

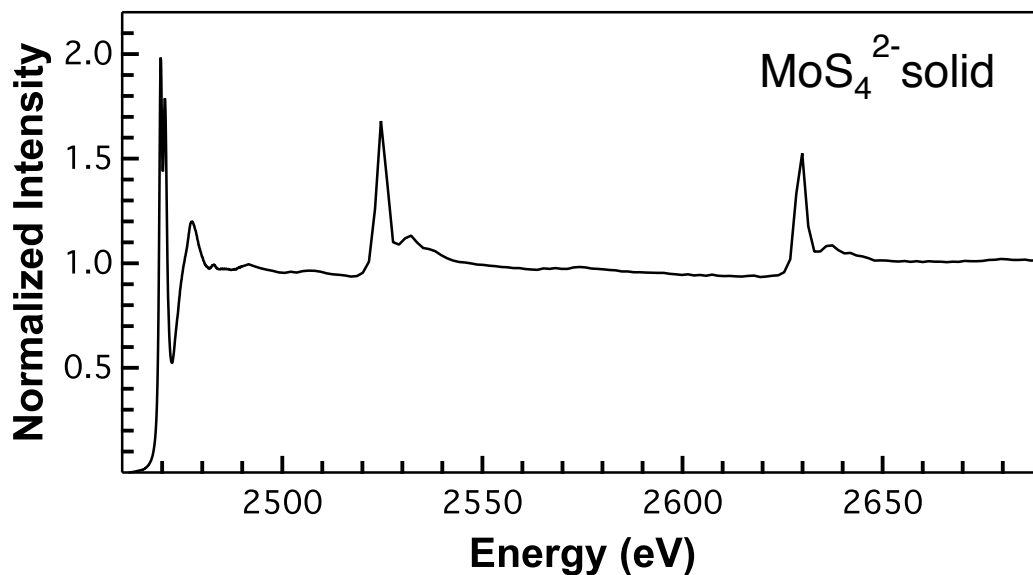
## ***Using Solution- and Solid-State S K-edge X-ray Absorption Spectroscopy with Density Functional Theory to Evaluate M–S Bonding for $MS_4^{2-}$ ( $M = Cr, Mo, W$ ) Dianions***

Angela C. Olson, Jason M. Keith, Enrique R. Batista,\* Kevin S. Boland, Scott R. Daly, Stosh A. Kozimor,\* Molly M. MacInnes, Richard L. Martin,\* and Brian L. Scott

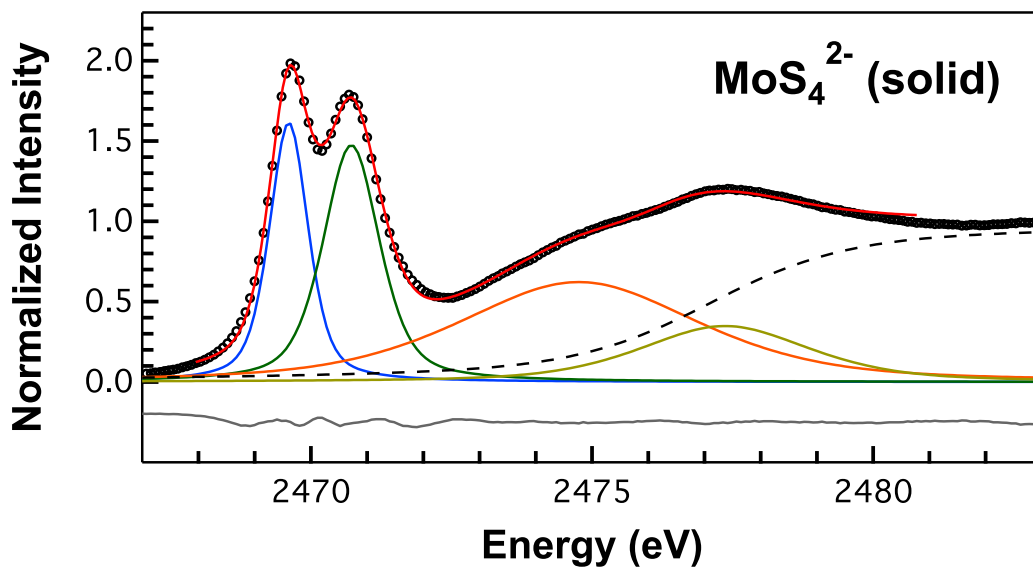
### **Supporting Information**

Complete Reference 71.....	S2
S K-edge XAS spectrum of $(PPh_4)_2MoS_4$ (Figure S1).....	S2
S K-edge XAS spectra and curve-fitting models for $MS_4^{2-}$ (Figures S2–S5).....	S3–S4
Atomic coordinates obtained from gas-phase DFT calculations (Table S1).....	S5
Atomic coordinates obtained from solution-phase DFT calculations (Table S2).....	S6
Waves for background-subtracted and normalized $MoS_4^{2-}$ solution-phase XAS spectra (Table S3).....	S6
Waves for background-subtracted and normalized $WS_4^{2-}$ solution-phase XAS spectra (Table S4).....	S18

