

Electronic Supplementary Information for:

The duality of electron localization and covalency in lanthanide and actinide metallocenes

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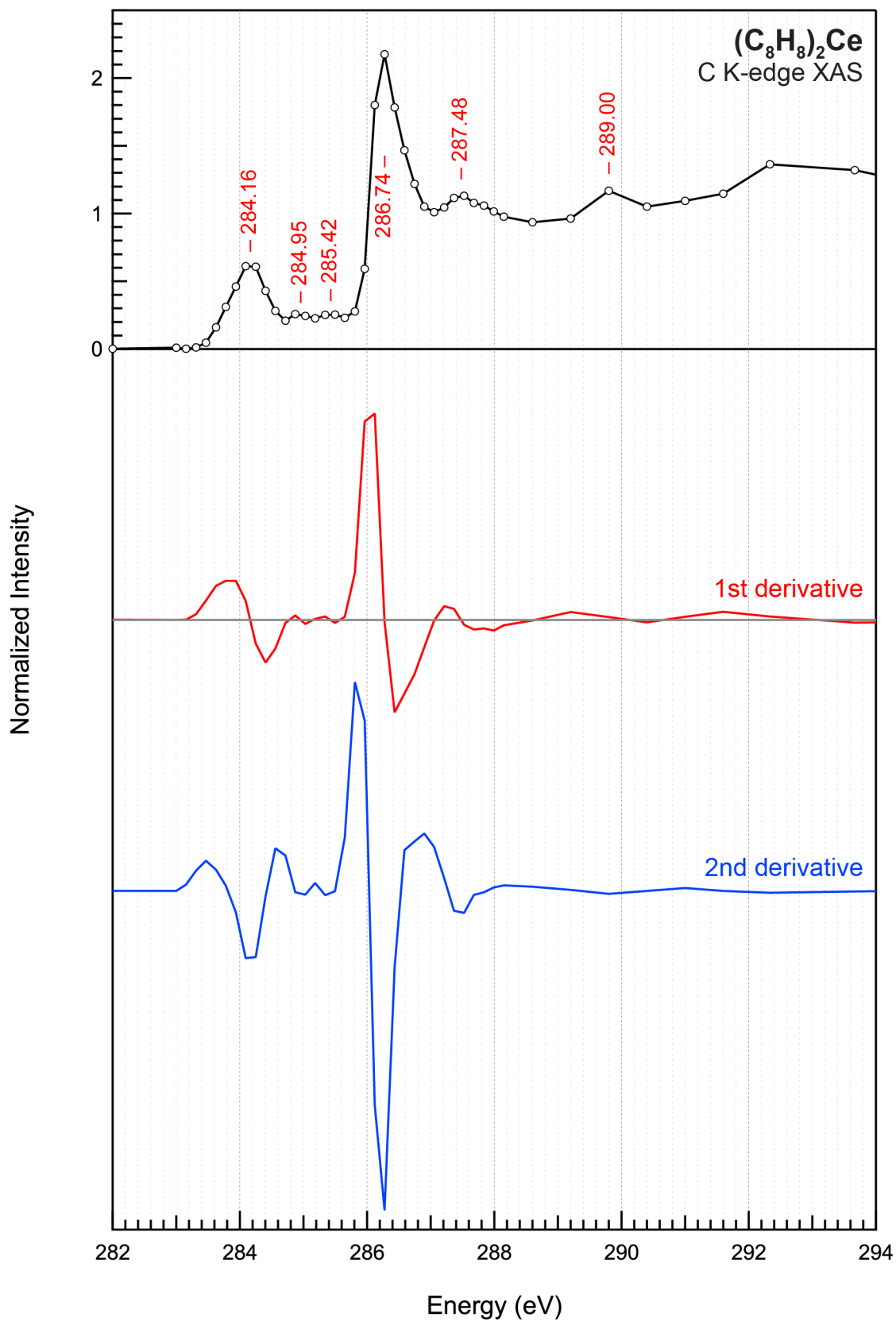


Figure S1. Experimental C K-edge XAS of $(C_8H_8)_2Ce$ (black circles) with 1st and 2nd derivatives of the data (red and blue). Energies of the C K-edge XAS features are provided, and were determined using either the zero-crossing of the 1st derivative or the minimum of the 2nd derivative.

