Optoelectronic Properties of $(ZnO)_{60}$ Isomers

(Supporting Information)

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1 MPMD computational details

The MPMD simulations are performed using the DL_POLY 3 code.[1] The interactions between atoms are described as the sum of electrostatic and Buckingham-type pair interaction potential.[2,3] All the electrostatic contributions are computed by the Ewald sum method with real space cutoff, $\rho_c = 8$ Å. The atomic trajectories are calculated using the Velocity Verlet algorithm with a timestep as small as 0.5 fs. Temperature is controlled by the Berendsen thermostat with relaxation costant $f = 0.5$ ps.

2 Additional DFT computational details

In all cases, the resolution of identity approximation is adopted for computing the electronic Coulomb interaction.[4] In addition, the multipole accelerated resolution of identity approximation[5] is used, enabling even more efficient calculations. In each SCF cycle, we require the energy to be converged within $3 \cdot 10^{-6}$ eV and the grid for numerical evaluation of the exchange-correlation operator is set to medium size.[6] No symmetry restraint have been applied during the relaxations.

3 Additional data

Table 1 reports a series of data on the ZnO isolated molecule as calculated with the BP86/TZVP scheme in comparison with other first principles results and available experimental data. In particular, column two reports very accurate Coupled Cluster (CC) data,[7] and column three reports the results obtained in Refs. 8,9. A very good agreement is found between our calculated properties and the corresponding experimental or CC data. In Figure 1 we report the optimized geometries of the hexagonal clusters, both unsaturated and saturated with 6 (W6) and 7 (W7) water molecules. Next two figures show the density of states for all the six unsaturated isomers (Figure 2) and for the two saturated hexagonal clusters (Figure 3). Table 2 shows a comparison between the B3LYP eigenvalues of the hexagonal and sodalite isomers, calculated on the BP86 and B3LYP optimized geometries. The two sets of data are consistent and differ only by a small rigid shift. Table 3 reports the energy of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the saturated and unsaturated clusters calculated with hybrid DFT, and the HOMO-LUMO gap, calculated both with hybrid DFT and TDDFT. The latter is calculated with both the SVP and 6-311G* basis sets for the sodalite and hexagonal clusters. In Figures 4 and 5 we report the spatial distribution of HOMO and LUMO for all the unsaturated isomers. From Figure 6, which reports the first 10 occupied and unoccupied energy levels, one can easily see that the band gap is well opened and there are no intra-band states. The optical absorption spectra of the saturated and unsaturated hexagonal clusters are compared in Figure 7.

Table 1: Comparison between calculated and experimental properties of the diatomic ZnO molecule. Bond lenghts (r_b) are in Å, energies (binding energy E_B, electron affinity EA and ionization energy IE) in eV and vibrational frequencies (ω_v) in cm^{-1}.

	this work	CC[a]	PBE/DSPP/DND[b]	Exp
r_b	1.71	1.72	1.73	-
E_B	1.78	1.63	2.12	1.61 ± 0.04[c]
ω_v	742	727.2	665	805 ± 40[d]
EA	2.21	2.03	-	2.09 ± 0.1[d]
IE	9.40	-	-	9.34[d]

[a] From Ref. 7
[b] From Refs. 8,9
[c] From Ref. 10
[d] From Ref. 11

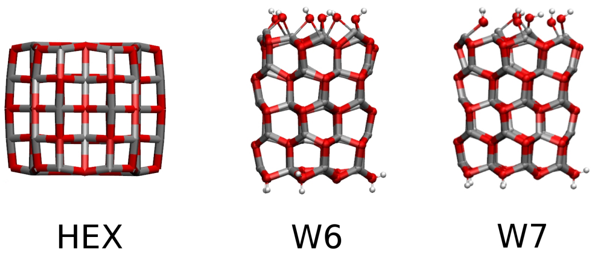


Figure 1: Optimized structures of the unsaturated hexagonal structure (HEX, left) and of its saturated counterparts: W6 (center) is saturated with 6 water molecules and W7 (right) with 7 water molecules.

