

Electronic Absorption Spectra of C_4O^- and C_4S^- in Neon Matrixes

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Received: February 7, 2001

The electronic spectra of the anions C_4O^- and C_4S^- have been observed by absorption spectroscopy in a neon matrix using mass selection. The symmetries of the states are determined on the basis of spectroscopic evidence and ab initio calculations. Two absorption systems of C_4O^- are assigned to the $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ and $\text{B}^2\Pi \leftarrow \text{X}^2\Pi$ electronic transitions, with band origins near 875 and 442 nm, respectively. The $\text{B}^2\Pi \leftarrow \text{X}^2\Pi$ system of C_4S^- , with the origin near 568 nm, has also been observed. After photobleaching, the $^3\Sigma^- \leftarrow \text{X}^3\Sigma^-$ electronic transition of C_4S is observed around 447 nm.

Introduction

Interest in the C_4O and C_4S molecules and their ions stems from the suggestion that both should be observable in dense interstellar clouds.^{1,2} The related smaller species, C_2O , C_3O , C_2S , C_3S , and also C_5S have in fact been detected.^{3–7} It has been proposed that C_4O may be produced in interstellar space via reactions between unsaturated hydrocarbons, such as C_3H_2^+ , and CO .¹ Although the C_4O molecule has not yet been observed in the interstellar medium, it has been studied experimentally in rare gas matrixes using electron spin resonance⁸ and infrared (IR) absorption techniques,⁹ and its microwave spectrum has been recorded in the gas phase.¹⁰ Photoelectron spectroscopy has provided a value for the electron affinity (EA) of 2.05 ± 0.15 eV.¹¹ Several theoretical studies of the vibrational and electronic states of the molecule have been undertaken, which indicate that the molecule has a $^3\Sigma^-$ ground state.^{12–15}

Mass spectrometry has demonstrated that the C_4O^- ion can be produced by the reaction between C_4^- and oxygen.¹⁶ Theoretical calculations predict that the electronic ground state of C_4O^- has $^2\Pi$ symmetry^{13,15} but give an EA of C_4O that is approximately 0.7 eV above the experimental value.¹⁵

It has been proposed that C_4S may also be formed in dense interstellar clouds via reaction between S^+ and diacetylene followed by dissociative recombination with an electron.¹⁷ Investigation of this reaction leads to the conclusion that it dominates over a competing charge-transfer process (the ionization potential of sulfur is higher than that of diacetylene) and could lead to observable amounts of C_4S .² Another possible production mechanism in dense interstellar clouds, which has common intermediates with the formation of hydrocarbons, was also proposed.¹⁸ The significance of this synthetic route is supported by the comparable abundances of C_nS and C_nH ($n = 1, 2, 3$) in dense interstellar clouds.¹⁸ The C_4S molecule has been detected experimentally in argon matrixes^{19,20} and its gas-phase microwave spectrum has also been recorded.²¹ Both experimental and theoretical²² studies indicate that the molecule has a $^3\Sigma^-$ electronic ground state. As far as the C_4S^- anion is concerned, neither theoretical nor experimental results have been reported to date. This paper reports the electronic absorption spectra of mass-selected C_4O^- and C_4S^- in neon matrixes. Assignments for the observed band systems are made, based

on ab initio calculations for the electronic excited states and ground-state vibrational frequencies.

Experimental Section

The experiment was carried out using an apparatus combining mass selection with matrix isolation spectroscopy.²³ The C_4O^- (or C_4S^-) ions were produced in a cesium sputter anion source containing a carbon rod with a 1 mm diameter channel, through which O_2 (or CS_2) was introduced. Two hours of co-deposition of ions (current in the 30–50 and 2–4 nA ranges for C_4O^- and C_4S^- , respectively) with neon at 6 K was sufficient to obtain detectable ion absorptions. The anions were subsequently neutralized by UV radiation (~ 5.4 eV) from a medium-pressure mercury lamp. Absorption spectra were recorded in the 220–1100 nm region using a waveguide technique with a path length of ~ 2 cm.

