



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

Structure Selection Based on High Vertical Electron Affinity for TiO_{2} Clusters

Noa Marom, Minjung Kim, and James R. Chelikowsky

Phys. Rev. Lett. **108**, 106801 — Published 5 March 2012

DOI: [10.1103/PhysRevLett.108.106801](https://doi.org/10.1103/PhysRevLett.108.106801)

Structure Selection Based on High Vertical Electron Affinity for TiO₂ Clusters

Noa Marom,^{1*} Minjung Kim,^{1,2} and James R. Chelikowsky^{1,2,3}

1. Center for Computational Materials, Institute for Computational Engineering and Sciences,
The University of Texas at Austin, Austin, TX 78712, USA

2. Department of Chemical Engineering, University of Texas, Austin, TX 78712, USA

3. Department of Physics, University of Texas, Austin, TX 78712, USA

We study the structure and electronic properties of (TiO₂)₂₋₁₀ clusters using basin hopping based on density functional theory, combined with many-body perturbation theory. We show that in photoemission experiments performed on anions isomers with high electron affinity are selectively observed rather than those with the lowest energy. These isomers possess a highly reactive Ti³⁺ site. The selectivity for highly reactive clusters may be exploited for applications in catalysis.

Clusters comprising up to few tens of atoms offer exciting prospects for designing new materials owing to the strong dependence of their electronic properties on their size and structure. However, selectivity remains a challenge, as there is little control over which isomers form in experiment. Moreover, such clusters are too small to enable direct structure characterization and their geometry can only be inferred by indirect means. A combination of photoemission spectroscopy (PES) and ab-initio simulations is often used to this end.^{1,2,3} This procedure typically involves a global minimum (GM) search, based on the assumption that the most energetically stable isomers are likely to form in experiment.

Metal oxide clusters in general and TiO₂ clusters in particular have attracted much attention due to their potential application in catalysis.^{4,5} Computational studies of TiO₂ clusters^{5,6,7} have employed a variety of algorithms to search for the most stable isomers and a variety of electronic structure methods to calculate their properties. However, to date, agreement with the PES experiment of Zhai and Wang⁸ has not been achieved. Previously published computed electron affinities (EA) and vertical detachment energies (VDE) agreed with experiment only for some cluster sizes, while for other cluster sizes differences as large as 1 eV were obtained. In addition, the qualitative trend of monotonically increasing EA and VDE with cluster size has not been reproduced theoretically. This and the fact that the clusters form in a highly non-equilibrium laser vaporization process,⁸ lead us to question the validity of the assumption that the most stable isomers are those observed in experiment.

Several cases have already been reported, in which the computed spectra of the most stable isomers did not agree

with PES experiments.^{1,9} Specifically, Kronik *et al.* have suggested the highest electron affinity as a predictor for cluster anion structures.¹ To explain this, they have suggested the following mechanism, illustrated in Figure 2e. The clusters initially form as neutral species. Several isomers form due to the high effective temperature. The clusters subsequently acquire an electron from the plasma (process 1→2 in Figure 2e). Then, an energetically favorable charge transfer process between anions and neutral species occurs,¹⁰ whereby the clusters with the higher vertical electron affinity (VEA) “win” the electron. In the mass spectrometry step only the charged species are selected, via acceleration in an electromagnetic field. Upon leaving the plasma region the anions cool down (process 2→3 in Figure 2e) and relax to the meta-stable state of the isomers with high VEA. The PES measurement is then performed for these isomers (process 3→4 in Figure 2e), assuming that the dwell-time before the measurement is significantly shorter than the time for conversion to a more stable isomer, which requires surmounting a considerable energy barrier.¹ Here, we examine whether such selection for TiO₂ clusters with high VEA may explain the experimentally observed size trend and its discrepancy with previous computational efforts.

We combine fully quantum mechanical configuration space exploration with many-body perturbation theory to find the GM and the high VEA isomers for (TiO₂)_n clusters with n=2-10. We obtain unprecedented agreement with experiment for the high VEA clusters and demonstrate unequivocally that these are indeed the isomers observed in PES. In addition, we find that a high VEA is associated with electron localization on a single

tricoordinated Ti atom, which may serve as an active site for catalysis.