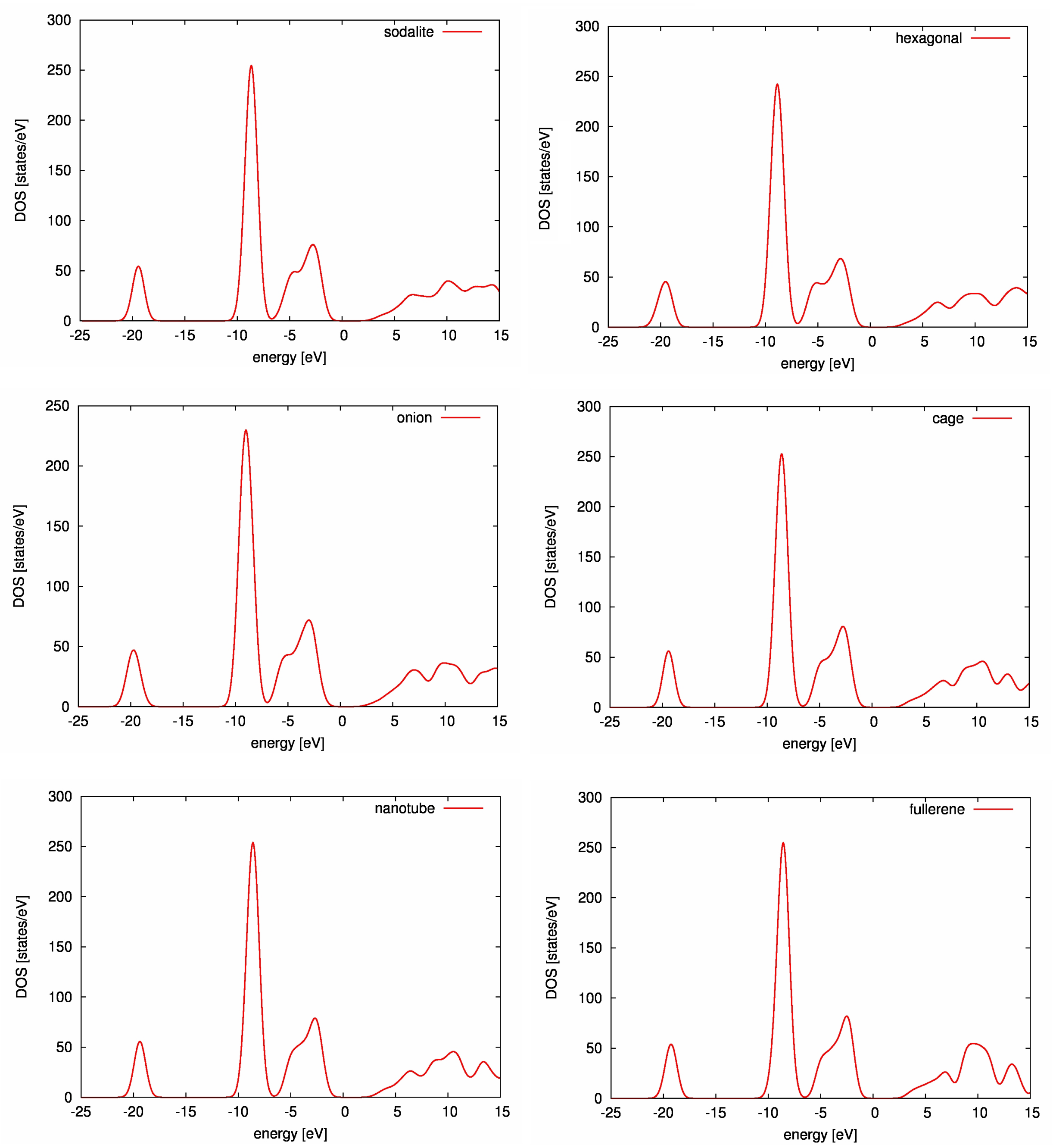


Figure 2: Density of states of the six isomers. Gaussian functions are plotted with arbitrary full width half maximum (FWHM) of 1.2 eV. The energy zero has been aligned to the Fermi energy.

