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Supporting information for:

Simulating X-ray Photoelectron Spectra With Strong Electron Correlation Using Multireference Algebraic Diagrammatic Construction Theory

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1 Benchmarking the Accuracy of CVS-MR-ADC: Active Spaces

Molecular orbitals computed using B3LYP that were selected for the CASSCF reference in MR-ADC calculations. Calculations were performed using PySCF with the cc-pCVTZ-X2C basis set and X2C scalar relativistic corrections. All listed orbitals were included in the CAS[Large] active space. The CAS[Small] active space orbitals are highlighted in blue.

1.1 Ethyne (C_2H_2)

CAS[Small]: CASSCF(4e,4o)
CAS[Large]: CASSCF(10e,10o)

```
MO #3 (A1g #2), energy= -0.753709855704024 occ= 2
MO #4 (A1u #2), energy= -0.570009189045261 occ= 2
MO #5 (A1g #3), energy= -0.499662044128499 occ= 2
MO #6 (E1uy #1), energy= -0.294822748341202 occ= 2
MO #7 (E1ux #1), energy= -0.294822748344717 occ= 2
MO #8 (E1gx #1), energy= 0.0280483176131281 occ= 0
MO #9 (E1gy #1), energy= 0.0280483176165779 occ= 0
MO #10 (A1u #3), energy= 0.0593050936717163 occ= 0
MO #11 (A1g #4), energy= 0.0799595025421912 occ= 0
MO #12 (A1g #5), energy= 0.178211647330189 occ= 0
```

1.2 Ethylene (C_2H_4)

CAS[Small]: CASSCF(2e,2o)
CAS[Large]: CASSCF(12e,12o)

```
MO #3 (Ag #2), energy= -0.761383036310425 occ= 2
MO #4 (B3u #2), energy= -0.580827025882971 occ= 2
MO #5 (B2u #1), energy= -0.47113724631324 occ= 2
MO #6 (Ag #3), energy= -0.421159845207843 occ= 2
MO #7 (B1g #1), energy= -0.357365543427001 occ= 2
MO #8 (B1u #1), energy= -0.275869023609227 occ= 2
MO #9 (B2g #1), energy= 0.000852609972134393 occ= 0
MO #10 (Ag #4), energy= 0.0582287597233807 occ= 0
MO #11 (B2u #2), energy= 0.0864183732990348 occ= 0
MO #12 (B3u #3), energy= 0.0868941072469934 occ= 0
MO #13 (B1g #2), energy= 0.15045553823567 occ= 0
MO #14 (Ag #5), energy= 0.241917054073259 occ= 0
```

1.3 Formaldehyde (CH_2O)

CAS[Small]: CASSCF(4e,3o)
CAS[Large]: CASSCF(12e,12o)

```
MO #3 (A1 #3), energy= -1.06518695797085 occ= 2
MO #4 (A1 #4), energy= -0.64001684233285 occ= 2
MO #5 (B2 #1), energy= -0.500960450578105 occ= 2
MO #6 (A1 #5), energy= -0.45546008007239 occ= 2
MO #7 (B1 #1), energy= -0.404616942998499 occ= 2
MO #8 (B2 #2), energy= -0.273688282777593 occ= 2
MO #9 (B1 #2), energy= -0.0525810128689245 occ= 0
MO #10 (A1 #6), energy= 0.0473482908720008 occ= 0
MO #11 (B2 #3), energy= 0.106362833221035 occ= 0
MO #12 (A1 #7), energy= 0.143028563128162 occ= 0
MO #14 (A1 #8), energy= 0.290153905540688 occ= 0
MO #15 (B2 #4), energy= 0.331289249945406 occ= 0
```

