Infrared Absorption Spectra of SSO⁻ Anion in Solid Argon

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When a high-frequency discharged CS_2:O_2:Ar sample was condensed at 4 K, new absorptions at 1003.1 and 567.7 cm⁻¹ were produced. Isotopic substitution ($^{13}CS_2$/O_2, $C^{34}S_2$/O_2, CS_2/$^{18}O_2$, and mixtures) shows that these new absorptions are due to S−O and S−S stretching vibrations, which involve two inequivalent S atoms and one O atom. The photosensitive behavior and the agreement with frequencies and isotopic frequency ratios from quantum chemical calculations substantiate assignment of these absorptions to the SSO⁻ anion, which was predicted to have a bent structure with elongated S−S and S−O bond lengths relative to those of S_2O.

Introduction

Sulfur oxides are potential important species in combustion, atmospheric, and planetary chemistry. Disulfur monoxide, S_2O, one of the simplest molecules incorporating both sulfur and oxygen elements, has been identified as the sulfur- and oxygen-containing species that resulted from volcanic activities on the surface of Jupiter's moon Io.[1−3] Numerous experimental and theoretical studies have been performed on the properties of S_2O.[4−13] Earlier mass and microwave spectroscopic studies showed that S_2O has a $^1A'$ ground state with unsymmetrical and bent equilibrium geometry (designated SSO).[4,5] The structural parameters and vibrational fundamentals were experimentally determined on subsequent microwave and infrared measurements.[6−9] Theoretical calculations indicated that the unsymmetrical SSO molecule is the most stable structure on the potential energy surface of S_2O. Two other S_2O isomers having C_{2v} symmetry were predicted to be stable, but they lie higher in energy than SSO.[13] Recently, the cyclic S_2O isomer with C_{2v} symmetry was produced by 308 nm excimer laser irradiation of matrix isolated SSO in solid argon. Its infrared and ultraviolet absorption spectra were reported.[14,15]

Although the S_2O neutral molecule has been well characterized, the S_2O^- anion has gained much less attention. However, the SSO⁻ anion has been produced by high-pressure dc glow discharge from the O_2/OCS or O_2/SO_2 mixtures, and its photoelectron spectrum was reported.[16] The electron affinity of SSO was measured to be 1.877 ± 0.008 eV. From a Franck−Condon analysis of the photoelectron spectra, the S−S bond length of SSO⁻ was determined to be 2.010 ± 0.020 Å. Previous investigations have shown that the isovalent O_3^-, SO_2^-, and S_3^- anions all can be trapped in solid matrices for spectroscopic study,[17−21] which suggests that the S_2O^- anion might also be produced and trapped in solid matrices. In this paper, we report a vibrational spectra and quantum chemical calculations of the SSO⁻ anion produced by condensation of a high-frequency discharged CS_2/O_2 mixture in excess argon.

Experimental and Computational Methods

The experimental setup for the high-frequency discharge and matrix isolation FTIR spectroscopic investigation has been described in detail previously.[22,23] Briefly, the gas stream containing CS_2/O_2/Ar was subjected to high-frequency discharge from a Tesla coil and was deposited onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. The matrix gas deposition rate was typically of 2−4 mmol per hour. In general, matrix samples were deposited for 1−2 h. The CS_2/O_2/Ar mixture was prepared in a stainless steel vacuum line using a standard manometric technique. CS_2 was cooled to 77 K using liquid N_2 and evacuated to remove volatile impurities. Isotopic labeled $^{18}O_2$ (Cambridge Isotope Laboratories, 99%), $^{13}CS_2$, and $C^{34}S_2$ (Isotec, 99%) were used without further purification. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer at 0.5 cm⁻¹ resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband irradiation using a high-pressure mercury arc lamp.

Quantum chemical theoretical calculations were performed using the Gaussian 98 program.[24] The Becke three-parameter hybrid functional with the Lee−Yang−Parr correlation corrections (B3LYP) was used.[25,26] Additional comparison ab initio calculations were also done at the CCSD(T) level.[27] The 6-311+G* basis set was used for O and S atoms.[28,29] Geometries were fully optimized and vibrational frequencies were calculated with analytical second derivatives, and zero-point vibrational energies (ZPVE) were derived.