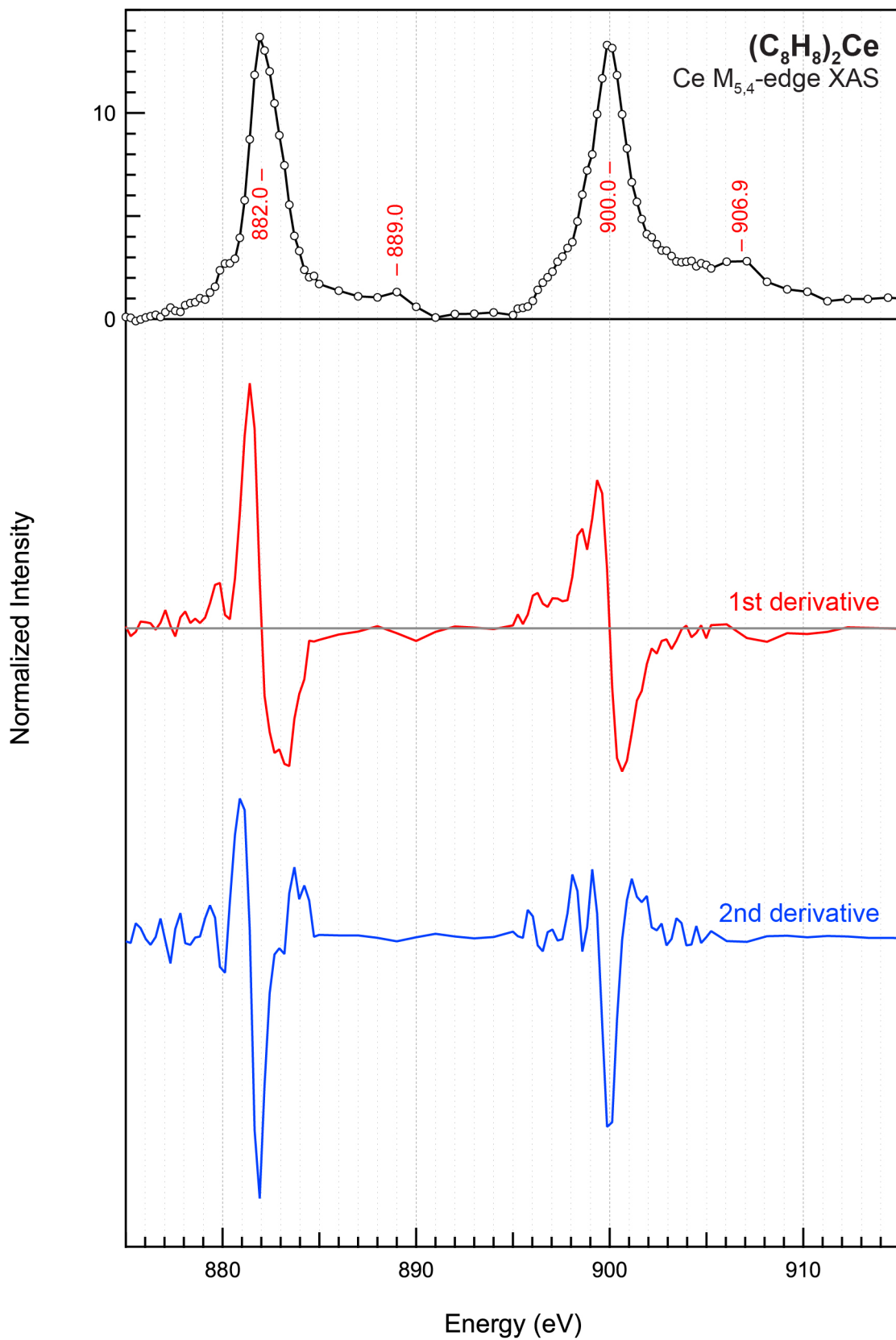


Figure S2. Experimental Ce M_{5,4}-edge XAS of (C₈H₈)₂Ce (black circles) with 1st and 2nd derivatives of the data (red and blue). Energies of the Ce M_{5,4}-edge XAS features are provided, and were determined using either the zero-crossing of the 1st derivative or the minimum of the 2nd derivative.

