Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Vibrationally Resolved Valence and Core Photoionization and Photoexcitation Spectra of an Electron-Deficient Trivalent Boron Compound: the Case of Catecholborane

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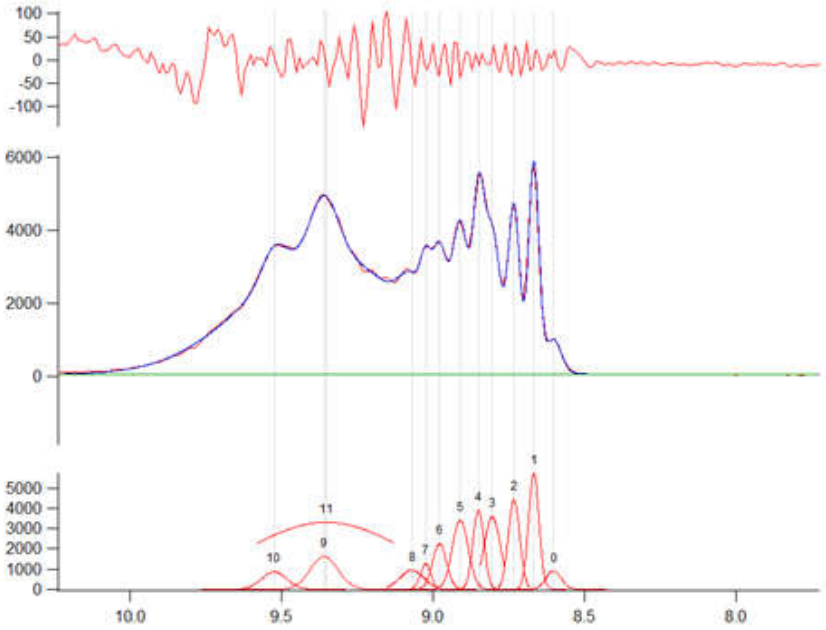


		Location	Location calibrated	Amplitude
Peak 0	Gauss	8.6026	8.6851	909.178
Peak 1	Gauss	8.6676	8.7501	5717.4
Peak 2	Gauss	8.73292	8.81542	4416.1
Peak 3	Gauss	8.80466	8.88716	3576.69
Peak 4	Gauss	8.85	8.9325	3901.1
Peak 5	Gauss	8.90981	8.99231	3412.09
Peak 6	Gauss	8.97846	9.06096	2259.65
Peak 7	Gauss	9.02391	9.10641	1259.83
Peak 8	Gauss	9.06973	9.15223	950.329
Peak 9	Gauss	9.35895	9.44145	1614.23
Peak 10	Gauss	9.52351	9.60601	867.152
Peak 11	Gauss	9.3526	9.4351	3308.39

Figure S1. The VUV-PES spectrum of catecholborane obtained at 50 eV photon energy; photon count = 550 cts/s; pressure p = 1.6 × 10^{-6} mbar; calibrated with respect to the Ar $3p_{3/2}$ and $3p_{1/2}$ lines (15.759 and 15.937 eV).

Table S1. Experimental setup parameters for the photoemission

Spectral region	$h\nu$ [eV]	Resolution [meV]	Reference gas	Reference energy [eV]
Valence		< 40	Ar(3p3/2)	15.76[a]
C(1s)	382	90	C(1s), CO_2	297.7[b]
O(1s)	628	300	O(1s), CO_2	541.3[c]
B(1s)	262	130	S($2p_{3/2}$) S($2p_{1/2}$), SF_6	180.2[d] 181.5[d]

[a] D. W. Turner et al. Molecular Photoelectron Spectroscopy, Wiley- Interscience, London (1970).

[b]G. Johansson, J. Hedman, A. Berndtsson, M. Klasson and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.* 1973, **2**, 295.

[c] T. D. Thomas and R. W. Shaw, Jr., *J. Electron Spectrosc. Relat. Phenom.* 1974, **5**, 1081.

[d]L. Pettersson, J. Nordgren, L. Selander, C. Nordling, K. Siegbahn and H. Ågren, *J. Electron Spectrosc. Relat. Phenom.*, 1982, **27**, 29.

