6888 *Inorg. Chem.* **2009**, *48*, 6888–6895
DOI: 10.1021/ic900869f

Inorganic Chemistry
Article

Infrared Spectra and Density Functional Calculations of the SUO_2 Molecule

Xuefeng Wang and Lester Andrews*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904-4319

Colin J. Marsden

Laboratoire de Chimie et Physique Quantiques, UMR 5626, IRSAMC, Universite Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 9, France

Received May 5, 2009

Reactions of laser-ablated U atoms with SO_2 molecules gave the very stable U(VI) molecule, SUO_2, as the major product. Infrared absorptions for two new O=U=O stretching modes were observed in solid argon and neon. The band assignments were confirmed by appropriate $^{34}SO_2$, $S^{18}O_2$, and $S^{16,18}O_2$ isotopic shifts. B3LYP and BPW91 density functional calculations were performed to determine molecular structure, vibrational frequencies, and isotopic shifts. The C_{2v} structure is analogous to those computed for UO_3 and US_3. Minor products were identified as SUO, the SUO_2^+ cation, and the $(SO_2)(SUO_2)$ adduct.

Introduction

The uranium(VI) oxide UO_3 molecule has an interesting almost T-shaped C_{2v} structure. This unique structure was first deduced from extensive oxygen isotopic substitution in argon matrix infrared spectra with normal coordinate analysis[1,2] and later confirmed by SCF and B3LYP calculations.[3−6] The UO_3 molecule evaporated from oxygen rich solid urania at 1550 °C, but the temperature had to be increased to near 1900 °C to produce significant UO_2 absorption in the matrix isolation experiments.[1,2] Both of these uranium oxide molecules were produced in the reaction of laser ablated U atoms with oxygen.[7] The sulfur analogues US_2 and US_3 were formed in the reaction of laser ablated U atoms with sulfur molecules, and calculations found the analogous T-shaped C_{2v} structure for US_3.[8] The known stability of U(VI) species prompted our investigation of the uranium reaction with SO_2 and the resulting analogous SUO_2 product.

Laser ablated uranium atoms have provided numerous new uranium bearing molecules with novel bonding, particularly the first examples of methylidene complexes such as $CH_2{=}UH_2$, $CH_2{=}UHF$, $CH_2{=}UF_2$, the methylidyne complexes $HC{\equiv}UF_3$ and $FC{\equiv}UF_3$, and the terminal pnictides $N{\equiv}UF_3$ and $P{\equiv}UF_3$.[9−13] Such simple product molecules are formed in straightforward reactions of U atoms with small precursor molecules during condensation in excess argon.

Experimental and Computational Methods

Laser-ablated U atoms were reacted with SO_2 in excess argon or neon during condensation at 5 K using methods described in our previous papers.[14−16] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating uranium target (Oak Ridge National Laboratory, high purity, depleted of ^{235}U). The uranium target was filed to remove oxide coating and

---

*To whom correspondence should be addressed. E-mail: lsa@virginia.edu.

[1] Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. *J. Chem. Phys.* **1973**, *58*, 4468 (UO_2).

[2] Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. *J. Chem. Phys.* **1973**, *59*, 6397 (UO_3).

[3] Pyykko, P.; Li, J.; Runeberg, N. J. *J. Phys. Chem.* **1994**, *98*, 4809.

[4] Zhou, M.; Andrews, L.; Ismail, N.; Marsden, C. *J. Phys. Chem A* **2000**, *104*, 5495 (UO_2 in solid neon).

[5] Shamov, G. A.; Schreckenbach, G.; Vo, T. N. *Chem.—Eur. J.* **2007**, *13*, 4932.

[6] Iché--Tarrat, N.; Marsden, C. J. *J. Phys. Chem A* **2008**, *112*, 7632.

[7] Hunt, R. D.; Andrews, L. *J. Chem. Phys.* **1993**, *98*, 3690 (UO_2 and UO_3).

[8] Liang, B.; Andrews, L.; Ismail, N.; Marsden, C. *Inorg. Chem.* **2002**, *41*, 2811 (US_2 and US_3). Unpublished neon matrix spectrum of US_2 reveals the antisymmetric stretching mode at 442.3 cm^{-1}.

[9] Lyon, J. T.; Andrews, L.; Malmqvist, P.-Å.; Roos, B. O.; Yang, T.; Bursten, B. E. *Inorg. Chem.* **2007**, *46*, 4917.

[10] Lyon, J. T.; Andrews, L. *Inorg. Chem.* **2006**, *45*, 1847. (U + CH_3X).

[11] Lyon, J. T.; Andrews, L.; Hu, H.-S.; Li, J. *Inorg. Chem.* **2008**, *47*, 1435.

[12] Lyon, J. T.; Hu, H.-S.; Andrews, L.; Li, J. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 18919.

[13] Andrews, L.; Wang, X.; Lindh, R.; Roos, B. O.; Marsden, C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 5366.

[14] Andrews, L.; Citra, A. *Chem. Rev.* **2002**, *102*, 885 and references therein.

[15] Andrews, L. *Chem. Soc. Rev.* **2004**, *33*, 123 and references therein.

[16] Andrews, L.; Cho, H.-G. *Organometallics* **2006**, *25*, 4040 (review article).

immediately placed in the vacuum chamber. Sulfur dioxide (Matheson) was condensed and outgassed before sample preparation with research grade argon and neon. A mixture of $S^{18}O_2$ and $S^{16,18}O_2$ with a trace of $S^{16}O_2$ was prepared by tesla coil discharge of $^{18}O_2$ (YEDA) (about 1 Torr) in a 2 L pyrex bulb containing a film of sulfur sublimed onto the walls (about 5 mg) by external heating using a hot air gun. A sample of $^{34}SO_2$ was prepared from sulfur-34 (98% ^{34}S, Cambridge Isotope Laboratories) and oxygen. The laser energy was varied about 10−20 mJ/pulse. FTIR spectra were recorded at 0.5 cm^{-1} resolution on Nicolet 750 with 0.1 cm^{-1} accuracy using an HgCdTe range B detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to photolysis by a medium pressure mercury arc lamp (Philips, 175W) with the globe removed.