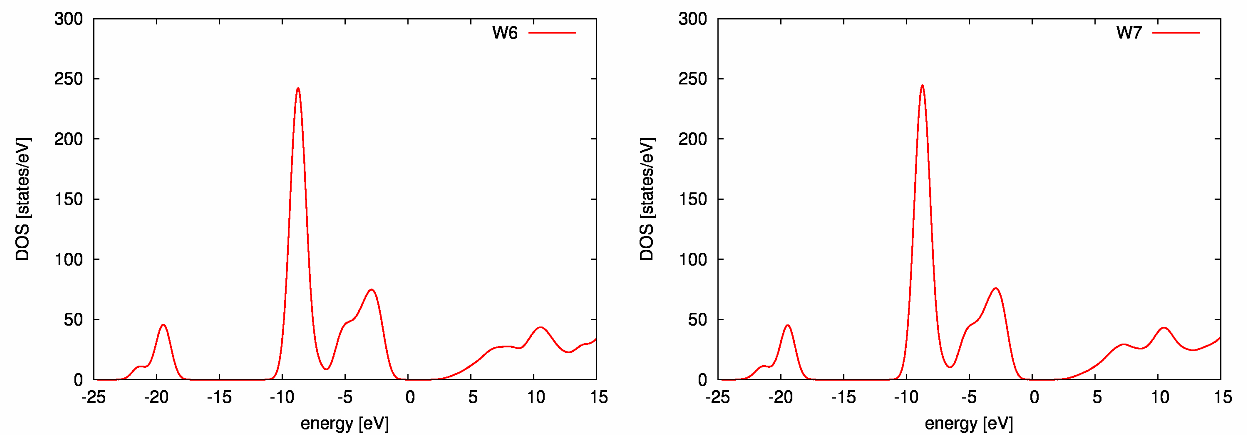


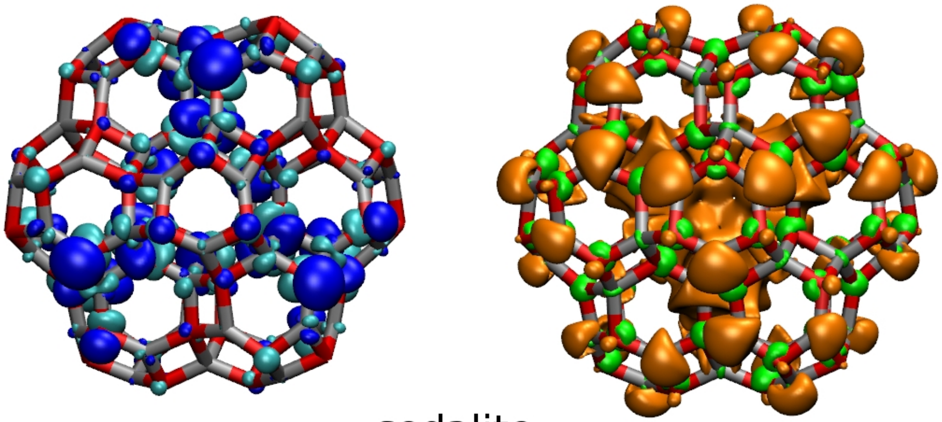
Figure 3: Same as Figure 2 for the two water saturated hexagonal nanoclusters.

Table 2: B3LYP eigenvalues corresponding to first five unoccupied (top) and occupied (bottom) molecular orbitals, calculated on the BP86 and B3LYP optimized geometries. The last row reports the electronic gap. All values are in eV.

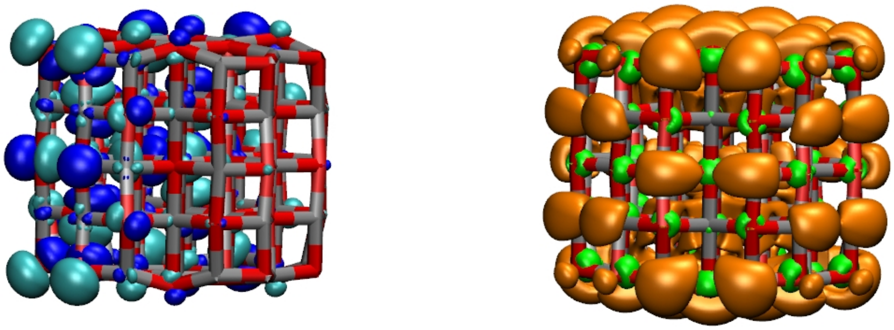
HEX		SOD	
BP86	B3LYP	BP86	B3LYP
-0.63	-0.46	-1.00	-0.90
-1.17	-0.90	-1.24	-1.12
-1.17	-0.90	-1.57	-1.48
-1.31	-1.06	-1.57	-1.48
-1.90	-1.58	-2.11	-2.02
-6.69	-6.37	-7.11	-7.06
-6.69	-6.37	-7.12	-7.07
-6.69	-6.37	-7.12	-7.07
-6.72	-6.37	-7.13	-7.10
-6.72	-6.39	-7.13	-7.11
E_g=4.79	E_g=4.79	E_g= 6.11	E_g= 6.16

Table 3: First three columns: HOMO, LUMO and HOMO-LUMO gap of the considered isomers. Last two columns: optical gap as computed by B3LYP TDDFT with SVP and 6-311G* basis sets, respectively. All values are in eV.

