The Electronic Structure of Dye-Sensitized TiO_2 Clusters from Many-Body Perturbation Theory

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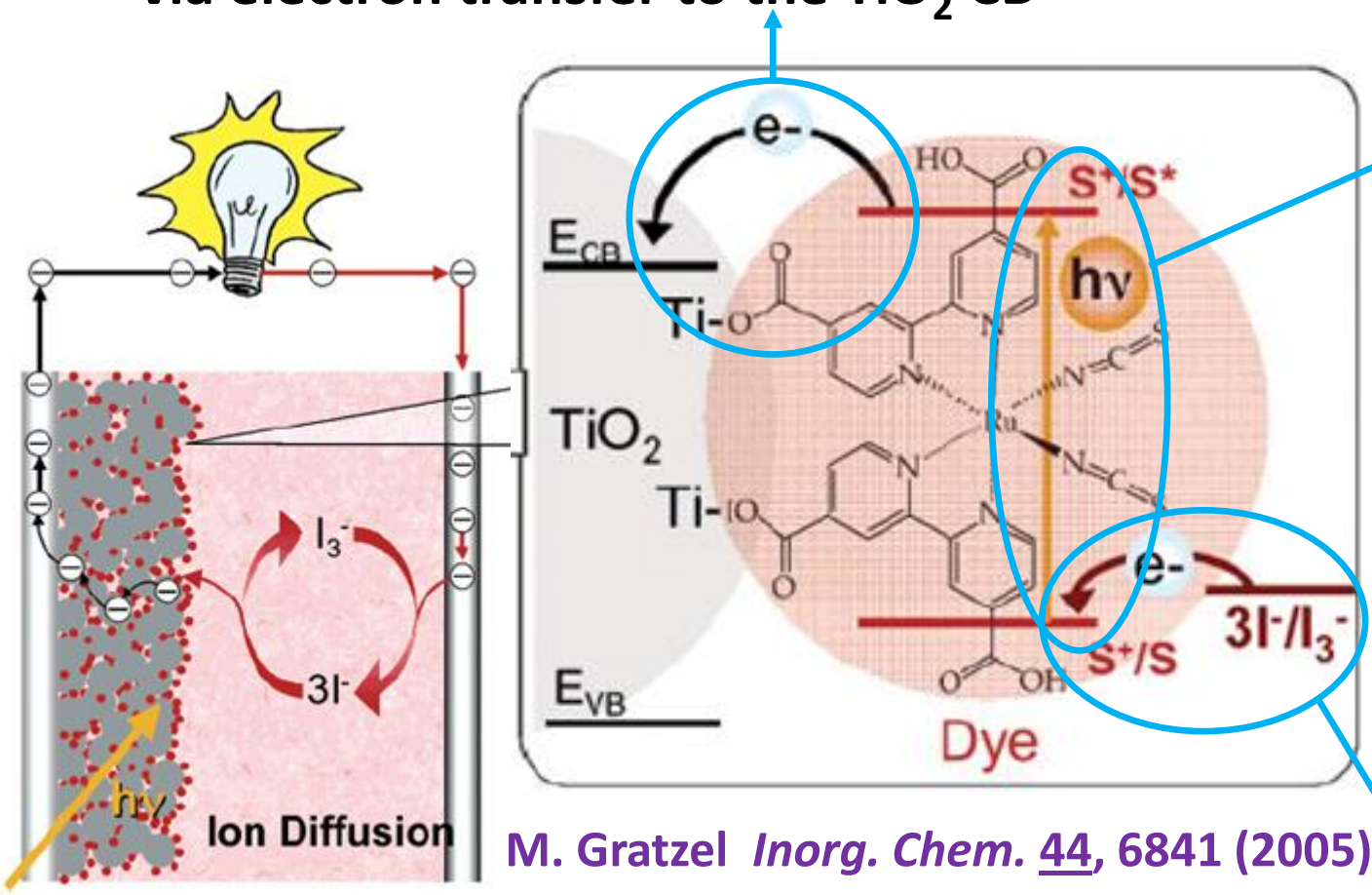
Dye-Sensitized Solar Cells

Charge separation occurs at the interface via electron transfer to the TiO_2 CB

The dye molecule (absorber) is photoexcited

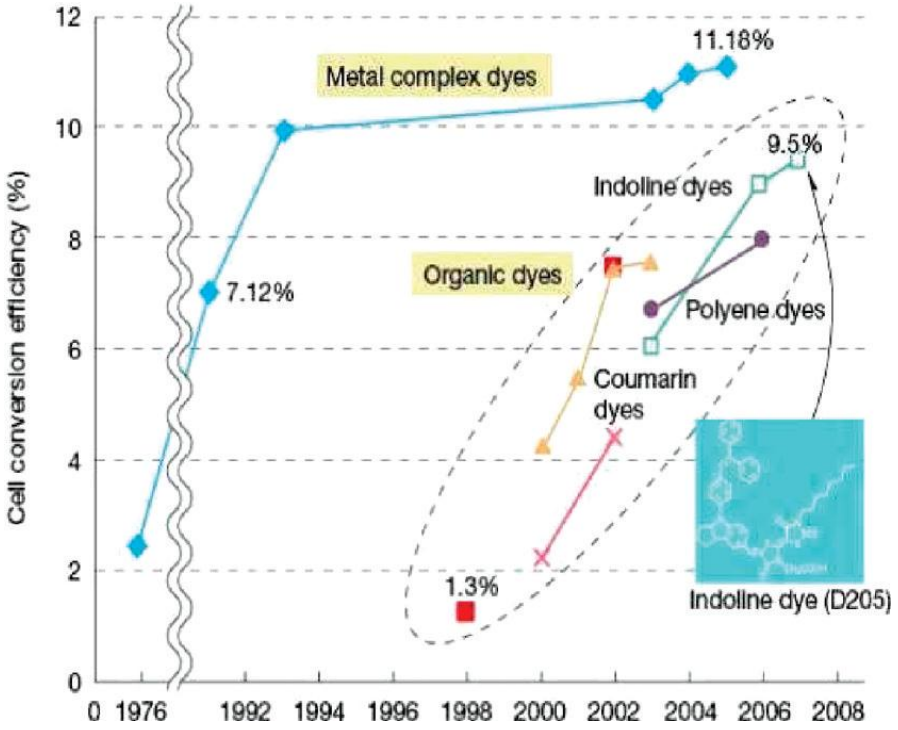


M. Gratzel *Inorg. Chem.* 44, 6841 (2005)

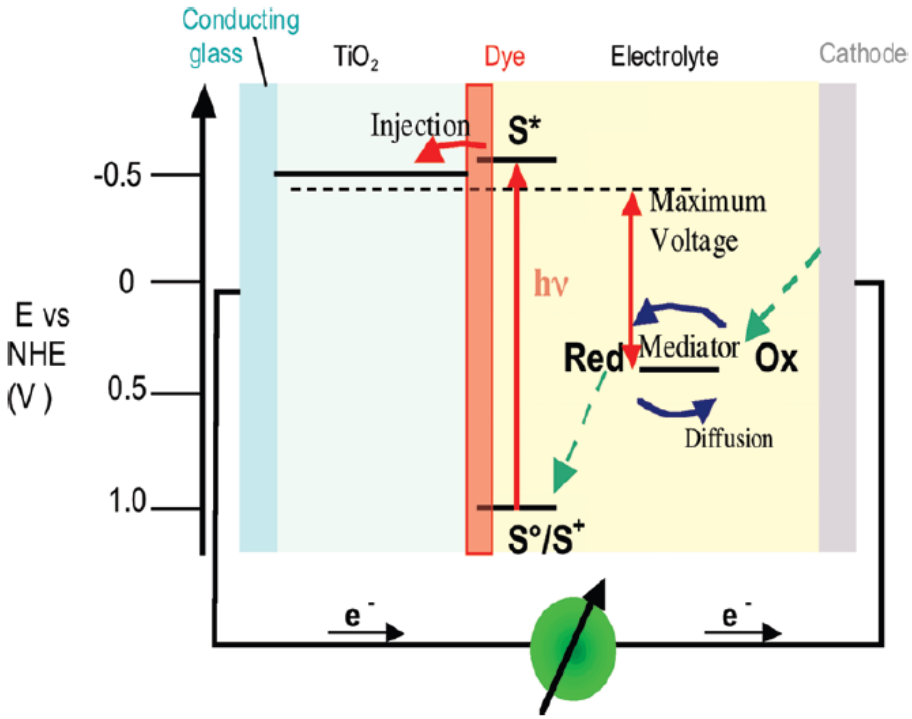
Regeneration is achieved by electron transfer from the electrolyte to the dye

Dye-Sensitized Solar Cells

How to make DSCs more efficient?



Make better dyes



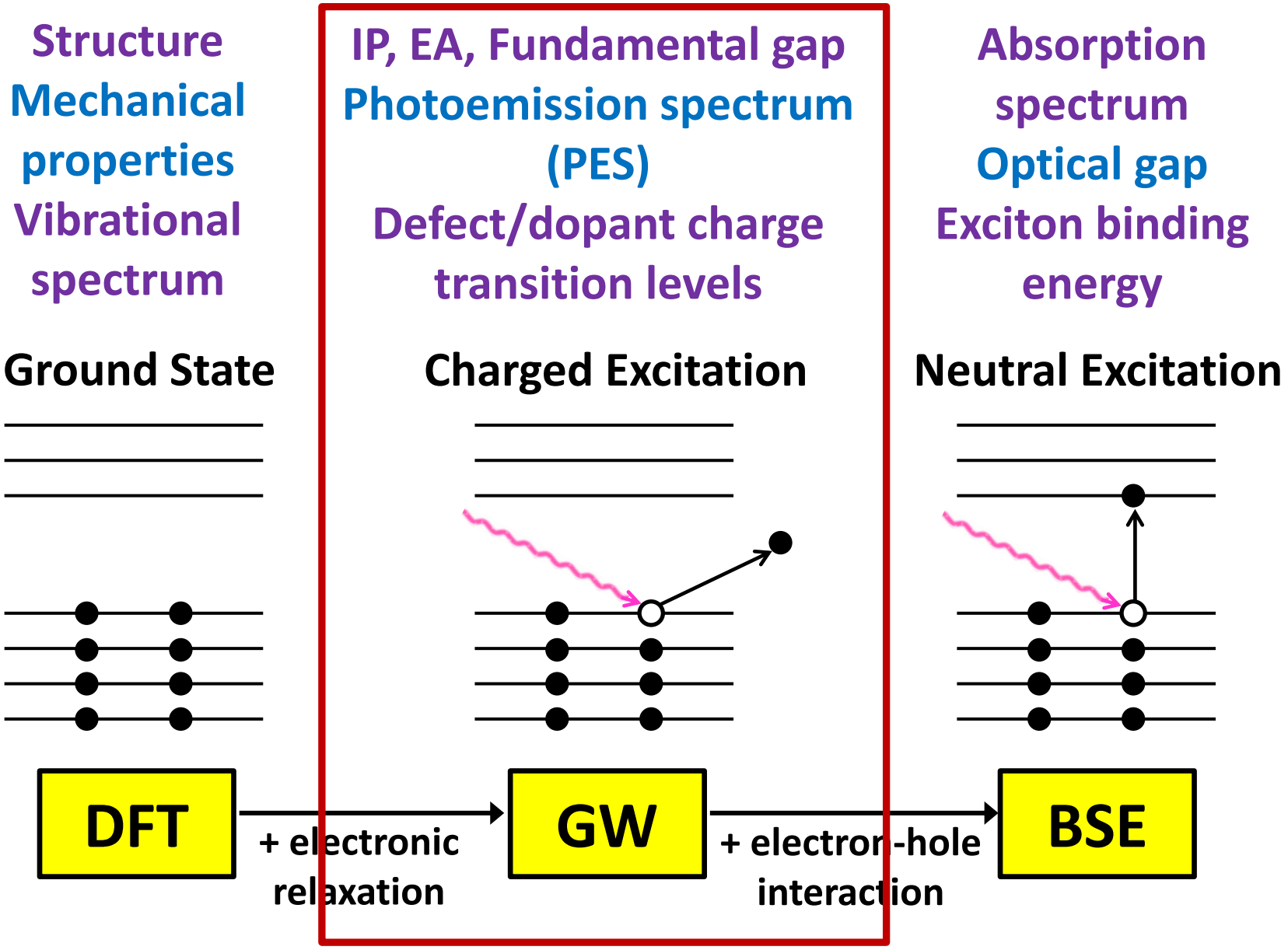
Reduce injection and regeneration losses

