Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Photoelectron Spectroscopy and Density Functional Calculations of $C_nS_m^-$ (n = 2-7; m = 1, 2) clusters

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Table S1 The relative energies and vertical detachment energies (VDEs) of C_nS^- (n = 2-4) calculated from the B3LYP/6-311+G(3d) and CCSD(T)/aug-cc-pVTZ level of theory.

Isomer		State	Sym.	ΔE(eV)		VDE(eV)	
				B3LYP[a]	CCSD(T)[b]	B3LYP[a]	CCSD(T)[b]
C_2S^-	2A	$^2\Pi$	$C_{\infty v}$	0.00	0.00	2.79	2.81
	2B	$^4A''$	C_s	2.70	2.76	0.80	0.63
C_3S^-	3A	$^2A'$	C_s	0.00	0.00	1.85	1.62
	3B	$^2B_2$	C_{2v}	0.56	0.40	2.74	2.48
	3C	$^4A''$	C_s	2.30	2.36	1.89	1.79
C_4S^-	4A	$^2\Pi$	$C_{\infty v}$	0.00	0.00	3.26	3.37
	4B	$^2B_1$	C_{2v}	1.34	1.20	3.24	3.01
	4C	$^2A''$	C_s	1.87	1.58	3.66	3.48

[a] B3LYP with 6-311+G(3d) basis set.

[b] CCSD(T) with aug-cc-pVTZ basis set.

Table S2 Cartesian coordinates for stable isomers of C_nS^- and $C_nS_2^-$ (n = 2-7) clusters.

C_2S^-

2A

	X	Y	Z
C	0.00000000	0.00000000	-0.66450500
C	0.00000000	0.00000000	-1.93886800
S	0.00000000	0.00000000	0.97626500

2B

	X	Y	Z
C	0.00000000	0.80597800	0.00000000
C	1.33613200	1.24811200	0.00000000
S	-0.50104900	-0.77028400	0.00000000

C_3S^-

3A

	X	Y	Z
C	1.14888400	0.73145400	0.00000000
C	0.00000000	0.12804200	0.00000000
C	2.26275000	1.37512500	0.00000000
S	-1.27936300	-0.83798300	0.00000000

3B

	X	Y	Z
C	0.00000000	0.00000000	-0.32849700
C	0.00000000	0.67567400	-1.58572400
C	0.00000000	-0.67567400	-1.58572400
S	0.00000000	0.00000000	1.31247900

3C

	X	Y	Z
C	1.25557500	0.20213500	0.00000000
C	0.00000000	0.61985600	0.00000000
C	2.53791900	-0.07056000	0.00000000
S	-1.42256000	-0.28178700	0.00000000

C_4S^-

4A

	X	Y	Z
C	0.00000000	0.00000000	0.50417900
C	0.00000000	0.00000000	-0.74594600
C	0.00000000	0.00000000	-2.07585200
C	0.00000000	0.00000000	-3.34369300
S	0.00000000	0.00000000	2.12299200

4B

	X	Y	Z
C	0.00000000	0.00000000	-0.94709500
C	0.00000000	0.00000000	0.33166000
C	0.00000000	0.66930900	-2.27376000
C	0.00000000	-0.66930900	-2.27376000
S	0.00000000	0.00000000	1.93610800

4C

	X	Y	Z
C	0.00000000	-0.43817000	0.00000000
C	-1.31123400	-0.78514800	0.00000000
C	1.31919600	-0.70024500	0.00000000
S	0.94342200	1.13704700	0.00000000
C	-2.52375300	-1.10856300	0.00000000

C_5S^-

5A

	X	Y	Z
C	0.00000000	0.00000000	1.11585200
C	0.00000000	0.00000000	-0.15679300
C	0.00000000	0.00000000	-1.43805600
C	0.00000000	0.00000000	-2.74464600
C	0.00000000	0.00000000	-4.02008100
S	0.00000000	0.00000000	2.71639700