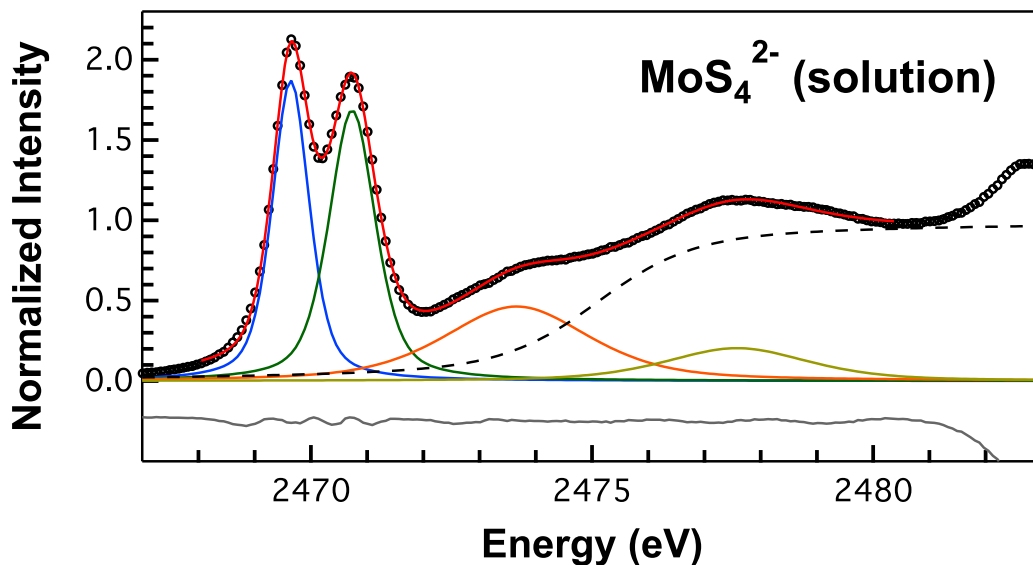
Complete Reference 71: Frisch, M. J. T. G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.01, Wallingford, CT; 2009.



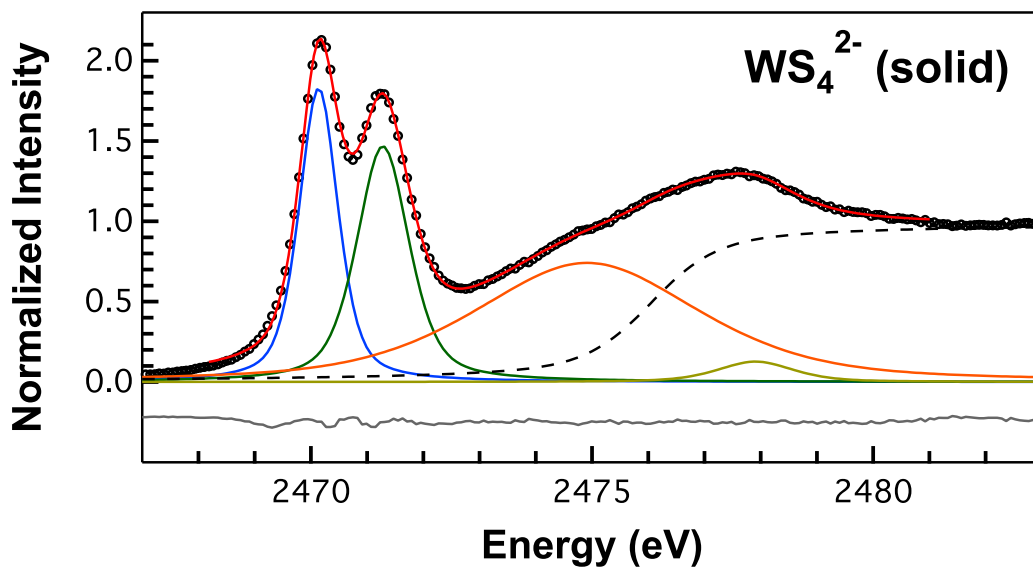
**Figure S1.** S K-edge X-ray absorption spectrum for (PPh<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> solid with Mo L<sub>3/2</sub>-edge absorptions at 2525 and 2630 eV.



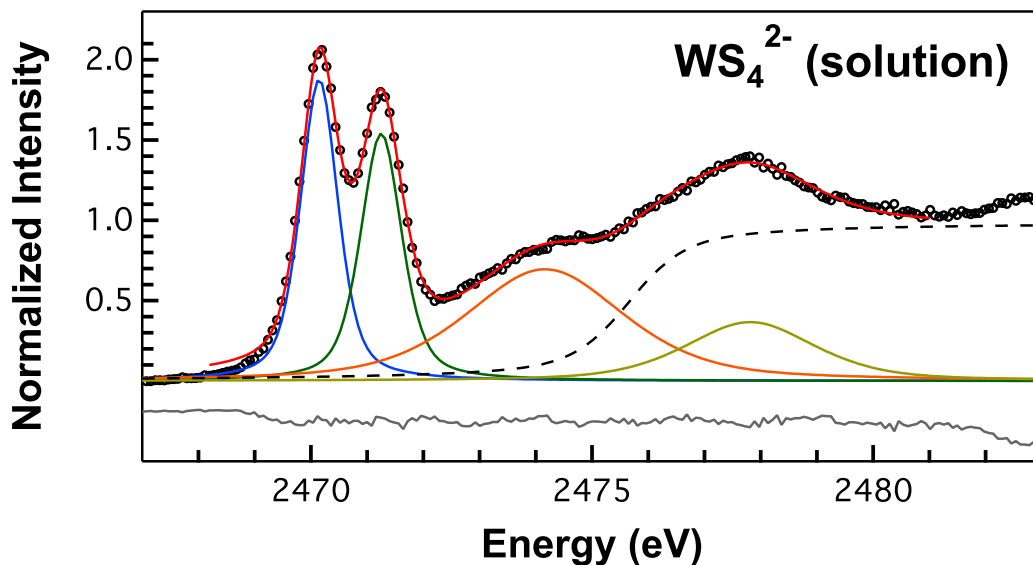
**Figure S2.** S K-edge X-ray absorption data (●) for (PPh<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> solid. Models for the data (red trace), pre-edge functions (blue and green traces), post-edge functions (orange and brown traces), as well as the step function (dashed line) are provided. Residual data (gray, offset) was determined by subtracting the curve fit from the experimental data.



