Supporting Information

Sulfur-Substituted Uranyl Stabilized by Fluoride Ligand: Matrix Preparation of $U(O)(S)F_2$ via Oxidation of U(0) by SOF_2

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Experimental and Theoretical Methods

The experimental apparatus and procedure for the preparation and characterization of $U(O)(S)F_2$ have been described previously.[1-3] The Nd: YAG laser fundamental (Continuum, Minilite II, 1064nm, 10 Hz repetition rate, 6 ns pulse width) was focused onto a rotating uranium target. The laser ablated U atoms were co-deposited with argon (99.999%, Xiangkun Special Gas, China) containing 0.5% SOF_2 or neon (99.999%, Dalian Special Gas, China) containing 0.5% SOF_2 onto a cryogenic CsI window maintained at 4 K for 60 (Ar) or 30 (Ne) minutes. ^{18}O-enriched SOF_2 sample was synthesized by the reaction of AgF (99.9%, Sigma-Aldrich) with sulfur powder (99.9%, Sinopharm Chemical Reagent, China) in the presence of $H_2{}^{18}O$, while $^{34}SOF_2$ was prepared via the reaction of AgF with ^{34}S powder (99.3%, ISOFLEX) in the presence of H_2O. The gaseous products were purified by several freeze-pump-thaw cycles using liquid nitrogen before use. The infrared spectra were recorded between 4000 and 400 cm^{-1} on a Bruker Vertex 70 V spectrometer at 0.5 cm^{-1} resolution with a DLaTGS detector. Matrix samples were annealed at different temperatures and cooled back to 4 K for spectral acquisition. Selected samples were subjected to $\lambda > 220$ nm UV-vis irradiation using a 250 W mercury arc lamp with the outer globe removed.

DFT calculation were performed using the Gaussian 09 program.[4] The hybrid B3LYP functional was employed together with the 6-311+G(d) basis set for O, S, F atoms and 60 electron core SDD pseudopotentials for U atom.[5-9] All of the structure parameters were fully optimized. Harmonic vibrational frequencies were obtained analytically, and zero-point energies were derived. Natural bond orbital (NBO) calculations were carried out with the NBO6 program.[10] Quantum theory of atoms in molecules (QTAIM)[11] analysis were

performed using Multiwfn[12] and the wave functions for QTAIM analysis were generated by Gaussian 09 at the B3LYP/6-311+G(d) level.

Results

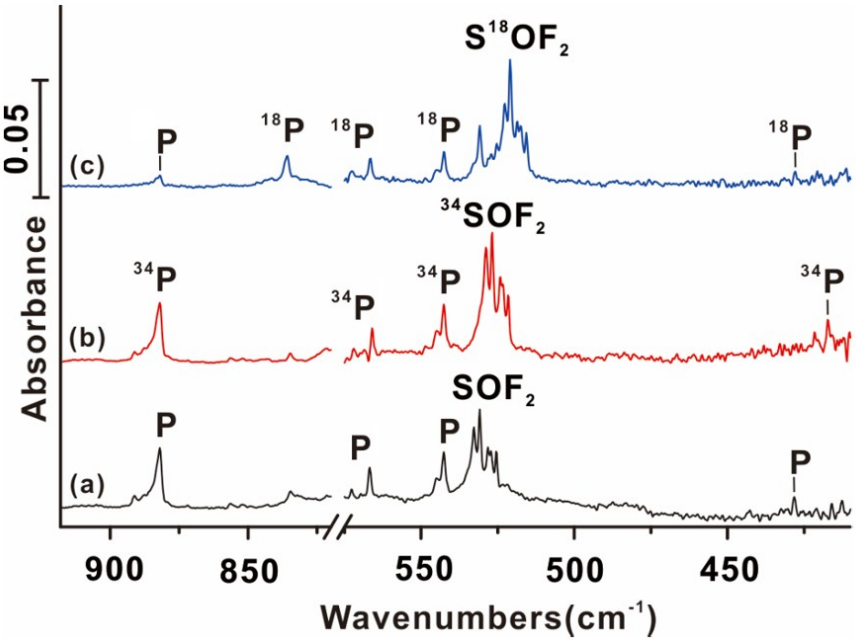

Figure S1. Infrared spectra of laser-ablated uranium atoms and isotopically substituted SOF_2 reaction products in excess argon at 4 K. Spectra were recorded after sample annealing to 30 K following $\lambda > 220$ nm irradiation. a) 0.5% SOF_2; b) 0.5% $^{34}SOF_2$; c) 0.5% $S^{18}OF_2$. P, ^{34}P and ^{18}P denote the bands of $U(O)(S)F_2$, $U(O)(^{34}S)F_2$ and $U(^{18}O)(S)F_2$, respectively.