Complementary density functional theory (DFT) calculations were performed using the Gaussian 03 program,[17] the hybrid B3LYP and pure BPW91 density functionals, and 6-311 + G(3df) basis set for sulfur and oxygen atoms, and the 60 electron SDD pseudopotential for uranium.[18−21] All of the geometrical parameters were fully optimized, and the harmonic vibrational frequencies were obtained analytically at the optimized structures.

Results

Infrared spectra of laser ablated uranium atom reaction products with SO_2 in excess argon or neon during condensation at 5 K will be presented in turn. Experiments were also done with $S^{18}O_2$ and $^{34}SO_2$, and the isotopic frequencies are listed in Table 1. Density functional calculations were performed to support the identification of new reaction products. Weak absorptions for common species, such as SO, SO_3, and uranium oxides, have been identified in previous papers.[4,7,22,23]

Table 1. Infrared Absorptions from Products of Laser-Ablated U Atom (and U^+) Reactions with Sulfur Dioxide in Excess Argon and Neon at 5 K

$^{32}S^{16}O_2$	$^{34}S^{16}O_2$	$^{32}S^{16,18}O_2$ + $^{32}S^{18}O_2$	ratio(16/18)	identity
		Argon		
1210.9	1198.0	1167.4	1.03726	$(SO_2)(SUO_2)$
987.5	987.5	969.4, 938.3	1.05244	SUO_2^+
952.5	952.5	904.8	1.05272	UO_2^+
927.3	927.3	910.3, 880.9	1.05267	$(SO_2)(SUO_2)$
891.2	891.1	875.5, 846.6	1.05268	SUO_2
857.0	857.0	811.5	1.05607	SUO
852.6	852.6	809.7	1.05298	UO_3
847.0	847.0	799	1.0600	$(SO_2)(SUO_2)$
821.7	821.5	793.0, 774.0	1.06163	SUO_2
775.7		736.7	1.05294	UO_2
745.6		705.0	1.05759	UO_3
		Neon		
1005.4	1005.4	986.8, 955.5	1.05222	SUO_2^+
980.2	980.2	931.0	1.05285	UO_2^+
936.0	936.0			$(SO_2)(SUO_2)$
915.2	915.2	869.7	1.0532	UO_2
904.5	904.4	888.7, 859.0	1.05297	SUO_2
871.5	871.5			SUO
865.5		822.0	1.05292	UO_3
855.0	855.5			$(SO_2)(SUO_2)$
835.5	835.3	805.4, 786.7	1.06203	SUO_2
760.4	760.4	719.2	1.05729	UO_3

Infrared Spectra of U + SO_2 Reaction Products. Infrared spectra of laser-ablated uranium atom reaction products with SO_2 in excess argon are illustrated in Figure 1 a−e. Sample co-deposition reveals two major new sharp bands at 891.2 and 821.7 cm^{-1}, a very weak 857.0 cm^{-1} absorption, a weak 775.7 cm^{-1} band for UO_2 in solid argon,[1,2,7] and weak broad bands at 1211, 927, 853, 848, and 746 cm^{-1}. Annealing the sample to 20 K increased all of these features including sharp subpeaks at 852.6 and 745.6 cm^{-1}, which are due to UO_3 in solid argon.[1,2,7] Ultraviolet irradiation (> 220 nm) further increased all bands except 857.0 cm^{-1} and UO_2. Subsequent annealing to 30 K again increased all absorptions, but a final annealing to 35 K increased only the 1211, 927, and 848 cm^{-1} bands with a sharp subpeaks at 1210.9, 927.4, and 847.0 cm^{-1} and slightly decreased the rest. Weak, sharp absorptions at 987.5, 952.5, and 857.0 cm^{-1} are shown clearly in Figure 2 using expanded absorbance scale. The 952.5 cm^{-1} absorption has been assigned to UO_2^+ in a previous report.[4] The 987.5 cm^{-1} peak is destroyed by ultraviolet irradiation but is reproduced on further annealing, which also increased the UO_2^+ absorption. Similar behavior is found for the 857.0 cm^{-1} peak.

Spectra from an experiment using $^{34}SO_2$ at lower concentration gave virtually the same spectra (Figure 1 f, g, h, i) except the major sharp bands were shifted slightly to 891.1 and 821.5 cm^{-1}. The same annealing and photolysis behavior was found: this time > 320 nm irradiation began the effect which > 220 nm light completed. The 987.5 and 857.0 cm^{-1} peaks were not shifted, as illustrated in Figure 2.

The discharge of $^{18}O_2$ with elemental sulfur in a pyrex bulb resulted in the preparation of a convenient $S^{18}O_2$ and $S^{16,18}O_2$ mixture, which enabled characterization of the new product absorptions. The major product bands shifted to 846.6 and 774.0 cm^{-1} with higher frequency mixed isotopic components at 875.5 and 793.0 cm^{-1} after the intensity pattern of the precursor molecules. The spectra shown in Figure 1 j, k, l, m reveal a slight growth with ultraviolet irradiation and continued increase on 30 K annealing of these new bands in concert. The $U^{18}O_2^+$ band shifted to 904.8 cm^{-1}, the $U^{18}O_3$ bands to 809.7 and 705.0 cm^{-1}, and the $U^{18}O_2$ to 736.7 cm^{-1}, as reported previously.[1,2,4,5] These oxygen-18 substituted uranium oxides show that most of the uranium oxide products come from the precursor reaction as a very weak $U^{16}O_2$ peak is detected at 775.8 cm^{-1}. The broadband that increased on final annealing shifted to 881 cm^{-1} with a subpeak at 880.9 cm^{-1} and exhibited a mixed isotopic component at 910.3 cm^{-1}. The sharp 987.5 cm^{-1} band shifted to 969.4 cm^{-1} mixed and 938.3 cm^{-1} pure oxygen-18 counterparts as shown in Figure 2 m.

Lower sample concentrations are required for neon matrix experiments, and weaker product absorptions result. Two experiments were done with different laser energies. The major peaks appear at 904.5 and 835.5 cm^{-1}

---

(17) Frisch, M. J. et al. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2004.