**Figure S3.** S K-edge X-ray absorption data (●) for (PPh<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> in acetonitrile (0.06 M). Models for the data (red trace), pre-edge functions (blue and green traces), post-edge functions (orange and brown traces), as well as the step function (dashed line) are provided. Residual data (gray, offset) was determined by subtracting the curve fit from the experimental data.



**Figure S4.** S K-edge X-ray absorption data (●) for (PPh<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> solid. Models for the data (red trace), pre-edge functions (blue and green traces), post-edge functions (orange and brown traces), as well as the step function (dashed line) are provided. Residual data (gray, offset) was determined by subtracting the curve fit from the experimental data.



**Figure S5.** S K-edge X-ray absorption data (●) for (PPh<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> in acetonitrile (0.06 M). Models for the data (red trace), pre-edge functions (blue and green traces), post-edge functions (orange and brown traces), as well as the step function (dashed line) are provided. Residual data (gray, offset) was determined by subtracting the curve fit from the experimental data.

**Table S1.** Atomic coordinates and Mulliken charges for the gas-phase DFT  $MS_4^{2-}$  structures.

<b>CrS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
Cr	1	0.000000	0.000000	0.000000	0.244403
S	2	1.205456	1.205456	1.205456	-0.561101
S	3	-1.205456	-1.205456	1.205456	-0.561101
S	4	-1.205456	1.205456	-1.205456	-0.561101
S	5	1.205456	-1.205456	-1.205456	-0.561101
<b>MoS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
Mo	1	0.000000	0.000000	0.000000	0.549911
S	2	1.278254	1.278254	1.278254	-0.637478
S	3	-1.278254	-1.278254	1.278254	-0.637478
S	4	-1.278254	1.278254	-1.278254	-0.637478
S	5	1.278254	-1.278254	-1.278254	-0.637478
<b>WS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
W	1	0.000000	0.000000	0.000000	0.409095
S	2	1.279307	1.279307	1.279307	-0.602274
S	3	-1.279307	-1.279307	1.279307	-0.602274
S	4	-1.279307	-1.279307	-1.279307	-0.602274
S	5	1.279307	-1.279307	-1.279307	-0.602274

**Table S2.** Atomic coordinates and Mulliken charges for the solution-phase DFT  $MS_4^{2-}$  structures.

<b>CrS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
Cr	1	0.000000	0.000000	0.000000	0.065773
S	2	1.201911	1.201911	1.201911	-0.516443
S	3	-1.201911	-1.201911	1.201911	-0.516443
S	4	-1.201911	1.201911	-1.201911	-0.516443
S	5	1.201911	-1.201911	-1.201911	-0.516443
<b>MoS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
Mo	1	0.000000	0.000000	0.000000	0.378618
S	2	1.273743	1.273743	1.273743	-0.594655
S	3	-1.273743	-1.273743	1.273743	-0.594655
S	4	-1.273743	1.273743	-1.273743	-0.594655
S	5	1.273743	-1.273743	-1.273743	-0.594655
<b>WS<sub>4</sub><sup>2-</sup></b>		Coordinates (Angstroms)			Mulliken Charges
Atom Type	Atom #	x	y	z	
W	1	0.000000	0.000000	0.000000	0.259149
S	2	1.276250	1.276250	1.276250	-0.564787
S	3	-1.276250	-1.276250	1.276250	-0.564787
S	4	-1.276250	1.276250	-1.276250	-0.564787
S	5	1.276250	-1.276250	-1.276250	-0.564787

**Table S3.** Waves for background-subtracted and normalized  $MoS_4^{2-}$  solution-phase XAS spectra.

MoS4_soln_Int	MoS4_soln_eV
0.0004939578099999999	2400.0095
0.0005932031491666669	2401.0105
0.001660703849166667	2402.0105
0.0002330755425	2403.0105
0.0017607427	2404.0095
0.000744332625	2405.0102
1.803931916666691e-05	2406.0098
0.001311184125	2407.0093
0.001302242669166666	2408.0093
0.001362301215	2409.0095

0.0009610863683333333	2410.0098
-0.0004398598508333334	2411.0105
-0.0012957847583333333	2412.0098
0.001463105798416666	2413.0093
0.0020641273625	2414.0107
-0.0008885830200000003	2415.0105
0.0014168834358333333	2416.0107
2.936022999999992e-05	2417.0095
-0.0024299847325	2418.01
-0.002646195083	2419.0093
-0.00121776591	2420.0102
-0.0024758172633333333	2421.0098
-0.0035005770866666666	2422.0095
0.0211458099833333333	2423.0093
-0.0010097769111666667	2424.0093
-0.0010653791108333333	2425.0095
-0.0013965813733333333	2426.0098
-0.0008051218583333331	2427.0102
9.542385833333331e-05	2428.0107
-0.0004386797049999998	2429.0098
-0.00199728358975	2430.0107
-0.0006631995516666665	2431.01
-0.001660411447413333	2432.0095
-0.0013416370416666667	2433.0107
-0.0017293413833333333	2434.0105
-0.0018559455041666666	2435.0102
-0.0003611638609999999	2436.01
-0.001522816860083334	2437.01
-0.0013583317383333334	2438.01
-0.0022633136133333333	2439.0102
-0.0013387604941666667	2440.0105
-0.0009620183883333333	2441.0107
-0.0042647835633333333	2442.0095
-0.0029785271716666666	2443.0098
-0.0005955246308333332	2444.0102
-0.004401809975	2445.0107
-0.0012351057266666667	2446.0098
-0.0010062207883333333	2447.0102
-0.0021156141416666666	2448.0107
-0.0038273691333333333	2449.0098
-0.0007571211916666668	2450.0105
-0.0008284691650000002	2451.0095
-0.001395977395	2452.01
-0.001215291825	2453.0107
-0.0018106459141666667	2454.0098
-0.001133088235	2455.0105