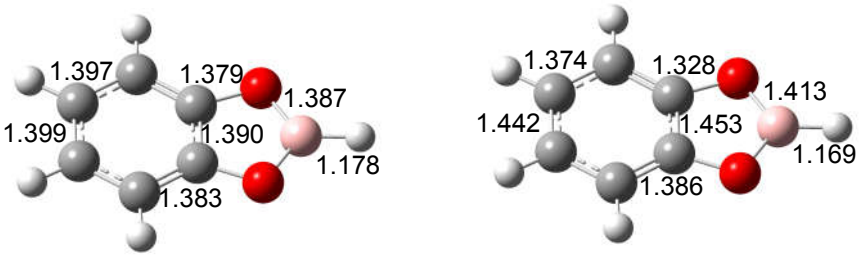
Table S2. Experimental setup parameters for the NEXAFS

Absorption edge	Resolution [meV]	Calibrant	Calibrant absorption energy [eV]
C K	100	C K of CO_2	290.77[a]
O K	160	O K of CO_2	535.4[b]
B K	25	N K (v = 1) of N_2 at the second order	401.1[c]

[a]M. Tronc, G. C. King and F. H. Read, *J. Phys. B: At. Mol. Op. Phys.*, 1979, **12**, 137.

[b]G. R. Wight and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **3**, 191.

[c]R. N. S. Sodhi and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 1984, **34**, 363.



MP2/cc-pVTZ; ground state

223.02	241.14	412.58	414.37	495.27	542.94	579.63	615.26	743.13
745.56	757.79	822.68	857.54	859.72	888.52	927.45	952.96	1021.62
1025.02	1106.84	1152.21	1162.10	1174.56	1295.76	1297.56	1316.36	1482.65
1499.03	1509.16	1657.57	1669.50	2791.81	3219.97	3234.67	3247.46	3250.76

MP2/cc-pVTZ; doublet cation

208.66	211.36	365.45	387.74	464.97	479.65	506.82	542.36	744.20
783.91	800.70	810.55	860.84	878.57	906.00	1010.12	1010.88	1015.75
1030.88	1098.06	1135.39	1172.05	1199.55	1239.79	1352.28	1391.53	1470.54
1478.09	1569.72	1616.75	1681.73	2872.51	3242.78	3249.00	3269.17	3269.62

Figure S2. MP2/cc-PVTZ equilibrium structures (C_{2v} symmetry) and harmonic vibrational frequencies (cm^{-1}) of the ground state and the lowest doublet cation of catecholborane. The distances are given in Å.

Table S3. The ground state bond lengths (Å) and the *A*, *B*, and *C* rotational constants (GHz) calculated at the MP2/cc-pVTZ and M06-2X/6-311+G(2d,p) level. The enumeration of the atoms follows Fig. 1.

	C1-C1'	C1-C2	C2-C3	C3-C3'	C1-O	B-O	B-H	*A*	*B*	*C*
MP2	1.390	1.383	1.397	1.399	1.379	1.387	1.178	3.869	1.696	1.179
M06-2X	1.387	1.376	1.395	1.392	1.374	1.379	1.177	3.914	1.702	1.186
exp.[a]								3.867	1.691	1.177

[a] Ref. 52

Table S4. The vibronic transitions that predominantly contribute to the X band. Positions of the peaks are given in cm^{-1} (Figure 2). The transitions with the largest intensity are boldfaced. The enumeration of the doublet cation frequencies follow Figure S2.

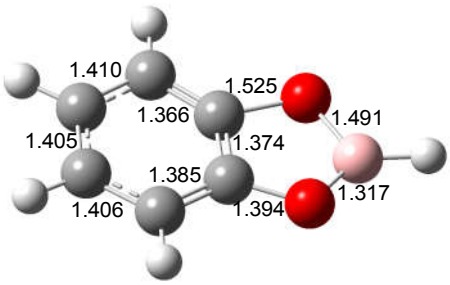
peak	542	1136	1536	2048	2652
modes	$\mathbf{8_0^1}$	$\mathbf{8_0^2}$; 20_0^1; 23_0^1	8_0^3; 26_0^1; $\mathbf{27_0^1}$; 29_0^1 30_0^1; $8_0^1 20_0^1$; $8_0^1 23_0^1$	$8_0^1 26_0^1$; $\mathbf{8_0^1 27_0^1}$ $8_0^1 29_0^1$; $8_0^1 30_0^1$	$8_0^2 26_0^1$; $\mathbf{8_0^2 27_0^1}$

Table S5. TD-CAM-B3LYP//mix shake-up spectrum of the B 1s core-ionized catecholborane. The monopole intensities are calculated from the overlaps of the TDDFT auxiliary CIS wave functions. The transitions used in Table 2 are highlighted in red.