(18) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, Y.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(19) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533 and references therein. (c) See also: Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.

(20) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(21) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535.

(22) Hopkins, A. G.; Brown, C. W. *J. Chem. Phys.* **1975**, *62*, 2511 (SO).

(23) Bondybey, V. E.; English, J. H. *J. Mol. Spectrosc.* **1985**, *109*, 221 (SO_3).

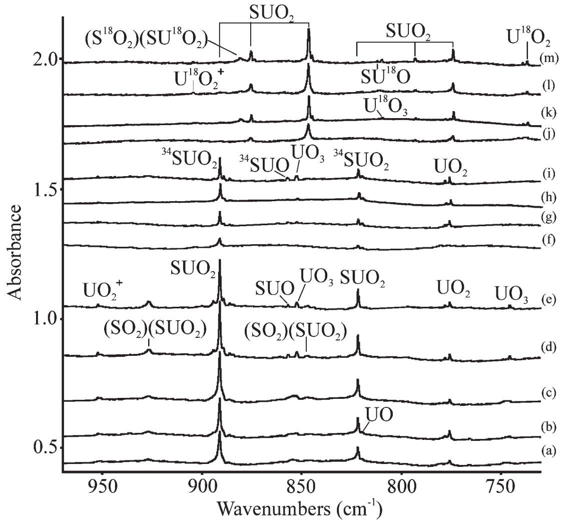

Figure 1. Infrared spectra in the 970−730 cm^{-1} region for products formed in the laser-ablated uranium atom reaction with sulfur dioxide during condensation in excess argon at 5 K. (a) Normal isotopic $^{32}SO_2$ isotopic sample at 0.4% in argon co-deposited for 60 min, (b) after annealing to 20 K, (c) after >220 nm irradiation, (d) after annealing to 30 K, (e) after annealing to 35 K, (f) $^{34}SO_2$ isotopic sample at 0.2% in argon co-deposited, (g) after annealing to 30 K, (h) after >220 nm irradiation, (i) after annealing to 35 K, (j) $S^{18}O_2$ and $S^{16,18}O_2$ isotopic mixture at 0.4% total co-deposited, (k) after >220 nm irradiation, (l) after annealing to 30 K, (m) after annealing to 35 K.

with broad red shoulders in solid neon. Annealing reduces the shoulder in favor of the sharp product bands, Figure 3 a, b, c. Sharp weak bands are observed for UO_2^+ at 980.2 cm^{-1}, for UO_3 at 865.5 and 760.4 cm^{-1}, and for UO_2 at 915.2 cm^{-1}.[4] Broad features increased on annealing at 936.0 and 855.0 cm^{-1}. The photosensitive, sharp 988.6 cm^{-1} band is common to other metal experiments with SO_2 in solid neon and is near absorptions for the isolated SO_2^- anion.[24]

Additional spectra are shown for the more productive $^{34}SO_2$ experiment, Figure 3 f−j. Again annealing decreases the broad red wing in favor of the sharp band. Next, 240−380 nm irradiation slightly increases the two bands together whereas >220 nm decreases them together. Subsequent annealing increases both sharp bands in concert with 3:1 relative intensity. All peaks measure the same as with natural isotopic precursor save the major sharp bands, which red-shifted 0.1 and 0.2 ± 0.05 cm^{-1}.

Reaction with the $S^{18}O_2$ and $S^{16,18}O_2$ mixture shifted the major product bands to 859.0 and 786.7 cm^{-1} with higher frequency mixed-isotopic components at 888.7 and 805.4 cm^{-1} after the intensity pattern of the precursor molecules. The spectra shown in Figure 3 k, l, m, n reveal a slight growth on annealing of these new bands in concert. The $U^{18}O_2^+$ band shifted to 931.0 cm^{-1}, the stronger $U^{18}O_3$ band to 822.0 cm^{-1}, and the $U^{18}O_2$ band to 869.7 cm^{-1}, as reported previously.[4] Another experiment was done with a different oygen-18 enrichment to confirm the above measurements.

Calculations. Density functional calculations were performed for several types of products whose stoichiometry is UO_2S, with different topologies, spin states, and oxidation states of uranium, to help assign the various IR bands. Since the reaction of U and CO_2 gave the insertion product OUCO,[25] the analogous species OUSO was examined in detail. Two linear triplet electronic states were characterized by computation; in the first, which is a true minimum, the unpaired electrons are in sigma and delta orbitals, whereas in the second, which is 8 kcal/mol lower in energy but which has two degenerate imaginary bending frequencies, they are in delta and phi orbitals. On relaxation, the O−U−S angle decreases to around 135°; the resulting species that contains U(IV) is a true minimum, 95 kcal/mol higher in energy than the $^1A_1$ uranium

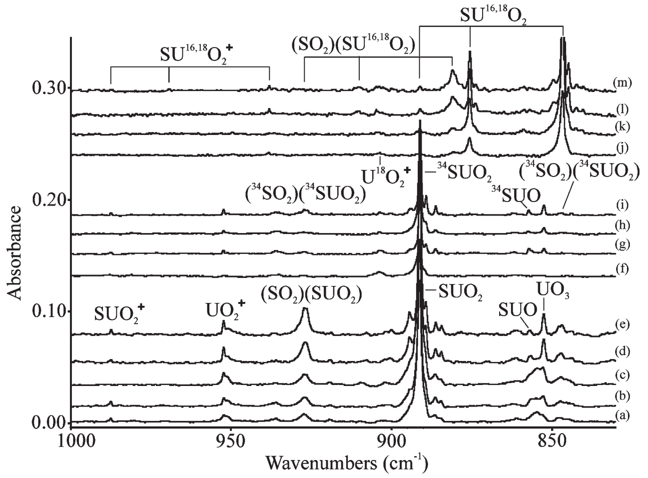

Figure 2. Infrared spectra in the 1000−830 cm^{-1} region for products formed in the laser-ablated uranium atom reaction with sulfur dioxide during condensation in excess argon at 5 K. Expanded absorbance scale for the same spectra presented in Figure 1.