1.4 Acetonitrile (CH_3CN)

CAS[Small]: CASSCF(4e,5o)
CAS[Large]: CASSCF(8e,8o)

```
MO #6 (A' #6), energy= -0.519034351580561 occ= 2
MO #9 (A' #8), energy= -0.365048291757122 occ= 2
MO #10 (A' #9), energy= -0.333092164486641 occ= 2
MO #11 (A" #2), energy= -0.333092115111118 occ= 2
MO #12 (A' #10), energy= 0.0221357501327724 occ= 0
MO #13 (A" #3), energy= 0.0281562950236036 occ= 0
MO #14 (A' #11), energy= 0.0281568943045158 occ= 0
MO #17 (A' #13), energy= 0.144753931581682 occ= 0
```

1.5 Methyl isocyanide (CH_3NC)

CAS[Small]: CASSCF(6e,5o)
CAS[Large]: CASSCF(8e,8o)

```
MO #6 (A' #6), energy= -0.55844053400229 occ= 2
MO #9 (A" #2), energy= -0.341040348162803 occ= 2
MO #10 (A' #8), energy= -0.341040292116585 occ= 2
MO #11 (A' #9), energy= -0.305221739413823 occ= 2
MO #12 (A" #3), energy= 0.0217878421314183 occ= 0
MO #13 (A' #10), energy= 0.021788187250358 occ= 0
MO #17 (A' #13), energy= 0.11023293246258 occ= 0
MO #18 (A' #14), energy= 0.20793629712743 occ= 0
```

1.6 Methanol (CH_3OH)

CAS[Small]: CASSCF(2e,2o)
CAS[Large]: CASSCF(10e,10o)

```
MO #5 (A' #5), energy= -0.506510267514489 occ= 2
MO #6 (A" #1), energy= -0.439102253625969 occ= 2
MO #7 (A' #6), energy= -0.424453562750573 occ= 2
MO #8 (A' #7), energy= -0.336077309996616 occ= 2
MO #9 (A" #2), energy= -0.27384733671465 occ= 2
MO #10 (A' #8), energy= 0.0328450339370898 occ= 0
MO #11 (A' #9), energy= 0.0695313666880206 occ= 0
MO #12 (A" #3), energy= 0.114575629113319 occ= 0
MO #13 (A' #10), energy= 0.115125000144423 occ= 0
MO #16 (A" #4), energy= 0.275230751417099 occ= 0
```

1.7 Methane (CH_4)

CAS[Small]: CASSCF(6e,4o)
CAS[Large]: CASSCF(8e,8o)

```
MO #2 (A #2), energy= -0.694340971129536 occ= 2
MO #3 (B1 #1), energy= -0.392309369389034 occ= 2
MO #4 (B2 #1), energy= -0.392308396048733 occ= 2
MO #5 (B3 #1), energy= -0.392308396047077 occ= 2
MO #6 (A #3), energy= 0.0469386464487306 occ= 0
MO #7 (B2 #2), energy= 0.123426598248532 occ= 0
MO #8 (B3 #2), energy= 0.123426598250132 occ= 0
MO #9 (B1 #2), energy= 0.12342688676113 occ= 0
```

1.8 Carbon monoxide (CO)

CAS[Small]: CASSCF(6e,5o)
CAS[Large]: CASSCF(10e,10o)

```
MO #3 (A1 #3), energy= -1.16802207358674 occ= 2
MO #4 (A1 #4), energy= -0.578736731942812 occ= 2
MO #5 (E1x #1), energy= -0.478277648710107 occ= 2
MO #6 (E1y #1), energy= -0.478277648717911 occ= 2
MO #7 (A1 #5), energy= -0.380252233145597 occ= 2
MO #8 (E1x #2), energy= -0.0302881506675582 occ= 0
MO #9 (E1y #2), energy= -0.0302881506730378 occ= 0
MO #10 (A1 #6), energy= 0.157981830474724 occ= 0
MO #13 (A1 #7), energy= 0.296458033420159 occ= 0
MO #14 (A1 #8), energy= 0.474224678460238 occ= 0
```

