

## *Supplementary Information*

### **Structural and Electronic Properties of $\text{HC}_n\text{S}^-$ ( $n = 4-11$ ): Anion Photoelectron Spectroscopy and Density Functional Calculations**

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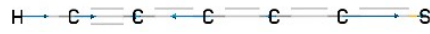


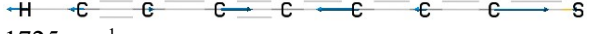



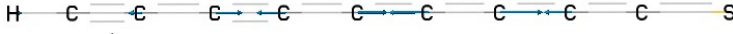


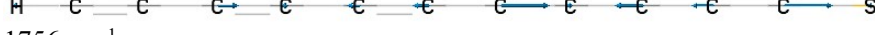

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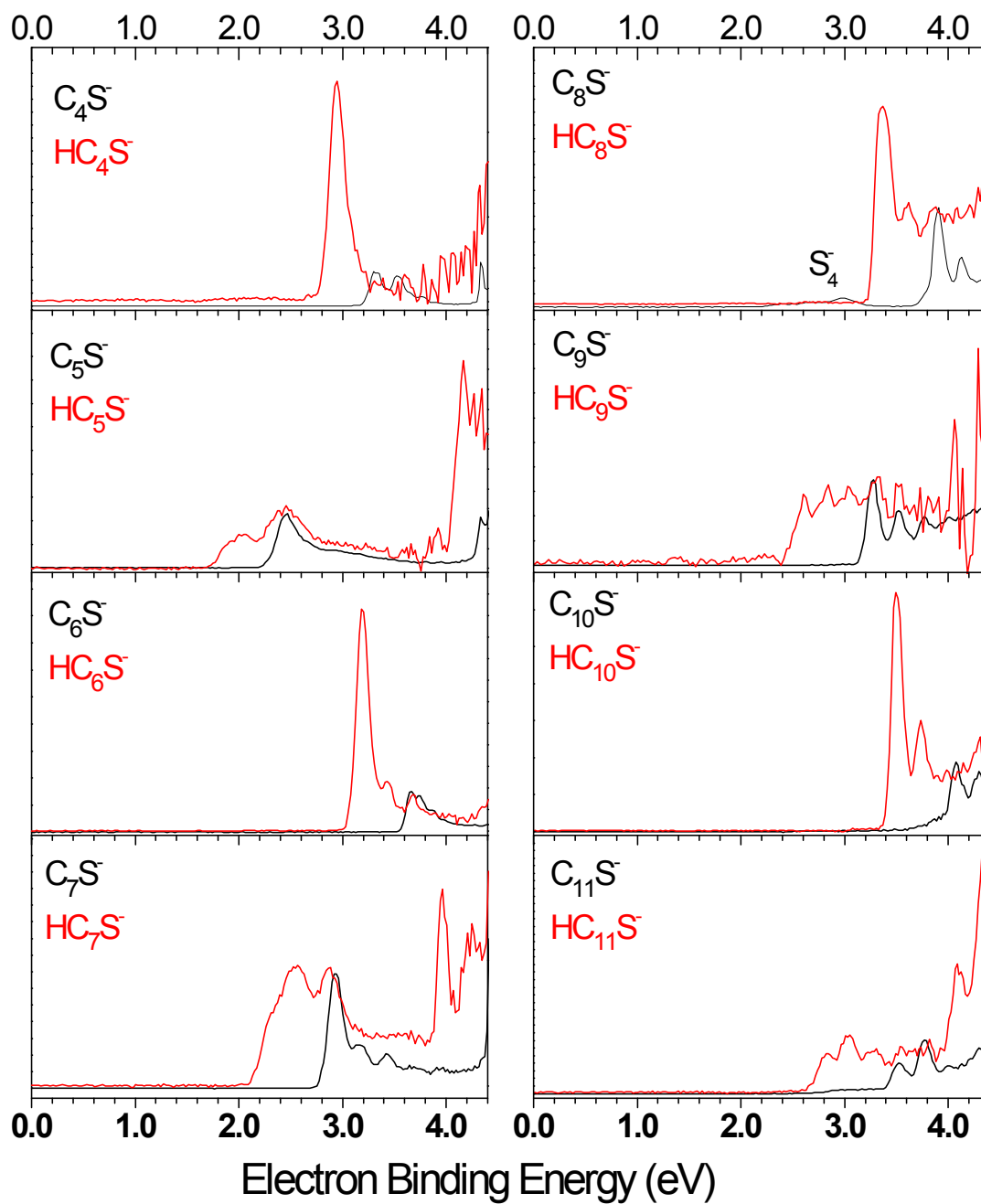
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**Table S1.** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) and infrared intensities ( $\text{km/mol}$ ) (in parentheses) of the most stable isomers of  $\text{HC}_n\text{S}$  ( $n = 4-11$ ) at the B3LYP/aug-cc-pVTZ level of theory.