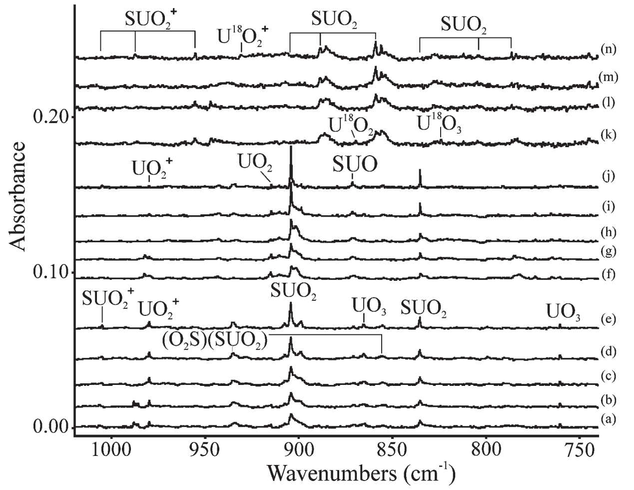

Figure 3. Infrared spectra in the 1020−740 cm^{-1} region for products formed in the laser-ablated uranium atom reaction with sulfur dioxide during condensation in excess neon at 5 K. (a) Normal isotopic $^{32}SO_2$ isotopic sample at 0.2% in argon co-deposited for 60 min, (b) after annealing to 8 K, (c) after >220 nm irradiation, (d) after annealing to 10 K, (e) after annealing to 12 K, (f) $^{34}SO_2$ isotopic sample at 0.2% in argon co-deposited, (g) after annealing to 8 K, (h) after >220 nm irradiation, (i) after annealing to 10 K, (j) after annealing to 12 K, (k) $S^{18}O_2$ and $S^{16,18}O_2$ isotopic mixture at 0.1% co-deposited, (l) after annealing to 8 K, (m) after annealing to 10 K, (n) after annealing to 12 K.

---

[24] Forney, D.; Kellogg, C. B.; Thompson, W. E.; Jacox, M. E. *J. Chem. Phys.* **2000**, *113*, 86 and references therein (SO_2^-).

[25] Andrews, L.; Zhou, M.; Liang, B.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **2000**, *122*, 11440 (OUCO).

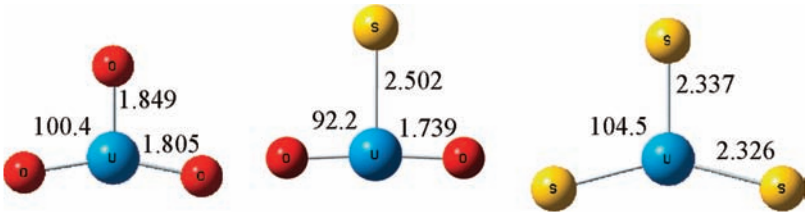

Figure 4. Structures for the series of molecules UO_3, SUO_2, and US_3 calculated at the (B3LYP/6-311+G(3df)/SDD) level of theory. Bond lengths in angstrom and angles in degrees.

Table 2. Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for U Atom and U^+ Cation Reaction Products with Sulfur Dioxide[a]

$^{32}SUO_2$	$^{34}SUO_2$	$^{32}SU^{16,18}O_2$	$^{32}SU^{18}O_2$	$^{32}SUO_2$	identity
B3LYP	B3LYP	B3LYP	B3LYP	BPW91	
918.86(403)	918.86	903.3	872.5	888.7(338)	B_2, OUO str
853.46(95)	853.40	821.5	804.7	825.0(83)	A_1, OUO str
426.8(65)	415.8	426.7	426.6	407.9(49)	A_1, US str
195.7(20)	195.5	191.0	185.7	162.8(19)	A_1, OUS bend
153.5(1)	151.9	150.5	148.2	139.2(1)	B_2, OUS bend
145.3(33)	145.2	141.8	138.3	138.8(30)	B_1, OUO bend

$^{32}SUO_2^+$	$^{34}SUO_2^+$	$^{32}SU^{16,18}O_2^+$	$^{32}SU^{18}O_2^+$	identity
B3LYP	B3LYP	B3LYP	B3LYP	
1027.5(282)	1027.5	1008.9	975.8	B_2, OUO str
939.9(34)	939.9	905.8	886.1	A_1, OUO str
340.4(20)	331.9	340.3	340.1	A_1, US str
211.2(12)	210.9	206.1	200.6	A_1, OUS bend
179.3(21)	179.3	174.8	170.3	B_1, OUO bend
128.3(0)	127.1	125.7	123.5	B_2, OUS bend

$(SO_2)(SUO_2)$	$(^{34}SO_2)-$	$(^{18}OSO)-$	identity
B3LYP[b]	B3LYP	B3LYP	
1245.7(259)	1233.0	1199.9	−S=O str
952.5(346)	952.5	952.5	antisym OUO str
882.8(108)	882.8	882.8	sym OUO str
765.3(117)	757.5	764.4	sym S−O str
522.6(128)	520.3	521.6	S=U−O bend
476.3(12)	472.2	467.8	SO_2 bend

^{32}SUO	^{34}SUO	$^{32}SU^{18}O$		identity
B3LYP[c]	B3LYP	B3LYP	B3LYP[d]	
904.6(290)	904.6(290)	856.4(265)	868(270)	U−O str
453.7(65)	441.7(62)	453.4(64)	426(79)	U−S str
80.9(21 × 2)	80.5(21 × 2)	77.9(20 × 2)	124(8)	SUO bend

[a] B3LYP or BPW91 density functionals and 6-311+G(3df)/SDD. The major product SUO_2 is a singlet state. [b] Singlet state. Only the six highest-frequency vibrations are listed, those in the spectral range available. [c] This triplet state is linear, SU, 2.326 Å and UO, 1.793 Å. [d] This triplet state is bent and 5 kcal/mol higher, SU, 2.407 Å, UO, 1.815 Å, SUO, 121°.