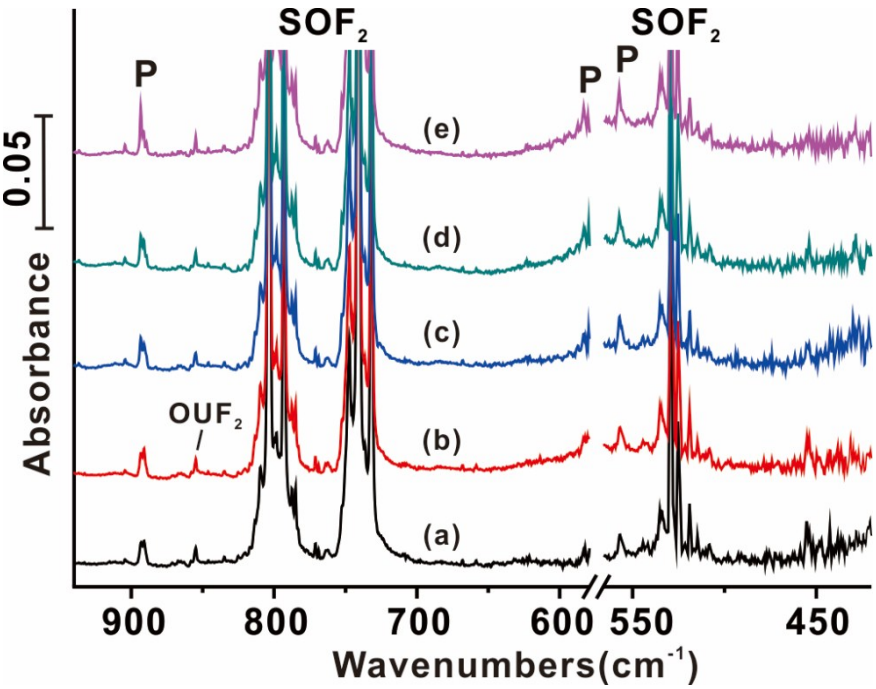

Figure S2. Infrared spectra of laser-ablated uranium atoms and SOF_2 reaction products in excess neon at 4 K. a) U + 0.5% SOF_2 deposition for 30 min; b) after annealing to 6 K; c) after $\lambda > 220$ nm UV-vis irradiation; d) after annealing to 8 K. e) after annealing to 10 K. P denotes the $U(O)(S)F_2$ absorptions.

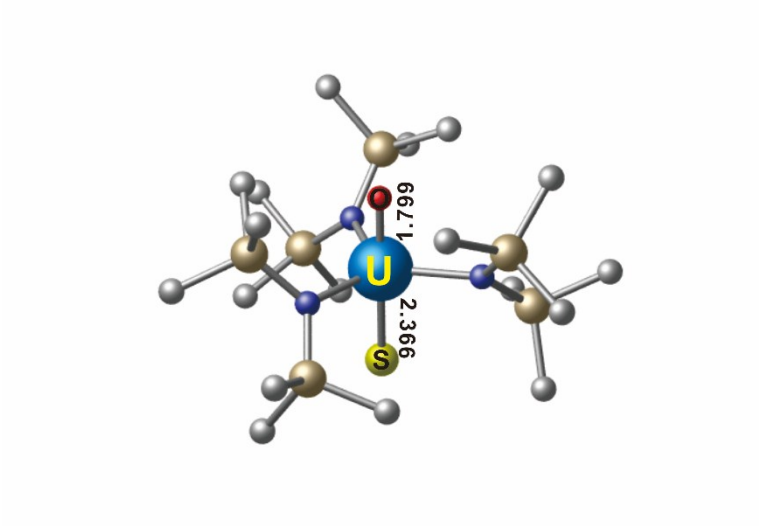

Figure S3. Optimized structure of $U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$) (bond lengths in angstroms) with C_3 symmetry at the B3LYP/6-311+G(d)/SDD level of theory. Hydrogen atoms are omitted for clarity.

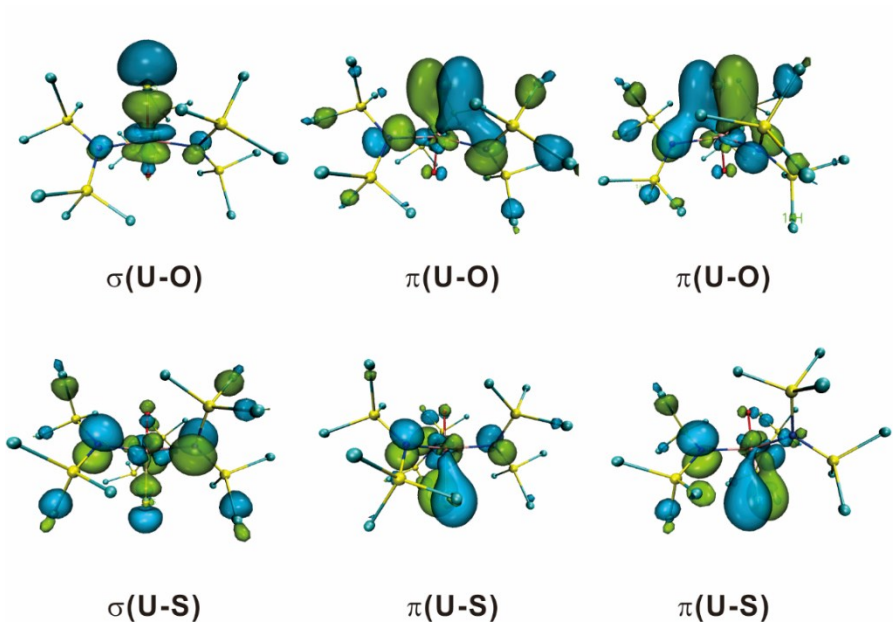

Figure S4. Natural bond orbitals of $U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$).