Also:

- **Reduce disorder, defects, and surface states**
- **Physically separate the TiO_2 and the electrolyte**

M. Gratzel *Acc. Chem.* Res. 42, 1788 (2009)

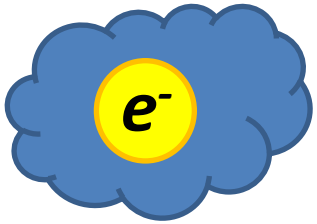
Methods


Structure
Mechanical properties
Vibrational spectrum
IP, EA, Fundamental gap
Photoemission spectrum (PES)
Defect/dopant charge transition levels
Absorption spectrum
Optical gap
Exciton binding energy
Ground State
Charged Excitation
Neutral Excitation
DFT
+ electronic relaxation
GW
+ electron-hole interaction
BSE

GW

Kohn-Sham: $\left(-\frac{1}{2}\nabla^2 + V_{ion} + V_{Hartree} + V_{xc}\right)\varphi_i(r) = \varepsilon_i^{KS}\varphi_i(r)$

The quasiparticle equation:



$$\left(-\frac{1}{2}\nabla^2 + V_{ion} + V_{Hartree} + \Sigma(r, r', E_i^{QP})\right)\psi_i(r) = E_i^{QP}\psi_i(r)$$

The GW approximation (Hedin, 1965):

The self-energy is approximated by the first order term in a perturbation series in the screened Coulomb interaction

$$\Sigma \approx iGW$$

G_0W_0

G_0W_0 (Hybertsen and Louie, 1986):

- Assume that the KS wave-function and eigenvalues are good approximations for the many-body wave-function and QP energies

- Calculate the QP energies non-self-consistently as perturbative corrections to the KS energies:

$$E_i^{G_0W_0} = \varepsilon_i^{KS} + \left\langle \varphi_i \left| \Sigma^{G_0W_0} - V_{xc} \right| \varphi_i \right\rangle$$

KS orbitals and energies are used to evaluate G_0 and W_0:

$$G_0(r,r';\omega) = \sum_i \frac{\varphi_i(r)\varphi_i^*(r')}{\omega - \varepsilon_i^{KS}}$$

$$W_0(r,r';\omega) = 1/\Omega \int \varepsilon^{-1}(r,r'';\omega) V^C(r''-r') d^3r''$$

The results of G_0W_0 depend on the underlying DFT functional!

Computational Details

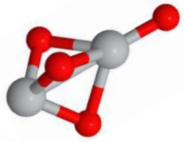
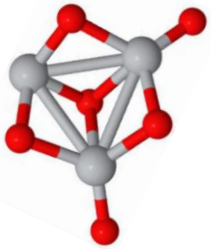
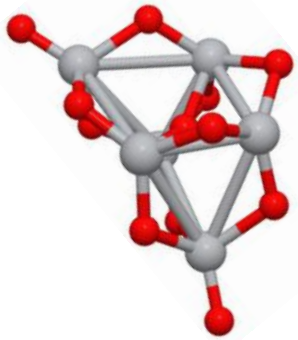
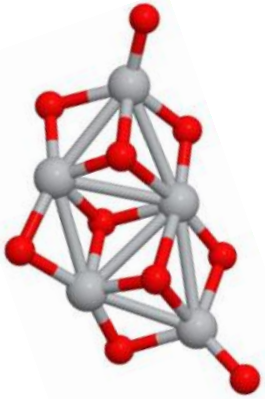
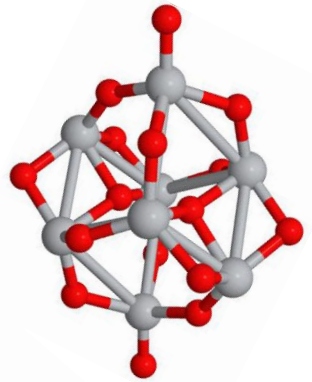
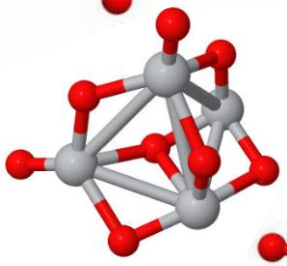
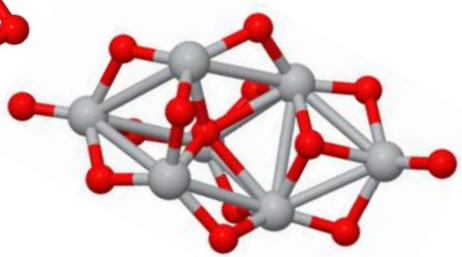
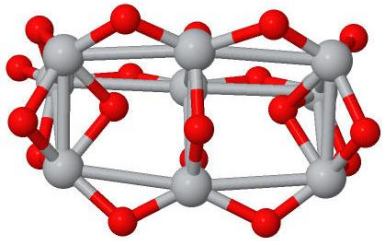
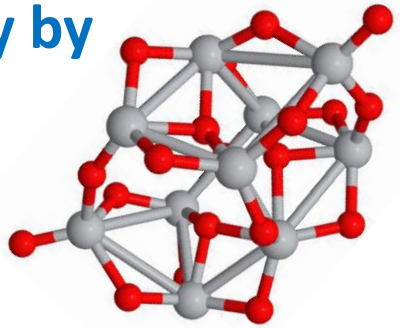
FHI-aims: all-electron code with numeric atom-centered orbital basis-sets

G_0W_0 implementation: X. Ren et al., *arXiv: 1201.0655v1*

- No pseudo-potential errors
- Periodic boundary conditions need not be imposed
  - No large vacuum regions
  - No artifacts from periodic replicas
- Good convergence behavior w/r to empty states
- The self-energy is calculated by analytical continuation

TiO_2 Clusters

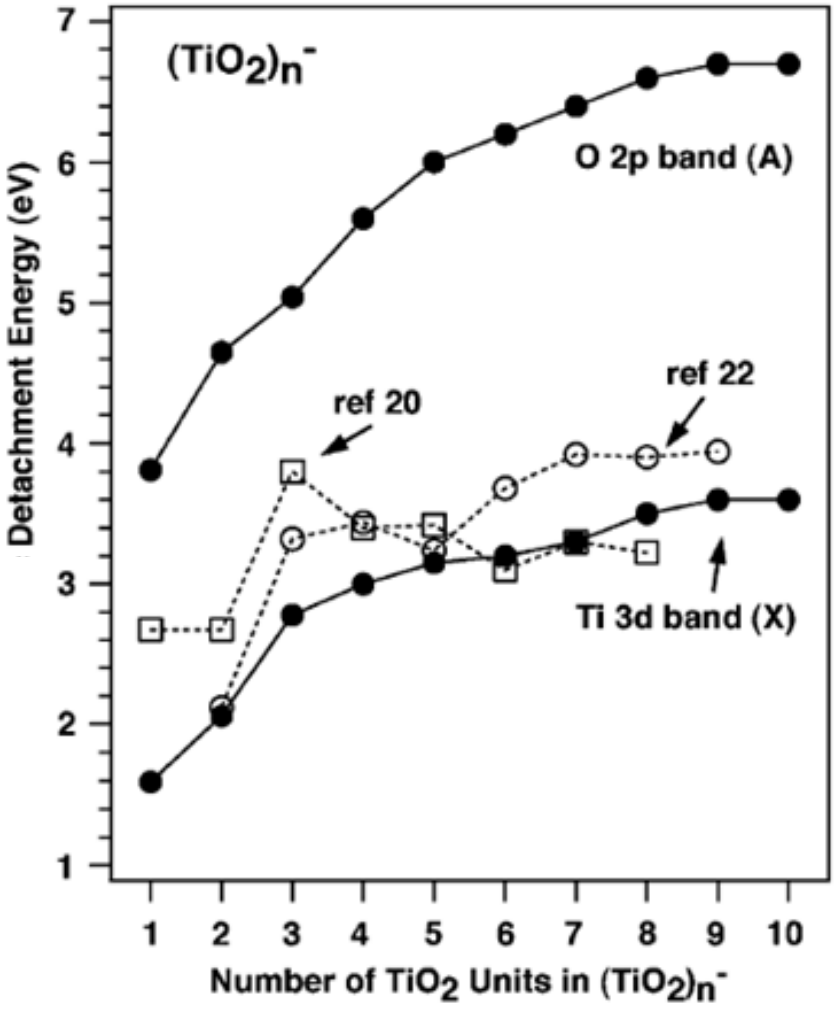
- TiO_2 clusters have potential applications in photocatalysis and photovoltaics
- Their properties are strongly dependent on their size and structure- highly tunable
- Selectivity is a challenge because there is little control over which isomers form in experiments
- Such clusters can be characterized only by indirect means

TiO_2 Clusters

- A combination of photoemission spectroscopy (PES) and *ab initio* simulations is often used to characterize clusters
- Typically a global minimum (GM) search is conducted, based on the assumption that the most stable isomers form in experiment