(VI) sulfido-dioxide SUO_2 molecule with a C_{2v} almost T-shaped structure. The lowest-energy quintet species (U(II)) has C_s symmetry, with SO_2 linked in a bidentate mode through the two oxygen atoms; it is 104 kcal/mol above SUO_2. The least unstable triplet species identified is planar, with an almost linear O−U−O grouping but with substantially different U−O distances and a very acute S−U−O angle of 43°; this system is 34 kcal/mol above SUO_2. It turns out that the observed IR spectra provide no evidence for any of these higher-energy species, and their computed spectra are sufficiently characteristic that they would have been detected had they been formed in significant quantity.

Structures for the series of molecules UO_3, SUO_2, and US_3 are compared in Figure 4. It is interesting to note that the unique U=S bond in the trisulfide is 0.045 Å shorter than this bond in SUO_2 where the U=O bonds are 0.022 Å shorter than the two equivalent U=O bonds in UO_3. Calculated vibrational frequencies for the SUO_2 molecule and related product molecules are listed in Table 2. Natural charges and electron configurations are listed in Table 3. As expected the charge on U decreases with S substitution. In principle, a T-shaped isomer of SUO_2 is possible in which an oxygen atom is on the stem of the T, making the two oxygen atoms non-equivalent; however, geometry optimizations for this isomer with C_s symmetry converged to the species shown in Figure 4, where the unique S atom is on the stem of the T.

Calculations were also done for the SUO triatomic molecule, the SUO_2^+ cation, and the precursor adducts,

Table 3. Structural Parameters and Physical Constants Computed for UO_3, SUO_2, and US_3 in Singlet States and C_{2v} Symmetry[a]

parameter	UO_3(B3)	SUO_2(B3)	SUO_2(BP)	US_3(B3)
r(U−O,S top)	1.849	2.382	2.390	2.337
r(U−O,S side)	1.845	1.783	1.801	2.327
(O,S−U−O,S)	100.4	100.6	101.4	104.5
q(O,S top)[b]	−0.68	−0.45	−0.0.38	−0.269
q(U)[b]	1.95	1.66	1.53	0.80
q(O,S side)[b]	−0.63	−0.61	−0.58	−0.265
U(s)[c]	0.06	0.15	0.14	0.15
U(d)[c]	1.52	1.64	1.56	2.24
U(f)[c]	2.75	2.81	2.98	2.87

[a] Bond lengths and angles are in anstrom and degrees (see Figure 4). All calculations performed at the B3LYP (listed as B3) or BPW91 (listed as BP)//6-311 + G(3df)//SDD level. [b] Natural atomic charges from NBO analysis. [c] Natural electron configuration for U valence orbitals.

$(O_2S)(SUO_2)$ and $(SO_2)(SUO_2)$, in which SO_2 binds to U through S or O, respectively, using both B3LYP hybrid and BPW91 pure density functionals to support the identification of new product absorptions. The C_s $(O_2S)(SUO_2)$ complex was bound by 6 kcal/mol at the B3LYP level (note that actinide thermochemistry is predicted much more reliably by hybrid DFT than by GGA functionals),[26] the OUO modes blue-shifted by 18 and 13 cm^{-1}, and the symmetric SO_2 mode red-shifted by 18 cm^{-1}. In contrast the C_1 $(SO_2)(SUO_2)$ complex is substantially more strongly bound, by 34 kcal/mol (B3LYP), the OUO modes are blue-shifted by 25 and 17 cm^{-1}, and a very strong −S=O stretch is computed 66 cm^{-1} above the symmetric SO_2 mode. The C_1 $(SO_2)(SUO_2)$ complex no doubt gains some stability from S−S bonding in the four-membered ring structure (see Figure 5).

Our B3LYP calculation for the $^2B_2$ ground state SUO_2^+ cation is straightforward. It is interesting that the B3LYP ionization energy for SUO_2 (191 kcal/mol) is almost as high as the value computed for UO_3 (221 kcal/mol). The latter is near the 10 eV appearance potential of the gaseous UO_3^+ cation in Knudsen effusion mass spectrometry experiments.[27] Although the SUO_2^+ cation has the same basic structure as the neutral molecule, the bond lengths and angles computed are slightly different (UO, 1.739 Å; US, 2.502 Å; OUS, 92.3°). The Mulliken atomic spin densities show that ionization comes essentially from the sulfur atom.

Several low-energy configurations for the SUO molecule, which has a triplet ground state, are located in our preliminary DFT calculations. Three orbitals are almost degenerate for linear SUO: non-bonding f-ϕ, non-bonding f-δ, and essentially non-bonding s-σ. At the B3LYP level of theory, the $\delta\phi$ configuration for SUO lies lowest, and we note that neutral UO_2, which is linear, has a $^3\Phi$ ($\phi\sigma$) ground state.[4,28]

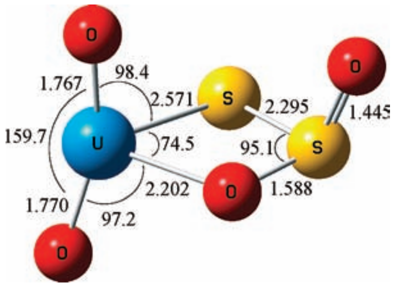

Figure 5. Structure calculated for the $(SO_2)(SUO_2)$ adduct at the (B3LYP/6-311 + G(3df)/SDD) level of theory. Bond lengths in angstrom and angles in degrees.

Discussion

The major product SUO_2 molecule will be identified, and bonding in the series of molecules UO_3, SUO_2, and US_3 considered. The minor triatomic product SUO, the SUO_2^+ cation, and the precursor adduct, $(O_2S)(SUO_2)$, will also be assigned.

SUO_2 Identification. The strong new argon matrix absorptions at 891.2 and 821.7 cm^{-1} shift to 846.6 and 774.0 cm^{-1} and define oxygen 16/18 isotopic frequency ratios of 1.05268 and 1.06163. The former ratio is characteristic of an antisymmetric O=U=O stretching mode,[4] and the latter ratio is slightly larger than the harmonic ratio for a totally symmetric O=U=O stretching mode (1.06080). The appearance of one intermediate mixed oxygen 16, 18 isotopic band for each mode, at 875.5 and at 793.3 cm^{-1} with relative intensities matching the $S^{18}O_2$ and $S^{16,18}O_2$ precursor bands, demonstrates that this new molecule contains two equivalent oxygen atoms. These sharp bands can be measured to an accuracy better than 0.1 cm^{-1}, and the $^{34}SO_2$ experiment reveals shifts to 891.1 and 821.5 cm^{-1}. Although the former 0.1 cm^{-1} shift may not be outside of experimental error, the latter 0.2 cm^{-1} difference indicates a measurable shift. Thus, this molecule contains sulfur even though the U=S stretching mode was not observed.