Theoretical Methods

Ab initio calculations have been performed²⁴ to provide insight into the assignments of the observed electronic absorption systems for C_4O^- and C_4S^- , as well as the vibrational band structure.

The energies of the ground and the excited electronic states of C_4O^- were computed using the Complete-Active-Space-Self-Consistent-Field (CASSCF) approach^{25,26} to produce a reference wave function for a Multi-Reference-Configuration-Interaction (MRCI) calculation.^{27,28} The energies were determined using the aug-cc-pVXZ, $X = \text{D, T, Q}$ (s, p, d, and f functions only) basis sets,^{29,30} with the atomic positions kept fixed in the linear geometry obtained in a CCSD(T)/aug-cc-pVDZ optimization for the $^2\Pi$ $([\text{core}]^{10}6\sigma^27\sigma^28\sigma^29\sigma^210\sigma^21\pi^42\pi^411\sigma^23\pi)$ ground state.¹⁵ The two lowest excited states for which transitions from the ground state are dipole allowed are found to be $\text{A}^2\Sigma^+$ and $\text{B}^2\Pi$, which result predominantly from the excitation of an electron from the 11σ to 3π and from the 2π to 3π orbital, respectively. The $\text{A}^2\Sigma^+$ state was established recently by CCSD(T) calculations ~ 1.42 eV above the ground state,¹⁵ and only the $\text{B}^2\Pi$ state has been considered here. Two selections of active orbitals, giving calculations of feasible size, were examined. In the CASSCF step, besides the core orbitals, the $6\sigma-8\sigma$ or $6\sigma-9\sigma$ and 1π valence orbitals were closed, giving an active space consisting of four σ ($9\sigma-12\sigma$ or $10\sigma-13\sigma$) and

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TABLE 1: Calculated Vertical Excitation Energies for the $B^2\Pi \leftarrow X^2\Pi$ Transition of C_4O^- at the MRCI/aug-cc-pVXZ, X = D, T, Q, Level Using Two Different Active Spaces

basis set	$E(X^2\Pi)/E_h$		$T_0(B^2\Pi \leftarrow X^2\Pi)/eV$	
	$10\sigma-13\sigma;$ $2\pi-5\pi$	$9\sigma-12\sigma;$ $2\pi-5\pi$	$10\sigma-13\sigma;$ $2\pi-5\pi$	$9\sigma-12\sigma;$ $2\pi-5\pi$
aug-cc-pVDZ	-226.49046	-226.57762	3.08	3.14
aug-cc-pVTZ	-226.56390	-226.68296	3.07	3.12
aug-cc-pVQZ	-226.57964	-226.70205	3.07	3.12

TABLE 2: Vertical Excitation Energies Relative to the Ground State of C_4O^- (Total Energy: -226.68296 E_h) Obtained in MRCI/aug-cc-pVQZ Calculations and the Lowest Singlet/Triplet Excited States of C_4O , Resulting from the Configuration [core] $^{10}6\sigma^27\sigma^28\sigma^29\sigma^210\sigma^21\pi^42\pi^311\sigma^23\pi^3$

electronic state		$\Delta E_{MRCI}/eV$
C_4O^-	$X^2\Pi$	0.00
	$B^2\Pi$	3.12
C_4O	$X^3\Sigma^-$	3.24
	$^1\Sigma^-$	6.11
	$^3\Delta$	6.23
	$^3\Sigma^+$	6.29
	$^3\Sigma^-$	7.00
	$^1\Delta$	7.82
	$^1\Sigma^+$	8.52

TABLE 3: Optimized Linear Geometry (pm) of C_4O^- and C_4S^- at the SCF/aug-cc-pVDZ Level

	C_1-C_2	C_2-C_3	C_3-C_4	C_4-S/O
C_4O^-	126.88	133.70	124.89	118.51
C_4S^-	126.17	133.87	123.93	163.10

four π ($2\pi-5\pi$) orbitals. In the CASSCF calculation the orbitals and their occupation numbers were optimized for the average of the X and B states. The subsequent MRCI calculation employed the same active orbitals and applied a cutoff of 0.01 in the configuration expansion. Table 1 lists the MRCI energies for the $X^2\Pi$ ground state and the vertical $B^2\Pi \leftarrow X^2\Pi$ transition energies obtained using the different selections of active space and basis set. The vertical excitation energies obtained in all calculations lie around 3.10 eV and are close to basis-set convergence at the level of accuracy required: the energies differ by less than 0.03 eV from aug-cc-pVDZ to aug-cc-pVTZ basis and no significant change is obtained with the aug-cc-pVQZ basis.