Results and Discussion

Low power microwave or high-frequency discharges have often been used in conjunction with the matrix isolation technique to produce and trap unstable species for spectroscopic studies. Numerous species such as free radicals and charged ions that are difficult to study in the gas phase have been produced and trapped in solid matrices.[30] The SSO⁻ anion reported here was produced by condensation of the CS_2/O_2/Ar mixture via high-frequency discharge. The products from condensation of discharged CS_2/Ar or O_2/Ar mixtures have been

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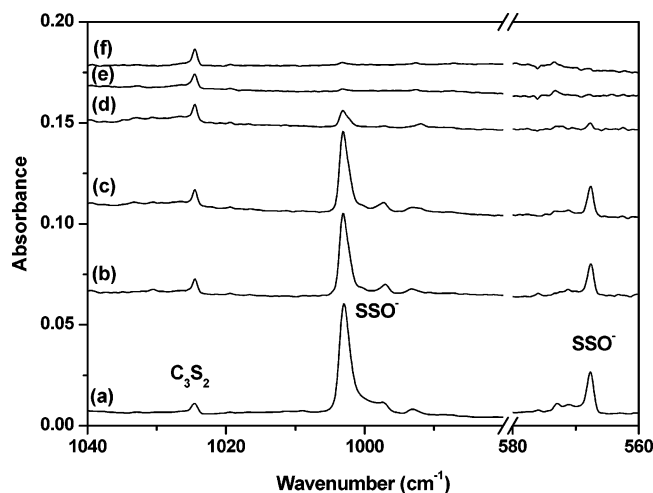‡ National Institute of Advanced Industrial Science and Technology.

Figure 1. Infrared spectra in the 1040−980 and 580−560 cm⁻¹ regions from deposition of a high-frequency discharged $CS_2/O_2/Ar$ (0.2:0.1:100) mixture at 4 K. (a) After 1 h of sample deposition, (b) after 25 K annealing, (c) after 15 min of $\lambda > 400$ nm irradiation, (d) after 15 min of $\lambda > 300$ nm irradiation, (e) after 15 min of $\lambda > 250$ nm irradiation, and (f) after 30 K annealing.

TABLE 1: Infrared Absorptions (cm⁻¹) of Various SSO⁻ Isotopomers in Solid Argon

	S−O stretching	S−S stretching
$^{32}S^{32}S^{16}O^-$	1003.0	567.7
$^{34}S^{32}S^{16}O^-$	1002.9	560.3
$^{32}S^{34}S^{16}O^-$	993.0	559.0
$^{34}S^{34}S^{16}O^-$	993.0	551.4
$^{32}S^{32}S^{18}O^-$	966.4	566.8

investigated previously.[31,32] Condensation of the CS_2/Ar products at 4 K after discharge resulted in strong CS absorptions at 1275.0 and 1270.0 cm⁻¹ and weak absorptions due to CS_2^+ (1200.5 cm⁻¹), $(CS)_2$ (1281.2 cm⁻¹), C_2S_2 (1180.5 cm⁻¹), CS_2^- (1160.5 cm⁻¹), and C_3S_2 (2078.2 and 1024.3 cm⁻¹).[32,33] Similarly, O_3 (1039.4 cm⁻¹), O_3^- (803.9 cm⁻¹),[17] O_4^- (953.6 cm⁻¹),[34] and O_4^+ (1118.4 cm⁻¹)[18,35] were produced after discharge of O_2/Ar and condensation. All of the charged species were eliminated on broadband irradiation.