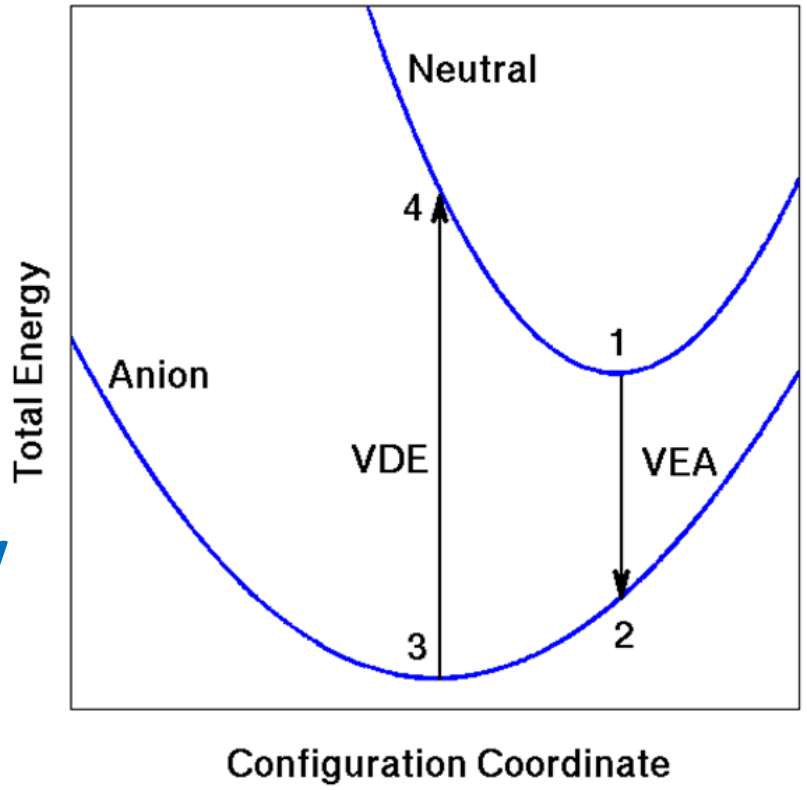
But… such calculations for TiO_2 clusters are not in agreement with PES experiments!



Zhai and Wang, *JACS.* *129*, 3022 (2007)

Selection Mechanism for High VEA

- The clusters initially form as neutrals
- Several low-energy isomers form
- The clusters acquire an electron from the plasma (process 1→2)
- The cluster with the highest VEA "wins" the electron via energetically favorable charge transfer reactions
- Only the charged clusters go through mass spectrometry



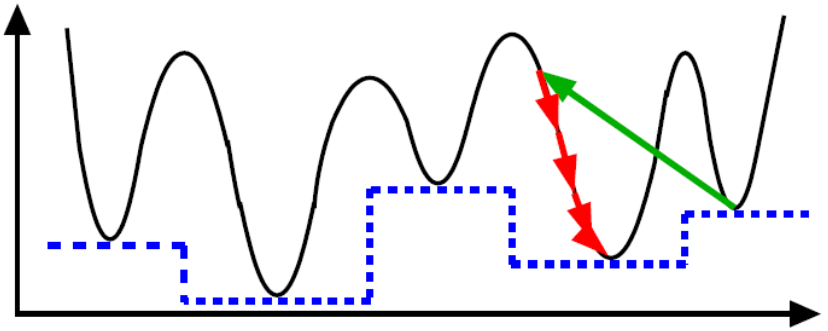
- The anions cool down and relax to the meta-stable state of the high VEA isomer (process 2→3)
- The VDE is then measured by PES (process 3→4)

L. Kronik et al. *Nature Materials* 1, 49 (2002)

Computational Details

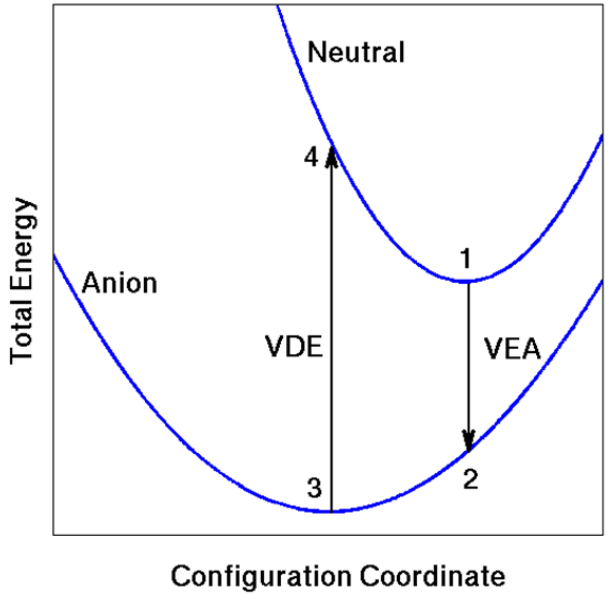
Step I: Structure Search:

A basin hopping algorithm based on DFT with the PBE functional was used to find isomers in a 1.25 eV interval from the GM

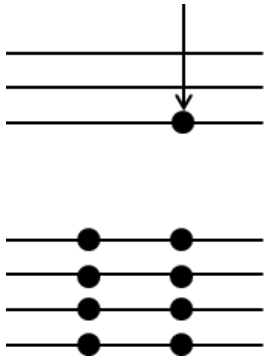


Gehrke and Reuter *PRB* 79, 085412 (2009)

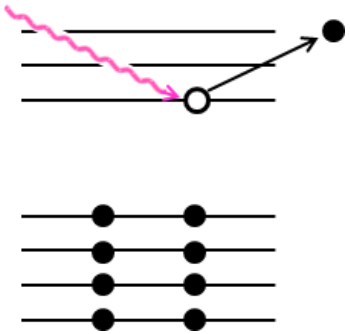
Step II: GW



The VEA (1→2) and VDE (3→4) are QP energies



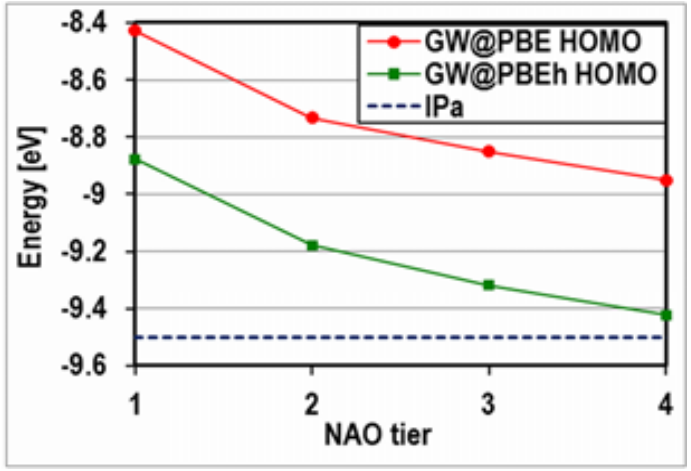
VEA= GW LUMO of the neutral

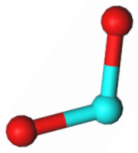


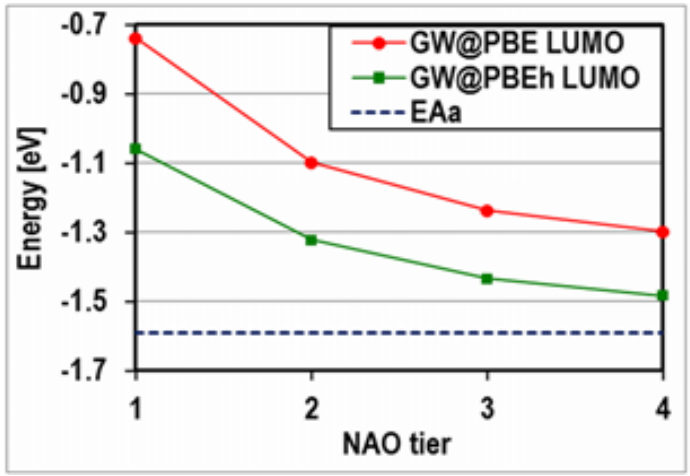
VDE= GW HOMO of the relaxed anion

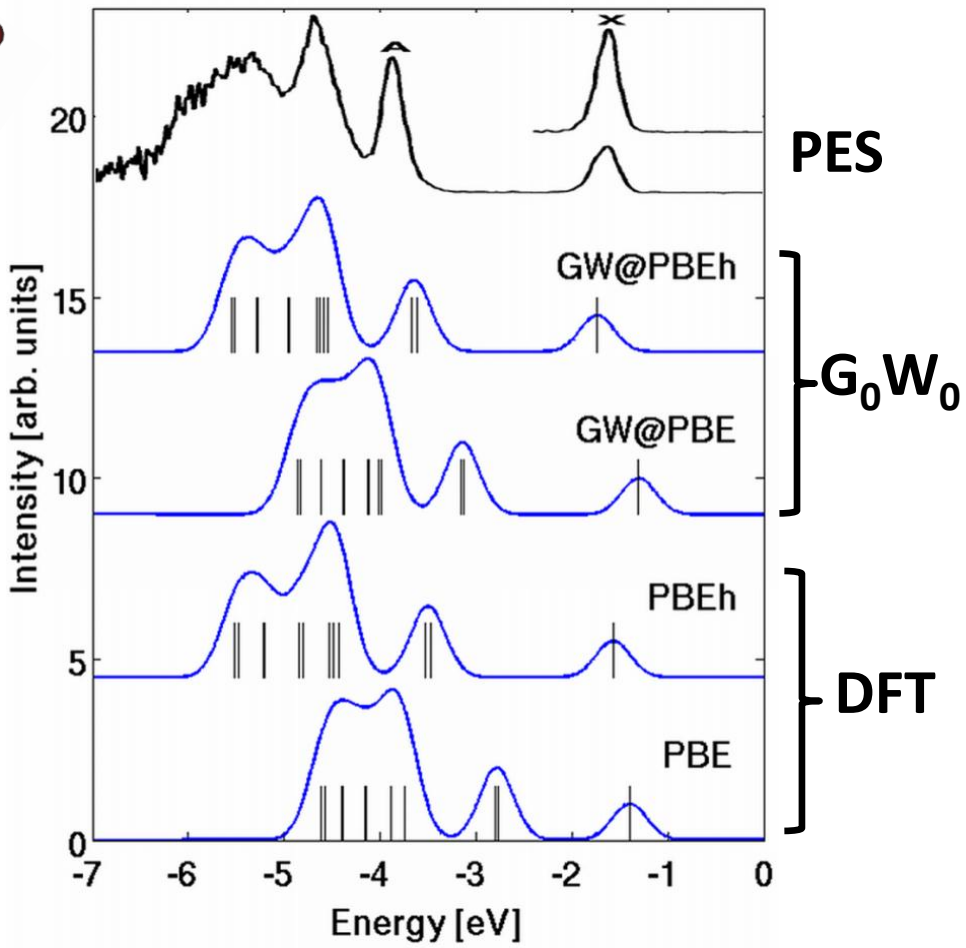
N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

