Electronic Supplementary Information

Observation and Investigation of the Uranyl Tetrafluoride Dianion ($UO_2F_4^{2-}$) and Its Solvation Complexes with Water and Acetonitrile

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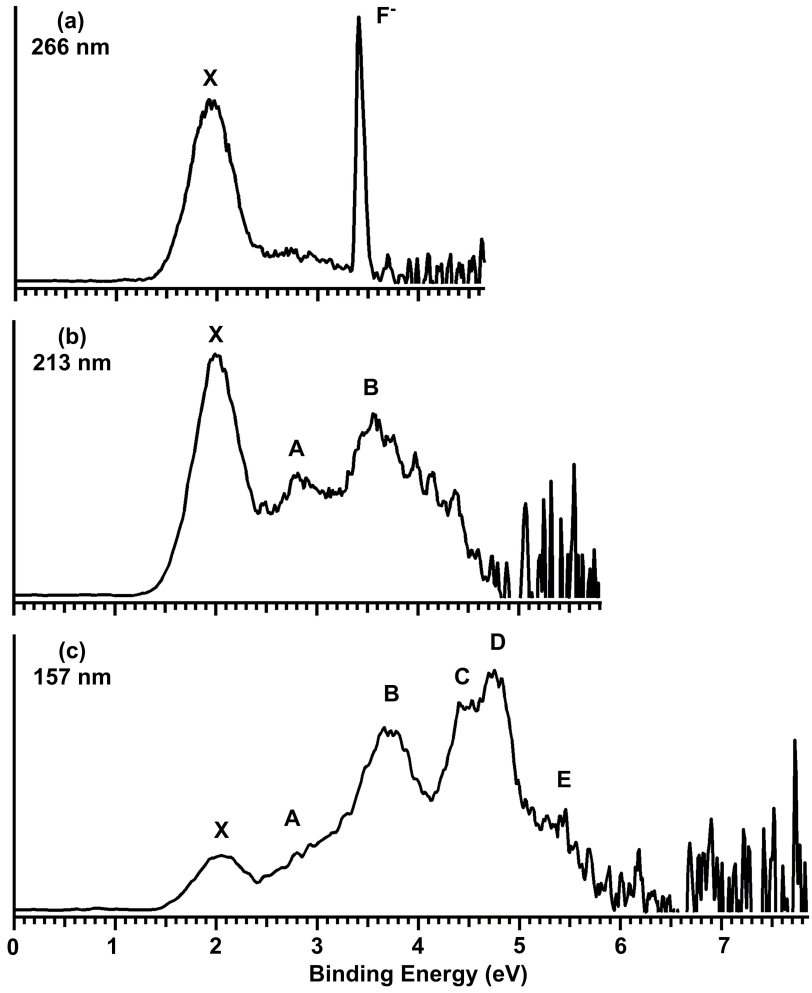

Fig. S1. Photoelectron spectra of $UO_2F_4(H_2O)^{2-}$ at (a) 266 nm, (b) 213 nm, and (c) 157 nm.

