Investigating the Character of Excited States in TiO_2 Nanoparticles from Topological Descriptors: Implications for Photocatalysis

Rosendo Valero*, Ángel Morales-García and Francesc Illas

Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona. c/ Martí i Franquès 1-11, 08028 Barcelona, Spain

e-mail: rosendo.valero@ub.edu

Contents

Detailed equations that define the topological descriptors

First, an attachment/detachment one-electron charge density function **Δ** is generated as the difference between excited state and the ground state density matrices represented by P_X and P_0, respectively.

$$\Delta = P_X - P_0 \Rightarrow \delta = U^{\dagger} \Delta U \quad (1),$$

which is subsequently transformed into the diagonal matrix **δ**. The **δ** matrix is further split into two matrices depending on the signs of its diagonal elements

$$\sigma_{\pm} = \frac{1}{2}\left(\sqrt{\delta^2} \pm \delta\right) \quad (2).$$

Finally, these two diagonal matrices are back-transformed into the attachment and detachment density matrices, $\boldsymbol{\gamma}^{\mathbf{A}}$ and $\boldsymbol{\gamma}^{\mathbf{D}}$, respectively:

$$\boldsymbol{\gamma}\mathbf{A} = U \sigma_{+} U^{\dagger} \quad (3a),$$

$$\boldsymbol{\gamma}\mathbf{D} = U \sigma_{-} U^{\dagger} \quad (3b).$$

Thus, the attachment density matrix represents the increment in density of the excited state with respect to the ground state, whereas the detachment density represents the density depletion. Representing these density matrices in the 3D-real space allows one to visualize the molecular regions exhibiting increase or decrease of charge density. Thus, we obtain the corresponding charge densities by summing over the *L* occupied canonical MOs:

$$n_A(r) = \sum_{r=1}^{L}\sum_{s=1}^{L} (\gamma^A)_{rs}\, \varphi_r(r)\, \varphi_s^*(r) \quad (4a),$$

$$n_D(r) = \sum_{r=1}^{L}\sum_{s=1}^{L} (\gamma^D)_{rs}\, \varphi_r(r)\, \varphi_s^*(r) \quad (4b).$$

From the attachment and detachment charge densities it is possible to derive different topological descriptors which are related to the degree of intramolecular charge transfer in the excited state. First, the overlap between the electron and the hole can be quantified by the Φ_S descriptor defined in Eq. 5a

$$\Phi_S = \Theta_X^{-1} \int_{R^3} \sqrt{n_A(r)\, n_D(r)}\, dr\,;\ \Phi_S \in [0, 1] \quad (5a),$$

where Θ_X is just a normalization factor defined as

$$\Theta_X = \frac{1}{2} \sum_{t=A,D} \int_{R^3} n_t(r)\, dr \quad (5b).$$

In order to have a measure of the degree of charge transfer induced by the electronic transition, one can compute the difference function of the charge densities

$$n_{\Delta}(r) = n_A(r) - n_D(r) \quad (6),$$

allowing one to define the charge displacement density functions are defined as in Eq. (7),

$$n_{\pm}(r) = \frac{1}{2}\left\{\sqrt{n_{\Delta}^2(r)} \pm n_{\Delta}(r)\right\} \quad (7).$$

Finally, the normalized displaced charge can be computed:

$$\Phi = \frac{\theta_X^{-1}}{2} \sum_{t=+,-} n_t(r)\, dr\,;\ \Phi \in [0,1] \quad (8).$$

Another measure of the efficiency of the photoinduced charge separation can be drawn from the hole-electron distance although this requires additional definitions. An estimate of that distance is provided by the distance between the attachment and detachment centroids radius. The centroids represent the barycenter of charge for the electron and for the hole. The centroid coordinates are obtained from the integrals of the product of each coordinate and the corresponding attachment and detachment densities:

$$x_i^{\tau} = \theta_{\tau}^{-1} \int_{R^3} \gamma_{\tau}(x)\, x_i\, d^3x, i = 1-3, \tau \equiv A, D \quad (9)$$

From the centroid coordinates, the norms of the radius vectors (r_{τ}) and the intercentroid distance (d_c) are defined as

$$r_{\tau} = \left\{\sum_{i=1}^{3} \left(x_i^{\tau}\right)^2\right\}^{1/2}; d_c = \left\{\sum_{i=1}^{3} \left(x_i^A - x_i^D\right)^2\right\}^{1/2} \quad (10)$$

For the NCs and NPs of interest in the present work, a representation of the centroids along with the coordinates of each NC or NP affords a concise picture of the charge-transfer character of a given electronic excitation.

Following with the topological analysis formalism,[1-2] a clear picture of the electronic excitation, and in particular of its charge transfer character, can be obtained from defining the so-called transition density matrix (TDM).[3] A TDDFT excited state wave function can be written as

$$|\Psi^X\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{L} N_X^{-\frac{1}{2}} \gamma_{ia}^{0X} |\Psi_a^i\rangle\,; |\Psi_a^i\rangle = \hat{a}^{\dagger}\, \hat{\imath}\, |\Psi^0\rangle \quad (11)$$

Here, γ_{ia}^{0X} is an element of the TDM from the ground state (0) to the *X* excited state, *L* is the number of orbitals, *N* the one of occupied MOs and, consequently, *L* – *N* is the number of virtual MOs; $N_X^{-\frac{1}{2}}$ is a normalization factor, and $\hat{a}^{\dagger}$, $\hat{\imath}$ are creation and annihilation operators for orbitals *a* and *i*, respectively.

From the γ matrix, one can derive a normalized N x (L - N) rectangular TDM (**T**) which can be transformed into a diagonal matrix by singular value decomposition[4]

$$\lambda = O^{\dagger}\, T\, V \qquad (12)$$

The diagonal elements of λ are the singular values, and its dimension is the smaller of N and $L - N$. Now, the left and right eigenvectors of **T** can be used to construct occupied and virtual natural transition orbital (NTO) spaces

$$|\Psi^X\rangle = \sum_{i=1}^{N} a_i^{v\,\dagger}\, a_i^o\, \lambda_{ii}\, |\Psi^0\rangle \qquad (13)$$

If $N < L$ - N, which is the usual case, we have N pairs of NTOs that represent electron/hole excitations. Note that the transitions are now from the i^{th} occupied (o) orbital to the i^{th} virtual (v) orbital.

Table S1. TDDFT PBE0 topological descriptors for $(TiO_2)_n$, n = 1-20 nanoclusters and n = 35, 78, 84, 97, 165, and 84_I-3-2 nanoparticles (anatase) and n = 51 (rutile). For definitions see main text.

Number of $(TiO_2)_n$ units	Φ		Φ_S		d_c / Å	
	Gas phase	Water	Gas phase	Water	Gas phase	Water
1	0.92	0.89	0.26	0.30	1.61	0.82
2	0.88	0.88	0.34	0.34	0.00	0.00
3	0.97	0.91	0.14	0.31	3.53	1.22
4	0.90	0.90	0.30	0.31	0.82	0.44
5	0.82	0.83	0.44	0.44	0.02	0.62
6	0.88	0.84	0.33	0.40	1.57	0.43
7	0.85	0.85	0.38	0.38	0.70	0.36
8	0.85	0.83	0.38	0.41	0.00	0.00
9	0.87	0.87	0.35	0.36	1.31	0.62
10	0.85	0.86	0.39	0.39	0.12	0.00
11	0.87	0.83	0.36	0.42	2.64	0.33
12	0.86	0.85	0.37	0.42	1.86	0.40
13	0.85	0.89	0.39	0.32	1.15	0.53
14	0.91	0.89	0.25	0.31	3.44	0.53
15	0.93	0.91	0.23	0.28	3.25	1.21
16	0.85	0.85	0.38	0.43	1.19	0.23
17	0.94	0.90	0.21	0.38	3.83	0.34
18	0.87	0.88	0.34	0.28	1.42	1.37

19	0.85	0.85	0.39	0.35	0.10	0.05
20	0.84	0.85	0.43	0.40	0.01	0.17
35	0.91	0.91	0.32	0.31	0.64	0.66
78	0.86	0.86	0.42	0.40	0.34	0.30
84	0.89	0.89	0.37	0.38	0.67	0.61
97	0.95	0.87	0.20	0.41	3.87	0.32
165	0.87	0.87	0.42	0.43	0.13	0.23
84 I-3-2	0.79	0.79	0.45	0.45	1.82	1.10
51	0.94	0.94	0.19	0.20	0.0	0.0

Table S2. Optical gap at TDDFT level, excited state character, and weight of NTOs for the $(TiO_2)_n$, n = 1-20 nanoclusters.

a) PBEx, gas phase

Number of $(TiO_2)_n$ units	Optical gap / eV	Excited state character	Weight of NTOs
1	2.34	HOMO – LUMO 98%	100%
2	3.67	HOMO – LUMO 95%	96%
3	2.67	HOMO – LUMO 98%	100%
4	3.71	HOMO – LUMO 85%	85%
5	3.69	HOMO – LUMO 92%	96%
6	3.65	HOMO – LUMO 98%	99%
7	3.87	HOMO – LUMO 90%	98%
8	3.78	HOMO – LUMO 95%	96%
9	3.69	HOMO – LUMO 85%	99%
10	4.25	HOMO-1 – LUMO 67%	93%
11	3.67	HOMO – LUMO 72% HOMO – LUMO+1 26%	99%
12	3.76	HOMO – LUMO 63% HOMO-1 – LUMO+1 27%	68% - 31%
13	3.84	HOMO – LUMO 65% HOMO – LUMO+1 25%	99%
14	3.57	HOMO-1 – LUMO 90%	100%
15	3.07	HOMO – LUMO 95%	100%
16	3.65	HOMO – LUMO 95%	100%
17	3.11	HOMO – LUMO 95%	100%
18	3.80	HOMO – LUMO 50% HOMO-1 – LUMO+1 39%	58% - 42%

19	3.74	HOMO – LUMO 95%	99%
20	4.09	HOMO – LUMO+1 37% HOMO – LUMO+2 32%	85%

b) PBEx, water

Number of $(TiO_2)_n$ units	Optical gap / eV	Excited state character	Weight of NTOs
1	3.69	HOMO – LUMO 95%	100%
2	4.32	HOMO – LUMO 98%	99%
3	3.98	HOMO – LUMO 92%	99%
4	4.06	HOMO – LUMO 87%	87%
5	3.95	HOMO – LUMO 92%	98%
6	4.07	HOMO – LUMO 92%	97%
7	4.13	HOMO – LUMO+1 61% HOMO-1 – LUMO+1 29%	98%
8	4.08	HOMO – LUMO+1 87%	88%
9	3.98	HOMO – LUMO 90%	97%
10	4.31	HOMO – LUMO+1 72%	96%
11	4.09	HOMO – LUMO 63% HOMO – LUMO+1 20%	95%
12	4.12	HOMO – LUMO 77%	82% - 16%
13	4.03	HOMO – LUMO 63% HOMO-1 – LUMO 29%	98%
14	3.99	HOMO-1 – LUMO 92%	98%
15	3.07	HOMO – LUMO 97%	100%
16	4.05	HOMO – LUMO 48% HOMO – LUMO+1 26%	91%
17	3.63	HOMO – LUMO 67%	100%
18	4.07	HOMO – LUMO 58% HOMO-1 – LUMO+1 32%	63% - 35%
19	3.83	HOMO – LUMO 95%	99%

20	4.11	HOMO-1 – LUMO 42% HOMO-1 – LUMO+1 32%	56% - 39%

c) PBE0, gas phase

Number of $(TiO_2)_n$ units	Optical gap / eV	Excited state character	Weight of NTOs
1	2.72	HOMO – LUMO 98%	100%
2	4.05	HOMO – LUMO 85%	89%
3	3.38	HOMO – LUMO 98%	100%
4	4.20	HOMO-1 – LUMO 67% HOMO – LUMO+1 25%	71% - 29%
5	4.24	HOMO-1 – LUMO 63%	91%
6	4.29	HOMO-1 – LUMO 67%	91%
7	4.43	HOMO-5 – LUMO+1 41% HOMO-3 – LUMO+1 34%	96%
8	4.40	HOMO – LUMO 61%	72% - 23%
9	4.32	HOMO-1 – LUMO 35%	90%
10	4.71	HOMO – LUMO+1 50% HOMO-1 – LUMO+1 20%	84%
11	4.31	HOMO – LUMO 46% HOMO – LUMO+1 32%	91%
12	4.48	HOMO-2 – LUMO 23%	49% - 39%
13	4.44	HOMO-3 – LUMO+4 42%	96%
14	4.31	HOMO-1 – LUMO 85%	98%
15	3.81	HOMO – LUMO 77%	100%
16	4.46	HOMO-5 – LUMO+4 12%	92%
17	3.88	HOMO – LUMO 79%	99%
18	4.47	HOMO-3 – LUMO+1 26% HOMO-2 – LUMO 25%	53% - 42%
19	4.37	HOMO – LUMO+1 50%	66% - 30%

20	4.62	HOMO-1 – LUMO 32%	78% - 11%

d) PBE0, water

Number of $(TiO_2)_n$ units	Optical gap / eV	Excited state character	Weight of NTOs
1	4.04	HOMO – LUMO 87%	100%
2	4.75	HOMO – LUMO 92%	96%
3	4.52	HOMO – LUMO 74%	96%
4	4.52	HOMO-1 – LUMO 77%	81% - 19%
5	4.40	HOMO – LUMO 82%	95%
6	4.58	HOMO-1 – LUMO 37% HOMO-4 – LUMO 26%	91%
7	4.58	HOMO-1 – LUMO 48%	97%
8	4.55	HOMO-1 – LUMO 70%	75% - 22%
9	4.53	HOMO – LUMO 56%	85%
10	4.79	HOMO – LUMO+1 52%	89%
11	4.63	HOMO-1 – LUMO 30%	85%
12	4.62	HOMO – LUMO+1 32% HOMO-3 – LUMO 32%	51% - 45%
13	4.57	HOMO – LUMO 63%	94%
14	4.57	HOMO – LUMO 77%	93%
15	4.06	HOMO – LUMO 74%	99%
16	4.53	HOMO-2 – LUMO 25%	97%
17	4.19	HOMO – LUMO 39%	99%
18	4.61	HOMO – LUMO 39% HOMO-1 – LUMO+1 34%	52% - 42%
19	4.44	HOMO – LUMO+1 50%	66% - 30%
20	4.66	HOMO-1 – LUMO 30%	88%

		HOMO – LUMO+1 25%	

Table S3. Optical gaps at TDDFT level, excited state character, and weight of NTOs for the $(TiO_2)_n$, n = 35, 78, 84, 97, 165, and 84_I-3-2 (anatase) and n = 51 (rutile) nanoparticles at the PBE0 level.

Gas phase			
35	3.77	HOMO – LUMO 79%	87%
78	3.84	HOMO-1 – LUMO 61%	88%
84	3.82	HOMO – LUMO 72%	89%
97	3.91	HOMO – LUMO 70%	88%
165	3.86	HOMO-1 – LUMO 35% HOMO-2 – LUMO 8% HOMO-4 – LUMO 12%	84%
84-I-3-2	1.03	HOMO – LUMO 25%	100%
51	2.94	HOMO-8 – LUMO 50% HOMO – LUMO 14%	85%
Water			
35	3.85	HOMO – LUMO 79%	91%
78	3.87	HOMO – LUMO 72%	88%
84	3.86	HOMO – LUMO 70%	90%
97	3.96	HOMO – LUMO 46%	82%
165	3.88	HOMO – LUMO 11% HOMO-2 – LUMO 19% HOMO-4 – LUMO 25%	84%
84-I-3-2	0.71	HOMO – LUMO 34%	100%
51	3.04	HOMO-6 – LUMO 58% HOMO – LUMO 13%	84%

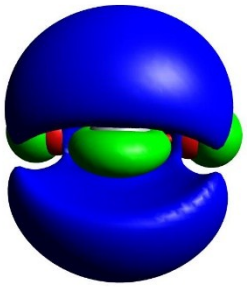
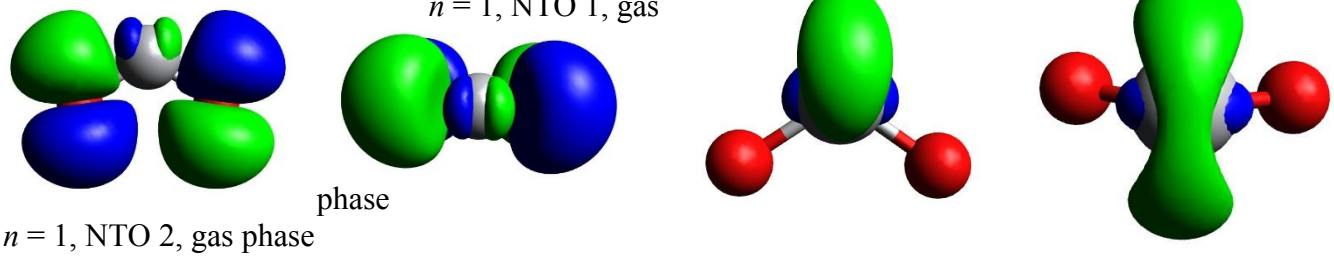
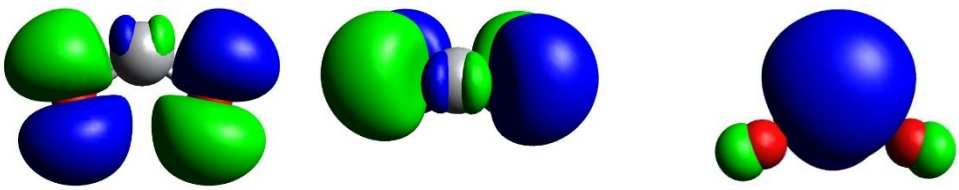


Fig. S1. Natural transition orbitals (NTOs) for the $(TiO_2)_n$ nanoclusters with n = 1-20 at the TDDFT PBEx level, in the gas phase and in water solvent. The first and second picture for each NTO correspond to two different views that differ by a 90º rotation. The grey and red spheres represent titanium and oxygen atoms, respectively.



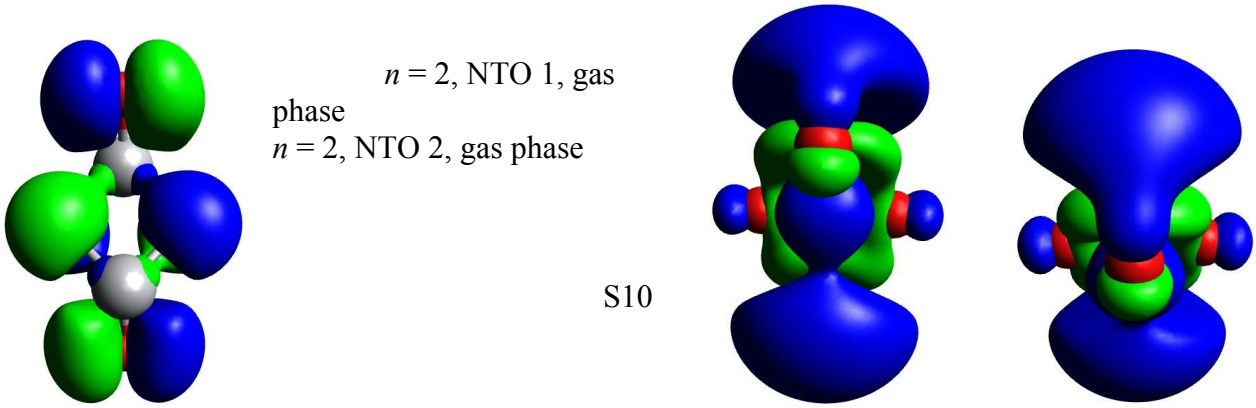
n = 1, NTO 1, gas phase

n = 1, NTO 2, gas phase



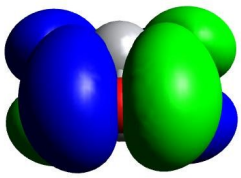
n = 1, NTO 1, water

n = 1, NTO 2, water

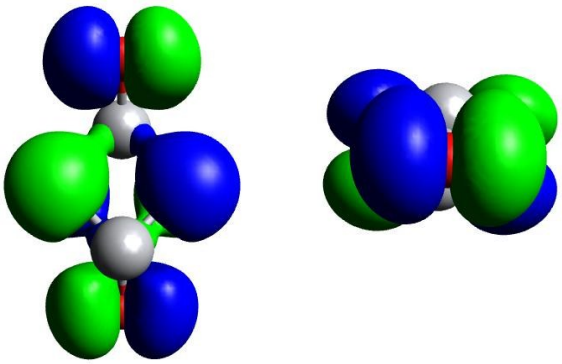


n = 2, NTO 1, gas phase

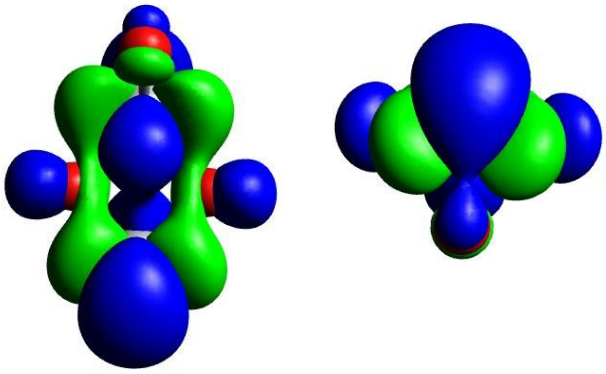
n = 2, NTO 2, gas phase



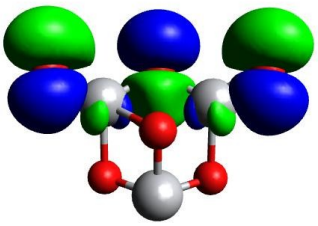
n = 2, NTO 1, water



n = 2, NTO 2, water



n = 3, NTO 1, gas phase



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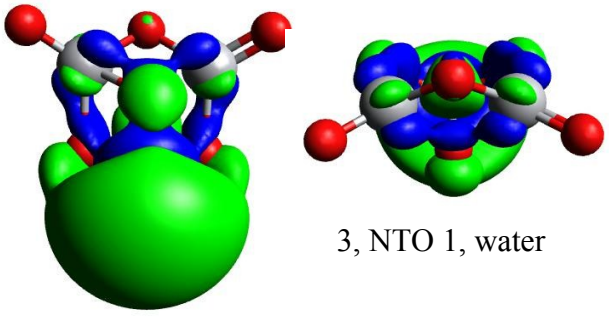
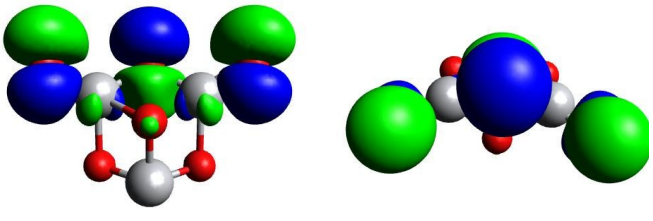
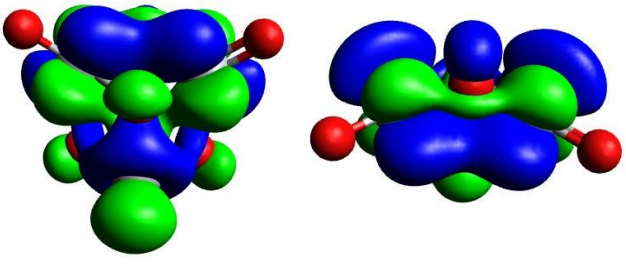


