\pi$ ,  $4\pi \rightarrow 5\pi$ ,  $3\pi \rightarrow 5\pi$ , and  $4\pi^2 \rightarrow 5\pi^2$  promotions, whereas  $9^2\Pi$  is a mixture of the  $3\pi \rightarrow 4\pi$ ,  $3\pi \rightarrow 5\pi$ ,  $4\pi \rightarrow 5\pi$ , ( $3\pi \rightarrow 4\pi$ ,  $3\pi \rightarrow 5\pi$ ),  $4\pi^2 \rightarrow 5\pi^2$ , and  $2\pi \rightarrow 5\pi$  excitations. In contrast to the  $4^2\Pi$  term of SC<sub>2</sub>H, there is almost no contamination of a  $\sigma \rightarrow \sigma^*$  excitation in any of these terms. Even though the MCSCF relative energies and oscillator strengths of these high-lying states might be inaccurate, we think it is safe to conclude that there are indeed valence high-intensity transitions from the ground state in SC<sub>4</sub>H and that these transitions should appear at energies close to 7 eV or higher.

The study of the  ${}^2\Sigma^+$  terms, which appear in the  $A_1$  irreducible representation of the  $C_{2v}$  point group, was quite difficult because the energy of the term arising from the  $13\sigma \rightarrow 4\pi$  excitation critically depends on the choice of the active space. Apart from this state, we have several sets of pairs of low-lying  ${}^2\Delta-{}^2\Sigma^+$  states, which arise mainly from the  $4\pi \rightarrow 14\sigma$  and  $4\pi \rightarrow 15\sigma$  excitations but are contaminated by simultaneous  $\pi \rightarrow \pi$  excitations. Inclusion of all valence  $\pi$  orbitals in the active space tends to bring up to three  ${}^2\Delta-{}^2\Sigma^+$  pairs below the  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$  term; the MRCI method is often unable to correct this energy gap. One could say that, to some extent, the dynamic

correlation effects are very important in the  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$  term, whereas the nondynamic correlation effects are essential in the  ${}^2\Delta-{}^2\Sigma^+$  pairs of states. Incorporating all valence electrons and orbitals in the active space would have been interesting but could not be done. Instead, we chose the active space in such way that the reference functions had similar weights in the MRCI wave function. Apart from the computations described in the preceding section, we also performed specific three-state computations for the  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$  term and the lowest  ${}^2\Delta-{}^2\Sigma^+$  pair with several basis sets ranging from the cc-pVDZ to the aug-cc-pVTZ basis set. The aug-cc-pVDZ basis set was used as it is and also truncated so it includes only s and p diffuse functions, whereas the aug-cc-pVTZ basis set was truncated so it includes diffuse functions only up to the d shell. We found that an active space of  $[12\sigma-14\sigma, 3\pi-4\pi]$  for nine electrons is sufficient to give a balanced description of the three states and makes the MRCI computation feasible with the largest basis sets. We have concluded that  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$  should be the lowest doublet state of  $A_1$  symmetry, but that the  $1^2\Sigma^+-1^2\Delta$  energy gap is highly uncertain. With a cc-pVTZ basis set an MRCI computation with the  $[12\sigma-14\sigma, 3\pi-4\pi]$  active space, using orbitals determined in an MCSCF computation with that same active space and three roots corresponding to the  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$ ,  ${}^2\Delta(4\pi \rightarrow 14\sigma)$ , and  ${}^2\Sigma^+(4\pi \rightarrow 14\sigma)$  states, one obtains 2.19 eV. Using an *uncontracted* cc-pVDZ basis set supplemented with the diffuse s–p functions defined in the aug-cc-pVTZ basis set, one obtains 0.26 eV. In the latter computation, the root of the  ${}^2\Sigma^+(13\sigma \rightarrow 4\pi)$  state is the third MCSCF root, whereas it is the first MCSCF root in the former computation. In both MRCI computations, the coefficients of the reference functions of the three states are very similar and lie close to 0.91. It seems that the use of diffuse functions tends to favor the terms arising from the  $4\pi \rightarrow 14\sigma$  excitation, but we did not encounter any dramatic effect of the diffuse functions in the nature of the  $13\sigma$ ,  $14\sigma$ , or  $4\pi$  orbitals. The  $1^2\Sigma^+-1^2\Delta$  energy gap of Table 3 is 0.51 eV. It is obvious that higher-level computations might be needed to obtain a reliable and accurate description of these states.

As in the case of SC<sub>2</sub>H, the lowest  ${}^2\Sigma^-$  term arises from a transition from the highest occupied  $\pi$  orbital, i.e., the HOMO, to the lowest virtual  $\sigma$  orbital, which is the LUMO in both cases. In the case of SC<sub>4</sub>H, however, the transition also has an important additional component ( $4\pi \rightarrow 15\sigma$ ). The smaller HOMO–LUMO energy gap of the four-carbon system as compared to SC<sub>2</sub>H might explain why a higher energy is found in the latter system. The  $1^2\Delta$  state is quite close in energy to the  ${}^2\Sigma^-$  state, and another  ${}^2\Delta$  state lies about 1 eV above  $1^2\Sigma^-$ . The  $1^2\Delta$  and  ${}^2\Sigma^+$  states are very close in energy, and the corresponding transitions have about the same oscillator strengths. The  $3\pi \rightarrow 14\sigma$  excitation is the most important in the very high-lying  $3^2\Delta$  state.

