# Investigation of Photo-Responsive Titania Surfaces

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## Background

Titania (TiO$_2$) is an oxide commonly used for photocatalysis. This proclivity to form free radicals when exposed to light has also prompted interest in applying porous TiO$_2$ as a reactive/responsive membrane. Surfaces of both main polymorphs of TiO$_2$ (especially rutile {110} and anatase {101}) have been shown [1,2] to be stable and photo-active.

PAA 10

H
C
O
Ti

TiO$_2$ Anatase Unit Cell

TiO$_2$ Rutile Unit Cell
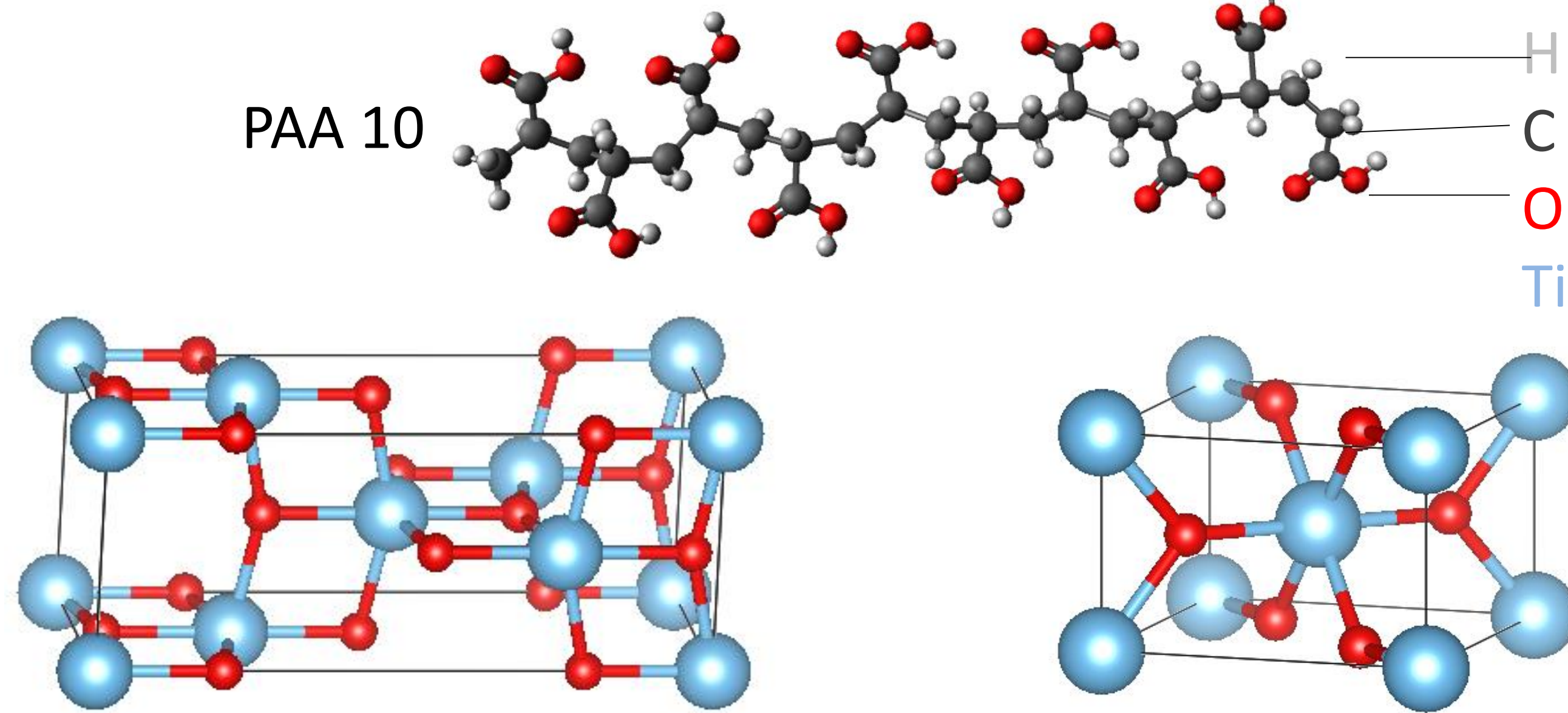
Polyacrylic acid (PAA) is a molecule of interest as changes in pH can cause the molecule to contract or expand [3,4], due to changes in the charge distribution relating to the carboxyl group. Due to TiO2's ability to generate photocarriers, we hypothesize that porous TiO2 substrates are able to induce light-mediated expansion/contraction in PAA. Photo-carriers from TiO2 modify charge distributions on PAA similar to how changes in pH have been shown to do.