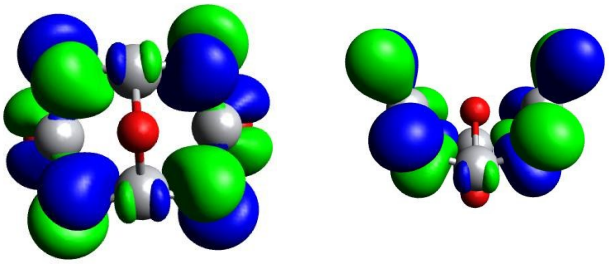
n = 3, NTO 2, water



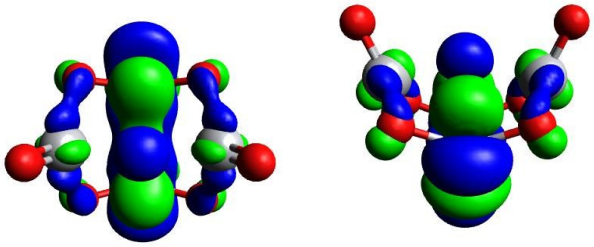
n = 3, NTO 1, water



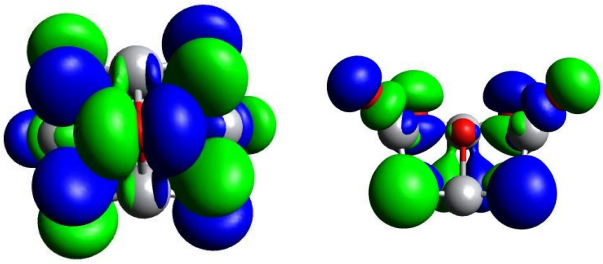
n = 4, NTO 1, gas phase



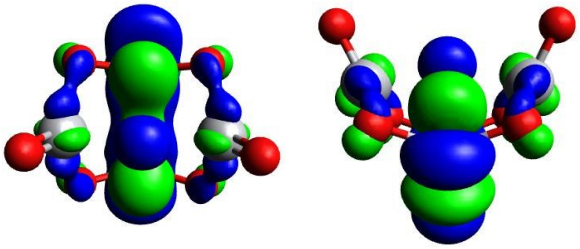
n = 4, NTO 2, gas phase



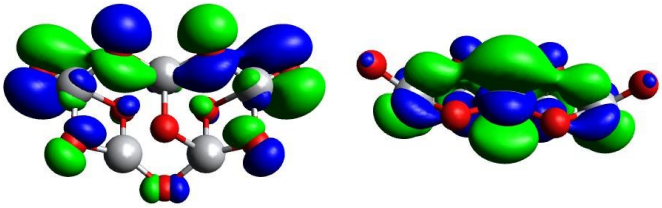
n = 4, NTO 1, water



n = 4, NTO 2, water



n = 5, NTO 1, gas phase



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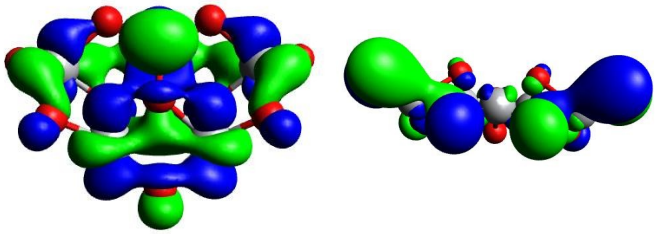

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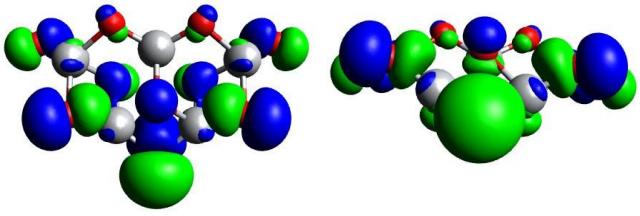
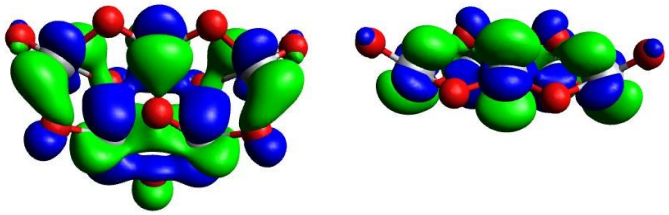
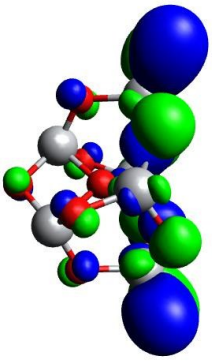


