

## Structure Selection Based on High Vertical Electron Affinity for $\text{TiO}_2$ Clusters

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We study the structure and electronic properties of  $(\text{TiO}_2)_{2-10}$  clusters by 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  $\text{Ti}^{3+}$  site. The selectivity for highly reactive clusters may be exploited for applications in catalysis.

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Clusters comprising up to a 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 [1–3]. 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  $\text{TiO}_2$  clusters, in particular, have attracted much attention due to their potential application in catalysis [4,5]. Computational studies of  $\text{TiO}_2$  clusters [5–7] 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 Wang [8] has not been achieved. Previously published computed electron affinities (EAs) and vertical detachment energies (VDEs) 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 EAs and VDEs with cluster size has not been reproduced theoretically. This and the fact that the clusters form in a highly nonequilibrium laser vaporization process [8] lead us to question the validity of the assumption that the most stable isomers are those observed in an 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 Fig. 1(e). 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  $\rightarrow$  2 in Fig. 1(e)]. 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  $\rightarrow$  3 in Fig. 1(e)] and relax to the metastable state of the isomers with high VEA. The PES measurement is then performed for these isomers [process 3  $\rightarrow$  4 in Fig. 1(e)], 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  $\text{TiO}_2$  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  $(\text{TiO}_2)_n$  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 by using the all-electron numerical atom-centered orbitals code FHI-AIMS [11]. The numerical atom-centered orbital 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 (tiers 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

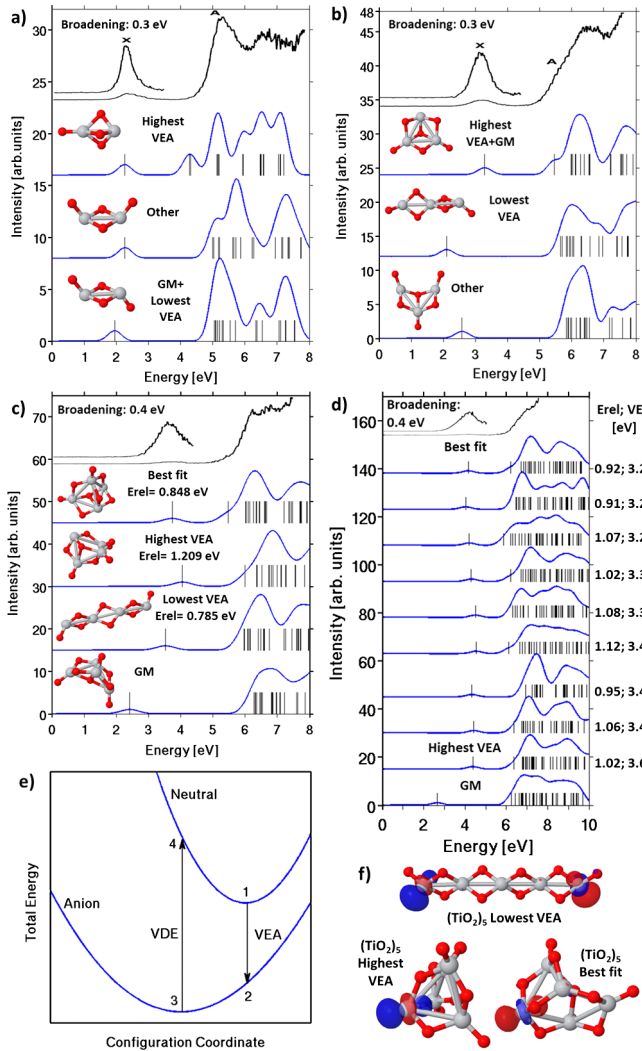


FIG. 1 (color online). Comparison of the anion GW@PBEh spectra of different isomers to PES [8], for clusters with (a)  $n = 2$ , (b)  $n = 3$ , (c)  $n = 4$ , and (d)  $n = 5$ . (e) Illustration of the path in energy and configuration space from neutral cluster formation to anion PES measurement. (f) Spatial distribution of the anion HOMO for the  $n = 5$  isomers with the lowest and highest VEAs and for the high VEA cluster that agrees best with the experiment.

based on Langevin molecular dynamics [1,2], performed by 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 [15]); 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 by using a larger tier 2 basis set, and their zero-point vibrational energy was calculated.