***E*/ eV**	**shifted**	**Monopole Intensities**	**Relative**
2.320	**199.75**	0.06289	**1.0000**
2.590	200.02	0.00000	0.0000
3.742	201.17	0.00000	0.0000
4.178	**201.60**	0.03474	**0.5524**
4.262	201.69	0.00000	0.0000
4.868	**202.29**	0.00520	**0.0827**
5.085	202.51	0.00000	0.0000
5.410	202.84	0.00277	0.0440
5.740	203.17	0.00000	0.0000
5.936	203.36	0.00264	0.0419
6.206	203.63	0.00000	0.0000
6.427	**203.85**	0.01989	**0.3163**
6.496	203.92	0.00000	0.0000
6.550	203.98	0.00000	0.0000
6.787	204.21	0.00000	0.0000
6.872	204.30	0.00000	0.0000
7.313	204.74	0.00349	0.0554
7.319	204.74	0.00000	0.0000
7.364	204.79	0.00000	0.0000
7.420	204.85	0.00000	0.0000

Table S6. Harmonic vibrational frequencies of the lowest B 1s core-ionized cation of catecholborane at the B3LYP//mix level of theory.

224.51	261.98	408.43	422.50	525.33	562.00	604.45	624.55	727.38
770.00	774.88	845.32	871.76	877.63	925.12	972.98	1008.33	1014.83
1061.09	1137.73	1139.13	1205.47	1208.23	1292.09	1324.50	1417.90	1469.28
1505.48	1568.52	1640.55	1690.84	3197.11	3208.16	3209.82	3228.19	3229.26



195.31	235.11	366.87	384.26	413.03	467.35	545.15	551.61	594.38
679.47	696.06	752.08	762.72	815.41	836.24	862.22	950.2	959.14
1003.58	1005.12	1031.6	1115.9	1165.42	1232.28	1278.41	1366.84	1386.04
1469.22	1493.81	1611.65	1729.31	2845.45	3197.04	3209.74	3220.23	3236.02

Figure S3. The minimum geometry and harmonic vibrational frequencies (cm^{-1}) of the O 1s core-ionized catecholborane at the B3LYP//mix level. The distances are given in Å.

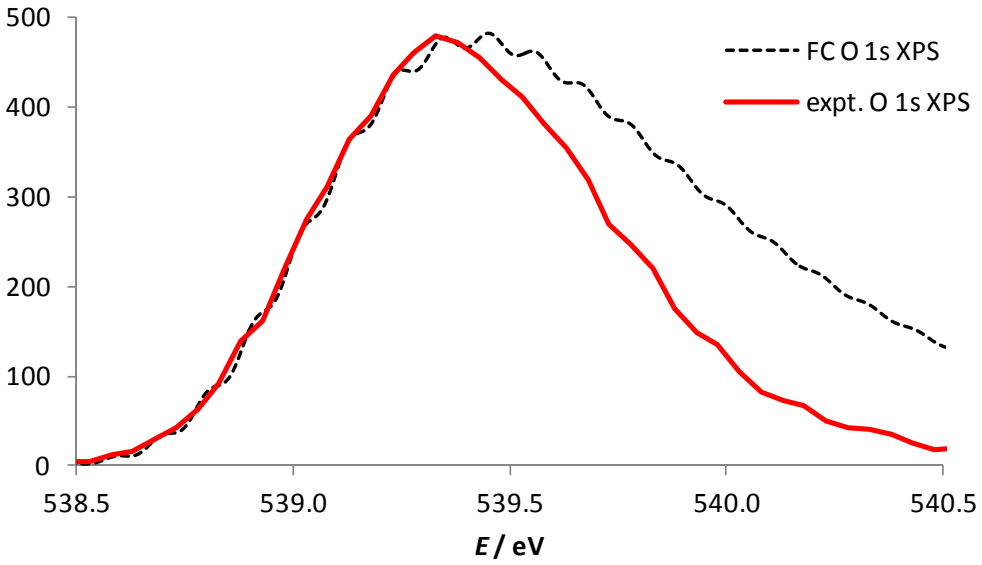
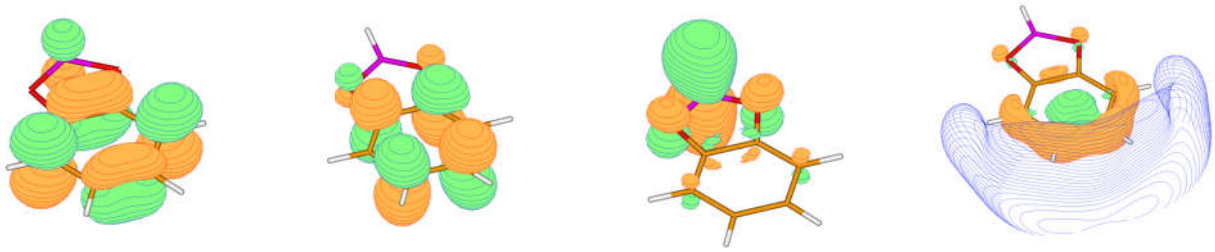
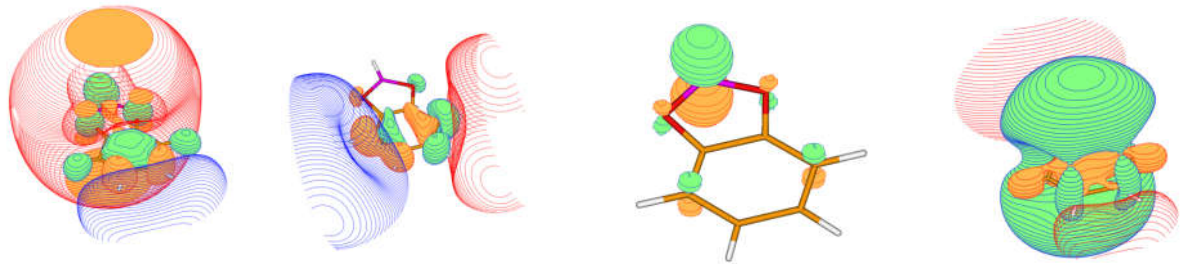


