

LA-UR-15-27576 (Accepted Manuscript)

## A Theoretical Study of Trimethylacetic Acid Adsorption on CeO<sub>2</sub>(111) Surface

Yang, Ping

Provided by the author(s) and the Los Alamos National Laboratory (0000-00-00).

**To be published in:** Journal of Physical Chemistry C ; Vol.120, iss.5, p.2655-2666, Feb. 11, 2016

**DOI to publisher's version:** 10.1021/acs.jpcc.5b09790

**Permalink to record:** <http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-15-27576>

**Disclaimer:**

Approved for public release. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

FOR DEMONSTRATION PURPOSES ONLY



# A Theoretical Study of Trimethylacetic Acid Adsorption on CeO<sub>2</sub>(111) Surface

Weina Wang,<sup>1,2</sup> S. Thevuthasan,<sup>2</sup> Wenliang Wang<sup>1\*</sup>, Ping Yang,<sup>2,3\*</sup>

1 Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, China

2 Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99352, USA

3 Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, 87545

Contacts: [wliwang@snnu.edu.cn](mailto:wliwang@snnu.edu.cn), [pyang@lanl.gov](mailto:pyang@lanl.gov)

**FOR DEMONSTRATION PURPOSES ONLY**

## Abstract

Trimethylacetic Acid (TMAA) adsorption on the stoichiometric and oxygen-deficient CeO<sub>2</sub>(111) surfaces was investigated using density functional theory that accounts for the on-site Coulomb interaction via a Hubbard term (DFT+U) and long-range dispersion correction. Both molecular state and dissociative state (TMAA → TMA<sup>-</sup> + H<sup>+</sup>) were identified on stoichiometric and oxygen-deficient CeO<sub>2</sub>(111) surfaces. For the stoichiometric surface, two thermodynamically favorable configurations with adsorption energies of the order of -30 kcal/mol are identified; one is molecule adsorption state and the other one is dissociative state. For the oxygen-deficient surface, dissociative states are more favorable than molecular states. The most favorable configuration is the dissociative adsorption of TMAA with the adsorption energy of the order of -77 kcal/mol. Dissociated TMA moiety takes the position of oxygen vacancy, forming three Ce-O bonds. The signature vibrational frequencies for these thermodynamically stable structures are reported as well as their electronic structures. The effects of long-range dispersion interactions are found to be negligible for geometries but important for adsorption energies.

Keywords: density functional calculations; dissociative adsorption; carboxylic acid; cerium oxide, electronic configuration, oxygen-deficient CeO<sub>2</sub>(111) surface; van der Waals interaction.

**FOR DEMONSTRATION PURPOSES ONLY**