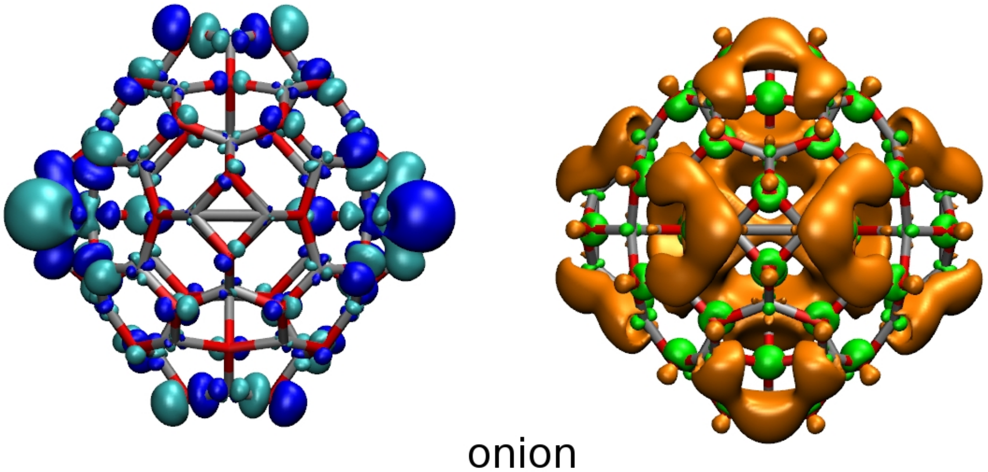
isomer	DFT B3LYP			TDDFT (SVP)	TDDFT (6-311G*)
	HOMO	LUMO	GAP	GAP	GAP
sodalite	-7.11	-2.11	5.00	4.24	4.30
hexagonal	-6.68	-1.90	4.79	4.06	4.09
onion	-6.81	-2.31	4.51	3.81	-
cage	-6.53	-1.53	5.00	4.37	-
nanotube	-6.53	-1.56	4.97	4.29	-
fullerene	-6.63	-1.38	5.26	4.50	-
W6	-7.10	-2.15	4.95	4.26	-
W7	-7.05	-2.15	4.89	4.19	-