Calculations for the electronic states of C_4O were performed using the same procedure as for C_4O^- . The geometry was kept fixed to that given in ref 15 (CCSD(T)/aug-cc-pVDZ) and the aug-cc-VTZ basis was employed with the $9\sigma-12\sigma$ and $2\pi-5\pi$ orbitals forming the active space. The CASSCF configurations with a cutoff at 0.01 were again taken as reference for the MRCI calculation, and the triplet and singlet states were treated separately. Only the electronic states produced by the excitation of a 2π electron to the 3π orbital, i.e., [core] $^{10}6\sigma^27\sigma^28\sigma^29\sigma^210\sigma^21\pi^42\pi^311\sigma^23\pi^3$, were studied. Table 2 gives the MRCI vertical excitation energies for the first seven electronic states of C_4O , along with that of the $B^2\Pi$ state of C_4O^- , with respect to the $X^2\Pi$ ground state of the anion.

Equilibrium geometries and harmonic vibrational frequencies for the ground states of both anions were calculated at the SCF/aug-cc-pVDZ level with the structures constrained to be linear. The bond lengths are listed in Table 3 and the frequencies in Table 4.

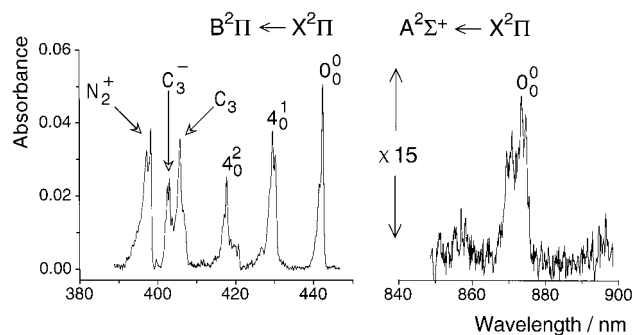
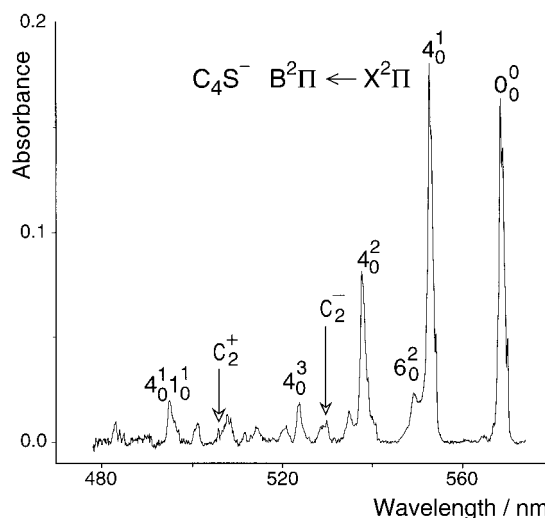
Results and Discussion

The spectrum observed after mass selected co-deposition of C_4O^- with neon shows two band systems (Figure 1). The one

TABLE 4: Harmonic Vibrational Frequencies (cm^{-1}) for the Ground State of C_4O^- and C_4S^- Calculated at the SCF/aug-cc-pVDZ Level and Comparison to the Experimental Values (± 10 cm^{-1}) for the $B^2\Pi$ States

	mode	C_4O^-		C_4S^-	
		$X^2\Pi$	$B^2\Pi$	$X^2\Pi$	$B^2\Pi$
σ^+	ν_1	2400		2329	1955
	ν_2	2042		1765	1861
	ν_3	1570		1196	
	ν_4	802	676	593	502
π^a	ν_5	608		470	
	ν_6	413		365	305
	ν_7	99		137	114

^a Average of calculated π_x, π_y frequencies.