All calculations were performed using the all-electron numerical atom-centered orbitals (NAO) code FHI-aims.¹¹ The NAO basis sets are grouped into a minimal basis, containing only basis functions for the core and valence electrons of the free atom, followed by four hierarchically constructed tiers of additional basis functions (*tier 1-4*).¹¹ A fully quantum mechanical configuration space exploration based on density functional theory (DFT) was conducted for the neutral species. For $(\text{TiO}_2)_{2-4}$ we compared simulated annealing based on Langevin molecular dynamics,¹¹ performed using the PARSEC real-space pseudopotential code,¹² to simulations based on basin hopping,¹³ performed with the Perdew-Burke-Ernzerhof (PBE)¹⁴ functional and a *tier 1* basis set. Both methods yielded the same isomers (see online supporting material); however basin hopping was found to be more efficient and was used for the larger clusters. To determine the relative energies accurately, the resulting structures were subsequently relaxed using a larger *tier 2* basis set and their zero-point vibrational energy (ZPE) was calculated.

A detailed account of the low-lying isomers found in basin hopping is provided as online supporting material. As expected, the number of low-energy isomers generally increases with cluster size. Clusters with $n=5,8,9$ have a more “glassy” energy landscape¹⁵ and exhibit an unusually large number of low-energy isomers. The prevalent Ti coordination in $(\text{TiO}_2)_{2-10}$ clusters is 4-fold. 6-fold Ti coordination emerges only for clusters with $n \geq 8$ and is expected to become prevalent for larger bulk-like clusters. The isomers reported previously in Ref. 6 are among the low energy isomers found here, however for $n=4,5,7,8,10$ a different GM was found. The different DFT functional used here may account for differences in the relative energies of the isomers. The emergence of newly found structures is attributed to the more thorough search procedure used by us.

We examined the electronic properties of the isomers found in a range of 1.25 eV from the GM for each cluster size.¹⁶ These were calculated using state-of-the-art many-body perturbation theory within the GW approximation, where G is the one-particle Green’s function and W is the dynamically screened Coulomb potential.¹⁷ Unlike the Kohn-Sham eigenvalues of DFT, the quasiparticle (QP) excitation energies obtained from GW are directly comparable to the particle removal energies measured in PES experiments. Owing to the high computational cost

of GW calculations, a perturbative approach, known as G_0W_0 , is often used. Within this approach, QP excitation energies are obtained as a first order correction to the DFT eigenvalues, using the single-electron DFT orbitals to calculate G and W . A complete account of the G_0W_0 implementation in FHI-aims is given elsewhere.¹⁸

The G_0W_0 results are sensitive to the choice of the underlying DFT functional, especially for systems with localized orbitals that have significant self-interaction errors (SIE).^{18,19,20} Hybrid functionals, which include a fraction of exact (Fock) exchange, mitigate SIE and serve better than semi-local functionals as a starting point for G_0W_0 . The G_0W_0 results presented here were obtained using the one-parameter PBE-based hybrid functional, PBEh.²¹ This is denoted as GW@PBEh. Highly converged *tier 4* NAO basis sets were used. Such calculations are converged to 0.1 eV for molecular TiO_2 .²⁰

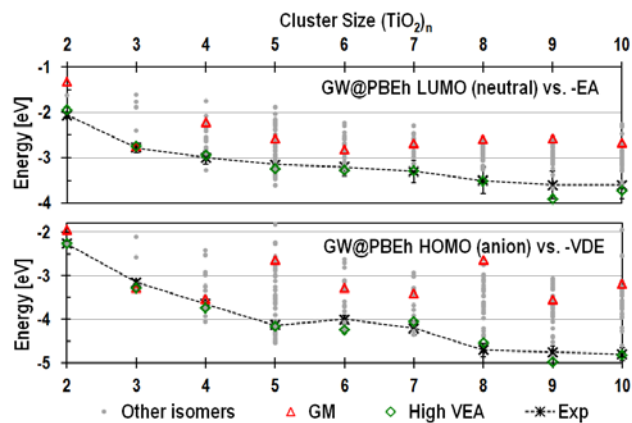


FIG. 1 The neutral LUMO and anion HOMO of low-energy isomers, obtained from GW@PBEh, compared to the experimental EA and VDE.⁸

