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**Alternation of the spin-orbit coupling in the 2Pi ground state of HCnS n=1-12 radicals**

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3 **Alternation of the spin-orbit coupling in the  $^2\Pi$  ground state of**  
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5  **$\text{HC}_n\text{S}$   $n = 1 - 12$  radicals**  
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32 (Dated: April 6, 2009)

33  
34 **Abstract**

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36 First-order calculations of spin-orbit constants, dipole moments and carbon-sulphur distances  
37 have been performed for the  $\text{HC}_n\text{S}$   $n = 1 - 12$  radicals in the  $^2\Pi$  electronic ground state. It is  
38 found that these molecular properties alternate with the even or odd number of carbon atoms in  
39 the chains and the spin-orbit constant  $A_{SO}$  is around  $-300 \text{ cm}^{-1}$  for  $n = \text{even}$  and about  $+120$   
40  $\text{cm}^{-1}$  for  $n = \text{odd}$  throughout the series. This agrees with the experimentally determined  $\sim -270$   
41  $\text{cm}^{-1}$  for  $\text{HC}_2\text{S}$ , but the theoretically predicted  $A_{SO}$  are much larger than the values given for  
42  $\text{HC}_3\text{S}$ ,  $\text{HC}_4\text{S}$  from a fit of their mm-wave spectra. Also in the analysis of the rotational spectra of  
43  $n = 4 - 8$  too low values were assumed.  
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3 The  $\text{HC}_n\text{S}$  ( $n = 1 - 12$ ) molecules in their  $X^2\Pi$  electronic ground state have two types of  
4 HOMO's:  $\pi^3$  or  $\pi^1$  depending on the even or odd number of carbon atoms in the chain. The  
5 alternation of the electronic configuration implies two different types of molecular properties  
6 depending on the number of carbon atoms. Because of the size of the chains first principle  
7 calculations can provide only semi-quantitative results. These are nevertheless useful as a  
8 guide for the analysis of experimental data.  
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12 The ground electronic states of the  $\text{HC}_n\text{S}$  radicals ( $n = 2 - 8$ ) have been studied by  
13 millimeter wave spectroscopy[1-4]. These show that the lowest doublet rotational pattern  
14 is regular (i.e. the  $^2\Pi_{1/2}$  component is the lowest in energy) for  $n = \text{odd}$  but inverted for  
15  $n = \text{even}$  ( $^2\Pi_{3/2}$  being the lowest). The linear structures of the  $\text{HC}_n\text{S}$  radicals in their  
16 ground states contrast with the isovalent  $\text{HC}_n\text{O}$  ( $n = 1 - 4$ ) species, in which either the  
17  $A_0$  ( $n = \text{odd}$ ) or  $A_{00}$  ( $n = \text{even}$ ) Renner-Teller components are the lowest bent electronic  
18 states. In addition the  $^2\Pi - X^2\Pi$  transitions in their electronic spectra[5] have been observed  
19 by a number of methods:  $\text{HC}_2\text{S}$ ,  $\text{HC}_4\text{S}$ , and  $\text{HC}_6\text{S}$  by fluorescence[6-8],  $\text{HC}_6\text{S}$  by resonant  
20 two-color two-photon ionization[9], and  $\text{HC}_8\text{S}$  and  $\text{HC}_{10}\text{S}$  by cavity ringdown absorption  
21 spectroscopy[9]. These data show that the wavelengths of the  $A^2\Pi - X^2\Pi$  origin band in the  
22  $\text{HC}_6\text{S}$ ,  $\text{HC}_8\text{S}$ , and  $\text{HC}_{10}\text{S}$  spectra exhibit a near linear relationship with chain length.  
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27 The analysis of the spectral data of multidimensional Renner-Teller open shell systems  
28 is very demanding. For instance, several close low-lying Renner-Teller bending levels, an-  
29 harmonic polyads and torsion modes make the assignments of the spin-orbit coupled states  
30 a challenge. Several effective Hamiltonians have been developed to interpret the spectra of  
31 the tetra-atomic radical  $\text{HC}_2\text{S}$  and so far the most detailed theoretical approach including  
32 Renner-Teller is that of Perić et al.[10]. Only recently a new variational method has been  
33 reported and applied to acetylene radical cation[11]. For open-shell Renner-Teller molecules  
34 with a larger number of atoms the determination of the electronic spin-orbit constant  $A_{SO}$   
35 is difficult.  
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40 In a recent study of the  $A^2\Pi_{3/2} - X^2\Pi_{3/2}$  electronic transition of  $\text{HC}_4\text{S}$  by cavity ringdown  
41 spectroscopy using a supersonic slit-jet expansion within a discharge[12], it was concluded  
42 that the spin-orbit splitting in the ground state can not be about  $-33 \text{ cm}^{-1}$  as indicated  
43 earlier[2]. In the cavity ringdown measurements at different temperatures,  $A_{SO}$  of the order  
44 of magnitude of  $-270 \text{ cm}^{-1}$  was consistent with the observations. It should be pointed out  
45 that  $A_{SO}$  of  $-33 \text{ cm}^{-1}$  in the ground state was not directly measured in the mm wave spec-  
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trum, but was used in the fit of the data, in analogy with  $\text{HC}_3\text{S}$ . This discrepancy prompted the current ab initio calculation of the spin-orbit constant in the whole homologous series,  $\text{HC}_n\text{S}$   $n = 1 - 12$ .