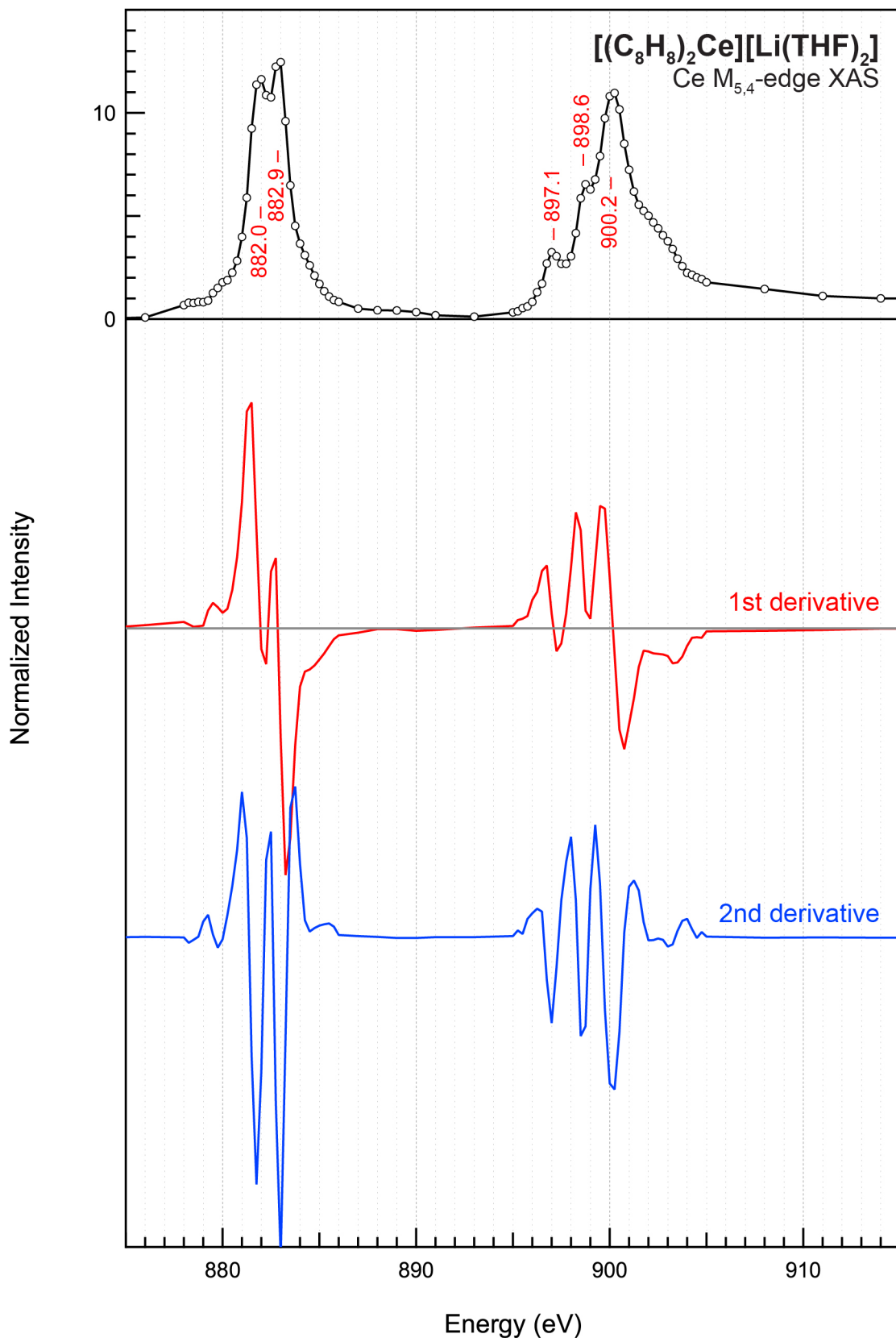


Figure S3. Experimental Ce M_{5,4}-edge XAS of [(C₈H₈)₂Ce][Li(THF)₂] (black circles) with 1st and 2nd derivatives of the data (red and blue). Energies of the Ce M_{5,4}-edge XAS features are provided, and were determined using either the zero-crossing of the 1st derivative or the minimum of the 2nd derivative.

Table S1. Atomic coordinates for Ce(C₈H₈)₂ used in the DFT calculations.