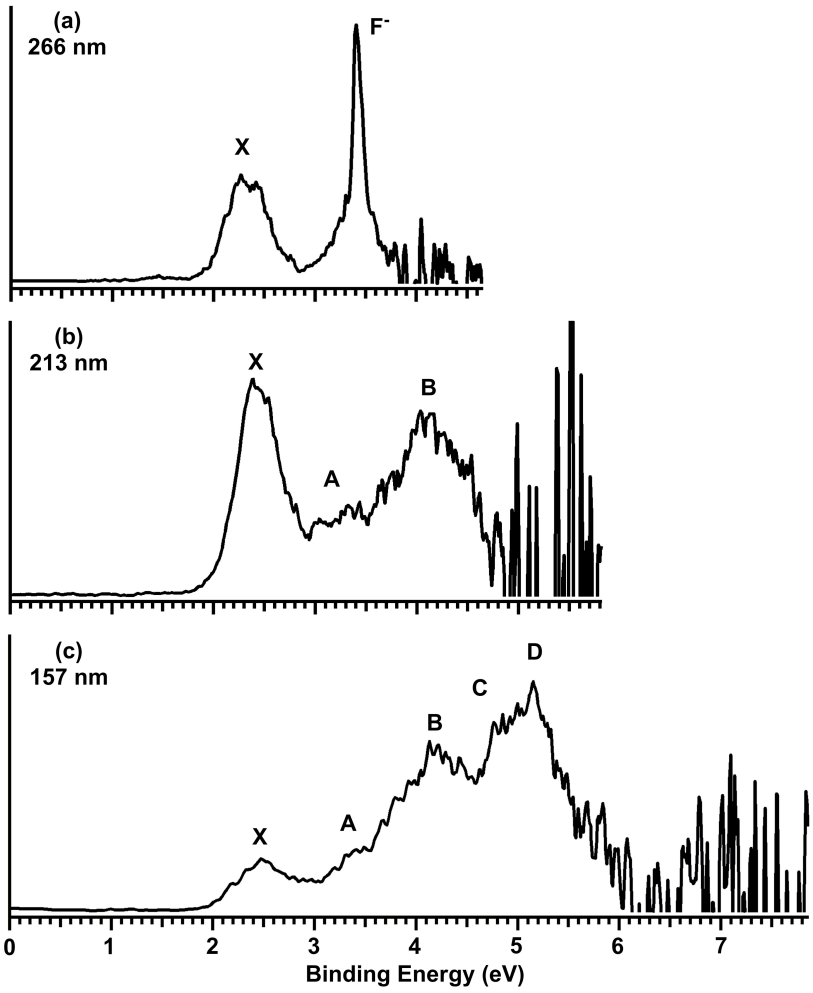

Fig. S2. Photoelectron spectra of $UO_2F_4(H_2O)_2^{2-}$ at (a) 266 nm, (b) 213 nm, and (c) 157 nm.

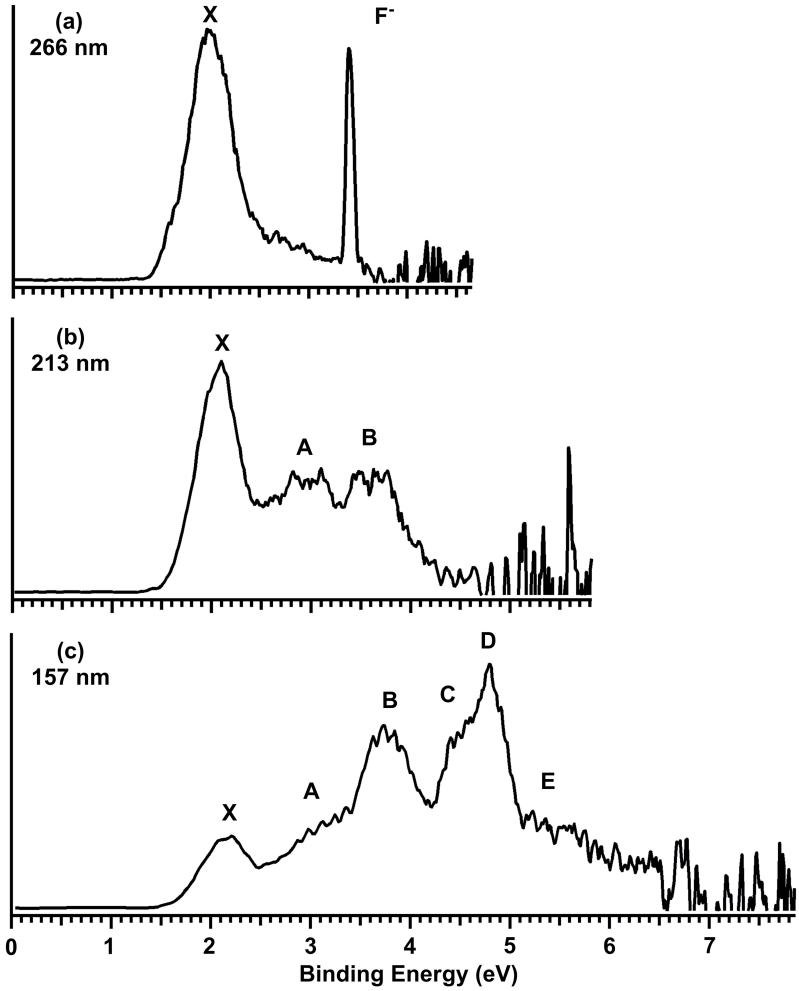

Fig. S3. Photoelectron spectra of $UO_2F_4(CH_3CN)^{2-}$ at (a) 266 nm, (b) 213 nm, and (c) 157 nm.

