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

How to stay out of trouble in RIXS calculations within equation-of-motion coupled-cluster damped response theory? Safe hitchhiking in the excitation manifold by means of core-valence separation.

Supporting information.

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1. ITERATIVE SCHEME FOR SOLVING DAMPED RESPONSE EQUATIONS

1.1. Iterative scheme for left response

For the left response equation given by [note that RHS in the equation below is different from RHS of Eq. (23) in the paper]

$$\left(\tilde{X}_{\mathrm{Re}} + i\tilde{X}_{\mathrm{Im}}\right)\left(\bar{H} - E_0 - (\omega + i\gamma)\right) = \tilde{D}, \tag{S1}$$

the corresponding iterative step is given by

$$\begin{aligned}
&\left(\tilde{X}_{\mathrm{Re}}^{(n+1)} + i\tilde{X}_{\mathrm{Im}}^{(n+1)}\right)\\
&= \left(\tilde{X}_{\mathrm{Re}}^{(n)} + i\tilde{X}_{\mathrm{Im}}^{(n)}\right) + \frac{\tilde{D} - \left(\tilde{X}_{\mathrm{Re}}^{(n)} + i\tilde{X}_{\mathrm{Im}}^{(n)}\right)\left(\bar{H} - E_0 - (\omega + i\gamma)\right)}{\left(\bar{H} - E_0 - (\omega + i\gamma)\right)^D}\\
&= \left(\tilde{X}_{\mathrm{Re}}^{(n)} + i\tilde{X}_{\mathrm{Im}}^{(n)}\right)\\
&\quad + \frac{\left(\tilde{D} - \left(\tilde{X}_{\mathrm{Re}}^{(n)} + i\tilde{X}_{\mathrm{Im}}^{(n)}\right)\left(\bar{H} - E_0 - \omega - i\gamma\right)\right)\left(\bar{H} - E_0 - \omega + i\gamma\right)^D}{\left(\bar{H}^D - E_0 - \omega\right)^2 + \gamma^2}\\
&= \left(\tilde{X}_{\mathrm{Re}}^{(n)} + i\tilde{X}_{\mathrm{Im}}^{(n)}\right) + \frac{\left(\tilde{B}_{\mathrm{Re}}^{(n)} - i\tilde{B}_{\mathrm{Im}}^{(n)}\right)\left(\bar{H} - E_0 - \omega + i\gamma\right)^D}{\left(\bar{H}^D - E_0 - \omega\right)^2 + \gamma^2},
\end{aligned} \tag{S2}$$

where $\tilde{B}_{\text{Re}}$ and $\tilde{B}_{\text{Im}}$ are the residuals given by

$$\tilde{B}^{\mu}_{\text{Re}} = \tilde{D}^{\mu} - \tilde{\sigma}^{\mu}_{\text{Re}} - \tilde{X}^{0}_{\text{Re}}\bar{H}^{0\mu} + \tilde{X}^{\mu}_{\text{Re}}\omega - \tilde{X}^{\mu}_{\text{Im}}\gamma \tag{S3}$$

and

$$\tilde{B}^{\mu}_{\text{Im}} = \tilde{X}^{\mu}_{\text{Re}}\gamma - \tilde{X}^{0}_{\text{Im}}\bar{H}^{0\mu} - \tilde{\sigma}^{\mu}_{\text{Im}} + \tilde{X}^{\mu}_{\text{Im}}\omega \tag{S4}$$

for excitation level μ (= 0, singles, doubles, etc.). Isolating the real and imaginary terms from the above equation gives

$$\tilde{X}^{(n+1)}_{\text{Re}} = \tilde{X}^{(n)}_{\text{Re}} + \frac{\tilde{B}^{(n)}_{\text{Re}}\left(\bar{H} - E_0 - \omega\right)^{D} + \tilde{B}^{(n)}_{\text{Im}}\gamma}{\left(\bar{H}^{D} - E_0 - \omega\right)^{2} + \gamma^{2}} \tag{S5}$$

and

$$\tilde{X}^{(n+1)}_{\text{Im}} = \tilde{X}^{(n)}_{\text{Im}} + \frac{\tilde{B}^{(n)}_{\text{Re}}\gamma - \tilde{B}^{(n)}_{\text{Im}}\left(\bar{H} - E_0 - \omega\right)^{D}}{\left(\bar{H}^{D} - E_0 - \omega\right)^{2} + \gamma^{2}} \tag{S6}$$

For $\mu = 0$,

$$\tilde{X}^{0}_{\text{Re}} = -\frac{\tilde{D}^{0}}{\omega\left(1 + \left(\frac{\gamma}{\omega}\right)^{2}\right)} \tag{S7}$$

and

$$\tilde{X}^{0}_{\text{Im}} = -\tilde{X}^{0}_{\text{Re}}\left(\frac{\gamma}{\omega}\right). \tag{S8}$$

1.2. Iterative scheme for right response

For the right response equation given by [note that RHS in the equation below is different from RHS of Eq. (22) in the paper]

$$\left(\bar{H} - E_0 - (\omega + i\gamma)\right)\left(X_{\text{Re}} + iX_{\text{Im}}\right) = D, \tag{S9}$$

the corresponding iterative step is given by

$$\begin{aligned}
&\left(X^{(n+1)}_{\text{Re}} + iX^{(n+1)}_{\text{Im}}\right) \\
&= \left(X^{(n)}_{\text{Re}} + iX^{(n)}_{\text{Im}}\right) + \frac{D - \left(\bar{H} - E_0 - (\omega + i\gamma)\right)\left(X^{(n)}_{\text{Re}} + iX^{(n)}_{\text{Im}}\right)}{\left(\bar{H} - E_0 - (\omega + i\gamma)\right)^{D}} \\
&= \left(X^{(n)}_{\text{Re}} + iX^{(n)}_{\text{Im}}\right) + \frac{\left(\bar{H} - E_0 - \omega + i\gamma\right)^{D}\left(D - \left(\bar{H} - E_0 - (\omega + i\gamma)\right)\left(X^{(n)}_{\text{Re}} + iX^{(n)}_{\text{Im}}\right)\right)}{\left(\bar{H}^{D} - E_0 - \omega\right)^{2} + \gamma^{2}} \\
&= \left(X^{(n)}_{\text{Re}} + iX^{(n)}_{\text{Im}}\right) + \frac{\left(\bar{H} - E_0 - \omega + i\gamma\right)^{D}\left(B^{(n)}_{\text{Re}} - iB^{(n)}_{\text{Im}}\right)}{\left(\bar{H}^{D} - E_0 - \omega\right)^{2} + \gamma^{2}},
\end{aligned} \tag{S10}$$

where B_{Re} and B_{Im} are the residuals given by

$$B^{\mu}_{\mathrm{Re}} = D^{\mu} - \sigma^{\mu}_{\mathrm{Re}} + \omega X^{\mu}_{\mathrm{Re}} - \gamma X^{\mu}_{\mathrm{Im}} \tag{S11}$$

and

$$B^{\mu}_{\mathrm{Im}} = -\gamma X^{\mu}_{\mathrm{Re}} + \sigma^{\mu}_{\mathrm{Im}} - \omega X^{\mu}_{\mathrm{Im}}. \tag{S12}$$

Isolating the real and imaginary terms from the above equation gives

$$X^{(n+1)}_{\mathrm{Re}} = X^{(n)}_{\mathrm{Re}} + \frac{\left(\bar{H} - E_0 - \omega\right)^D B_{\mathrm{Re}} + \gamma B_{\mathrm{Im}}}{\left(\bar{H}^D - E_0 - \omega\right)^2 + \gamma^2} \tag{S13}$$

and

$$X^{(n+1)}_{\mathrm{Im}} = X^{(n)}_{\mathrm{Im}} + \frac{\gamma B_{\mathrm{Re}} - \left(\bar{H} - E_0 - \omega\right)^D B_{\mathrm{Im}}}{\left(\bar{H}^D - E_0 - \omega\right)^2 + \gamma^2}. \tag{S14}$$

Finally, for $\mu = 0$,

$$X^{0}_{\mathrm{Re}} = \frac{-D^0 + \bar{H}^{0\mu} X^{\mu}_{\mathrm{Re}} + \frac{\gamma}{\omega} \bar{H}^{0\mu} X^{\mu}_{\mathrm{Im}}}{\omega \left(1 + \left(\frac{\gamma}{\omega}\right)^2\right)} \tag{S15}$$

and

$$X^{0}_{\mathrm{Im}} = \frac{-\gamma X^{0}_{\mathrm{Re}} + \bar{H}^{0\mu} X^{\mu}_{\mathrm{Im}}}{\omega}. \tag{S16}$$

2. VALIDATION OF THE ANALYTICAL FC-CVS-EOM-EE-CCSD DAMPED RESPONSE APPROACH FOR RIXS MOMENTS WITH NUMERICAL SUM-OVER-STATE CALCULATIONS

System: LiH (bond length = 1.6 Å)

Computational details: STO-3G basis set with frozen-core approximation

Symmetry group imposed = C_{2v}

Initial state = 1A$_1$ (CCSD)

Final state = 2A$_1$ (excitation energy = 3.6295 eV)

Incident photon frequency = 2.12430931 a.u. (resonant with excitation energy of the 1B$_2$ state in Q-Chem symmetry notation)

Emitted photon frequency = 1.99092715 a.u.