-0.001184181925	2456.0095
0.002875839459166667	2457.01
0.001536834410916667	2458.0107
0.0012208717925	2459.0095
0.00237144836	2460.0102
0.005964471341666667	2461.0107
0.005172977133333334	2462.0095
0.009616038333333332	2463.01
0.012004696383333333	2464.0102
0.017500131083333333	2465.0105
0.018053677	2465.0908
0.020249236	2465.1709
0.02015237691666667	2465.2493
0.02100109441666667	2465.3293
0.02230749716666667	2465.4097
0.022203099833333333	2465.4897
0.023491631333333333	2465.5698
0.025556629083333333	2465.6499
0.024364714583333334	2465.7302
0.026640161083333334	2465.8103
0.02640792075	2465.8906
0.029226399583333333	2465.9707
0.027702648	2466.0493
0.02851526891666667	2466.1296
0.03196899475	2466.2097
0.03264402466666667	2466.29
0.035208877	2466.3704
0.034593127083333333	2466.4507
0.03624642491666666	2466.5293
0.03957466866666667	2466.6096
0.04036932525	2466.6897
0.04164631150000001	2466.77
0.04242632925	2466.8503
0.044216587583333333	2466.9307
0.04692416625	2467.0095
0.050823326333333333	2467.0898
0.053548603083333332	2467.1702
0.054167907833333334	2467.2505
0.059065179833333332	2467.3293
0.06117183991666666	2467.4097
0.06820325200000001	2467.49
0.071806329	2467.5703
0.07609262641666667	2467.6492
0.08196357191666666	2467.7297
0.08787260891666666	2467.81
0.09324404966666666	2467.8906



0.1022024348333333	2467.9692
0.1095473825	2468.0498
0.1216024333333334	2468.1304
0.1331005283333333	2468.2107
0.1465799683333333	2468.2895
0.1658224575	2468.3701
0.1814372566666666	2468.4507
0.2074953708333334	2468.5295
0.2394111183333333	2468.6101
0.2733375991666666	2468.6907
0.3170409725	2468.7695
0.3783565466666667	2468.8501
0.4503606533333334	2468.9307
0.5512195375	2469.0095
0.6826899850000001	2469.0903
0.8465295725	2469.1692
1.0658176583333333	2469.2497
1.3191267833333333	2469.3303
1.588647	2469.4094
1.8412155833333334	2469.49
2.0442128	2469.5708
2.12692835	2469.6496
2.0864523416666666	2469.7305
1.96373355	2469.8096
1.778088875	2469.8901
1.5976582916666667	2469.9692
1.4576270666666667	2470.05
1.3886107583333333	2470.1306
1.3860778166666667	2470.2097
1.441816125	2470.2905
1.5381982416666667	2470.3696
1.6522219083333333	2470.4504
1.7684822916666666	2470.5295
1.8437418916666667	2470.6103
1.893579425	2470.6894
1.8877161666666666	2470.7703
1.8233266916666667	2470.8494
1.7088376833333333	2470.9302
1.5509971916666667	2471.0095
1.377381975	2471.0903
1.1904426666666667	2471.1697
1.01649376	2471.2505
0.870264975	2471.3296
0.7368695499999999	2471.4106
0.6410806475	2471.4897
0.566853455	2471.5708

0.5146624408333333	2471.6499
0.4748613999999999	2471.7292
0.4510946641666667	2471.8103
0.43501735	2471.8894
0.4294811566666667	2471.9704
0.4301107875000001	2472.0498
0.4320538899999999	2472.1308
0.4465048216666666	2472.2102
0.4592194458333334	2472.2895
0.4743921083333333	2472.3704
0.4875453058333334	2472.4499
0.5082238766666666	2472.5293
0.5213239175000001	2472.6103
0.5356155375	2472.6897
0.5484019425	2472.7707
0.5646260408333332	2472.8501
0.578081555	2472.9297
0.59603569	2473.0107
0.6021823175	2473.0901
0.6102384366666668	2473.1697
0.628362305	2473.2507
0.6436455208333333	2473.3301
0.6617515300000001	2473.4097
0.6808168458333332	2473.4907
0.6855197733333332	2473.5703
0.6991889341666667	2473.6499
0.7116065441666667	2473.7295
0.7211174558333333	2473.8105
0.7257160433333333	2473.8901
0.7333912408333333	2473.9697
0.7383018425	2474.0493
0.7433331299999999	2474.1304
0.7496320958333333	2474.21
0.7491566141666666	2474.2895
0.751447275	2474.3691
0.7563771983333334	2474.4504
0.7550349116666667	2474.53
0.7663830633333334	2474.6099
0.7731730350000001	2474.6894
0.7748966841666668	2474.7707
0.7814053991666667	2474.8503
0.7881634841666667	2474.9302
0.7917785400000001	2475.0098
0.8004676233333333	2475.0896
0.8124641991666666	2475.1709
0.8170086825	2475.2505