#	Atom	Coordinates (Angstroms)			Mulliken
		x	y	z	Population
1	C	1.997186	-0.687286	-1.714694	-0.119976
2	C	1.997191	-1.698539	-0.726517	-0.119989
3	C	1.996915	-1.714764	0.687381	-0.119965
4	C	1.99687	-0.726584	1.69863	-0.119977
5	C	1.99698	1.714793	-0.687221	-0.11997
6	C	1.997245	0.726613	-1.698472	-0.119992
7	H	1.898628	-1.090693	-2.721225	0.068611
8	H	1.898615	-2.695503	-1.153012	0.068624
9	H	1.898173	-2.721281	1.090773	0.068611
10	H	1.898088	-1.153066	2.69558	0.068624
11	H	1.898272	2.721305	-1.090637	0.068612
12	H	1.898706	1.15309	-2.695448	0.068624
13	C	1.996911	1.698567	0.726678	-0.11998
14	C	1.996725	0.687314	1.714854	-0.119959
15	H	1.898135	2.695523	1.153148	0.068624
16	H	1.897859	1.090714	2.721356	0.068611
17	C	-1.996853	1.713959	0.689526	-0.119955
18	C	-1.997027	1.699455	-0.72438	-0.119991
19	C	-1.997188	0.689464	-1.713862	-0.119965
20	C	-1.996963	-1.699421	0.724533	-0.119985
21	C	-1.996819	-0.689431	1.714014	-0.11995
22	C	-1.996772	0.724474	1.699513	-0.119979
23	H	-1.898141	2.719952	1.094214	0.068614
24	H	-1.898414	2.696963	-1.149609	0.068616
25	H	-1.898712	1.094162	-2.719875	0.068614
26	H	-1.898322	-2.696936	1.149739	0.068616
27	H	-1.898112	-1.094134	2.720002	0.068614
28	H	-1.898004	1.149684	2.697013	0.068616
29	C	-1.997226	-0.724441	-1.69936	-0.119997
30	C	-1.997129	-1.713926	-0.689371	-0.119962
31	H	-1.898612	-2.719928	-1.094085	0.068614
32	H	-1.898752	-1.149659	-2.696886	0.068616
33	Ce	0.000005	-0.000029	-0.000148	0.82173

Table S2. Normalized C K-edge and Ce M_{5,4}-edge XAS of (C₈H₈)₂Ce, and Ce M_{5,4}-edge XAS of [(C₈H₈)₂Ce][Li(THF)₂].

COT2Ce_CK_Int	COT2Ce_CK_eV
-0.069757863	278.000
-0.007396651	279.000
-0.001929973	280.000
-0.001908494	281.000
0.002172743	282.000
0.009336405	283.000
0.001884876	283.156
0.01101664	283.312
0.047124143	283.468
0.159997103	283.624
0.309962104	283.780
0.461123883	283.936
0.611399332	284.092
0.608278849	284.248
0.4300155	284.404
0.280427346	284.560
0.209715568	284.716
0.258514134	284.872
0.244174457	285.028
0.227476999	285.184
0.2527276	285.340
0.253587671	285.496
0.23040883	285.652
0.27754795	285.808
0.591545528	285.964
1.800656629	286.120
2.176731452	286.276
1.78417323	286.432
1.467337374	286.588
1.219404615	286.744
1.050176184	286.900
1.009350973	287.056
1.045268803	287.212
1.115233096	287.368
1.130845322	287.524
1.07897567	287.680
1.057929374	287.836
1.01469184	287.992
0.976448888	288.148
0.936166974	288.600
0.963578745	289.200
1.167703912	289.800
1.050117436	290.400
1.094208228	291.000
1.146813023	291.600
1.364052441	292.333

1.320008376	293.666
1.190567428	294.999
1.232351729	296.332
1.2085334	300.417
1.068548867	305.834
0.905790274	311.251
0.851976783	316.668
0.823383415	322.085
0.792000895	327.502
0.764510549	332.919
0.737072356	338.336
0.715100675	343.753
0.702743979	349.170
0.682326591	354.587
0.649807569	360.004
0.614760838	365.421

COT2Ce_CeM_Int	COT2Ce_CeM_Int
0.167450213	860.000
0.119737903	861.000
0.049156385	862.000
-0.0222325	863.000
-0.013826954	864.000
0.127205566	865.000
0.192780638	866.000
0.080241607	867.000
-0.023495491	868.000
-0.242516287	869.000
-0.1677228	870.000
-0.052302674	871.000
-0.07536352	872.000
-0.038523284	873.000
-0.047723933	874.000
0.106912845	875.000
0.06991798	875.256
-0.089496594	875.512
-0.015400488	875.768
0.074812721	876.024
0.136733167	876.280
0.203183713	876.536
0.104894069	876.792
0.343753633	877.048
0.557135751	877.304
0.402953941	877.560
0.354967711	877.816
0.67871254	878.072
0.776320025	878.328
0.814354494	878.584
1.016277578	878.840
0.947546424	879.096
1.283085333	879.352

1.570633576	879.608
2.365822838	879.864
2.696252298	880.120
2.70191994	880.376
2.924204041	880.632
3.943827498	880.888
5.765373926	881.144
8.724168394	881.400
11.84927591	881.656
13.68657414	881.912
13.03969343	882.168
12.01302427	882.424
10.46405583	882.680
8.917181429	882.936
7.458838244	883.192
5.547927204	883.448
4.037605377	883.704
3.302588987	883.960
2.401701627	884.216
2.034607477	884.472
2.091997824	884.728
1.707732574	884.984
1.379831166	886.000
1.101707349	887.000
1.060791351	888.000
1.30996923	889.000
0.595615698	890.000
0.073867003	891.000
0.251891844	892.000
0.264976398	893.000
0.32828293	894.000
0.195517831	895.000
0.50435312	895.256
0.541387104	895.512
0.610462176	895.768
0.88338241	896.024
1.421761343	896.280
1.764429284	896.536
2.032689122	896.792
2.298901458	897.048
2.779985222	897.304
3.037984281	897.560
3.451407394	897.816
3.737396743	898.072
4.740896118	898.328
6.043307592	898.584
7.21153785	898.840
7.993488147	899.096
9.943468823	899.352
11.6742504	899.608
13.29514158	899.864