A detailed account of the low-lying isomers found in basin hopping is provided in [15]. As expected, the number

of low-energy isomers generally increases with cluster size. Clusters with  $n = 5, 8, 9$  have a more “glassy” energy landscape [16] and exhibit an unusually large number of low-energy isomers. The prevalent Ti coordination in  $(\text{TiO}_2)_{2-10}$  clusters is fourfold. Sixfold Ti coordination emerges only for clusters with  $n \geq 8$  and is expected to become prevalent for larger bulklike 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 [17]. These were calculated by 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 [18]. 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, by 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 [19].

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 [19–21]. Hybrid functionals, which include a fraction of exact (Fock) exchange, mitigate self-interaction errors and serve better than semilocal functionals as a starting point for  $G_0W_0$ . The  $G_0W_0$  results presented here were obtained by using the one-parameter PBE-based hybrid functional PBEh [22]. This is denoted as GW@PBEh. Highly converged tier 4 numerical atom-centered orbital basis sets were used. Such calculations are converged to 0.1 eV for molecular  $\text{TiO}_2$  [21].

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  $1 \rightarrow 2$  in Fig. 1(e), 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  $3 \rightarrow 4$  in Fig. 1(e), i.e., the particle removal energy, which is of equal magnitude and opposite sign to the VDE.

Figure 2 shows a comparison of the GW@PBEh HOMO of the neutral species and the GW@PBEh LUMO of the anions to (minus) the experimental EAs and VDEs [8],

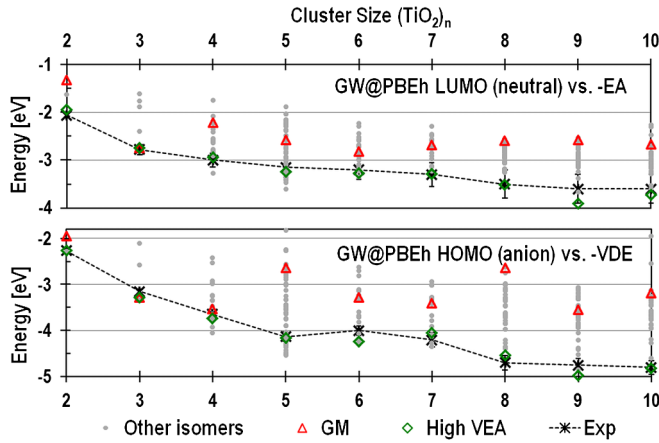


FIG. 2 (color online). The neutral LUMO and anion HOMO of low-energy isomers, obtained from GW@PBEh, compared to the experimental EAs and VDEs [8].

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. 2, 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 Figs. 1(c) and 1(d)]. These are shown as green diamonds in Fig. 2. Unlike the GM isomers, the isomers with high VEAs not only agree with experiment quantitatively but also possess the correct size trend. The selection for high VEAs 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 PES [8] is shown in Figs. 1(a)–1(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 the experiment. In any case, the high VEA isomers are in better agreement with experiment than the GM isomer. Thus, the detailed comparison to PES reaffirms our conclusion that isomers with high VEAs are selectively observed.

A connection between the structure of the isomers and their VEAs 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. 1(f)] 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  $109.5^\circ$  [23]. The anion HOMO is highly localized on that Ti atom. Examples of two  $n = 5$  clusters with high VEAs are shown in Fig. 1(f). Threefold Ti coordination is particularly common in this cluster size. The structural feature possessed by  $\text{TiO}_2$  clusters with high VEAs is reminiscent of the  $\text{Ti}^{3+}$  sites, also known as *F* centers, on  $\text{TiO}_2$  surfaces, which are known to play an essential role in photocatalysis and dissociative chemisorption [24]. 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.

In summary, we employed a combination of DFT-based basin hopping and many-body perturbation theory in the  $G_0W_0$  approximation to study  $(\text{TiO}_2)_{2-10}$  clusters. We demonstrated unequivocally that isomers with high VEAs are observed in PES experiments rather than the GM isomers. These clusters possess a highly reactive  $\text{Ti}^{3+}$  site. The selectivity for high VEA clusters may be exploited for applications in catalysis. The fact that such selectivity for high VEAs has been demonstrated for anion clusters of two dissimilar materials, deuterated silicon [1] and  $\text{TiO}_2$ , 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.

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