When a $CS_2/O_2/Ar$ mixture was subjected to discharge and condensed, the CS, C_3S_2, and CS_2^+ absorptions were still presented, but the absorptions due to CS_2^-, O_3^-, O_3, O_4^-, and O_4^+ were not observed. Strong absorptions due to CO (2138.3 cm⁻¹), SO_2 (1350.8, 1147.0, and 517.2 cm⁻¹), OCS (2049.5 and 858.7 cm⁻¹), and SSO (1157.1 and 672.6 cm⁻¹), together with two new absorptions at 1003.0 and 567.7 cm⁻¹, were produced. The spectra in the 1050−960 and 600−560 cm⁻¹ regions with 0.2% CS_2 + 0.1% O_2 in Ar, which are of particularly interest here, are shown in Figure 1. The new 1003.0 and 567.7 cm⁻¹ absorptions that were observed after sample deposition were reduced 20% upon sample annealing to 25 K (trace b). Filtered irradiation ($\lambda > 400$ nm) using the high-pressure mercury lamp has little effect on these absorptions (trace c), but continued irradiation with $\lambda > 300$ nm reduced the absorptions about 80% (trace d). Additional broadband irradiation without filter ($\lambda > 250$ nm) virtually destroyed the absorptions (trace e). Both absorptions were not reproduced on further annealing to 30 K (trace f).

Similar experiments were performed with the $^{13}CS_2:O_2$, $CS_2:^{18}O_2$, $C^{34}S_2:O_2$, $CS_2:^{16}O_2 + ^{18}O_2$, and $C^{32}S_2 + C^{34}S_2:O_2$ samples. The isotopic shifts and splittings of the product absorptions will be discussed below. Table 1 lists the vibrational frequencies of various SSO⁻ isotopomers. The infrared spectra in the 1030−
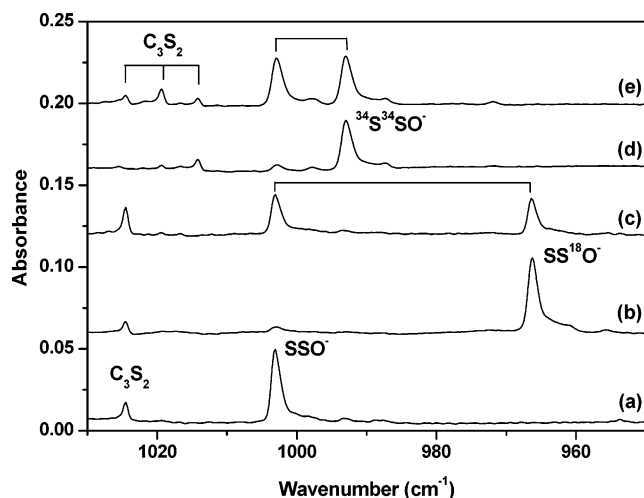

Figure 2. Infrared spectra in the 1030−950 cm⁻¹ region from deposition of a high-frequency discharged $CS_2/O_2/Ar$ mixture at 4 K. (a) 0.2% CS_2 + 0.1% O_2, (b) 0.2% CS_2 + 0.1% $^{18}O_2$, (c) 0.2% CS_2 + 0.05% $^{16}O_2$ + 0.05% $^{18}O_2$, (d) 0.2% $C^{34}S_2$ + 0.1% O_2, and (e) 0.1% $C^{32}S_2$ + 0.1% $C^{34}S_2$ + 0.1% O_2.
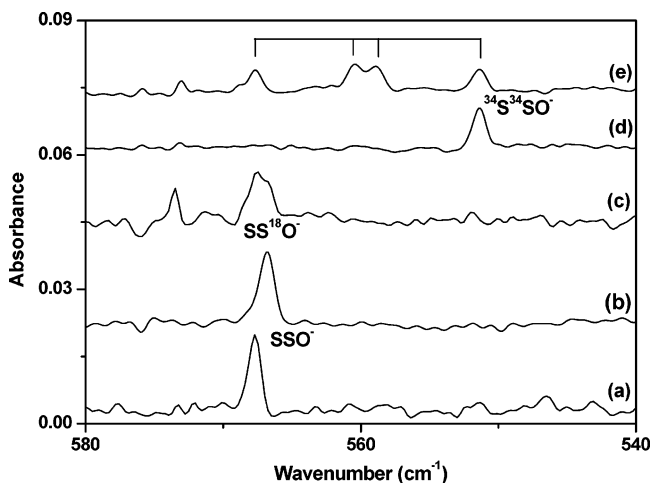