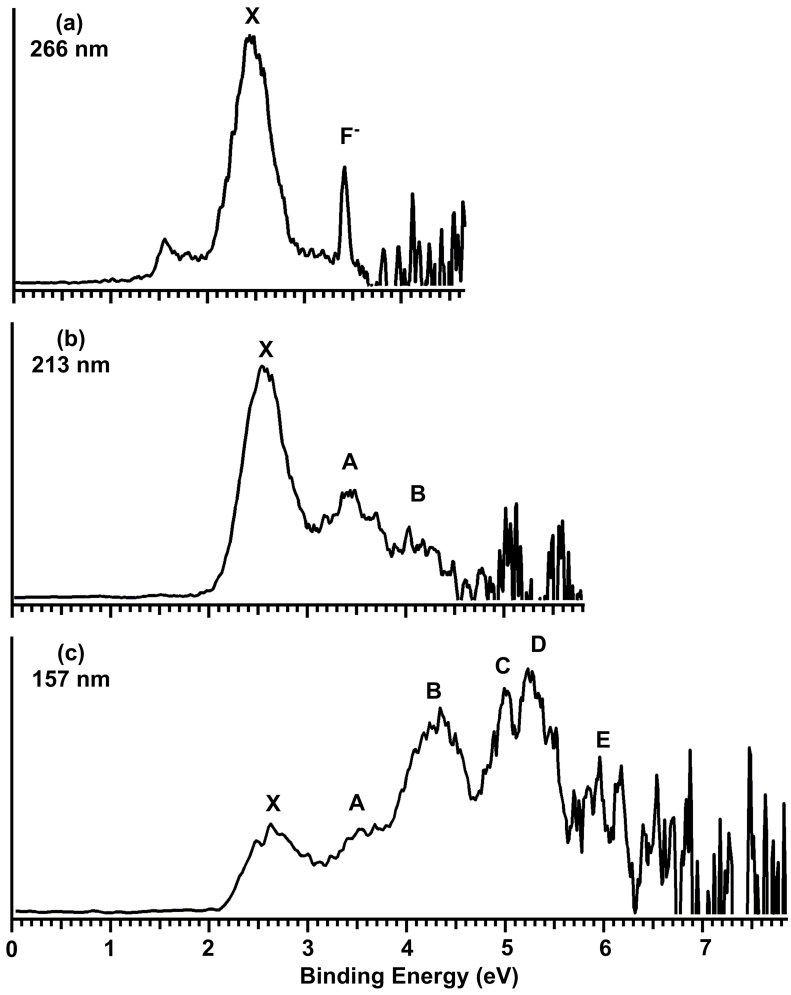

Fig. S4. Photoelectron spectra of $UO_2F_4(CH_3CN)_2^{2-}$ at (a) 266 nm, (b) 213 nm, and (c) 157 nm. The sharp peak at 3.5 eV in (a) is from detachment of F^-, which is produced from photodissociation of the parent dianion. The weak feature at ~1.5 eV in (a) is also due to detachment of photodissociation product.

Table S1 VDE values and the corresponding MOs of $UO_2F_4^{2-}$. VDE_1 is shifted to be 1.5 eV to align with the experimental data, see the corresponding MOs of SR and SO in Fig. 4