The GW@PBEh quasiparticle excitation energies are directly comparable to PES. Specifically, the lowest unoccupied molecular orbital (LUMO) of the neutral species, obtained from GW@PBEh, corresponds to the QP excitation 1→2 in Fig. 2e, i.e., the particle addition energy, which is of equal magnitude and opposite sign to the VEA. By the same token, the highest occupied molecular orbital (HOMO) of the anions (at their optimized geometries), obtained with GW@PBEh, corresponds to the QP excitation 3→4 in Fig. 2e, i.e., the particle removal energy, which is of equal magnitude and opposite sign to the VDE.

Figure 1 shows a comparison of the GW@PBEh HOMO of the neutral species and the GW@PBEh LUMO of the anions to (minus) the experimental EA and VDE,⁸ respectively. All isomers found in the search energy

window are shown. The strong structure dependence of the electronic properties is reflected in the wide range of 1-3 eV spanned by the VEAs and VDEs of different isomers of the same cluster size. The values obtained for the GM clusters (red triangles) are quite far from the experimental values, except for the $n=3$ cluster for which the GM isomer also happens to have the highest VDE. Moreover, the GM isomers do not have the experimentally observed size trend.

For most cluster sizes, the values obtained for the isomers with the highest VDE in the search window, shown as green diamonds in Fig. 1, are in excellent agreement with experimental EAs and VDEs. For $(\text{TiO}_2)_{4,5}$ the isomers with the highest VEA in the search window significantly overshoot the experimental values. For these cluster sizes other isomers were found, with a somewhat lower energy, whose VEA and VDE are in better agreement with experiment (see also Figure 2c,d). These are shown as green diamonds in Fig. 1. Unlike the GM isomers, the isomers with high VEA not only agree with experiment quantitatively but also possess the correct size trend. The selection for high VEA rather than low energy isomers finally provides the sought after explanation for the experimental findings of Zhai and Wang.⁸

A detailed comparison of the anion GW@PBEh QP excitation energies of different isomers to PES⁸ is shown in Figure 2a-d for clusters with $n=2-5$. The calculated spectra are broadened by convolution with a Gaussian to simulate experimental broadening. For the larger clusters the experimental spectra become quite featureless due to significant broadening, making such a comparison uninformative. For $(\text{TiO}_2)_{2,3}$ the spectra of the highest VEA isomers are in better agreement with PES than other isomers. For $(\text{TiO}_2)_{4,5}$, the VDE of the highest VEA isomer is somewhat higher than the experimental value, although still within the range of the experimental broadening. Other isomers with high VEA and a somewhat lower energy, which agree better with experiment, were found in the search window. For $n=5$, we find several isomers with a high VEA about 1 eV above the global minimum. We cannot determine with certainty which isomer is the one observed in experiment solely on the basis of the first PES peak and the onset of the second peak. It is also possible that more than one isomer is present in experiment. In any case, the high VEA isomers are in better agreement with experiment than the GM isomer. Thus, the detailed comparison to