Figure S4. The region of the O 1s CEBE with superimposed vibrationally resolved FC spectrum computed at the B3LYP//mix level of theory.



V1 (π*) V2 (π*) V3 (π*) V4 (3s)



V5 ($3p_z$) V6 ($3p_y$) V7 (mixed $3p_x + Bp_x$) V8 ($3d_z^2$)

Figure S5. Virtual orbitals (V1 ≡ LUMO) of catecholborane at the SRC2-BLYP/6-311(2+)G** level of theory and their assignment to the valence or Rydberg manifold.

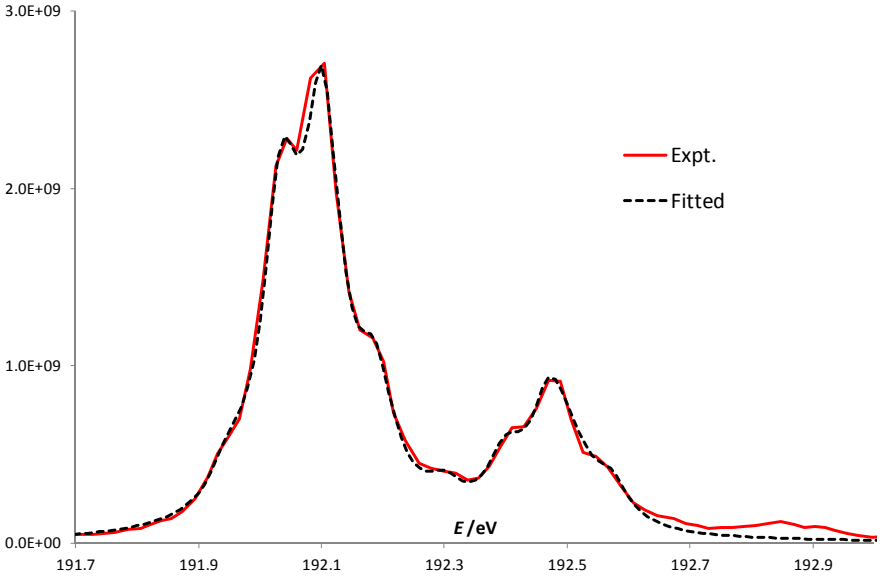
Table S7. Excitation energies (eV) and oscillator strengths of the first 20 B 1s core-excitations of diborane (B_2H_6) at the TD-SRC2-BLYP/6-311(2+)G** level of theory.

190.30	190.31	193.03	193.04	193.67	193.68	193.70	193.70	193.72	193.73
0.0001	0.1151	0.0043	0.0000	0.0000	0.0106	0.0012	0.0136	0.0000	0.0010
193.73	193.75	194.20	194.20	194.21	194.22	194.33	194.33	194.47	194.48
0.0279	0.0000	0.0022	0.0000	0.0028	0.0000	0.0016	0.0000	0.0000	0.0000

Table S8. Harmonic vibrational frequencies (in cm^{-1}) of the ground state and the first B 1s core-excited state of catecholborane at the $BH^{0.58}$LYP/6-311+G(2d,p) level of theory.