TABLE S1: Comparison of analytical and numerical RIXS moments (all values in a.u.)

γ	RIXS moments	Analytical		Numerical		% differences	
		Re	Im	Re	Im	Re	Im
0.005	$M_{xx}^{f\leftarrow 0}/M_{yy}^{f\leftarrow 0}$	-0.023583	0.801039	-0.023526	0.801052	0.2	-0.0
	$M_{zz}^{f\leftarrow 0}$	-0.289587	0.022319	-0.284753	0.022095	1.7	1.0
	$M_{xx}^{0\leftarrow f}/M_{yy}^{0\leftarrow f}$	-0.005944	0.218572	-0.005941	0.216755	0.1	0.8
	$M_{zz}^{0\leftarrow f}$	-0.253951	-0.019780	-0.253735	-0.019769	0.1	0.1
0.5	$M_{xx}^{f\leftarrow 0}/M_{yy}^{f\leftarrow 0}$	-0.002387	0.000857	-0.002379	0.000874	0.3	-1.9
	$M_{zz}^{f\leftarrow 0}$	0.001909	0.044622	0.002012	0.044452	-5.1	0.4
	$M_{xx}^{0\leftarrow f}/M_{yy}^{0\leftarrow f}$	-0.000953	0.003688	-0.000951	0.003670	0.2	0.5
	$M_{zz}^{0\leftarrow f}$	0.001625	-0.039605	0.001662	-0.039616	-2.2	-0.0

The maximum difference of 5 % is for the real part of $M_{zz}^{f\leftarrow 0}$ with γ=0.5, although the base numbers are small in magnitude. The slightly larger differences are due to the accumulation of numerical noise during the addition of 9 and 15 terms in the sum-over-state expressions of the xx/yy and zz components.

3. WATER

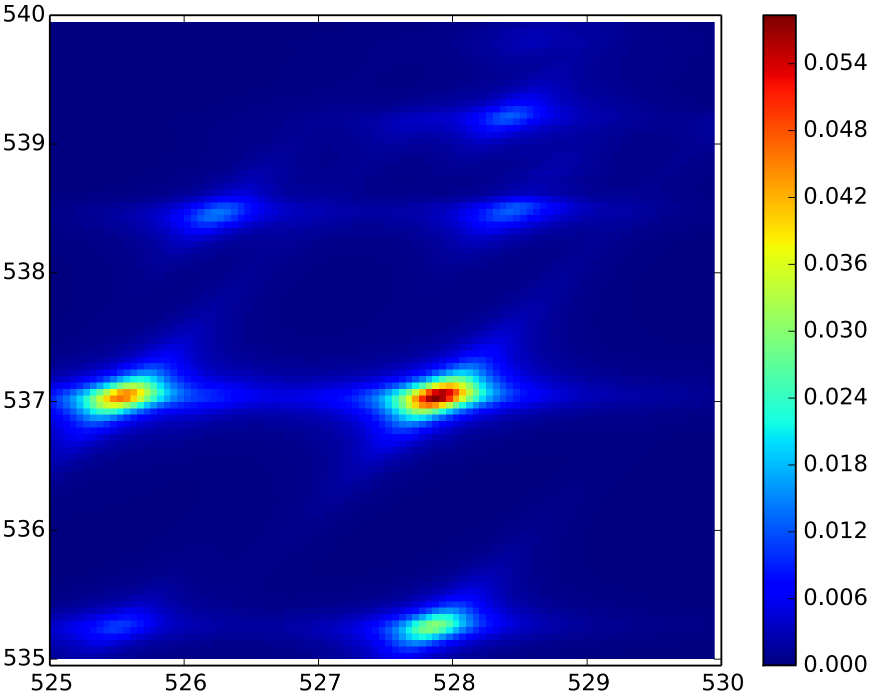

FIG. S1: Computed RIXS spectrum for water,

3.1. Basis set used for water

```
H     0
S   3   1.00
     33.8650000              0.0254938
      5.0947900              0.1903730
      1.1587900              0.8521610
S   1   1.00
      0.3258400              1.0000000
S   1   1.00
      0.1027410              1.0000000
S   1   1.00
      0.0360000              1.0000000
P   1   1.00
      0.7500000              1.0000000
****
O     0
S   6   1.00
   8588.5000000              0.00189515
   1297.2300000              0.0143859
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```
    299.2960000              0.0707320
     87.3771000              0.2400010
     25.6789000              0.5947970
      3.7400400              0.2808020
SP   3   1.00
     42.1175000              0.1138890              0.0365114
      9.6283700              0.9208110              0.2371530
      2.8533200             -0.00327447             0.8197020
SP   1   1.00
      0.9056610              1.0000000              1.0000000
SP   1   1.00
      0.2556110              1.0000000              1.0000000
SP   1   1.00
      0.0845000              1.0000000              1.0000000
D   1   1.00
      1.2920000              1.0000000
S   1   1.00
 0.0058583805        1.0000000000
S   1   1.00
 0.0033459739        1.0000000000
S   1   1.00
 0.0020484225        1.0000000000
P   1   1.00
        0.0099882106        1.0000000000
P   1   1.00
        0.0056893607        1.0000000000
P   1   1.00
 0.0034756797        1.0000000000
```

4. BENZENE AND ITS CATION

4.1. Geometries

Benzene: Ground state

H	2.4750347531	0.0000000000	0.0000000000
C	1.3935929418	0.0000000000	0.0000000000
C	0.6967964709	1.2068868901	0.0000000000
H	1.2375173766	2.1434429715	0.0000000000
C	-0.6967964709	1.2068868901	0.0000000000
H	-1.2375173766	2.1434429715	0.0000000000
C	-1.3935929418	0.0000000000	0.0000000000
H	-2.4750347531	0.0000000000	0.0000000000
C	-0.6967964709	-1.2068868901	0.0000000000
H	-1.2375173766	-2.1434429715	0.0000000000
C	0.6967964709	-1.2068868901	0.0000000000
H	1.2375173766	-2.1434429715	0.0000000000

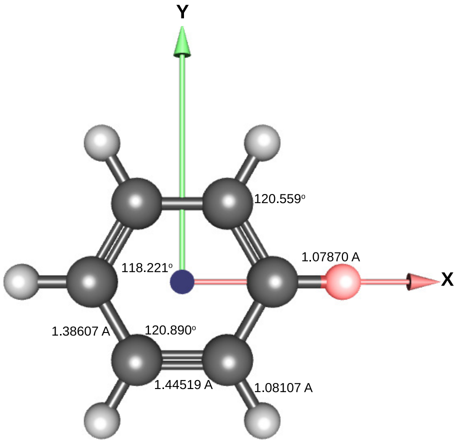
Nuclear Repulsion Energy = 203.71874490 hartrees

Benzene cation: B_{3g} relaxed

H	1.2392908131	-2.1390691708	0.0000000000
C	0.7225974533	-1.1894682957	0.0000000000
C	-0.7225974533	-1.1894682957	0.0000000000
H	-1.2392908131	-2.1390691708	0.0000000000
C	-1.4341864916	0.0000000000	0.0000000000
H	-2.5128824541	0.0000000000	0.0000000000
C	-0.7225974533	1.1894682957	0.0000000000
H	-1.2392908131	2.1390691708	0.0000000000
C	0.7225974533	1.1894682957	0.0000000000
H	1.2392908131	2.1390691708	0.0000000000
C	1.4341864916	0.0000000000	0.0000000000
H	2.5128824541	0.0000000000	0.0000000000

Nuclear Repulsion Energy = 202.30075690 hartrees

FIG. S2: Geometric parameters and orientation of the optimized benzene cation structure ($^2B_{3g}$)



4.2. Benzene: Core and valence ionization energies

TABLE S2: Benzene: Valence and core ionization energies (eV) using EOM-IP-CCSD and CVS-EOM-IP-CCSD with 6-311(2+,+)G**(uC)

State	MO	IE
c2 ^{2}A$_g$	$1a_g$	290.992
c1 ^{2}B$_{2u}$/c1 ^{2}B$_{3u}$	$1b_{2u}/1b_{3u}$	290.975
c1 ^{2}B$_{1g}$/c1 ^{2}A$_g$	$1b_{1g}/2a_g$	290.934
c1 ^{2}B$_{3u}$	$2b_{3u}$	290.914
4 ^{2}A$_g$	$3a_g$	22.963
3 ^{2}B$_{2u}$/3 ^{2}B$_{3u}$	$2b_{2u}/3b_{3u}$	21.000
2 ^{2}B$_{1g}$/3 ^{2}A$_g$	$2b_{1g}/4a_g$	19.598
2 ^{2}A$_g$	$5a_g$	17.365
2 ^{2}B$_{3u}$	$4b_{3u}$	15.818
2 ^{2}B$_{2u}$	$3b_{2u}$	14.802
1 ^{2}B$_{2u}$/1 ^{2}B$_{3u}$	$4b_{2u}/5b_{3u}$	14.402
1 ^{2}B$_{1u}$	$1b_{1u}$	12.547
1 ^{2}B$_{1g}$/1 ^{2}A$_g$	$3b_{1g}/6a_g$	12.108
1 ^{2}B$_{2g}$/1 ^{2}B$_{3g}$	$1b_{2g}/1b_{3g}$	9.224

Note that the numbering of MOs is opposite from the numbering of the EOM-IP states.

