

Electronic Absorption Spectra of C₅S, C₆S, and C₆S⁻ in Neon Matrixes

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Electronic absorption spectra of C₅S, C₆S, and C₆S⁻ have been observed in 6 K matrixes after co-deposition of mass-selected ions with excess of neon. The ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ electronic transition of C₅S, ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ of C₆S, and B ${}^2\Pi \leftarrow X {}^2\Pi$ of the C₆S⁻ anion are detected with origin bands at 284, 574, and 608 nm, respectively. The band systems of the neutral chains show vibrational structure to higher energy of the origins which is assigned to the excitation of modes in the upper electronic states.

Introduction

Carbon-chain molecules terminated with a sulfur atom C_nS represent an interesting field for investigation of the electronic properties with implications for nanoscience¹ and play a role in the chemistry of the interstellar medium.² The smaller members of this series C_nS *n* = 1–5 have already been identified in dense interstellar clouds or in the envelope of carbon stars based on the laboratory microwave data.³ Chemical models for a number of dense interstellar clouds suggest that the C_nS species with *n* > 5 may also occur therein.^{4,5} Their detection by mm wave spectroscopy is favored because of their unusually large dipole moments, in the range 3–5 D.

The structural and energetic characteristics of the low lying excited states of the C_nS polyatomics have been studied by electronic spectroscopy in the gas phase for C₂S by laser induced fluorescence,⁶ and in neon matrixes for C₂S and C₂S⁻⁷ and C₄S and C₄S⁻.⁸ The experimental information in the literature on the larger chains C_nS *n* = 4–9 comes mainly from gas-phase rotational spectra.³ Also a few infrared vibrations have been observed in argon matrixes for C_nS *n* = 1–5.⁹ In the latter work as well as in that of ref 10 on C_nS *n* = 2–9, theoretically predicted vibrational frequencies and bonding characteristics in the ground electronic states are given. Neither theoretical nor experimental investigations on the electronic excited states of these molecules with *n* > 4 have been performed. In the present work, the C₅S, C₆S, and C₆S⁻ species have been isolated in neon matrixes following mass selection and their electronic absorption spectra measured and assigned.

Experimental Section

The C_nS species were produced and studied employing the same methods as described.¹¹ A cesium sputter ion source was used to generate the C₅S⁻ and C₆S⁻ anions from a graphite rod and CS₂. The anions were then mass selected and co-deposited with neon during 4 h at a 6 K temperature. Ion currents of 0.3 and 0.7 nA were achieved for C₅S⁻ and C₆S⁻, respectively. The light of a medium-pressure mercury lamp (~5.4 eV) was used to produce the neutral species by electron detachment. The 220–1100 nm region was scanned before and after the photobleaching.

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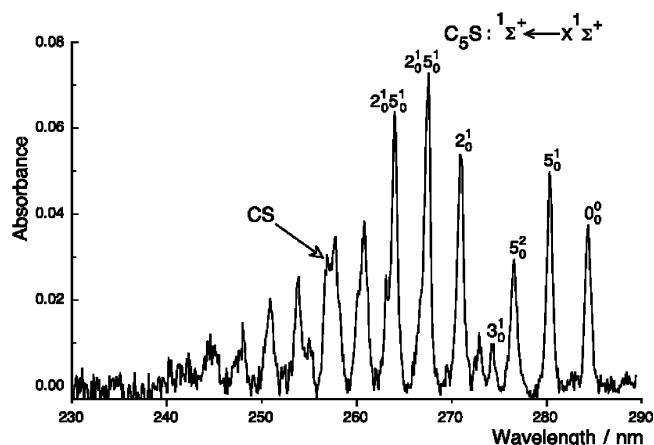


Figure 1. Electronic absorption spectrum of the ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ electronic transition of C₅S observed after mass-selected co-deposition with neon to form a 6 K matrix followed by exposure to the UV radiation.

Depending on the ion kinetic energy chosen, fragmentation can take place. Numerous experiments in the past have shown that this can lead to the detection of diatomic species, in the present case CS, C₂⁺. Polyatomic fragments are not usually observed; thus, though the spectra of C₂S/C₂S⁻ and C₄S/C₄S⁻ are known,^{7,8} they are not detected. To observe the latter species, their masses have to be selected for the co-deposition.

Results and Discussion

After co-deposition of mass selected C₅S⁻ with an excess of neon to produce a matrix containing the isolated ions at 6 K, only the known A ${}^1\Pi \leftarrow X {}^1\Sigma^+$ origin band of CS, near 258 nm, was observed. This diatomic is formed when the C₅S⁻ ions hit the matrix surface with ~60 eV kinetic energy. No other absorptions were detected. However, exposure to UV radiation produced an intense system at 284 nm (Figure 1). The band system which appears after photodetachment of the electron from C₅S⁻ is due the neutral C₅S.