Our density functional frequency calculations at the B3LYP level of theory find strong 918.86 cm^{-1} (403 km/mol) and 853.46 cm^{-1} (95 km/mol) frequencies (infrared intensities). The former frequency does not shift with sulfur-34, but the latter sustains a 0.06 cm^{-1} shift as this symmetric O=U=O stretching mode couples very slightly with the symmetric U=S stretching mode. Both modes shift considerably with oxygen-18 substitution at both atomic positions, and harmonic 16/18 ratios of 1.05318 and 1.06064 are defined. Single oxygen-18 substitution gives observed 1.01793 and 1.03619 oxygen 16/18 ratios for comparison to computed 1.01727 and 1.03895 harmonic values. The asymmetry in the mixed isotopic components within the oxygen isotopic triplets (grouped in Figures 1 and 3), which is manifested in the different 16,16/16,18 isotopic ratios 1.01793 and 1.03619 arises because of interaction between these two modes in the mixed isotopic molecule of lower symmetry and demonstrates further that the two major bands are due to modes of different symmetry in the same molecule. Very good agreement between calculated and observed values for single and double oxygen-18 substitution in both antisymmetric and symmetric O=U=O stretching modes for the SUO_2 molecule

---

(26) Clavaguéra, C.; Marsden, C. J.; Bégue, D.; Pouchan, C. *Chem. Phys.* **2004**, *302*, 1.

(27) Guido, M.; Balducci, G. *J. Chem. Phys.* **1991**, *95*, 5373 and references therein.

(28) (a) Gagliardi, L.; Heaven, M. C.; Krogh, J. W.; Roos, B. O. *J. Am. Chem. Soc.* **2005**, *127*, 86. (b) Fleig, T.; Jensen, H. J. Aa.; Olsen, J.; Visscher, L. *J. Chem. Phys.* **2006**, *124*, 104106. (c) Infante, I.; Eliav, E.; Vilkas, M. J.; Ishikawa, Y.; Kaldor, U.; Visscher, L. *J. Chem. Phys.* **2007**, *127*, 124308.

verifies these assignments and the identification of this new U(VI) molecule.

Similar information is found in the neon matrix spectrum. The major bands are 13.3 and 13.8 cm^{-1} higher in the more weakly interacting neon matrix host, but the isotopic characteristics are almost identical to the argon matrix values. See for example the oxygen 16/18 isotopic frequency ratios and the $^{32}S^{16,18}O_2$ and $^{32}S^{18}O_2$ frequency patterns in Table 1. Nearly the same 12.9 and 14.8 cm^{-1} blue shifts from argon to neon are observed for two modes of the $^1A_1$ ground state UO_3 molecule, which are typical matrix shifts.[29] These comparisons further support our identification of the SUO_2 molecule.

It is interesting the compare harmonic frequencies calculated for the SUO_2 molecule using the B3LYP hybrid density functional and the BPW91 pure density functional. As is generally found, the hybrid functional predicts slightly higher frequencies than the pure density functional.[26,30] The O=U=O stretching frequencies for the SUO_2 molecule are predicted about 30 cm^{-1} higher with the hybrid functional. The gaseous molecule is not known, but extrapolating from argon to neon to gas phase predicts these two modes near 925 and 855 cm^{-1}, which are very close to the B3LYP values. Note that the lower BPW91 frequencies are within 5 cm^{-1} of the argon matrix values. So here the BPW91 functional clearly underestimates the O=U=O stretching frequencies, and the B3LYP functional predicts frequencies very close to extrapolated gas phase values for the SUO_2 molecule.

It is also interesting to compare the calculated and observed frequencies for the SUO_2 molecule with those for the analogous UO_3 molecule. The calculated O=U=O angle in the SUO_2 molecule, 158.8°, is slightly smaller than the corresponding 159.2° angle for the UO_3 molecule presumably owing to greater repulsions for the larger sulfur electron cloud. This is attested by the still smaller 151.0° S=U=S angle in US_3 calculated here with the same method. On going from UO_3 to SUO_2 the antisymmetric O=U=O stretching mode is blue-shifted 42.1 cm^{-1} (B3LYP) or 39.0 cm^{-1} (neon matrix), and the symmetric mode is red-shifted 27.4 cm^{-1} (B3LYP), but this much weaker mode is not observed for the UO_3 molecule in solid neon. Hence, the small decrease in the O=U=O angle and interaction with S lone pairs triple the infrared intensity of the symmetric O=U=O stretching mode in the SUO_2 molecule.

The SUO_2 molecule is formed directly in the concerted highly exothermic reaction 1, which is computed as −196 kcal/mol at the B3LYP level in the absence of spin orbit coupling. The O atom dissociation from SO_2 is sufficiently high (121 kcal/mol)[31] to make UO stripping unlikely as attested by the detection of only a trace of UO at 819.7 cm^{-1} beside the major product band in Figure 1. Reaction 1 may proceed through insertion to form OUSO followed by immediate rearrangement in the matrix cage to the more stable U(VI) product SUO_2. The clear increase of the major SUO_2 absorptions in solid argon and neon on annealing indicates that reaction 1 is spontaneous and requires no activation energy.

$$U + SO_2 \rightarrow SUO_2 \qquad (1)$$

SUO_2 Structure. The computed C_{2v} structure for SUO_2, is analogous to that for UO_3.[1−6] Two bond length changes in the UO_3, SUO_2, and US_3 molecule series, Figure 4, are noteworthy. The O=U=O bond lengths decrease 0.022 Å on sulfur substitution in the third position, and this U=S bond is 0.045 Å longer than computed for US_3. Our NBO analysis reveals an increase in the U 5f configuration from 2.75 to 2.81 to 2.87 and U 6d configuration from 1.52 to 1.64 to 2.24 in the series UO_3, SUO_2, and US_3. The natural charges on U decrease 1.95→1.66→0.80 in the series, as less charge is withdrawn by the less electronegative S, seems to sustain stronger U−O bonds in UO_3 compared to SUO_2.