1.9 Carbon dioxide (CO_2)

CAS[Small]: CASSCF(4e,4o)
CAS[Large]: CASSCF(12e,12o)

```
MO #6 (A1g #4), energy= -0.567144481930019 occ= 2
MO #7 (A1u #3), energy= -0.524501970579976 occ= 2
MO #8 (E1uy #1), energy= -0.520612769284549 occ= 2
MO #9 (E1ux #1), energy= -0.520612769296507 occ= 2
MO #10 (E1gx #1), energy= -0.376386581998685 occ= 2
MO #11 (E1gy #1), energy= -0.376386581994475 occ= 2
MO #12 (E1uy #2), energy= 0.0307089963219225 occ= 0
MO #13 (E1ux #2), energy= 0.0307089963176131 occ= 0
MO #14 (A1g #5), energy= 0.0383120782941207 occ= 0
MO #15 (A1u #4), energy= 0.221901282044402 occ= 0
MO #16 (E1uy #3), energy= 0.255198686134203 occ= 0
MO #17 (E1ux #3), energy= 0.255198686131851 occ= 0
```

1.10 Fluorine molecule (F_2)

CAS[Small]: CASSCF(4e,5o)
CAS[Large]: CASSCF(10e,10o)

```
MO #5 (A1g #3), energy= -0.601214551725558 occ= 2
MO #6 (E1uy #1), energy= -0.539080179633189 occ= 2
MO #7 (E1ux #1), energy= -0.539080179636322 occ= 2
MO #8 (E1gx #1), energy= -0.41087775780382 occ= 2
MO #9 (E1gy #1), energy= -0.410877757803504 occ= 2
MO #10 (A1u #3), energy= -0.151290595211936 occ= 0
MO #12 (E1uy #2), energy= 0.653277759542451 occ= 0
MO #13 (E1ux #2), energy= 0.653277759543147 occ= 0
MO #15 (E1gx #2), energy= 0.785293802226026 occ= 0
MO #16 (E1gy #2), energy= 0.785293802225121 occ= 0
```

1.11 Water (H_2O)

CAS[Small]: CASSCF(2e,2o)
CAS[Large]: CASSCF(8e,8o)

```
MO #2 (A1 #2), energy= -1.00805981691294 occ= 2
MO #3 (B1 #1), energy= -0.524924075882725 occ= 2
MO #4 (A1 #3), energy= -0.383198708379786 occ= 2
MO #5 (B2 #1), energy= -0.306345167609433 occ= 2
MO #6 (A1 #4), energy= 0.0269390612903103 occ= 0
MO #7 (B1 #2), energy= 0.0999761120368496 occ= 0
MO #8 (B1 #3), energy= 0.370710248446375 occ= 0
MO #9 (A1 #5), energy= 0.420219006967604 occ= 0
```

1.12 Hydrogen cyanide (HCN)

CAS[Small]: CASSCF(4e,4o)
CAS[Large]: CASSCF(10e,10o)

```
MO #3 (A1 #3), energy= -0.925793545186558 occ= 2
MO #4 (A1 #4), energy= -0.611800113199697 occ= 2
MO #5 (A1 #5), energy= -0.388001771333186 occ= 2
MO #6 (E1x #1), energy= -0.366886126503612 occ= 2
MO #7 (E1y #1), energy= -0.36688612649997 occ= 2
MO #8 (E1x #2), energy= 0.00456272892244339 occ= 0
MO #9 (E1y #2), energy= 0.00456272893292538 occ= 0
MO #10 (A1 #6), energy= 0.0420115374708675 occ= 0
MO #11 (A1 #7), energy= 0.118684706207165 occ= 0
MO #14 (A1 #8), energy= 0.334793618943826 occ= 0
```