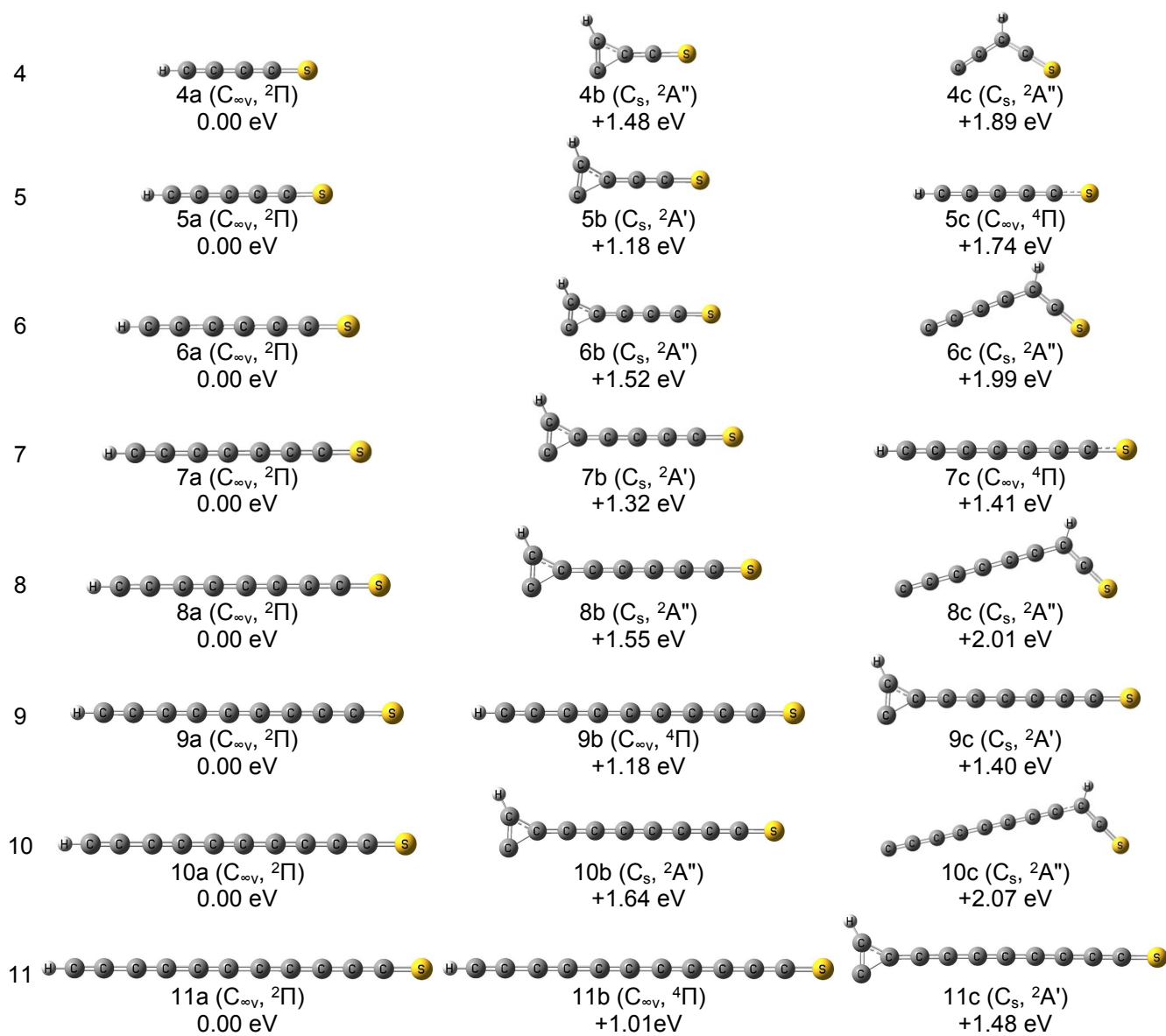
Isomers	Vibrational frequencies (Infrared intensity)
$\text{HC}_4\text{S}$ ( $^2\Pi$ )	3458 (123); 2069 (0.1); 1979 (54); 1183 (38); 678 (29); 583 (3); 530 (3); 521 (55); 470 (5); 390 (0); 365 (1); 130 (2); 120 (3).
$\text{HC}_5\text{S}$ ( $^2\Pi$ )	3458 (167); 2081 (111); 2027 (334); 1678 (226); 1053 (79); 717 (29); 574 (2); 526 (4); 490 (2); 443 (38); 400 (22); 369 (2); 261 (1); 220 (0); 92 (1); 84 (2).
$\text{HC}_6\text{S}$ ( $^2\Pi$ )	3459 (166); 2144 (71); 2060 (9); 1941 (209); 1369 (43); 908 (54); 677 (33); 575 (1); 569 (50); 517 (3); 501 (0); 460 (1); 459 (3); 392 (2); 371 (3); 196 (1); 185 (1); 69 (1); 66 (1).
$\text{HC}_7\text{S}$ ( $^2\Pi$ )	3459 (222); 2158 (337); 2083 (47); 1952 (708); 1725 (399); 1248 (79); 830 (76); 697 (338); 603 (33); 540 (1); 528 (52); 475 (2); 469 (0); 433 (0); 420 (2); 391 (0); 290 (20); 266 (1); 151 (1); 146 (1); 53 (0.5); 53 (0.8).
$\text{HC}_8\text{S}$ ( $^2\Pi$ )	3460 (215); 2192 (114); 2131 (175); 2005 (125); 1905 (276); 1464 (111); 1115 (40); 742 (59); 693 (0); 674 (35); 651 (1); 597 (50); 557 (0); 519 (0); 486 (2); 451 (0); 394 (0); 377 (2); 375 (0); 237 (2); 225 (2); 122 (1); 118 (0); 43 (0); 42 (1).