The C_{2v} structure for UO_3 is well established, and the related SUO_2 molecule follows suit with a very similar structure. This is in marked contrast to the pyramidal, C_{3v}, structure of the similar WO_3 molecule.[32,33] One is thus tempted to conclude that the special angular properties of the UO_3, SUO_2, and US_3 molecular structures are due to the involvement of U 5f orbitals, which are not present with the symmetrical WO_3 molecule. Dyall has carefully discussed the consequences of f-orbital participation on molecular shapes.[34] We note above the increase in both U 5f and 6d configurations with increasing electron density at the U center (decrease in positive charge), but the increase in 6d is much more pronounced that that for 5f. As a result the U−S bond lengths are more nearly equal in US_3 (difference 0.01 Å) than are the U−O bonds in UO_3 (difference 0.042 Å) where the latter has the more dominant 5f involvement.

SUO_2^+ Identification. The sharp 987.5 cm^{-1} band shows no sulfur-34 shift so this absorption is not due to a precursor mode, and in this region it is therefore most likely due to an antisymmetric O=U=O vibration. The shift to 938.3 cm^{-1} and the oxygen 16/18 isotopic frequency ratio 1.05244 are again characteristic of an antisymmetric O=U=O vibration, and the weak mixed 16, 18 component at 969.4 cm^{-1} with 16,18/16,16 ratio 1.01867 completes this characterization as found in similar isotopic frequency ratios for SUO_2 above. In solid neon this band blue shifts 18.0 cm^{-1} to 1005.5 cm^{-1}. The dioxygen-18 counterpart at 955.5 cm^{-1} again defines the antisymmetric O=U=O vibration isotopic ratio 1.05233, and the mixed oxygen isotopic counterpart at 986.8 cm^{-1} gives almost the same single oxygen isotopic substitution ratio, 1.01895, as the argon matrix observations.

The position of this antisymmetric O=U=O vibration above that for UO_2^+ itself (Table 1) suggested the possible SUO_2^+ assignment, so calculations were performed for the latter cation. Our B3LYP calculation predicted a very strong antisymmetric O=U=O vibration for this $^2B_2$ ground state cation at 1027.5 cm^{-1} with no sulfur-34 shift

---

(29) Jacox, M. E. *Chem. Phys.* **1994**, *189*, 149.

(30) (a) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502. (b) Andersson, M. P.; Uvdal, P. L. *J. Phys. Chem. A* **2005**, *109*, 2937. (c) von Frantzius, G.; Streubel, R.; Brandhorst, K.; Grunenberg, J. *Organometallics* **2006**, *25*, 118. (d) Iché-Tarrat, N.; Marsden, C. J. *J. Phys. Chem. A* **2008**, *112*, 7632.

(31) Okabe, H. *J. Am. Chem. Soc.* **1969**, *73*, 762. D[OS-O].

(32) Bare, W. D.; Souter, P. F.; Andrews, L. *J. Phys. Chem. A* **1998**, *102*, 8279. (Mo, W + O_2).

(33) Zhou, M.; Andrews, L. *J. Chem. Phys.* **1999**, *111*, 4230. (Cr, Mo, W + O_2 in neon).

(34) Dyall, K. *Mol. Phys.* **1999**, *96*, 511.

and 1.05298 harmonic 16,16/18,18 and 1.01844 harmonic 16,16/16,18 isotopic frequency ratios. The order-of-magnitude weaker symmetric counterpart predicted at 939.9 cm^{-1} was not observed. The above agreement with the frequency calculation and isotopic effects for SUO_2^+ and the comparison with UO_2^+ all support our matrix identification of SUO_2^+.

The SUO_2^+ cation can be prepared three different ways in these experiments. First, ionization of the neutral product using hard ultraviolet radiation in the ablation plume as shown in reaction 2 is the most direct process. Annealing can foster the reaction of U^+, also produced by laser ablation and proposed to react with dioxygen to form UO_2^+ on annealing in earlier experiments,[4] with SO_2, as in highly exothermic reaction 3, which is computed as −149 kcal/mol at the B3LYP level in the absence of spin orbit coupling. Finally, the reaction of S with UO_2^+ can also give the SUO_2^+ cation, reaction 4, which is 42 kcal/mol exothermic.

$$SUO_2 + \text{vac uv} \rightarrow SUO_2^+ \qquad (2)$$

$$U^+ + SO_2 \rightarrow SUO_2^+ \qquad (3)$$

$$S + UO_2^+ \rightarrow SUO_2^+ \qquad (4)$$

SUO Identification. The very weak 857.0 cm^{-1} band increases on annealing, decreases on ultraviolet irradiation, but restores on subsequent annealing as illustrated in Figures 1 and 2 (to absorbance 0.005). The band shows no sulfur-34 shift but a large oxygen-18 shift to 811.5 cm^{-1} (ratio 1.05607). There is no evidence for a mixed oxygen isotopic counterpart in the 820−840 cm^{-1} region. This oxygen 16/18 isotopic frequency ratio is appropriate for a single O vibrating against U as in UO itself, but UO absorbs at 819.7 cm^{-1} in solid argon.[1,2,4,7] A neon matrix counterpart was observed at 871.5 cm^{-1} with both sulfur isotopes, but no oxygen-18 counterpart could be detected. This blue neon matrix shift is near those observed for SUO_2, and larger than that found for US_2 (3.6 cm^{-1}).[8] These relatively small argon−neon matrix shifts suggest that the electronic state is the same in both matrix hosts, in marked contrast to the large change in UO_2 on going from solid argon to neon.[4]

Our preliminary B3LYP calculations for the SUO molecule, a relative of OUO and SUS,[1,2,4,7,8] find a linear triplet low energy state with strong computed U−O stretching mode at 904.6 cm^{-1} and 16/18 ratio 1.0561 with no sulfur-34 displacement. The much weaker U−S stretching mode computed at 453.7 cm^{-1} is too low for us to observe. Another low energy triplet state is bent (121°) and has a calculated U−O stretch at 867.6 cm^{-1} (16/18 ratio1.0566). Hence, the U−O stretching mode of SUO is expected to fall in the 850−900 cm^{-1} range.

