The Structure and UV Spectroscopy of Benzene-Water (Bz-W$_6$) Clusters using Time-Dependent Density Functional Theory

Divya Sharma,[a] and Martin J. Paterson*[a]
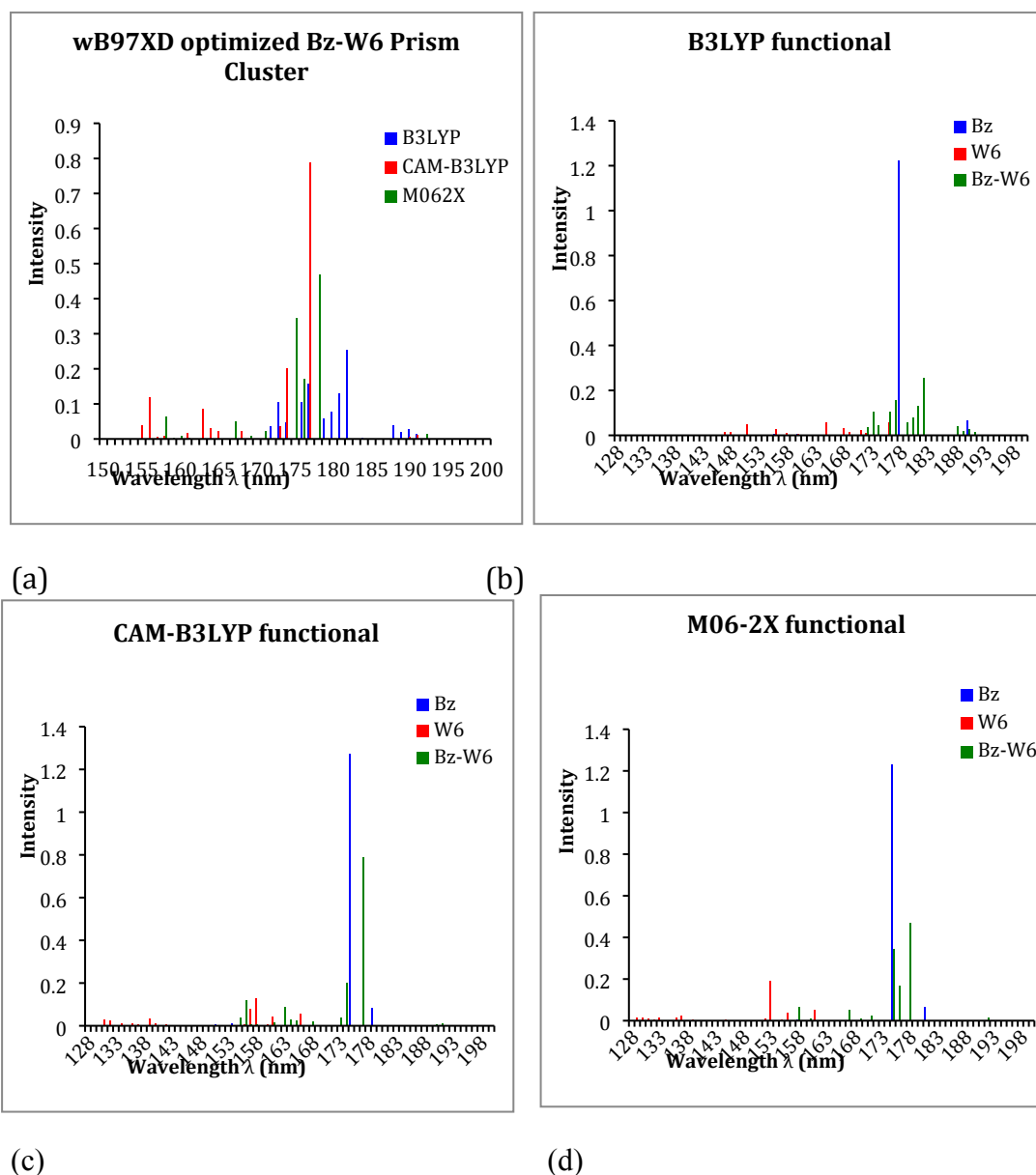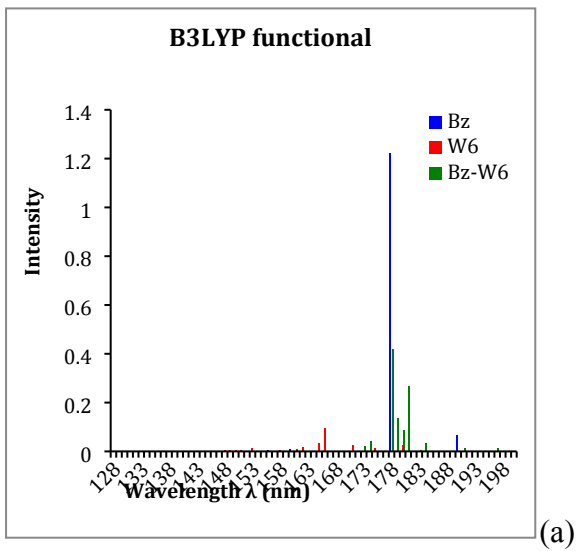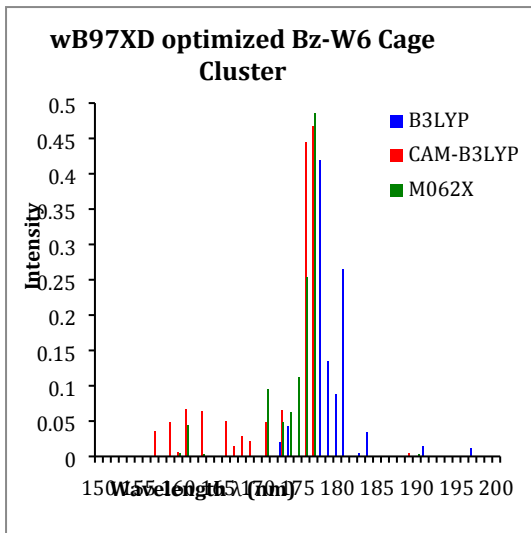
Supporting information