Results: TiO_2 Molecule









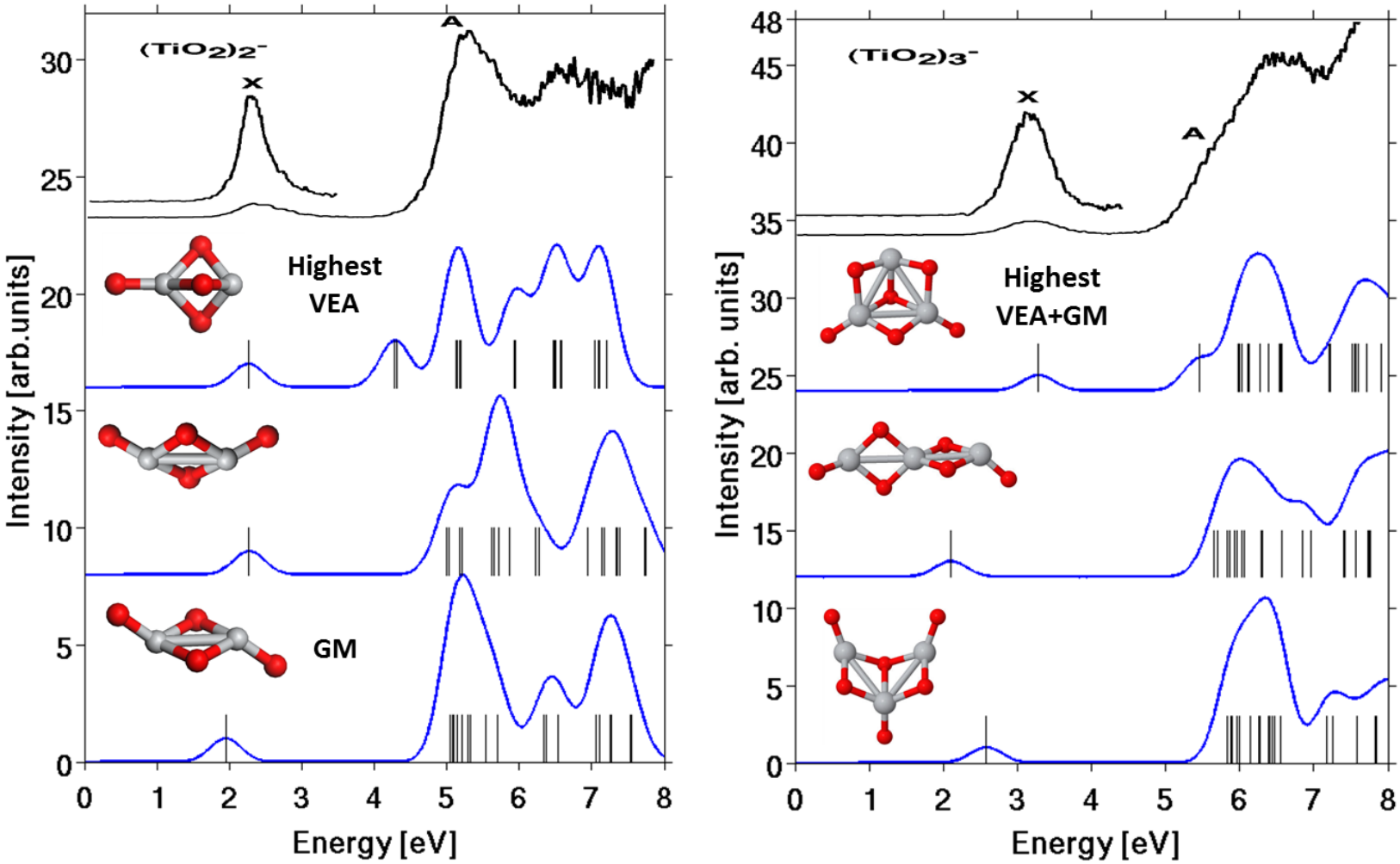
Tier 4 converged to 0.1 eV from experiment

G_0W_0@PBEh is in excellent agreement with experiment

N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, PRB 84, 245115 (2011)

Results: $(TiO_2)_{2,3}$ Clusters Spectra

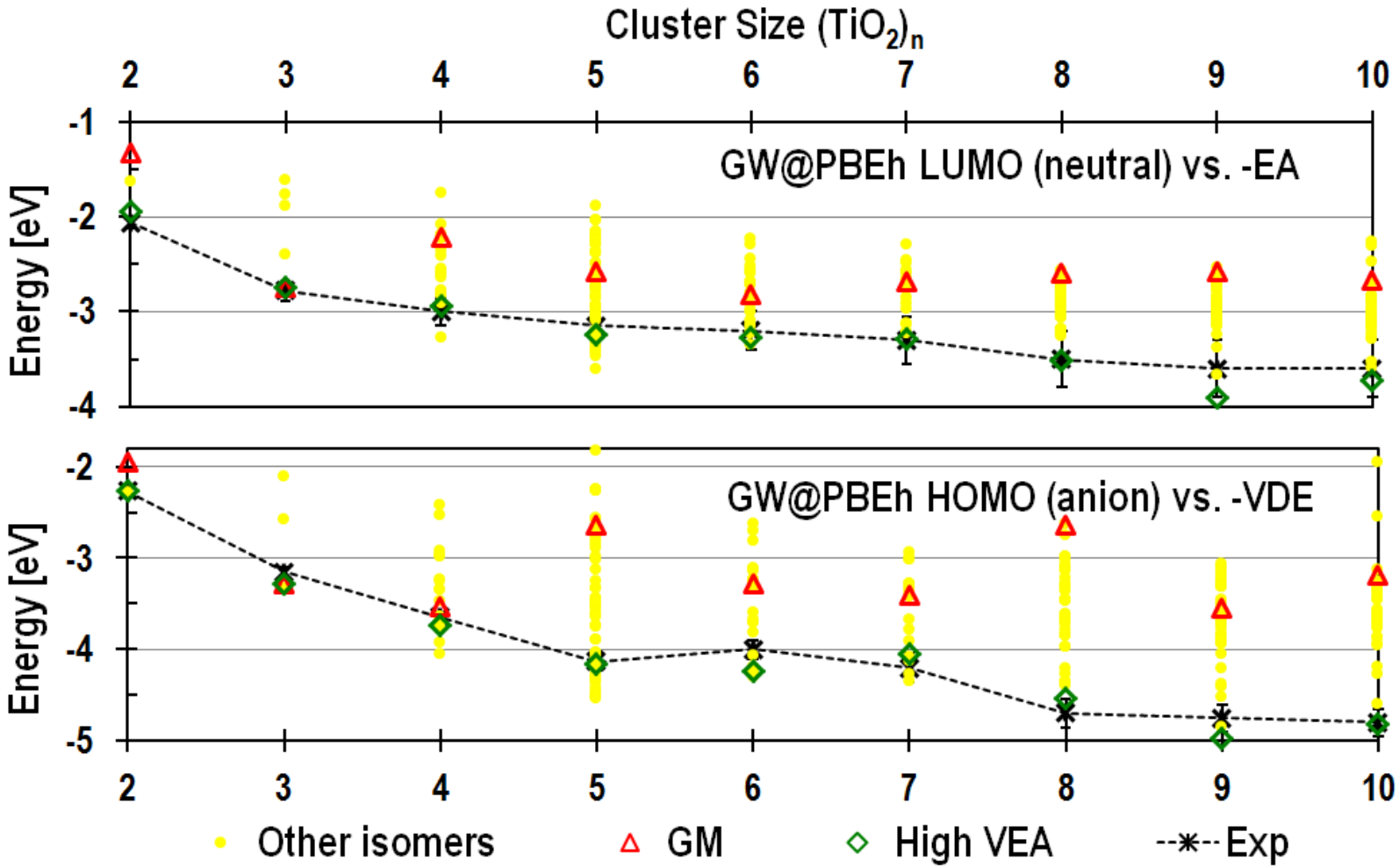
GW@PBEh, broadening 0.3 eV



Highest VEA isomers are in agreement with PES

N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

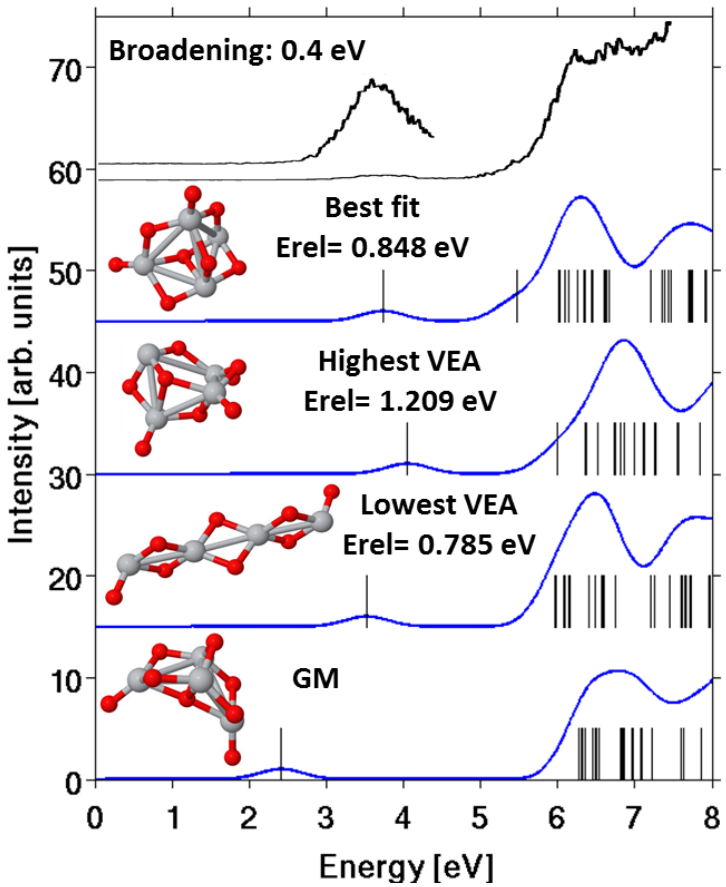
Results: $(TiO_2)_{2\text{-}10}$ Clusters VEA and VDE