VDE#	Energy/eV	Main component of MOs (SR)	MOs(SO)
1	1.50	U-O σ_u	$5e_{1/2u}$
2	2.24	U-O π_u	$4e_{3/2u}$
3	2.39	U-O π_g	$4e_{3/2g}$
4	2.41	U-O π_g	$5e_{1/2g}$
5	2.72	U-O π_u	$4e_{1/2u}$
6	3.03	F 2p	$4e_{1/2g}$
7	3.23	U-O σ_g	$3e_{1/2g}$
8	3.38	F 2p	$3e_{3/2u}$
9	3.40	F 2p	$2e_{3/2u}$
10	3.41	F 2p	$3e_{1/2u}$
11	3.67	F 2p	$2e_{1/2u}$
12	3.72	F 2p	$1e_{3/2u}$
13	3.77	F 2p	$1e_{1/2u}$
14	3.99	F 2p	$3e_{3/2g}$
15	4.13	F 2p	$2e_{3/2g}$
16	4.16	F 2p	$2e_{1/2g}$
17	4.54	F 2p	$1e_{1/2g}$
18	4.57	F 2p	$1e_{3/2g}$
19	11.96	O 2s, U 6p	$e_{1/2u}$

Table S2 Comparisons of state energies between CR-EOMCCSD(T) and CCSD(T) calculations denoted as E_{EOM} and E_{CC}, respectively, for $UO_2F_4^{2-}$. SC: small-core frozen concerning 1s of O and F; LC: large-core frozen concerning 5s, 5p, 5d of U

state	Configuration	contribution	$E_{EOM}(SC)$/eV	$E_{EOM}(LC)$/eV	E_{CC}/eV
aA_{2u}	SOMO:$2a_{2u}$	1	*0*	*0*	*0*
aE_u	$3e_u \rightarrow 2a_{2u}$	0.780	0.64	0.64	0.82
	$2e_u \rightarrow 2a_{2u}$	0.515			
	$1e_u \rightarrow 2a_{2u}$	0.149			
aE_g	$2e_g \rightarrow 2a_{2u}$	0.863	0.72	0.73	0.84
	$1e_g \rightarrow 2a_{2u}$	0.378			
aA_{1g}	$2a_{1g} \rightarrow 2a_{2u}$	0.903	1.17	1.19	1.48
	$1a_{1g} \rightarrow 2a_{2u}$	0.132			
aA_{2g}	$1a_{2g} \rightarrow 2a_{2u}$	0.939	1.76	1.75	1.64
bE_u	$2e_u \rightarrow 2a_{2u}$	0.691	2.00	2.00	1.95
	$3e_u \rightarrow 2a_{2u}$	0.514			
	$1e_u \rightarrow 2a_{2u}$	0.382			
aB_{2u}	$1b_{2u} \rightarrow 2a_{2u}$	0.938	2.21	2.20	2.13
cE_u	$1e_u \rightarrow 2a_{2u}$	0.852	2.26	2.25	2.19
	$2e_u \rightarrow 2a_{2u}$	0.387			
aA_{2u}	$1a_{2u} \rightarrow 2a_{2u}$	0.936	2.45	2.45	2.40
aB_{1u}	$2a_{2u} \rightarrow 4b_{1u}(5f\delta_u)$	0.932	2.76	2.79	2.68
	$1a_{2u} \rightarrow 4b_{1u}(5f\delta_u)$	0.156			
aB_{2g}	$1b_{2g} \rightarrow 2a_{2u}$	0.939	2.89	2.88	2.81
bE_g	$1e_g \rightarrow 2a_{2u}$	0.885	2.97	2.98	2.93
	$2e_g \rightarrow 2a_{2u}$	0.387			
bB_{2u}	$2a_{2u} \rightarrow 2b_{2u}(5f\delta_u)$	0.930	3.02	3.05	2.97
	$1a_{2u} \rightarrow 2b_{2u}(5f\delta_u)$	0.160			
bA_{1g}	$1a_{1g} \rightarrow 2a_{2u}$	0.916	3.30	3.29	3.29
	$2a_{1g} \rightarrow 2a_{2u}$	0.159			
aB_{1g}	$1b_{1g} \rightarrow 2a_{2u}$	0.938	3.40	3.39	3.34
dE_u	$2a_{2u} \rightarrow 4e_u(5f\phi_u)$	0.877	3.48	3.57	3.38
	$1a_{2u} \rightarrow 4e_u(5f\phi_u)$	0.158			
	$1a_{2u} \rightarrow 5e_u(\pi_u^*)$	0.275			