0.8342167666666667	2475.3303
0.8343756466666666	2475.4099
0.8455670624999999	2475.4897
0.8575056075000002	2475.5696
0.8609495925	2475.6492
0.8753511166666667	2475.7307
0.8901979191666665	2475.8105
0.9021656199999999	2475.8904
0.9079509583333333	2475.97
0.9224188400000001	2476.0498
0.93582024	2476.1296
0.9484717075000001	2476.2095
0.9673564850000002	2476.2893
0.9750150275	2476.3694
0.9919180049999999	2476.4507
1.007708344166667	2476.5308
1.024232633333333	2476.6106
1.0420573	2476.6904
1.05246305	2476.7703
1.065969425	2476.8503
1.074067183333333	2476.9302
1.088682925	2477.01
1.1008045	2477.0901
1.110094408333333	2477.1699
1.115945541666667	2477.25
1.124632025	2477.3298
1.1233578	2477.4099
1.127889533333333	2477.49
1.122293516666667	2477.5698
1.12300175	2477.6499
1.128132358333333	2477.73
1.127284608333333	2477.81
1.118502516666667	2477.8901
1.118723033333333	2477.97
1.115170783333333	2478.05
1.108491083333333	2478.1301
1.1067358	2478.2102
1.099920633333333	2478.2903
1.102278983333333	2478.3704
1.096546491666666	2478.4507
1.097015441666667	2478.5308
1.088947983333333	2478.6091
1.088330508333333	2478.6894
1.083675675	2478.7695
1.0836255	2478.8496
1.081089516666667	2478.9297

1.072000016666667	2479.01
1.067036316666667	2479.0901
1.064379933333333	2479.1704
1.056691	2479.2505
1.046703425	2479.3308
1.043113141666667	2479.4094
1.036415033333333	2479.4895
1.027030941666667	2479.5698
1.025604258333333	2479.6501
1.009467756666667	2479.7305
1.009070809166667	2479.8105
1.000097186666667	2479.8894
0.9936257891666666	2479.9695
0.9918252558333335	2480.0498
0.9889498258333335	2480.1301
0.9806361300000001	2480.2104
0.9797851766666668	2480.2893
0.9796722491666666	2480.3696
0.9802159441666668	2480.4499
0.9776642283333334	2480.5303
0.9780302758333331	2480.6106
0.98383867	2480.6894
0.9832188024999998	2480.7698
0.9823219974999998	2480.8501
0.9921074416666666	2480.9307
0.9931716216666667	2481.0093
0.9948268075000001	2481.0898
0.9989469891666666	2481.1702
1.0073610275	2481.2507
1.019823058333333	2481.3296
1.027907325	2481.4099
1.043407816666667	2481.4905
1.046554433333333	2481.5693
1.064218266666667	2481.6496
1.080866325	2481.7302
1.101114208333333	2481.8108
1.113576108333333	2481.8896
1.145902925	2481.9702
1.165250441666666	2482.0508
1.195810008333333	2482.1296
1.218062075	2482.2102
1.2555631	2482.2908
1.283510308333333	2482.3696
1.311077116666667	2482.4504
1.334184875	2482.5293
1.350622208333333	2482.6099

1.3506392	2482.6904
1.351617341666667	2482.7695
1.349202291666667	2482.8501
1.327332741666667	2482.9309
1.314198666666667	2483.0098
1.287593683333333	2483.0906
1.260023216666667	2483.1694
1.226380258333333	2483.2502
1.2021027	2483.3293
1.16658695	2483.4099
1.132393208333333	2483.4907
1.100366925	2483.5698
1.074995633333333	2483.6506
1.056888216666666	2483.7297
1.0335184525	2483.8103
1.02693775	2483.8894
1.017041326666666	2483.9702
0.990861728333333	2484.0493
0.980420441666666	2484.1301
0.974408694166666	2484.2095
0.965457091666666	2484.2903
0.961689335	2484.3694
0.960020237499999	2484.4502
0.955637090000001	2484.5293
0.949317924166666	2484.6103
0.948953531666666	2484.6894
0.952685774166667	2484.7703
0.943486342500001	2484.8496
0.949866401666666	2484.9304
0.941389985000002	2485.0098
0.943021935833333	2485.0906
0.948169581666666	2485.1699
0.944927513333333	2485.2493
0.946003560833333	2485.3301
0.946367131666667	2485.4094
0.94473861	2485.4905
0.950566299999999	2485.5698
0.952487836666666	2485.6506
0.955332069166665	2485.73
0.953730724166667	2485.8093
0.954922702499999	2485.8904
0.953281179166665	2485.9697
0.956049625	2486.0508
0.9615359	2486.1301
0.956642794166665	2486.2095
0.960076294999999	2486.2908

