



HAL
open science

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

Alexander Mitrushchenkov, Roberto Linguerri, Pavel Rosmus, John P. Maier

► **To cite this version:**

Alexander Mitrushchenkov, Roberto Linguerri, Pavel Rosmus, John P. Maier. Alternation of the spin-orbit coupling in the 2Π ground state of HCnS $n=1-12$ radicals. *Molecular Physics*, 2009, 107 (15), pp.1549-1553. 10.1080/00268970902973842 . hal-00513294

HAL Id: hal-00513294

<https://hal.science/hal-00513294v1>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



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

| | |
|--|---|
| Journal: | <i>Molecular Physics</i> |
| Manuscript ID: | TMPh-2009-0103.R1 |
| Manuscript Type: | Research Note |
| Date Submitted by the Author: | 06-Apr-2009 |
| Complete List of Authors: | Mitrushchenkov, Alexander; Universite Paris-Est Marne la Vallee, Chimie Theorique Linguerrri, Roberto; Universite Paris-Est Marne la Vallee, Chimie Theorique Rosmus, Pavel; Universite Paris-Est Marne la Vallee, Chimie Theorique Maier, John P.; Universitat Basel |
| Keywords: | spin-orbit coupling, HCnS radicals |
| <p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>articlerev.tex</p> | |



1
2
3 **Alternation of the spin-orbit coupling in the $^2\Pi$ ground state of**
4
5 **HC_nS $n = 1 - 12$ radicals**
6
7

8 A. Mitrushchenkov, R. Linguerri, and P. Rosmus

9 *Université Paris-Est,*

10 *Laboratoire Modélisation et Simulation Multi Echelle,*

11 *MSME FRE 3160 CNRS,*

12 *5 boulevard Descartes,*

13 *77454 Marne-la-Vallée CEDEX 2, France.*

14
15
16
17
18
19
20
21 J. P. Maier

22 *Department of Chemistry,*

23 *University of Basel,*

24 *Klingelbergstrasse 80,*

25 *CH-4056 Basel,*

26 *Switzerland.*

27
28
29
30
31
32 (Dated: April 6, 2009)

33
34 **Abstract**

35
36 First-order calculations of spin-orbit constants, dipole moments and carbon-sulphur distances
37 have been performed for the HC_nS $n = 1 - 12$ 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 cm^{-1} for $n = \text{even}$ and about $+120$
40 cm^{-1} for $n = \text{odd}$ throughout the series. This agrees with the experimentally determined ~ -270
41 cm^{-1} for HC_2S , but the theoretically predicted A_{SO} are much larger than the values given for
42 HC_3S , HC_4S 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.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 The HC_nS ($n = 1 - 12$) molecules in their $X^2\Pi$ electronic ground state have two types of
4 HOMO's: π^3 or π^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.
9

10
11
12 The ground electronic states of the HC_nS 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 HC_nS radicals in their
16 ground states contrast with the isovalent HC_nO ($n = 1 - 4$) 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: HC_2S , HC_4S , and HC_6S by fluorescence[6-8], HC_6S by resonant
20 two-color two-photon ionization[9], and HC_8S and HC_{10}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 HC_6S , HC_8S , and HC_{10}S spectra exhibit a near linear relationship with chain length.
23
24

25
26
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 HC_2S 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.
36
37

38
39
40 In a recent study of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ electronic transition of HC_4S 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 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 cm^{-1} was consistent with the observations. It should be pointed out
45 that A_{SO} of -33 cm^{-1} in the ground state was not directly measured in the mm wave spec-
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

trum, but was used in the fit of the data, in analogy with HC_3S . This discrepancy prompted the current ab initio calculation of the spin-orbit constant in the whole homologous series, HC_nS $n = 1 - 12$.