'c' denotes core states.

4.3. Benzene: XAS energies and oscillator strengths

TABLE S3: Benzene: fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) excitation energies ω_i (eV) and oscillator strengths f. Only bright transitions are shown.

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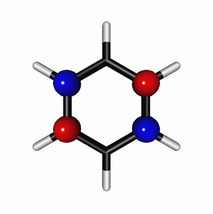
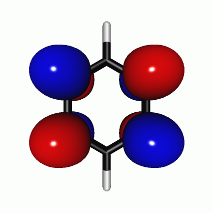
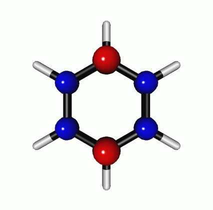
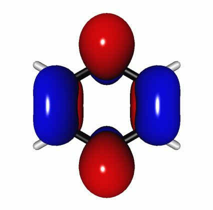
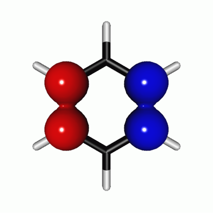
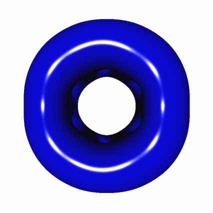
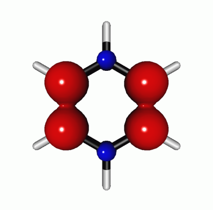
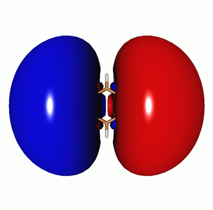
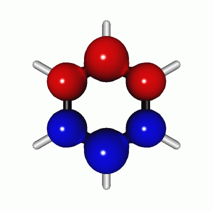
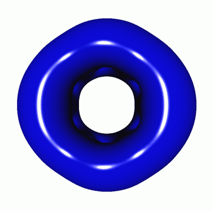
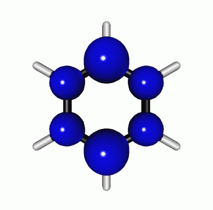
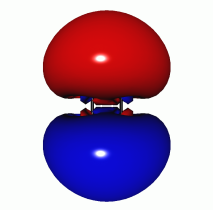
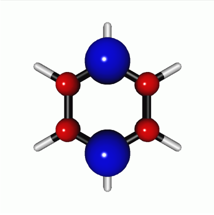
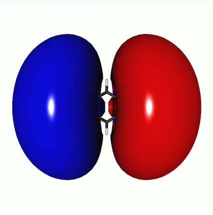
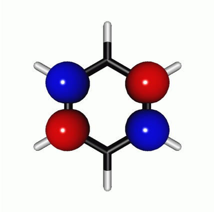
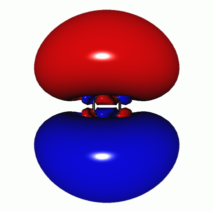
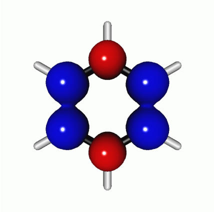
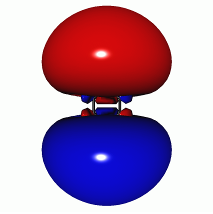
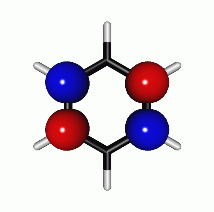
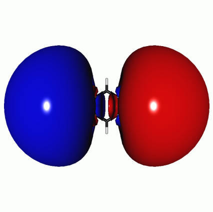
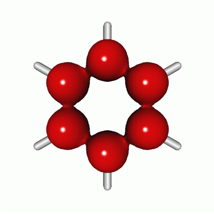
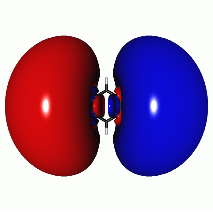
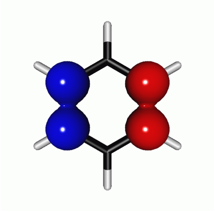
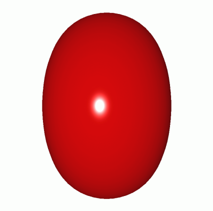
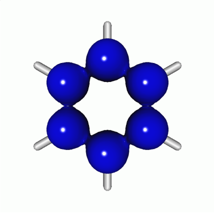
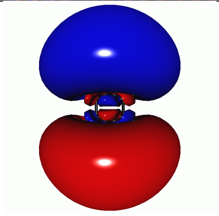
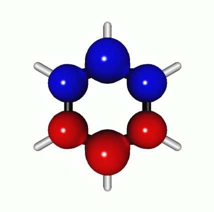
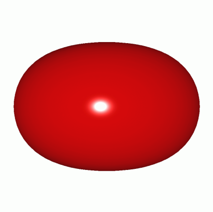
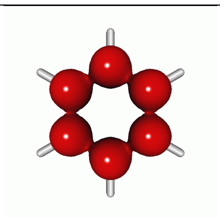
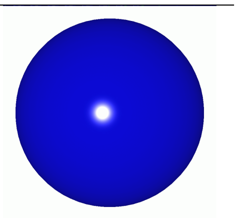
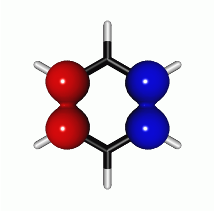
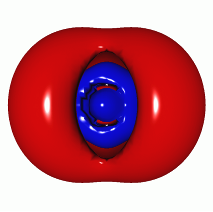
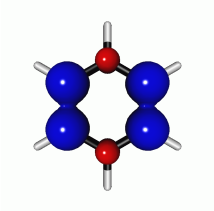
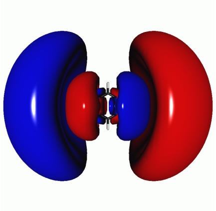
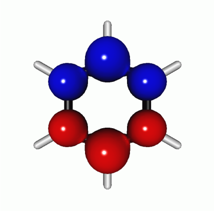
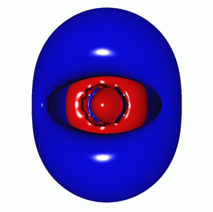
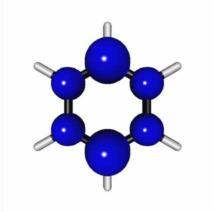
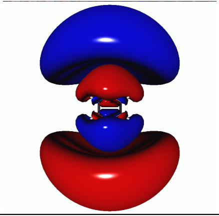
Symm.	ω_i	f	Assignment
c2B$_{1u}$	285.97	0.30677	(A)
c1B$_{2u}$/c2B$_{3u}$	287.80	0.04405	(B)
c3B$_{2u}$/c4B$_{3u}$	288.79	0.00355	(C1)
c4B$_{2u}$/c5B$_{3u}$	288.83	0.01005	(C2)
c5B$_{1u}$	288.91	0.00543	(C3)
c5B$_{2u}$/c7B$_{3u}$	289.35	0.00324	
c6B$_{2u}$/c8B$_{3u}$	289.40	0.00246	
c7B$_{2u}$/c10B$_{3u}$	289.46	0.00027	
c8B$_{1u}$	289.66	0.00270	
c9B$_{2u}$/c12B$_{3u}$	289.75	0.02059	(D)
c10B$_{2u}$/c13B$_{3u}$	290.12	0.00120	
c11B$_{2u}$/c14B$_{3u}$	290.14	0.00037	
c14B$_{2u}$/c16B$_{3u}$	290.21	0.00001	
c9B$_{1u}$	290.28	0.00270	
c12B$_{1u}$	290.83	0.00067	
c15B$_{1u}$	291.07	0.02991	

4.4. Benzene: XAS NTOs

TABLE S4: Benzene: fc-CVS-EOM-CCSD/6-311(2+,+)G**(uC). NTOs of the relevant core excited states. NTO isosurface is 0.005.