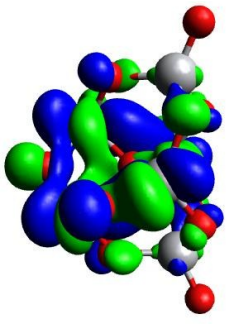
n = 5, NTO 2, water

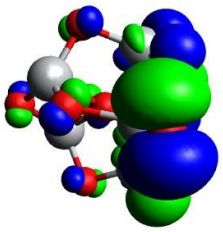


n = 6, NTO 1, gas phase

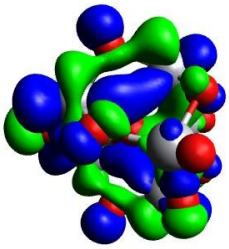


n = 6, NTO 2, gas phase

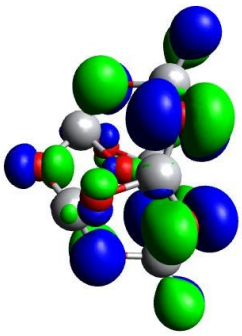


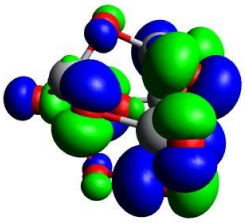


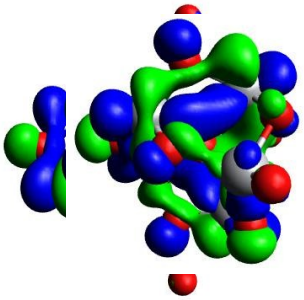
n = 6, NTO 1, water



n = 6, NTO 2, water

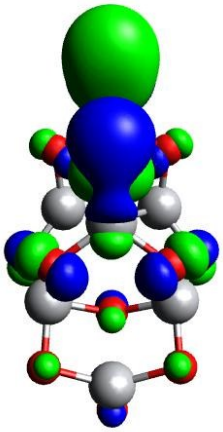


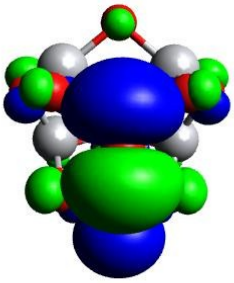


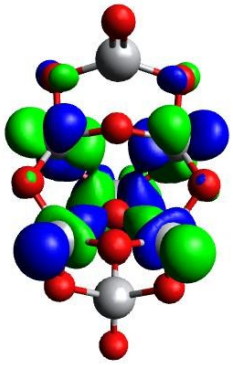


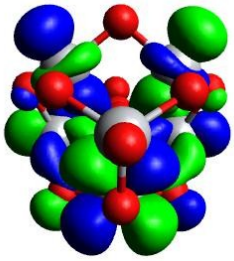
n = 7, NTO 1, gas phase

n = 7, NTO 2, gas phase



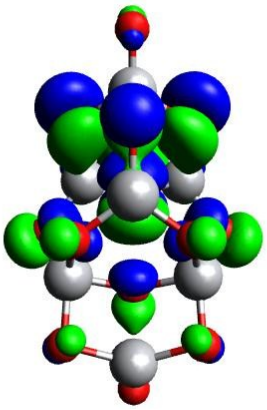




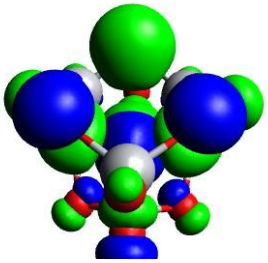


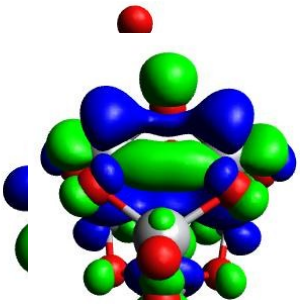
n = 7, NTO 1, water

n = 7, NTO 2, water

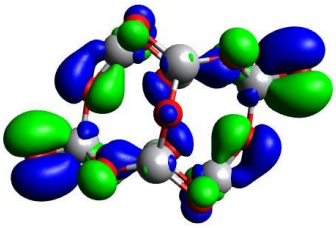


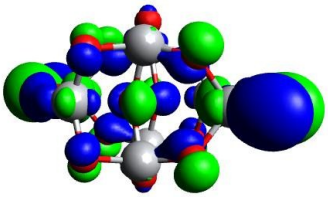
n = 8, NTO 1, gas phase

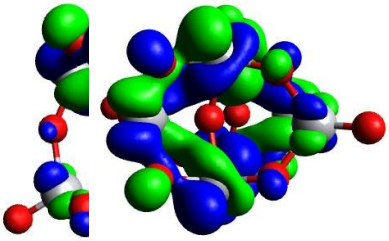




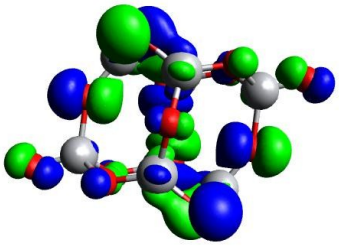
n = 8, NTO 2, gas phase



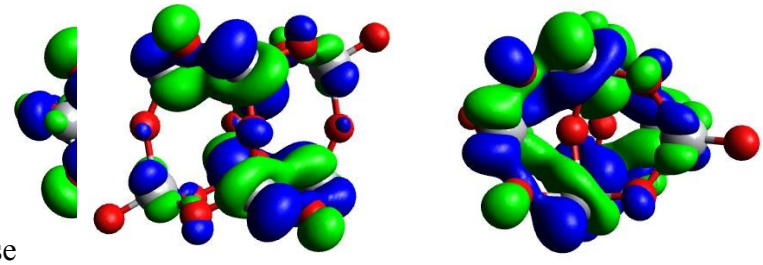




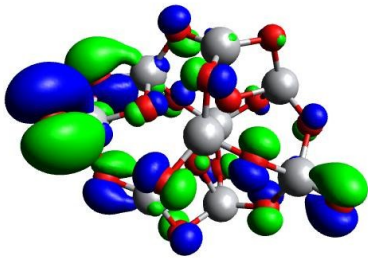
n = 8, NTO 1, water



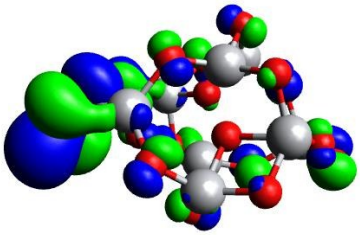
n = 8, NTO 2, water



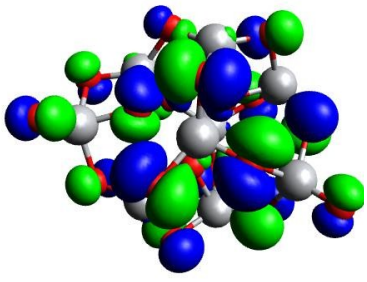
n = 9, NTO 1, gas phase



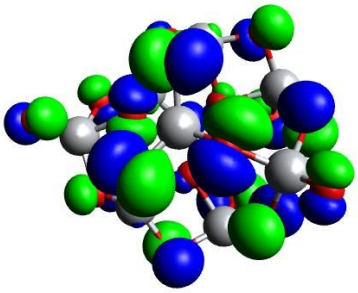
n = 9, NTO 2, gas phase



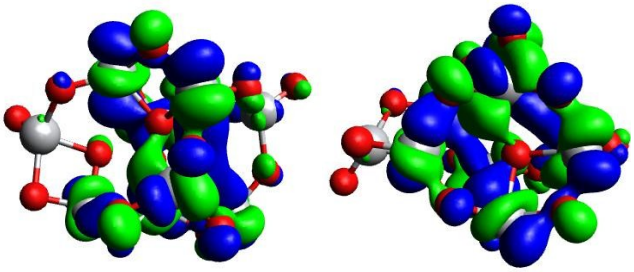
n = 9, NTO 1, water



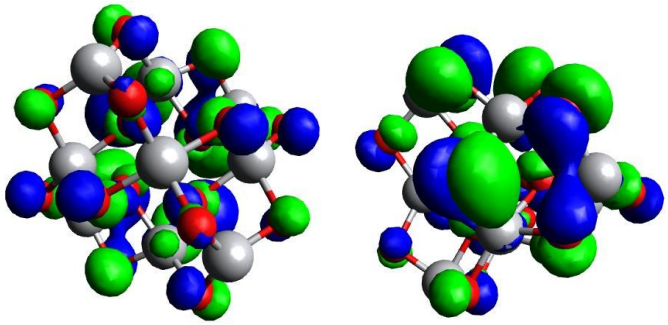
n = 9, NTO 2, water



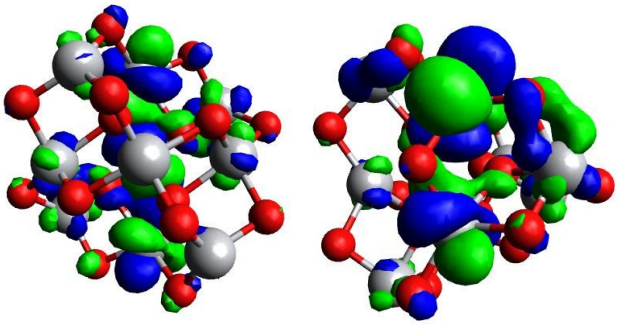
n = 10, NTO 1, gas phase



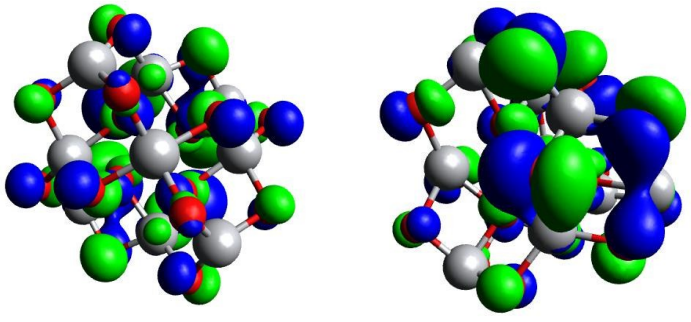
n = 10, NTO 2, gas phase

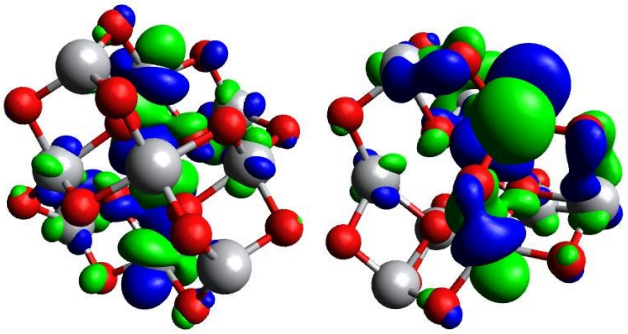


n = 10, NTO 1, water

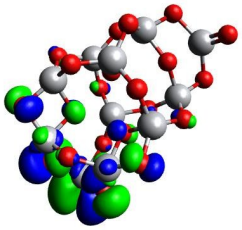


n = 10, NTO 2, water

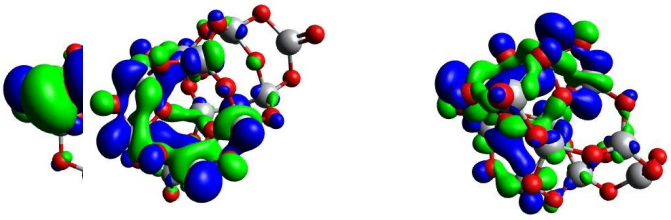




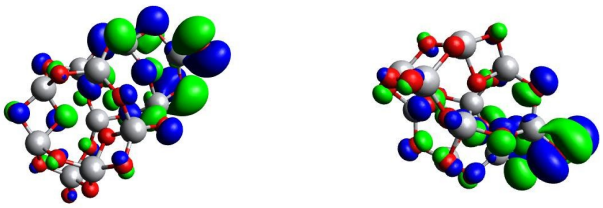
n = 11, NTO 1, gas phase



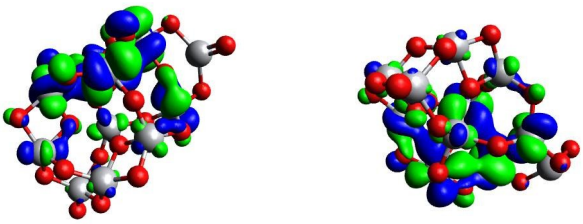
n = 11, NTO 2, gas phase



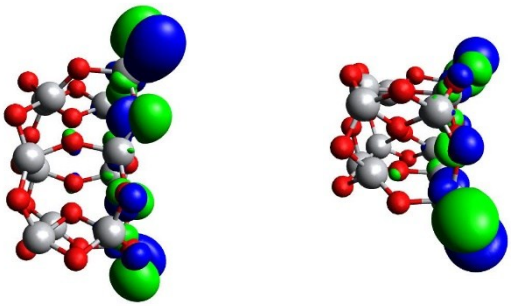
n = 11, NTO 1, water



n = 11, NTO 2, water

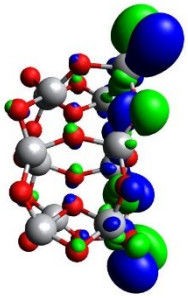


n = 12, NTO 1, gas phase



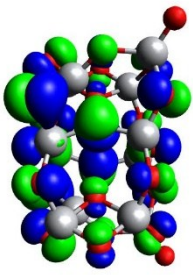
n = 12, NTO 2, gas phase

n = 12, NTO 3, gas phase

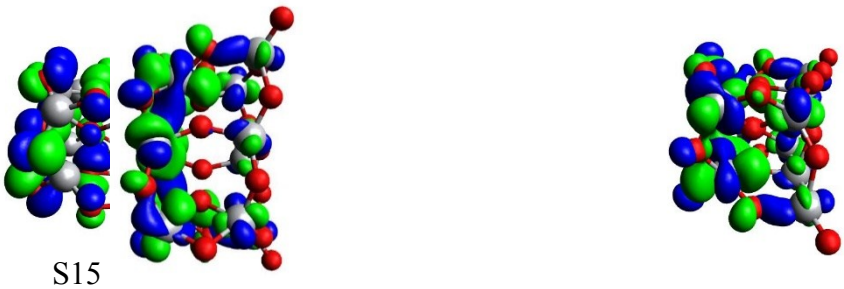


n = 12, NTO 4, gas phase

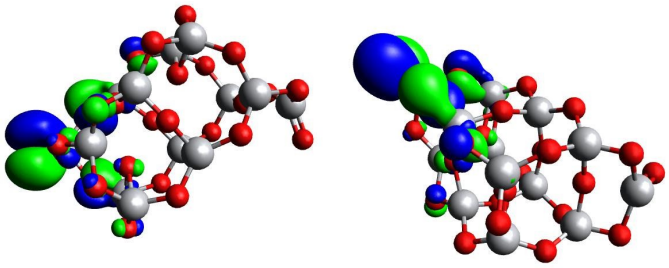
n = 12, NTO 1, water



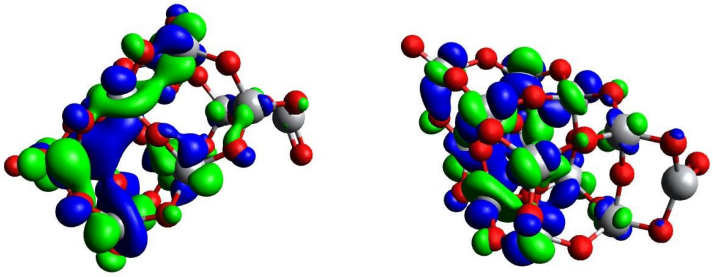
n = 12, NTO 2, water



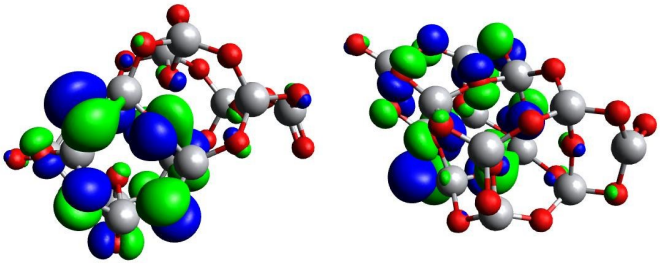
n = 13, NTO 1, gas phase



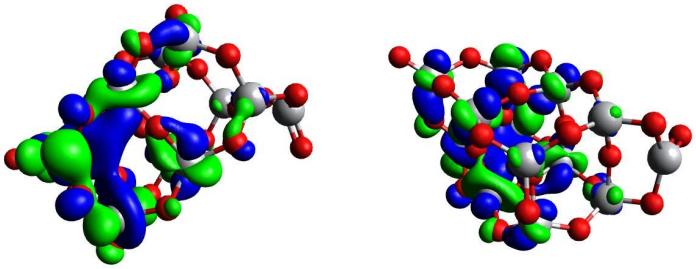
n = 13, NTO 2, gas phase



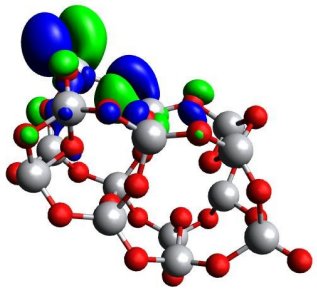
n = 13, NTO 1, water



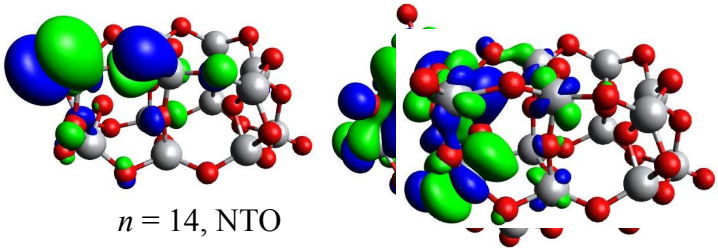
n = 13, NTO 2, water



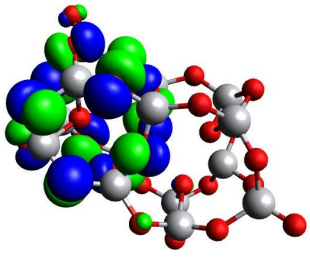
n = 14, NTO 1, gas phase



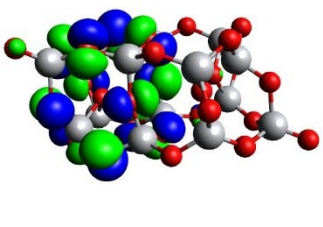
n = 14, NTO 2, gas phase

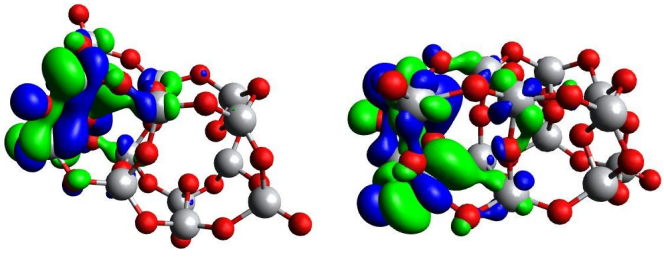


n = 14, NTO 1, water

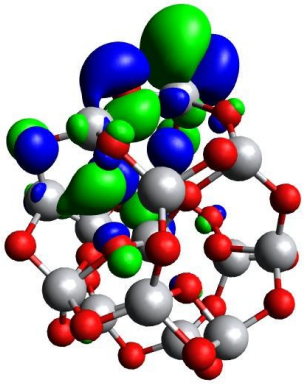


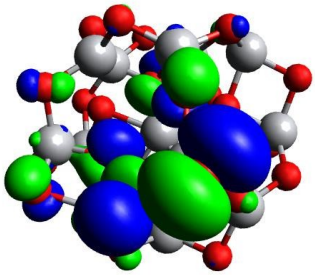
n = 14, NTO 2, water





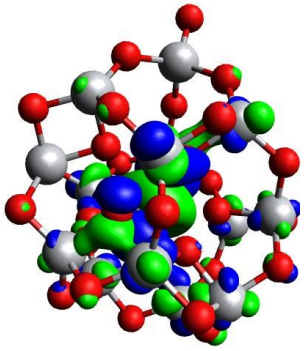
n = 15, NTO 1, gas phase

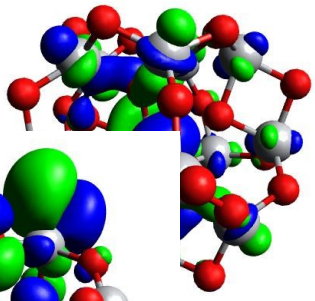


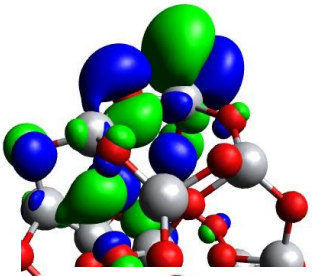


n = 15, NTO 1, water

n = 15, NTO 2, gas phase

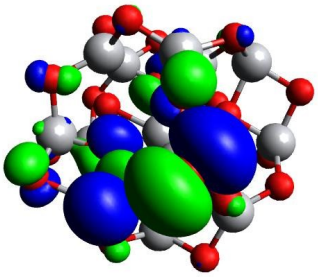


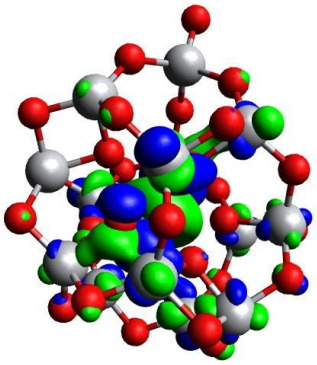




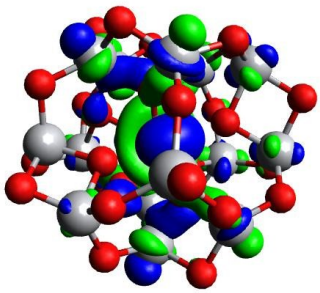
n = 15, NTO 2, water

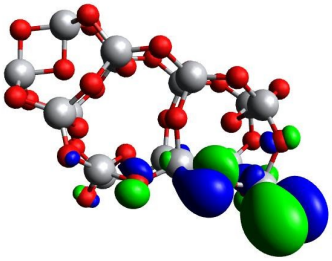
n = 16, NTO 1, gas phase

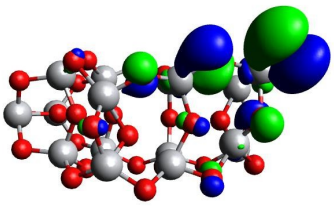




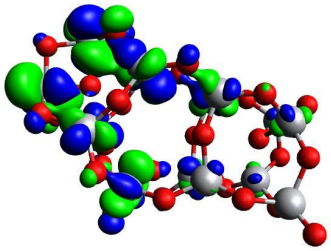
n = 16, NTO 2, gas phase

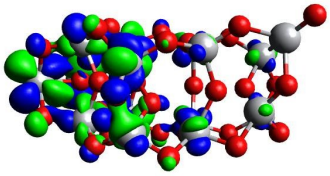




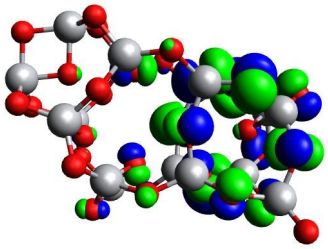


n = 16, NTO 1, water

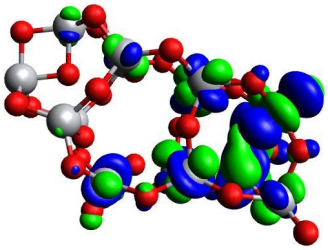


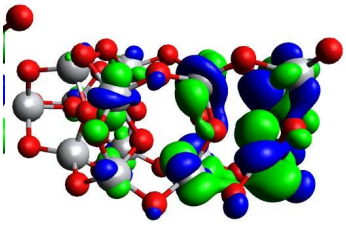


n = 16, NTO 2, water

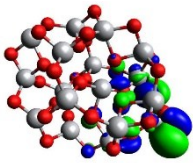


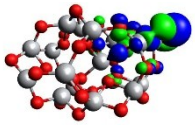
n = 17, NTO 1, gas phase



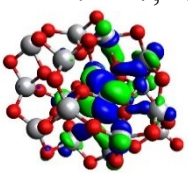


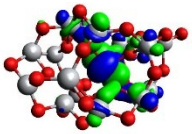
n = 17, NTO 2, gas phase



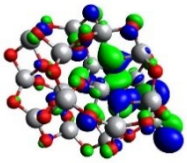


n = 17, NTO 1, water

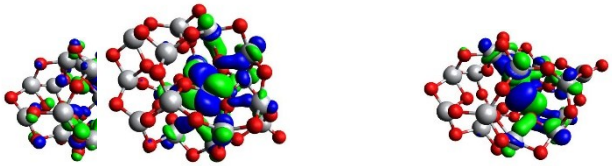




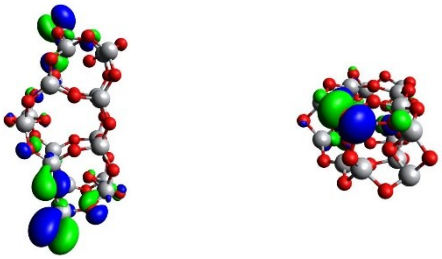
n = 17, NTO 2, water



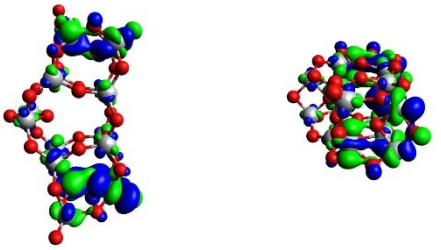
n = 18, NTO 1, gas phase



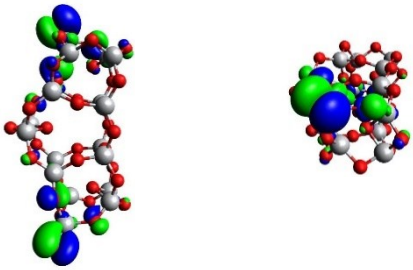
n = 18, NTO 2, gas phase



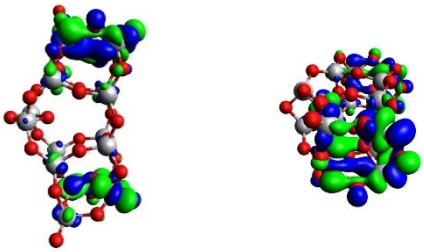
n = 18, NTO 3, gas phase



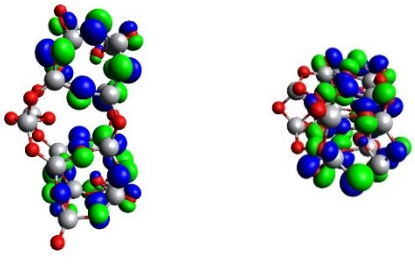
n = 18, NTO 4, gas phase



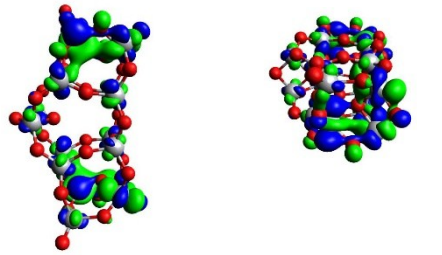
n = 18, NTO 1, water



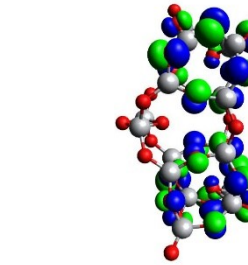
n = 18, NTO 2, water



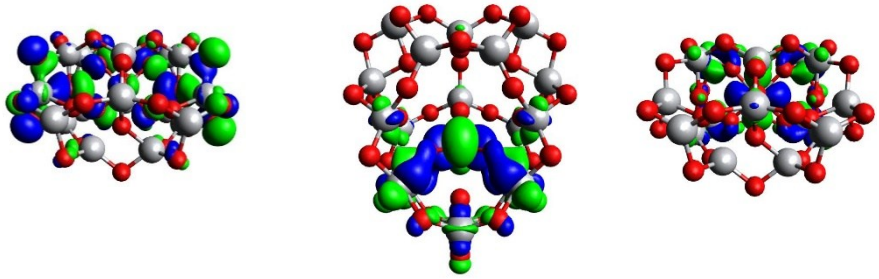
n = 18, NTO 3, water



n = 18, NTO 4, water



n = 19, NTO 1, gas phase



n = 19, NTO 2, gas phase

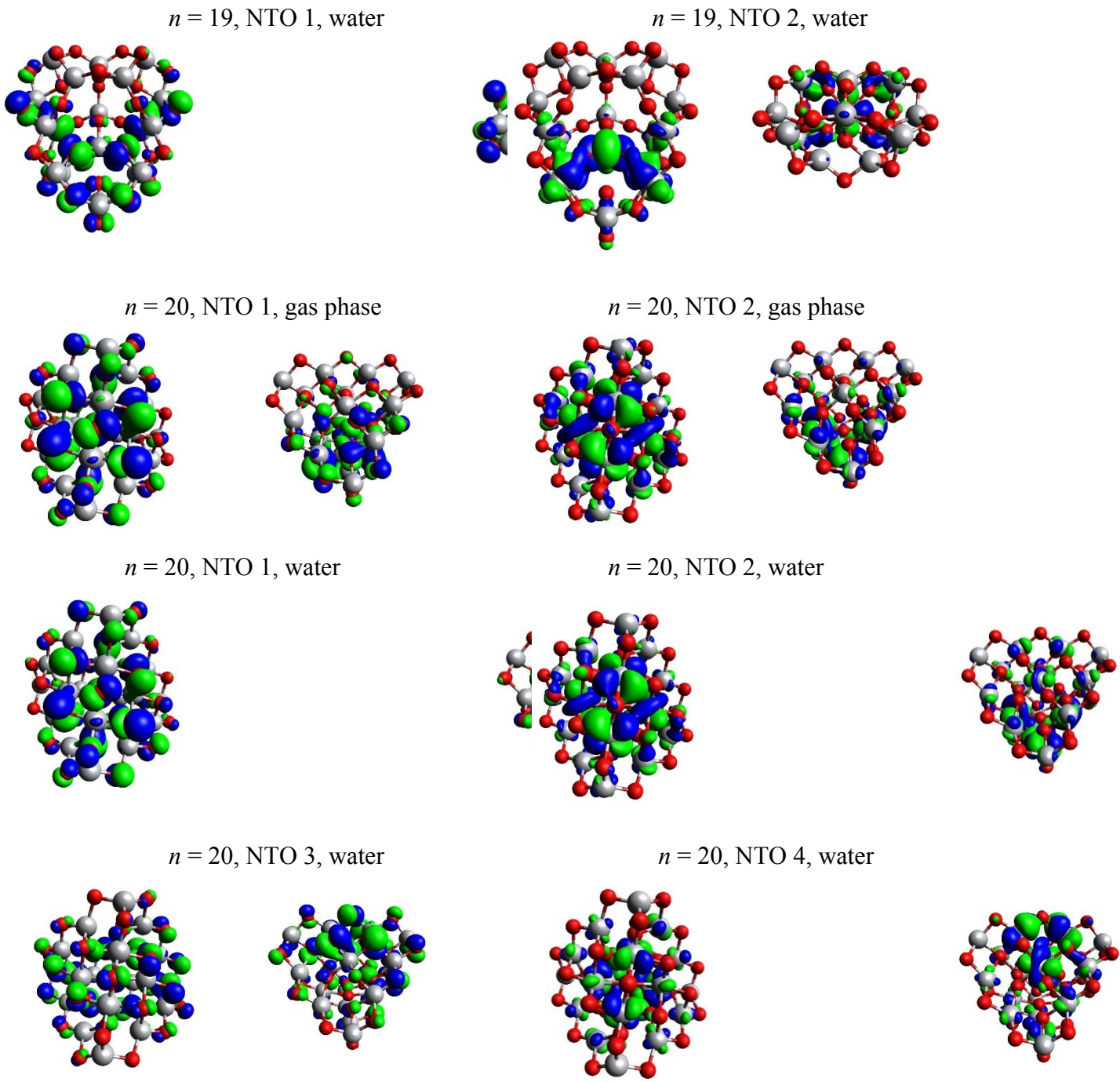
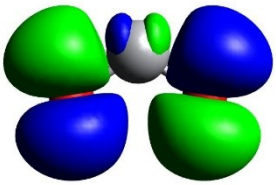
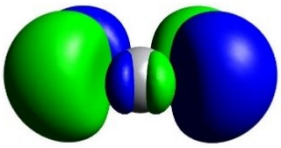


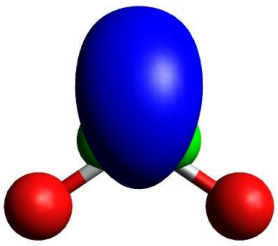
Fig. S2. Natural transition orbitals (NTOs) for the $(TiO_2)_n$ nanoclusters with n = 1-20 at the TDDFT PBE0 level, in the gas phase and in water solvent. The first and second picture for each NTO correspond to two different views that differ by a 90º rotation. The grey and red spheres represent titanium and oxygen atoms, respectively.