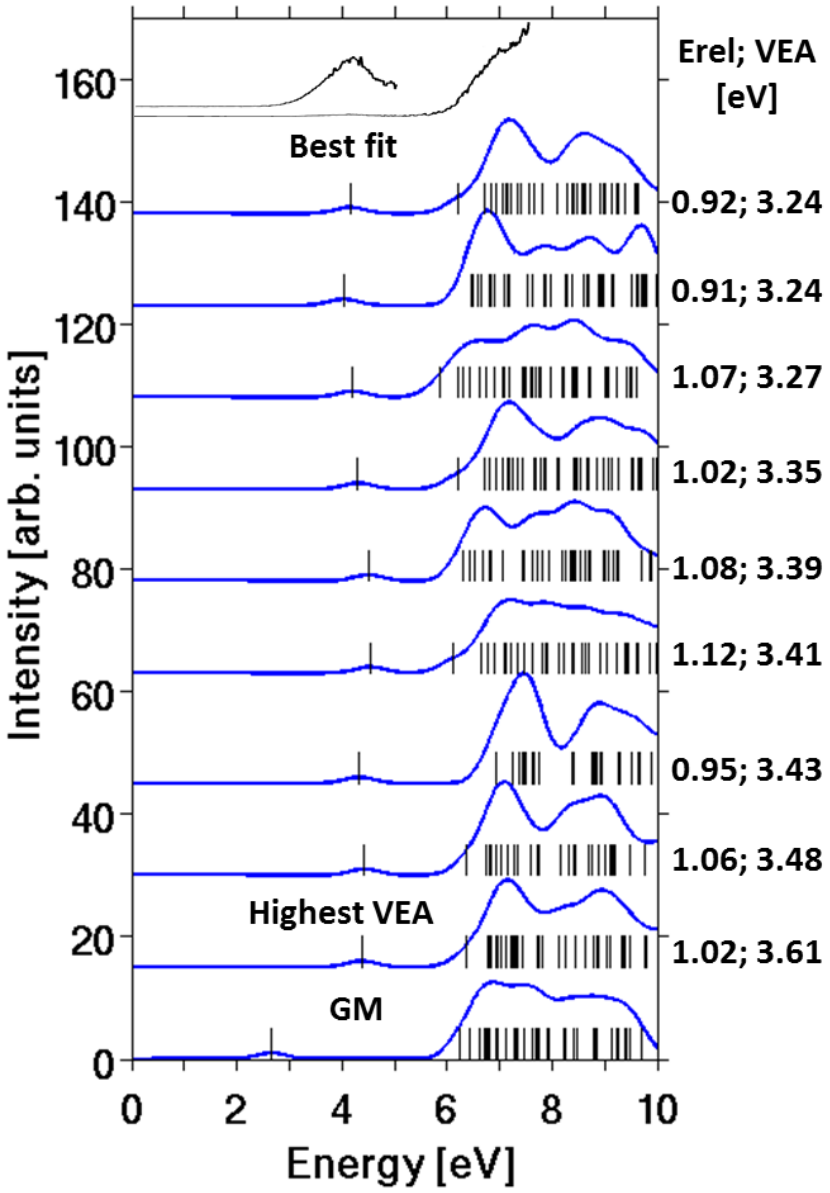


Isomers with high VEA are in agreement with PES…
unlike the GM isomers!

N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

Results: $(TiO_2)_{4,5}$ Clusters Spectra





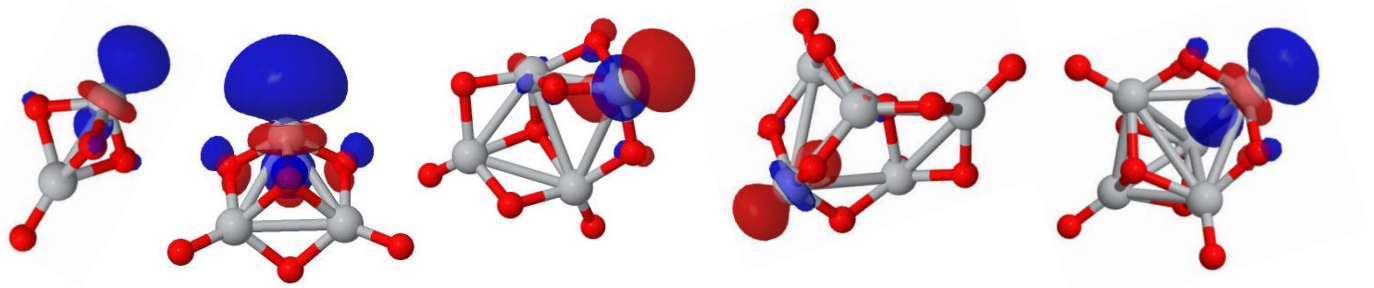
For some cluster sizes several isomers with high VEA were found. An isomer with lower Erel agrees with experiment better than the one with the highest VEA. A combination of isomers in the experimental spectra is also possible

N. Marom, et al. *PRL* 108, 106801 (2012)

Structure-Property Relation

Experiments on anions select for clusters with high VEA rather than the most energetically stable isomers!

LUMO Orbital of high VEA clusters:



Localization on a single tri-coordinated Ti atom leads to high VEA!

Ti^{3+} sites on TiO_2 surfaces are highly reactive and play an essential role in photocatalysis and dissociative chemisorption

The selection for clusters with this feature may be useful for catalysis

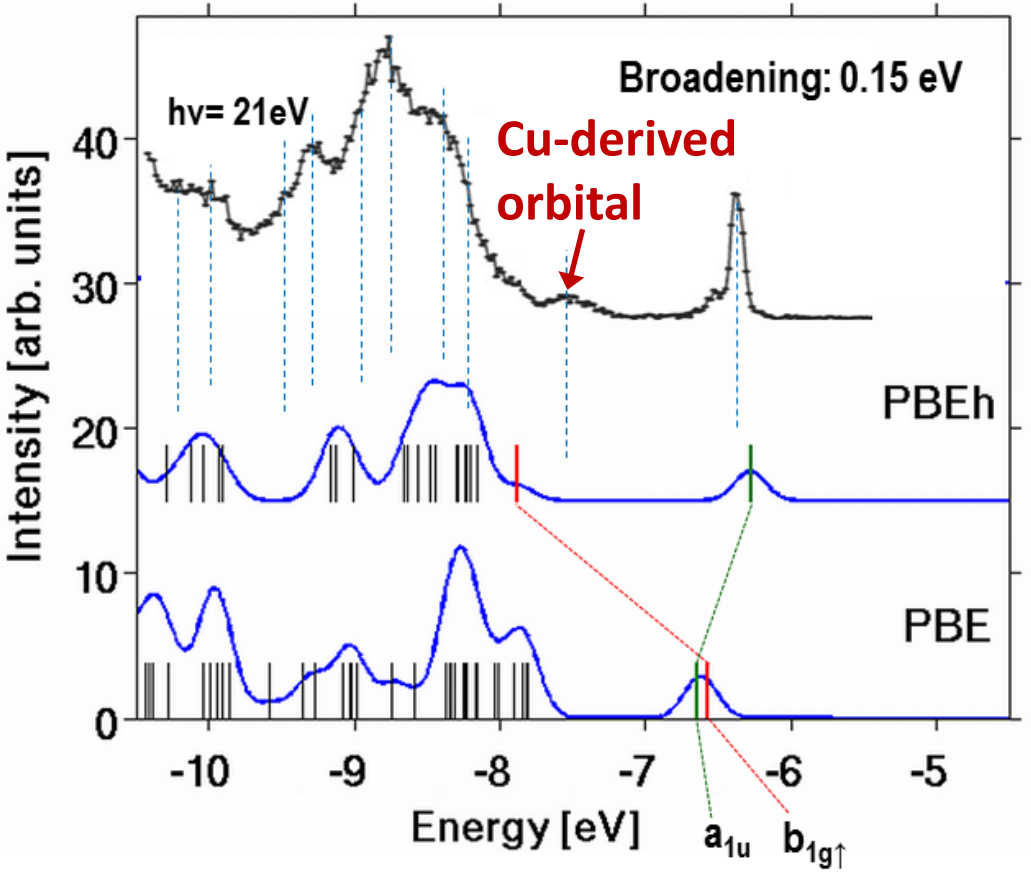
N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

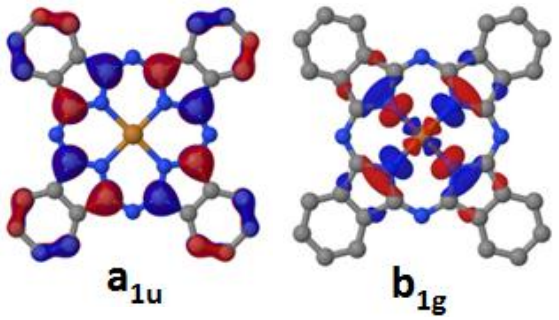
CuPc: Self-Interaction Error

Self interaction error (SIE) – the spurious Coulomb interaction of an electron with itself

With the semi-local PBE functional, the repulsion caused by SIE shifts the highly localized b_{1g} orbital to a higher energy

The addition of a fraction of exact exchange in the hybrid functional mitigates the SIE