In Table I results are given for the spin-orbit constants of the smaller HC_nS $n = 1 - 4$ 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 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 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 cm^{-1} . With the aug-cc-pV5Z basis set we obtained 372 cm^{-1} (all states) and 366 cm^{-1} (3P only) for the 3P_1 - 3P_2 splitting and 171 cm^{-1} (all states) and 183 cm^{-1} (3P only) for the 3P_0 - 3P_1 splitting. For semi-quantitative trends of molecular properties in HC_nS radical chains the present approach is expected to give results with an accuracy better than about 10 – 30 percent.

In Figure 1 the α 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

spin-orbit coupling at sulphur atom and is calculated for any n as being larger than -150 cm^{-1} .

The present calculations show that for the species HC_nS with $n = \text{even}$ A_{SO} is around -300 cm^{-1} , whereas for $n = \text{odd}$ it is $+120$ cm^{-1} in magnitude. This is of significance in view of the analysis of the mm-wave spectra which have been measured for the species HC_nS $n = 2 - 8$. In the case of HC_2S the value $A_{SO} = -185$ cm^{-1} was obtained by fitting the rotational transitions observed for both the ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ components[17]. In a latter investigation the intensity variation of the lines within these two components led to $A_{SO} = -270$ cm^{-1} [18], in agreement with the presently ab initio calculated value. According to the authors of the latter study, the quality of the fit to the experimental lines is the same whether $A_{SO} = -270$ or -185 cm^{-1} is used. The analysis of the ${}^2\Pi - X$ ${}^2\Pi$ electronic spectrum of HC_2S also led to the larger value of -259 cm^{-1} [19].

In the mm-wave spectrum of HC_3S , transitions within both spin-orbit manifolds were observed. By means of a fit of the appropriate Hamiltonian a spin-orbit splitting in the $X^2\Pi$ ground state of $+44$ cm^{-1} was inferred[3]. This is much smaller than the $+120$ cm^{-1} constant calculated here. It can be excluded that the ab initio values are too big by a factor of 3. Quenching of the spin-orbit by Renner-Teller is possible but this would be an unusually large effect. It is thus suggested that the determination of the A_{SO} from the fit of the lines in the rotational spectrum is too insensitive to give a reliable value. In all the other studied species HC_nS $n = 4 - 8$ the fits of the rotational line positions assumed the A_{SO} of $+43$ or -33 cm^{-1} , for $n = \text{odd}$ or $n = \text{even}$ respectively[4]. The specific case of HC_4S was discussed in connection with the ${}^2\Pi - X$ ${}^2\Pi$ electronic spectrum of HC_4S [4]. There it was argued that the observations are consistent with $A_{SO} -270$ but not -33 cm^{-1} and furthermore the re-fit of the rotational spectrum with $A_{SO} = -270$ cm^{-1} gave agreement not significantly different to the original work. The results of the present study show that the values of A_{SO} of around $+120$ cm^{-1} and -270 cm^{-1} should be used for the $n = \text{even}$ or odd chains respectively. The results of this note are also expected to reflect the pattern in some other carbon-heteroatom chains.

Acknowledgements

The work in Basel has been supported by the Swiss National Science Foundation (project [200020-124349/1](#)).