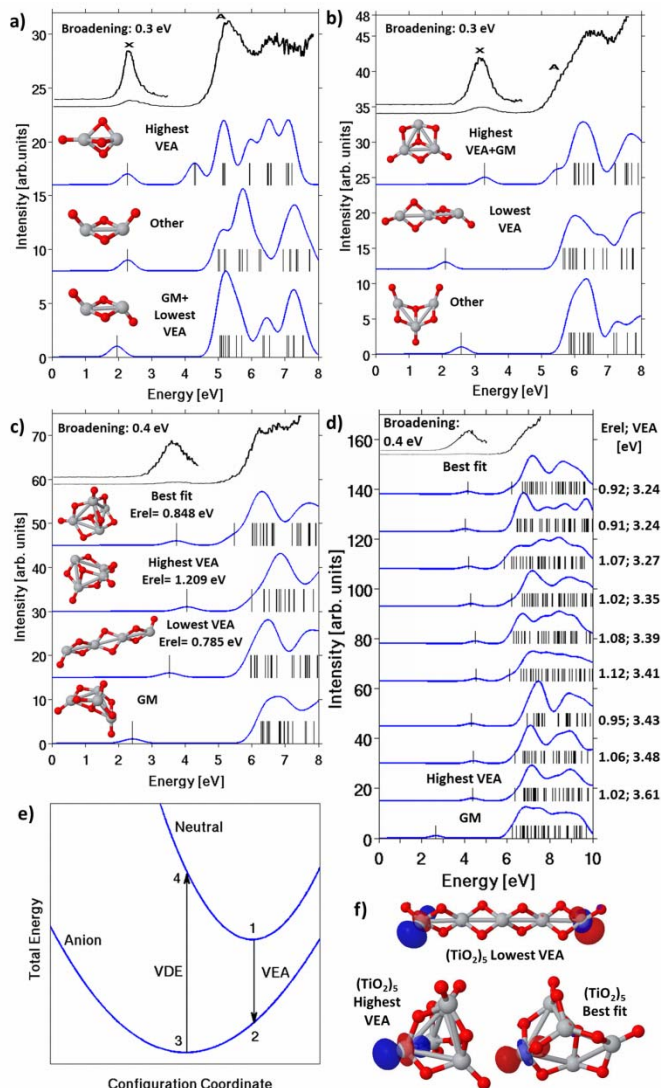


FIG. 2 Comparison of the anion GW@PBEh spectra of different isomers to PES,⁸ for clusters with a) $n=2$, b) $n=3$, c) $n=4$ and d) $n=5$. e) Illustration of the path in energy and configuration space from neutral cluster formation to anion PES measurement. f) Spatial distribution of the anion HOMO for the $n=5$ isomers with the lowest and highest VEA, and for the high VEA cluster that agrees best with experiment.

PES reaffirms our conclusion that isomers with high VEA are selectively observed.

A connection between the structure of the isomers and their VEA is revealed by examining their geometrical features and the spatial distribution of the anion HOMO orbital. We observe that localization of the anion HOMO generally leads to a higher VEA while delocalization leads to a lower VEA. We find that for linear clusters the anion HOMO has lobes on the Ti atoms on both ends of the cluster (an example for the $n=5$ cluster is shown in Fig.

2f) and this is associated with a very low VEA. All the high VEA clusters found here have one tricoordinated Ti atom with O-Ti-O angles close to the tetrahedral angles of 109.5° .²² The anion HOMO is highly localized on that Ti atom. Examples of two $n=5$ clusters with high VEA are shown in Figure 5f. 3-fold Ti coordination is particularly common in this cluster size. The structural feature possessed by TiO_2 clusters with high VEA is reminiscent of the Ti^{3+} sites, also known as F-centers, on TiO_2 surfaces, which are known to play an essential role in photocatalysis and dissociative chemisorption.²³ The fact that the anion cluster formation procedure typically used for PES experiments selects for isomers with these highly reactive sites may be exploited for applications in catalysis.

To summarize, we employed a combination of DFT-based basin hopping and many-body perturbation theory with in the G_0W_0 approximation to study $(\text{TiO}_2)_{2-10}$ clusters. We demonstrated unequivocally that isomers with high VEA are observed in PES experiments rather

than the GM isomers. These clusters possess a highly reactive Ti^{3+} site. The selectivity for high VEA clusters may be exploited for applications in catalysis. The fact that such selectivity for high VEA has been demonstrated for anion clusters of two dissimilar materials, deuterated silicon¹ and TiO_2 , indicates that it is likely a more general phenomenon. This calls for a paradigm shift in the computational interpretation of PES experiments on charged clusters.

We thank X. Ren, V. Blum, E. C. Beret, and L. Ghiringhelli from the Fritz Haber Institut der MPG and J. E. Moussa from Sandia National Laboratory for their interest and advice. This work was supported under NSF grants DMR-0941645 and OCI-1047997, and DOE grant DE-SC0001878. Computational resources were provided by National Energy Research Scientific Computing Center (NERSC) and the Texas Advanced Computing Center (TACC) under grant TG-DMR090026.