The electronic ground state of linear C₅S has ${}^1\Sigma^+$ symmetry¹⁰ and the relevant π electron configuration is ... $4\pi^4$. The X ${}^2\Pi$ ground electronic state of C₅S⁻ then corresponds to ... $4\pi^4 5\pi^1$. The lowest, dipole accessible, excited electronic state of C₅S and C₅S⁻ involves the $5\pi^* \leftarrow 4\pi$ electron promotion and the transition energies will lie in a similar wavelength region. Because C₅S is a closed shell species, it is not surprising that

TABLE 1: Positions of the Band Maxima (± 0.2 nm) Observed for the ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ Electronic Transition of C₅S in a 6 K Neon Matrix

λ/nm	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
284.3	35169	0	0_0^0
280.3	35672	503	5_0^1
276.5	36160	991	5_0^2
274.3	36458	1289	3_0^1
272.9	36650	1481	5_0^3
271.0	36903	1734	2_0^1
269.5	37107	1938	5_0^4
267.5	37384	2215	$2_0^1 5_0^1$
264.0	37881	2712	$2_0^1 5_0^2$
260.8	38343	3174	
257.7	38800	3631	
253.8	39399	4230	
250.9	39861	4692	
248.0	40327	5158	
244.6	40889	5720	

the expected, strong, ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ electronic transition lies in the UV, with observed origin near 284 nm in a neon matrix (Figure 1). The electronic transition of C₅S⁻ corresponding to the same electron excitation should lie nearby. The reason no band system is observed after mass-selected co-deposition is probably because the excited electronic state (c.a. 4 eV above the ground state) lies above the electron detachment threshold of C₅S⁻. Thus, there is no bound excited-state accessible. On photodetachment of the electron, however, the ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ band system of the neutral C₅S is detected.

The electronic absorption spectrum of C₅S shows rich vibrational structure. It is dominated by the excitation of two vibrational progressions (and their combinations), one with a frequency around 500 cm⁻¹ and the other with 1734 cm⁻¹. These vibrations are excited in the upper ${}^1\Sigma^+$ electronic state because only the zero-point energy level in the electronic ground state is populated in the neon matrix at 6 K. These clearly involve the totally symmetric modes, and comparison with the frequencies calculated for the X ${}^1\Sigma^+$ electronic ground state of the molecule ($\nu_1 = 2178$, $\nu_2 = 2013$, $\nu_3 = 1594$, $\nu_4 = 1091$, $\nu_5 = 543$ cm⁻¹)¹⁰ shows that the 503 cm⁻¹ spacing is due to the ν_5 mode, essentially the C–S stretch, and the 1734 cm⁻¹ one is probably the ν_2 mode (asymmetric stretching motions of the C–C bonds). Because the $5\pi^* \leftarrow 4\pi$ electron excitation is from a bonding to less bonding orbital, a lowering of the C–C stretch frequencies is expected (and the theoretical values are usually too high though the experimentally determined value of $\nu_1 = 2124$ cm⁻¹ in the X ${}^1\Sigma^+$ electronic state⁹ agrees well with the theory value of 2178 cm⁻¹).¹⁰ In addition, the excitation of the ν_3 mode (1289 cm⁻¹), though weaker, is seen. The assignments are given in Table 1 where the maxima of the bands in the spectrum of Figure 1 are summarized. Below around 260 nm, the bands become broader, show irregularities, and thus, assignment is not given.

In the case of C₆S⁻ mass selection, three absorption bands were observed at 530, 608, and 574 nm in the 6 K neon matrix (bottom trace Figure 2). The first of these is the origin band of the B ${}^2\Sigma_u^+ \leftarrow X {}^2\Sigma_g^+$ electronic transition of C₂⁻,¹² produced by fragmentation during co-deposition, but the other two are new, unknown absorptions. Exposure of the matrix to the UV light resulted in the disappearance of the 608 nm band and concurrently to a considerable increase in intensity of the one at 574 nm. Moreover, a number of new bands appeared between 490 and 580 nm which belong to the same system, with the 574 nm band being its origin. In view of the mass selection and the photodetachment behavior upon UV irradiation, the 574 nm band is associated with C₆S whereas the 608 nm with the

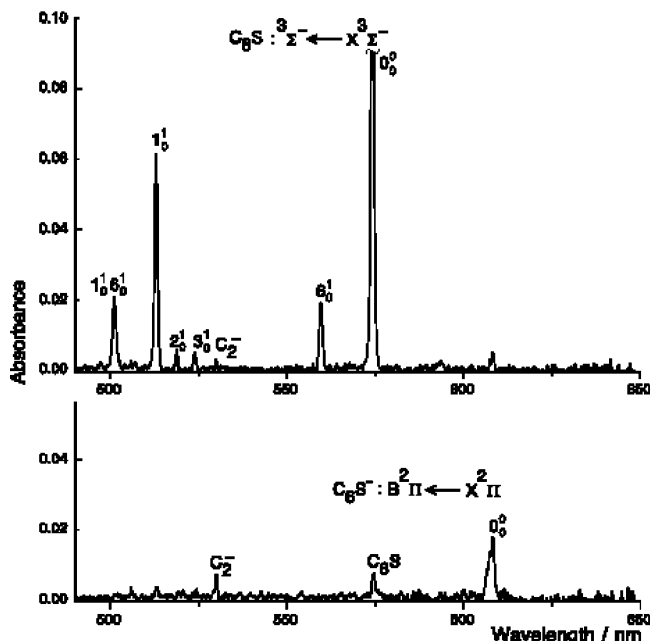


Figure 2. Electronic absorption spectra of the ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ and B ${}^2\Pi \leftarrow X {}^2\Pi$ electronic transitions of C₆S and C₆S⁻ observed after mass-selected co-deposition with neon to form a 6 K matrix (bottom trace) and subsequent UV irradiation (top trace).