0.9598739391666666	2486.3701
0.9616697533333332	2486.4495
0.9619307499999999	2486.5305
0.9658217358333334	2486.6101
0.9578056483333336	2486.6894
0.9606564799999999	2486.7705
0.9658821841666668	2486.8501
0.9622691199999998	2486.9294
0.9612220674999999	2487.0107
0.9618397	2487.0901
0.9645029908333335	2487.1697
0.9671317091666668	2487.2493
0.9606907399999999	2487.3303
0.9679686508333334	2487.4099
0.9702352200000001	2487.4895
0.9712415600000001	2487.5708
0.9744763116666668	2487.6504
0.9744591324999999	2487.7297
0.9763070716666667	2487.8093
0.9778144958333335	2487.8906
0.9722754408333335	2487.9702
0.9755079416666667	2488.0498
0.9845850799999999	2488.1296
0.9792202500000001	2488.2109
0.9843079600000001	2488.2905
0.9923023125	2488.3701
0.9876567508333333	2488.4497
0.9907245750000001	2488.5295
0.9949683783333333	2488.6108
0.9931727608333333	2488.6904
0.9948428674999999	2488.7703
0.9964734999999999	2488.8498
0.9946271666666665	2488.9297
1.0001970208333333	2489.0093
0.9943884299999999	2489.0908
1.00024203	2489.1704
1.0007145041666667	2489.2502
0.9967397666666667	2489.3301
0.9997623008333333	2489.4097
0.9926178641666666	2489.4895
1.0018613266666667	2489.5693
0.9988333524999998	2489.6509
0.9990538058333334	2489.7307
1.0035865591666666	2489.8105
1.0040313208333333	2489.8904
1.0014459333333333	2489.9702

1.002360979166667	2490.01
0.9981545650000001	2491.0107
0.9990237591666665	2492.51
1.002417401666667	2494.0095
1.0036269	2495.5107
1.010911948333333	2497.01
1.013286770833333	2498.5095
1.010850919166667	2500.0105
1.01015766	2501.5095
1.005933053333333	2503.0105
1.0052777175	2504.5095
1.010212174166667	2506.01
1.014141915	2507.5105
1.009687848333333	2509.0093
1.009628440833333	2510.5093
1.000423176666667	2512.0093
0.9858534916666669	2513.509
0.9969300358333334	2515.0105
0.9978102674999999	2516.51
1.0042109375	2518.0107
1.022214041666667	2519.5098
1.07090755	2521.01
1.237868358333333	2522.5102
1.892901816666667	2524.01
2.253322491666666	2525.5098
1.361612641666667	2527.0107
1.239245133333333	2528.5095
1.264348266666667	2530.01
1.321422	2531.51
1.329525366666667	2533.0095
1.283568991666667	2534.5105
1.259829591666667	2536.0093
1.245391275	2537.5095
1.237769041666667	2539.0093
1.220099958333333	2540.5105
1.211531516666666	2542.0095
1.20674125	2543.5098
1.200392	2545.0095
1.195675316666667	2546.5105
1.194023608333333	2548.0093
1.195242208333333	2549.5093
1.189951483333333	2551.0107
1.198311566666667	2552.5098
1.192225908333333	2554.01
1.1976655	2555.5098
1.191988358333333	2557.0107

1.197991016666667	2558.5093
1.199324216666667	2560.0107
1.197730741666667	2561.51
1.200077508333333	2563.0102
1.2095918	2564.51
1.207887958333333	2566.011
1.218857166666667	2567.5093
1.220218083333333	2569.0107
1.231108641666667	2570.5095
1.242912941666667	2572.0095
1.239120516666667	2573.5107
1.248603741666667	2575.0093
1.248911925	2576.5107
1.256190233333333	2578.0098
1.247780491666666	2579.5098
1.254245683333333	2581.0107
1.253460858333333	2582.5093
1.258762566666667	2584.0105
1.25780515	2585.5093
1.255181275	2587.011
1.259495991666667	2588.5098
1.255017358333333	2590.0098
1.261562925	2591.5107
1.26219895	2593.0107
1.263505333333333	2594.51
1.262611466666667	2596.0102
1.268386566666667	2597.5095
1.264538475	2599.0098
1.272788183333333	2600.509
1.269869625	2602.0093
1.274192275	2603.5107
1.274425208333333	2605.011
1.2803941	2606.5102
1.2792612	2608.0105
1.283735825	2609.5095
1.283511441666667	2611.0098
1.288947983333333	2612.5107
1.288876583333333	2614.0107
1.28861045	2615.5098
1.2921796	2617.0095
1.293273416666667	2618.51
1.300126266666667	2620.0098
1.307779116666667	2621.51
1.311123566666667	2623.0095
1.324579016666666	2624.5095
1.364136366666667	2626.0105



1.509610591666666	2627.5102
2.052726358333333	2629.011
2.00496685	2630.5105
1.549569583333333	2632.0107
1.499590141666667	2633.5098
1.5165837	2635.0095
1.561107208333333	2636.51
1.566370666666667	2638.0095
1.544956433333333	2639.5095
1.529392958333333	2641.0105
1.52802325	2642.51
1.528993916666667	2644.0102
1.523559108333333	2645.5093
1.520423091666667	2647.009
1.516656916666666	2648.5095
1.519380216666667	2650.0105
1.52188075	2651.5102
1.517056816666667	2653.0107
1.523801675	2654.51
1.524181191666667	2656.0098
1.53032065	2657.51
1.532495158333333	2659.009
1.538098808333333	2660.511
1.542845316666667	2662.009
1.544336266666667	2663.51
1.546595416666666	2665.0095
1.552226525	2666.5095
1.557172383333333	2668.0102
1.563389883333334	2669.5095
1.566507558333334	2671.0093
1.568816741666667	2672.5098
1.5719604	2674.0105
1.5819454	2675.51
1.592235233333333	2677.01
1.597538125	2678.5105
1.597505483333333	2680.0095
1.598593	2681.509
1.610163691666667	2683.009
1.609548775	2684.5095
1.6160121	2686.0105
1.615427775	2687.51
1.620023508333333	2689.01
1.614634991666667	2690.01