233.57	255.75	436.29	441.44	517.84	575.86	618.71	652.93	792.04
801.35	811.22	877.33	897.07	926.05	934.14	1000.25	1042.79	1061.45
1072.34	1163.04	1214.78	1217.80	1222.53	1318.07	1370.39	1378.02	1418.84
1582.57	1591.71	1747.74	1753.02	2835.11	3299.89	3313.92	3326.64	3329.94

212.92	245.22	341.28	442.70	452.72	576.82	607.36	661.44	787.02
796.37	806.44	869.93	903.38	918.89	962.76	992.53	1039.27	1071.45
1162.61	1195.56	1221.58	1229.08	1263.57	1348.50	1376.64	1427.79	1430.21
1581.26	1598.03	1745.43	1765.04	3301.83	3316.08	3329.19	3332.24	3363.67



band	*E*	OS
1	191.950	0.45
2	192.035	3.40
3	192.102	4.40
4	192.188	1.35
5	192.300	0.31
6	192.401	0.70
7	192.470	1.28
8	192.501	0.40
9	192.520	0.19
10	192.570	0.45

Figure S6. The magnified region of the first band in the B 1s NEXAFS spectrum of catecholborane. Ten Lorentzian profiles (fwhm = 600 cm^{-1}) are used for a faithful reconstruction of this spectral region. The corresponding band centres (eV) and oscillator strengths (OS) are shown in the table below.

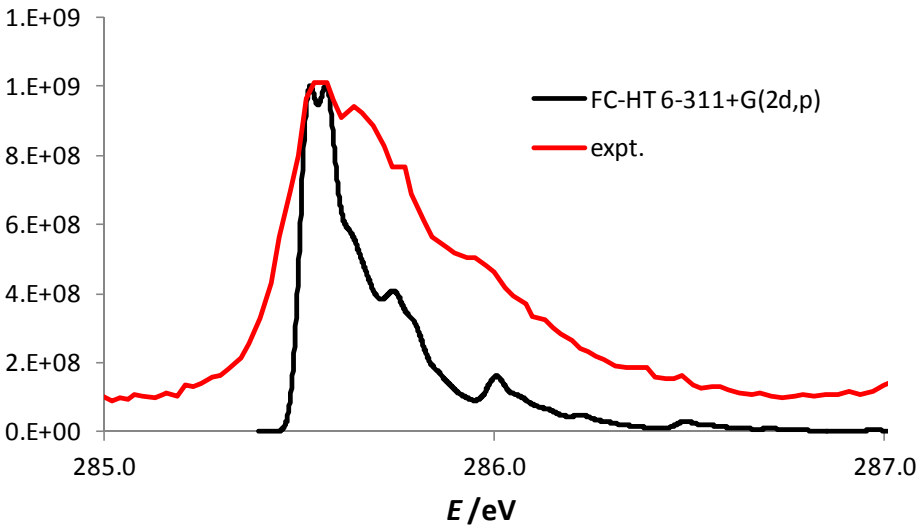


Figure S7. The superimposed experimental and FC-HT vibrationally resolved spectra ($BH^{0.58}$LYP/6-311+G(2d,p) level) in the region of the first band of the C 1s NEXAFS spectrum of catecholborane

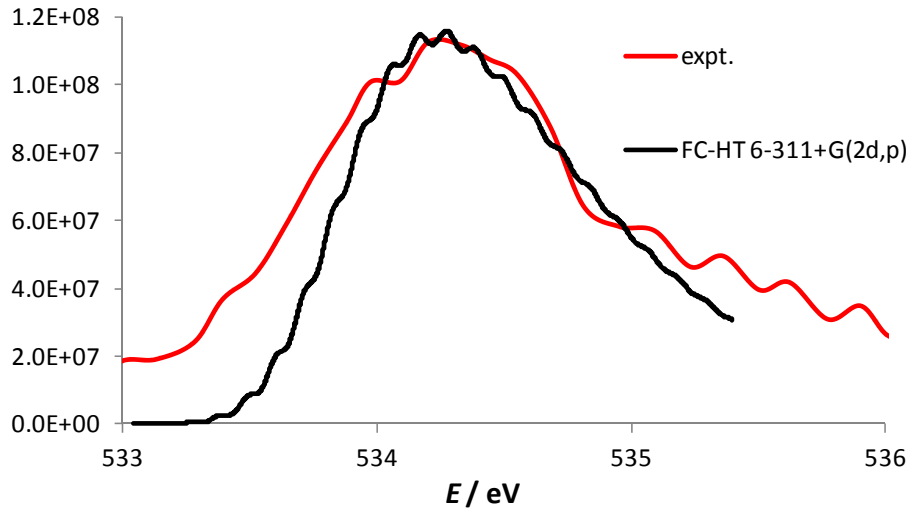


Figure S8. The superimposed experimental and FC-HT vibrationally resolved spectra ($BH^{0.58}$LYP/6-311+G(2d,p) level) in the region of the first band of the O 1s NEXAFS spectrum of catecholborane