$\text{HC}_9\text{S}$ ( $^2\Pi$ )	3460 (272); 2186 (141); 2149 (432); 2063 (504); 1877 (901); 1746 (603); 1363 (161); 1031 (65); 749 (1); 689 (71); 684 (35); 669 (0); 603 (0); 575 (49); 527 (1); 520 (0); 462 (1); 452 (0); 400 (1); 350 (1); 311 (1); 294 (0); 194 (1); 190 (2); 100 (0); 100 (0); 35 (0); 35 (0).
$\text{HC}_{10}\text{S}$ ( $^2\Pi$ )	3461 (265); 2214 (0); 2169 (330); 2100 (321); 1997 (348); 1837 (289); 1521 (117); 1244 (114); 941 (37); 669 (37); 630 (59); 615 (46); 556 (1); 547 (0); 521 (0); 508 (1); 493 (2); 475 (0); 462 (0); 432 (0); 391 (1); 369 (1); 319 (1); 261 (1); 248 (0); 163 (1); 157 (1); 83 (0); 81 (0); 29 (0); 29 (0).
$\text{HC}_{11}\text{S}$ ( $^2\Pi$ )	3461 (320); 2212 (28); 2162 (104); 2117 (1469); 2058 (283); 1800 (748); 1756 (13593); 1437 (152); 1168 (158); 881 (55); 675 (37); 602 (46); 598 (1); 591 (65); 587 (1); 534 (0); 531 (0); 497 (1); 488 (0); 468 (1); 446 (0); 430 (0); 395 (0); 316 (1); 305 (1); 299 (0); 222 (0); 218 (0); 137 (1); 137 (1); 71 (0); 70 (0); 25 (0); 25 (0).