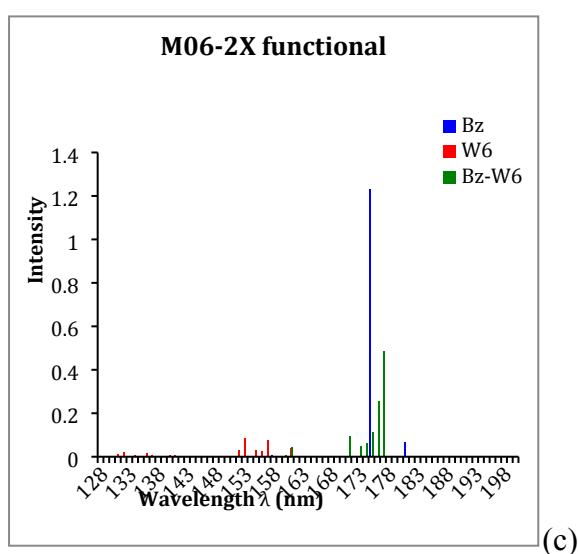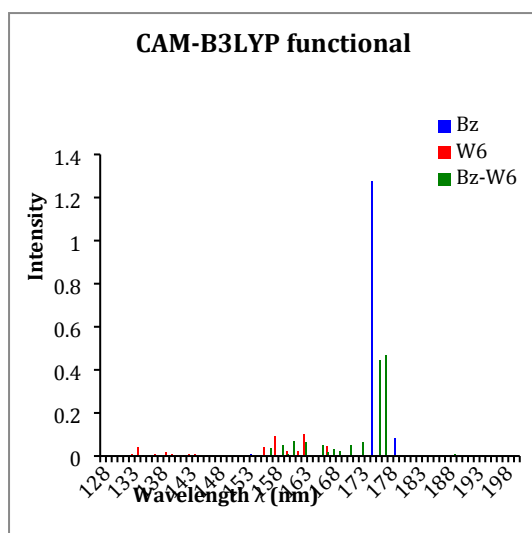Figure S1. Simulated UV spectra obtained from TD-DFT calculations on wB97XD optimized ground state geometries of prism shaped water W$_6$ cluster, Bz-W$_6$ cluster and Bz using 6-31++G(d,p) basis set. (a) Comparison of B3LYP, CAM-B3LYP and M062X functionals performance on Bz-W$_6$ prism cluster (b) Performance of B3LYP functional (c) Performance of CAM-B3LYP functional (d) Performance of M06-2X functional.