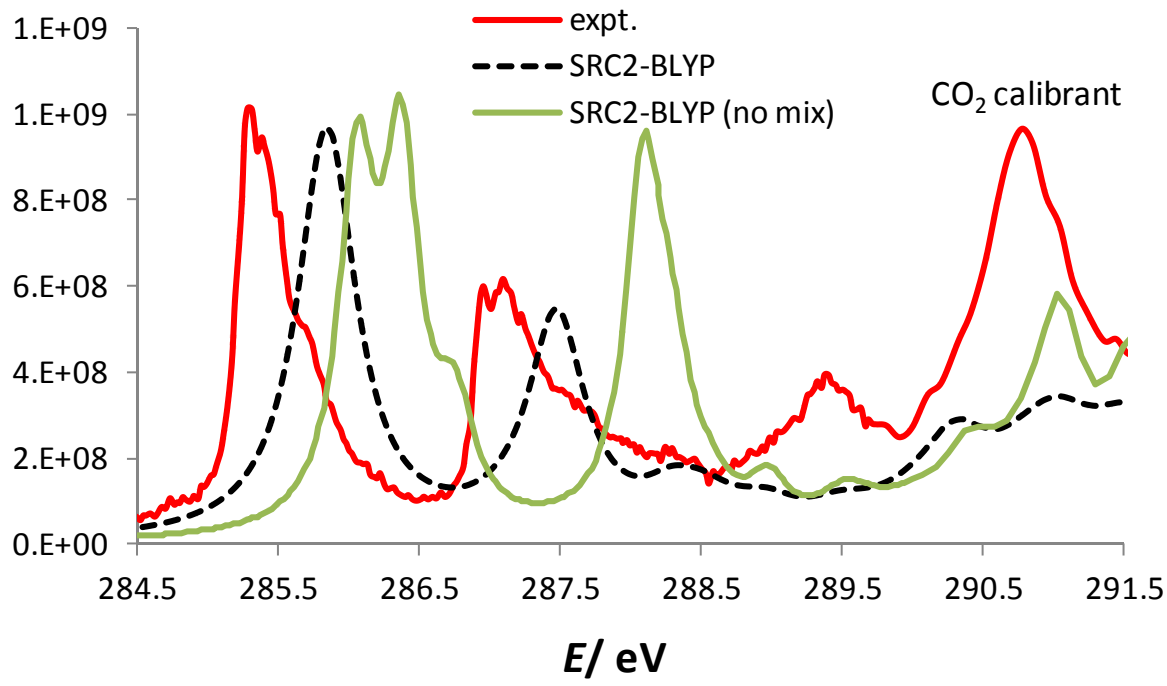


Figure S9. The comparison between the C 1s NEXAFS spectra obtained with the one-at-a-time approach (SRC2-BLYP no mix) and the approach that allows for the mixings of excitations originating from different cores (SRC2-BLYP)

Table S9. Cartesian coordinates (Å) and harmonic vibrational frequencies (cm^{-1}) of the stationary points discussed in the paper (the remaining vibrational frequencies are given in Figures S2 and S3, and Tables S6 and S8).

Ground state M06-2X/6-311+G(2d,p)

H	3.028462	1.226202	-0.000026
C	2.085267	0.696081	-0.000021
C	2.085241	-0.696061	-0.000014
H	3.028420	-1.226212	-0.000012
C	0.895881	-1.424621	0.000006
H	0.881702	-2.505866	0.000030
C	-0.269755	-0.693523	0.000005
C	-0.269676	0.693456	0.000002
C	0.895888	1.424620	0.000005
H	0.881582	2.505861	0.000024
O	-1.569334	1.139641	0.000060
O	-1.569337	-1.139622	0.000050
B	-2.345132	0.000025	-0.000162
H	-3.522208	0.000019	0.000019