1.13 Hydrogen fluoride (HF)

CAS[Small]: CASSCF(4e,5o)
CAS[Large]: CASSCF(8e,8o)

```
MO #2 (A1 #2), energy= -1.19441800815719 occ= 2
MO #3 (A1 #3), energy= -0.541305795471805 occ= 2
MO #4 (E1x #1), energy= -0.404133471288317 occ= 2
MO #5 (E1y #1), energy= -0.404133471287291 occ= 2
MO #6 (A1 #4), energy= 0.0246577936761579 occ= 0
MO #7 (A1 #5), energy= 0.380176806409049 occ= 0
MO #9 (E1x #2), energy= 0.654227797688523 occ= 0
MO #10 (E1y #2), energy= 0.654227797687241 occ= 0
```

1.14 Nitrogen molecule (N_2)

CAS[Small]: CASSCF(6e,5o)
CAS[Large]: CASSCF(10e,10o)

```
MO #3 (A1g #2), energy= -1.12558659908461 occ= 2
MO #4 (A1u #2), energy= -0.553188466215462 occ= 2
MO #5 (E1uy #1), energy= -0.465752458739695 occ= 2
MO #6 (E1ux #1), energy= -0.46575245873735 occ= 2
MO #7 (A1g #3), energy= -0.430762301019936 occ= 2
MO #8 (E1gx #1), energy= -0.0246106067507891 occ= 0
MO #9 (E1gy #1), energy= -0.0246106067489361 occ= 0
MO #10 (A1u #3), energy= 0.289874264346667 occ= 0
MO #13 (A1g #4), energy= 0.394241516968607 occ= 0
MO #14 (A1g #5), energy= 0.416661589518888 occ= 0
```

1.15 Nitrous oxide (N_2O)

CAS[Small]: CASSCF(4e,4o)
CAS[Large]: CASSCF(12e,12o)

```
MO #6 (A1 #6), energy= -0.607416167411539 occ= 2
MO #7 (E1x #1), energy= -0.566016740850906 occ= 2
MO #8 (E1y #1), energy= -0.566016740854362 occ= 2
MO #9 (A1 #7), energy= -0.47968309860303 occ= 2
MO #10 (E1x #2), energy= -0.345309937231378 occ= 2
MO #11 (E1y #2), energy= -0.345309937222059 occ= 2
MO #12 (E1x #3), energy= -0.0175965537538933 occ= 0
MO #13 (E1y #3), energy= -0.0175965537476182 occ= 0
MO #14 (A1 #8), energy= 0.102963380946563 occ= 0
MO #15 (A1 #9), energy= 0.271816933871534 occ= 0
MO #16 (E1x #4), energy= 0.381466721505024 occ= 0
MO #17 (E1y #4), energy= 0.381466721506446 occ= 0
```

1.16 Ammonia (NH_3)

CAS[Small]: CASSCF(2e,2o)
CAS[Large]: CASSCF(6e,6o)

```
MO #3 (A' #3), energy= -0.456184541235006 occ= 2
MO #4 (A" #1), energy= -0.45618365813654 occ= 2
MO #5 (A' #4), energy= -0.263118097242816 occ= 2
MO #6 (A' #5), energy= 0.0326225130420952 occ= 0
MO #7 (A' #6), energy= 0.113374412642921 occ= 0
MO #8 (A" #2), energy= 0.113374469692072 occ= 0
```

2 Core-Ionized States of Ozone

2.1 Atomic coordinates

The ozone geometry was optimized at the CASSCF(12e,9o) level of theory using the cc-pCVTZ basis. The optimized Cartesian geometry (in Å) is given below.

```
O          0.0000000000          0.0000000000         -0.4477034680
O          0.0000000000          1.0918051524          0.2238517340
O          0.0000000000         -1.0918051524          0.2238517340
```