In Table I results are given for the spin-orbit constants of the smaller  $\text{HC}_n\text{S}$   $n = 1 - 4$  radicals calculated with different basis sets[13] by HF, CASSCF[14] or MRCI[15] methods using the Breit-Pauli formulation as coded in MOLPRO[16]. Depending on the size of the molecule, either full-valence or very large active spaces have been used. The resulting CASSCF expansions were used as reference wavefunctions in subsequent MRCI computations. The geometric parameters have been taken from the published data (Table I) and from geometry optimisation at the open-shell SCF/cc-pVTZ level of the linear molecular structures (Table II). The ground state configurations given in Table I are found to be the dominating ones in all correlated wavefunctions.

We have performed a series of calculations of the spin-orbit splitting in the  $^3P$  ground state of the sulphur atom. The atomic orbital basis sets used in these computations are the cc-pVTZ, cc-pVQZ, cc-pV5Z and the corresponding augmented basis sets[13]. The experimental energy difference between the  $^3P_1$  and  $^3P_2$ , and the  $^3P_0$  and  $^3P_1$  components are 396 and 178  $\text{cm}^{-1}$ , respectively. The neglect of the core-valence contributions in the RHF and full-valence CASSCF wavefunctions results in deviations from the experimental values up to 30  $\text{cm}^{-1}$ . The influence of the  $^1D$  and  $^1S$  states on the spin-orbit splitting in the ground state has been investigated as well and the deviations from the full-valence-CASSCF computations with the  $^3P$  only are calculated to be few  $\text{cm}^{-1}$ . With the aug-cc-pV5Z basis set we obtained 372  $\text{cm}^{-1}$  (all states) and 366  $\text{cm}^{-1}$  ( $^3P$  only) for the  $^3P_1$ - $^3P_2$  splitting and 171  $\text{cm}^{-1}$  (all states) and 183  $\text{cm}^{-1}$  ( $^3P$  only) for the  $^3P_0$ - $^3P_1$  splitting. For semi-quantitative trends of molecular properties in  $\text{HC}_n\text{S}$  radical chains the present approach is expected to give results with an accuracy better than about 10 – 30 percent.

In Figure 1 the  $\alpha$  spin densities are plotted. The densities within the thiocarbonyl group strongly alternate, mainly due to corresponding neighboring C-C moiety. This result leads to  $n$  dependent even/odd saw-tooth pattern of molecular properties such as the spin-orbit constants (Tables I, II and Figure 2), thiocarbonyl distances (Table II and Figure 2) or dipole moments (Figure 2). The spin densities also suggest different carbenoid type reactivity along the carbon chains. For the species with odd number of carbons the density is larger at the atom next to the sulphur. Hence the size of  $A_{SO}$  is mainly determined by the

