Electronic Supplementary Information (ESI)

Effect of Electron Correlation in the Decomposition of Core Level Binding Energy Shifts into Initial and Final State Contributions

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Table S1. DFT (B3LYP) vibrational mode frequencies of the set of molecules studied in the present work at the geometries reported in Table 1 using Basis set 3. Note that the bending mode is twofold degenerate

Molecule	**Normal Modes Frequencies (cm^{-1})**		
	Bending	Symmetric stretch	Antisymmetric stretch
CO_2	668.03	1372.39	2414.06
CS_2	402.96	668.51	1544.26
CSe_2	319.75	375.87	1315.36
SiO_2	290.96	981.34	1427.45
SiS_2	179.57	503.61	904.54
$SiSe_2$	142.92	290.01	742.76
GeO_2	193.58	872.58	1048.20
GeS_2	119.44	469.52	639.16
$GeSe_2$	91.77	272.36	482.06

Table S2. Hartree-Fock total energy (in hartrees) for ground state (neutral) and 1s core-hole state (cation) of the set of molecules studied in the present work at the geometries reported in Table 1 of the main text and as computed with the three basis sets employed

Core	Molecule	Basis	Neutral	Cation
C(1s)	CO_2	1	-187.722487	-176.723249
		2	-187.714527	-176.711286
		3	-187.699411	-176.693299
	CS_2	1	-832.978168	-822.146356
		2	-832.969641	-822.133191
		3	-832.941915	-822.102249
	CSe_2	1	-4837.631063	-4826.821948
		2	-4837.621668	-4826.807643
		3	-4837.459354	-4826.645391
Si(1s)	SiO_2	1	-438.738256	-370.832349
		2	-438.729819	-370.819369
		3	-438.693784	-370.767899
	SiS_2	1	-1084.098460	-1016.250241
		2	-1084.088826	-1016.236033
		3	-1084.055524	-1016.193582
	$SiSe_2$	1	-5088.783850	-5020.946813
		2	-5088.774101	-5020.932598
		3	-5088.604390	-5020.757956
Ge(1s)	GeO_2	1	-2225.132314	-1821.638616
		2	-2225.121899	-1821.623414
		3	-2225.028544	-1821.507372
	GeS_2	1	-2870.555482	-2467.111302
		2	-2870.545036	-2467.096100
		3	-2870.449432	-2466.980776
	$GeSe_2$	1	-6875.252996	-6471.820821
		2	-6875.242807	-6471.806102
		3	-6875.007657	-6471.554468

Table S3. Hartree-Fock total energy (in hartrees) for ground state (neutral) and Si(2s), Ge(2s) and Ge(3s) core-hole state (cation) of the set of molecules studied in the present work at the geometries reported in Table 1 using Basis 3

Core	Molecule	Neutral	Cation
Si(2s)	SiO_2	-438.693784	-432.684188
	SiS_2	-1084.055524	-1078.103901
	$SiSe_2$	-5088.604390	-5082.667195
Ge(2s)	GeO_2	-2225.028544	-2173.716191
	GeS_2	-2870.449432	-2819.186969
	$GeSe_2$	-6875.007657	-6823.760179
Ge(3s)	GeO_2	-2225.028544	-2218.008526
	GeS_2	-2870.449432	-2863.481008
	$GeSe_2$	-6875.007657	-6868.054660

Table S4. CASSCF (8,6) total energy (in hartrees) for ground state (neutral) and 1s core-hole state (cation) of the set of molecules studied in the present work at the geometries reported in Table 1 and Basis 3

Core	Molecule	Neutral	Cation
C(1s)	CO_2	-187.781602	-176.852737
	CS_2	-833.009804	-822.235054
	CSe_2	-4837.528723	-4826.779273
Si(1s)	SiO_2	-438.746104	-370.852973
	SiS_2	-1084.087873	-1016.262657
	$SiSe_2$	-5088.636172	-5020.827946
Ge(1s)	GeO_2	-2225.082902	-1821.587165
	GeS_2	-2870.481605	-2467.042564
	$GeSe_2$	-6875.038874	-6471.616441

Table S5. Total revTPSS energy (in hartrees) for ground state (neutral), and core-hole state (cation) of the set of molecules studied in the present work at the geometries reported in Table 1 using Basis 3. For the cation frozen orbital and ΔSCF values are reported