2.2 Active space orbitals

Hartree–Fock molecular orbitals selected for the CASSCF reference in the MR-ADC calculations. Calculations were performed using PySCF with the cc-pCVTZ basis set.

```
MO #7 (A1 #5), energy= -0.82656652419632 occ= 2
MO #8 (B1 #3), energy= -0.794898855502317 occ= 2
MO #9 (B2 #1), energy= -0.774564524768685 occ= 2
MO #10 (B1 #4), energy= -0.562083600757817 occ= 2
MO #11 (A1 #6), energy= -0.551181361808789 occ= 2
MO #12 (A2 #1), energy= -0.484637877340836 occ= 2
MO #13 (B2 #2), energy= -0.0453100941444691 occ= 0
MO #14 (A1 #7), energy= 0.282958139900081 occ= 0
MO #15 (B1 #5), energy= 0.363890283049254 occ= 0
```

2.3 Atomic charges

Table S1: Atomic charges from Mulliken population analysis. Calculations were performed using PySCF with the cc-pCVTZ basis set. Multiconfigurational calculations used CASSCF(12e,9o).

Atom	RHF	CASSCF
O1	0.402	0.301
O2	−0.201	−0.151
O3	−0.201	−0.151

2.4 Core ionization energies and spectroscopic factors

Table S2: Oxygen K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of ozone calculated using the SR-ADC methods. O_C and O_T stand for the central and terminal oxygen atoms, respectively. Calculations were done using the cc-pCVTZ basis set. Also shown results with the X2C scalar relativistic corrections computed using the cc-pCVTZ-X2C basis set.

ionization		SR-ADC(2)		SR-ADC(2)-X		SR-ADC(3)	
		Ω	P	Ω	P	Ω	P
O_T $(1a_1^{-1})$		540.64	1.461	540.49	1.471	548.17	1.635
	X2C	541.02	1.461	540.87	1.471	548.55	1.635
O_T $(1b_2^{-1})$		540.64	1.461	540.49	1.471	548.17	1.635
	X2C	541.02	1.461	540.87	1.471	548.55	1.635
O_C $(2a_1^{-1})$		546.46	1.491	546.09	1.492	551.37	1.664
	X2C	546.83	1.490	546.46	1.492	551.75	1.664

Table S3: Oxygen K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of ozone calculated using the MR-ADC methods. O_C and O_T stand for the central and terminal oxygen atoms, respectively. All multireference methods used the CASSCF(12e,9o) reference wavefunction using the cc-pCVTZ basis set. Also shown results with the X2C scalar relativistic corrections computed using the cc-pCVTZ-X2C basis set.

ionization		MR-ADC(2)		MR-ADC(2)-X	
		Ω	P	Ω	P
O_T $(1a_1^{-1})$		543.47	1.531	540.62	1.291
	X2C	543.85	1.531	541.00	1.291
O_T $(1b_2^{-1})$		543.47	1.531	540.63	1.291
	X2C	543.85	1.531	541.00	1.291
O_C $(2a_1^{-1})$		548.11	1.552	545.06	1.380
	X2C	548.48	1.552	545.43	1.380

3 Simulating the X-Ray Photoelectron Spectra of Benzyne Diradicals

3.1 Atomic coordinates

The geometries of benzynes were optimized at the CASSCF(8e,8o) level of theory using the cc-pCVTZ basis. The optimized Cartesian geometries (in Å) are given below.

3.1.1 *ortho*-benzyne (*o*-C_6H_4)

C	0.0000000000	1.4472101359	-0.1184655749
C	0.0000000000	-1.4472101359	-0.1184655749
C	0.0000000000	0.7094872559	1.0585035705
C	0.0000000000	-0.7094872559	1.0585035705
C	0.0000000000	0.6246857178	-1.2487043065
C	0.0000000000	-0.6246857178	-1.2487043065
H	0.0000000000	2.5176207916	-0.1268328540
H	0.0000000000	-2.5176207916	-0.1268328540
H	0.0000000000	1.2230014455	2.0016161649
H	0.0000000000	-1.2230014455	2.0016161649

3.1.2 *meta*-benzyne (*m*-C_6H_4)