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3 spin-orbit coupling at sulphur atom and is calculated for any  $n$  as being larger than  $-150$   
4  $\text{cm}^{-1}$ .  
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7 The present calculations show that for the species  $\text{HC}_n\text{S}$  with  $n = \text{even}$   $A_{SO}$  is around  
8  $-300 \text{ cm}^{-1}$ , whereas for  $n = \text{odd}$  it is  $+120 \text{ cm}^{-1}$  in magnitude. This is of significance  
9 in view of the analysis of the mm-wave spectra which have been measured for the species  
10  $\text{HC}_n\text{S}$   $n = 2 - 8$ . In the case of  $\text{HC}_2\text{S}$  the value  $A_{SO} = -185 \text{ cm}^{-1}$  was obtained by fit-  
11 ting the rotational transitions observed for both the  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  components[17]. In a  
12 latter investigation the intensity variation of the lines within these two components led to  
13  $A_{SO} = -270 \text{ cm}^{-1}$ [18], in agreement with the presently ab initio calculated value. Accord-  
14 ing to the authors of the latter study, the quality of the fit to the experimental lines is the  
15 same whether  $A_{SO} = -270$  or  $-185 \text{ cm}^{-1}$  is used. The analysis of the  ${}^2\Pi - X \text{ } {}^2\Pi$  electronic  
16 spectrum of  $\text{HC}_2\text{S}$  also led to the larger value of  $-259 \text{ cm}^{-1}$ [19].  
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20 In the mm-wave spectrum of  $\text{HC}_3\text{S}$ , transitions within both spin-orbit manifolds were  
21 observed. By means of a fit of the appropriate Hamiltonian a spin-orbit splitting in the  
22  $X^2\Pi$  ground state of  $+44 \text{ cm}^{-1}$  was inferred[3]. This is much smaller than the  $+120 \text{ cm}^{-1}$   
23 constant calculated here. It can be excluded that the ab initio values are too big by a factor  
24 of 3. Quenching of the spin-orbit by Renner-Teller is possible but this would be an unusually  
25 large effect. It is thus suggested that the determination of the  $A_{SO}$  from the fit of the lines  
26 in the rotational spectrum is too insensitive to give a reliable value. In all the other studied  
27 species  $\text{HC}_n\text{S}$   $n = 4 - 8$  the fits of the rotational line positions assumed the  $A_{SO}$  of  $+43$  or  
28  $-33 \text{ cm}^{-1}$ , for  $n = \text{odd}$  or  $n = \text{even}$  respectively[4]. The specific case of  $\text{HC}_4\text{S}$  was discussed  
29 in connection with the  ${}^2\Pi - X \text{ } {}^2\Pi$  electronic spectrum of  $\text{HC}_4\text{S}$ [4]. There it was argued that  
30 the observations are consistent with  $A_{SO} -270$  but not  $-33 \text{ cm}^{-1}$  and furthermore the re-fit  
31 of the rotational spectrum with  $A_{SO} = -270 \text{ cm}^{-1}$  gave agreement not significantly different  
32 to the original work. The results of the present study show that the values of  $A_{SO}$  of around  
33  $+120 \text{ cm}^{-1}$  and  $-270 \text{ cm}^{-1}$  should be used for the  $n = \text{even}$  or  $\text{odd}$  chains respectively. The  
34 results of this note are also expected to reflect the pattern in some other carbon-heteroatom  
35 chains.  
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TABLE I: Bond distances (Å) and spin-orbit coupling constants  $A_{SO}$  ( $\text{cm}^{-1}$ ) in the lowest  $^2\Pi$  state of  $\text{CS}^+$  and linear  $\text{HC}_n\text{S}$  ( $n = 1 - 4$ ).