**Figure 1.** The $A^2\Sigma^+ \leftarrow X^2\Pi$ and $B^2\Pi \leftarrow X^2\Pi$ electronic absorption spectra of C_4O^- observed at 6 K after mass-selected co-deposition of C_4O^- with excess neon.**Figure 2.** The $B^2\Pi \leftarrow X^2\Pi$ electronic absorption spectrum of C_4S^- observed after co-deposition of C_4S^- with excess of neon to form a matrix at 6 K.

in the near-IR contains only a weak band at 875 nm. The origin band of the other system is about 15 times stronger and lies at 442 nm. This higher energy system shows a single strong vibrational progression with a mean separation of 670 cm^{-1} . Both band systems disappeared after the matrix had been exposed to UV radiation, supporting the assignment to the anionic species. No new bands were observed after the photobleaching.

Deposition of C_4S^- gives rise to a single observable absorption system, with the origin band near 568 nm, which possess a rich vibrational structure (Figure 2). All bands disappear after exposure to UV radiation and a new system starting at 447 nm evolves in their place (Figure 3). This new band system is close

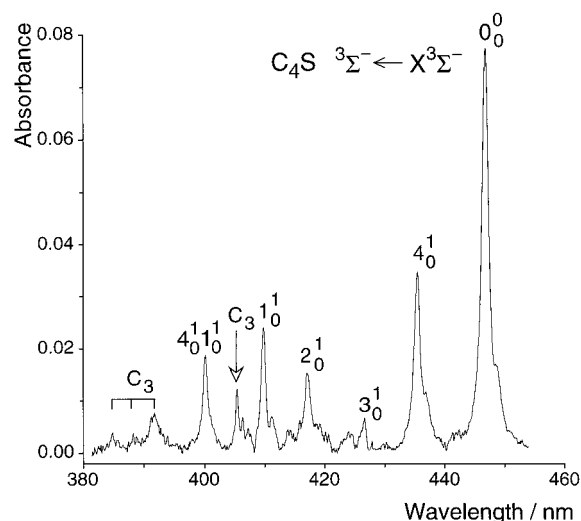


Figure 3. The ${}^3\Sigma^- \leftarrow X^3\Sigma^-$ spectrum of C_4S recorded after UV irradiation of the matrix grown by deposition of mass-selected C_4S^- ions with neon at 6 K.

to the origin of the electronic transition of neutral C_4S in an argon matrix (450 nm).¹⁹ The evidence from mass selection and photodetachment experiments thus supports the assignment of the carrier of the 568 nm band system as C_4S^- .

Absorptions belonging to C_3 , C_3^- ,³¹ C_2^- , C_2^+ , and N_2^+ , are also present in both spectra. These molecules are formed either by fragmentation during the deposition or as products of reactions of the fragments with impurities (e.g., N_2). The peaks corresponding to these species are indicated in the figures.

Electronic Transitions. The vertical excitation energy for the dipole-allowed $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition of the C_4O^- anion has been calculated previously as 1.42 eV.¹⁵ This is in excellent agreement with the position of the near-IR absorption in the matrix spectrum (1.41 eV) attributed to C_4O^- , and this single weak band is therefore assigned as the origin of the $A^2\Sigma^+ \leftarrow X^2\Pi$ system. The difference between the vertical excitation energy for the $B^2\Pi \leftarrow X^2\Pi$ transition calculated here (3.10 eV) and the position of the higher energy band system in the neon matrix (2.80 eV) is larger, but the agreement is nevertheless sufficient to support the assignment of the latter absorption to this transition. This higher energy absorption system is near to the measured EA (2.05 eV) of C_4O .¹¹ A previous theoretical investigation¹⁵ gives a value of 2.99 eV for the EA and thus casts doubt on the experimental measurement. The present MRCI calculation (3.24 eV) for the EA is in reasonable agreement with this more accurate result, obtained at the restricted coupled cluster RCCSD(T) level of theory. It is therefore not clear whether the excited $B^2\Pi$ electronic state is a bound or a long-lived quasi-bound state.