Table S1. List of important electronic transitions corresponding to highest peak intensities (oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functionals on wB97XD optimized Bz-W$_6$ prism shaped clusters using 6-31++G(d,p) basis set. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transition of an isolated benzene molecule).

DFT functional	E (eV)	λ (nm)	Oscillator strength (*f*)	Electronic transition
M06-2X	7.08 (7.10)	175.0 (174.6)	0.3433 (0.6154)	$\pi \rightarrow \pi^*$
	6.98	177.8	0.3025	$\pi \rightarrow \pi^*$
	6.95	178.5	0.1647	$\pi \rightarrow \pi^*$
	7.06	175.7	0.1696	$\pi \rightarrow \pi^*$
	7.85	157.9	0.0376	W-Rydberg State
CAM-B3LYP	6.99 (7.08)	177.5 (175.0)	0.4032 (0.637)	$\pi \rightarrow \pi^*$
	7.00	176.9	0.3839	$\pi \rightarrow \pi^*$
	7.94	173.6	0.2023	$\pi \rightarrow \pi^*$
	7.14	156.2	0.0993	W-Rydberg state
	7.62	162.6	0.0869	W-Rydberg state
B3LYP	6.82 (6.97)	181.8 (177.9)	0.2545 (0.6122)	Water CT state
	7.02	176.7	0.0923	Bz Diffuse state
	6.99	177.2	0.0643	Bz CT state
	6.85	180.9	0.1286	Water CT state
	7.15	173.4	0.1062	Bz CT state
	7.03	176.4	0.1046	Bz diffuse state

(a)

(b)

(c)

(d)

Figure S2. Simulated UV spectra obtained from TDDFT calculations on wB97XD optimized ground state geometries of cage shaped water W_6 cluster, Bz-W_6 cluster and Bz using 6-31++G(d,p) basis set (a) Comparison of B3LYP, CAM-B3LYP and M062X functionals performance on Bz-W_6 prism cluster (b) Performance of B3LYP functional (c) Performance of CAM-B3LYP functional (d) Performance of M06-2X functional.

Table S2. List of important electronic transitions corresponding to highest peak intensities (oscillator strengths) obtained using B3LYP, CAM-B3LYP and M062X hybrid functionals on wB97XD optimized Bz-W_6 cage clusters using 6-31++G(d,p) basis set. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transition of an isolated benzene molecule).

DFT functional	E (eV)	λ (nm)	Oscillator strength (f)	Electronic transition
M06-2X	7.00 (7.10)	177.0 (174.6)	0.3278 (0.6154)	$\pi \rightarrow \pi^*$
	7.01	176.8	0.1586	$\pi \rightarrow \pi^*$
	7.03	176.3	0.2542	$\pi \rightarrow \pi^*$
	7.09	174.7	0.1126	Bz CT state
	7.12	174.6	0.0631	$\pi \rightarrow \pi^*$
	7.23	171.5	0.0433	Bz CT state
	7.27	170.5	0.0526	Bz CT state
CAM-B3LYP	7.02 (7.08)	176.7 (175.0)	0.4669 (0.637)	$\pi \rightarrow \pi^*$
	7.05	175.9	0.4455	$\pi \rightarrow \pi^*$
	7.71	160.9	0.0673	W-Rydberg state
	7.62	162.8	0.0635	W-Rydberg state
B3LYP	6.96 (6.97)	178.0 (177.9)	0.3113 (0.6122)	$\pi \rightarrow \pi^*$
	6.95	178.3	0.1080	W-Rydberg State
	6.87	180.6	0.1823	W-Rydberg state
	6.92	179.1	0.1352	Bz-Diffuse state
	6.89	180.0	0.0881	Bz CT state
	6.84	181.3	0.0833	W-Rydberg state