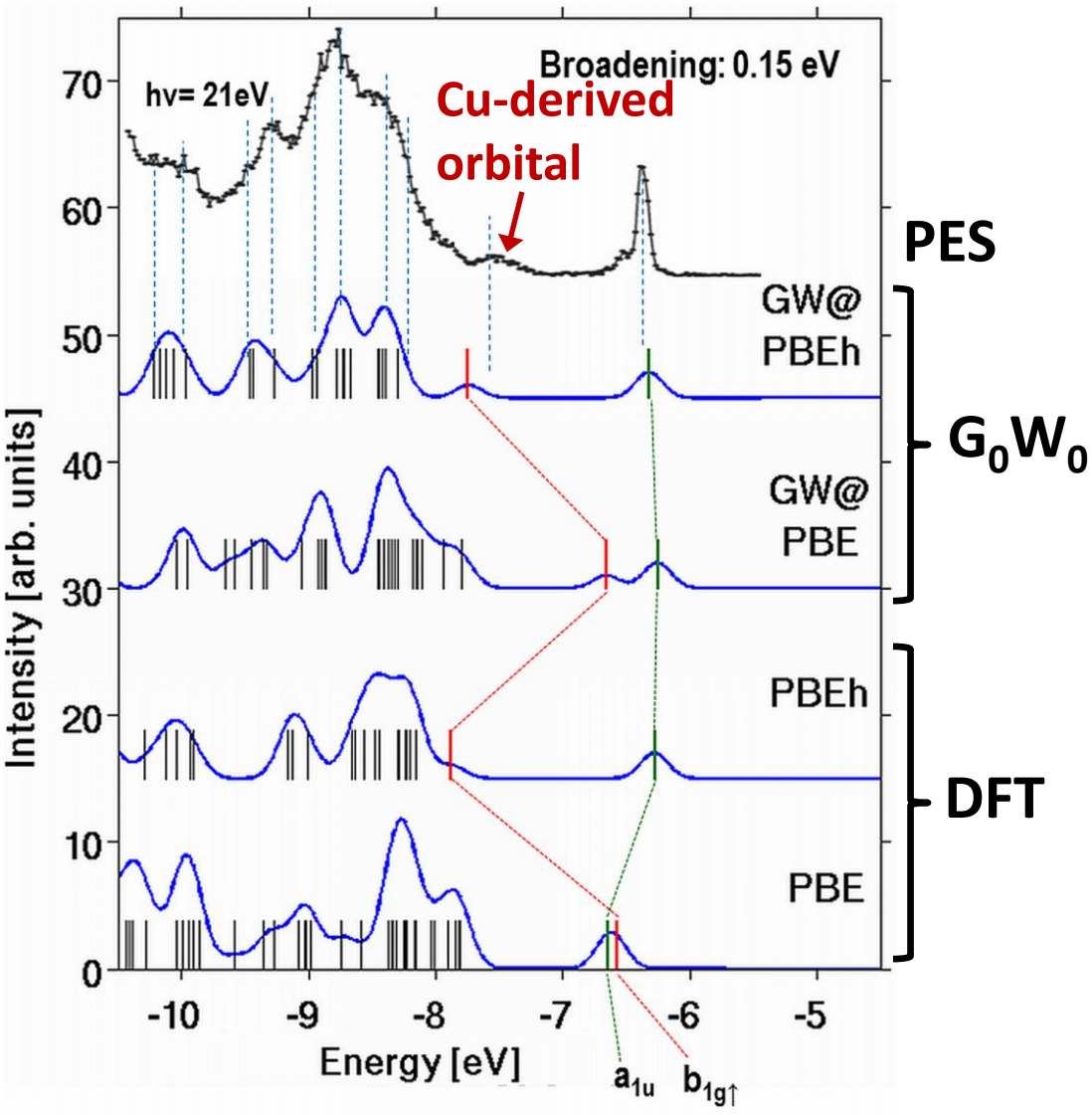




N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, JCP 128, 164107 (2008)

N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, PRB 84, 195143 (2011)

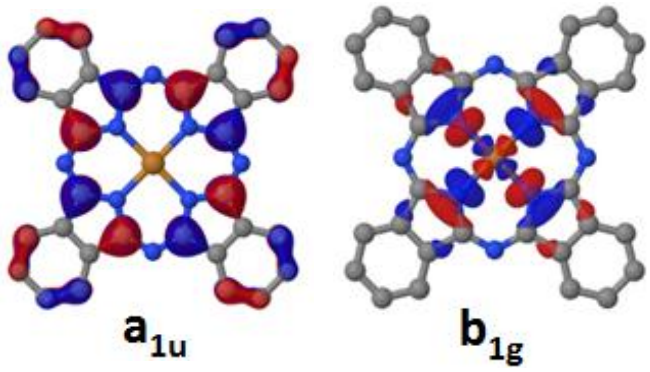
CuPc: G_0W_0 Starting Point Dependence



N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, PRB 84, 195143 (2011)

The SIE propagates from DFT to G_0W_0 leading to a strong starting point dependence for the position of the highly localized b_{1g} orbital

GW@PBEh is in excellent agreement with experiment unlike GW@PBE



A Crystalline Phase of Dye-Sensitized TiO_2 Clusters

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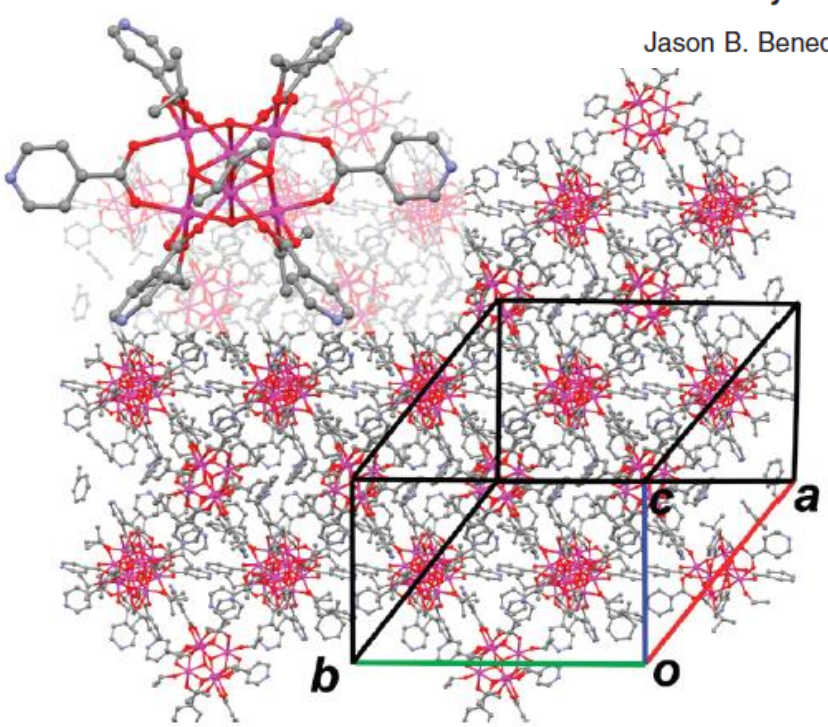
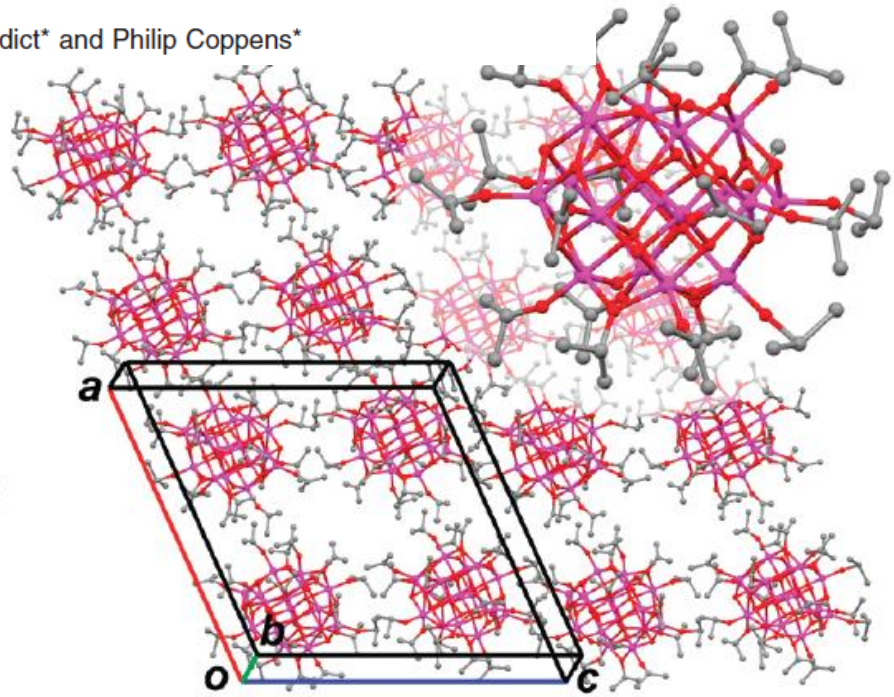
ARTICLES

Published on Web 02/10/2010

The Crystalline Nanocluster Phase as a Medium for Structural and Spectroscopic Studies of Light Absorption of Photosensitizer Dyes on Semiconductor Surfaces

Jason B. Benedict* and Philip Coppens*





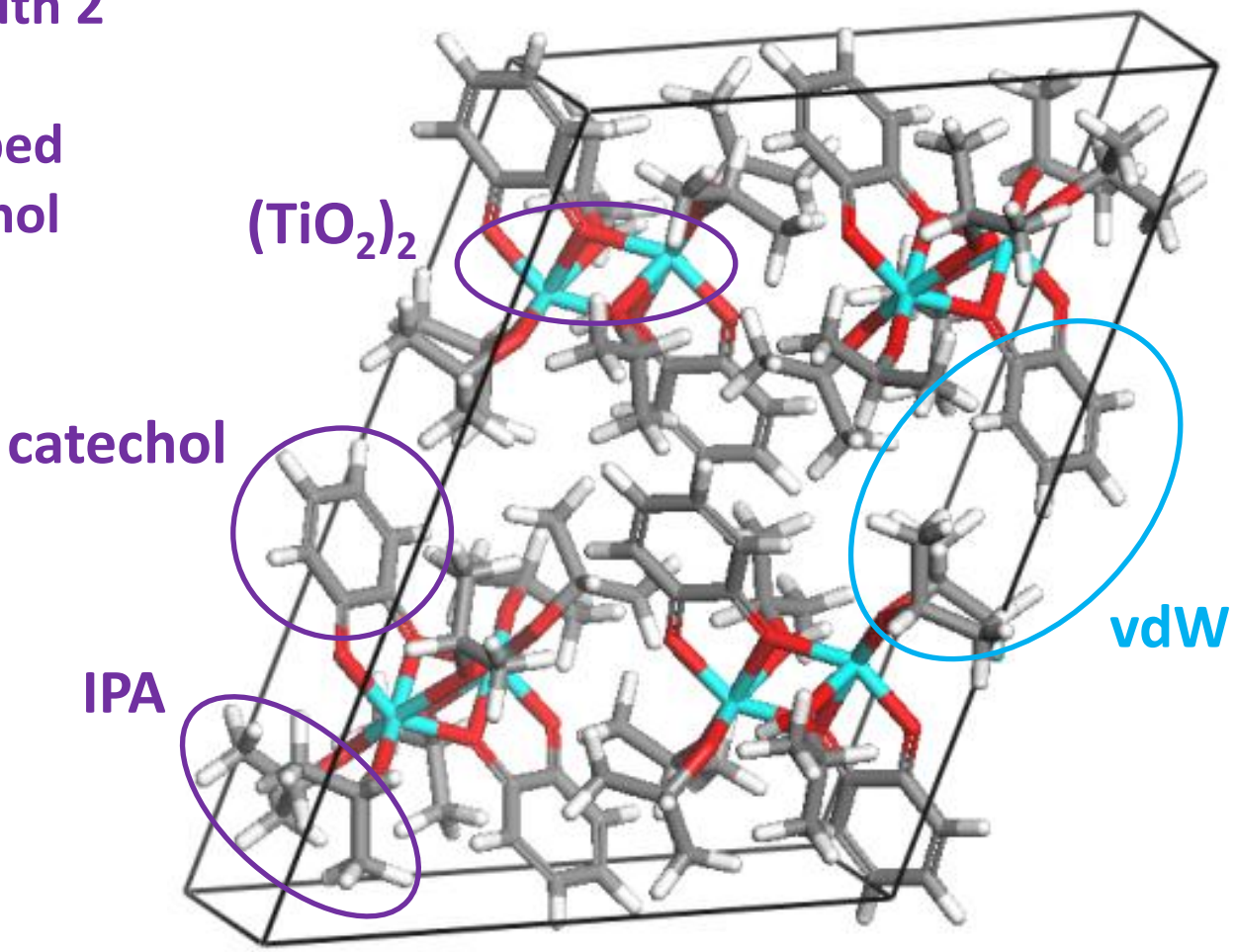
Good test bed for theory because the structure is well defined and a direct comparison to experiment is possible

Ti_2cat_2

Four units of $(TiO_2)_2$ cluster sensitized with 2 catechol (cat) dye molecules and capped with isopropyl alcohol (IPA) groups.