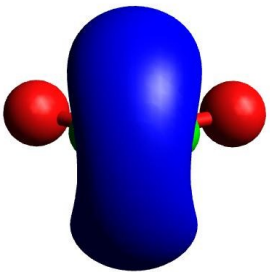
n = 1, NTO 1, gas phase *n* = 1, NTO 2, gas phase



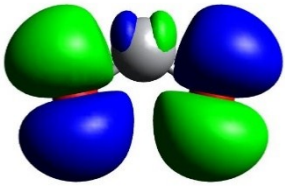


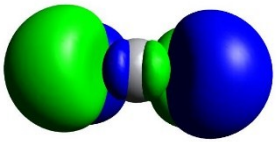
n = 1, NTO 1, water



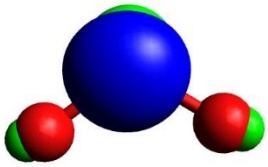


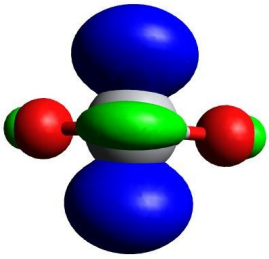
n = 1, NTO 2, water



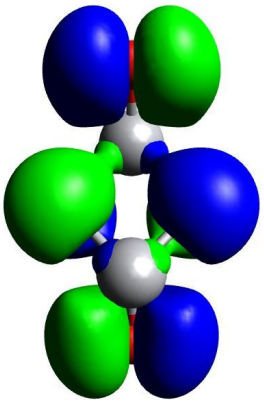


n = 2, NTO 1, gas phase

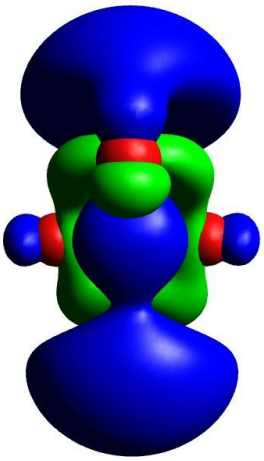


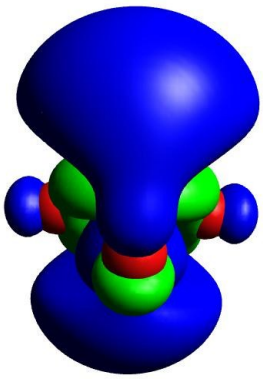


n = 2, NTO 2, gas phase

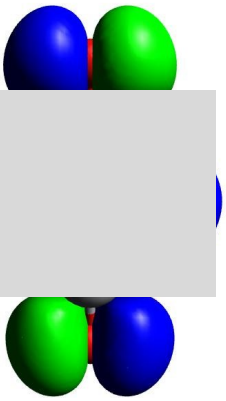


n = 2, NTO 1, water

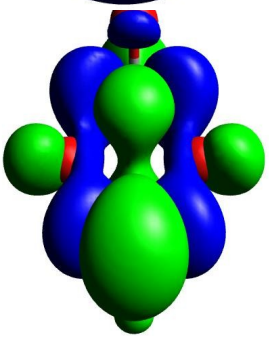




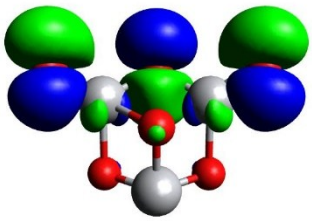
n = 2, NTO 2, water



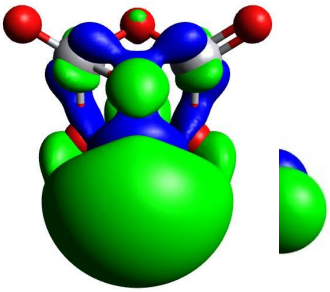
n = 3, NTO 1, gas phase

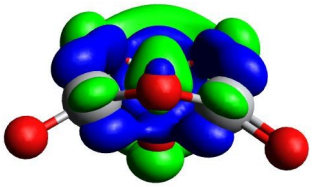


n = 3, NTO 2, gas phase

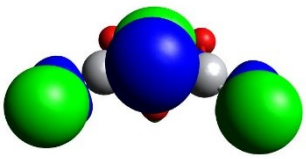


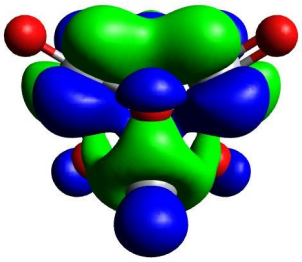
n = 3, NTO 1, water

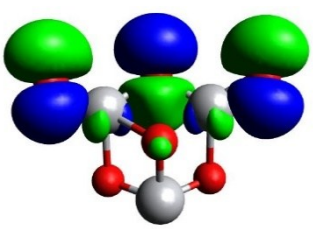


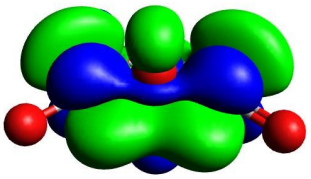


n = 3, NTO 2, water



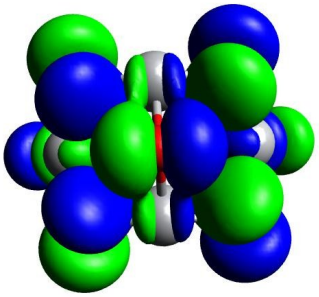


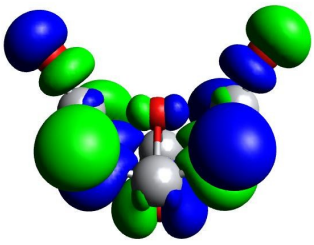


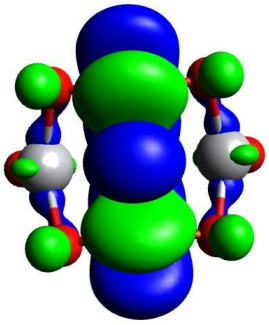


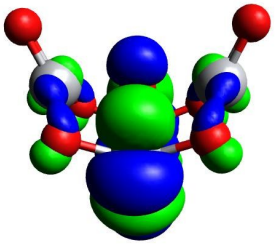
n = 4, NTO 1, gas phase

n = 4, NTO 2, gas phase



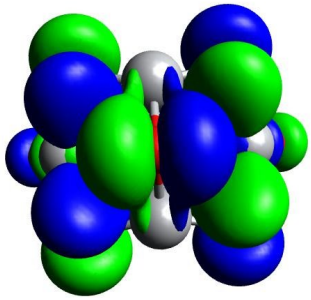


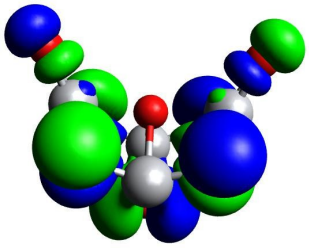


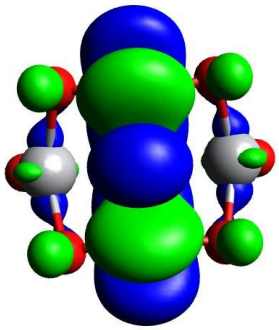


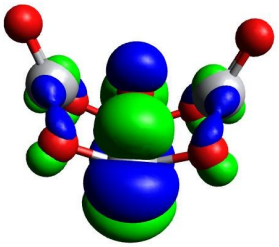
n = 4, NTO 1, water

n = 4, NTO 2, water



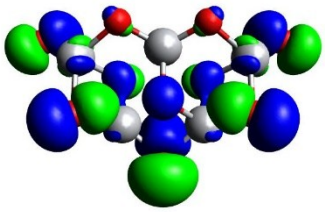




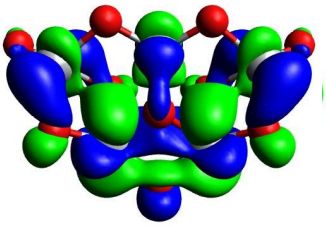


n = 5, NTO 1, gas phase

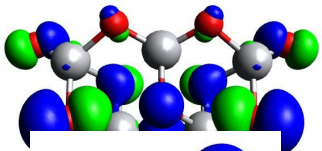
n = 5, NTO 2, gas phase

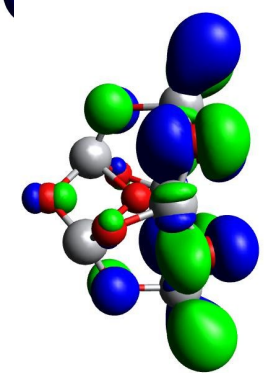


n= 5, NTO 1, water

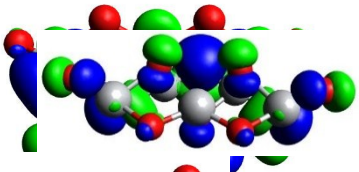


n = 5, NTO 2, water

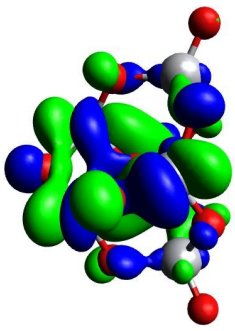


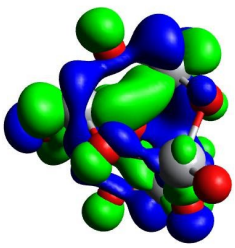


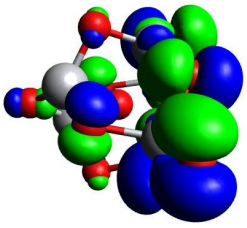
n = 6, NTO 1, gas phase



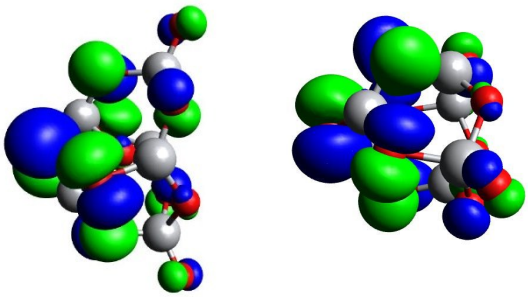
n = 6, NTO 2, gas phase



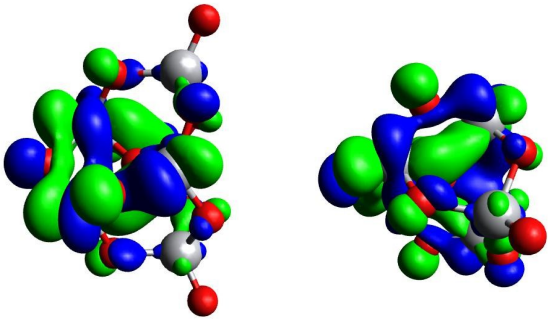




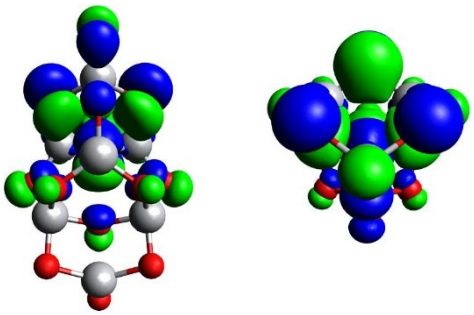
n = 6, NTO 1, water



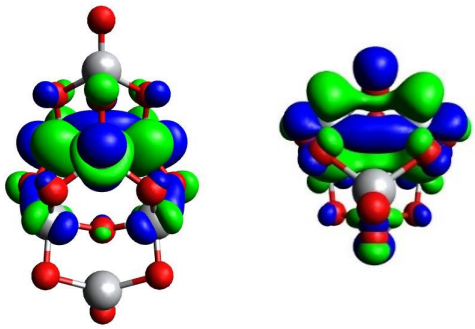
n = 6, NTO 2, water



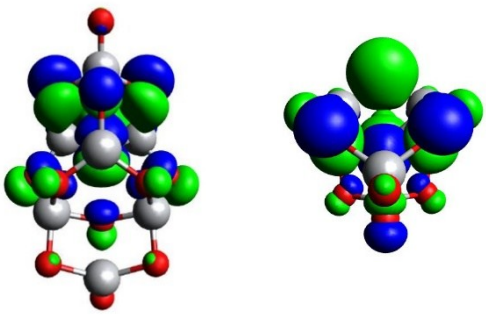
n = 7, NTO 1, gas phase



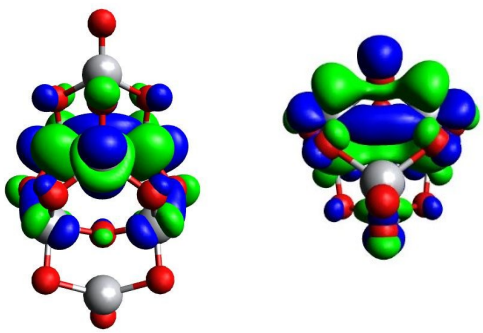
n = 7, NTO 2, gas phase



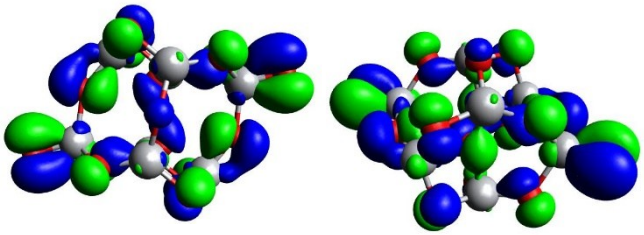
n = 7, NTO 1, water



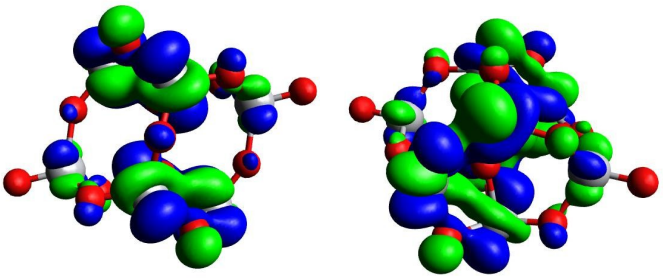
n = 7, NTO 2, water



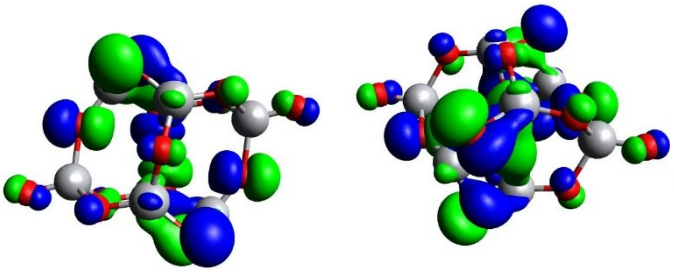
n = 8, NTO 1, gas phase



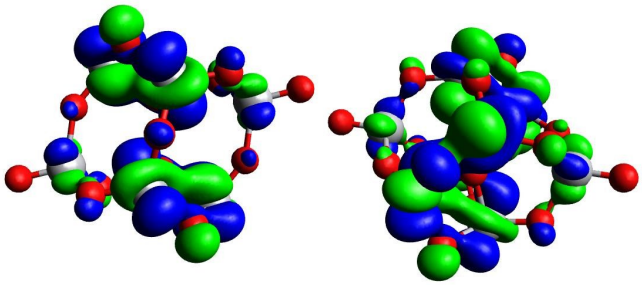
n = 8, NTO 2, gas phase



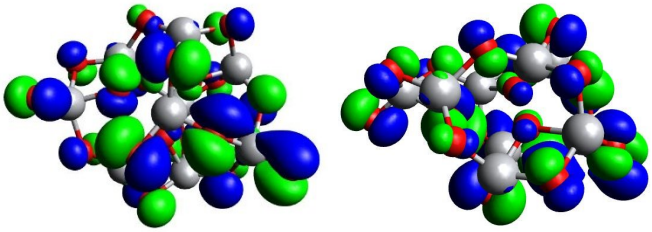
n = 8, NTO 1, water



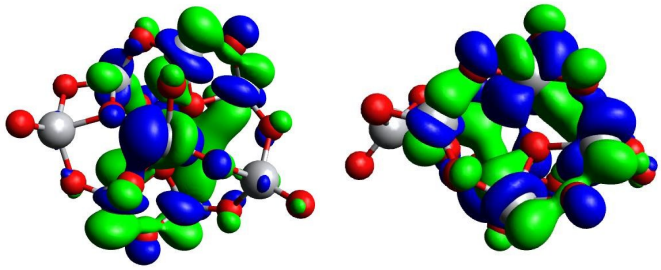
n = 8, NTO 2, water



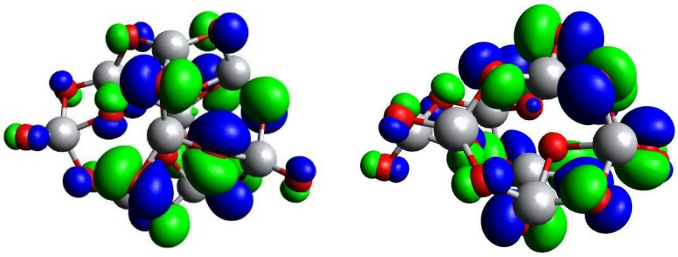
n = 9, NTO 1, gas phase



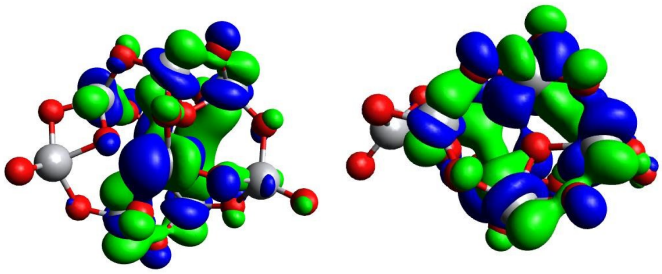
n = 9, NTO 2, gas phase



n = 9, NTO 1, water

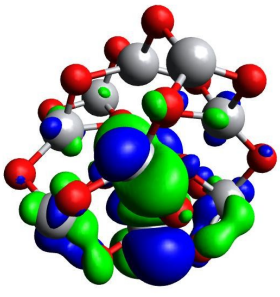


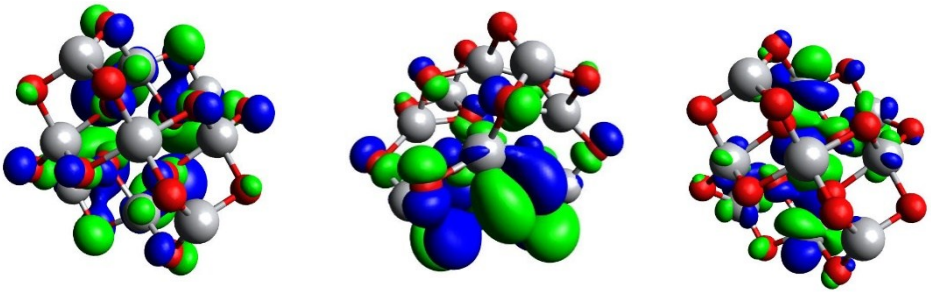
n = 9, NTO 2, water



n = 10, NTO 1, gas phase

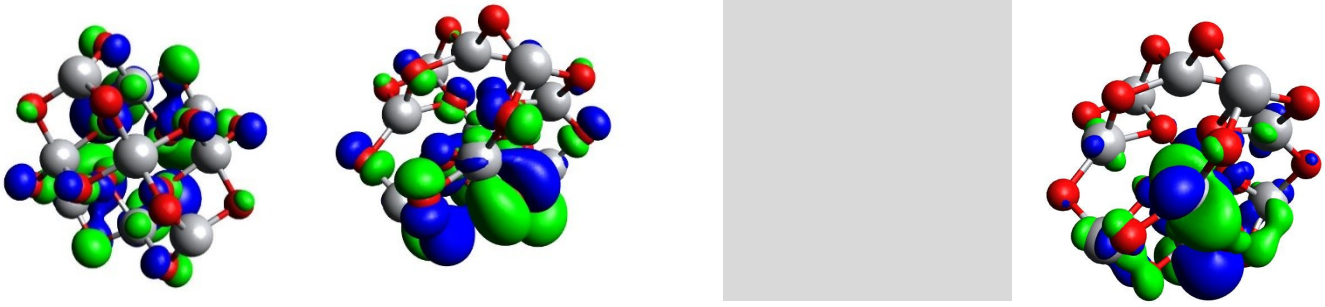
n = 10, NTO 2, gas phase





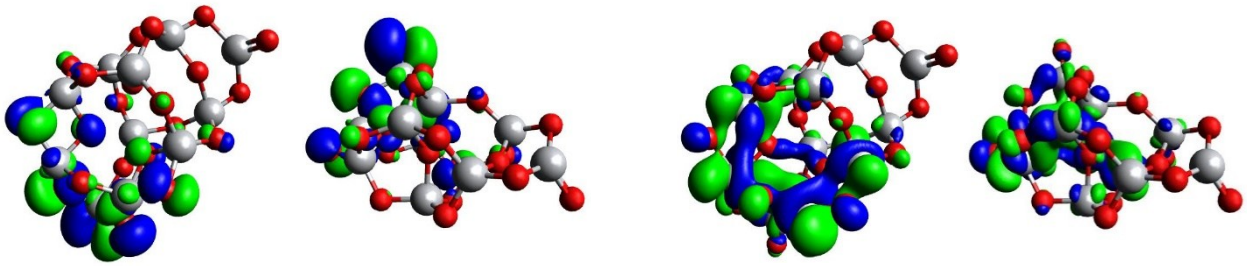
n = 10, NTO 1, water

n = 10, NTO 2, water



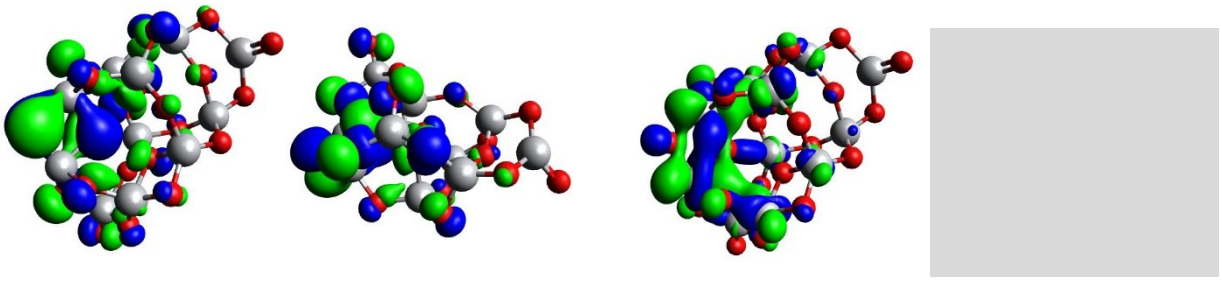
n = 11, NTO 1, gas phase

n = 11, NTO 2, gas phase



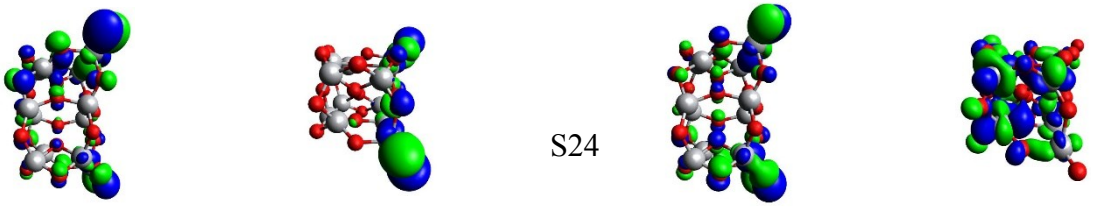
n = 11, NTO 1, water

n = 11, NTO 2, water

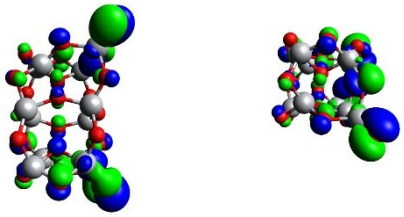


n = 12, NTO 1, gas phase

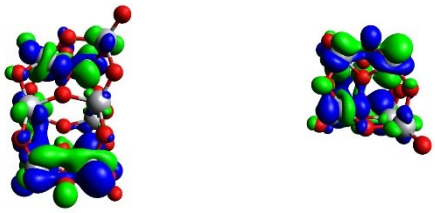
n = 12, NTO 2, gas phase



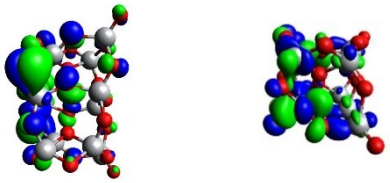
n = 12, NTO 3, gas phase