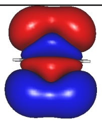
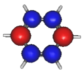
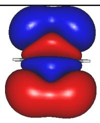
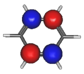
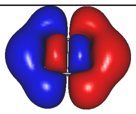
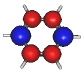
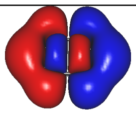
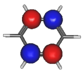
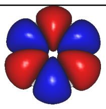
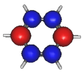
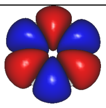
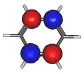
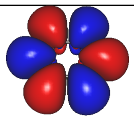
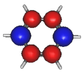
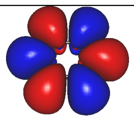
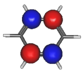
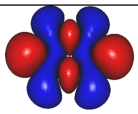
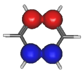
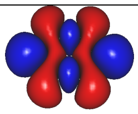
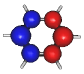
Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.35	
		0.35	
(B) B_{2u}		0.50	
		0.20	
(B) B_{3u}		0.50	
		0.20	

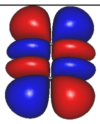
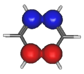
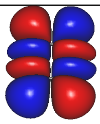
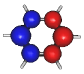
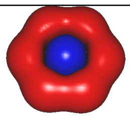
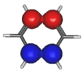
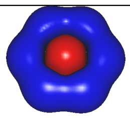
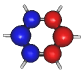
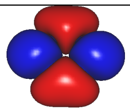
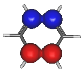
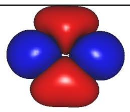
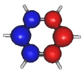
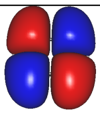
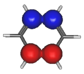
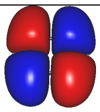
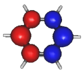
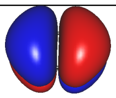
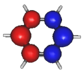
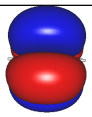
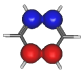
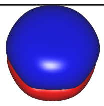
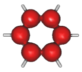
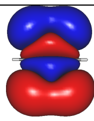
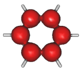
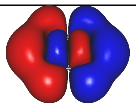
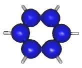
(C1) B_{2u}		0.33	
		0.23	
(C1) B_{3u}		0.33	
		0.24	
(C2) B_{2u}		0.38	
		0.35	
(C2) B_{3u}		0.38	
		0.35	

(C3) B_{1u}		0.69	
(D) B_{2u}		0.46	
		0.19	
(D) B_{3u}		0.45	
		0.20	

4.5. Benzene: XES energies, oscillator strengths, and NTOs

TABLE S5: Benzene: Relevant oscillator strengths, emitted photon frequencies (eV) and NTOs between fc-CVS-EOMIP-CCSD states (with core holes corresponding to XAS peaks A and B) and EOM-IP-CCSD states with 6-311(2+,+)G**(uC) basis. NTO isosurface is 0.05. *c* denotes a core-ionized state. See Table S2 for states-to-orbitals mapping.

Transition	ω_e	Orb. trans.	f (a.u.)	Particle NTO	σ_K^2	Core-hole NTO
$1\mathrm{B}_{2u} \rightarrow \mathrm{c}1\mathrm{A}_g$	276.5323	$4b_{2u} \rightarrow 2a_g$	0.019835		0.82	
$1\mathrm{B}_{2u} \rightarrow \mathrm{c}1\mathrm{B}_{1g}$	276.5323	$4b_{2u} \rightarrow 1b_{1g}$	0.019835		0.84	
$1\mathrm{B}_{3u} \rightarrow \mathrm{c}1\mathrm{A}_g$	276.5323	$5b_{3u} \rightarrow 2a_g$	0.019835		0.84	
$1\mathrm{B}_{3u} \rightarrow \mathrm{c}1\mathrm{B}_{1g}$	276.5323	$5b_{3u} \rightarrow 1b_{1g}$	0.019835		0.82	
$2\mathrm{B}_{2u} \rightarrow \mathrm{c}1\mathrm{A}_g$	276.1319	$3b_{2u} \rightarrow 2a_g$	0.040857		0.83	
$2\mathrm{B}_{2u} \rightarrow \mathrm{c}1\mathrm{B}_{1g}$	276.1319	$3b_{2u} \rightarrow 1b_{1g}$	0.040857		0.83	
$2\mathrm{B}_{3u} \rightarrow \mathrm{c}1\mathrm{A}_g$	275.1160	$4b_{3u} \rightarrow 2a_g$	0.008829		0.80	
$2\mathrm{B}_{3u} \rightarrow \mathrm{c}1\mathrm{B}_{1g}$	275.1160	$4b_{3u} \rightarrow 1b_{1g}$	0.008829		0.80	
$1\mathrm{A}_g \rightarrow \mathrm{c}1\mathrm{B}_{2u}$	278.8670	$6a_g \rightarrow 1b_{2u}$	0.000311		0.85	
$1\mathrm{A}_g \rightarrow \mathrm{c}2\mathrm{B}_{3u}$	278.8670	$6a_g \rightarrow 1b_{3u}$	0.000311		0.85	

$1B_{1g} \rightarrow c1B_{2u}$	278.8670	$3b_{1g} \rightarrow 1b_{2u}$	0.000311		0.85	
$1B_{1g} \rightarrow c2B_{3u}$	278.8670	$3b_{1g} \rightarrow 1b_{3u}$	0.000311		0.85	
$2A_g \rightarrow c1B_{2u}$	273.6100	$5a_g \rightarrow 1b_{2u}$	0.021223		0.79	
$2A_g \rightarrow c2B_{3u}$	273.6100	$5a_g \rightarrow 1b_{3u}$	0.021223		0.79	
$3A_g \rightarrow c1B_{2u}$	271.3764	$4a_g \rightarrow 1b_{2u}$	0.009497		0.76	
$3A_g \rightarrow c2B_{3u}$	271.3764	$4a_g \rightarrow 1b_{3u}$	0.009497		0.76	
$2B_{1g} \rightarrow c1B_{2u}$	271.3764	$2b_{1g} \rightarrow 1b_{2u}$	0.009497		0.76	
$2B_{1g} \rightarrow c2B_{3u}$	271.3764	$2b_{1g} \rightarrow 1b_{3u}$	0.009497		0.76	
$1B_{2g} \rightarrow c2B_{3u}$	281.7503	$1b_{2g} \rightarrow 1b_{3u}$	0.067681		0.89	
$1B_{3g} \rightarrow c1B_{2u}$	281.7503	$1b_{3g} \rightarrow 1b_{2u}$	0.067683		0.89	
$1B_{1u} \rightarrow c2A_g$	278.4453	$1b_{1u} \rightarrow 1a_g$	0.051099		0.81	
$1B_{2u} \rightarrow c2A_g$	276.5907	$4b_{2u} \rightarrow 1a_g$	0.012181		0.83	
$1B_{3u} \rightarrow c2A_g$	276.5907	$5b_{3u} \rightarrow 1a_g$	0.012181		0.83	

4.6. Benzene: RIXS cross sections

TABLE S6: Benzene: fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) valence excitation energies Ω_{f0} (eV) of gerade states and their RIXS cross sections (a.u.) for θ=0°, 45°, 90°.

Final state	Ω_{f0}	$\omega_i = 285.97$ eV			$\omega_i = 287.80$ eV		
		$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$	$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$
$1A_g$	0.00	1.271070	1.938659	2.606247	0.038017	0.061142	0.084266
$2A_g$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$3A_g$	7.88	0.000419	0.000619	0.000818	0.000065	0.000083	0.000102
$4A_g$	9.10	0.000000	0.000000	0.000000	0.000001	0.000001	0.000001
$5A_g$	9.23	0.000000	0.000000	0.000001	0.000020	0.000022	0.000024
$6A_g$	9.32	0.000000	0.000000	0.000000	0.000036	0.000039	0.000042
$7A_g$	10.06	0.000000	0.000000	0.000000	0.000001	0.000001	0.000001
$8A_g$	10.13	0.000985	0.001405	0.001825	0.000344	0.000673	0.001001
$9A_g$	10.42	0.000042	0.000045	0.000049	0.001100	0.001192	0.001284
$10A_g$	10.54	0.000000	0.000016	0.000033	0.000211	0.000600	0.000990
$11A_g$	10.54	0.000009	0.000010	0.000011	0.000186	0.000202	0.000217
$12A_g$	10.58	0.000047	0.000071	0.000095	0.000025	0.000054	0.000084
$13A_g$	10.67	0.000000	0.000000	0.000000	0.000004	0.000004	0.000004
$14A_g$	11.15	0.000000	0.000000	0.000000	0.000000	0.000000	0.000001
$15A_g$	11.70	0.000016	0.000017	0.000018	0.000246	0.000266	0.000287
$16A_g$	11.74	0.000026	0.000041	0.000057	0.000148	0.000412	0.000676
$17A_g$	11.91	0.000000	0.000000	0.000000	0.000008	0.000008	0.000009
$18A_g$	12.03	0.000029	0.000031	0.000034	0.000403	0.000437	0.000470
$19A_g$	12.06	0.000071	0.000106	0.000140	0.000212	0.000584	0.000956
$20A_g$	12.24	0.000021	0.000022	0.000024	0.000975	0.001056	0.001138
$21A_g$	12.25	0.000079	0.000128	0.000177	0.001827	0.004988	0.008149
$1B_{1g}$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$2B_{1g}$	7.91	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$3B_{1g}$	9.10	0.000000	0.000000	0.000000	0.000001	0.000001	0.000001