sodalite

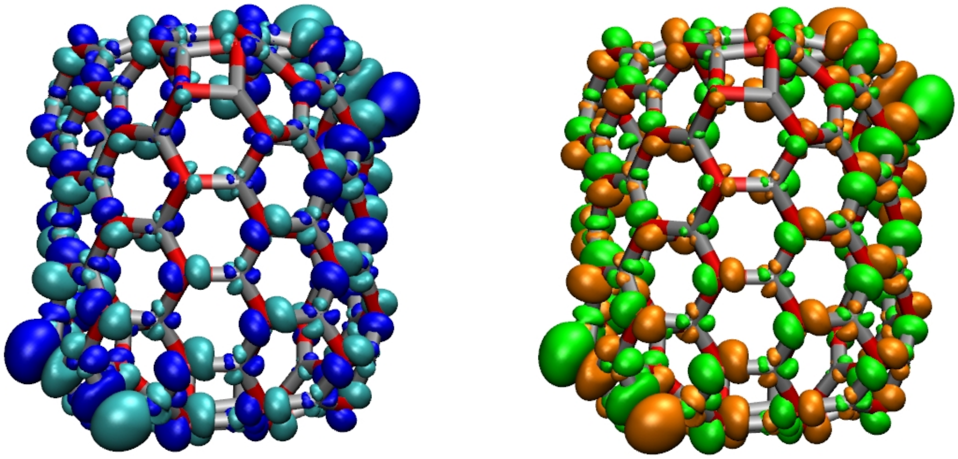


hexagonal

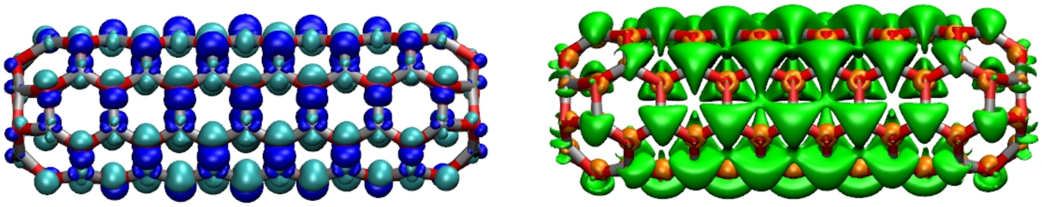


onion

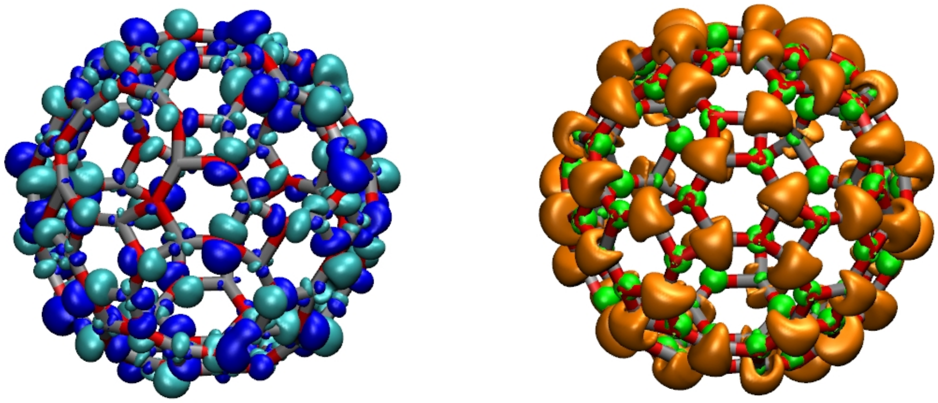
Figure 4: Orbital spatial localization (HOMO left, LUMO right) of the sodalite, hexagonal and onion isomers.



cage



nanotube



fullerene-like cage

Figure 5: Orbital spatial localization (HOMO left, LUMO right) of the cage, nanotube and fullerene-like cage isomers.