5B

	X	Y	Z
C	0.00000000	0.00000000	-1.63954300
C	0.00000000	0.00000000	-0.30891400
C	0.00000000	0.67462100	-2.90069300
C	0.00000000	-0.67462100	-2.90069300
C	0.00000000	0.00000000	0.94045300
S	0.00000000	0.00000000	2.55352100

5C

C	0.00000000	0.00000000	1.11774700
C	0.00000000	0.00000000	-0.15195700
C	0.00000000	0.00000000	-1.45573600
C	0.00000000	0.00000000	-2.75359400
C	0.00000000	0.00000000	-4.06144300
S	0.00000000	0.00000000	2.73936900

C_6S^-

6A

	X	Y	Z
C	0.00000000	0.00000000	-3.42292500
C	0.00000000	0.00000000	-2.09794500
C	0.00000000	0.00000000	-0.84922300
C	0.00000000	0.00000000	0.46673000
C	0.00000000	0.00000000	1.71875200
C	0.00000000	0.00000000	-4.68926500
S	0.00000000	0.00000000	3.32770400

6B

	X	Y	Z
C	0.00000000	0.00000000	-0.97781000
C	0.00000000	0.00000000	0.31987200
C	0.00000000	0.00000000	1.58061800
C	0.00000000	0.00000000	-2.26093000
C	0.00000000	0.66742900	-3.57627900
C	0.00000000	-0.66742900	-3.57627900
S	0.00000000	0.00000000	3.18405300

6C

C	1.68454600	-2.89787900	0.00000000
C	1.10774600	-1.74501100	0.00000000
C	0.53541100	-0.57108600	0.00000000
C	0.00000000	0.56577700	0.00000000
C	-0.49438300	1.80744900	0.00000000
C	2.26123100	-4.05837200	0.00000000
S	-1.91045700	2.58717100	0.00000000

C_7S^-

7A

	X	Y	Z
C	0.00000000	0.00000000	-2.76743500
C	0.00000000	0.00000000	-1.49961500
C	0.00000000	0.00000000	-0.21519700
C	0.00000000	0.00000000	1.07319400
C	0.00000000	0.00000000	2.33971800
C	0.00000000	0.00000000	3.93666300
C	0.00000000	0.00000000	-4.07878100
S	0.00000000	0.00000000	-5.34965400

7B

	X	Y	Z
C	0.00000000	0.00000000	-1.61083400
C	0.00000000	0.00000000	-0.36015900
C	0.00000000	0.00000000	0.95055000
C	0.00000000	0.00000000	-2.93784600
C	0.00000000	0.67385000	-4.20014800
C	0.00000000	-0.67385000	-4.20014800
C	0.00000000	0.00000000	2.20296700
S	0.00000000	0.00000000	3.80835700

7C

C	0.00000000	0.00000000	-2.78516800
C	0.00000000	0.00000000	-1.50040900
C	0.00000000	0.00000000	-0.22316900
C	0.00000000	0.00000000	1.08143500
C	0.00000000	0.00000000	2.34495100
S	0.00000000	0.00000000	3.95705900
C	0.00000000	0.00000000	-4.08921200
C	0.00000000	0.00000000	-5.38058700

$C_2S_2^-$

2A'

	X	Y	Z
C	0.00000000	0.00000000	0.62434600
S	0.00000000	0.00000000	2.25877200
C	0.00000000	0.00000000	-0.62434600
S	0.00000000	0.00000000	-2.25877200

2B'

	X	Y	Z
C	0.00000000	0.39687100	0.00000000
C	-1.28577700	0.78145900	0.00000000
S	-1.14979100	-1.09113400	0.00000000
S	1.63195700	0.64926000	0.00000000

2C'

S	-1.55827100	-0.57014600	0.00000000
C	2.67992600	-0.38765500	0.00000000
C	1.47546200	-0.02152900	0.00000000
S	0.00000000	0.72359000	0.00000000

$C_3S_2^-$

3A'

	X	Y	Z
C	0.00000000	0.00000000	1.27855100
S	0.00000000	0.00000000	2.88743300
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-1.27855100
S	0.00000000	0.00000000	-2.88743300

3B'