- [1] L. Kronik et al., Nat Mater **1**, 49 (2002)
- [2] See e.g., N. Binggeli and J. R. Chelikowsky, Phys. Rev. Lett. **75**, 493 (1995); Müller et al. Phys. Rev. Lett. **85**, 1666 (2000); Phys. Rev. B, **71**, 165433 (2006)
- [3] O. Guliamov, L. Kronik, and K. A. Jackson, J. Chem. Phys. **123**, 204312 (2005); H. J. Zhai et al. J. Am. Chem. Soc. **129**, 13270 (2007); H. J. Zhai et al. J. Am. Chem. Soc. **130**, 5167 (2008); A. Aguado and O. Kostko, J. Chem. Phys. **134**, 164304 (2011)
- [4] C. R. A. Catlow et al. Phys. Chem. Chem. Phys. **12**, 786 (2010); H. J. Zhai, L. S. Wang Chem. Phys. Lett. **500**, 185 (2010)
- [5] M. Calatayud, L. Maldonado, and C. Minot J. Phys. Chem. C **112**, 16087 (2008); O. A. Syzgantseva et al. J. Phys. Chem. C **115**, 15890 (2011)
- [6] Z. W. Qu and G. J. Kroes J. Phys. Chem. B **110**, 8998 (2006); J. Phys. Chem. C **111**, 16808 (2007)
- [7] S. Hamad et al. J. Phys. Chem. B **109**, 15741 (2005); S. Li and D. A. Dixon J. Phys. Chem. A **112**, 6646 (2008); D. J. Mowbray J. Phys. Chem. C **113**, 12301 (2009); S. A. Shevlin, and S. M. Woodley J. Phys. Chem. C **114**, 17333 (2010); W. Zhang et al. Mater. Chem. Phys. **130**, 196 (2011); L. Tang et al. J. Comput Chem **33**, 163 (2012)
- [8] H.-J. Zhai and L.-S. Wang, J Am Chem Soc **129**, 3022 (2007)
- [9] See e. g., B. Kiran et al. Proc. Nat. acad. Sci. **102**, 961 (2005); Ji et al. Angew Chem Int Ed **44**, 7119 (2005); I. Iordanov and J. O. Sofo, J Chem Phys **134**, 184310 (2011)
- [10] O. V. Boltalina et al. Chem. Phys. Lett. **256**, 253 (1996).
- [11] V. Blum et al., Comput Phys Commun **180**, 2175 (2009)
- [12] J. R. Chelikowsky J. Phys. D **33**,R33 (2000)
- [13] R. Gehrke and K. Reuter, Phys. Rev. B **79**, 085412 (2009)
- [14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys Rev Lett **77**, 3865 (1996); Phys Rev Lett **78**, 1396 (1997)
- [15] S. De et al., Phys Rev Lett **106**, 225502 (2011)
- [16] We have chosen a large enough energy range to reflect the highly non-equilibrium conditions of cluster formation by laser vaporization, as we have no means to precisely determine the effective temperature of this process.⁸
- [17] L. Hedin, Physical Review **139**, A796 (1965); M. S. Hybertsen and S. G. Louie, Phys Rev B **34**, 5390 (1986)
- [18] X. Ren, P. Rinke, V. Blum, J. Wierink, A. Tkatchenko, A. Sanfilipo, K. Reuter, and M. Scheffler, to be published
- [19] N. Marom et al. Phys. Rev. B **84**, 195143 (2011)
- [20] N. Marom et al. Phys. Rev. B **84**, 245115 (2011)
- [21] C. Adamo and V. Barone, J Chem Phys **110**, 6158 (1999)
- [22] The $(\text{TiO}_2)_7$ highest VEA cluster is the only exception to this rule.
- [23] G. Lu, A. Linsebigler, and J. T. Yates, Jr., J. Phys. Chem. **98**, 11733 (1994); T. L. Thompson and J. T. Yates, Jr. Chem. Rev. **106**, 4428 (2006); U. Diebold Surf. Sci. Rep. **48**, 53 (2003)