$4\mathrm{B}_{1g}$	9.23	0.000000	0.000000	0.000001	0.000020	0.000022	0.000024
$5\mathrm{B}_{1g}$	9.32	0.000000	0.000000	0.000000	0.000036	0.000039	0.000042
$6\mathrm{B}_{1g}$	10.06	0.000000	0.000000	0.000000	0.000001	0.000001	0.000001
$7\mathrm{B}_{1g}$	10.17	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$8\mathrm{B}_{1g}$	10.42	0.000042	0.000045	0.000049	0.001101	0.001193	0.001284
$9\mathrm{B}_{1g}$	10.43	0.000067	0.000050	0.000033	0.001592	0.001194	0.000796
$10\mathrm{B}_{1g}$	10.54	0.000009	0.000010	0.000011	0.000186	0.000201	0.000217
$11\mathrm{B}_{1g}$	10.67	0.000000	0.000000	0.000000	0.000004	0.000004	0.000004
$12\mathrm{B}_{1g}$	11.15	0.000000	0.000000	0.000000	0.000000	0.000000	0.000001
$13\mathrm{B}_{1g}$	11.67	0.000017	0.000013	0.000008	0.000222	0.000166	0.000111
$14\mathrm{B}_{1g}$	11.70	0.000016	0.000017	0.000018	0.000246	0.000266	0.000287
$15\mathrm{B}_{1g}$	11.91	0.000000	0.000000	0.000000	0.000008	0.000008	0.000009
$16\mathrm{B}_{1g}$	12.03	0.000029	0.000031	0.000034	0.000403	0.000436	0.000470
$17\mathrm{B}_{1g}$	12.04	0.000026	0.000019	0.000013	0.000246	0.000185	0.000123
$18\mathrm{B}_{1g}$	12.24	0.000021	0.000022	0.000024	0.000974	0.001055	0.001136
$19\mathrm{B}_{1g}$	12.37	0.000004	0.000003	0.000002	0.000473	0.000355	0.000236
$20\mathrm{B}_{1g}$	12.59	0.000014	0.000015	0.000016	0.000459	0.000497	0.000535
$1\mathrm{B}_{2g}$	6.45	0.000203	0.000178	0.000153	0.020316	0.017777	0.015238
$2\mathrm{B}_{2g}$	7.57	0.000179	0.000153	0.000127	0.001242	0.001090	0.000938
$3\mathrm{B}_{2g}$	7.64	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$4\mathrm{B}_{2g}$	7.65	0.000005	0.000005	0.000004	0.000097	0.000085	0.000073
$5\mathrm{B}_{2g}$	8.29	0.000092	0.000079	0.000066	0.000538	0.000473	0.000409
$6\mathrm{B}_{2g}$	8.87	0.000016	0.000013	0.000011	0.000096	0.000084	0.000072
$7\mathrm{B}_{2g}$	8.88	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$8\mathrm{B}_{2g}$	9.18	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$9\mathrm{B}_{2g}$	9.19	0.000054	0.000046	0.000039	0.000091	0.000079	0.000068
$10\mathrm{B}_{2g}$	9.60	0.001500	0.001308	0.001116	0.000113	0.000110	0.000106
$11\mathrm{B}_{2g}$	10.43	0.000249	0.000213	0.000177	0.002641	0.002309	0.001977
$12\mathrm{B}_{2g}$	10.57	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$13\mathrm{B}_{2g}$	10.67	0.260048	0.227553	0.195058	0.005970	0.005224	0.004478

14B$_{2g}$	10.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
15B$_{2g}$	10.76	0.001171	0.001025	0.000878	0.000027	0.000024	0.000021
16B$_{2g}$	10.85	0.009982	0.008736	0.007490	0.000255	0.000212	0.000169
17B$_{2g}$	10.95	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{2g}$	10.99	0.032880	0.028769	0.024658	0.000763	0.000670	0.000576
19B$_{2g}$	11.23	0.001044	0.000917	0.000791	0.000158	0.000127	0.000096
20B$_{2g}$	11.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
1B$_{3g}$	6.45	0.000203	0.000178	0.000153	0.020318	0.017778	0.015239
2B$_{3g}$	7.57	0.000179	0.000153	0.000127	0.001242	0.001090	0.000938
3B$_{3g}$	7.63	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{3g}$	7.65	0.000005	0.000005	0.000004	0.000097	0.000085	0.000073
5B$_{3g}$	8.29	0.000093	0.000080	0.000067	0.000538	0.000473	0.000409
6B$_{3g}$	8.85	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7B$_{3g}$	8.87	0.000016	0.000013	0.000011	0.000096	0.000084	0.000072
8B$_{3g}$	9.19	0.000054	0.000046	0.000039	0.000091	0.000079	0.000068
9B$_{3g}$	9.20	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
10B$_{3g}$	9.60	0.001500	0.001308	0.001116	0.000113	0.000110	0.000106
11B$_{3g}$	10.43	0.000249	0.000213	0.000177	0.002641	0.002309	0.001977
12B$_{3g}$	10.67	0.259967	0.227483	0.194998	0.005968	0.005222	0.004476
13B$_{3g}$	10.76	0.001185	0.001037	0.000889	0.000027	0.000024	0.000021
14B$_{3g}$	10.77	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
15B$_{3g}$	10.80	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
16B$_{3g}$	10.85	0.009976	0.008731	0.007486	0.000255	0.000212	0.000169
17B$_{3g}$	10.97	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{3g}$	10.99	0.032878	0.028767	0.024656	0.000763	0.000670	0.000576
19B$_{3g}$	11.23	0.001040	0.000914	0.000788	0.000158	0.000127	0.000096
20B$_{3g}$	11.73	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

TABLE S7: Benzene: fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) valence excitation energies Ω_{f0} (eV) of gerade states and their RIXS cross sections (a.u.) for θ=0°, 45°, 90°.

Final state	Ω_{f0}	$\omega_i = 288.79$ eV			$\omega_i = 288.83$ eV		
		$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$	$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$
$1A_g$	0.00	0.012223	0.027252	0.042281	0.011861	0.026960	0.042060
$2A_g$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$3A_g$	7.88	0.000867	0.001220	0.001572	0.000960	0.001351	0.001741
$4A_g$	9.10	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$5A_g$	9.23	0.000002	0.000003	0.000003	0.000003	0.000003	0.000003
$6A_g$	9.32	0.000081	0.000088	0.000094	0.000074	0.000080	0.000086
$7A_g$	10.06	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$8A_g$	10.13	0.000766	0.000947	0.001128	0.000807	0.000991	0.001175
$9A_g$	10.42	0.000759	0.000822	0.000885	0.000806	0.000873	0.000940
$10A_g$	10.54	0.000332	0.000679	0.001026	0.000380	0.000740	0.001100
$11A_g$	10.54	0.000209	0.000226	0.000243	0.000214	0.000232	0.000250
$12A_g$	10.58	0.001322	0.002247	0.003172	0.001562	0.002651	0.003740
$13A_g$	10.67	0.000027	0.000029	0.000032	0.000028	0.000030	0.000032
$14A_g$	11.15	0.000006	0.000007	0.000007	0.000007	0.000007	0.000008
$15A_g$	11.70	0.000069	0.000075	0.000080	0.000071	0.000077	0.000083
$16A_g$	11.74	0.000029	0.000106	0.000183	0.000031	0.000113	0.000196
$17A_g$	11.91	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001
$18A_g$	12.03	0.000122	0.000132	0.000142	0.000119	0.000129	0.000138
$19A_g$	12.06	0.000051	0.000169	0.000288	0.000053	0.000180	0.000306
$20A_g$	12.24	0.000275	0.000297	0.000320	0.000304	0.000330	0.000355
$21A_g$	12.25	0.000711	0.001980	0.003250	0.000823	0.002306	0.003789
$1B_{1g}$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$2B_{1g}$	7.91	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$3B_{1g}$	9.10	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
$4B_{1g}$	9.23	0.000002	0.000003	0.000003	0.000003	0.000003	0.000003