Figure 3. Infrared spectra in the 580−540 cm⁻¹ region from deposition of a high-frequency discharged $CS_2/O_2/Ar$ mixture at 4 K. (a) 0.2% CS_2 + 0.1% O_2, (b) 0.2% CS_2 + 0.1% $^{18}O_2$, (c) 0.2% CS_2 + 0.05% $^{16}O_2$ + 0.05% $^{18}O_2$, (d) 0.2% $C^{34}S_2$ + 0.1% O_2, and (e) 0.1% $C^{32}S_2$ + 0.1% $C^{34}S_2$ + 0.1% O_2.

950 and 580−540 cm⁻¹ regions using different isotopic samples are shown in Figures 2 and 3, respectively.

The 1003.0 and 567.7 cm⁻¹ bands can be grouped together by their consistent behavior upon annealing and broadband irradiation, which suggests different vibrational modes of the same species. Both bands showed no shifts when a $^{13}CS_2/O_2$ sample was used, which suggests that no carbon atom is involved in the product absorptions. The 1003.0 cm⁻¹ band shifted to 966.4 cm⁻¹ with $CS_2/^{18}O_2$, and to 993.0 cm⁻¹ with $C^{34}S_2/O_2$, giving the $^{16}O/^{18}O$ isotopic frequency ratio of 1.0379 and $^{32}S/^{34}S$ ratio of 1.0101. These ratios are very close to the harmonic isotopic frequency ratios of the diatomic SO molecule (1.0392 and 1.0100), indicating that the 1003.0 cm⁻¹ band is due to a S−O stretching vibration. In the mixed $CS_2/^{16}O_2 + ^{18}O_2$ experiment (Figure 2, trace c), only the pure isotopic counterparts were observed, indicating that only one O atom is involved in this vibrational mode. In the mixed $C^{32}S_2 + C^{34}S_2/O_2$ experiment (Figure 2, trace e), a doublet also was observed; however, the band center of the two absorptions is 0.1 cm⁻¹ lower and 0.05 cm⁻¹ higher, respectively, than that of the pure isotopic counterparts, which suggests that one S atom is involved
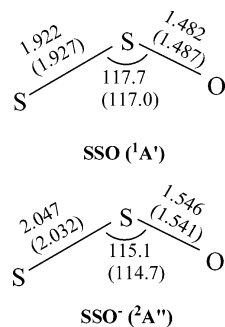
Figure 4. Optimized structures (bond lengths in angstroms, bond angles in degrees) of the SSO neutral and SSO⁻ anion at the B3LYP and CCSD(T) (values in parentheses) levels.

TABLE 2: Calculated Vibrational Frequencies (cm⁻¹) and Intensities (in Parentheses, km/mol) for SSO and SSO⁻

		S—O stretching	S—S stretching	bending
B3LYP	$^{32}S^{32}S^{16}O$	1140.2(176)	650.9(48)	372.3(12)
	$^{32}S^{32}S^{16}O^-$	955.0(212)	519.7(75)	312.2(5)
	$^{34}S^{32}S^{16}O^-$	955.0(212)	513.2(72)	309.4(4)
	$^{32}S^{34}S^{16}O^-$	945.5(208)	511.3(74)	310.4(5)
	$^{34}S^{34}S^{16}O^-$	945.5(208)	504.7(72)	307.8(5)
	$^{32}S^{32}S^{18}O^-$	919.2(196)	518.8(73)	302.8(4)
CCSD(T)	SSO	1107.2	628.9	369.6
	SSO⁻	983.1	537.2	318.5

in this vibrational mode but is very weakly coupled by another S atom. The 567.7 cm⁻¹ absorption showed a very small shift (0.9 cm⁻¹) with $CS_2/^{18}O_2$, but shifted to 551.4 cm⁻¹ with $C^{34}S_2/O_2$. The $^{32}S/^{34}S$ isotopic frequency ratio of 1.0296 indicates that the 567.7 cm⁻¹ band is mainly due to a S—S stretching vibration. The very small oxygen isotopic shift suggests that this S—S stretching vibration is also slightly coupled by another O atom. In the mixed $C^{32}S_2 + C^{34}S_2/O_2$ experiment (Figure 3, trace d), a quartet at 567.7, 560.3, 559.0, and 551.4 cm⁻¹ with approximately 1:1:1:1 relative intensities was observed. This quartet isotopic structure confirms that two slightly inequivalent S atoms are involved in this vibrational mode.