**Table S2.** Forms of the calculated vibration modes of  $\text{HC}_n\text{S}$  ( $n = 4, 6-11$ ), corresponding to the observed vibrational progressions.

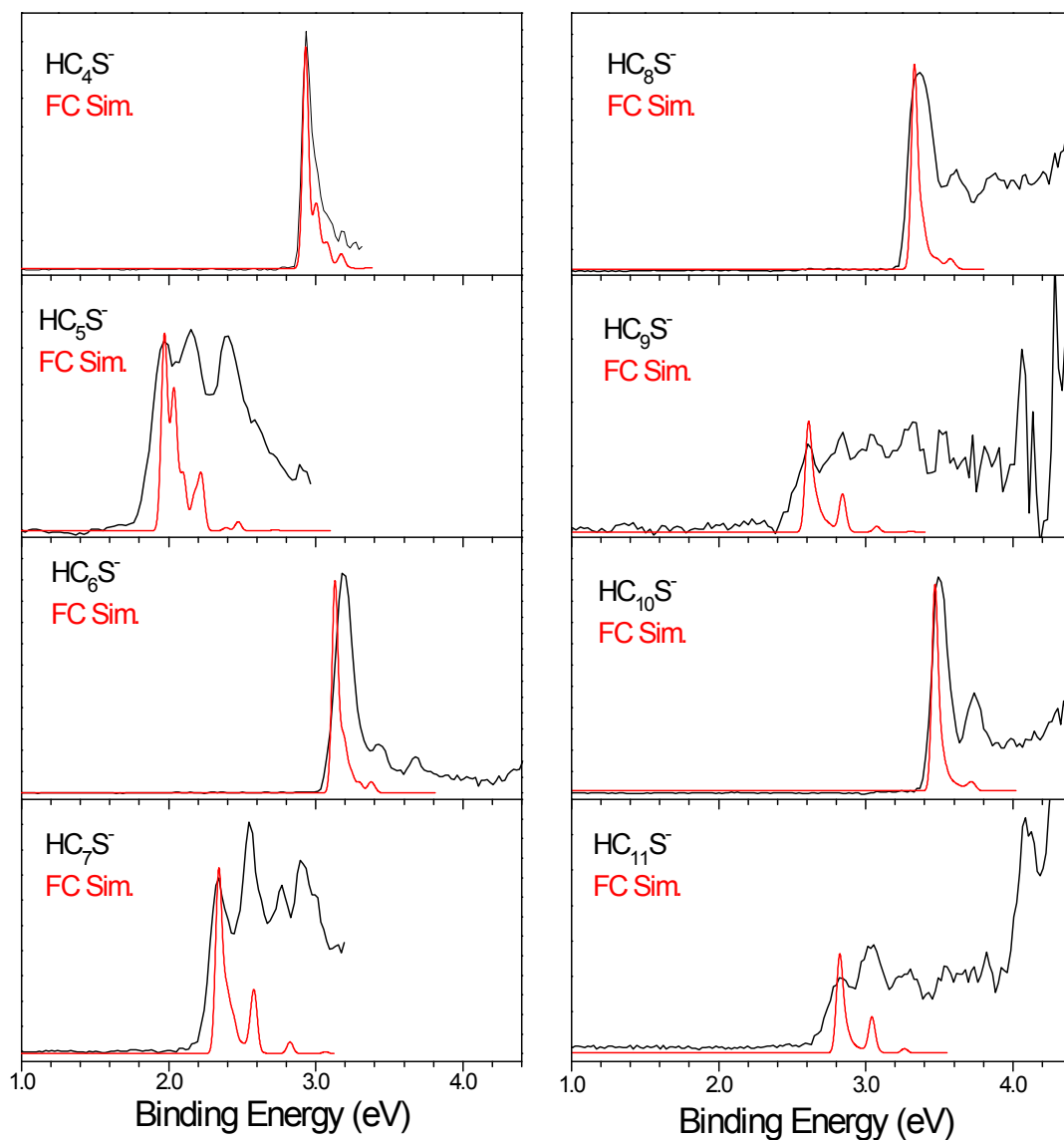
cluster	Vibration mode
$\text{HC}_4\text{S}$	 1979 $\text{cm}^{-1}$
$\text{HC}_5\text{S}$	 1678 $\text{cm}^{-1}$
$\text{HC}_6\text{S}$	 1941 $\text{cm}^{-1}$  2144 $\text{cm}^{-1}$
$\text{HC}_7\text{S}$	 1725 $\text{cm}^{-1}$  1952 $\text{cm}^{-1}$
$\text{HC}_8\text{S}$	 1905 $\text{cm}^{-1}$
$\text{HC}_9\text{S}$	 1746 $\text{cm}^{-1}$  1877 $\text{cm}^{-1}$
$\text{HC}_{10}\text{S}$	 1837 $\text{cm}^{-1}$  2100 $\text{cm}^{-1}$
$\text{HC}_{11}\text{S}$	 1756 $\text{cm}^{-1}$  1800 $\text{cm}^{-1}$