Examination of the configuration expansion for the $B^2\Pi$ state of C_4O^- suggests that electron detachment will produce excited states of the neutral molecule corresponding to $[core]^{10}6\sigma^27\sigma^28\sigma^29\sigma^210\sigma^21\pi^42\pi^311\sigma^23\pi^3$. This configuration gives rise to ${}^3\Sigma^{+/-}$, ${}^3\Delta$, ${}^1\Sigma^{+/-}$, and ${}^1\Delta$ states lying more than 2.9 eV above the ${}^3\Sigma^-$ ground state of C_4O and therefore at least 3 eV higher in energy than the $B^2\Pi$ state of the anion (Table 2). Thus, if the $B^2\Pi$ state lies above the photodetachment threshold, it will correspond to a class of states termed Feshbach resonances in electron-scattering terminology,^{32,33} for which electron detachment to the neutral ground state occurs by a concerted two-electron process. Recently, electron-detachment studies of C_3^- and C_5^- in the gas phase have determined lifetimes between 200 fs and 3 ps for Feshbach states lying up

TABLE 5: Positions of the Band Maxima (± 0.2 nm) in the Absorption Spectrum of C_4O^- in a Neon Matrix at 6 K

λ/nm	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
$C_4O^-: A^2\Sigma^+ \leftarrow X^2\Pi$			
874.6	11 434	0	0_0^0
870.8	11 484	50	site structure
$C_4O^-: B^2\Pi \leftarrow X^2\Pi$			
442.3	22 610	0	0_0^0
429.4	23 286	676	4_0^1
417.7	23 942	1332	4_0^2

to 1.5 eV above the electron detachment threshold.^{31,34} Thus, even if the $B^2\Pi$ state of C_4O^- is a Feshbach rather than a bound state, it may be sufficiently long-lived to give rise to observable absorption bands.

The C_4S^- anion is valence isoelectronic with C_4O^- and could be expected to possess a similar set of electronic states. The absorption band system observed at 568 nm for C_4S^- is therefore assigned to the $B^2\Pi \leftarrow X^2\Pi$ transition because it lies in the same energy region as the corresponding transition of C_4O^- (442 nm). The fact that no absorption system was observed in the near-IR, where the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition can be expected, may be due to the low intensity of this absorption. The absorption system (origin band at 447 nm) observed for neutral C_4S is most likely assigned as a ${}^3\Sigma^- \leftarrow X^3\Sigma^-$ transition on the basis of the intensity of the system. This absorption has been observed previously in an argon matrix (origin at 450 nm) after its preparation by photolysis, though no assignment of symmetry was given.¹⁹

Vibrational Structure. Harmonic vibrational frequencies in the ground electronic states were calculated for both anions (Table 4) to aid the assignment of the vibrational structure within the observed absorption systems. In the neon matrix at 6 K transitions will originate from the lowest vibrational level of the ground electronic state and all of the observed vibrational structure is associated with the excited state. Because calculated vibrational frequencies in the excited states were not available, the ground-state frequencies were used to guide the assignment.

Only the origin band is observed for the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of C_4O^- . The strong vibration progression observed in the $B^2\Pi \leftarrow X^2\Pi$ system, with separation of 670 cm^{-1} , is assigned to excitation of a ν_4 stretching mode by comparison with the values calculated for the ground state (Table 4). The third member of the progression is followed by strong absorptions due to C_3 , C_3^- , and N_2^+ , which obscure further features (Figure 1). The band maxima for the $A^2\Sigma^+ \leftarrow X^2\Pi$ and $B^2\Pi \leftarrow X^2\Pi$ systems of C_4O^- are listed in Table 5.