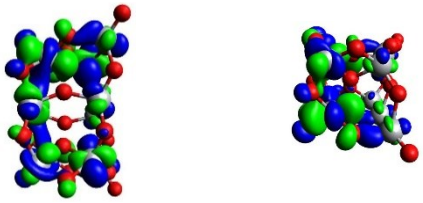
n = 12, NTO 4, gas phase



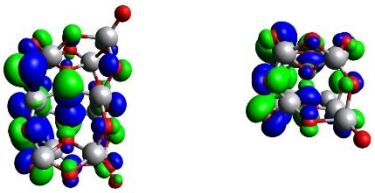
n = 12, NTO 1, water



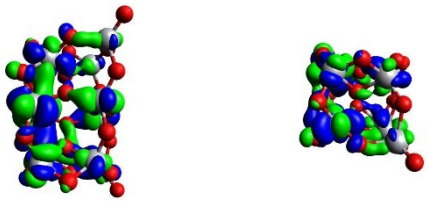
n = 12, NTO 2, water



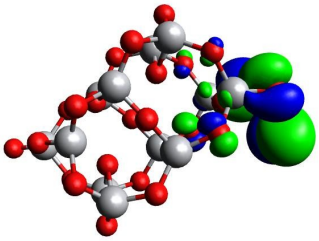
n = 12, NTO 3, water



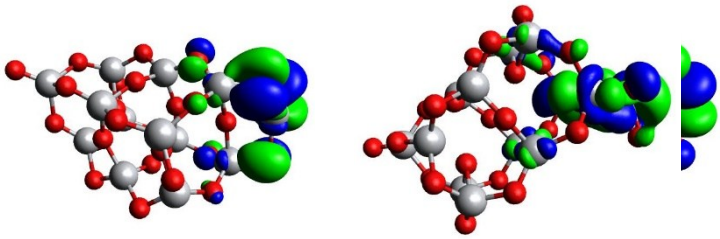
n = 12, NTO 4, water



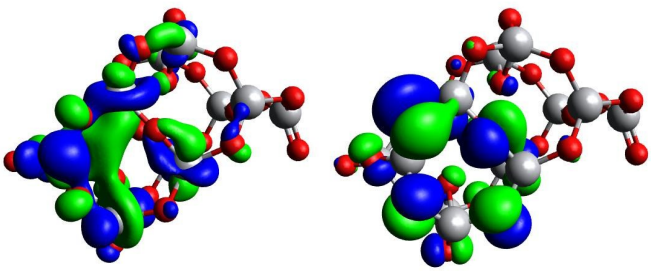
n = 13, NTO 1, gas phase



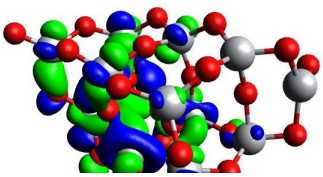
n = 13, NTO 2, gas phase

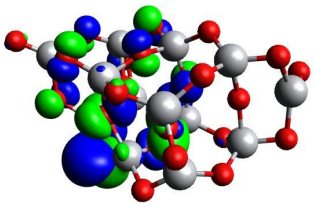


n = 13, NTO 1, water



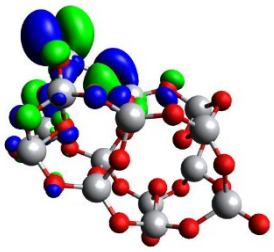
n = 13, NTO 2, water





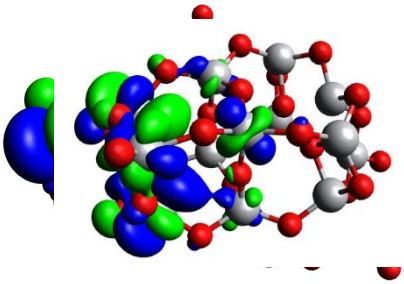
n = 14, NTO 1, gas phase

n = 14, NTO 2, gas phase

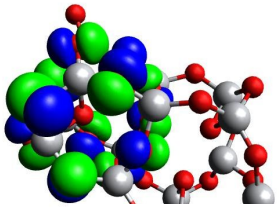


n = 14, NTO 1, water

n = 14, NTO 2, water

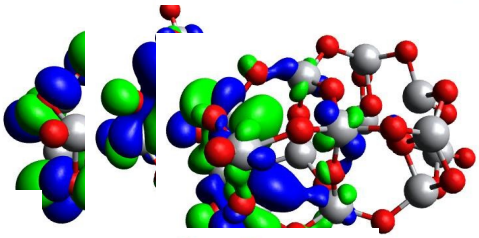


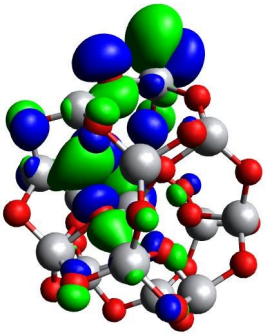
n = 15, gas phase

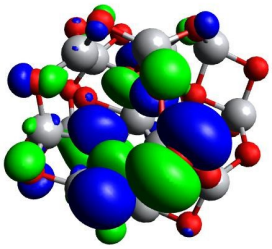


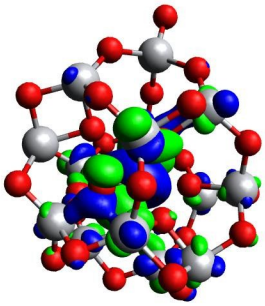
NTO 1, gas phase

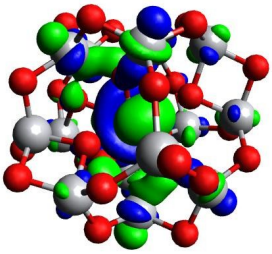
n = 15, NTO 2, gas phase





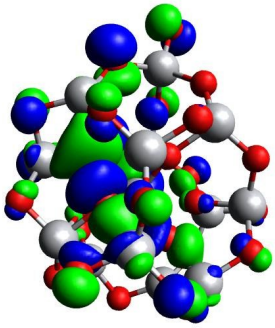






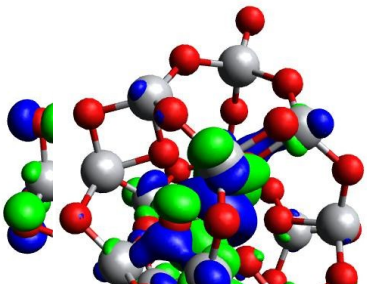
n = 15, NTO 1, water

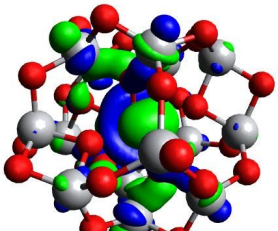
n = 15, NTO 2, water

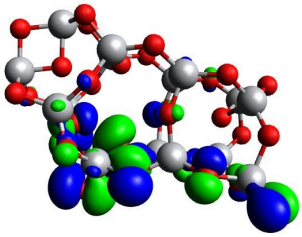


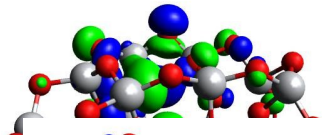
n = 16, NTO 1, gas phase

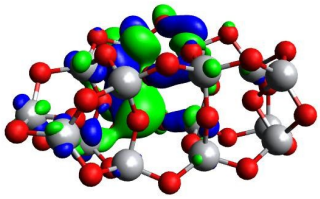
n = 16, NTO 2, gas phase

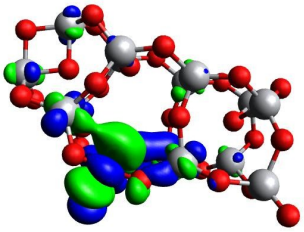






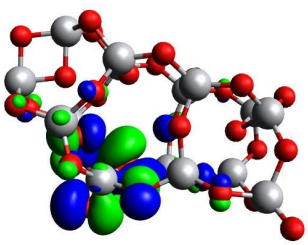


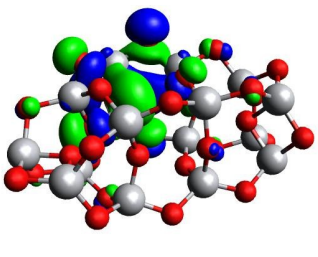


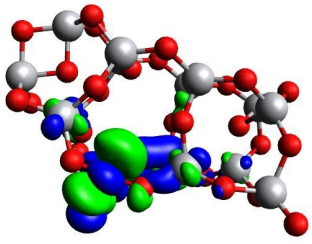


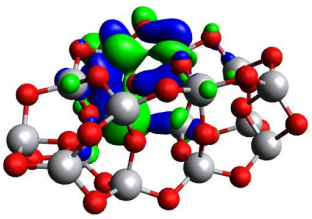
n = 16, NTO 1, water

n = 16, NTO 2, water

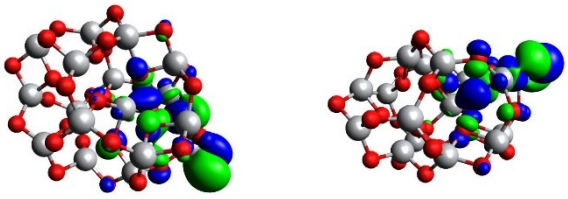




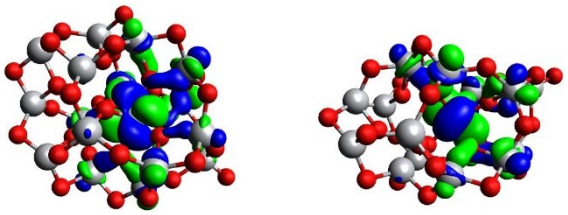




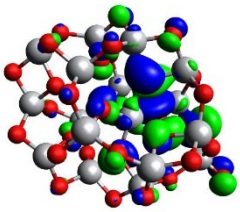
n = 17, NTO 1, gas phase



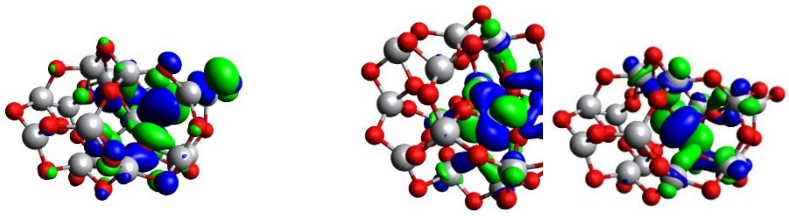
n = 17, NTO 2, gas phase



n = 17, NTO 1, water

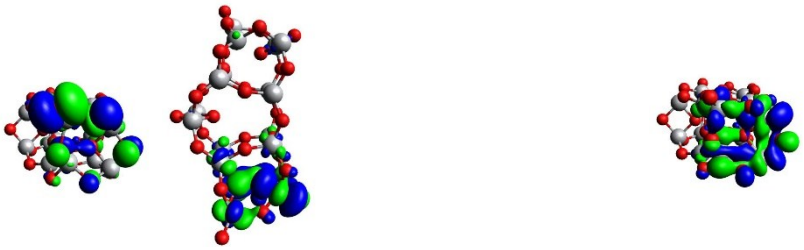


n= 17, NTO 2, water



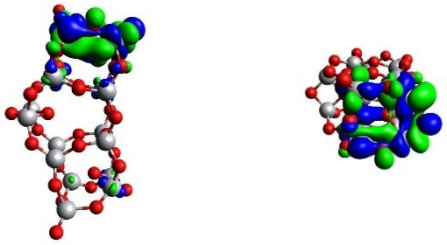
n = 18, NTO 1, gas phase

n = 18, NTO 2, gas phase

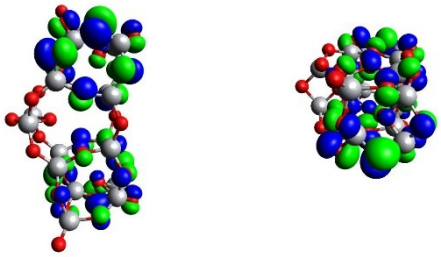


n = 18, NTO 3, gas phase

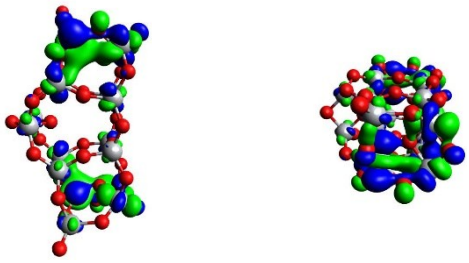
n = 18, NTO 4, gas phase



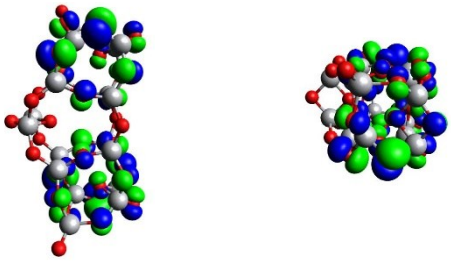
n = 18, NTO 1, water



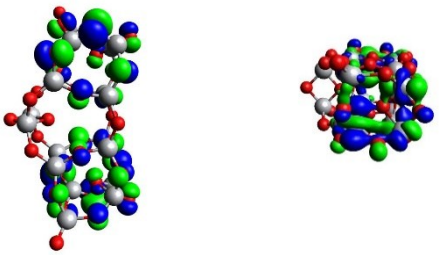
n = 18, NTO 2, water



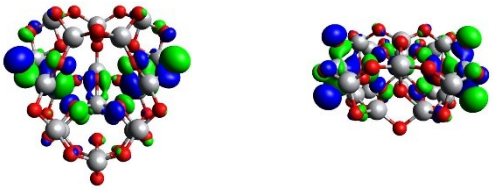
n = 18, NTO 3, water



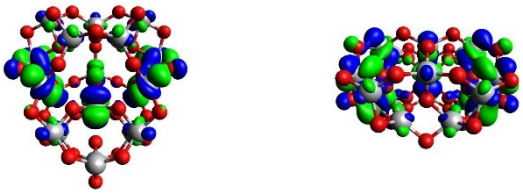
n = 18, NTO 4, water



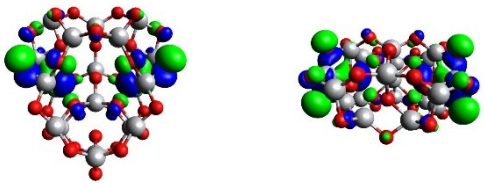
n = 19, NTO 1, gas phase



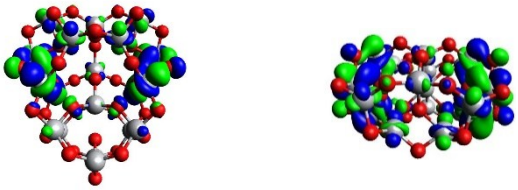
n = 19, NTO 2, gas phase



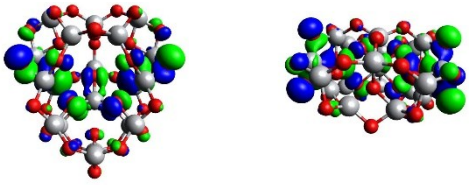
n = 19, NTO 3, gas phase



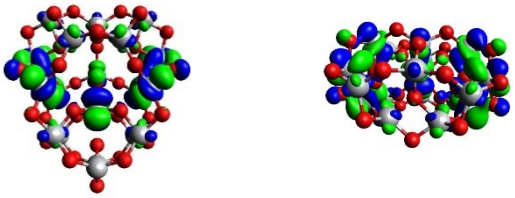
n = 19, NTO 4, gas phase



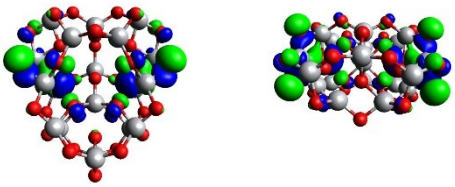
n = 19, NTO 1, water



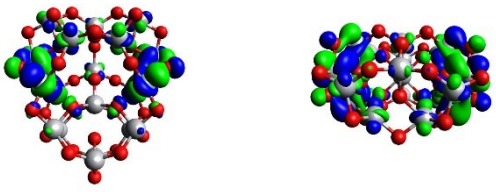
n = 19, NTO 2, water



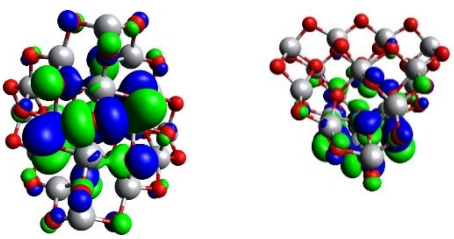
n = 19, NTO 3, water



n = 19, NTO 4, water

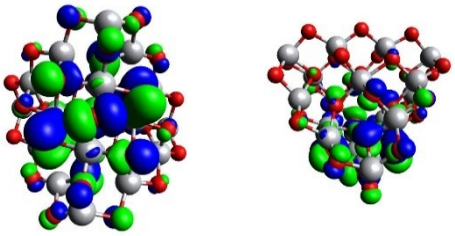


n = 20, NTO 1, gas phase



n = 20, NTO 2, gas phase

n = 20, NTO 1, water



n = 20, NTO 2, water

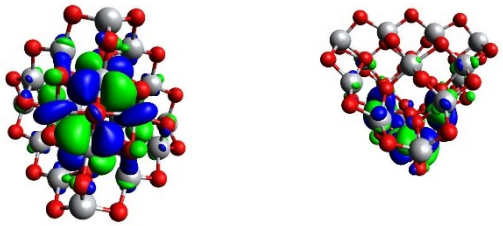
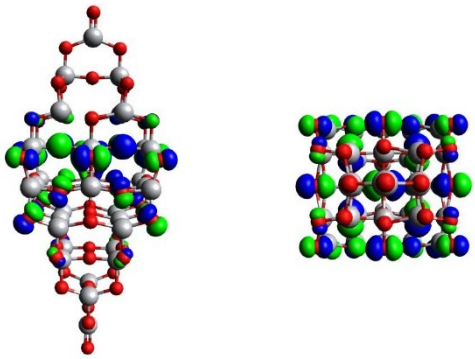
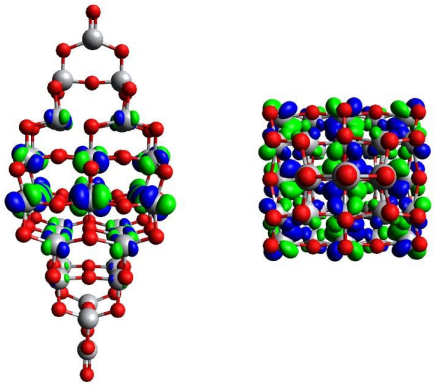


Fig. S3. Natural transition orbitals (NTOs) for $(TiO_2)_n$ nanoparticles with n = 35, 78, 84, 84-I-3-2, 97, 165 (anatase), and 51 (rutile) at the TDDFT PBEx and PBE0 levels, in the gas phase and in water solvent. The grey and red spheres represent titanium and oxygen atoms, respectively.