C₆S⁻ anion. Consideration of the electron configurations of the electronic states involved supports this interpretation. The ground state of C₆S is a triplet X ${}^3\Sigma^- \dots 4\pi^4 5\pi^2$ and that of C₆S⁻ a doublet X ${}^2\Pi \dots 4\pi^4 5\pi^3$. The excited electronic states in both cases have as an important contribution the configuration involving the $5\pi \leftarrow 4\pi$ promotion, i.e., within the bonding orbital manifold. Thus, it is not surprising that the electronic transitions lie energetically nearby as Figure 2 shows, and in the visible rather than in the UV as for C₅S with the $5\pi^* \leftarrow 4\pi$ bonding–antibonding electron promotion.

In a homologous series such as C_{2n}S or C_{2n}S⁻, the molecules usually possess (for larger *n*) the same electronic ground-state symmetry and similar sets of excited states. In addition, the wavelength of the origin band of the same electronic transition within a series is blue shifted as *n* decreases and a monotonic trend should be apparent. The trend is linear for cumulenic systems (i.e., similar bond lengths) such as the carbon chains C_n¹³ but shows curvature for alternating bond distances (e.g., polyenes HC_{2n}H *n* = 8–13).¹⁴ The C_{2n}S chains (*n* < 9) have been shown to be cumulenic like.^{3,10}

The electronic spectra of C₂S⁷ and C₄S⁸, identified previously in neon matrixes, show origin bands in their ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ transition and at 327 and 447 nm, respectively. A linear extrapolation of the wavelength versus number of chain atoms leads to the prediction that C₆S would absorb near 570 nm, exactly as observed (Figure 2), confirming the symmetry assignment. The anions C₂S⁻ and C₄S⁻ have the origin bands of the B ${}^2\Pi \leftarrow X {}^2\Pi$ electronic transition at 449 and 568 nm. As the observed origin band for C₆S⁻ is at 608 nm (Figure 2), the wavelength versus chain length dependence has significant curvature (though this is just based on three points and often the smallest members of the homologous series show anomalous behavior). If this trend is established when the data become available for longer members of the C_nS⁻ *n* > 6 series, the implication would be that these anions exhibit bond length alternation.

The analysis of the vibrational structure in the ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ absorption spectrum of C₆S indicates the excitation of four of

TABLE 2: Positions of the Band Maxima (± 0.2 nm) Observed for the ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ Electronic Transition of C_6S in a 6 K Neon Matrix

λ/nm	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
574.2	17416	0	0_0^0
559.7	17868	452	6_0^1
523.9	19089	1673	3_0^1
518.7	19279	1863	2_0^1
512.9	19497	2081	1_0^1
507.0	19723	2307	$2_0^1 6_0^1$
501.1	19957	2541	$1_0^1 6_0^1$

the totally symmetric stretching vibrations in the upper electronic state. The assignment in Table 2 is made by reference to the calculated values in the $X {}^3\Sigma^-$ electronic state: $\nu_1 = 2069$, $\nu_2 = 2025$, $\nu_3 = 1773$, $\nu_4 = 1357$, $\nu_5 = 902$, $\nu_6 = 460$ cm^{-1} and the expectation that the observed frequencies will be smaller than in the ground state because of the excitation of an electron from the 4π orbital to one with more nodes, 5π . In the $B {}^2\Pi \leftarrow X {}^2\Pi$ system of the C_6S^- anion, only the origin band at 608 nm was detected.

Conclusion

The ${}^1\Sigma^+ \leftarrow X {}^1\Sigma^+$ electronic transition of C_5S , ${}^3\Sigma^- \leftarrow X {}^3\Sigma^-$ of C_6S , and $B {}^2\Pi \leftarrow X {}^2\Pi$ of C_6S^- have been observed in 6 K neon matrixes. According to theoretical models, these neutral species are expected to be present in the interstellar medium and to play a role in its chemistry. Whereas the C_5S molecule has already been detected in space, C_6S is still awaiting the identification. As far as the C_nS^- anions are concerned,

laboratory gas-phase spectra, rotational or electronic, are a prerequisite for astronomical searches. The transitions identified in this present article provide the basis for studies of the electronic spectra of these neutral and anionic chains with a terminal sulfur atom in the gas phase.

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