C	0.0000000000	0.0000000000	1.5728754863
C	0.0000000000	1.0863738460	0.7317665704
C	0.0000000000	-1.0863738460	0.7317665704
C	0.0000000000	1.1826495874	-0.6422303680
C	0.0000000000	-1.1826495874	-0.6422303680
C	0.0000000000	0.0000000000	-1.3808089873
H	0.0000000000	0.0000000000	2.6394747532
H	0.0000000000	2.1456227945	-1.1137534570
H	0.0000000000	-2.1456227945	-1.1137534570
H	0.0000000000	0.0000000000	-2.4554887432

3.1.3 *para*-benzyne (p-C_6H_4)

```
C          0.0000000000        0.0000000000        1.3479873989
C          0.0000000000        1.2167804968        0.7039480999
C          0.0000000000        1.2167804968       -0.7039480999
C          0.0000000000        0.0000000000       -1.3479873989
C          0.0000000000       -1.2167804968       -0.7039480999
C          0.0000000000       -1.2167804968        0.7039480999
H          0.0000000000        2.1445324245        1.2415193958
H          0.0000000000        2.1445324245       -1.2415193958
H          0.0000000000       -2.1445324245       -1.2415193958
H          0.0000000000       -2.1445324245        1.2415193958
```

3.2 Active spaces

Hartree–Fock molecular orbitals selected for the CASSCF(8e,8o) reference in the MR-ADC calculations. Calculations were performed using PySCF with the cc-pCVDZ-X2C basis set with the X2C scalar relativistic corrections.

3.2.1 *ortho*-benzyne (o-C_6H_4)

```
MO #17 (B2 #1), energy= -0.524413026355899 occ= 2
MO #18 (A1 #10), energy= -0.373441668216938 occ= 2
MO #19 (A2 #1), energy= -0.353213737911319 occ= 2
MO #20 (B2 #2), energy= -0.352783089873779 occ= 2
MO #21 (B1 #8), energy= 0.0653467292889115 occ= 0
MO #22 (B2 #3), energy= 0.11420078970953 occ= 0
MO #23 (A2 #2), energy= 0.15198136782739 occ= 0
MO #28 (A2 #3), energy= 0.36317585872199 occ= 0
```

3.2.2 *meta*-benzyne (m-C_6H_4)

```
MO #17 (B1 #1), energy= -0.528637094818258 occ= 2
MO #18 (B1 #2), energy= -0.363267572748615 occ= 2
MO #19 (A2 #1), energy= -0.349290447267701 occ= 2
MO #20 (A1 #11), energy= -0.305163835064116 occ= 2
MO #21 (B2 #7), energy= 0.0289363833246175 occ= 0
MO #22 (B1 #3), energy= 0.115065600053355 occ= 0
MO #23 (A2 #2), energy= 0.140452951138588 occ= 0
MO #28 (B1 #4), energy= 0.34216006022487 occ= 0
```

3.2.3 *para*-benzyne (p-C_6H_4)

```
MO #17 (B3u #1), energy= -0.522313211510342 occ= 2
MO #18 (B1g #1), energy= -0.361701470371551 occ= 2
MO #19 (B2g #1), energy= -0.346809247283215 occ= 2
MO #20 (B1u #5), energy= -0.26885925252202 occ= 2
MO #21 (Ag #6), energy= -0.0458080556925598 occ= 0
MO #22 (Au #1), energy= 0.108865756647446 occ= 0
MO #23 (B3u #2), energy= 0.141591340372341 occ= 0
MO #28 (B2g #2), energy= 0.345641045162728 occ= 0
```

3.3 Atomic charges

Table S4: Atomic charges from Mulliken population analysis. Calculations were performed using PySCF with the cc-pCVDZ-X2C basis set and the X2C scalar relativistic corrections. Multiconfigurational calculations correspond to CASSCF(8e,8o).