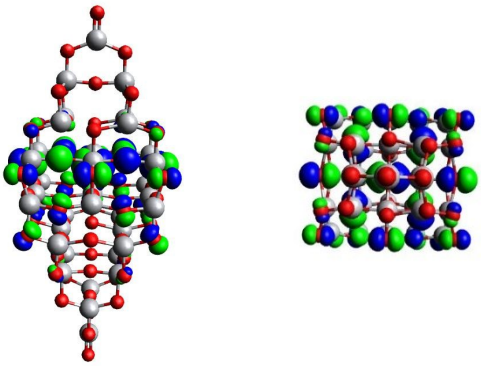
n = 35, PBEx, NTO 1, gas phase



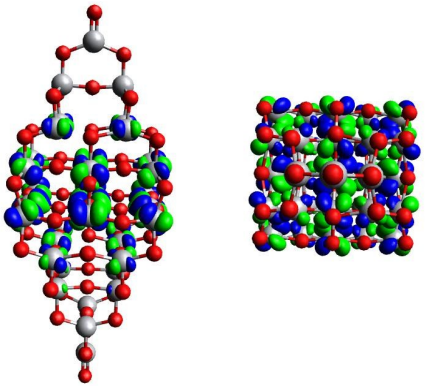
n = 35, PBEx, NTO 2, gas phase



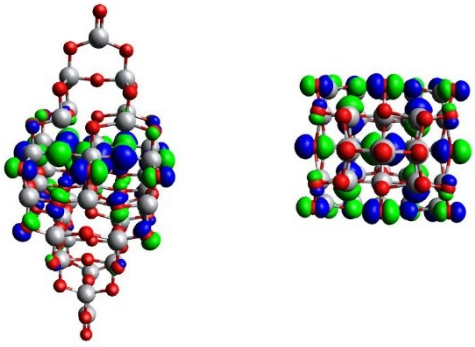
n = 35, PBEx, NTO 1, water



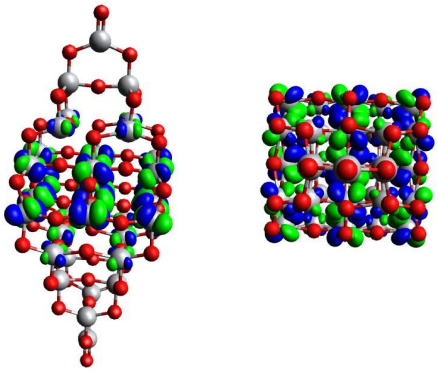
n = 35, PBEx, NTO 2, water



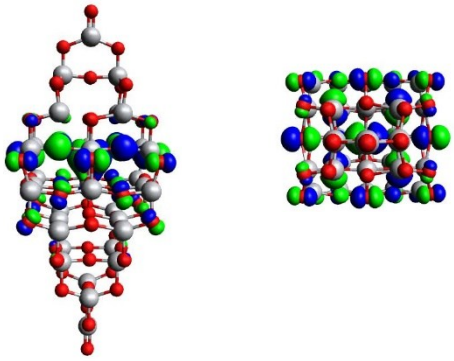
n = 35, PBE0, NTO 1, gas phase



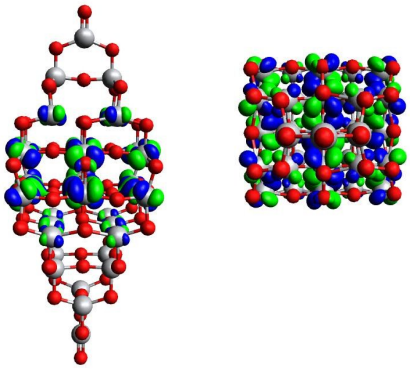
n = 35, PBE0, NTO 2, gas phase



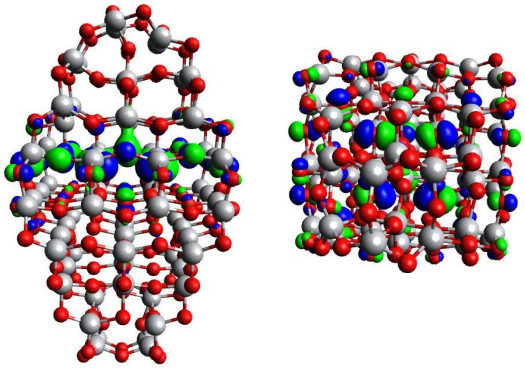
n = 35, PBE0, NTO 1, water



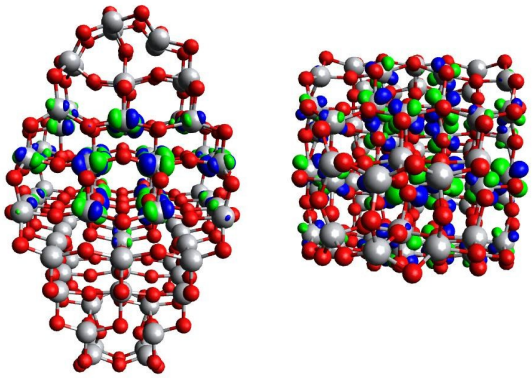
n = 35, PBE0, NTO 2, water



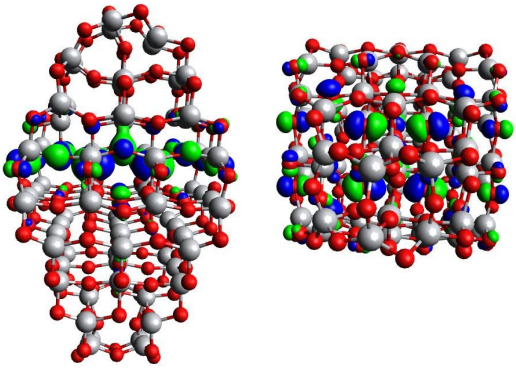
n = 78, PBEx, NTO 1, gas phase



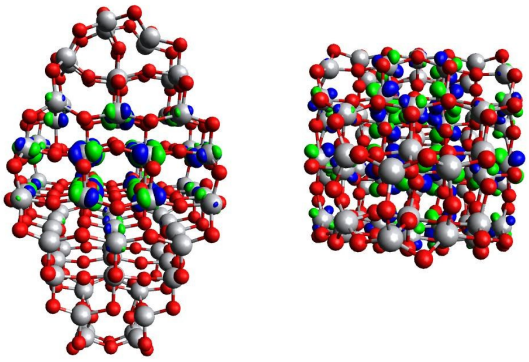
n = 78, PBEx, NTO 2, gas phase



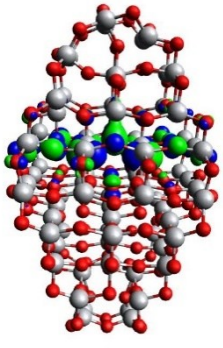
n = 78, PBEx, NTO 1, water



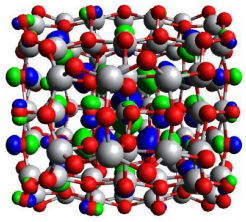
n = 78, PBEx, NTO 2, water



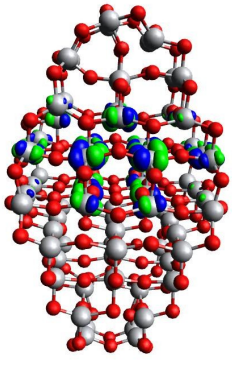
= 78,



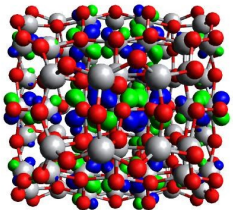
n = 78, PBE0, NTO 1, PBE0, NTO 2, gas



gas phase

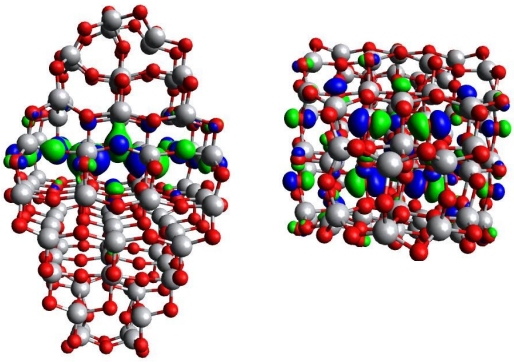


phase

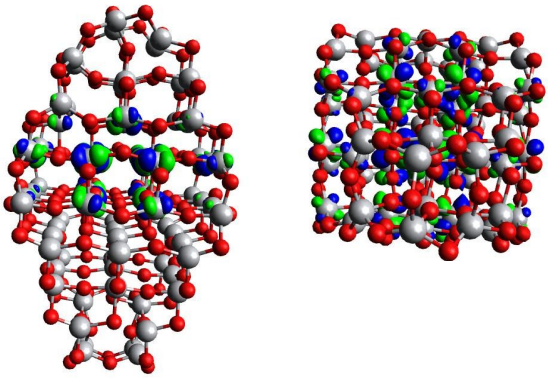


n

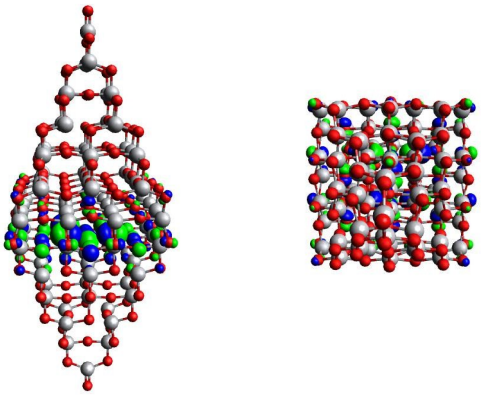
n = 78, PBE0, NTO 1, water



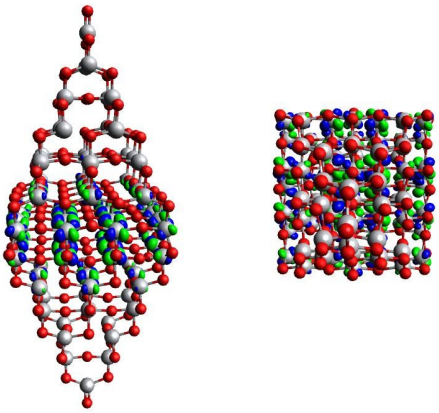
n = 78, PBE0, NTO 2, water



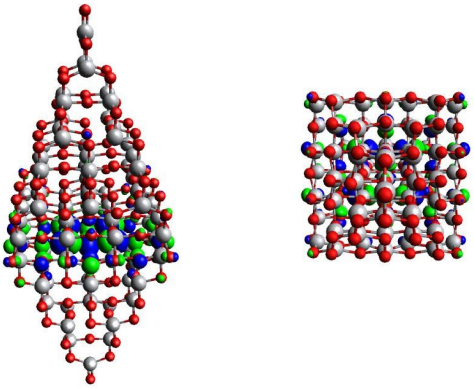
n = 84, PBEx, NTO 1, gas phase



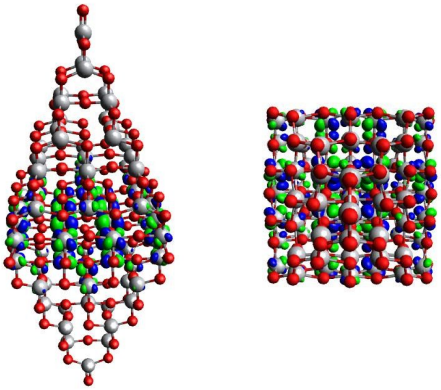
n = 84, PBEx, NTO 2, gas phase



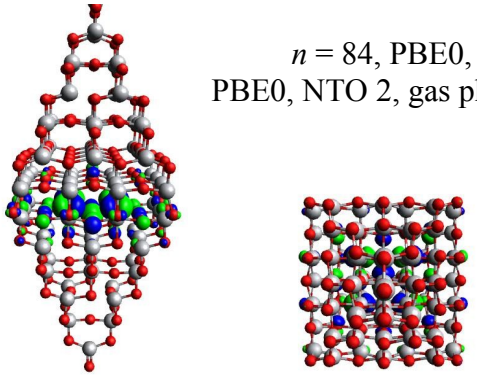
n = 84, PBEx, NTO 1, water



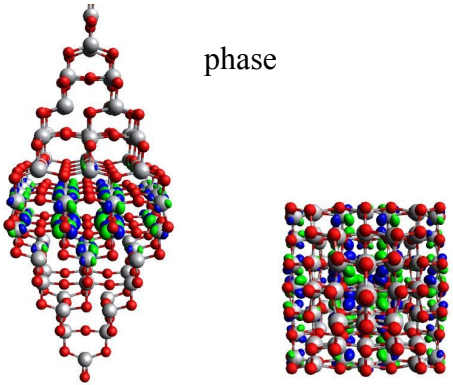
n = 84, PBEx, NTO 2, water



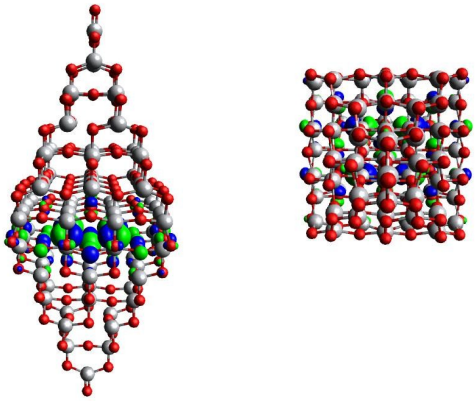
n = 84, PBE0, NTO 1, gas phase



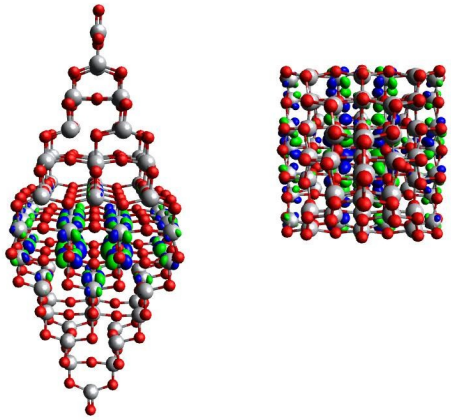
n = 84, PBE0, NTO 2, gas phase



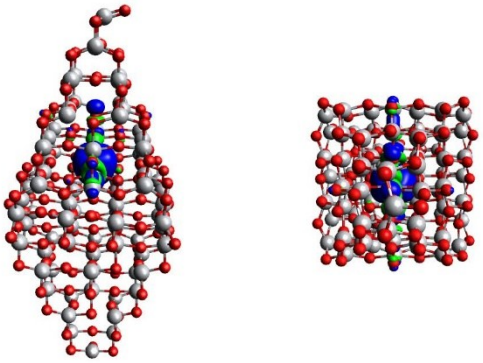
n = 84, PBE0, NTO 1, water



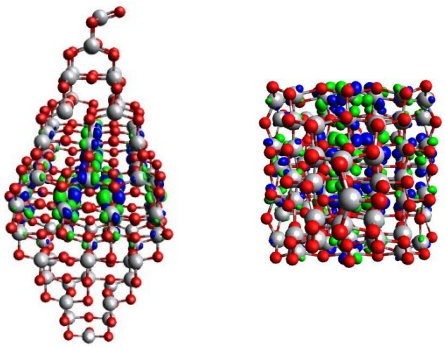
n = 84, PBE0, NTO 2, water



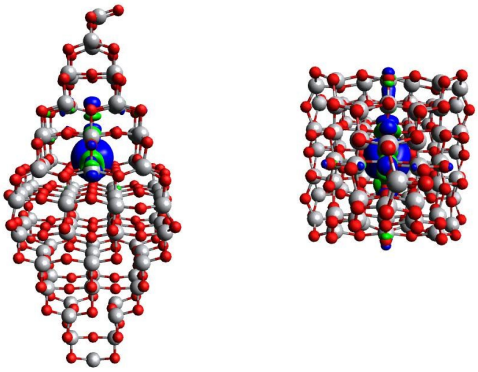
n = 84-I-3-2, PBEx, NTO 1, gas phase



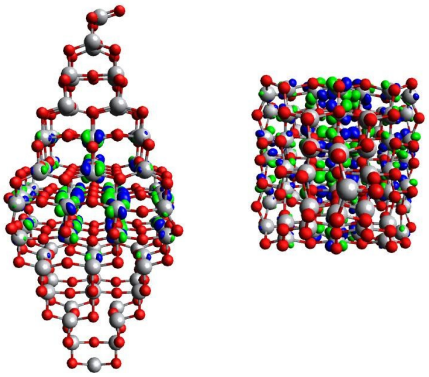
n = 84-I-3-2, PBEx, NTO 2, gas phase



n = 84-I-3-2, PBEx, NTO 1, water

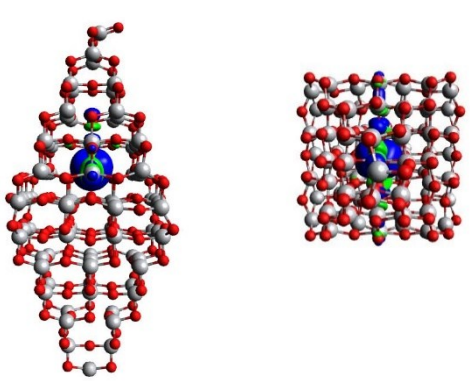


n = 84-I-3-2, PBEx, NTO 2, water

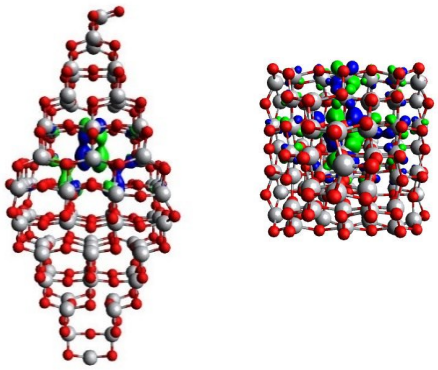