On the basis of above-mentioned isotopic substitution, we can conclude that the 1003.0 and 567.7 cm⁻¹ absorptions are due to the S—O and S—S stretching vibrations of a S_2O species with two inequivalent S atoms. This species is photosensitive; both the 1003.0 and the 567.7 cm⁻¹ absorptions were destroyed on full-arc irradiation and never came back on further sample annealing. The band positions are about 154.1 and 105.0 cm⁻¹ lower than those of the neutral SSO molecule, which was observed at 1157.1 and 672.7 cm⁻¹ in solid argon. These observations strongly suggest the assignment of the 1003.0 and 567.7 cm⁻¹ bands to the SSO⁻ anion in solid argon. The SSO⁻ anion has been produced by high-pressure dc glow discharge from the O_2/OCS or O_2/SO_2 mixtures in the gas phase. The S—S stretching frequency has been determined to be 620 ± 150 cm⁻¹ from the photoelectron spectroscopic study.[16]

Quantum chemical computations were performed to support the experimental assignment and to provide insight into the geometry and electronic structure in the SSO⁻ anion. Comparison calculations were also done on the neutral SSO molecule as well. The optimized geometric parameters are shown in Figure 4, and the calculated vibrational frequencies and intensities are listed in Table 2. As can be seen, excellent agreement was found between the B3LYP and CCSD(T) calculations. The geometric parameters calculated for the ¹A′ ground-state SSO molecule with B3LYP are: S—S, 1.922 Å; S—O, 1.482 Å; and ∠SSO, 117.7°. The bond lengths are slightly longer than the experimental values: S—S, 1.885 Å; and S—O, 1.459 Å, while

TABLE 3: Comparison of the Observed and Calculated Isotopic Frequency Ratios of the SSO and SSO⁻ Species

		$^{16}O/^{18}O$		$^{32}S/^{34}S$	
	mode	calcd	obsd	calcd	obsd
SSO	SO str.	1.0382	1.0372	1.0103	1.0106
	SS str.	1.0023	1.0025	1.0297	1.0291
SSO⁻	SO str.	1.0389	1.0379	1.0100	1.0101
	SS str.	1.0017	1.0016	1.0297	1.0296