	o-C_6H_4		m-C_6H_4		p-C_6H_4	
Atom	RHF	CASSCF	RHF	CASSCF	RHF	CASSCF
C1	−0.072	−0.076	−0.081	−0.098	−0.067	−0.013
C2	−0.072	−0.076	−0.028	−0.014	−0.104	−0.103
C3	−0.093	−0.090	−0.028	−0.014	−0.104	−0.103
C4	−0.093	−0.090	−0.139	−0.121	−0.067	−0.013
C5	−0.052	−0.037	−0.139	−0.121	−0.104	−0.103
C6	−0.052	−0.037	−0.046	−0.066	−0.104	−0.103
H1	0.112	0.106	0.122	0.120	0.138	0.109
H2	0.112	0.106	0.119	0.110	0.138	0.109
H3	0.105	0.098	0.119	0.110	0.138	0.109
H4	0.105	0.098	0.101	0.096	0.138	0.109

3.4 Core ionization energies and spectroscopic factors

3.4.1 *ortho*-benzyne (*o*-C_6H_4)

Table S5: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *ortho*-benzyne computed using the SR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

SR-ADC(2)		SR-ADC(2)-X		SR-ADC(3)	
Ω	P	Ω	P	Ω	P
292.15	1.509	291.13	1.454	295.46	1.581
292.23	1.508	291.20	1.452	295.49	1.581
292.64	1.541	291.40	1.474	295.50	1.582
292.67	1.541	291.43	1.473	295.58	1.581
293.09	1.531	291.93	1.470	295.96	1.583
293.09	1.531	291.93	1.470	295.96	1.583

Table S6: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *ortho*-benzyne computed using the MR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

MR-ADC(2)		MR-ADC(2)-X	
Ω	P	Ω	P
292.66	1.538	290.90	1.415
292.69	1.538	290.93	1.415
292.94	1.545	291.12	1.396
293.02	1.544	291.19	1.394
293.20	1.538	291.36	1.404
293.20	1.538	291.36	1.404

3.4.2 *meta*-benzyne (*m*-C_6H_4)

Table S7: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *meta*-benzyne computed using the SR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

SR-ADC(2)		SR-ADC(2)-X		SR-ADC(3)	
Ω	P	Ω	P	Ω	P
292.09	1.456	291.16	1.398	295.57	1.593
292.09	1.456	291.16	1.398	295.58	1.594
292.54	1.534	291.44	1.481	295.66	1.579
292.54	1.534	291.44	1.481	296.11	1.575
292.98	1.537	291.73	1.466	296.12	1.567
293.41	1.533	292.32	1.478	296.17	1.588

Table S8: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *meta*-benzyne computed using the MR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

MR-ADC(2)		MR-ADC(2)-X	
Ω	P	Ω	P
292.70	1.538	290.92	1.415
292.70	1.538	290.93	1.415
292.85	1.536	291.08	1.415
293.25	1.535	291.47	1.374
293.41	1.529	291.49	1.355
293.41	1.529	291.53	1.398

3.4.3 *para*-benzyne (*p*-C_6H_4)

Table S9: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *para*-benzyne computed using the SR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

SR-ADC(2)		SR-ADC(2)-X		SR-ADC(3)	
Ω	P	Ω	P	Ω	P
290.77	1.409	290.32	1.397	295.71	1.597
290.77	1.409	290.32	1.397	295.71	1.597
292.73	1.519	291.74	1.472	295.74	1.596
292.73	1.519	291.74	1.472	295.74	1.596
292.76	1.519	291.77	1.471	296.16	1.597
292.76	1.519	291.77	1.471	296.16	1.597

Table S10: Carbon K-edge core ionization energies (Ω, eV) and spectroscopic factors (P) of *para*-benzyne computed using the MR-ADC methods. Calculations were performed using the cc-pCVDZ-X2C basis set and X2C scalar relativistic corrections.

MR-ADC(2)		MR-ADC(2)-X	
Ω	P	Ω	P
292.82	1.539	291.02	1.412
292.82	1.539	291.02	1.412
292.85	1.538	291.05	1.411
292.86	1.538	291.06	1.411
293.45	1.542	291.63	1.390
293.45	1.542	291.63	1.390