n = 84-I-3-2, PBE0, NTO 1, gas phase

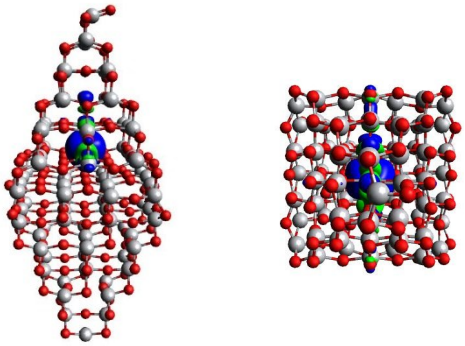
n = 84-I-3-2, PBE0, NTO 2, gas phase



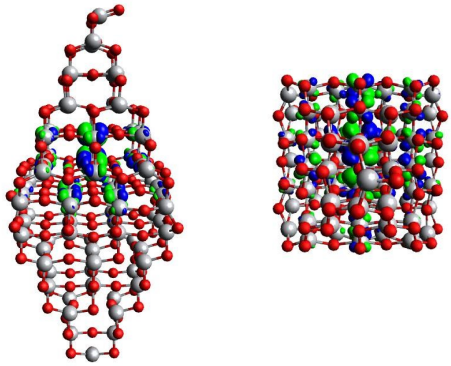
n = 84-I-3-2, PBE0, NTO 1, water



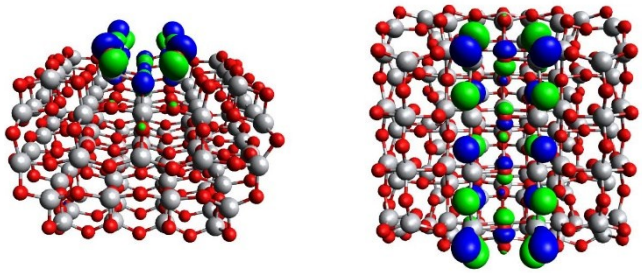
n = 84-I-3-2, PBE0, NTO 2, water



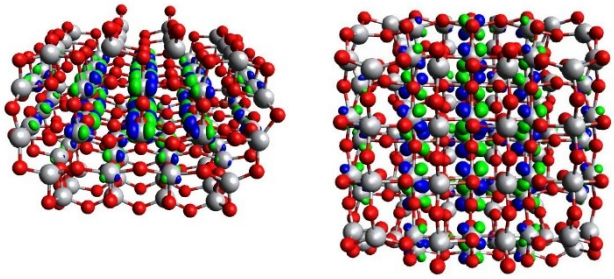
n = 97, PBEx, NTO 1, gas phase



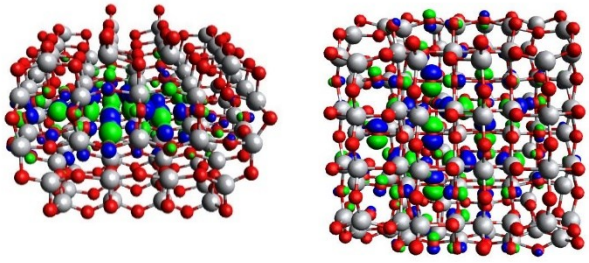
n = 97, PBEx, NTO 2, gas phase



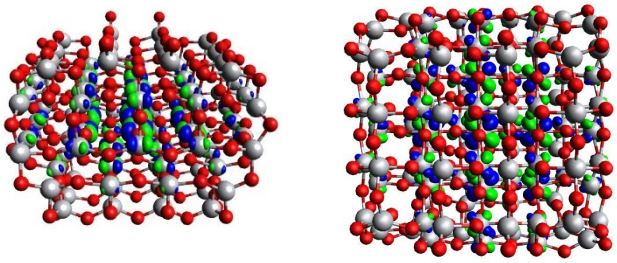
n = 97, PBEx, NTO 1, water



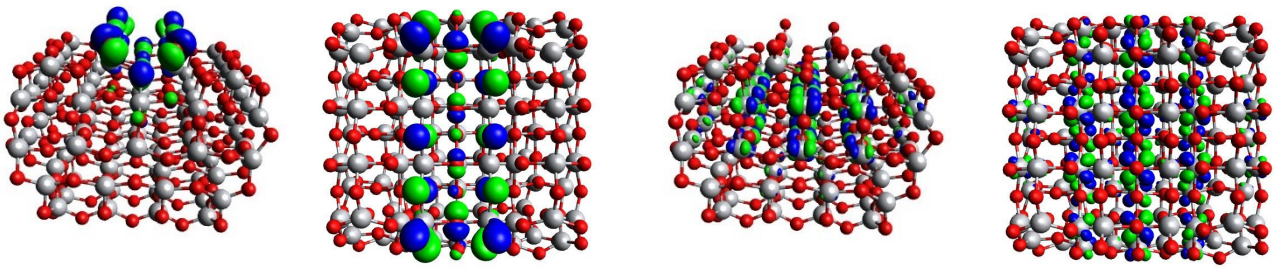
n = 97, PBEx, NTO 2, water



n = 97, PBE0, NTO 1, gas phase

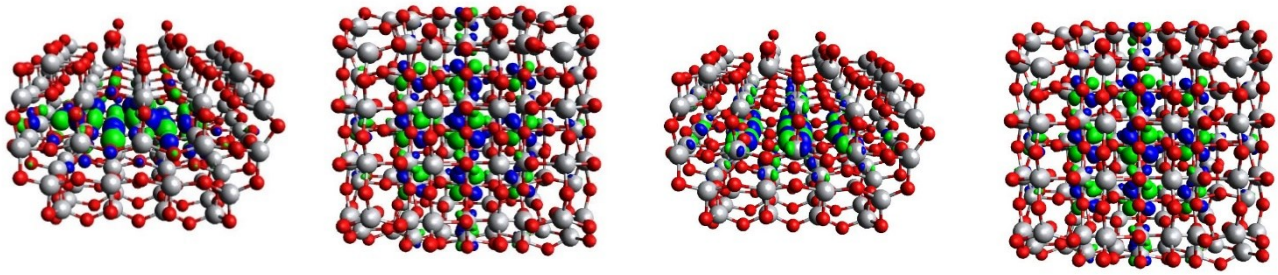


n = 97, PBE0, NTO 2, gas phase



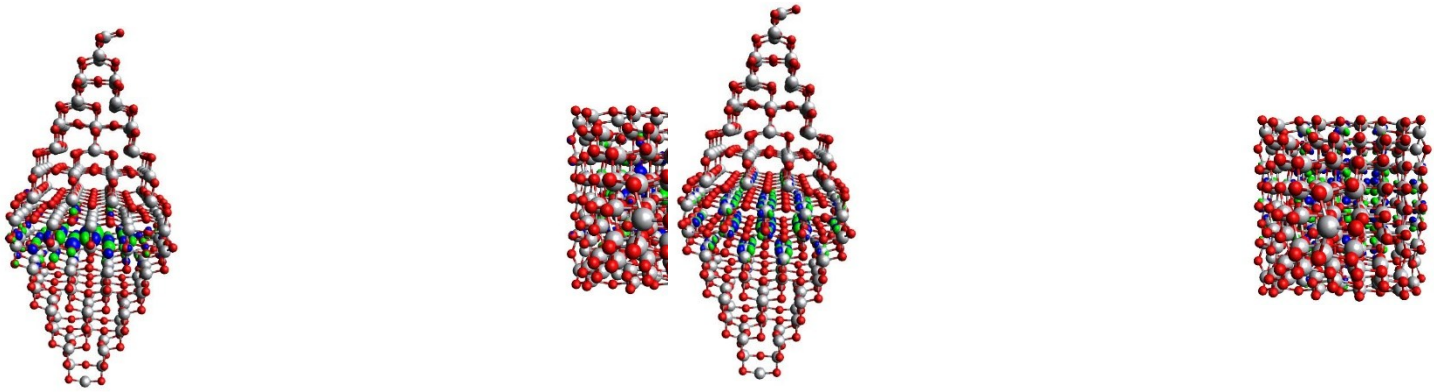
n = 97, PBE0, NTO 1, water

n = 97, PBE0, NTO 2, water



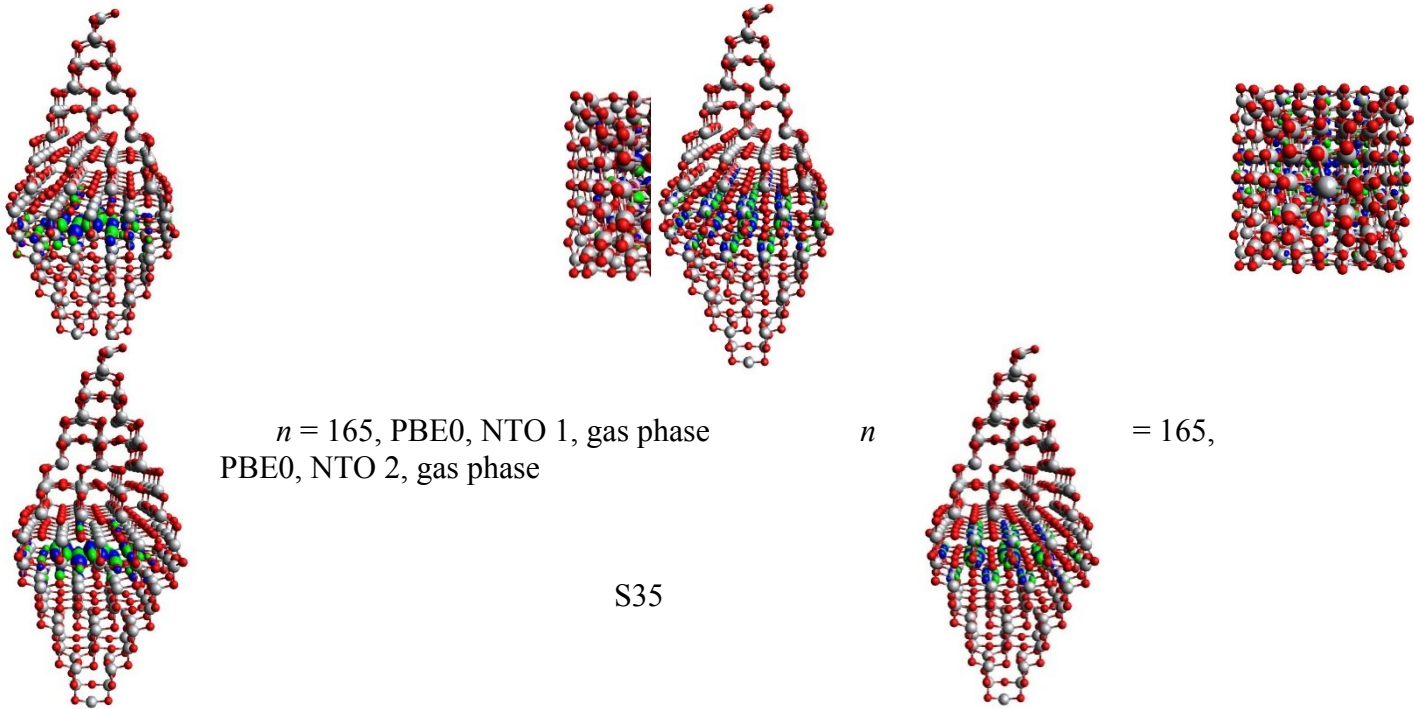
n = 165, PBEx, NTO 1, gas phase

n = 165, PBEx, NTO 2, gas phase



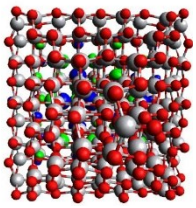
n = 165, PBEx, NTO 1, water

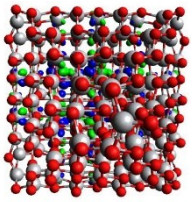
n = 165, PBEx, NTO 2, water



n = 165, PBE0, NTO 1, gas phase

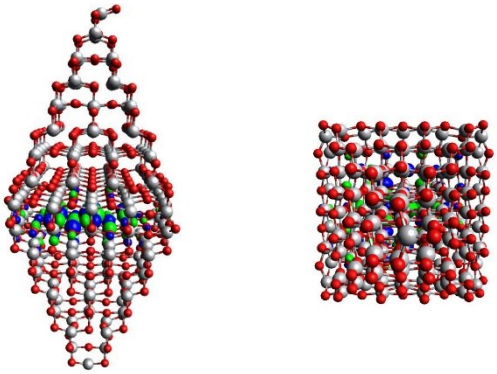
n = 165, PBE0, NTO 2, gas phase

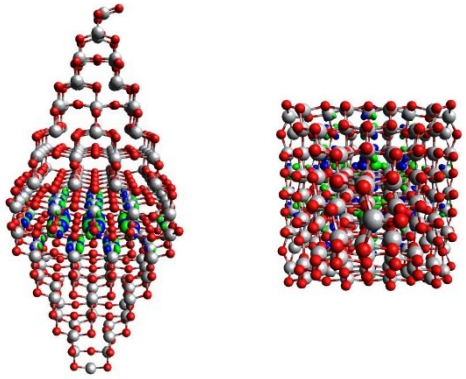




n = 165, PBE0, NTO 1, water

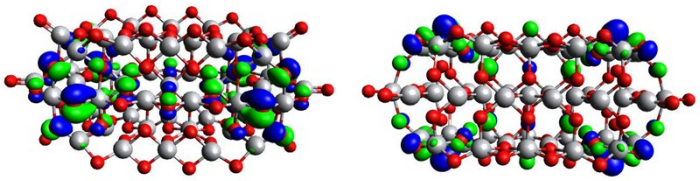
n = 165, PBE0, NTO 2, water

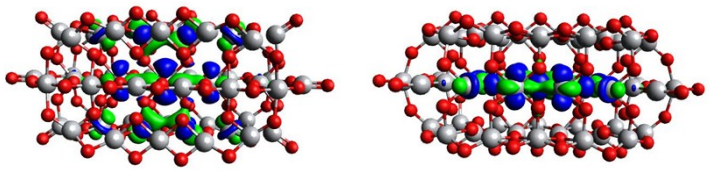




n = 51, PBEx, NTO 1, gas phase

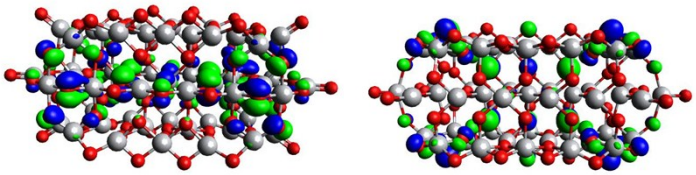
n = 51, PBEx, NTO 2, gas phase

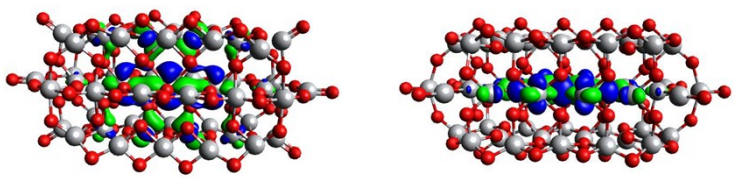




n = 51, PBEx, NTO 1, water

n = 51, PBEx, NTO 2, water





n = 51, PBE0, NTO 1, gas phase

n = 51, PBE0, NTO 2, gas phase

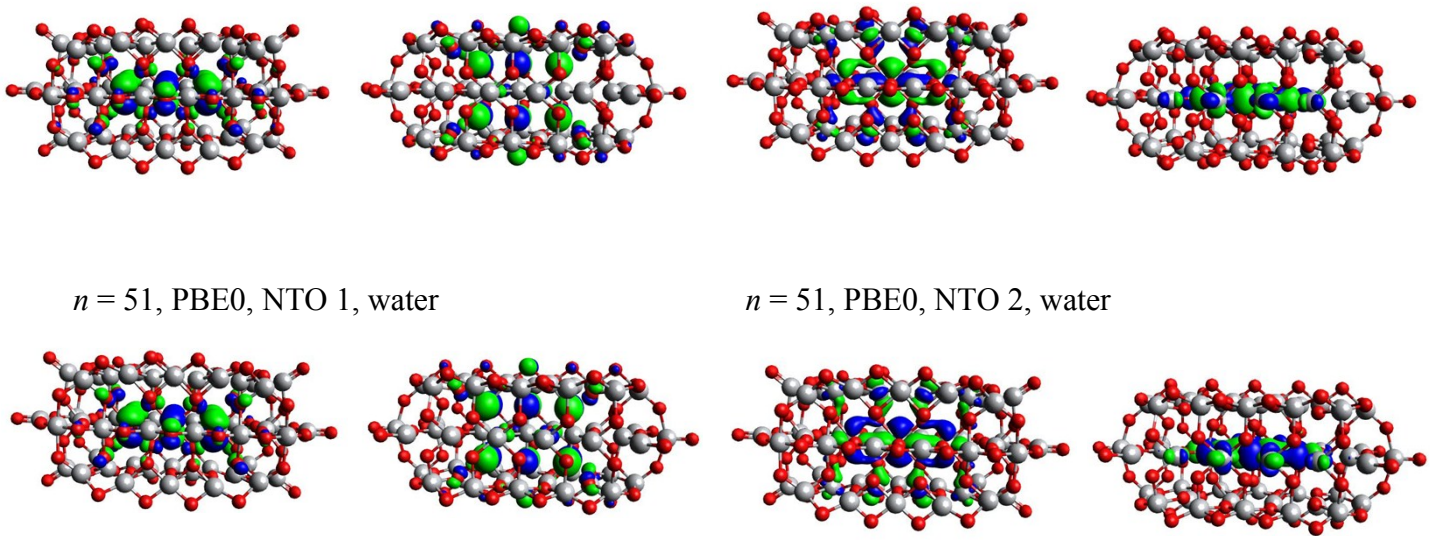
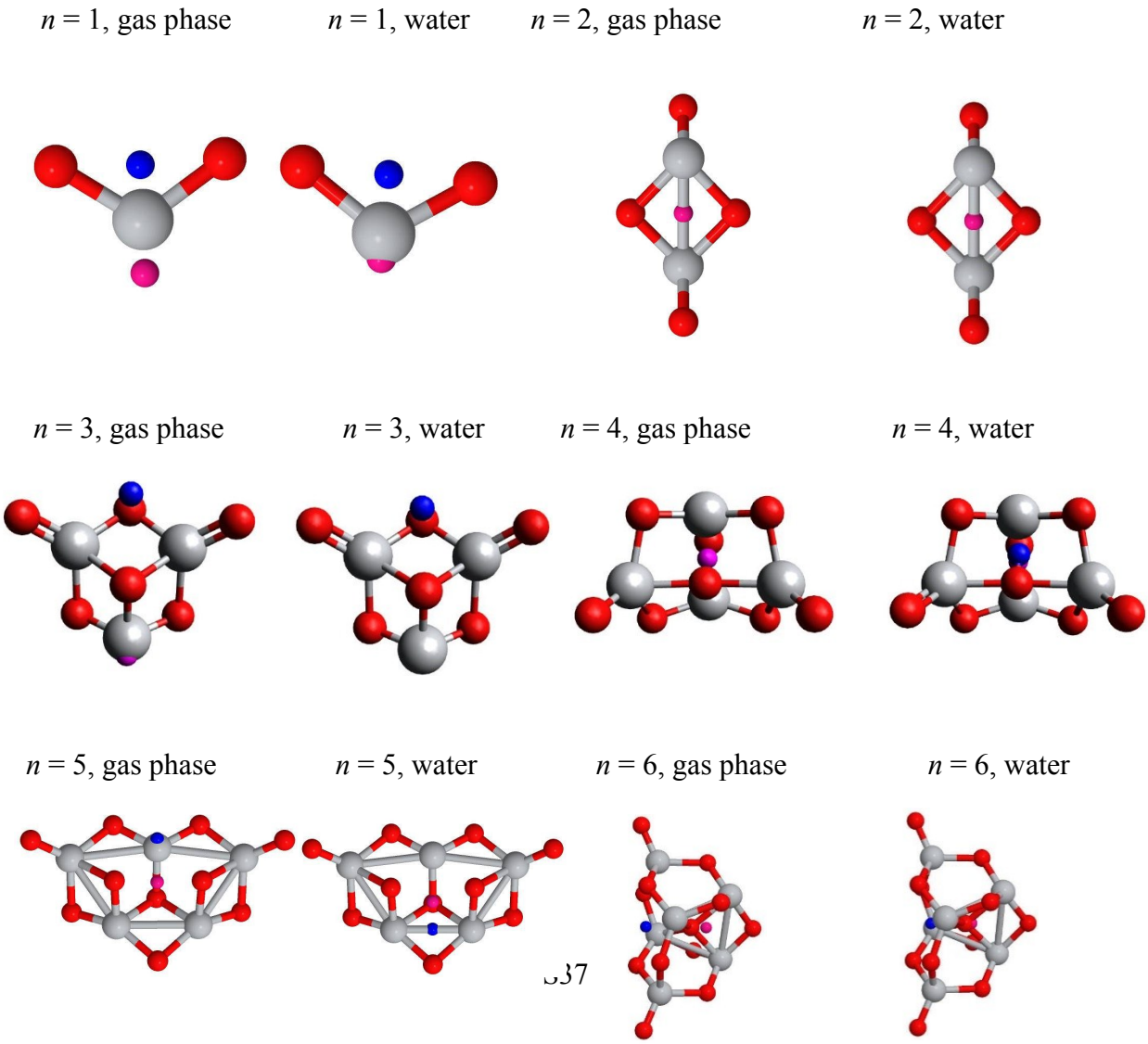
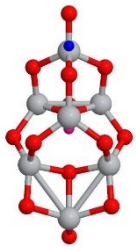


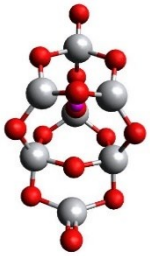
Fig. S4. Centroids for the $(TiO_2)_n$ nanoclusters with n = 1-20 at the TDDFT PBEx level, in the gas phase and in water solvent. The centroids always correspond to the NTOs 1 and 2. The blue and pink spheres represent the positive (hole) and negative (electron) centroids, respectively, whereas the grey and red spheres depict the titanium and oxygen atoms, respectively.