B3LYP functional on Bz-W6 Prism cluster

CAM-B3LYP functional

M06-2X functional

(a)

(b)

(c)

Figure S3. Comparison of UV spectra obtained from TDDFT calculations on MP2 and wB97XD optimized ground state geometries of prism shaped Bz-W$_6$ cluster: (a) Performance of B3LYP functional (b) Performance of CAM-B3LYP functional (c) Performance of M06-2X functional.

B3LYP functional on Bz-W6 Cage Cluster

(a)

CAM-B3LYP functional
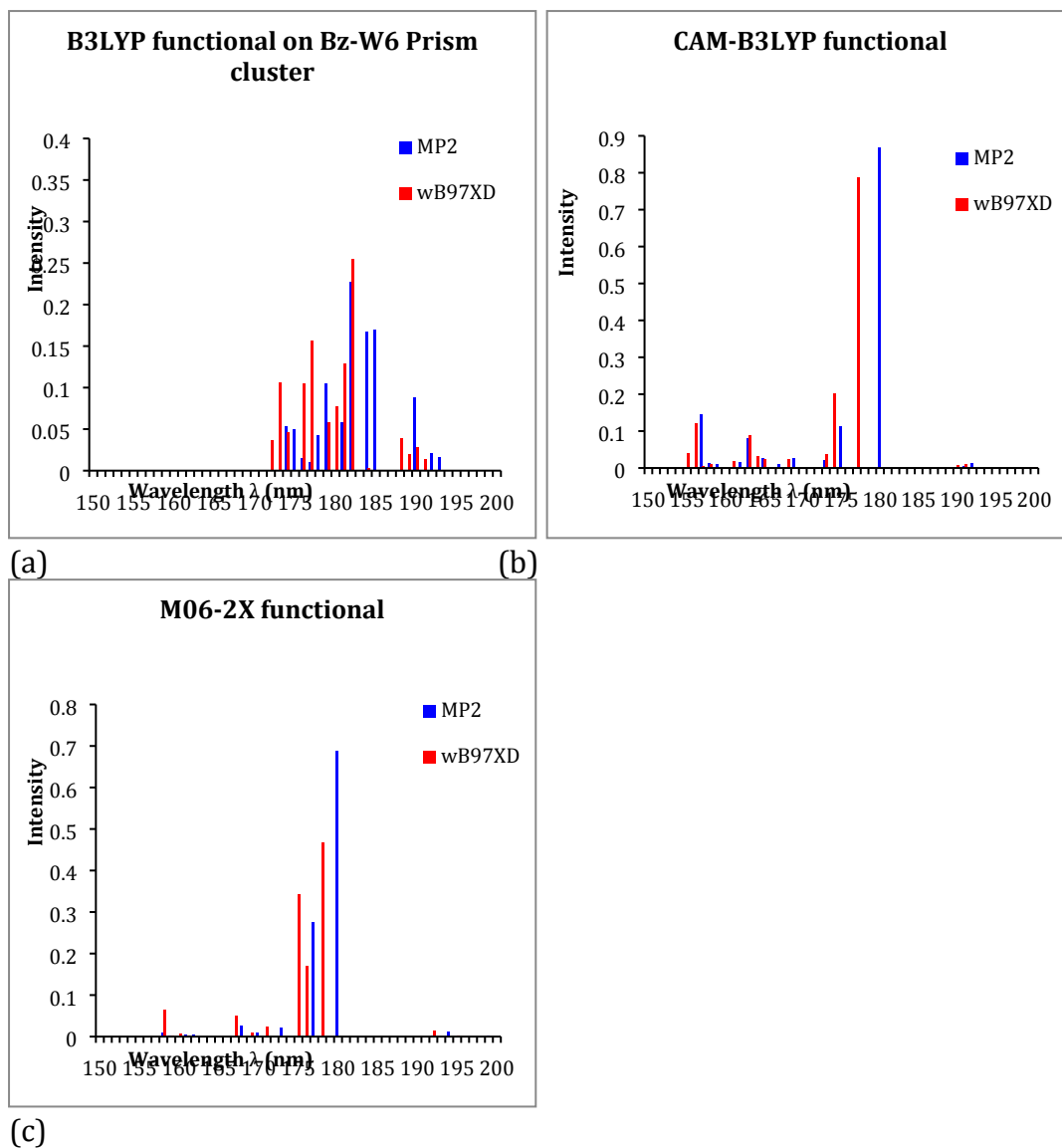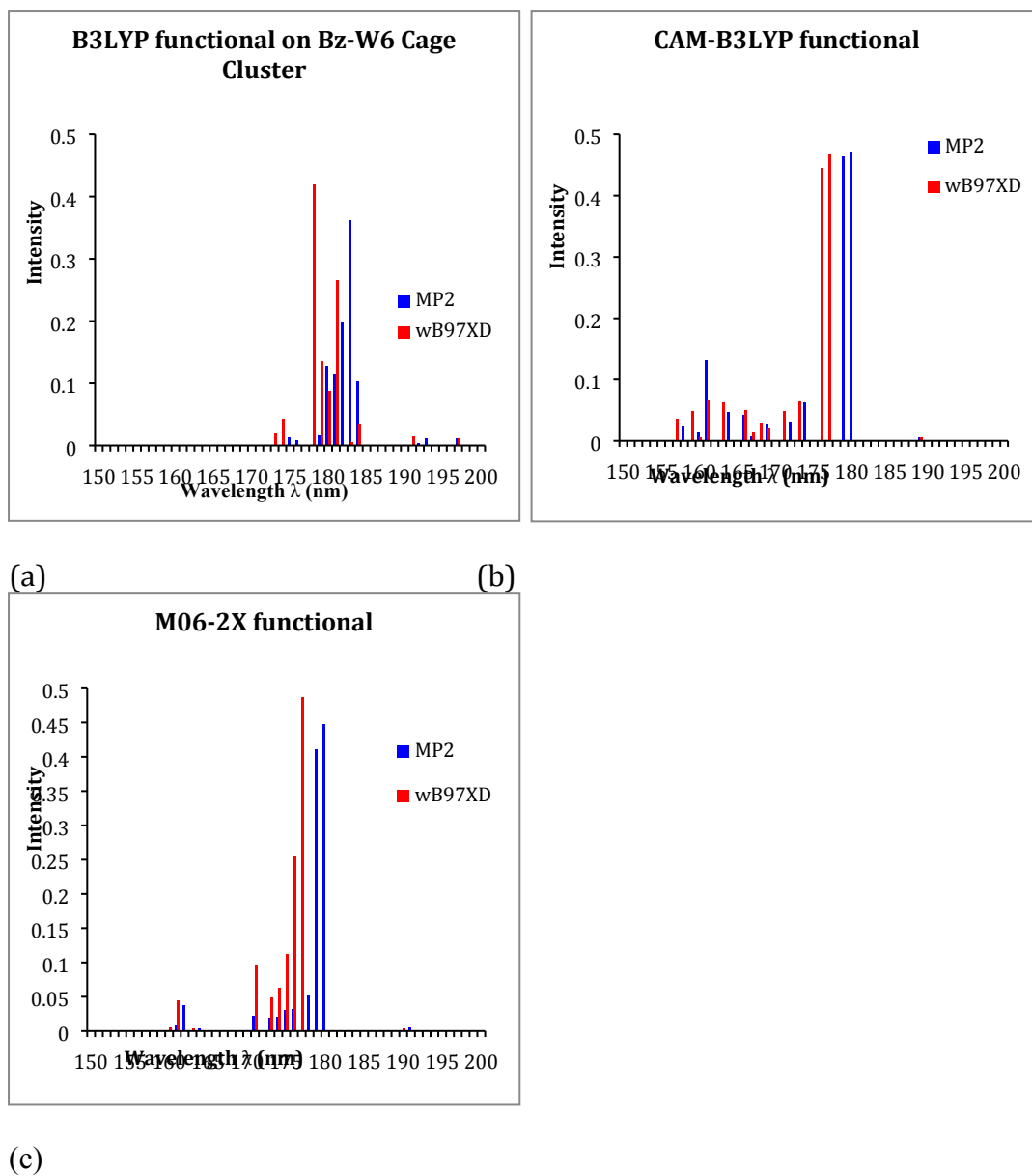
(b)