Three of the vibrational excitations observed for C_4S^- , including the strongest one with a separation of 500 cm^{-1} , are assigned to stretches (Table 6) according to the calculated harmonic frequencies. Weak absorptions involving the excitation of the ν_6 bending vibration are also tentatively assigned. In addition, a very weak band corresponding to single excitation of the ν_7 bending mode, forbidden by symmetry for a gas-phase transition, is also observable, possibly due to the influence of the neon environment. The same effect was observed in the matrix absorption spectrum of C_2O^- .³⁵ Considering the approximations inherent in the comparison, the calculated harmonic frequencies (Table 4) are in a satisfactory agreement with the experimental observations. The two most intense progressions present in the spectra of C_4O^- and C_4S^- (670 and 500 cm^{-1} , respectively) are assigned to the ν_4 stretching mode. The ratios $\nu_4(C_4O^-)/\nu_4(C_4S^-)$ from the experimental spectrum and

TABLE 6: Positions of the Band Maxima (± 0.2 nm) in the Absorption Spectra of C₄S⁻ and C₄S in a Neon Matrix at 6 K

λ/nm	$\tilde{\nu}/\text{cm}^{-1}$	$\Delta\tilde{\nu}/\text{cm}^{-1}$	assignment
C ₄ S ⁻ : B ² Π ← X ² Π			
568.4	17 593	0	0 ₀ ⁰
564.7	17 708	114	7 ₀ ¹
552.6	18 095	502	4 ₀ ¹
549.4	18 202	609	6 ₀ ²
537.8	18 595	1002	4 ₀ ²
534.7	18 702	1109	4 ₀ ¹ 6 ₀ ²
531.4	18 816	1223	6 ₀ ⁴
523.6	19 096	1503	4 ₀ ³
520.8	19 198	1605	4 ₀ ² 6 ₀ ²
514.0	19 454	1861	2 ₀ ¹
511.5	19 548	1955	1 ₀ ¹
507.7	19 695	2102	4 ₀ ³ 6 ₀ ²
501.1	19 955	2362	4 ₀ ¹ 2 ₀ ¹
494.9	20 205	2612	4 ₀ ¹ 1 ₀ ¹
483.1	20 699	3106	4 ₀ ² 1 ₀ ¹
C ₄ S: ³ Σ ⁻ ← X ³ Σ ⁻			
446.8	22 380	0	0 ₀ ⁰
435.5	22 964	584	4 ₀ ¹
426.6	23 440	1060	3 ₀ ¹
423.9	23 586	1206	4 ₀ ²
417.1	23 975	1595	2 ₀ ¹
409.8	24 402	2022	1 ₀ ¹
400.1	24 993	2613	4 ₀ ¹ 1 ₀ ¹

TABLE 7: Comparison of the Calculated Vibrational Frequencies (cm⁻¹) from Ref 22 (BLYP/6-311G*) for the X³Σ⁻ Electronic Ground State of C₄S with the Experimental Values (± 10 cm⁻¹) for its ³Σ⁻ Excited Electronic State

	mode	X ³ Σ ⁻ $\tilde{\nu}$ (calc)	³ Σ ⁻ $\tilde{\nu}$ (exp)
σ^+	ν_1	2045	2022
	ν_2	1745	1595
	ν_3	1171	1060
	ν_4	587	584
π	ν_5	402	
	ν_6	279	
	ν_7	117	

theoretical values are in excellent agreement (both are around 1.350).

The vibrational bands observed for neutral C₄S resemble those in the argon matrix spectrum reported previously.¹⁹ The vibrations observed in the excited ³Σ⁻ state are assigned to stretching modes by comparison with density functional calculations of frequencies for the ground state of the molecule (Table 7).²²

Conclusion

Carbon chain molecules containing a heteroatom represent a vast and interesting subject for spectroscopic investigations, particularly in light of their possible role in the chemistry of

the interstellar medium. The A²Σ⁺ ← X²Π and B²Π ← X²Π transitions of C₄O⁻ and B²Π ← X²Π of C₄S⁻ have been observed in neon matrixes and assigned with reference to ab initio calculations. These results provide the basis for the measurement of these spectra in the gas phase.

Acknowledgment. This study was supported by the Swiss National Science Foundation (project 20-55285.98) and the Roche Research Foundation. Calculations were performed at the Swiss Centre for Scientific Computing (CSCS).

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