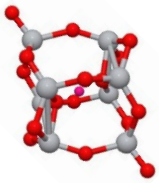
n = 7, gas phase



n = 7, water

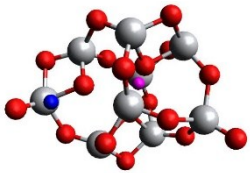


n = 8, gas phase

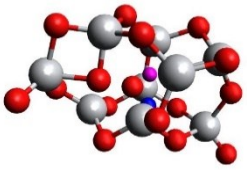


n = 8, water

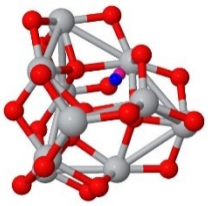
n = 9, gas phase



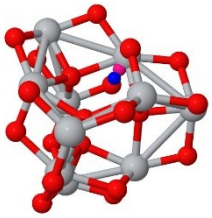
n = 9, water



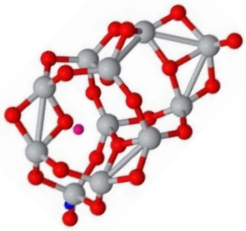
n = 10, gas phase



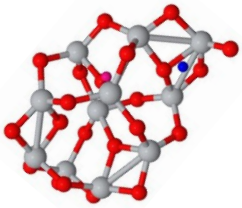
n = 10, water



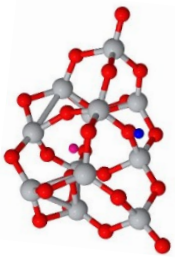
n = 11, gas phase



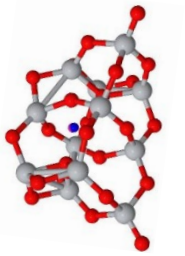
n = 11, water



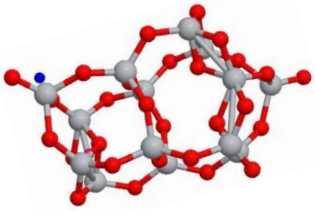
n = 12, gas phase



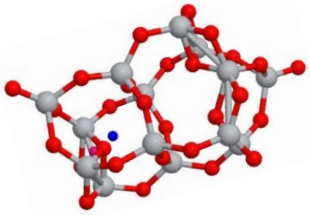
n = 12, water



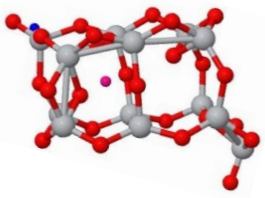
n = 13, gas phase



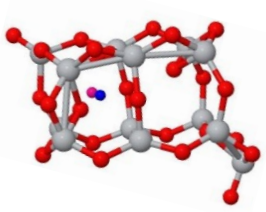
n = 13, water



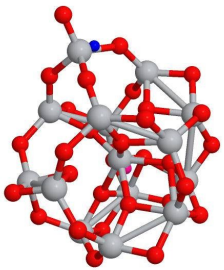
n = 14, gas phase



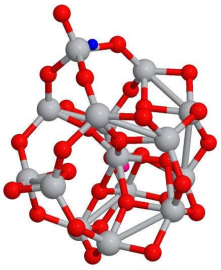
n = 14, water



n = 15, gas phase

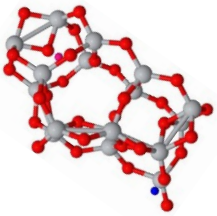


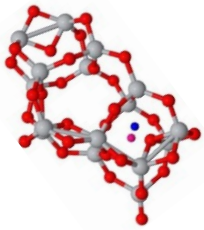
n = 15, water



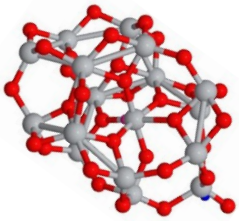
n = 16, gas phase

n = 16, water

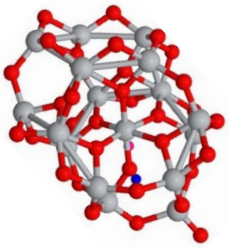




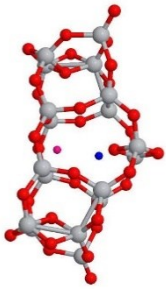
n = 17, gas phase



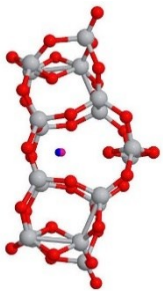
n = 17, water



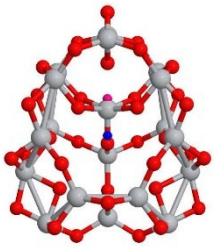
n = 18, gas phase



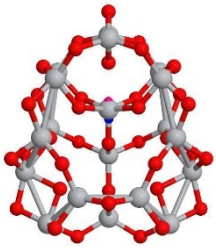
n = 18, water



n = 19, gas phase



n = 19, water



n = 20, gas phase

n = 20, water

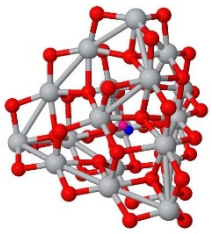
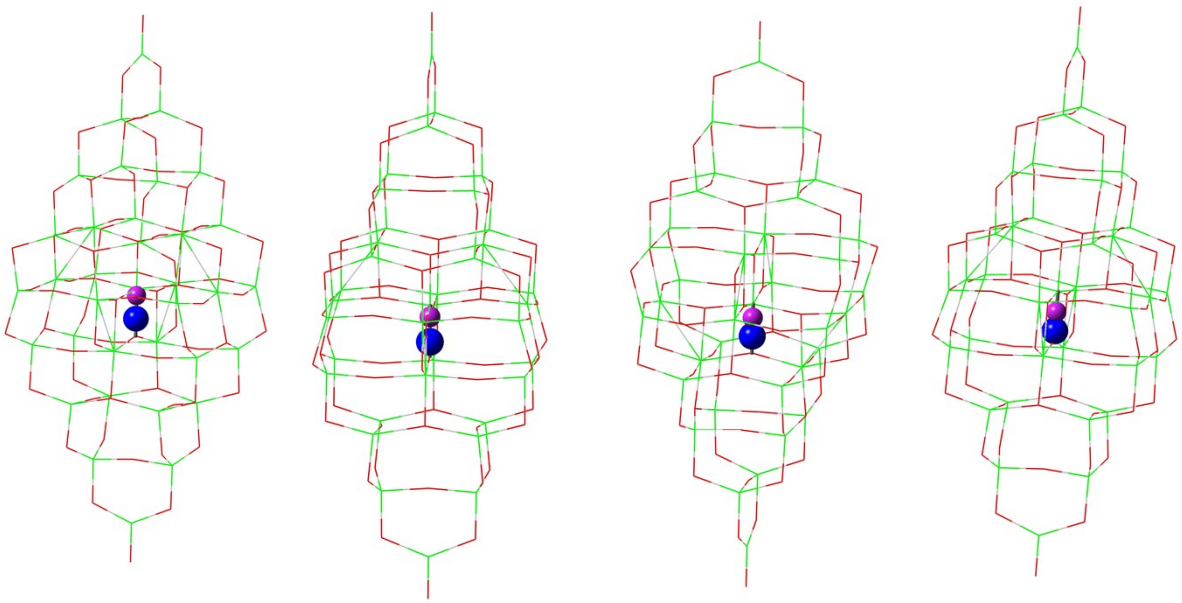
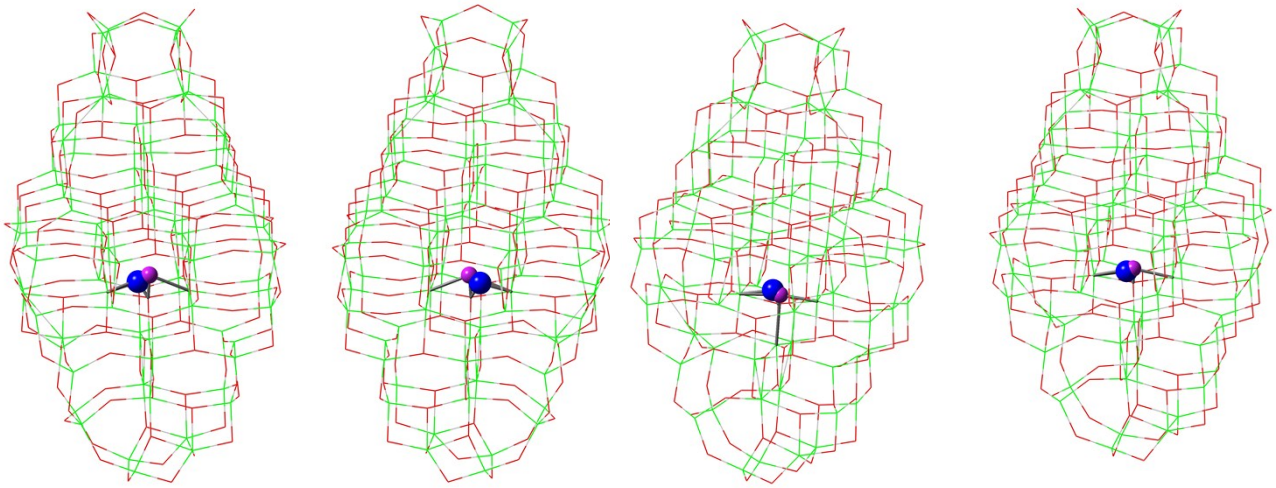


Fig. S5. Centroids for the $(TiO_2)_n$ nanoparticles with n = 35, 78, 84, 84_I-3-2, 97, and 165 (anatase) and n = 51 (rutile) at the TDDFT PBEx and PBE0 levels in the gas phase and in water solvent. The centroids always correspond to the NTOs 1 and 2. The blue and pink spheres represent the positive (hole) and negative (electron) centroids, respectively, whereas the green and red sticks depict the titanium and oxygen atoms, respectively.

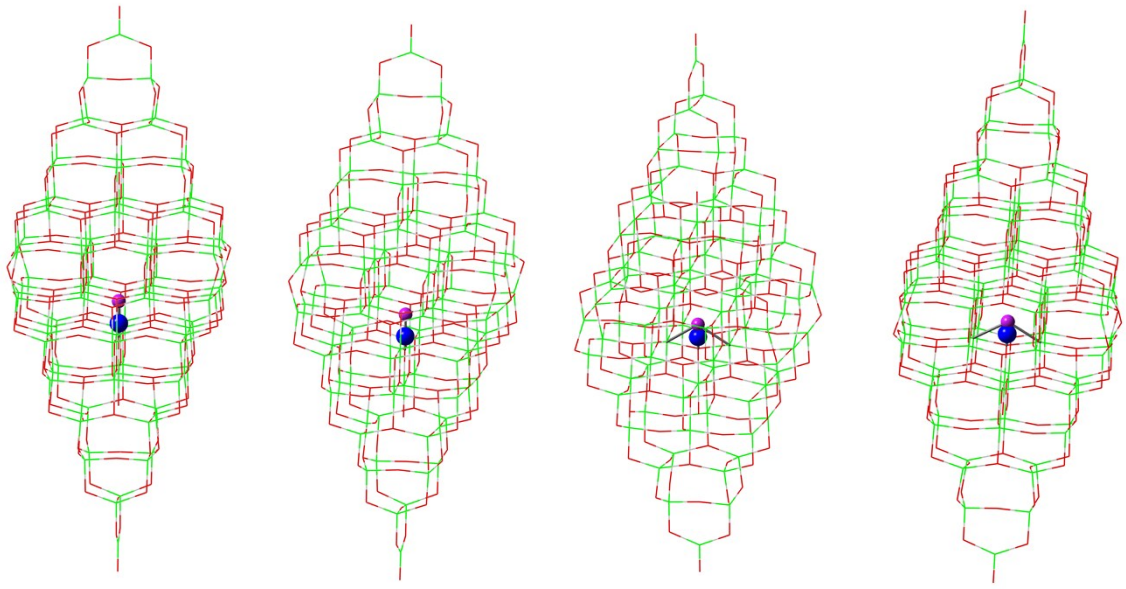
PBEx: n = 35, gas phase n = 35, water PBE0: n = 35, gas phase n = 35, water



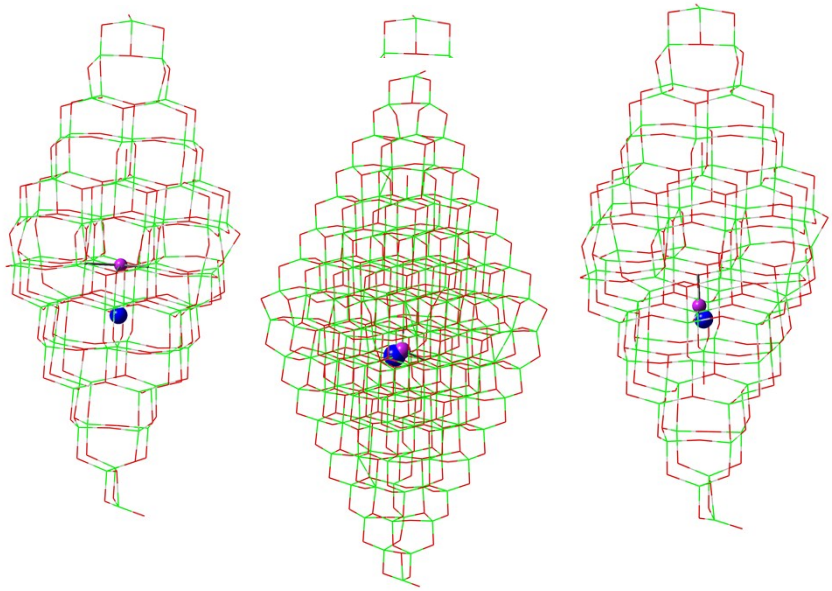
PBEx: n = 78, gas phase n = 78, water PBE0: n = 78, gas phase n = 78, water



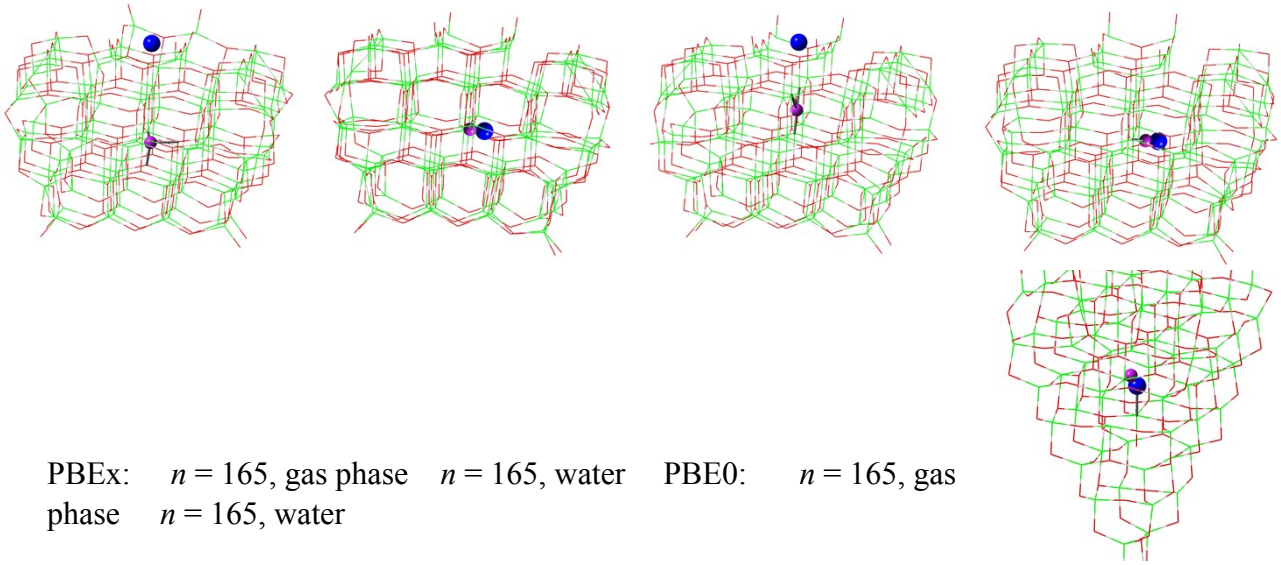
PBEx: n = 84, gas phase n = 84, water PBE0: n = 84, gas phase n = 84, water



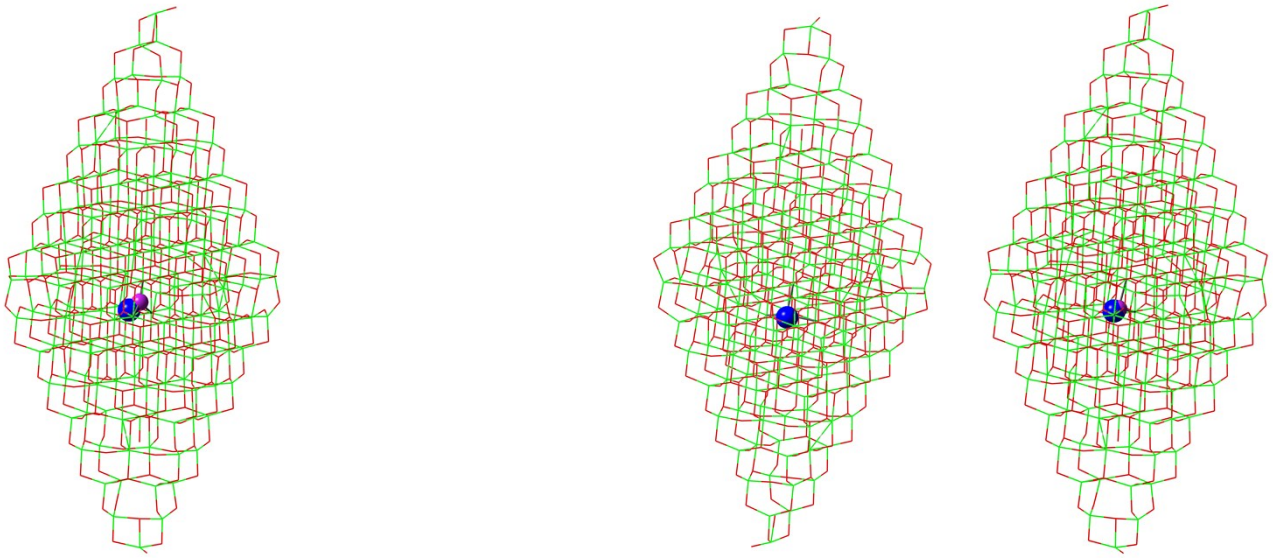
PBEx: n = 84_I-3-2, gas phase n = 84_I-3-2, water PBE0: n = 84_I-3-2, gas phase n = 84_I-3-2, water



PBEx: n = 97, gas phase n = 97, water PBE0: n = 97, gas phase n = 97, water



PBEx: n = 165, gas phase n = 165, water PBE0: n = 165, gas phase n = 165, water



PBEx: n = 51, gas phase n = 51, water PBE0: n = 51, gas phase n = 51, water

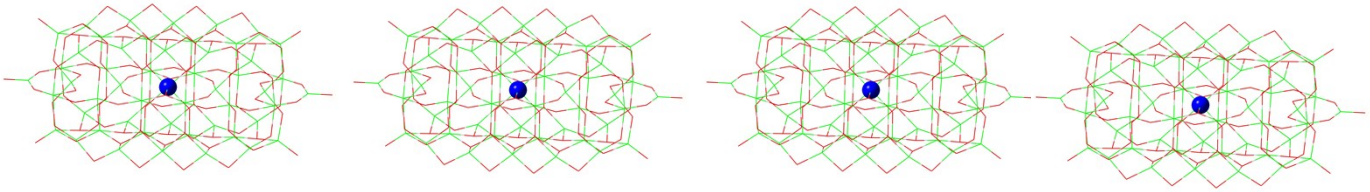
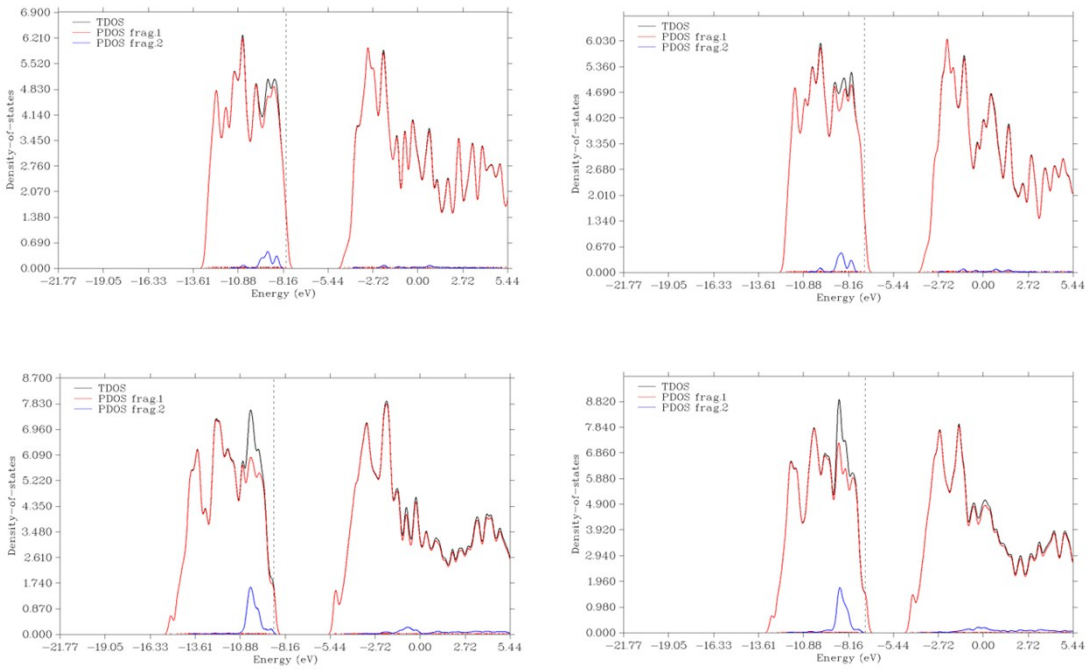
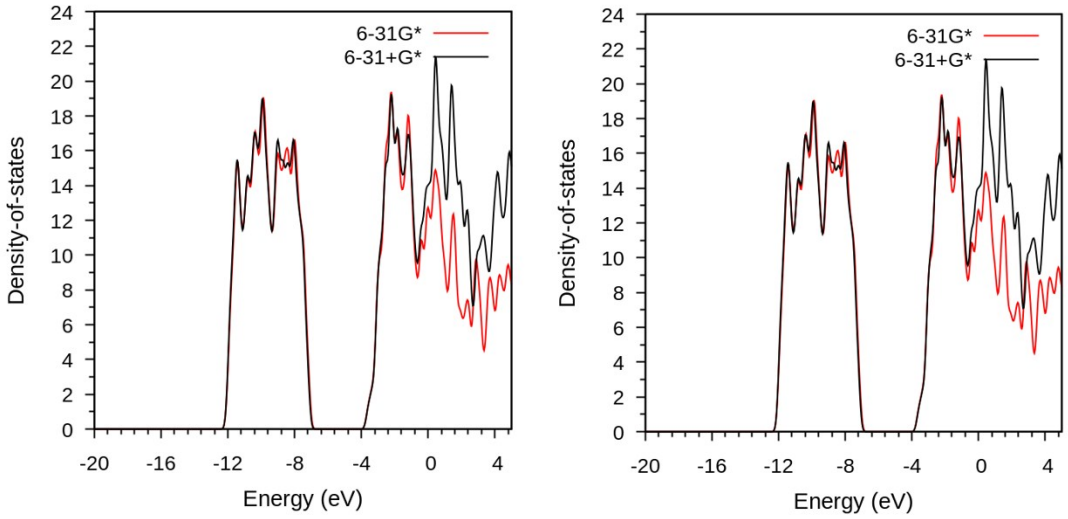


Fig. S6. (a) Plots of the total and partial density of states (DOS) of DFT ground state for n = 35 (upper figures, for gas phase and water solvent on the left and right, respectively) and n = 51 (lower plots, for gas phase and water solvent on the left and right, respectively) nanoparticles, at the PBEx/6-31G* level. Total DOS is shown in black, PDOS for the single-coordinated atoms in blue, and PDOS for the rest of atoms in red. Plots were prepared with the Multiwfn program.[5] (b) Plots of the total DOS of DFT ground state for n = 35 nanoparticles for gas phase and water solvent on the left and right, respectively, at the PBEx/6-31G* and PBEx/6-31+G* levels. Plots were prepared with the GaussSum program.[6]

(a)



(b)



REFERENCES

1 T. Etienne, X. Assfeld and A. Monari, Toward a Quantitative Assessment of Electronic Transitions´ Charge Transfer, *J. Chem. Theory Comput.*, 2014, **10**, 3896-3905.

2 T. Etienne, Probing the Locality of Excited States with Linear Algebra*, J. Chem. Theory Comput.*, 2015, **11**, 1692-1699.

3 R. L. Martin, Natural Transition Orbitals, *J. Chem. Phys.* 2003, **118**, 4775-4777.

4 A. T. Amos and G. G. Hall, Single Determinant Wave Functions*, Proc. R. Soc. Lond. A Math. Phys. Sci.*, 1961, **263**, 483-493.

5 T. Lu and F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comp. Chem.* **2012**, *33*, 580-592.

6 N. M. O'boyle, A. L. Tenderholt, and K. M. Langner, cclib: A Library for Package-Independent Computational Chemistry Algorithms, *J. Comp. Chem.*, **2008**, *29*, 839-845.