224.1011	244.7416	416.7511
421.6953	498.8986	552.0549
592.8001	627.1105	760.7332
763.1985	775.3840	846.2340
863.3280	880.5553	891.0566
951.5889	993.7731	1018.7640
1034.7542	1118.4130	1169.1172
1174.3540	1183.2578	1281.6830
1310.4023	1328.4717	1379.5973
1518.9832	1525.7103	1686.4667
1690.8495	2789.6115	3213.7949
3226.0251	3236.4604	3239.8182

Ground state MP2/cc-pVTZ

H	-3.032034	1.227807	-0.000041
C	-2.089234	0.699599	-0.000047
C	-2.089233	-0.699597	-0.000047
H	-3.032031	-1.227808	-0.000041
C	-0.898693	-1.430856	0.000015
H	-0.885620	-2.510711	0.000078
C	0.271860	-0.695103	-0.000003
C	0.271854	0.695098	-0.000003
C	-0.898694	1.430856	0.000015
H	-0.885612	2.510710	0.000077
O	1.573009	1.151202	0.000169
O	1.573010	-1.151201	0.000169
B	2.347037	0.000004	-0.000499
H	3.524802	-0.000001	0.000139

Doublet cation MP2/cc-pVTZ

H	-3.005501	1.223203	-0.000008
C	-2.048140	0.721221	-0.000009
C	-2.048161	-0.721203	-0.000009
H	-3.005533	-1.223162	-0.000009
C	-0.894618	-1.468475	0.000003
H	-0.888670	-2.547612	0.000013
C	0.275974	-0.726601	0.000001
C	0.275981	0.726602	0.000001
C	-0.894582	1.468484	0.000003
H	-0.888627	2.547621	0.000013
O	1.533183	1.153906	0.000028
O	1.533159	-1.153926	0.000029
B	2.348296	-0.000006	-0.000088
H	3.517378	-0.000028	0.000032

Ground state $BH^{0.58}$LYP/6-311+G(2d,p)

H	3.006969	1.216489	0.019003
H	3.006967	-1.216494	0.019019
H	0.879346	-2.483912	-0.001543
H	0.879350	2.483911	-0.001576
H	-3.494937	0.000003	-0.043796
O	-1.555134	1.127797	-0.025068
O	-1.555136	-1.127793	-0.025053
C	2.072855	0.690602	0.009976
C	2.072854	-0.690605	0.009985
C	0.890611	-1.412650	-0.001435
C	-0.265891	-0.687602	-0.012610
C	-0.265890	0.687603	-0.012620
C	0.890613	1.412649	-0.001454
B	-2.325575	0.000002	-0.032493

B 1s first core-excited state $BH^{0.58}$LYP/6-311+G(2d,p)

H	2.992843	1.216112	-0.032336
H	2.992840	-1.216116	-0.032316
H	0.863733	-2.484273	0.006898
H	0.863739	2.484273	0.006860
H	-3.312885	0.000003	-0.342932
O	-1.565052	1.120500	0.039389
O	-1.565053	-1.120497	0.039391
C	2.059495	0.689320	-0.015903
C	2.059493	-0.689323	-0.015894
C	0.875221	-1.413252	0.007102
C	-0.276360	-0.685772	0.028193
C	-0.276359	0.685773	0.028187
C	0.875223	1.413252	0.007083
B	-2.349876	0.000002	0.176612

C 1s first core-excited state $BH^{0.58}$LYP/6-311+G(2d,p)

H	1.126960	-1.008376	-0.243060
C	0.593499	-0.085732	-0.127069
C	1.342846	1.056826	-0.070048
H	2.408963	1.044415	-0.117231
C	0.734337	2.295267	0.102174
H	1.232742	3.154136	-0.061070
C	-0.626233	2.279240	0.154412
C	-1.356814	1.154332	0.101759
C	-0.791717	-0.105629	-0.046135
H	-1.370008	-1.001805	-0.095218
O	-2.669319	1.507830	0.234320
O	-1.410697	3.375136	0.336204
B	-2.680538	2.865230	0.375163
H	-3.644181	3.513849	0.509220

155.1787	268.7616	314.2821
369.2385	441.0116	492.8461
560.5136	580.4901	664.6637
673.1491	692.9012	772.3034
792.9975	883.5860	918.2478
924.0503	1005.1349	1061.8394
1080.0607	1154.4637	1176.8282
1219.0019	1273.2463	1344.9722
1374.0038	1404.0256	1433.5701
1563.0230	1627.9099	1737.8035
1835.6988	2835.1748	3311.5964
3359.9137	3364.1753	3898.4617