The first quartet state is  $1^4\Pi$ , which arises from a  $4\pi \rightarrow 5\pi$  promotion from the ground state, i.e., the same kind of promotion associated with the lowest quartet state of SC<sub>2</sub>H. The fact that the  $4\pi-5\pi$  energy gap is smaller than the  $3\pi-4\pi$  gap of SC<sub>2</sub>H might account for the smaller  $1^4\Pi-X^2\Pi$  gap of the six-atom system. The next three terms of the quartet  $\Pi-\Phi$  system originate in a  $3\pi \rightarrow 4\pi$  excitation from the  $1^4\Pi$  state, just as in the two-carbon radical, where the corresponding excitation is  $2\pi \rightarrow 3\pi$ . The lowest  $4^2\Sigma^-$  state is due to a HOMO–LUMO promotion in both the two- and four-carbon systems. However, it is the second quartet state in SC<sub>2</sub>H, where it lies only 0.78 eV above  $1^4\Pi$ , whereas it lies 2.52 eV higher than  $1^4\Pi$  in the four-carbon system. It is almost coincident in energy

with the  $2^4\Sigma^-$  term of  $\text{SC}_2\text{H}$ , which arises from a promotion from the HOMO to the second virtual orbital ( $11\sigma$ ). The  $2^4\Sigma^-$  state of  $\text{SC}_4\text{H}$  also arises from this kind of promotion. We could also locate a  $1^4\Delta$  state arising from a  $3\pi \rightarrow 14\sigma$  promotion from the ground state, which is equivalent in character to the  $1^4\Delta$  state of  $\text{SC}_2\text{H}$ .

We optimized the geometry of the lowest quartet state of the  $\text{SC}_4\text{H}$  chain at the B3LYP/6-311G\*\* level and obtained a bent geometry ( $\angle\text{SC}_2\text{C}_3 = 130.7^\circ$ ,  $\angle\text{C}_4\text{C}_5\text{H} = 146.6^\circ$ ; the other angles are close to  $180^\circ$ ). This geometry variation with respect to the ground state should decrease the doublet–quartet energy gap by about 0.93 eV with respect to the vertical value.

#### 4. Conclusions

The electronic spectra of the  $\text{SC}_n\text{H}$  radicals ( $n = 2-4$ ) have been studied by means of the MCSCF and MRCI methods. The ground state is  $^2\Pi$ , and the lowest quartet is  $^4\Pi$  in the three molecules. The  $\text{X}^2\Pi-1^4\Pi$  vertical energy gaps are 4.94 eV ( $n = 2$ ), 2.87 eV ( $n = 3$ ), and 3.71 eV ( $n = 4$ ), whereas the adiabatic electronic energy gaps should be about 1.95, 0.42, and 0.93 eV smaller, respectively. The lowest-lying excited doublet states arise from electronic excitation to the HOMO, which is a  $\pi$  orbital, from the highest inner-valence  $\pi$  orbital. The corresponding transitions are intense in the case of the two- and four-carbon radicals, and there is also a relatively intense one in the case of  $\text{SC}_3\text{H}$ . We also found very intense transitions to high-lying  $^2\Pi$  terms:  $4^2\Pi \leftarrow \text{X}^2\Pi$  ( $n = 2$ ),  $(6,7)^2\Pi \leftarrow \text{X}^2\Pi$  ( $n = 3$ ),  $(7,8,9)^2\Pi \leftarrow \text{X}^2\Pi$  ( $n = 4$ ). In addition, there are moderately intense transitions to lower-lying terms [ $1^2\Pi \leftarrow \text{X}^2\Pi$ ,  $1^2\Sigma^+ \leftarrow \text{X}^2\Pi$  ( $n = 2$ ),  $(2,3,4)^2\Pi \leftarrow \text{X}^2\Pi$  ( $n = 3$ ), and  $1^2\Pi \leftarrow \text{X}^2\Pi$  ( $n = 4$ )]. The  $^2\Delta-^2\Sigma^{+-}$  terms appear at rather high energies. The lowest term of this kind is  $1^2\Sigma^+$ , which arises from an excitation from the highest occupied  $\sigma$  orbital to the HOMO in the case of the two- and four-carbon systems, whereas it is due to a HOMO–LUMO promotion ( $4\pi \rightarrow 12\sigma$ ) in the case of  $\text{SC}_3\text{H}$ . The corresponding transitions should be quite intense. The relative energy of the  $1^2\Sigma^+$  state of the four-carbon system is difficult to compute and presently quite uncertain. Comparison with experimental values is possible in the case of the  $1^2\Pi \leftarrow \text{X}^2\Pi$  transitions of the - and four-carbon radicals; our vertical excitation energies are 0.3 eV ( $n = 2$ ) and 0.24 eV ( $n = 4$ ) higher than the experimental  $T_0$  values.

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