**Table S4.** Waves for background-subtracted and normalized WS<sub>4</sub><sup>2-</sup> solution-phase XAS spectra.

WS4_soln_Int	WS4_soln_eV
-0.0006104078588084491	2465.1499
0.0008656534040060995	2465.231
0.002881069561764113	2465.3108
0.0007247784842353325	2465.3909
0.001297259078029847	2465.4709
-0.004284295737236634	2465.5508
0.001563484387308609	2465.6309
0.003565328279087724	2465.7119
0.001526076767267263	2465.792
0.0005463232642492113	2465.8718
-0.003828485761854265	2465.9519
-0.0015960179038478	2466.031
0.001291226990352054	2466.1108
-0.008520138124058812	2466.1909
0.007501123362676025	2466.271
-0.004295470856700172	2466.3508
-0.003489819586079726	2466.4319
0.0001212702460699618	2466.512
0.001012569334381513	2466.5918
0.00236875230103089	2466.6719
0.005624204849393256	2466.7529
-0.001793190592496599	2466.833
-0.01025745669436256	2466.9128
0.0007785430199037416	2466.9939
-0.001121430329152563	2467.072
-0.001028342577140234	2467.1528
0.004780387501083698	2467.2329
0.004377005191034926	2467.313
0.00316462248710515	2467.3938
0.009589677498854782	2467.4739
0.01105621420903635	2467.5549
0.0128698082788569	2467.6328
0.02268290036588444	2467.7139
0.0173190190721791	2467.7939
0.01768268187104947	2467.874
0.01823144637832746	2467.9548
0.02097187002066667	2468.0339
0.03544065517081341	2468.114
0.03306550636339556	2468.1948
0.03753883012316446	2468.2749
0.04236951991503011	2468.356
0.05022716043108397	2468.4338

0.05791927933546362	2468.5149
0.06382456951380845	2468.5959
0.07083093357759428	2468.6758
0.08485243669303942	2468.7559
0.1092526003687782	2468.8359
0.1277245438069573	2468.916
0.1334752287723682	2468.9958
0.1809726631099029	2469.0759
0.200908095013416	2469.156
0.256239089867706	2469.2368
0.3148730483830687	2469.3169
0.3789408952762238	2469.396
0.4961579795289893	2469.4768
0.6195612173694524	2469.5569
0.77468760887808	2469.637
0.9971672303746324	2469.7168
1.241120252970433	2469.7979
1.494741819162979	2469.877
1.724432874438099	2469.958
1.948481574475024	2470.0378
2.031544400633581	2470.1169
2.061014774748091	2470.198
1.957264768029482	2470.2788
1.821835456731999	2470.3579
1.580321773986902	2470.439
1.436319032796147	2470.5188
1.293905576411087	2470.5979
1.250418442474477	2470.679
1.233679940146069	2470.7578
1.292595585417742	2470.8389
1.419231302436648	2470.9199
1.541049607798485	2470.999
1.703078311975546	2471.0798
1.75125144691962	2471.1589
1.799120766293153	2471.24
1.767828775960978	2471.3188
1.670687627328338	2471.3999
1.520597041230305	2471.479
1.345095467729486	2471.5598
1.198411063722576	2471.6409
0.9894336358280464	2471.72
0.8295306443898015	2471.8008
0.7335287636255505	2471.8809
0.6178407723512663	2471.9619
0.5673875286665975	2472.041
0.5378338188925829	2472.1218

0.497591129566849	2472.2009
0.5121264053030686	2472.282
0.5107724152397616	2472.3608
0.5233312606102458	2472.4419
0.532246609331833	2472.522
0.5383267532237678	2472.6008
0.5750046746049949	2472.6819
0.5935213780917381	2472.762
0.6084818501896915	2472.843
0.6046072123606883	2472.9219
0.6446390762061776	2473.0029
0.6530523339482206	2473.083
0.6697913358240482	2473.1638
0.6811825470262722	2473.2429
0.7027282791749679	2473.323
0.6924167167210838	2473.4038
0.7320586542271079	2473.4829
0.759612646618096	2473.564
0.7574022055545034	2473.6438
0.7890273913189906	2473.7229
0.802865019360821	2473.8049
0.8029188719206547	2473.8838
0.8168367849157032	2473.9629
0.8107267346347583	2474.0449
0.8194842533747214	2474.124
0.8221628396994531	2474.2039
0.8655247420591714	2474.2849
0.8787927991002281	2474.365
0.875614188361569	2474.4438
0.8692214728932126	2474.5249
0.8770893539170479	2474.605
0.8760273265500537	2474.6848
0.9076772172190239	2474.7659
0.8996002061713357	2474.8459
0.8858062639041491	2474.9248
0.882647604268696	2475.0049
0.8890205308042154	2475.0859
0.8989158090870355	2475.166
0.9103727810341985	2475.2458
0.8969597851426162	2475.3269
0.9264694739953168	2475.407
0.9505442041700216	2475.4858
0.9435652537492928	2475.5659
0.9936959677423101	2475.646
0.9863197268131345	2475.7268
1.045075890876095	2475.8069