Core	Molecule	Neutral	Cation	
			Frozen Orbital	ΔSCF
C(1s)	CO_2	-188.782725	-177.365211	-177.848446
	CS_2	-834.892549	-823.528864	-824.111959
	CSe_2	-4841.976523	-4830.584657	-4831.221824
Si(1s)	SiO_2	-440.242308	-371.337120	-372.392209
	SiS_2	-1086.423960	-1017.556594	-1018.639942
	$SiSe_2$	-5093.533191	-5024.649324	-5025.766418
Ge(1s)	GeO_2	-2227.943745	-1822.762547	-1824.698384
	GeS_2	-2874.168831	-2469.022458	-2470.977421
	$GeSe_2$	-6881.285979	-6476.129378	-6478.111044

Table S6. Total TPSS energy (in hartrees) for ground state (neutral), and core-hole state (cation) of the set of molecules studied in the present work at the geometries reported in Table 1 using Basis 3. For the cation frozen orbital and ΔSCF values are reported

Core	Molecule	Neutral	Frozen Orbital	Cation
C(1s)	CO_2	-188.686383	-177.275217	-177.762499
	CS_2	-834.585478	-823.223233	-823.809809
	CSe_2	-4841.039194	-4829.678312	-4830.289649
Si(1s)	SiO_2	-440.045277	-371.175008	-372.235026
	SiS_2	-1086.019931	-1017.186246	-1018.273198
	$SiSe_2$	-5092.498944	-5023.678054	-5024.769747
Ge(1s)	GeO_2	-2227.440571	-1822.376193	-1824.306978
	GeS_2	-2873.455841	-2468.425064	-2470.374970
	$GeSe_2$	-6879.942173	-6474.930693	-6476.878164

BASIS SETS

Basis set 1. Primitive GTO basis used in the present work, these correspond to the fully uncontracted basis from EMSL web page (https://bse.pnl.gov/bse/portal). Note that Basis 2 is obtained from Basis 1 by simply removing f and g functions

Carbon (13s,7p,4d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
33980.0000000	34.5100000	1.8480000	1.4190000	1.0110000
5089.0000000	7.9150000	0.6490000	0.4850000	0.4240000
1157.0000000	2.3680000	0.2280000	0.1870000	
326.6000000	0.8132000	0.0766000		
106.1000000	0.2890000			
38.1100000	0.1007000			
14.7500000	0.0321800			
6.0350000				
2.5300000				
0.7355000				
0.2905000				
0.1111000				
0.0414500				

Silicon (17s,12p,4d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
513000.0000000	1122.0000000	0.1200000	0.2120000	0.4610000
76820.0000000	266.0000000	0.3020000	0.5410000	0.2120000
17470.0000000	85.9200000	0.7600000	0.0846000	
4935.0000000	32.3300000	0.0435000		
1602.0000000	13.3700000			
574.1000000	5.8000000			
221.5000000	2.5590000			
90.5400000	1.1240000			
38.7400000	0.3988000			
16.9500000	0.1533000			
6.4520000	0.0572800			
2.8740000	0.0200000			
1.2500000				
0.3599000				
0.1699000				
0.0706600				
0.0275000				

Germanium (22s,17p,13d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
12360507.0000000	24017.4660000	864.6741100	0.5492000	0.4681000
1850697.8000000	5685.7175000	261.0376300	0.2190000	0.2143000
421131.4200000	1846.4859000	101.7703000	0.0884000	
119278.2600000	706.2498100	45.1166410		
38912.2770000	299.4561000	21.4306860		
14048.6820000	136.4390400	10.6598610		
5480.6992000	65.3901550	5.3922870		
2274.2055000	32.3937350	2.7044970		
992.2412900	16.4156160	1.3285440		
450.9996600	8.2877870	0.6264520		
211.8202400	4.1126340	0.2660130		
101.4110200	1.9988540	0.1063000		
46.9140900	0.9442910	0.0397000		
23.5089500	0.3412110			
11.6813110	0.1343500			
5.4345260	0.0517350			
2.6088080	0.0185500			
1.1984420				
0.3298080				
0.1554330				
0.0669130				
0.0263900				

Oxygen (13s,7p,4d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
61420.0000000	63.4200000	3.7750000	2.6660000	1.8460000
9199.0000000	14.6600000	1.3000000	0.8590000	0.7140000
2091.0000000	4.4590000	0.4440000	0.3240000	
590.9000000	1.5310000	0.1540000		
192.3000000	0.5302000			
69.3200000	0.1750000			
26.9700000	0.0534800			
11.1000000				
4.6820000				
1.4280000				
0.5547000				
0.2067000				
0.0695900				