System	Bond distances	Basis set	Method	Occupied/Closed <sup>a</sup>	CSF's	Configuration	$A_{SO}$ [Theory]	$A_{SO}$ [Exp.]
$\text{CS}^+$	$r_{CS}=1.639^b$	cc-pVQZ	HF			$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^3$	-304	
		aug-cc-pV5Z	MRCI	8,3,3/4,1,1	738124		-268	-294 <sup>g</sup>
HCS	$r_{CH}=1.063^c$	cc-pVQZ	HF			$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 3\pi$	135	
		cc-pVQZ	CASSCF	9,3,3/4,1,1	1512		163	
HCCS	$r_{CH}=1.060^d$	cc-pVQZ	MRCI			$6\sigma^2 \dots 9\sigma^2 2\pi^4 3\pi^3$	156	
		cc-pVQZ	HF				-302	
	$r_{CC}=1.232$	cc-pVTZ	CASSCF	12,4,4/8,1,1	6940		-268	
		cc-pVTZ	CASSCF	12,4,4/5,1,1	245338		-275	
	$r_{CS}=1.631$	cc-pVQZ	CASSCF	12,4,4/5,1,1	245338		-276	-185 <sup>h</sup> , -270 <sup>i</sup>
		cc-pVQZ	HF			$7\sigma^2 \dots 11\sigma^2 2\pi^4 3\pi^4 4\pi$	129	
HC <sub>3</sub> S	$r_{CC}=1.195, 1.385$	cc-pVTZ	CASSCF	15,5,5/10,1,1	245448		151	
		cc-pVTZ	CASSCF	15,5,5/9,1,1	1073660		152	
	$r_{CS}=1.527$	cc-pVQZ	CASSCF	15,5,5/8,1,1	4089800		147	44 <sup>j</sup>
		cc-pVQZ	HF			$8\sigma^2 \dots 13\sigma^2 2\pi^4 3\pi^4 4\pi^3$	-261	
HC <sub>4</sub> S	$r_{CH}=1.06^f$	cc-pVQZ	CASSCF	18,6,6/13,1,1	1561970		-252	
		cc-pVTZ	CASSCF	18,6,6/12,1,1	8849330		-232	-33 <sup>k</sup>

<sup>a</sup>The active space is specified by the number of occupied and closed-shell orbitals in the  $A_1$ ,  $B_1$  and  $B_2$

irreducible representations of  $C_{2v}$  point group.

<sup>b</sup>Ref.[20].

<sup>c</sup>Geometry at the barrier to linearity. Ref.[21].

<sup>d</sup>Ref.[10].

<sup>e</sup>Ref.[3].

<sup>f</sup>F. J. Mazzotti and Z. Jamshidi, private communication.

<sup>g</sup>Ref.[20].

<sup>h</sup>Ref.[17].

<sup>i</sup>Ref.[18].

<sup>j</sup>Estimated. Ref.[3].

<sup>k</sup>Assumed. Ref.[2].

TABLE II: Spin-orbit coupling constants  $A_{SO}$  ( $\text{cm}^{-1}$ ) and optimized bond distances ( $\text{\AA}$ ), calculated at the HF/cc-pVTZ level, for the lowest  ${}^2\Pi$  state of  $\text{CS}^+$  and linear  $\text{HC}_n\text{S}$  ( $n = 1 - 12$ ).

System	$A_{SO}$	System	$A_{SO}$
$\text{CS}^+$	-302	$\text{HC}_7\text{S}$	120
HCS	136	$\text{HC}_8\text{S}$	-309
$\text{HC}_2\text{S}$	-302	$\text{HC}_9\text{S}$	120
$\text{HC}_3\text{S}$	121	$\text{HC}_{10}\text{S}$	-310
$\text{HC}_4\text{S}$	-311	$\text{HC}_{11}\text{S}$	120
$\text{HC}_5\text{S}$	121	$\text{HC}_{12}\text{S}$	-310
$\text{HC}_6\text{S}$	-309		

$n$	$r_{\text{C}_n\text{S}}$	$r_{\text{HC}_1}$	$r_{\text{C}_1\text{C}_2}$	$r_{\text{C}_2\text{C}_3}$	$r_{\text{C}_3\text{C}_4}$	$r_{\text{C}_4\text{C}_5}$	$r_{\text{C}_5\text{C}_6}$	$r_{\text{C}_6\text{C}_7}$	$r_{\text{C}_7\text{C}_8}$	$r_{\text{C}_8\text{C}_9}$	$r_{\text{C}_9\text{C}_{10}}$	$r_{\text{C}_{10}\text{C}_{11}}$	$r_{\text{C}_{11}\text{C}_{12}}$
1	1.531	1.058											
2	1.664	1.054	1.189										
3	1.537	1.054	1.196	1.340									
4	1.653	1.054	1.184	1.377	1.194								
5	1.538	1.054	1.186	1.369	1.205	1.325							
6	1.650	1.054	1.183	1.379	1.187	1.371	1.196						
7	1.537	1.054	1.183	1.377	1.190	1.361	1.208	1.322					
8	1.650	1.054	1.183	1.379	1.187	1.373	1.188	1.370	1.196				
9	1.537	1.054	1.183	1.379	1.187	1.371	1.192	1.360	1.208	1.321			
10	1.650	1.054	1.183	1.379	1.187	1.374	1.188	1.372	1.189	1.370	1.196		
11	1.537	1.054	1.183	1.379	1.187	1.373	1.188	1.370	1.192	1.359	1.209	1.320	
12	1.650	1.054	1.183	1.379	1.186	1.374	1.188	1.373	1.188	1.372	1.189	1.370	1.196