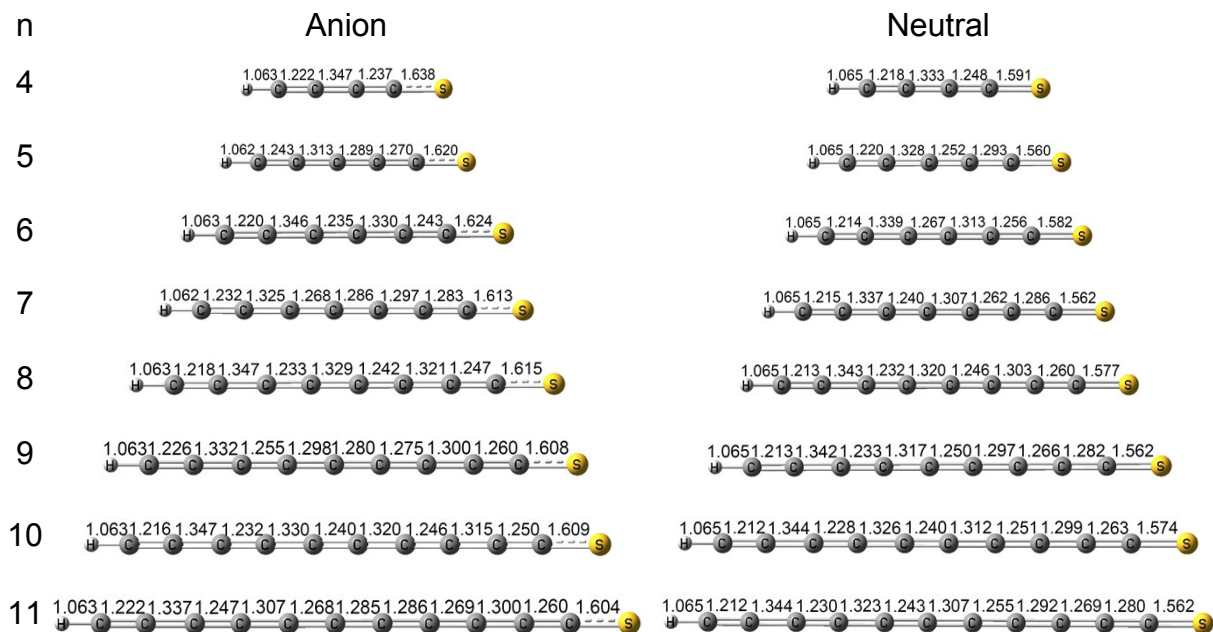
**Fig. S1** Comparison of photoelectron spectra of  $\text{HC}_n\text{S}^-$  and  $\text{C}_n\text{S}^-$  ( $n = 4-11$ ) clusters taken with 266 nm photons. The red lines represent the spectra of  $\text{HC}_n\text{S}^-$  clusters and the black lines represent the spectra of  $\text{C}_n\text{S}^-$  clusters. The photoelectron spectra of  $\text{C}_n\text{S}^-$  ( $n = 8-11$ ) clusters obtained by us have not been reported.