-
- [1] E. Kim, H. Habara, and S. Yamamoto, *J. Mol. Spectrosc.* **212**, 83 (2002).
 - [2] Y. Hirahara, Y. Ohshima, and Y. Endo, *J. Chem. Phys.* **101**, 7342 (1994).
 - [3] M. C. McCarthy, J. M. Vrtilik, E. W. Gottlieb, F.-M. Tao, C. A. Gottlieb, and P. Thaddeus, *Astrophys. J.* **431**, L127 (1994).
 - [4] V. D. Gordon, M. C. McCarthy, A. J. Apponi, and P. Thaddeus, *Astrophys. J. Suppl. S.* **138**, 297 (2002).
 - [5] N. J. Reilly, G. C. Cupitt, S. H. Kable, and T. W. Schmidt, *J. Chem. Phys.* **124**, 194310 (2006), and references therein.
 - [6] M. Nakajima, Y. Sumiyoshi, and Y. Endo, *Chem. Phys. Lett.* **351**, 359 (2002).
 - [7] S.-G He and D. J. Clouthier, *J. Chem. Phys.* **123**, 014317 (2005).
 - [8] M. Nakajima, Y. Sumiyoshi, and Y. Endo, *Chem. Phys. Lett.* **355**, 116 (2002), and references therein.
 - [9] A. Denisov, T. W. Schmidt, A. E. Boguslavskiy, H. Ding, M. Araki, and J. P. Maier, *Int. J. Mass Spectrom.* **233**, 131 (2004).
 - [10] M. Perić, C. M. Marian, and S. D. Peyerimhoff, *J. Chem. Phys.* **114**, 6086 (2001), and references therein.
 - [11] L. Jutier, C. Léonard, and F. Gatti, *J. Chem. Phys.*, (2009) in press.
 - [12] F. J. Mazzotti, R. Chauhan, Z. Jamshidi, M. Tulej, P. P. Radi, and J. P. Maier, *Mol. Phys.* **106**, 2709 (2008).
 - [13] T.H. Dunning, Jr. *J. Chem. Phys.* **90**, 1007 (1989); D.E. Woon and T.H. Dunning, Jr. *J. Chem. Phys.* **98**, 1358 (1993).
 - [14] H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
 - [15] H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).

- 1
2
3 [16] MOLPRO, version 2008.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R.
4 Lindh, F. R. Manby, M. Schtz, and others , see <http://www.molpro.net>.
5
6
7 [17] J. M. Vrtilik, C. A. Gottlieb, E. W. Gottlieb, W. Wang, and P. Thaddeus, *Astrophys. J.* **398**,
8 L73 (1992).
9
10 [18] J. Tang and S. Saito, *J. Chem. Phys.* **105**, 8020 (1996).
11
12 [19] S. -G. He and D. J. Clouthier, *J. Chem. Phys.* **120**, 8544 (2004).
13
14 [20] Y. Liu, C. Duan, J. Liu, L. Wu, C. Xu, Y. Chen, P. A. Hamilton, and P. B. Davies, *J. Chem.*
15 *Phys.* **116**, 9768 (2002).
16
17 [21] J. Senekowitsch, S. Carter, P. Rosmus, and H.-J. Werner, *Chem. Phys.* **147**, 281 (1990).
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TABLE I: Bond distances (Å) and spin-orbit coupling constants A_{SO} (cm^{-1}) in the lowest ${}^2\Pi$ state of CS^+ and linear HC_nS ($n = 1 - 4$).

| System | Bond distances | Basis set | Method | Occupied/Closed ^a | CSF's | Configuration | A_{SO} [Theory] | A_{SO} [Exp.] |
|-------------------|-----------------------|-------------|--------|------------------------------|---------|---|-------------------|---------------------------------------|
| 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 ^g |
| 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 ^h , -270 ⁱ |
| | | cc-pVQZ | HF | | | $7\sigma^2 \dots 11\sigma^2 2\pi^4 3\pi^4 4\pi$ | 129 | |
| HC ₃ 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 ^j |
| | | cc-pVQZ | HF | | | $8\sigma^2 \dots 13\sigma^2 2\pi^4 3\pi^4 4\pi^3$ | -261 | |
| HC ₄ 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 ^k |

^aThe 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.

^bRef.[20].

^cGeometry at the barrier to linearity. Ref.[21].

^dRef.[10].

^eRef.[3].

^fF. J. Mazzotti and Z. Jamshidi, private communication.

^gRef.[20].

^hRef.[17].

ⁱRef.[18].

^jEstimated. Ref.[3].

^kAssumed. Ref.[2].