M06-2X functional

(c)

Figure S4. Comparison of UV spectra obtained from TDDFT calculations on MP2 and wB97XD optimized ground state geometries of cage shaped Bz-W_6 cluster: (a) Performance of B3LYP functional (b) Performance of CAM-B3LYP functional (c) Performance of M06-2X functional.

Table S3. List of important electronic transitions corresponding to highest peak intensities (or oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functionals with aug-cc-pVTZ basis set on MP2 optimized Bz-W$_6$ prism shaped clusters. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transition of an isolated benzene molecule).

DFT functional	E (eV)	λ (nm)	Oscillator strength (f)	Electronic transition
M06-2X	6.81 (6.91)	181.9 (179.4)	0.4083 (0.6084)	$\pi \rightarrow \pi^*$
	6.81	182.1	0.3876	$\pi \rightarrow \pi^*$
	6.96	178.1	0.1047	$\pi \rightarrow \pi^*$
CAM-B3LYP	6.81 (6.91)	181.9 (179.6)	0.4362 (0.6301)	$\pi \rightarrow \pi^*$
	6.83	181.6	0.4359	$\pi \rightarrow \pi^*$
	7.61	162.9	0.0731	W-Rydberg state
	7.05	175.8	0.0811	$\pi \rightarrow \pi^*$
B3LYP	6.66 (6.80)	186.1 (182.4)	0.2346 (0.6064)	$\pi \rightarrow \pi^*$
	6.70	185.1	0.2194	$\pi \rightarrow \pi^*$
	6.84	181.4	0.0687	Bz CT state
	6.77	183.2	0.0576	W CT state

Table S4. List of important electronic transitions corresponding to highest peak intensities (or oscillator strengths) obtained using B3LYP, CAM-B3LYP and M06-2X hybrid functionals with aug-cc-pVTZ on MP2 optimized Bz-W$_6$ cage shaped clusters. (Value in parenthesis correspond to singlet $\pi \rightarrow \pi^*$ transition of an isolated benzene molecule).

DFT functional	E (eV)	λ (nm)	Oscillator strength (f)	Electronic transition
M06-2X	6.83 (6.92)	181.6 (179.4)	0.4480 (0.5826)	$\pi \rightarrow \pi^*$
	6.85	180.9	0.4173	$\pi \rightarrow \pi^*$
	6.98	177.7	0.0423	Bz CT State
CAM-B3LYP	6.83 (6.91)	181.5 (179.6)	0.4675 (0.6068)	$\pi \rightarrow \pi^*$
	6.86	180.6	0.4488	$\pi \rightarrow \pi^*$
	7.10	174.6	0.0582	

				Diffused $\pi \to \pi^*$
B3LYP	6.74 (6.80)	183.8 (182.4)	0.2215 (0.5824)	$\pi \to \pi^*$
	6.70	184.9	0.2009	$\pi \to \pi^*$
	6.72	184.6	0.1730	$\pi \to \pi^*$
	6.67	185.8	0.157	Bz Diffuse state
	6.89	180.0	0.0932	W CT state