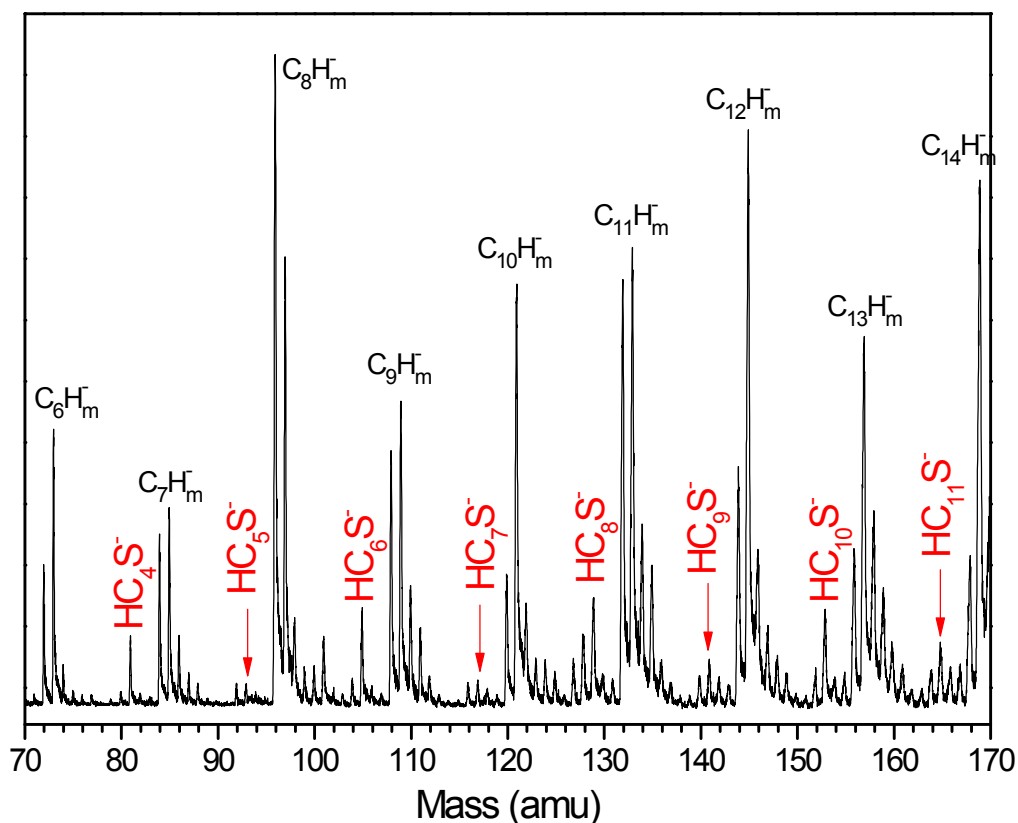
**Fig. S2** Geometries, electronic states, and relative energies of the low-lying isomers of  $HC_nS$  ( $n = 4-11$ ) neutrals.



**Fig. S3** Comparison of Franck-Condon simulations with the experimental spectra. The black lines represent the photoelectron spectra of  $\text{HC}_n\text{S}^-$  ( $n = 4-11$ ) clusters. The red lines come from the Franck-Condon simulations.



**Fig. S4** Bond lengths of the most stable isomers of the anionic and neutral  $\text{HC}_n\text{S}$  ( $n = 4-11$ ) clusters. The bond lengths are in angstrom.



**Fig. S5** A typical mass spectrum of  $HC_nS^-$  ( $n = 4-11$ ) cluster anions. The major series of the mass peaks is that of  $C_nH_m^-$  ( $n = 6-14$ ;  $m \geq 0$ ) while the minor series is that of  $H_mC_nS^-$  ( $m \geq 0$ ;  $n = 4-11$ ). The assignments of the mass peaks were carefully confirmed by the natural isotopic distributions of the C and S elements. For the  $H_mC_nS^-$  ( $m \geq 0$ ;  $n = 4-11$ ) series, we only assigned the  $HC_nS^-$  ( $n = 4-11$ ) clusters. The ion intensities of  $HC_nS^-$  ( $n = 4-11$ ) are high enough for us to proceed with the photoelectron spectroscopic study although their mass peaks are relatively weak compared with those of  $C_nH_m^-$ .