the bond angle is very close to the experimental value of 118.1°.[6-9] Calculations at the CCSD(T) level gave slightly longer bond lengths. Due mainly to the neglect of anharmonicity, computed vibrational frequencies are generally higher than the experimental values. However, the vibrational frequencies of SSO were underestimated at both levels of theory. The S—O and S—S stretching frequencies of SSO were computed at 1140.2 and 650.9 cm⁻¹ (B3LYP), which are 16.9 and 22.2 cm⁻¹ lower than the frequencies observed in solid argon (1157.1 and 672.7 cm⁻¹). As listed in Table 3, the calculated isotopic frequency ratios are in excellent agreement with the experimental values. Present DFT/B3LYP calculations predicted that the unsymmetric SSO⁻ anion is the most stable structure on the doublet potential energy surface of S_2O^-. Two other isomers having bent C_{2v} symmetry were predicted to lie much higher in energy than the SSO⁻ isomer (with B3LYP, a ²B₁ state C_{2v} structure with S—O, 1.701 Å and ∠SOS, 124.6° is 34.1 kcal/mol above SSO⁻; another ²B₂ state C_{2v} structure with S—O, 1.751 Å and ∠SOS, 97.4° is 45.9 kcal/mol above SSO⁻). The bent SSO⁻ anion was predicted to have a ²A″ ground state. The bond lengths calculated at the B3LYP level (S—S, 2.047 Å and S—O, 1.546 Å) are 0.125 and 0.064 Å longer than those of neutral SSO calculated at the same level of theory. The calculated bond angle (115.2°) is only slightly smaller than that of SSO. The calculated S—S bond length is slightly longer than that estimated from a Franck—Condon analysis of the photoelectron spectra (2.010 ± 0.020 Å).[16] The S—O and S—S stretching vibrational frequencies of SSO⁻ were calculated at 955.0 and 519.7 cm⁻¹ (B3LYP), respectively, which are both 48.0 cm⁻¹ lower than the observed values. Calculations at the CCSD(T) level gave slightly higher vibrational frequencies than those of B3LYP, but still lower than the experimental values. Obviously the S—O and S—S stretching frequencies of SSO⁻ anion were also underestimated, similar to those of the neutral SSO molecule.[36] Although the calculated vibrational frequencies were systematically underestimated, the calculated IR intensities and isotopic frequency ratios are in excellent agreement with the observed values, which add strong support for the anion assignment. Taking the B3LYP calculation results, for example, the calculated intensity ratio of these two observed modes is 212:75, while the experimental band intensities gave a ratio of 0.130:0.042. As listed in Table 3, the calculated isotopic frequency ratios for these two modes (upper mode, $^{16}O/^{18}O$, 1.0389, $^{32}S/^{34}S$, 1.0100; low mode, $^{16}O/^{18}O$, 1.0017, $^{32}S/^{34}S$, 1.0297) are in excellent agreement with the experimental values (upper mode, $^{16}O/^{18}O$, 1.0379, $^{32}S/^{34}S$, 1.0101; low mode, $^{16}O/^{18}O$, 1.0016, $^{32}S/^{34}S$, 1.0296). The bending vibration of SSO⁻ was predicted at 312.2 cm⁻¹, which is out of the range of our spectrometer. This mode was predicted to have much lower IR intensity (5 km/mol) than the other two modes.

The observed S—O and S—S stretching vibrational frequencies of SSO⁻ in solid argon are 154.1 and 105.0 cm⁻¹ lower than those of neutral SSO molecule. SSO has been found to be a closed-shell molecule with an electronic configuration of (core) $(15a')^2 (16a')^2 (5a'')^0$. As shown in Figure 5, the 5a″ LUMO of SSO is an antibonding π orbital, which mainly consists of the
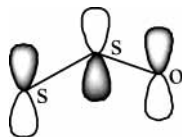
Figure 5. Depiction of the lowest unoccupied molecular orbital (5a″) of SSO.

S 3p and O 2p atomic orbitals perpendicular to the molecular plane. Addition of an electron to the 5a″ orbital results in a ²A″ ground-state SSO⁻ anion. As the 5a″ MO is both S−S and S−O antibonding in character, an electron adding in this orbital elongates both the S−S and the S−O bond lengths and results in a reduction of the S−O and S−S stretching vibrational frequencies.