5B$_{1g}$	9.32	0.000081	0.000088	0.000095	0.000074	0.000080	0.000086
6B$_{1g}$	10.06	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7B$_{1g}$	10.17	0.000001	0.000001	0.000000	0.000001	0.000001	0.000000
8B$_{1g}$	10.42	0.000759	0.000823	0.000886	0.000806	0.000873	0.000941
9B$_{1g}$	10.43	0.001739	0.001304	0.000869	0.001832	0.001374	0.000916
10B$_{1g}$	10.54	0.000208	0.000226	0.000243	0.000214	0.000232	0.000249
11B$_{1g}$	10.67	0.000027	0.000029	0.000032	0.000028	0.000030	0.000032
12B$_{1g}$	11.15	0.000006	0.000007	0.000007	0.000007	0.000007	0.000008
13B$_{1g}$	11.67	0.000090	0.000067	0.000045	0.000095	0.000071	0.000047
14B$_{1g}$	11.70	0.000069	0.000075	0.000080	0.000071	0.000077	0.000083
15B$_{1g}$	11.91	0.000001	0.000001	0.000001	0.000001	0.000001	0.000001
16B$_{1g}$	12.03	0.000122	0.000132	0.000142	0.000119	0.000129	0.000138
17B$_{1g}$	12.04	0.000153	0.000115	0.000076	0.000153	0.000115	0.000076
18B$_{1g}$	12.24	0.000274	0.000297	0.000320	0.000304	0.000329	0.000355
19B$_{1g}$	12.37	0.000701	0.000526	0.000350	0.000887	0.000665	0.000443
20B$_{1g}$	12.59	0.000254	0.000275	0.000296	0.000290	0.000315	0.000339
1B$_{2g}$	6.45	0.004988	0.004356	0.003724	0.004199	0.003667	0.003134
2B$_{2g}$	7.57	0.001955	0.001711	0.001467	0.001921	0.001680	0.001439
3B$_{2g}$	7.64	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{2g}$	7.65	0.000165	0.000145	0.000126	0.000196	0.000173	0.000149
5B$_{2g}$	8.29	0.000725	0.000637	0.000549	0.000727	0.000639	0.000550
6B$_{2g}$	8.87	0.000026	0.000023	0.000020	0.000025	0.000022	0.000019
7B$_{2g}$	8.88	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
8B$_{2g}$	9.18	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
9B$_{2g}$	9.19	0.000037	0.000033	0.000028	0.000035	0.000031	0.000026
10B$_{2g}$	9.60	0.000098	0.000097	0.000095	0.000101	0.000099	0.000097
11B$_{2g}$	10.43	0.000998	0.000867	0.000736	0.001042	0.000904	0.000766
12B$_{2g}$	10.57	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
13B$_{2g}$	10.67	0.002730	0.002398	0.002067	0.002594	0.002282	0.001969
14B$_{2g}$	10.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

15B$_{2g}$	10.76	0.000015	0.000014	0.000013	0.000016	0.000015	0.000014
16B$_{2g}$	10.85	0.000132	0.000106	0.000081	0.000124	0.000100	0.000076
17B$_{2g}$	10.95	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{2g}$	10.99	0.000361	0.000316	0.000270	0.000345	0.000301	0.000256
19B$_{2g}$	11.23	0.000161	0.000129	0.000098	0.000161	0.000130	0.000098
20B$_{2g}$	11.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
1B$_{3g}$	6.45	0.004965	0.004336	0.003707	0.004125	0.003601	0.003078
2B$_{3g}$	7.57	0.001999	0.001750	0.001500	0.001840	0.001609	0.001378
3B$_{3g}$	7.63	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{3g}$	7.65	0.000165	0.000145	0.000126	0.000221	0.000194	0.000168
5B$_{3g}$	8.29	0.000712	0.000626	0.000540	0.000717	0.000630	0.000543
6B$_{3g}$	8.85	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7B$_{3g}$	8.87	0.000026	0.000022	0.000019	0.000026	0.000022	0.000019
8B$_{3g}$	9.19	0.000036	0.000032	0.000028	0.000036	0.000031	0.000027
9B$_{3g}$	9.20	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
10B$_{3g}$	9.60	0.000105	0.000103	0.000101	0.000106	0.000103	0.000101
11B$_{3g}$	10.43	0.001011	0.000878	0.000745	0.001150	0.000998	0.000846
12B$_{3g}$	10.67	0.002730	0.002398	0.002067	0.002591	0.002281	0.001970
13B$_{3g}$	10.76	0.000015	0.000014	0.000013	0.000016	0.000015	0.000014
14B$_{3g}$	10.77	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
15B$_{3g}$	10.80	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
16B$_{3g}$	10.85	0.000131	0.000105	0.000080	0.000125	0.000101	0.000076
17B$_{3g}$	10.97	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{3g}$	10.99	0.000358	0.000312	0.000267	0.000344	0.000300	0.000255
19B$_{3g}$	11.23	0.000159	0.000127	0.000096	0.000164	0.000132	0.000100
20B$_{3g}$	11.73	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

TABLE S8: Benzene: fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) valence excitation energies Ω_{f0} (eV) of gerade states and their RIXS cross sections (a.u.) for θ=0°, 45°, 90°.

Final	Ω_{f0}	ω_i = 288.91 eV			ω_i = 289.75 eV		
state		$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$	$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$
1A$_g$	0.00	0.011441	0.025323	0.039206	0.005942	0.020005	0.034068
2A$_g$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
3A$_g$	7.88	0.000970	0.001370	0.001770	0.000216	0.000316	0.000415
4A$_g$	9.10	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
5A$_g$	9.23	0.000003	0.000003	0.000003	0.000001	0.000001	0.000002
6A$_g$	9.32	0.000052	0.000056	0.000060	0.000001	0.000001	0.000001
7A$_g$	10.06	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
8A$_g$	10.13	0.000759	0.000926	0.001093	0.000065	0.000187	0.000308
9A$_g$	10.42	0.000745	0.000807	0.000870	0.000110	0.000119	0.000128
10A$_g$	10.54	0.000420	0.000734	0.001049	0.000202	0.000244	0.000286
11A$_g$	10.54	0.000182	0.000197	0.000212	0.000028	0.000030	0.000033
12A$_g$	10.58	0.001970	0.003305	0.004639	0.000561	0.000935	0.001309
13A$_g$	10.67	0.000024	0.000026	0.000028	0.000002	0.000002	0.000003
14A$_g$	11.15	0.000006	0.000007	0.000007	0.000005	0.000005	0.000005
15A$_g$	11.70	0.000062	0.000067	0.000073	0.000007	0.000007	0.000007
16A$_g$	11.74	0.000028	0.000109	0.000190	0.000008	0.000025	0.000042
17A$_g$	11.91	0.000001	0.000001	0.000001	0.000000	0.000000	0.000000
18A$_g$	12.03	0.000093	0.000101	0.000109	0.000000	0.000000	0.000000
19A$_g$	12.06	0.000050	0.000177	0.000304	0.000001	0.000009	0.000016
20A$_g$	12.24	0.000350	0.000379	0.000408	0.000065	0.000070	0.000076
21A$_g$	12.25	0.000971	0.002745	0.004519	0.000138	0.000430	0.000723
1B$_{1g}$	7.86	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
2B$_{1g}$	7.91	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
3B$_{1g}$	9.10	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{1g}$	9.23	0.000002	0.000003	0.000003	0.000001	0.000001	0.000001

5B$_{1g}$	9.32	0.000052	0.000056	0.000060	0.000001	0.000001	0.000001
6B$_{1g}$	10.06	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7B$_{1g}$	10.17	0.000001	0.000000	0.000000	0.000000	0.000000	0.000000
8B$_{1g}$	10.42	0.000746	0.000808	0.000870	0.000110	0.000119	0.000128
9B$_{1g}$	10.43	0.001660	0.001246	0.000831	0.000236	0.000177	0.000118
10B$_{1g}$	10.54	0.000182	0.000197	0.000212	0.000028	0.000030	0.000033
11B$_{1g}$	10.67	0.000024	0.000026	0.000028	0.000002	0.000002	0.000003
12B$_{1g}$	11.15	0.000006	0.000007	0.000007	0.000005	0.000005	0.000006
13B$_{1g}$	11.67	0.000088	0.000066	0.000044	0.000007	0.000005	0.000003
14B$_{1g}$	11.70	0.000062	0.000068	0.000073	0.000006	0.000007	0.000008
15B$_{1g}$	11.91	0.000001	0.000001	0.000001	0.000000	0.000000	0.000000
16B$_{1g}$	12.03	0.000093	0.000101	0.000109	0.000000	0.000000	0.000000
17B$_{1g}$	12.04	0.000125	0.000094	0.000063	0.000006	0.000004	0.000003
18B$_{1g}$	12.24	0.000350	0.000379	0.000408	0.000065	0.000070	0.000076
19B$_{1g}$	12.37	0.001110	0.000833	0.000557	0.000100	0.000075	0.000050
20B$_{1g}$	12.59	0.000324	0.000350	0.000377	0.000025	0.000028	0.000030
1B$_{2g}$	6.45	0.002406	0.002099	0.001793	0.000057	0.000050	0.000043
2B$_{2g}$	7.57	0.001229	0.001072	0.000914	0.000342	0.000295	0.000248
3B$_{2g}$	7.64	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{2g}$	7.65	0.000283	0.000249	0.000215	0.000011	0.000010	0.000009
5B$_{2g}$	8.29	0.000608	0.000534	0.000460	0.000467	0.000405	0.000343
6B$_{2g}$	8.87	0.000024	0.000021	0.000018	0.000060	0.000052	0.000044
7B$_{2g}$	8.88	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
8B$_{2g}$	9.18	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
9B$_{2g}$	9.19	0.000027	0.000024	0.000020	0.000008	0.000007	0.000006
10B$_{2g}$	9.60	0.000085	0.000083	0.000082	0.000119	0.000113	0.000107
11B$_{2g}$	10.43	0.001312	0.001138	0.000963	0.000151	0.000128	0.000106
12B$_{2g}$	10.57	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
13B$_{2g}$	10.67	0.002328	0.002056	0.001783	0.001371	0.001209	0.001047
14B$_{2g}$	10.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