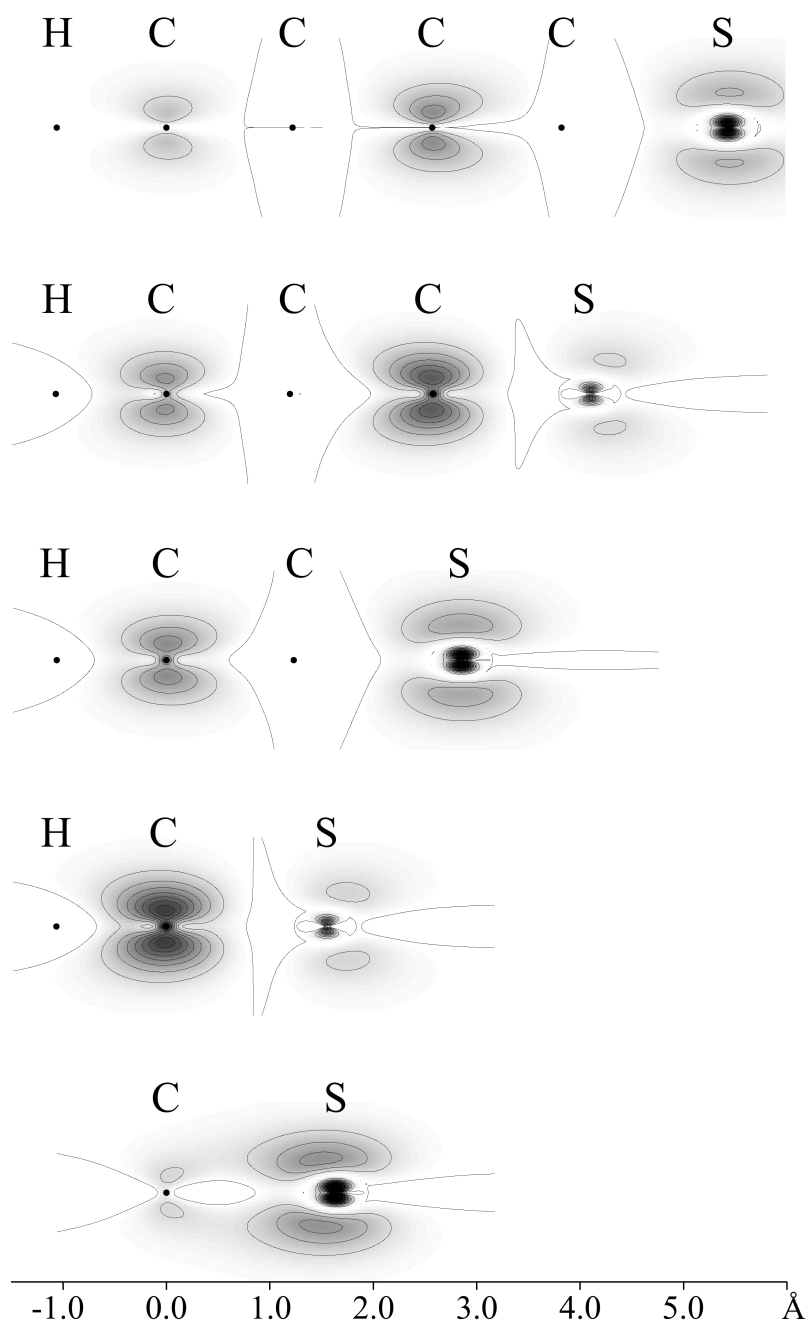
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## Figure Captions:

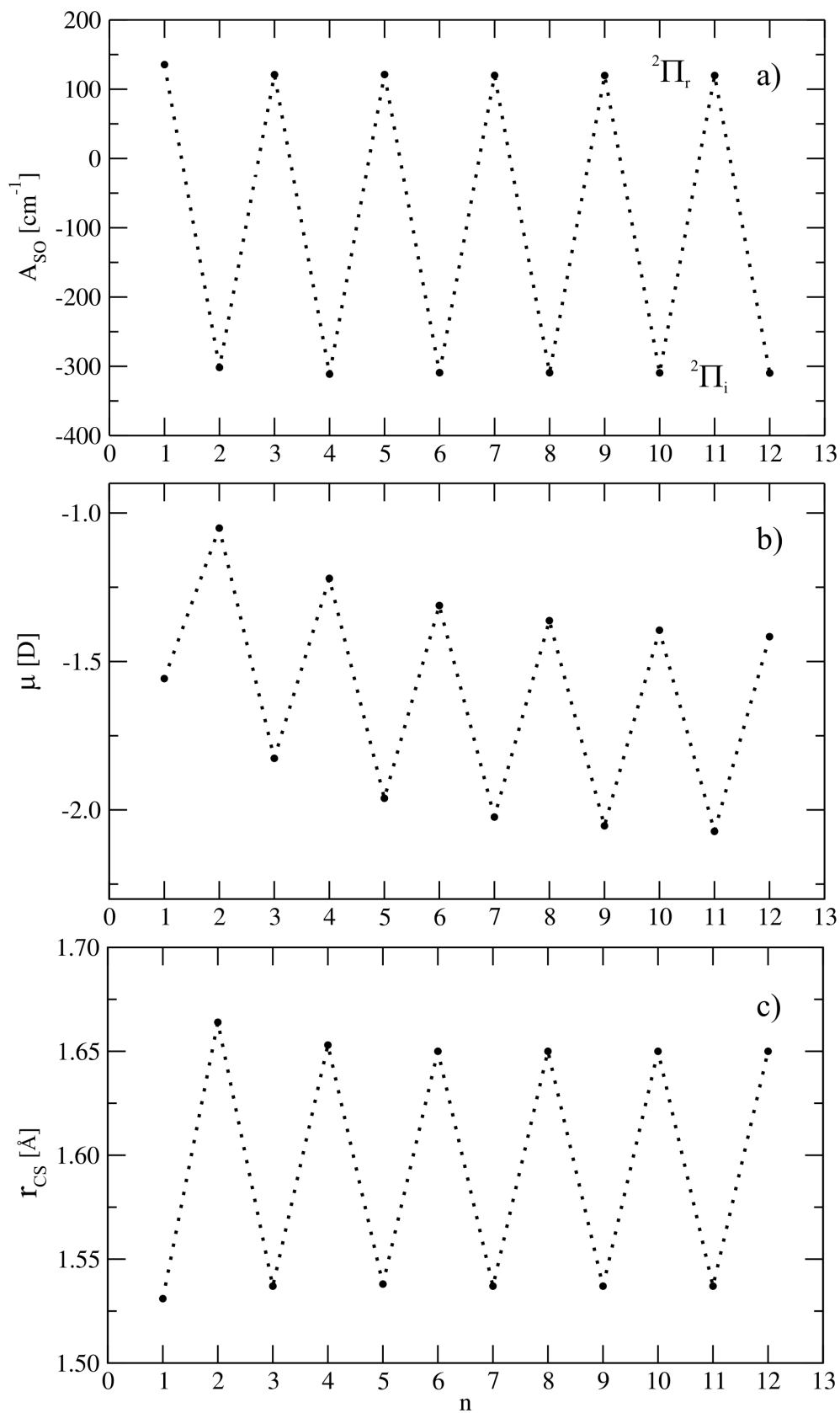
**Figure 1:** Contour cuts of the electron spin density distribution in  $\text{CS}^+$  radical cation and  $\text{HC}_n\text{S}$  chain radicals  $n = 1 - 4$ . Spin densities are obtained from CASSCF wavefunctions (Table I).

**Figure 2:** Molecular properties calculated at the HF/cc-pVTZ level for  $\text{HC}_n\text{S}$  chain radicals ( $n = 1 - 12$ ).

- a) Electron spin-orbit coupling constants in  $\text{cm}^{-1}$ . Values in the upper and lower part refer to regular and inverted  $^2\Pi$  ground states respectively.
- b) Dipole moments in debye.
- c) Equilibrium carbon-sulfur bond lengths in ångström.



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