The SSO⁻ anion must be formed by electron capture of the neutral SSO molecule during condensation. Strong SSO absorptions were observed after sample deposition in the present experiments. The electron affinity of SSO was determined to be 1.877 ± 0.008 eV from previous photoelectron spectroscopic study.[16] Present calculations predicted the electron affinity of SSO to be 2.37 eV (B3LYP) or 1.65 eV (CCSD(T)). The B3LYP value is 0.5 eV higher than the experimental value, whereas the CCSD(T) value is 0.23 eV lower than the experimental value. The SSO⁻ anion absorptions decreased on $\lambda > 300$ nm irradiation, during which the SSO absorptions slightly increased. This observation provides further support for the experimental assignment of the SSO⁻ anion. It is interesting to note that the CS_2^-, O_3^-, and O_4^- anion absorptions were observed in the pure CS_2/Ar and O_2/Ar discharge experiments, but were not presented in the mixed CS_2/O_2/Ar discharge experiments. Although strong SO_2 and OCS absorptions were produced in the mixed CS_2/O_2/Ar discharge experiments, the corresponding SO_2^- and OCS⁻ anion absorptions were not observed.[19,20,37] The absence of O_3^- and O_4^- anion absorptions can be rationalized by the low O_2 concentration in the mixed experiments, because a large number of O_2 reacted with CS_2 to form CO, OCS, SO_2, and SSO during discharge. The only observation of the SSO⁻ anion absorptions in the mixed experiments suggests that the SSO neutral has a larger electron affinity than those of the CS_2, OCS, and SO_2 neutrals. The electron affinity of SO_2 has been determined to be 1.107 ± 0.008 eV,[16] lower than that of S_2O. There are no experimental data on the electron affinities of OCS and CS_2. DFT/B3LYP calculations predicted the electron affinities of OCS, CS_2, and SO_2 to be 0.23, 0.59, and 1.67 eV, respectively, significantly lower than that of SSO calculated at the same level of theory. Hence, the SSO molecule serves as an electron trap; it will dominate electron capture reactions and minimize the formation of other anions such as CS_2^-, OCS⁻, and SO_2^- during the condensation process. The same effect has been observed in previous pulsed laser ablation experiments when CCl_4 was used as an electron trap.[38,39]

Conclusion

The SSO⁻ anion has been studied by matrix isolation infrared absorption spectroscopy and quantum chemical calculations. The SSO⁻ anion was produced by condensation of a high-frequency discharged CS_2/O_2 mixture in excess argon. On the basis of isotopic substitution experiments, photosensitive absorptions at 1003.0 and 567.7 cm⁻¹ are assigned to the S−O and S−S stretching vibrations of the SSO⁻ anion, which was predicted to have a ²A″ ground state with bent structure. The anion was formed via electron capture by the neutral SSO molecule during the condensation process. As the captured electron occupies the

LUMO of SSO that is S−O and S−S antibonding in character, both the S−S and the S−O bond lengths are elongated, which results in a reduction of the S−O and S−S stretching vibrational frequencies relative to those of SSO.