	X	Y	Z
C	0.00000000	0.74165600	0.48321700
C	0.00000000	0.00000000	1.64617400
C	0.00000000	-0.74165600	0.48321700
S	0.00000000	2.06533300	-0.48986400
S	0.00000000	-2.06533300	-0.48986400

3C'

C	0.00000000	0.00000000	0.15840100
C	0.00000000	0.00000000	1.53105600
C	0.00000000	0.00000000	2.78573200
S	0.00000000	1.38723700	-0.83909800
S	0.00000000	-1.38723700	-0.83909800

$C_4S_2^-$

4A'

	X	Y	Z
C	0.00000000	0.00000000	1.91125900
C	0.00000000	0.00000000	0.66110500
C	0.00000000	0.00000000	-0.66110500
C	0.00000000	0.00000000	-1.91125900
S	0.00000000	0.00000000	3.53037000
S	0.00000000	0.00000000	-3.53037000

4B'

	X	Y	Z
C	0.00000000	0.42910300	0.00000000
C	1.08041400	1.04575500	0.00000000
C	-1.12602600	-0.30008700	0.00000000
C	-2.45623900	-0.48810900	0.00000000
S	-1.54014600	-2.11912100	0.00000000
S	2.47834100	1.86162300	0.00000000

4C'

C	0.00000000	1.95110900	0.49730900
C	0.00000000	0.62910600	0.38477400
C	0.00000000	-0.62910600	0.38477400
C	0.00000000	-1.95110900	0.49730900
S	0.00000000	3.34509200	-0.33078100
S	0.00000000	-3.34509200	-0.33078100

$C_5S_2^-$

5A'

	X	Y	Z
C	0.00000000	0.00000000	2.55663100
C	0.00000000	0.00000000	1.28940300
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-1.28940300
C	0.00000000	0.00000000	-2.55663100
S	0.00000000	0.00000000	4.16157600
S	0.00000000	0.00000000	-4.16157600

5B'

	X	Y	Z
C	0.00000000	0.00000000	2.56861200
C	0.00000000	0.00000000	1.29731700
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-1.29731700
C	0.00000000	0.00000000	-2.56861200
S	0.00000000	0.00000000	4.18766600
S	0.00000000	0.00000000	-4.18766600

5C'

C	0.00000000	0.00000000	-0.76973200
C	0.00000000	0.00000000	0.60013000
S	0.00000000	1.40210500	-1.73640500
S	0.00000000	-1.40210500	-1.73640500
C	0.00000000	0.00000000	1.83650600
C	0.00000000	0.00000000	3.16778900
C	0.00000000	0.00000000	4.42613200

$C_6S_2^-$

6A'

	X	Y	Z
C	0.00000000	0.00000000	3.19231500
C	0.00000000	0.00000000	1.94035500
C	0.00000000	0.00000000	0.62531900
C	0.00000000	0.00000000	-0.62531900
C	0.00000000	0.00000000	-1.94035500
S	0.00000000	0.00000000	4.80259400
C	0.00000000	0.00000000	-3.19231500
S	0.00000000	0.00000000	-4.80259400

6B'

	X	Y	Z
C	0.58643900	3.11676000	0.00000000
C	0.28985900	1.87077700	0.00000000
C	0.00000000	0.62812500	0.00000000
C	-0.30568600	-0.64511800	0.00000000
C	-0.61052200	-1.86530900	0.00000000
S	0.94786000	4.67585200	0.00000000
C	-1.02622800	-3.12524700	0.00000000
S	-0.54805900	-4.66834700	0.00000000

6C'

C	-0.88777000	-0.49919700	0.00000000
C	0.00000000	0.36935400	0.00000000
C	0.93157400	1.30239600	0.00000000
C	-1.81132800	-1.47497200	0.00000000
C	-3.07715000	-1.93300200	0.00000000
S	-1.81017200	-3.31224400	0.00000000
C	1.81219600	2.18784600	0.00000000
S	2.94735100	3.33008500	0.00000000

$C_7S_2^-$

7A'