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

| System | A_{SO} | System | A_{SO} |
|-----------------------|----------|--------------------------|----------|
| CS^+ | -302 | HC_7S | 120 |
| HCS | 136 | HC_8S | -309 |
| HC_2S | -302 | HC_9S | 120 |
| HC_3S | 121 | HC_{10}S | -310 |
| HC_4S | -311 | HC_{11}S | 120 |
| HC_5S | 121 | HC_{12}S | -310 |
| HC_6S | -309 | | |

| n | $r_{\text{C}_n\text{S}}$ | r_{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 |

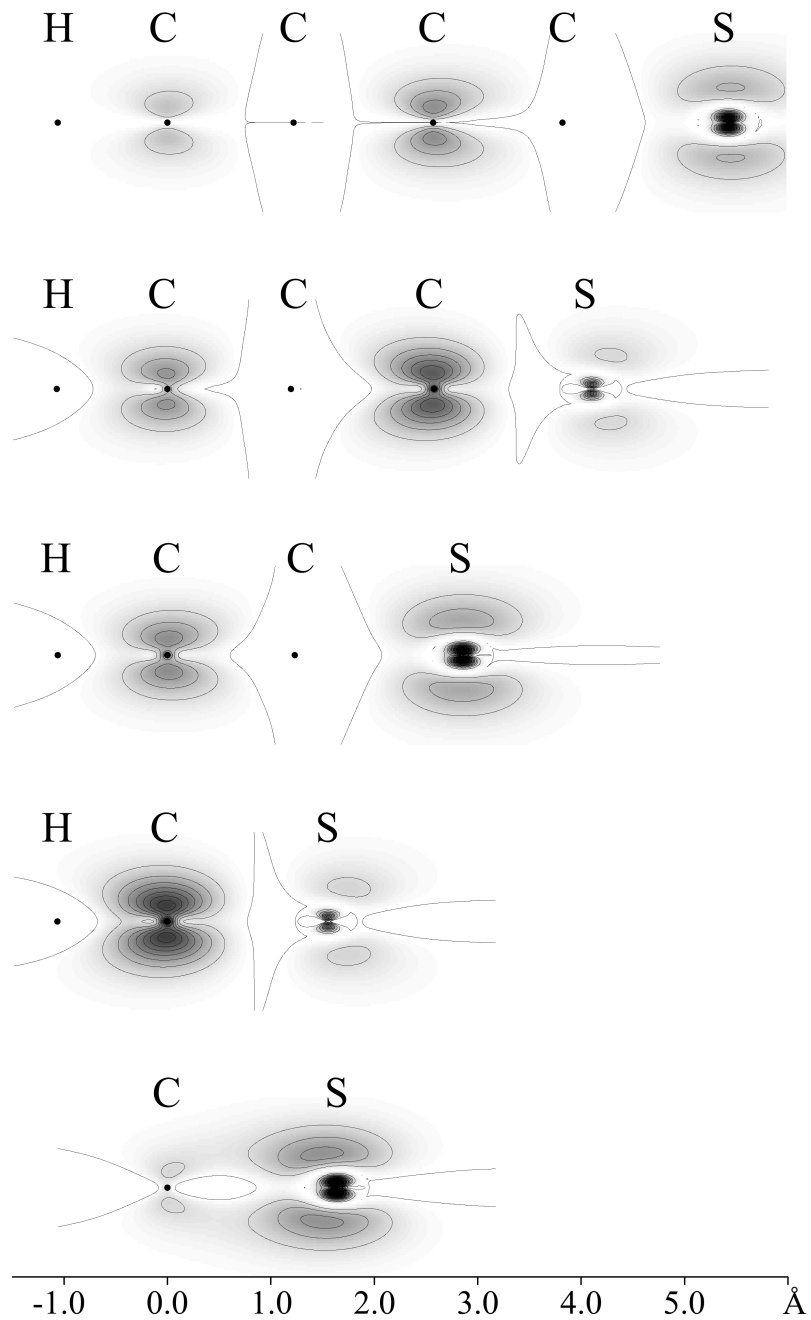
∞

Figure Captions:

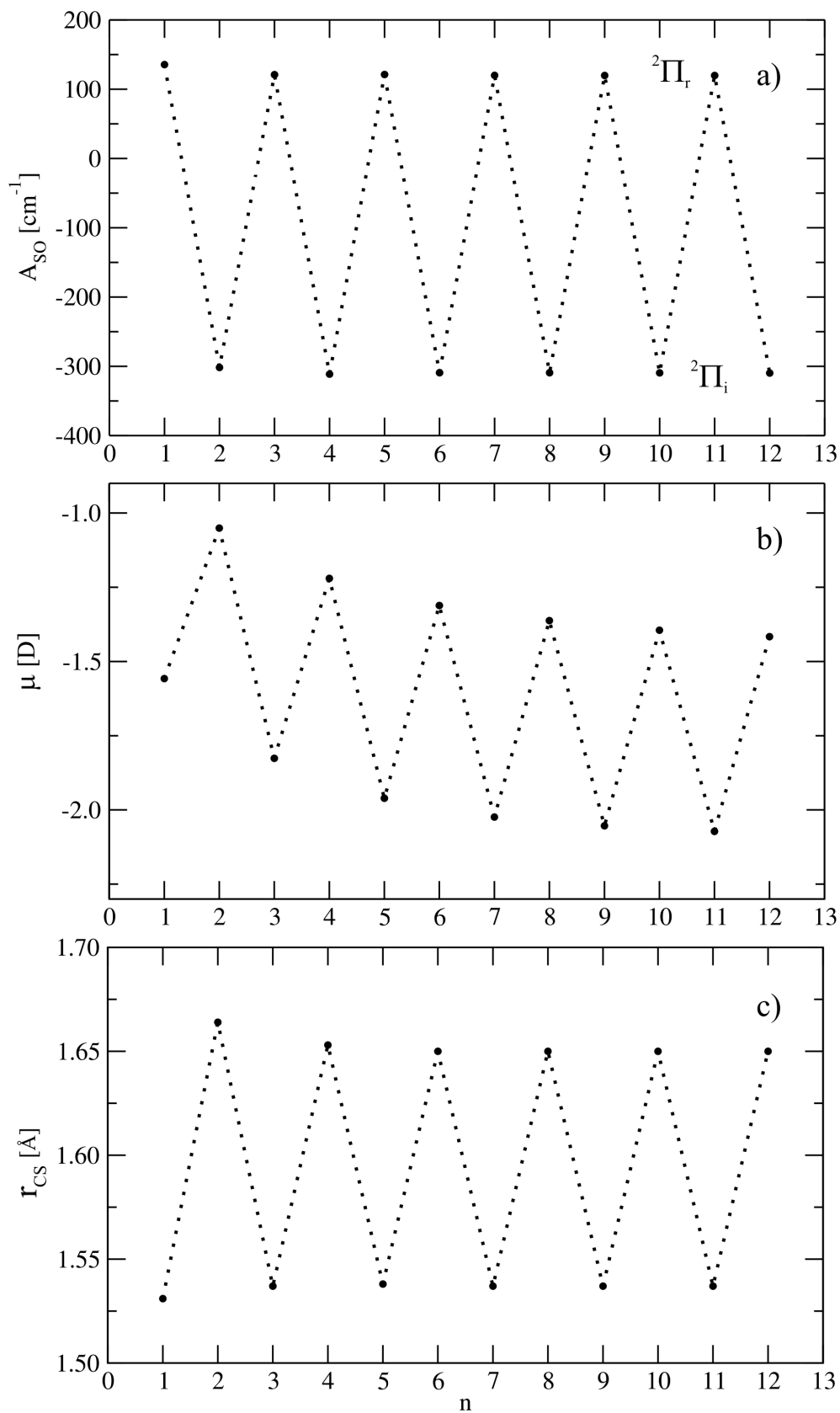
Figure 1: Contour cuts of the electron spin density distribution in CS^+ radical cation and HC_nS chain radicals $n = 1 - 4$. Spin densities are obtained from CASSCF wavefunctions (Table I).

Figure 2: Molecular properties calculated at the HF/cc-pVTZ level for HC_nS chain radicals ($n = 1 - 12$).

- a) Electron spin-orbit coupling constants in 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.



[1] A. Mitrushchenkov *et al.*



[2] A. Mitrushchenkov *et al.*