1.048600956199896	2475.887
1.071108721204209	2475.9668
1.084753985540003	2476.0479
1.08623883249525	2476.1279
1.132998964451788	2476.208
1.12635726383726	2476.2878
1.134485478503237	2476.3679
1.146151353639832	2476.447
1.178357404755777	2476.5288
1.201414157120977	2476.6089
1.185160927586413	2476.689
1.242052439770004	2476.7678
1.236118789811467	2476.8479
1.25324762218766	2476.928
1.283790494091758	2477.0078
1.302875736562352	2477.0898
1.301660762869768	2477.1699
1.341868294989558	2477.25
1.330387879797027	2477.3298
1.349559073677677	2477.4099
1.354930726894333	2477.49
1.374238968933028	2477.5688
1.384232382389628	2477.6499
1.393466432682291	2477.73
1.398502912596029	2477.8088
1.359062218947079	2477.8909
1.390933374325573	2477.9709
1.327812050246504	2478.0508
1.352901418927734	2478.1309
1.321344224064467	2478.2109
1.282666740950898	2478.291
1.331195603911036	2478.3708
1.276329849367919	2478.4519
1.270032339726069	2478.532
1.248575122009253	2478.6118
1.23398594605882	2478.6919
1.21083854856987	2478.772
1.203920090500908	2478.8518
1.200325580629718	2478.9319
1.172436326473491	2479.0129
1.146612216159405	2479.093
1.136600001837326	2479.1729
1.124840547980012	2479.2529
1.153305511351381	2479.333
1.144452419602348	2479.4128
1.14179761048205	2479.4939

1.117215861420831	2479.572
1.107422906467093	2479.6519
1.101854718939958	2479.7329
1.101526100359248	2479.813
1.084067682870401	2479.8928
1.082288225403292	2479.9729
1.081837892904074	2480.054
1.063401624630946	2480.1338
1.093702310231201	2480.2139
1.059143056940895	2480.2949
1.102402100948607	2480.375
1.035360316362826	2480.4539
1.052803948775415	2480.5339
1.058584993471926	2480.615
1.048817770612485	2480.6948
1.038945855590494	2480.7749
1.01777397950197	2480.856
1.030738039787664	2480.9338
1.064945445326356	2481.0149
1.030334639668557	2481.095
1.022882604467416	2481.1758
1.030997963151065	2481.2559
1.021167162382463	2481.3369
1.04897490788661	2481.417
1.033026090169933	2481.4958
1.057376166151814	2481.5759
1.043610559561436	2481.657
1.038455612022464	2481.7368
1.043567280324526	2481.8159
1.045440150622622	2481.897
1.066312788003036	2481.9768
1.074280175308858	2482.0579
1.077074228448107	2482.137
1.107697332296969	2482.2168
1.107834659723884	2482.2979
1.102492670457884	2482.3779
1.136829535708358	2482.4568
1.121578272418317	2482.5378
1.141043178317245	2482.6179
1.141941279138758	2482.699
1.145098013929989	2482.7778
1.124851910893249	2482.8579
1.132907786279262	2482.939
1.124905498923592	2483.0178
1.122670735436902	2483.0989
1.103515543760951	2483.1799

1.079638333944767	2483.2578
1.10501444626527	2483.3389
1.076311225613259	2483.4199
1.073689504536558	2483.499
1.053222423712306	2483.5798
1.042978358278521	2483.6589
1.017863169879843	2483.739
1.021053337490153	2483.8198
1.022947869930127	2483.8989
1.011496811937964	2483.98
0.9982285062365305	2484.0608
0.9983519059643382	2484.1399
0.978637493800225	2484.2209
0.9914640891511046	2484.2998
0.9788682295215909	2484.3809
0.9954336353766776	2484.4619
0.974576057202084	2484.541
0.9796183067743468	2484.6208
0.9657519997109824	2484.7009
1.004651411249523	2484.782
0.9759662219670461	2484.8608
0.9744882807244222	2484.9419
0.9616166420715685	2485.0229
0.9881208674008172	2485.1018
0.9583366183711699	2485.1829
0.9722477200544675	2485.262
0.9690729567052039	2485.343
0.9945538635328627	2485.4219
0.9892693037442899	2485.5029
0.9511390753887867	2485.5818
0.9452743156821746	2485.6628
0.9377519641184969	2485.7429
0.9724626843139628	2485.824
0.9781337072086541	2485.9028
0.9977781398241052	2485.9829
0.9580300032248855	2486.064
0.9947871599661493	2486.1428
0.9706521273820251	2486.2239
0.9704428048515943	2486.303
0.957349588193885	2486.3838
0.9335450907825052	2486.4639
0.9455575475475178	2486.5449
0.9466206724055788	2486.624
0.9638809060531616	2486.7039
0.9514995049282559	2486.7849
0.9573647077633065	2486.864

1.004193180507102	2486.9448
0.9625754959030676	2487.0249
0.9924823882222101	2487.104
0.9851006628602	2487.1848
0.9625933075281372	2487.2649
0.9904685426897971	2487.3459
0.9549462262232328	2487.4258
0.954753710825662	2487.5049
0.9467953131162578	2487.5859
0.9417578814028322	2487.666
1.005151124345067	2487.7449
0.9634193290118791	2487.8269
0.9924088025095487	2487.906
0.9664606009477491	2487.9858
0.9886043035556082	2488.0669
0.9732391688186004	2488.147
0.9807811794349792	2488.2258
0.962504248629839	2488.3079
0.9525519196390535	2488.387
0.9483849219071711	2488.4668
0.9722267199147512	2488.5479
0.973657533412163	2488.6279
0.9473454854935661	2488.708
0.9636465722426769	2488.7869
0.9797823692997328	2488.8689
0.9705394340035367	2488.948
0.9511087437028654	2489.0278
0.9781148479419863	2489.1079
0.9742242870066067	2489.189
0.950846544755457	2489.2688
0.9426365750544262	2489.3489
0.9752411352492133	2489.429
0.9691562616339877	2489.5078
0.9529071020518486	2489.5898
0.9645163982813161	2489.6699
0.9496483220202708	2489.749
0.9797965157775848	2489.8289
0.9577701152076603	2489.9089
0.9301218021318295	2489.99
0.9264459117707229	2490.0698
0.9650798392187545	2490.1499