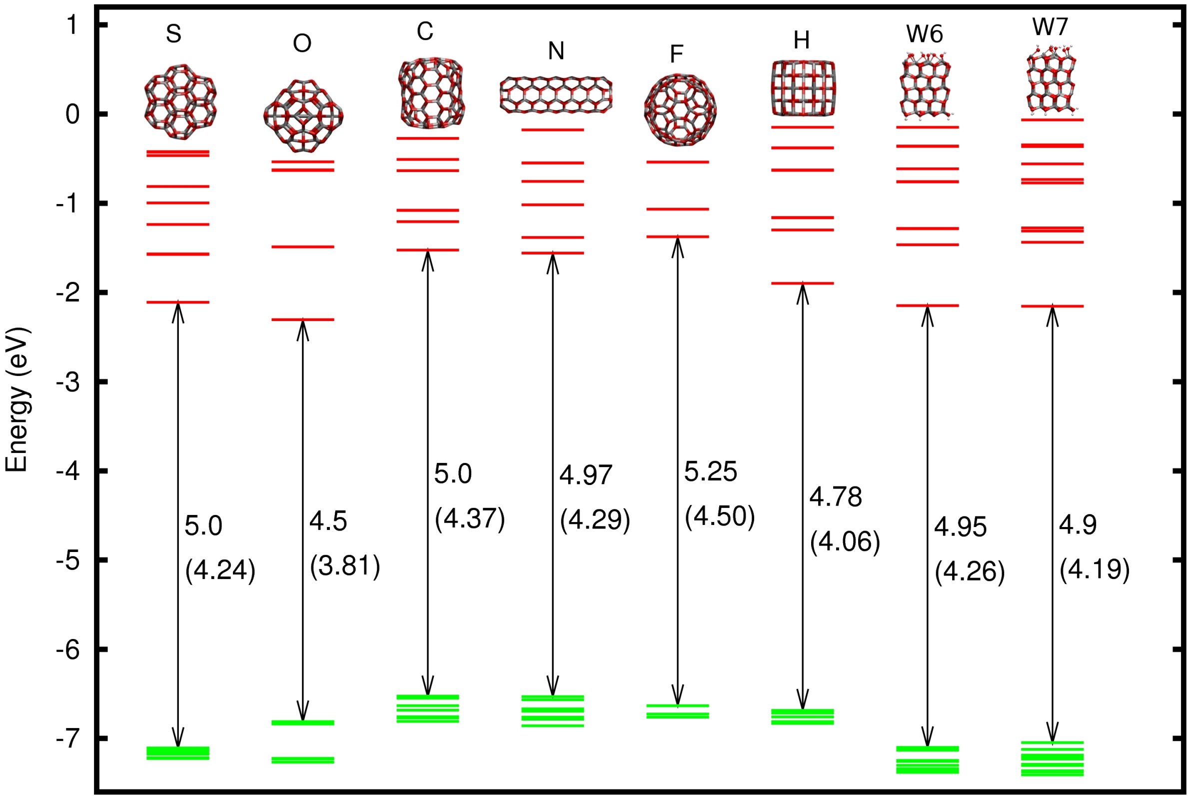


Figure 6: First ten occupied and unoccupied levels as obtained with the modified B3LYP functional. The values in parenthesis correspond to the TDDFT optical gap. Capital letters on top refer to different isomers as follows: S=sodalite, H=hexagonal, O=onion, C=cage, N=nanotube, F=fullerene-like cage, W6= hexagonal saturated with 6 water molecules, W7= hexagonal saturated with 7 water molecules.

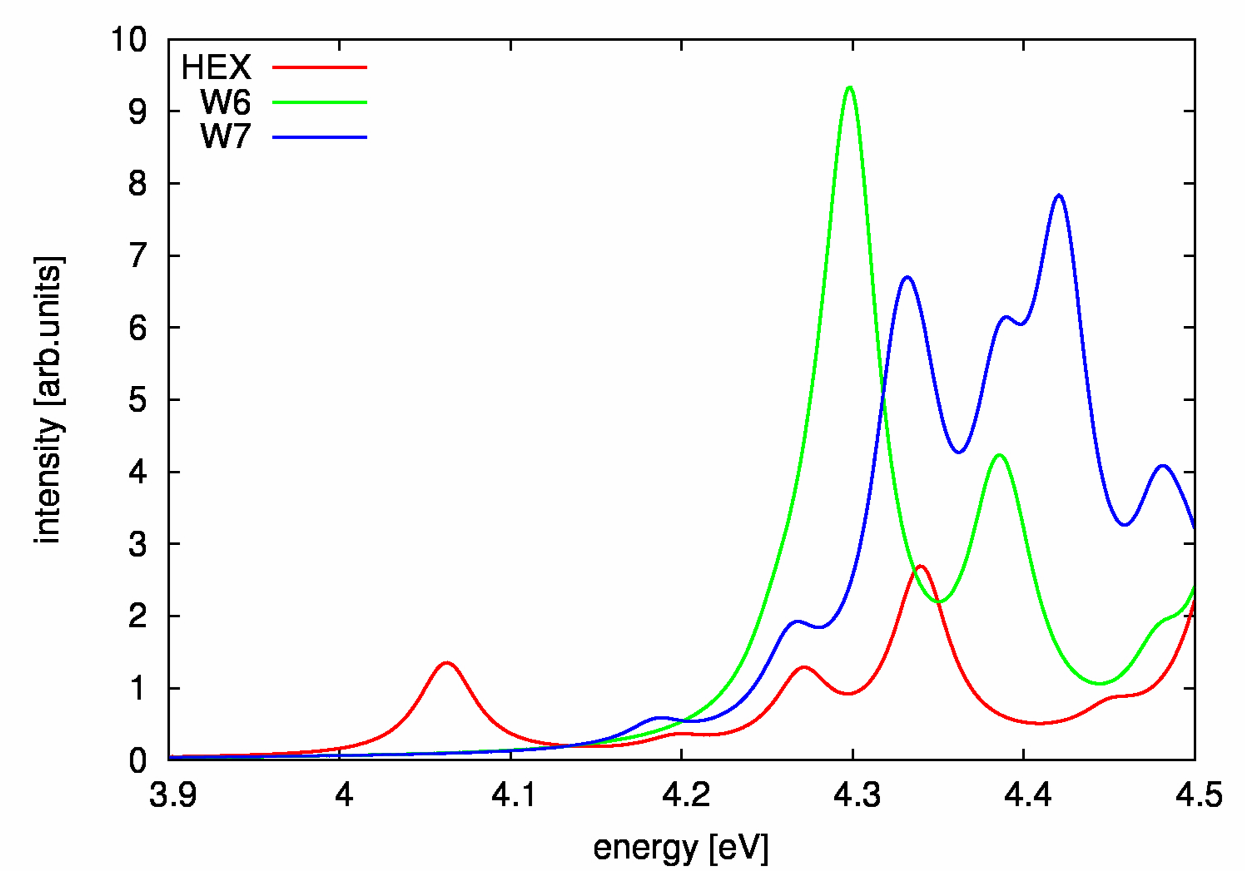


Figure 7: Comparison between the optical absorption spectra of the unsaturated hexagonal cluster and its two saturated counterparts.

Full reference for Ref. 41:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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