Table S1. Observed Infrared Absorptions (cm^{-1}) of $U(O)(S)F_2$, $U(^{18}O)(S)F_2$ and $U(O)(^{34}S)F_2$ in Argon and Neon (in Parenthesis) Matrixes at 4 K.

mode	$U(O)(S)F_2$	$U(^{18}O)(S)F_2$	$U(O)(^{34}S)F_2$
U-O str.	882.0 (893.4)	835.8	882.0
sym. F-U-F str.	566.8 [a] (583.2)	566.6	566.0
antisym. F-U-F str.	542.6 [a] (557.3)	542.5	542.6
U-S str.	428.2	428.0	417.2

[a] Argon matrix site splittings observed at 572.7 and 545.1 cm^{-1}, 572.6 and 545.0 cm^{-1} (^{18}O), 572.0 and 545.1 cm^{-1} (^{34}S).

Table S2. Calculated Infrared Absorptions (cm^{-1}) and Intensities (km/mol) of $U(O)(S)F_2$, $U(^{18}O)(S)F_2$ and $U(O)(^{34}S)F_2$ at the B3LYP/6-311+G(d)/SDD Level.

$U(O)(S)F_2$		$U(^{18}O)(S)F_2$		$U(O)(^{34}S)F_2$	
freq	int	freq	int	freq	int
914.7	288	866.4	264	914.7	288
566.7	80	566.7	80	566.0	82
544.5	168	544.4	168	544.5	168
449.5	69	449.0	68	438.3	65
195.5	9	188.9	8	195.5	9
184.2	13	181.0	12	184.1	13
143.9	6	142.6	7	142.2	6
141.5	19	138.6	19	140.3	19

92.2	4	91.8	4	92.1	4

Table S3. Orbital Compositions (%) of the U-O and U-S Bonds in $U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$) from NBO Calculations at the B3LYP/6-311+G(d)/SDD Level.

	bond type	%	s	p	d	f
U-S	σ	S(70.86)	16.73	83.12	0.15	
		U(29.14)	3.44	1.11	44.75	50.70
	π	S(76.87)	0.00	99.91	0.09	
		U(23.13)	0.00	0.16	50.86	48.98
	π	S(76.87)	0.00	99.91	0.09	
		U(23.13)	0.00	0.16	50.86	48.98
U-O	σ	O(75.25)	18.48	81.43	0.09	
		U(24.75)	0.91	1.32	42.55	55.22
	π	O(81.58)	0.00	99.93	0.07	
		U(18.42)	0.00	0.33	46.09	53.58
	π	O(81.58)	0.00	99.93	0.07	
		U(18.42)	0.00	0.33	46.09	53.58

Table S4. Electron Density ρ(r) and Electronic Energy Density H(r) at Selected Bond Critical Points of $U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$)

	ρ(r)	H(r)
U-S	0.128	-0.058
U-O	0.282	-0.241
U-N	0.087	-0.022

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Cartesian coordinates for $U(O)(S)F_2$ and $U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$) obtained at the B3LYP/6-311+G(d)/SDD level of theory

$U(O)(S)F_2$

0 1

F	0.83696600	0.76889200	1.65978900
F	0.83696600	0.76889200	-1.65978900
S	0.83696600	-1.99504900	0.00000000
U	-0.18515200	0.07872700	0.00000000
O	-1.42785800	1.35472900	0.00000000

$U(O)(S)(NR_2)_3^-$ ($R=SiMe_3$)

-1 1

C	0.43930600	5.16656400	0.36077700
H	0.87605500	5.80867500	1.13552900
H	-0.47008100	5.66109700	0.01199600
H	1.14649400	5.14770400	-0.47423100
C	-0.89265900	3.66649200	2.64392700
H	-1.03828000	2.72347800	3.17516900
H	-1.88043300	4.06297000	2.38951400
H	-0.42262400	4.37308300	3.33841000
C	1.93955100	2.97350900	1.64716300
H	2.64326800	3.01306700	0.80992600
H	2.02260500	1.99183000	2.11271300
H	2.27591400	3.71569100	2.38187200
C	-0.75872700	3.81071800	-2.68193700
H	0.01632200	3.18994800	-3.14095300
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H	3.46343400	1.98098000	-2.68664700

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H	3.88479500	-3.56674500	-0.47423100
H	4.59243300	-3.66302400	1.13552900
H	5.13769500	-2.42344600	0.01199600
C	1.60535900	-3.16645600	1.64716300
H	1.28775900	-3.79567100	0.80992600
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