15B$_{2g}$	10.76	0.000019	0.000018	0.000016	0.000011	0.000010	0.000010
16B$_{2g}$	10.85	0.000114	0.000092	0.000070	0.000093	0.000071	0.000049
17B$_{2g}$	10.95	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{2g}$	10.99	0.000318	0.000276	0.000234	0.000193	0.000173	0.000153
19B$_{2g}$	11.23	0.000150	0.000121	0.000092	0.000098	0.000079	0.000059
20B$_{2g}$	11.72	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
1B$_{3g}$	6.45	0.002436	0.002126	0.001815	0.000037	0.000032	0.000028
2B$_{3g}$	7.57	0.001470	0.001283	0.001096	0.000378	0.000326	0.000274
3B$_{3g}$	7.63	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4B$_{3g}$	7.65	0.000293	0.000257	0.000222	0.000013	0.000012	0.000010
5B$_{3g}$	8.29	0.000613	0.000538	0.000464	0.000435	0.000377	0.000319
6B$_{3g}$	8.85	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7B$_{3g}$	8.87	0.000020	0.000018	0.000015	0.000053	0.000046	0.000039
8B$_{3g}$	9.19	0.000028	0.000024	0.000021	0.000008	0.000007	0.000005
9B$_{3g}$	9.20	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
10B$_{3g}$	9.60	0.000090	0.000088	0.000087	0.000104	0.000100	0.000095
11B$_{3g}$	10.43	0.001175	0.001018	0.000861	0.000162	0.000139	0.000115
12B$_{3g}$	10.67	0.002330	0.002056	0.001782	0.001373	0.001212	0.001050
13B$_{3g}$	10.76	0.000020	0.000018	0.000016	0.000012	0.000011	0.000010
14B$_{3g}$	10.77	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
15B$_{3g}$	10.80	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
16B$_{3g}$	10.85	0.000111	0.000090	0.000069	0.000088	0.000067	0.000046
17B$_{3g}$	10.97	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18B$_{3g}$	10.99	0.000313	0.000271	0.000230	0.000178	0.000159	0.000140
19B$_{3g}$	11.23	0.000159	0.000128	0.000097	0.000094	0.000076	0.000057
20B$_{3g}$	11.73	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

4.7. Benzene: RIXS 2D maps

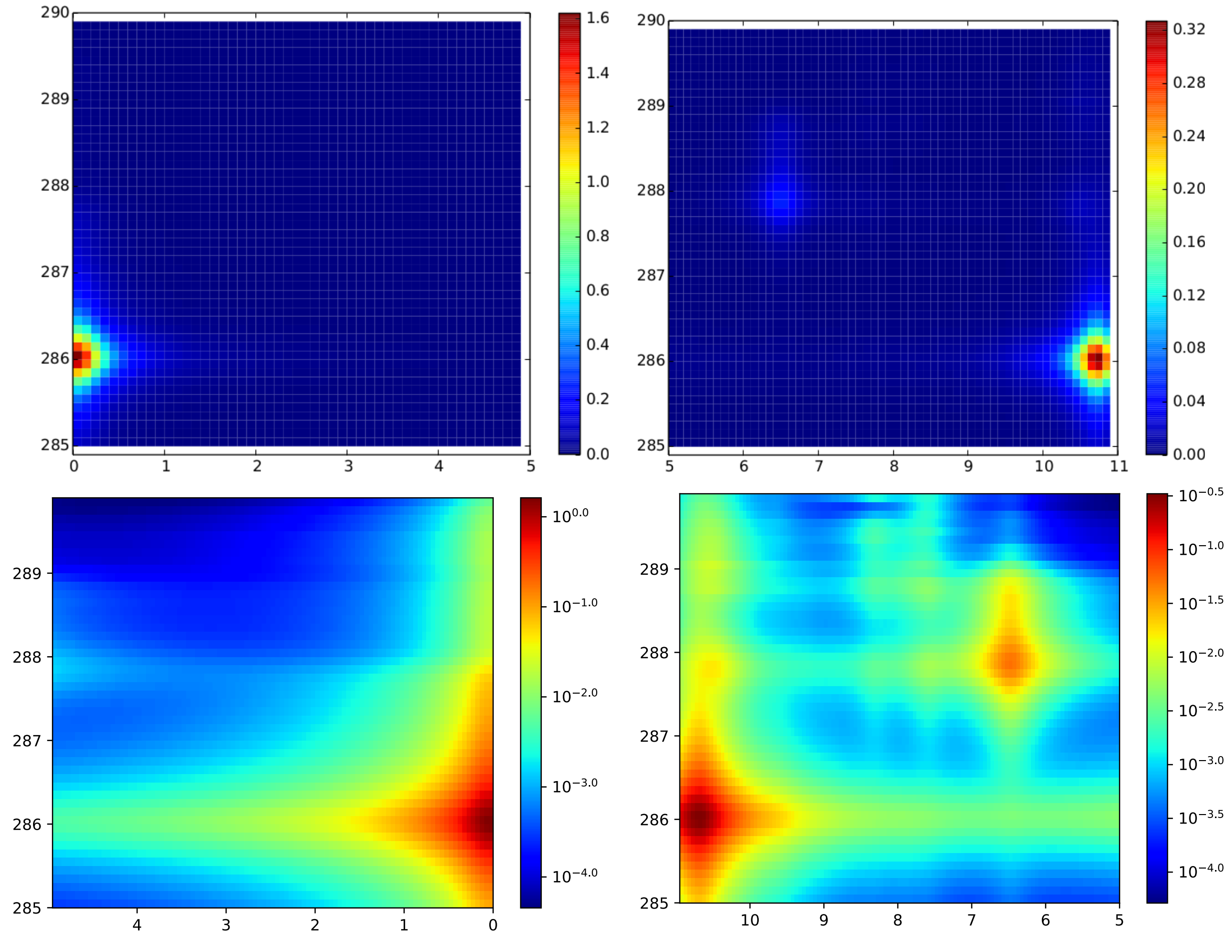


FIG. S3: Computed REXS (left) and RIXS (right) two-dimensional energy-loss (X axis) spectra; fc-CVS-EOM-CCSD/6-311(2+,+)G**(uC). The bottom panels show the spectra on the logarithmic scale.

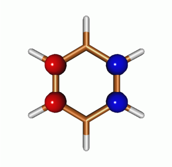
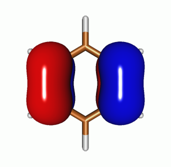
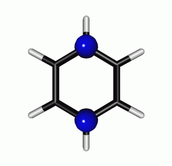
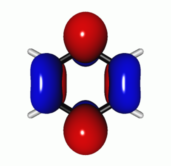
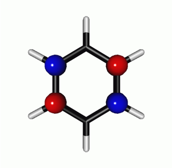
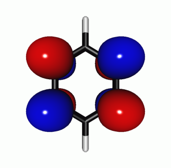
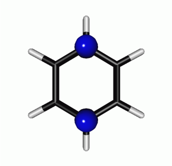
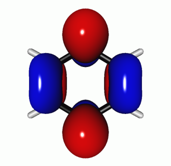
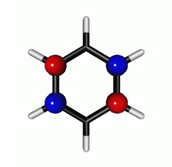
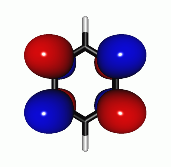
4.8. Benzene cation: XAS energies and oscillator strengths

TABLE S9: Benzene cation ($^2B_{3g}$): fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) core excitation energies ω_i (eV) and oscillator strengths f at the neutral unrelaxed and relaxed geometries.

Unrelaxed B_{3g}			Relaxed B_{3g}			
Symm.	ω_i	f	Symm.	ω_i	f	Assignment
B_{1u}	281.37	0.08192	B_{1u}	281.67	0.08182	(A)
B_{1u}	285.01	0.02219	B_{1u}	285.11	0.02229	(B)
B_{1u}	285.90	0.08098	B_{1u}	285.79	0.08674	(C)
B_{1u}	286.35	0.09080	B_{1u}	286.47	0.09145	(D)
B_{1u}	287.57	0.08782	B_{1u}	287.53	0.08012	(E)
B_{1u}	288.43	0.00432	B_{1u}	288.56	0.00713	
B_{1u}	288.88	0.00022	B_{1u}	288.98	0.00014	
B_{3u}	289.23	0.00060	B_{3u}	289.27	0.00057	
B_{3u}	289.67	0.01692	B_{3u}	289.72	0.01668	
B_{3u}	290.09	0.00076	B_{3u}	290.16	0.00071	
B_{2u}	290.11	0.00176	B_{2u}	290.18	0.00179	
B_{3u}	290.51	0.00495	B_{3u}	290.56	0.00500	
B_{3u}	290.62	0.01234	B_{3u}	290.69	0.01102	
B_{2u}	290.65	0.03305	B_{2u}	290.71	0.03350	
B_{3u}	290.75	0.00771	B_{3u}	290.80	0.00744	
B_{2u}	291.02	0.00000	B_{2u}	291.06	0.00007	
B_{1u}	291.09	0.00302	B_{1u}	291.16	0.00275	
B_{3u}	291.20	0.00008	B_{3u}	291.27	0.00006	
B_{2u}	291.23	0.00000	B_{2u}	291.27	0.00007	
B_{1u}	291.32	0.00302	B_{1u}	291.38	0.00254	
B_{3u}	291.47	0.00029	B_{3u}	291.53	0.00018	
B_{3u}	291.52	0.00184	B_{3u}	291.59	0.00183	
B_{2u}	291.55	0.00681	B_{2u}	291.61	0.00662	
B_{3u}	291.72	0.00405	B_{2u}	291.73	0.00189	
B_{2u}	291.76	0.00056	B_{3u}	291.79	0.00425	
B_{2u}	291.76	0.01346	B_{2u}	291.82	0.01257	
B_{2u}	292.00	0.00100	B_{2u}	291.99	0.00116	
B_{1u}	292.04	0.00639	B_{1u}	292.04	0.00611	

4.9. Benzene cation: XAS NTOs

TABLE S10: Benzene cation (B_{3g}): fc-CVS-EOM-CCSD/6-311(2+,+)G**(uC) NTOs of the relevant core excited states.

