ATOMIC INSIGHT INTO THE ADSORPTION OF MOLECULAR O$_2$ ON THE RUTILE TiO$_2$(110) (1X1) SURFACE

Igor Sokolović[a], Michele Reticcioli[b], Martin Čalkovský[a] , Cesare Franchini[b], Michael Schmid[a], Ulrike Diebold[a], Martin Setvin[a]

[a]E134 - Institute of Applied Physics, TU Wien
[b]Center for Computational Materials Science, Faculty of Physics, University of Vienna, Vienna, Austria

INTRODUCTION

Transition metal oxides attract significant research attention due to their various application possibilities and intriguing phenomena at their surfaces [1, 2]. Rutile TiO$_2$ is considered a prototypical example of this class of materials and its (110) facet is the most studied transition metal-oxide surface up to date [1]. It attracts attention for its possible applications in photocatalysis [3], photochemical solar cells [4], memsistors [5] and a transparent conductors [6].

The use of local-probe techniques in a controlled environment of ultra-high vacuum (UHV), together with quantum-mechanical simulations, is a well-established approach for resolving fundamental questions related to the applications. This research focuses on the interaction of O$_2$ molecules with the reduced rutile TiO$_2$(110) surface; a long-standing question on this material, which still does not have a widely-accepted solution [7].

EXAMINATIONS

We employed the non-contact atomic force microscopy (AFM) as a non-intrusive local technique. The AFM, in constant height imaging mode, provides atomic resolution as can be seen in panels (a-b) of the Figure. The Figure clearly shows the as-adsorbed molecular oxygen with atomic resolution, together with the rows of bridging oxygen atoms (with some bridging oxygen vacancies) characteristic for this surface. The theoretical treatment utilizes U-corrected density functional theory (DFT). The precise ground state of the clean, reduced surface, was determined in previous studies [8,9] and can be seen in the panel (c) of the Figure. It is characterized by the presence of electronic small polarons induced by the presence of electron-donating bridging oxygen vacancy. This theoretical approach enables us to non-ambiguously determine the charge associated with each of the adsorbed molecular species, illustrated in panel (d) of the Figure.
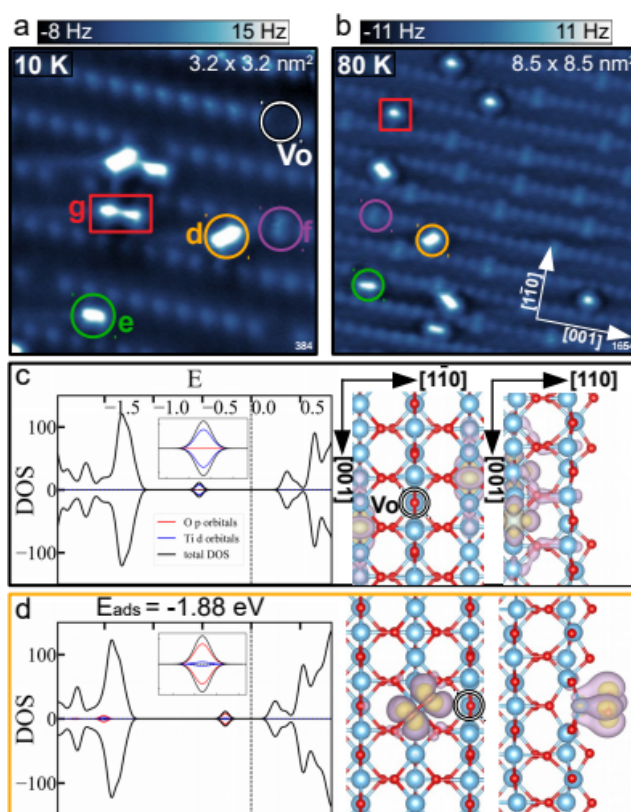
Adsorption of molecular O$_2$ to the reduced rutile TiO$_2$ (110) surface: (a,b) constant-height AFM images of the surface exposed to O$_2$ (c,d) DFT calculations of the adsorption showing charge transfer to the adsorbed O$_2$.

RESULTS AND DISCUSSION

The O_2 molecules adsorb to the reduced TiO_2 (110) surface in three molecular configurations below 100 K: one type of O_2 molecule filling the oxygen vacancy and two types of O_2 molecules adsorbed on Ti_{5c} sites. All the adsorbed O_2 are predicted by the DFT+U to have undergone a charge transfer from the polaron-hosting Ti_{6c} sites, making them chemisorbed (ionosorbed) in the peroxo form. The chemisorbed character of the molecules is confirmed by their presence on the surface after annealing up to room temperature. The increase in temperature also reveals dissociation channels. As already indicated by a STM study [10], we find that the application of bias voltage between the sample and the tip also dissociates the adsorbed O_2, which explains the current ambiguities in the literature and highlights the importance of nc-AFM in this research. The assignment of the calculated properties of the adsorbed O_2 to the experimentally observed ones is further confirmed by comparing the measured and calculated force-distance curves. This procedure, in particular, supports the adsorbed O_2^{2-} charge assignment, a long-standing discussion in the literature. The effect of UV light on the adsorbed molecules is investigated, and the possible reaction pathways are observed.

CONCLUSION

This research unambiguously identified the adsorption configurations of molecular O_2 on the reduced rutile TiO_2 (110) surface, and determined all the adsorbed species to be chemisorbed with two excess electrons O_2^{2-}. The methodology used in this research can be applied to adsorption studies of other gases on this surface [11], and to other reducible transition-metal oxide surfaces.

REFERENCES

[1] Diebold U., *Surface Science Reports* 48, 53 (2003).

[2] Fujishima A., Zhang X., and Tryk D. A., *Surface Science Reports* 63, 515 (2008).

[3] Henderson M.A., *Surface Science Reports* 66, 185 (2011).

[4] Linsebigler, A.L., Lu, G. and Yates Jr, J.T., *Chemical Reviews* 95, 735 (1995)

[5] Szot, K., Rogala, M., Speier, W., Klusek, Z., Besmehn, A., and Waser, R., *Nanotechnology* 22, 254001 (2011).

[6] Furubayashi, Y., Hitosugi, T., Yamamoto, Y., Inaba, K., Kinoda, G., Hirose, Y., Shimada, T. and Hasegawa, T., *Applied Physics Letters* 86, 252101 (2005).

[7] Henderson, M.A. and Lyubinetsky, I., *Chemical Reviews* 113, 4428 (2013).

[8] Setvin, M., Franchini, C., Hao, X., Schmid, M., Janotti, A., Kaltak, M., Van de Walle, C.G., Kresse, G. and Diebold, U., *Physical Review Letters* 113, 086402 (2014).

[9] Reticcioli, M., Setvin, M., Schmid, M., Diebold, U., and Franchini, C. , *Physical Review B* 98, 045306 (2018).

[10] Scheiber, P., Riss, A., Schmid, M., Varga, P. and Diebold, U., *Physical Review Letters* 105, 216101 (2010).

[11] Reticcioli, M., Sokolović, I., Schmid, M., Diebold, U., Setvin, M. and Franchini, C., *Physical Review Letters* 122, 016805 (2019).