The weak 857.0 cm^{-1} argon matrix and 871.5 cm^{-1} neon matrix bands are probably due to the SUO molecule although our case would be stronger with more intense bands and the observation of both stretching modes. This molecule is interesting because of its relationship to OUO (linear) and SUS (bond angle near 120°), which have been investigated in our laboratories.[3,7,8] In addition SUO is surely a multireference problem that will require higher levels of computational theory than the preliminary estimates offered here.

The SUO molecule is probably made in these experiments by the U reaction with the SO byproduct of sample irradiation during deposition. The SUO molecule

$$U + SO \rightarrow SUO \qquad (5)$$

absorption increases on annealing while the SO band decreases. Recall that the U and O_2 reaction proceeds on annealing.[4] Reaction 5 is exothermic by 164 kcal/mol (B3LYP, computed in the absence of spin orbit coupling). Ultraviolet irradiation likely leads to S detachment, which may preclude a significant yield on sample deposition under exposure to the intense ablation plume.

$$SUO + \text{uv} \rightarrow S + UO + \text{anneal} \rightarrow SUO \qquad (6)$$

$(SO_2)(SUO_2)$ identification. The 927.3 cm^{-1} absorption increases on annealing and reveals isotopic characteristics similar to the major 891.2 cm^{-1} band for SUO_2, namely, the progressive shifts with one oxygen-18 to 910.3 cm^{-1} (ratio 1.01868) and two oxygen-18's to 880.9 cm^{-1} (ratio 1.05267). No sulfur-34 shift was observed. A weaker associated lower band was observed at 847.0 cm^{-1} (16/18 isotopic ratio 1.0600) again with no sulfur-34 shift. Another weaker band at 1210.9 cm^{-1} with the same profile as the above bands tracks with them on annealing and reaches a final absorbance of one-fourth of the 927.3 cm^{-1} band (not shown). This band is blue-shifted 63.7 cm^{-1} from the symmetric SO_2 stretching mode in solid argon at 1147.2 cm^{-1}, but its 12.9 and 43.5 cm^{-1} sulfur-34 and oxygen-18 shifts are close to values for a simple S−O vibration. The above 16/18 isotopic frequency ratios again point to antisymmetric and symmetric O=U=O stretching modes as found for the major product molecule. The steady increase of these new absorptions on annealing suggests a precursor adduct, but the blue shifts (36.1 and 25.3 cm^{-1}) in the O=U=O stretching modes are unusual. This indicates that any intermolecular interaction does not directly involve the oxide centers. Only natural isotopic counterparts of the major bands were observed in solid neon at 936 and 855 cm^{-1}, which represent 9 and 8 cm^{-1} blue shifts from the argon matrix values.

Calculations were launched for this probable adduct using both S and O coordination, and the C_1 $(SO_2)(SUO_2)$ complex is predicted to be more strongly bound, by 34 kcal/mol instead of only 6. The preference for SO_2 to bind to U in SUO_2, which is a fairly hard center, through O rather than through S should not be a surprise: SO_2 protonates preferentially on O rather than on S, with a difference of proton affinity at the B3LYP level of theory of 53 kcal/mol. The OUO modes in the C_1 $(SO_2)(SUO_2)$ complex are blue-shifted by 25 and 17 cm^{-1}, and a very strong −S=O stretch is computed 66 cm^{-1} above the symmetric SO_2 mode. This is significant because the weak band observed 63.7 cm^{-1} above the symmetric SO_2 mode exhibits 1.01077 and 1.03726 isotopic 32/34 and 16/18 frequency ratios, which are in excellent agreement with the 1.01030 and 1.03817 computed values. Furthermore, no red-shifted symmetric SO_2 mode counterpart was found like that predicted for the S-bonded adduct. The weaker, lower bond stretching modes were not observed here. Overall the agreement between the observed and computed spectra for the C_1 (SO_2)(SUO_2) complex is excellent and it substantiates this assignment.

$$SO_2 + SUO_2 \rightarrow (SO_2)(SUO_2) \qquad (7)$$

Since the binding of SO_2 to SUO_2 turns out to be more favorable than we had anticipated (34 kcal/mol), we investigated the interaction between a simpler Lewis base (H_2O) and SUO_2. The binding energy is still appreciable, at 23 kcal/mol. It thus appears that there is a rich coordination chemistry of SUO_2 (and presumably also for UO_3) awaiting discovery.

Conclusions

Laser ablated U atoms react with SO_2 on deposition and on annealing in solid argon and neon to form the SUO_2 molecule, which is identified from two strong O=U=O stretching modes as predicted by DFT. These infrared absorptions exhibit oxygen 16/18 isotopic frequency ratios for antisymmetric and symmetric O=U=O stretching modes and mixed isotopic components for the vibration of two equivalent oxygen atoms. The UO_3, SUO_2, US_3 molecules have analogous C_{2v} structures, based on density functional calculations, but the analogous group 6 metal containing molecules have pyramidal structures.[33,35,36] The SUO_2 molecule acts as a fairly strong Lewis acid toward SO_2 and H_2O, so a rich coordination chemistry of these molecules can safely be anticipated. The SUO_2^+ molecular cation and the SUO molecule have been detected through their strongest absorptions. The SUO molecule promises to be a computational challenge like its UO_2 and US_2 counterparts.

Acknowledgment. We gratefully acknowledge financial support from Subgrant 6855694 under Prime Contract No. DE-AC02-05CH11231 to the Lawrence Berkeley National Laboratory from the DOE and NCSA computing Grant CHE07-0004N to L.A.

---

(35) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2009**, *113*, in press. (Gr 6 + SO_2).

(36) Liang, B.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 6945. (Cr, Mo, W + S_2).