Excitation	Hole	σ_K^2	Particle
(A) B_{1u}		0.67	
(B) B_{1u}		0.58	
(C) B_{1u}		0.59	
(D) B_{1u}		0.77	
(E) B_{1u}		0.77	

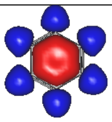
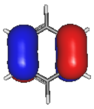
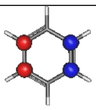
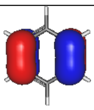
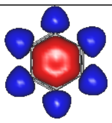
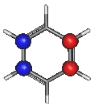
4.10. Benzene cation: RIXS cross sections

TABLE S11: Benzene cation: fc-CVS-EOMEE-CCSD/6-311(2+,+)G**(uC) valence excitation energies Ω_{f0} (eV) of gerade states and their RIXS cross sections (a.u.) for θ=0° for Frank-Condon and B_{3g} relaxed geometries with ω_i equal to 281.37 eV and 281.67 eV, respectively.

Transition	Unrelaxed geom.				Relaxed geom.			
	Ω_{f0}	$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$	Ω_{f0}	$\sigma^{RIXS}(0°)$	$\sigma^{RIXS}(45°)$	$\sigma^{RIXS}(90°)$
1A$_g$	0.00	0.37922	0.58543	0.79163	0.00	0.37921	0.58837	0.79753
2A$_g$	7.72	0.00902	0.01351	0.01801	7.72	0.00920	0.01380	0.01839
3A$_g$	9.71	0.00071	0.00106	0.00142	9.75	0.00063	0.00095	0.00126
4A$_g$	10.22	0.00001	0.00002	0.00003	10.31	0.00006	0.00009	0.00011
1B$_{1g}$	0.20	0.00000	0.00000	0.00000	0.66	0.00000	0.00000	0.00000
2B$_{1g}$	7.95	0.00000	0.00000	0.00000	7.65	0.00000	0.00000	0.00000
3B$_{1g}$	9.45	0.00000	0.00000	0.00000	9.12	0.00000	0.00000	0.00000
1B$_{2g}$	3.05	0.00195	0.00170	0.00146	3.42	0.00270	0.00236	0.00202
2B$_{2g}$	8.37	0.00001	0.00001	0.00001	8.56	0.00001	0.00001	0.00001
3B$_{2g}$	8.50	0.00001	0.00001	0.00001	8.70	0.00001	0.00001	0.00001
4B$_{2g}$	9.38	0.00259	0.00227	0.00194	9.32	0.01232	0.01078	0.00924
5B$_{2g}$	9.53	0.00179	0.00156	0.00133	9.59	0.00126	0.00110	0.00095
6B$_{2g}$	9.86	0.03024	0.02646	0.02268	9.75	0.00445	0.00389	0.00333
7B$_{2g}$	10.03	0.00780	0.00683	0.00585	9.90	0.01686	0.01475	0.01264
8B$_{2g}$	10.14	0.00012	0.00011	0.00009	10.23	0.02827	0.02474	0.02121
9B$_{2g}$	10.31	0.00073	0.00063	0.00054	10.32	0.00042	0.00037	0.00031
1B$_{3g}$	3.04	0.00194	0.00170	0.00146	3.24	0.00127	0.00111	0.00095
2B$_{3g}$	8.24	0.17948	0.15704	0.13461	8.41	0.18660	0.16327	0.13995
3B$_{3g}$	9.24	0.00000	0.00000	0.00000	8.93	0.00006	0.00005	0.00005
4B$_{3g}$	9.76	0.00191	0.00167	0.00143	9.80	0.00160	0.00140	0.00120
5B$_{3g}$	10.08	0.01292	0.01130	0.00969	9.92	0.00211	0.00184	0.00158
6B$_{3g}$	10.18	0.00253	0.00222	0.00190	10.26	0.00000	0.00000	0.00000
7B$_{3g}$	10.29	0.00330	0.00289	0.00247	10.32	0.00707	0.00619	0.00530

4.11. Benzene cation: Orbitals involved in dominant RIXS transitions

TABLE S12: Benzene cation (unrelaxed geometry): Orbitals involved in the dominant RIXS transition using the dominant sum-over-state term in the RIXS moments and the corresponding NTOs of one-photon absorption and emission processes involving the initial, final, and intermediate states. NTO isosurface is 0.05. c denotes a core-level transition.

Electronic transition	f (a.u.)	Orbital transition	Hole NTO	σ_K^2	Particle NTO
2B$_{3g}$	0.000000	$5a_g \rightarrow 1b_{3g}$		0.74	
cB$_{1u}$ (absorption)	0.081929	$1b_{2u} \rightarrow 1b_{3g}$		0.68	
cB$_{2u}$ (emission)	0.019527	$5a_g \rightarrow 1b_{2u}$		0.56	

Net 2B$_{3g}$ RIXS orbital transition: $5a_g \rightarrow 1b_{2u} \rightarrow 1b_{3g}$

4.12. Benzene: Experimental RIXS

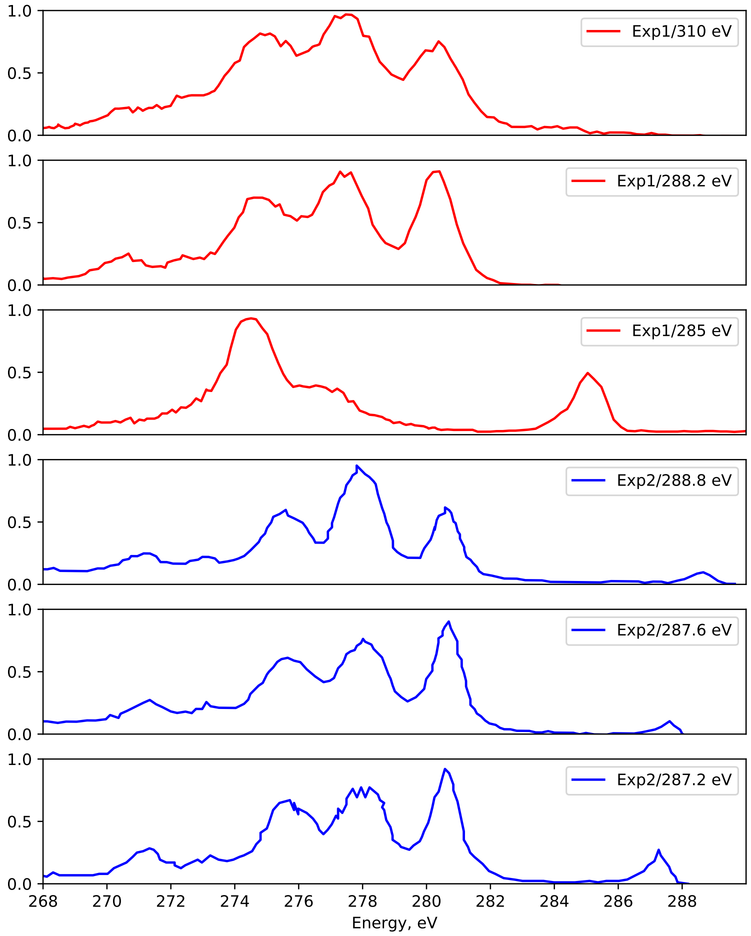


FIG. S4: Benzene XES and RIXS spectra from Refs. 1 (marked as 'Exp1', in red) and 2 (marked as 'Exp2', in blue).

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[1] P. Skytt, J. Guo, N. Wassdahl, J. Nordgren, Y. Luo, and H. Ågren, Probing symmetry breaking upon core excitation with resonant x-ray fluorescence, Phys. Rev. A **52**, 3572 (1995).

[2] F. Hennies, S. Polyutov, I. Minkov, A. Pietzsch, M. Nagasono, H. Ågren, L. Triguero, M.-N. Piancastelli, W. Wurth, F. Gel'mukhanov, and A. Föhlisch, Dynamic interpretation of resonant x-ray Raman scattering: Ethylene and benzene, Phys. Rev. A **76**, 032505 (2007).