376 atoms/cell
94 atoms/unit

Bound by weak van der Waals interactions



The TS Dispersion Correction

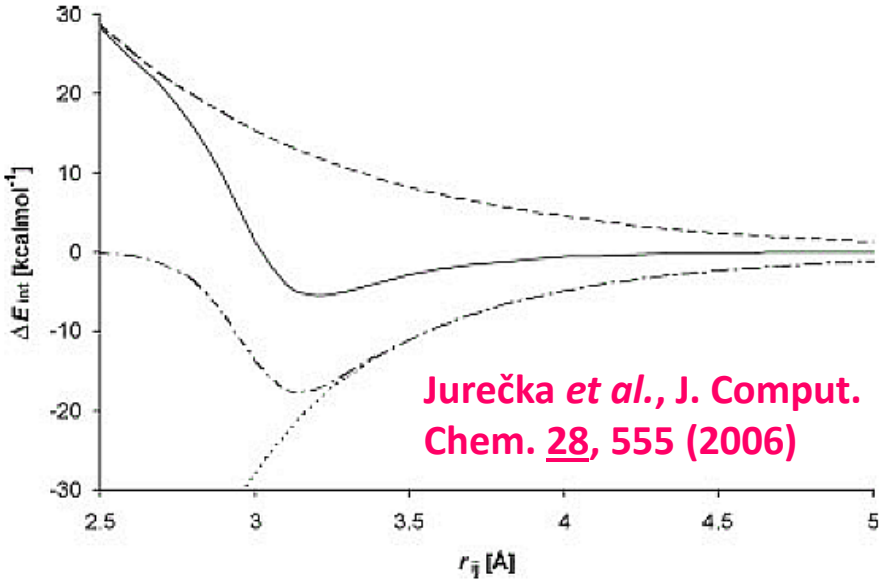
Functionals that rely on semi-local correlation do not provide a proper treatment of dispersion interactions!

C_6/R^6 corrections:

The vdW interaction is added pair-wise to the inter-nuclear energy term:

$$E_{disp} = -\sum_{j>i} f_{damp}(R_{ij}, R_{ij}^0) C_{6ij} R_{ij}^{-6}$$

$$f_{damp}(R_{ij}, R_{ij}^0) = \left[1 + \exp\left(-d\left(\frac{R_{ij}}{s_R R_{ij}^0} - 1\right)\right)\right]^{-1}$$



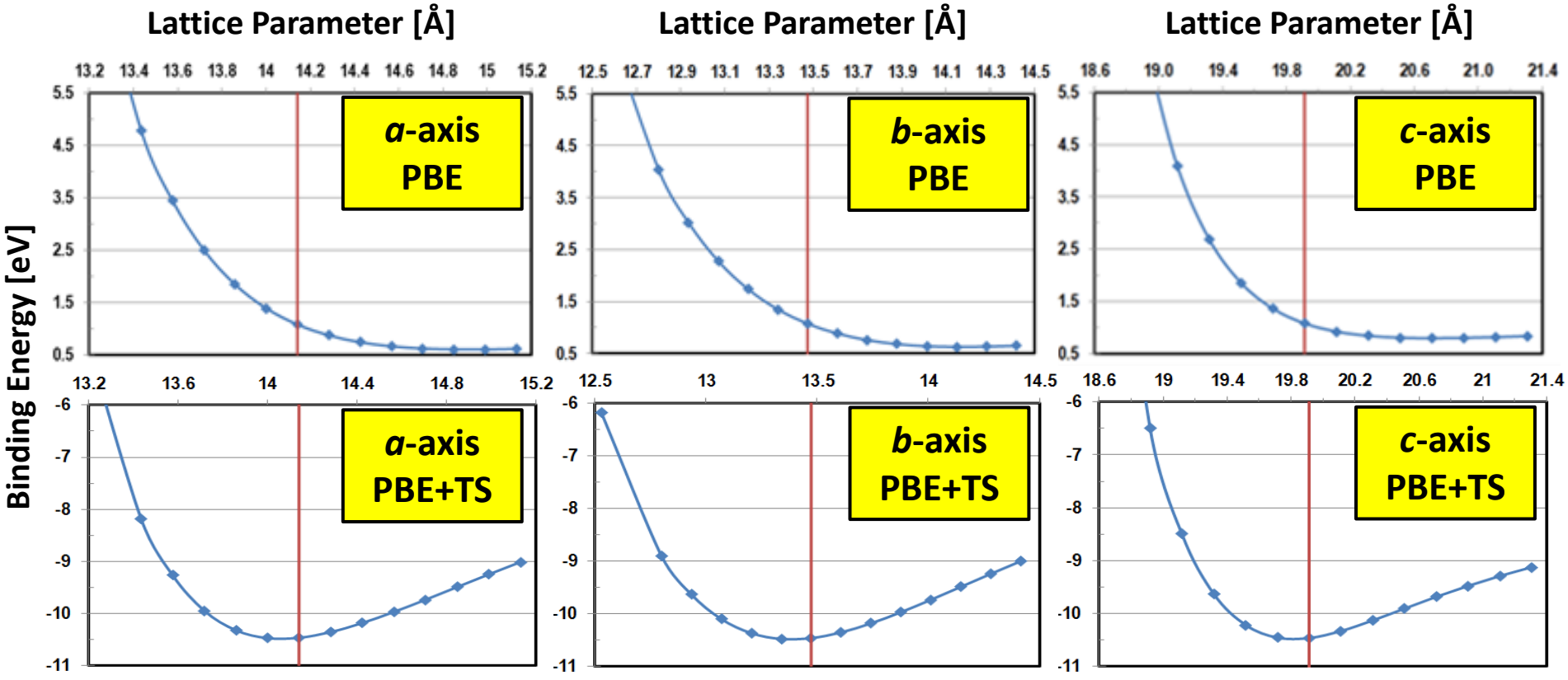
Jurečka *et al.*, J. Comput. Chem. 28, 555 (2006)

The Tkatchenko-Scheffler (TS) scheme:

- C_{6ij} and R^0_{ij} are determined from first principles considerations, based on Hirshfeld partitioning of the DFT charge density
- S_R is determined once per functional by fitting to the S22 data set

A. Tkatchenko and M. Scheffler, *PRL* 102, 073005 (2009)

Ti_2cat_2 Geometry Optimization

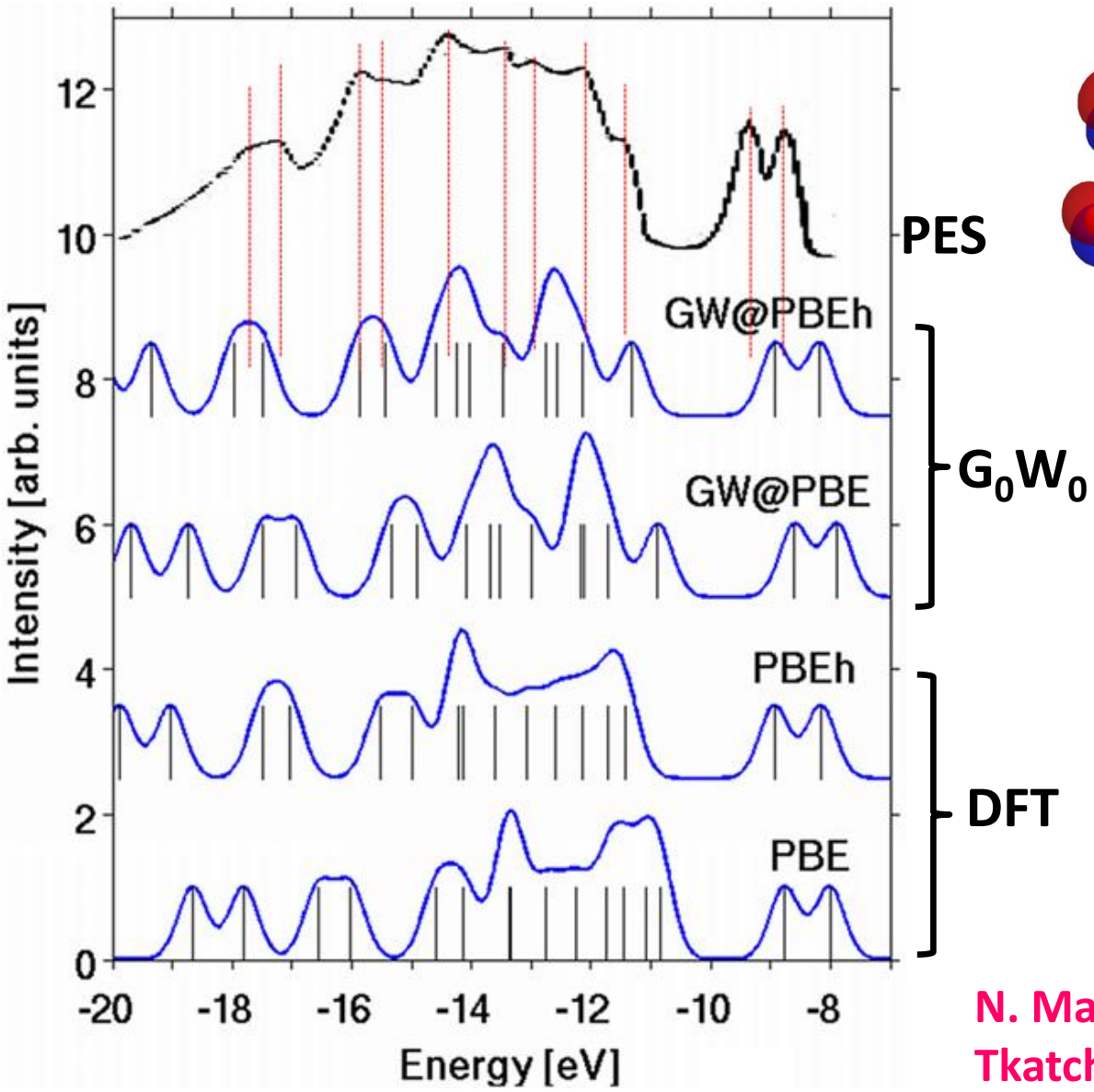


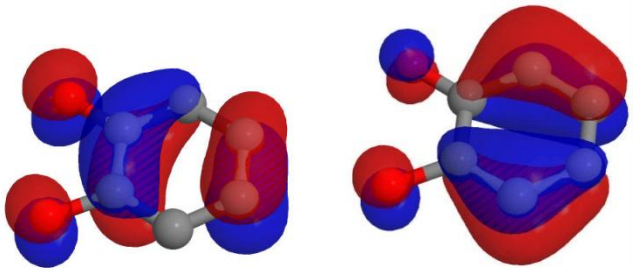
PBE gives no binding!