O 1s first core-excited state $BH^{0.58}$LYP/6-311+G(2d,p)

H	3.009642	1.226832	-0.028199
H	2.994417	-1.208670	-0.038476
H	0.885766	-2.480961	-0.005636
H	0.860296	2.488327	0.008932
H	-3.422423	0.050461	-0.357803
O	-1.519814	1.116107	-0.001636
O	-1.542745	-1.139751	0.037734
C	2.076366	0.702050	-0.014696
C	2.060955	-0.681371	-0.019287
C	0.886351	-1.410225	-0.000225
C	-0.294415	-0.707337	0.024099
C	-0.228285	0.658929	0.037247
C	0.892062	1.418169	0.007739
B	-2.421174	-0.032561	0.250543

186.6704	250.5697	341.4225
426.5466	444.7358	569.8665
604.5682	640.7005	679.3245
749.3115	776.6106	793.3446
853.6770	902.0983	915.6944
931.8071	996.4106	1045.9517
1048.5892	1069.9792	1087.7372
1178.9336	1220.3527	1281.9542

```
1337.6700    1379.2754    1436.0784
1587.3412    1618.5907    1734.7432
1771.8527    2764.0594    3304.8032
3324.6364    3335.0037    3340.4952
```

Ground state B3LYP//mix

```
H   3.0484964037   1.2387684600  -0.0009164708
H   3.0485656288  -1.2386166516   0.0003738823
H   0.8806533113  -2.5298594367   0.0005220124
H   0.8805748387   2.5298094592   0.0017705515
H  -3.5323874780   0.0003825365  -0.0003689812
O  -1.5838044698   1.1450549271  -0.0004773885
O  -1.5838134779  -1.1452045787   0.0003708829
C   2.0931741715   0.7023672162  -0.0006072912
C   2.0932472664  -0.7023715092  -0.0001123319
C   0.8973935190  -1.4360252242   0.0001637235
C  -0.2751910579  -0.6965416498  -0.0001828812
C  -0.2751909854   0.6963393302  -0.0004358700
C   0.8972855055   1.4359916996  -0.0000540230
B  -2.3520021761  -0.0000945790  -0.0000798148

 226.8819     245.8142     416.7740
 419.7744     496.4336     543.0611
 580.7377     617.6377     749.3241
 753.7719     757.3316     829.9859
 843.2323     860.4479     878.2143
 933.6672     967.7898    1012.4642
1019.1469    1091.2267    1140.2665
1149.0794    1162.8945    1260.4799
1282.3084    1308.4190    1404.6655
1490.6593    1496.0115    1665.7237
1673.8697    2734.0239    3169.4215
3185.8652    3201.6201    3204.9957
```

B 1s first core-ionized state B3LYP//mix

```
H    3.0276078130   1.2330860421  -0.0000672684
H    3.0276452287  -1.2330473397  -0.0006898120
H    0.8755868029  -2.5544522931   0.0002058008
H    0.8754941618   2.5544088232  -0.0000702389
H   -3.4266571943   0.0001857993   0.0005827241
O   -1.6067973428   1.0981355781  -0.0002043085
O   -1.6067453186  -1.0982003508   0.0004843493
C    2.0669015168   0.7079843278  -0.0000917139
C    2.0669115175  -0.7079850786  -0.0003924469
C    0.8903519915  -1.4618150511  -0.0001348130
C   -0.2633983763  -0.6937359952   0.0001541639
C   -0.2634294088   0.6937165067  -0.0001179287
C    0.8903334153   1.4617675178   0.0000469054
B   -2.3168038067  -0.0000484858   0.0002605865
```

O 1s first core-ionized state B3LYP//mix

H	3.0768494081	1.2333181559	-0.0006713721
H	3.0409637573	-1.2399812555	-0.0002544788
H	0.8719677453	-2.5288984312	0.0007355956
H	0.9152983597	2.5730619638	-0.0002873552
H	-3.6072814393	0.0151498816	-0.0006089657
O	-1.6232425236	1.1404791315	-0.0000145985
O	-1.5978451959	-1.1282120607	0.0004437709
C	2.1162324046	0.7082244250	-0.0003110766
C	2.0907823598	-0.6965461467	-0.0000413079
C	0.8943579314	-1.4354831949	0.0004753375
C	-0.2738794095	-0.6906884084	0.0004888406
C	-0.1694654409	0.6795430448	0.0002241400
C	0.9363993997	1.4808957942	-0.0001531796
B	-2.4341363568	-0.1108628994	-0.0000593504