13.15027125	900.120
11.83434583	900.376
9.92841394	900.632
8.28142132	900.888
6.644991952	901.144
5.686099776	901.400
4.854129489	901.656
4.12960655	901.912
3.965331484	902.168
3.631974591	902.424
3.335938085	902.680
3.3190832	902.936
3.064159614	903.192
2.805303892	903.448
2.758783487	903.704
2.780551944	903.960
2.82412165	904.216
2.558797681	904.472
2.71072215	904.728
2.630138749	904.984
2.463141435	905.240
2.789463212	906.042
2.812428675	907.084
1.804057818	908.126
1.44749077	909.168
1.328736486	910.210
0.866511329	911.252
0.975941892	912.294
0.977885553	913.336
1.041647504	914.378
0.972512581	915.420
0.970645096	916.462
0.717467618	917.504
0.51473781	918.546
0.802564009	919.588
0.807618479	920.630
0.956412277	921.672
0.770022935	922.714
0.865339691	923.756
0.870252232	924.798
0.791817459	925.840
0.928382084	926.882
0.946796507	927.924
0.964894498	928.966
0.909156756	930.008
1.049895494	931.050

COT2Ce_anion_CeM_Int	COT2Ce_anion_CeM_eV
0.004482834	860.000
-0.003102229	862.000

0.024636628	864.000
-0.032400294	866.000
0.018490346	868.000
-0.019212679	870.000
-0.023394107	872.000
0.030499501	874.000
0.080640418	876.000
0.675045159	878.000
0.792643293	878.250
0.775304809	878.500
0.829217205	878.750
0.824618585	879.000
0.89305008	879.250
1.263095814	879.500
1.512316571	879.750
1.778215955	880.000
1.889987434	880.250
2.253989203	880.500
2.822168341	880.750
3.98276473	881.000
5.88520692	881.250
9.244991742	881.500
11.36208298	881.750
11.62815893	882.000
10.85805476	882.250
10.76047415	882.500
12.23670134	882.750
12.46622828	883.000
9.59976458	883.250
6.484955024	883.500
4.51872976	883.750
3.655725091	884.000
3.103217253	884.250
2.60782149	884.500
2.110225453	884.750
1.706670799	885.000
1.352839643	885.250
1.098469066	885.500
0.921216769	885.750
0.835438868	886.000
0.502242081	887.000
0.428922218	888.000
0.417155727	889.000
0.342871545	890.000
0.187774795	891.000
0.122640317	893.000
0.330462176	895.000
0.375709291	895.250
0.534365643	895.500
0.60861021	895.750
0.830667078	896.000

1.299236236	896.250
1.717008922	896.500
2.690609101	896.750
3.23755966	897.000
3.050243142	897.250
2.686157618	897.500
2.684384043	897.750
3.046918961	898.000
4.161391067	898.250
5.856246819	898.500
6.541298589	898.750
6.284795646	899.000
6.773316681	899.250
7.899238365	899.500
9.740806281	899.750
10.80221373	900.000
10.96417049	900.250
10.17105851	900.500
8.508389703	900.750
7.24196054	901.000
6.182696775	901.250
5.552391559	901.500
5.243041271	901.750
5.011597016	902.000
4.683734538	902.250
4.403531103	902.500
4.068035572	902.750
3.77290558	903.000
3.39900031	903.250
2.92799772	903.500
2.569453629	903.750
2.24528544	904.000
2.149022277	904.250
2.017772026	904.500
1.935634086	904.750
1.786754471	905.000
1.457500975	908.000
1.121415761	911.000
0.997616338	914.000
1.026179167	917.000
0.964055354	920.000
0.953488601	923.000
1.011402012	926.000
1.037764566	929.000
1.07488402	932.000
1.029751219	935.000
0.98107353	938.000
0.98456409	941.000
0.948748502	944.000
0.958473174	947.000
0.96305029	950.000

1.030443898	953.000
1.005575358	956.000
1.016223602	959.000
1.00734101	962.000
1.001419283	965.000
0.954941869	968.000