PBE+TS gives lattice parameters in good agreement with experiment

N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, PRB 84, 245115 (2011)

Catechol

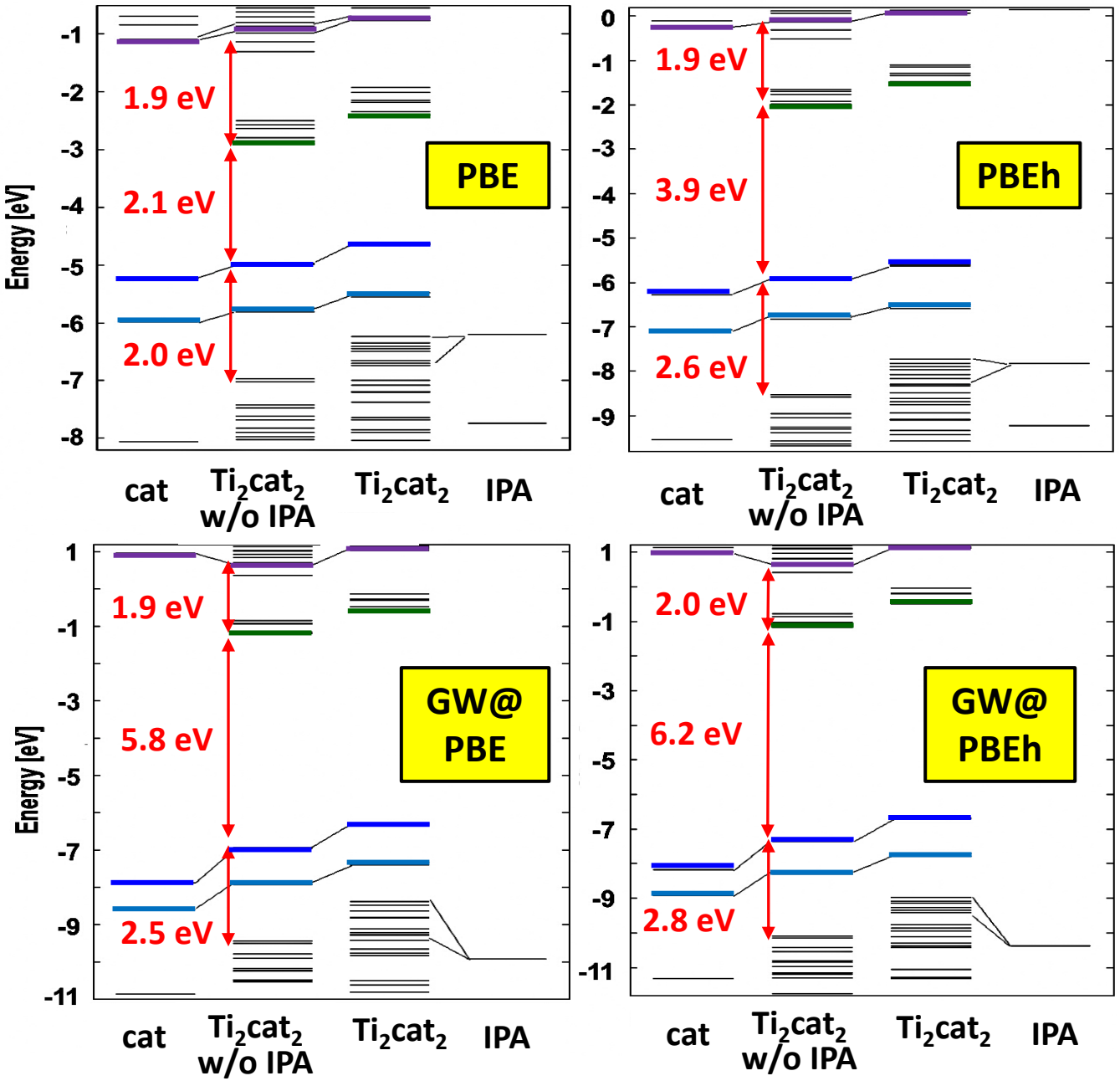


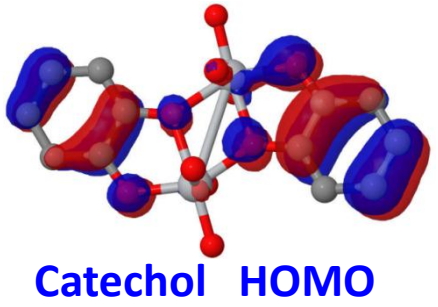


GW@PBEh is in excellent agreement with experiment

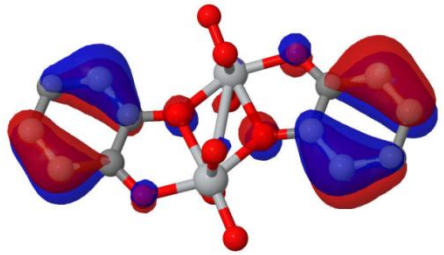
N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, PRB 84, 245115 (2011)

Ti_2cat_2 Level Alignment

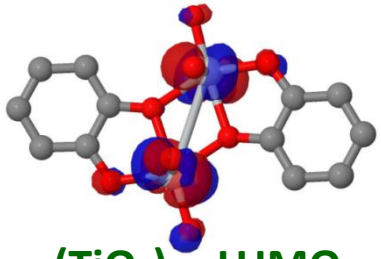




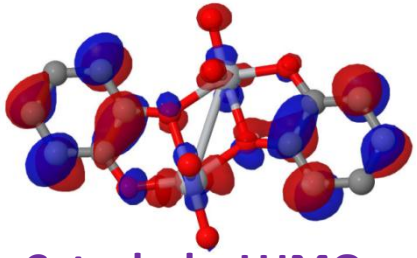
Catechol HOMO



Catechol HOMO-1

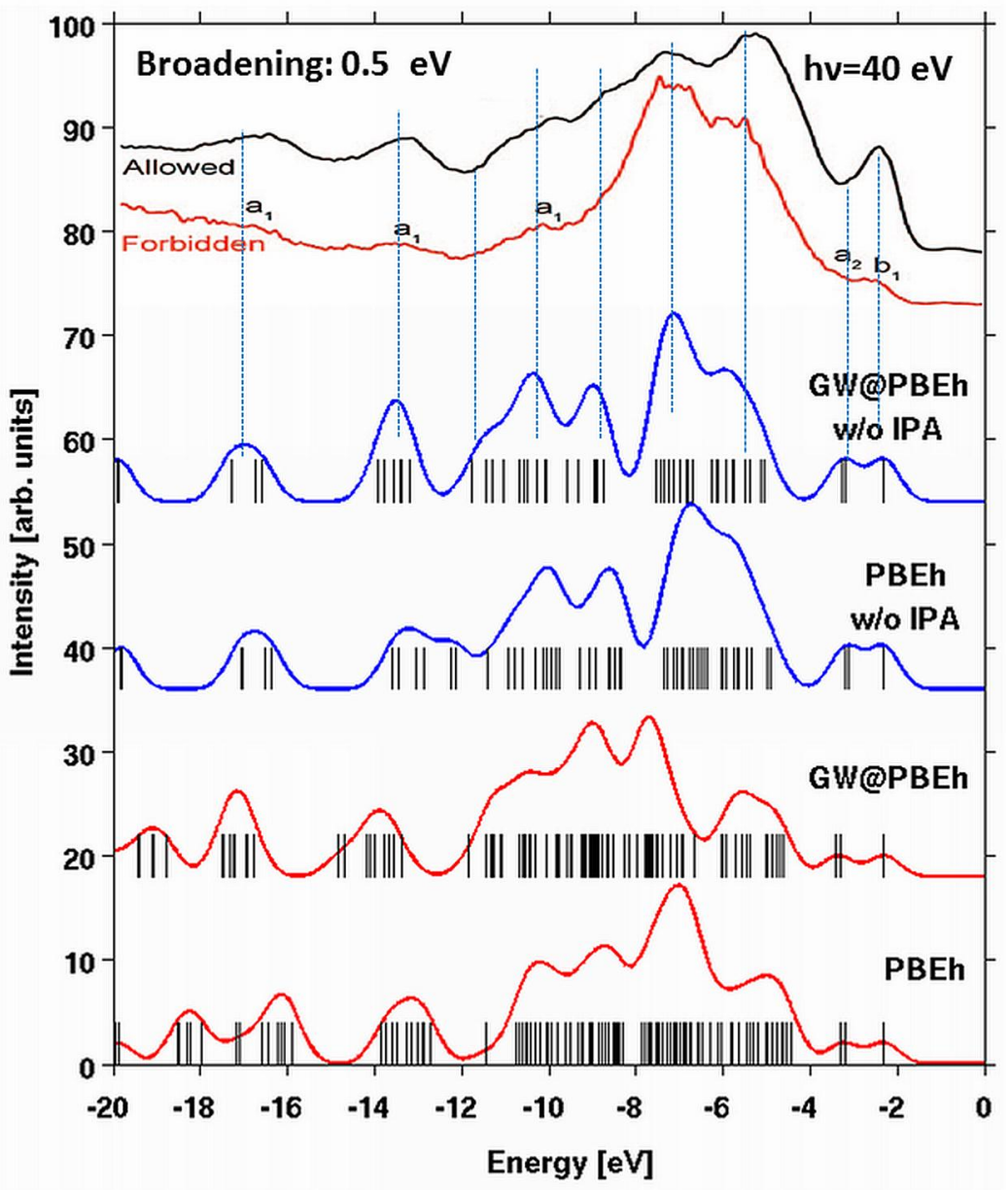


$(TiO_2)_2$ LUMO



Catechol LUMO

Ti_2cat_2 Spectrum



- The spectra of Ti_2cat_2 without IPA are in good agreement with the PES of a monolayer of catechol on a TiO_2 surface
- The small model system captures the essence of the dye-TiO_2 interaction
- The addition of IPA changes the shape of the spectrum but the signature of catechol on TiO_2 is still clearly visible

N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, PRB 84, 245115 (2011)

Conclusion

MBPT within the G_0W_0 approximation gives:

- **Accurate VEAs and VDEs that enable identifying the $(TiO_2)_{2\text{-}10}$ isomers observed in PES**
- **Accurate description of the electronic structure of metal-organic dyes, particularly with respect to the metal *d*-states**
- **Reliable predictions of the fundamental gaps and level alignment for dye-sensitized TiO_2 clusters**

TiO_2 clusters: N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

CuPc: N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, *PRB* 84, 195143 (2011)

Dye-sensitized TiO_2 clusters : N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, *PRB* 84, 245115 (2011)