Sulfur (17s,12p,4d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
727800.0000000	1546.0000000	0.2030000	0.3350000	0.6830000
109000.0000000	366.4000000	0.5040000	0.8690000	0.2970000
24800.0000000	118.4000000	1.2500000	0.1400000	
7014.0000000	44.5300000	0.0748000		
2278.0000000	18.3800000			
814.7000000	7.9650000			
313.4000000	3.5410000			
127.7000000	1.5910000			
54.4800000	0.6205000			
23.8500000	0.2420000			
9.4280000	0.0901400			
4.2900000	0.0317000			
1.9090000				
0.6270000				
0.2873000				
0.1172000				
0.0428000				

Selenium (22s,17p,13d,3f,2g)				
s primitives	p primitives	d primitives	f primitives	g primitives
15011000.0000000	25217.0000000	1143.4000000	0.2840000	0.5730000
2247500.0000000	5969.9000000	345.3300000	0.7097000	0.2630000
511450.0000000	1938.9000000	134.4600000	0.1240000	
144870.0000000	741.6600000	59.5670000		
47261.0000000	314.5000000	28.2830000		
17062.0000000	143.3100000	14.0610000		
6654.5000000	68.6500000	7.1390000		
2759.8000000	33.9950000	3.6148000		
1203.2000000	17.1850000	1.8072000		
546.5300000	8.5740000	0.8694400		
256.6300000	4.2206000	0.3703600		
123.1400000	2.0521000	0.1530000		
58.2630000	0.9615600	0.0619000		
29.0230000	0.4215100			
14.4650000	0.1762600			
6.9348000	0.0706630			
3.3299000	0.0265690			
1.5600000				
0.4929100				
0.2352500				
0.1003700				
0.0381520				

Basis set 3. Primitive GTO basis used in the present work, these correspond to the fully uncontracted basis from EMSL web page (https://bse.pnl.gov/bse/portal)

Carbon (10s,6p,1d)		
s primitives	p primitives	d primitives
8506.0384000	34.7094960	0.8000000
1275.7329000	7.9590883	
290.3118700	2.3786972	
82.0562000	0.81540065	
26.4796410	0.28953785	
9.2414585	0.10084754	
3.3643530		
0.87174164		
0.36352352		
0.12873135		

Silicon (12s,9p,1d)		
s primitives	p primitives	d primitives
79079.4340000	483.0235200	0.3500000
11855.0100000	14.2508100	
2697.7051000	36.3877860	
762.8722700	3.4117040	
247.2845500	5.2884033	
87.9312400	2.1374219	
33.8232840	0.86468463	
13.8681080	0.25489855	
3.9920017	0.079397031	
1.4659925		
0.25271086		
0.092491673		

Germanium (14s,11p,6d)		
s primitives	p primitives	d primitives
538981.208590	3196.8571212	74.776447903
80785.7689540	758.78574707	21.307762727
18387.3215390	246.40186162	7.3452966023
5210.3369514	94.429089481	2.5656881541
1707.4890772	39.602333266	0.81988587339
627.54854073	17.394023219	0.2460000
250.56696133	7.5468872383	
102.39333101	3.1497947773	
25.923923344	1.2651485767	
11.389081191	0.30024031728	
3.7472808901	0.087319187211	
1.5027733307		
0.24441033890		
0.091205393545		

Oxygen (10s,6p,1d)		
s primitives	p primitives	d primitives
15902.6474590	63.270524011	1.2000000
2384.9537829	14.623312295	
542.71957182	4.4489518003	
153.40407874	1.5281513180	
49.545716140	0.52997315870	
17.339649897	0.17509445998	
6.3303355272		
1.6995882201		
0.68954491271		
0.23936028181		

Sulfur (12s,9p,1d)		
s primitives	p primitives	d primitives
103953.9500000	606.6936700	0.5500000
15583.7860000	143.5069600	
3546.1293000	45.7461600	
1002.6808000	16.8729120	
324.9028800	6.6399196	
115.5122500	2.6727135	
44.5282100	1.0000089	
18.3978920	0.35438942	
5.5100683	0.11671305	
2.1259867		
0.43691893		
0.15730851		

Selenium (14s,11p,6d)		
s primitives	p primitives	d primitives
609461.5616500	3656.2658173	94.493793993
91349.7284690	868.08211673	27.186508933
20791.8449100	282.38879090	9.5088741989
5892.0009402	108.68249518	3.4175441801
1931.5795523	45.880428373	1.1481458665
711.02173299	20.313633210	0.3380000
284.76563000	8.9138677790	
116.67280336	3.8029430087	
29.611379847	1.5911663461	
13.118921596	0.44755579009	
4.5252274573	0.13236319065	
1.8747678530		
0.35857737666		
0.13617743845		