	X	Y	Z
C	0.00000000	0.00000000	2.57136800
C	0.00000000	0.00000000	1.27713100
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-1.27713100
C	0.00000000	0.00000000	-2.57136800
C	0.00000000	0.00000000	-3.83410400
S	0.00000000	0.00000000	-5.43485800
C	0.00000000	0.00000000	3.83410400
S	0.00000000	0.00000000	5.43485800

7B'

	X	Y	Z
C	0.00000000	0.00000000	2.58148800
C	0.00000000	0.00000000	1.28069600
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-1.28069600
C	0.00000000	0.00000000	-2.58148800
C	0.00000000	0.00000000	-3.84600700
S	0.00000000	0.00000000	-5.45681400
C	0.00000000	0.00000000	3.84600700
S	0.00000000	0.00000000	5.45681400

7C'

C	0.00000000	0.00000000	-1.80915600
C	0.00000000	0.00000000	-0.43475200
S	0.00000000	1.41154000	-2.75361700
S	0.00000000	-1.41154000	-2.75361700
C	0.00000000	0.00000000	0.80054300
C	0.00000000	0.00000000	2.12309400
C	0.00000000	0.00000000	3.36478800
C	0.00000000	0.00000000	4.69047600
C	0.00000000	0.00000000	5.95096500

Table S3 Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km/mol) (in parentheses) of the most stable isomers of C_nS (n = 2-7) at the B3LYP/6-311+G(3d) level of theory. The frequencies labeled in bold are π modes.

clusters	Vibrational frequency (Infrared intensiy)
C_2S ($^3\sum^-$)	1714(48); 862(13); **276(7)**
C_3S ($^1\sum^+$)	2127(1598); 1562(67); 739(12); **493(0)**; **160(4)**.
C_4S ($^3\sum^-$)	2098(44); 1801(541); 1221 (3); 611 (6); **500(0)**; **319(6)**; **127(5)**.
C_5S ($^1\sum^+$)	2219(4150); 2073(0); 1649(635); 1088(76); 5**79(3)**; 542(6); **456(0)**; **213(5)**; **85(3)**.
C_6S ($^3\sum^-$)	2113(68); 2074(1518); 1827(13); 1405(272); 936(29); **560(0)**; 475(4); **469(0)**; **338(1)**; **183(6)**; **70(3)**.
C_7S ($^1\sum^+$)	2215(513); 2191(5737); 1996(3131); 1705(147); 1281(263); 853(87); **594(5)**; **530(0)**; 4**41(0)**; 430(3); **244(2)**; **138(4)**; **52(2)**.

Table S4 Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km/mol) (in parentheses) of the most stable isomers of C_nS_2 (n = 2-7) at the B3LYP/ B3LYP/6-311+G(3d) level of theory. The frequencies labeled in bold are π modes.

clusters	Vibrational frequency (Infrared intensiy)
C_2S_2 ($^3\sum_g^-$)	1958(0); 1182(132); 553(0); **420(0)**; **176(1).**
C_3S_2 ($^1\sum_g^+$)	2153(3166); 1713(0); 1037(353); **505(0)**; 501(0); **415(0)**; **98(0)**.
C_4S_2 ($^3\sum_g^-$)	2116(0); 1927(845); 1411(0); 883(156); **511(0)**; 440(0); **425(1)**; **252(0)**; **79(0)**.
C_5S_2 ($^1\sum_g^+$)	2191(6176); 2117(0); 1726(1646); 1276(0); 807(273); **562(2)**; **474(0)**; **417(1)**; 404(0); **165(0)**; **54(0)**.
C_6S_2 ($^3\sum_g^-$)	2111(2051); 2089(0); 1910(0); 1521(635); 1118(0); 721(159); **552(0)**; **486(0)**; **421(0)**; 365(0); **293(1)**; **138(0)**; **46(0)**.
C_7S_2 ($^1\sum_g^+$)	2215(0); 2162(6267); 2024(7163); 1762(0); 1399(1098); 1031(0); 670(233); **586(3)**; **528(0)**; **459(1)**; **417(0)**; 339(0); **209(0)**; **104(0)**; **35(0)**.