References and Notes

(1) Na, C. Y.; Esposito, L. W. *Icarus* **1997**, *125*, 364.
(2) Spencer, J. R.; McEwen, A. S.; McGrath, M. A.; Sartoretti, P.; Nash, D. B.; Noll, K. S.; Gilmore, D. *Icarus* **1997**, *127*, 221.
(3) Zolotov, M. Y.; Fegley, B., Jr. *Icarus* **1998**, *133*, 293. Moses, J. I.; Zolotov, M. Y. *Icarus* **2002**, *156*, 76.
(4) Meschi, D. J.; Myers, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 6220.
(5) Meschi, D. J.; Myers, R. J. *J. Mol. Spectrosc.* **1959**, *3*, 405.
(6) Cook, R. L. *J. Mol. Spectrosc.* **1973**, *46*, 276. Tiemann, E.; Hoeft, J.; Lovas, F. J.; Johnson, D. R. *J. Chem. Phys.* **1974**, *60*, 5000.
(7) Blukis, U.; Myers, R. J. *J. Phys. Chem.* **1965**, *69*, 1154.
(8) Hopkins, A. G.; Tang, S. Y.; Brown, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 3486. Hopkins, A. G.; Daly, F. P.; Brown, C. W. *J. Phys. Chem.* **1975**, *79*, 1849.
(9) Lindenmayer, J.; Jones, H. *J. Mol. Spectrosc.* **1985**, *112*, 71. Lindenmayer, J.; Rudolph, H. D.; Jones, H. *J. Mol. Spectrosc.* **1986**, *119*, 56.
(10) Lakshminarayana, G. *J. Mol. Spectrosc.* **1975**, *55*, 141. Tsukiyama, K.; Kobayashi, D.; Obi, K.; Tanaka, I. *Chem. Phys.* **1984**, *84*, 337. Clouthier, D. J.; Rutherford, M. L. *Chem. Phys.* **1988**, *127*, 189.
(11) Zhang, Q.; Dupre, P.; Grzybowski, B.; Vaccaro, P. H. *J. Chem. Phys.* **1995**, *103*, 67.
(12) Muller, T.; Vaccaro, P. H.; Perez-Bernal, F.; Iachello, F. *J. Chem. Phys.* **1999**, *111*, 5038. Iachello, F.; Perez-Bernal, F.; Muller, T.; Vaccaro, P. H. *J. Chem. Phys.* **2000**, *112*, 6507.
(13) Jones, R. O. *Chem. Phys. Lett.* **1986**, *125*, 221. Fueno, T.; Buenker, R. J. *Theor. Chim. Acta* **1988**, *73*, 123.
(14) Lo, W. J.; Wu, Y. J.; Lee, Y. P. *J. Chem. Phys.* **2002**, *117*, 6655.
(15) Lo, W. J.; Wu, Y. J.; Lee, Y. P. *J. Phys. Chem. A* **2003**, *107*, 6944.
(16) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574.
(17) Andrews, L.; Ault, B. S.; Grzybowski, J. M.; Allen, R. O. *J. Chem. Phys.* **1975**, *62*, 2461. Wight, C. A.; Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *65*, 1244.
(18) Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **1989**, *91*, 3826. Lugez, C. L.; Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **1996**, *105*, 2153.
(19) Bencivenni, L.; Ramondo, F.; Teghil, R.; Polino, M. *Inorg. Chim. Acta* **1986**, *121*, 207.
(20) Forney, D.; Kellogg, C. B.; Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **2000**, *113*, 86.
(21) Brabson, G. D.; Mielke, Z.; Andrews, L. *J. Phys. Chem.* **1991**, *95*, 79.
(22) Chen, M. H.; Wang, X. F.; Zhang, L. N.; Yu, M.; Qin, Q. Z. *Chem. Phys.* **1999**, *242*, 81.
(23) Kong, Q. Y.; Zeng, A. H.; Chen, M. H.; Zhou, M. F.; Xu, Q. *J. Chem. Phys.* **2003**, *118*, 7267. Kong, Q. Y.; Zeng, A. H.; Chen, M. H.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 1531.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(26) Lee, C.; Yang, E.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(27) Pople, J. A.; Gordon, M. H.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(28) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
(29) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(30) See for example: Jacox, M. E. *Rev. Chem. Intermed.* **1978**, *2*, 1. Langford, V. S.; McKinley, A. J.; Quickenden, T. I. *J. Am. Chem. Soc.* **2000**, *122*, 12859. Zhou, M. F.; Zeng, A. H.; Wang, Y.; Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 11512.

(31) Bohn, R. B.; Hannachi, Y.; Andrews, L. *J. Am. Chem. Soc.* **1992**, *114*, 6452.

(32) Zhou, M. F.; Hacaloglu, J.; Andrews, L. *J. Chem. Phys.* **1999**, *110*, 9450.

(33) Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **2000**, *112*, 6576.

(34) Chertihin, G. V.; Andrews, L. *J. Chem. Phys.* **1998**, *108*, 6404.

(35) Chertihin, G. V.; Saffel, W.; Yustein, J. T.; Andrews, L.; Neurock, M.; Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem.* **1996**, *100*, 5261.

(36) A reviewer has pointed out that they have recently studied a series of compounds having sulphur−oxygen linkages using the B3LYP functional with the 6-311++G** basis set. Their results showed that the calculated frequencies are systematically underestimated when compared with experimental data in argon matrix.

(37) Lugez, C. L.; Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **2001**, *115*, 166.

(38) Zhou, M. F.; Andrews, L. *J. Am. Chem. Soc*. **1998**, *120*, 11499. Zhou, M. F.; Andrews, L. *J. Chem. Phys*. **1999**, *110*, 10370.

(39) Zhou, M. F.; Zhang, L. N.; Chen, M. H.; Qin, Q. Z. *J. Chem. Phys*. **2000**, *112*, 7089. Zhang, L. N.; Dong, J.; Zhou, M. F. *J. Chem. Phys*. **2000**, *113*, 8700.