pH

Light?

e$^-$
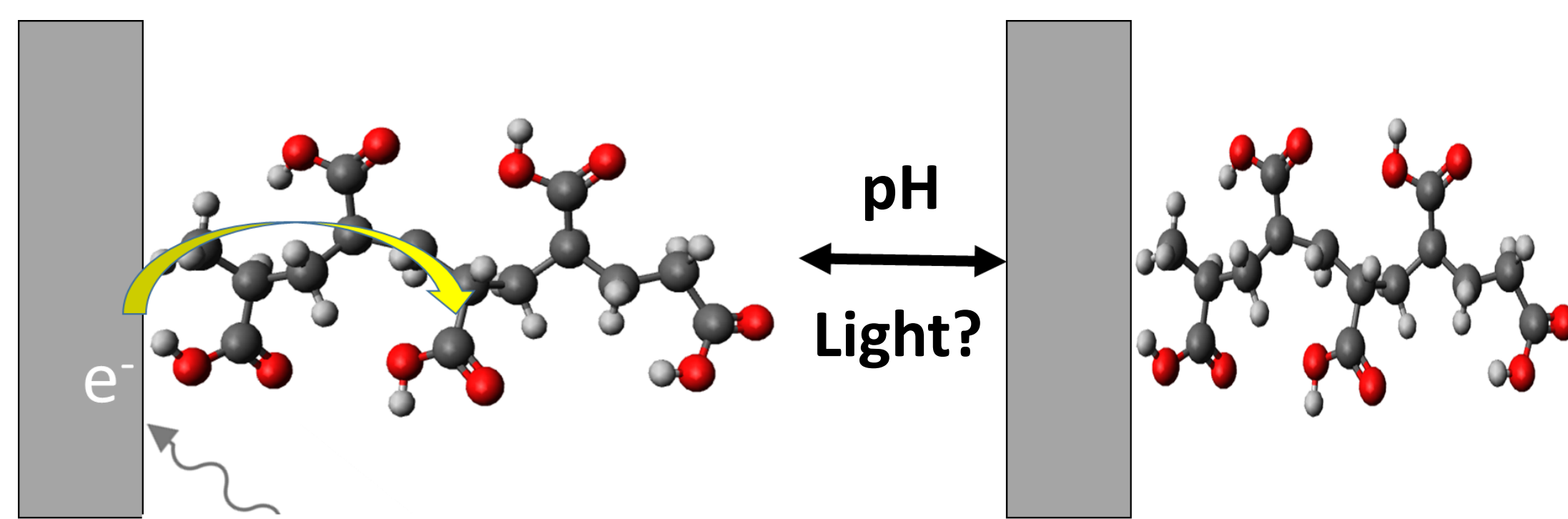
## Methods

The Vienna ab-initio software package (VASP) was used to perform Density Functional Theory (DFT) calculations to determine the minimum energy arrangement of atoms. One intermediate value we are interested in knowing is the adsorption energy as a function of coverage for water molecules, which determines surface structure.

$$E_{H_2O,ads} = \frac{E_{total} - n_{TiO_2}E_{TiO_2} - A_{hkl}\gamma_{hkl} - n_{H_2O}E_{H_2O}}{n_{H_2O}}$$
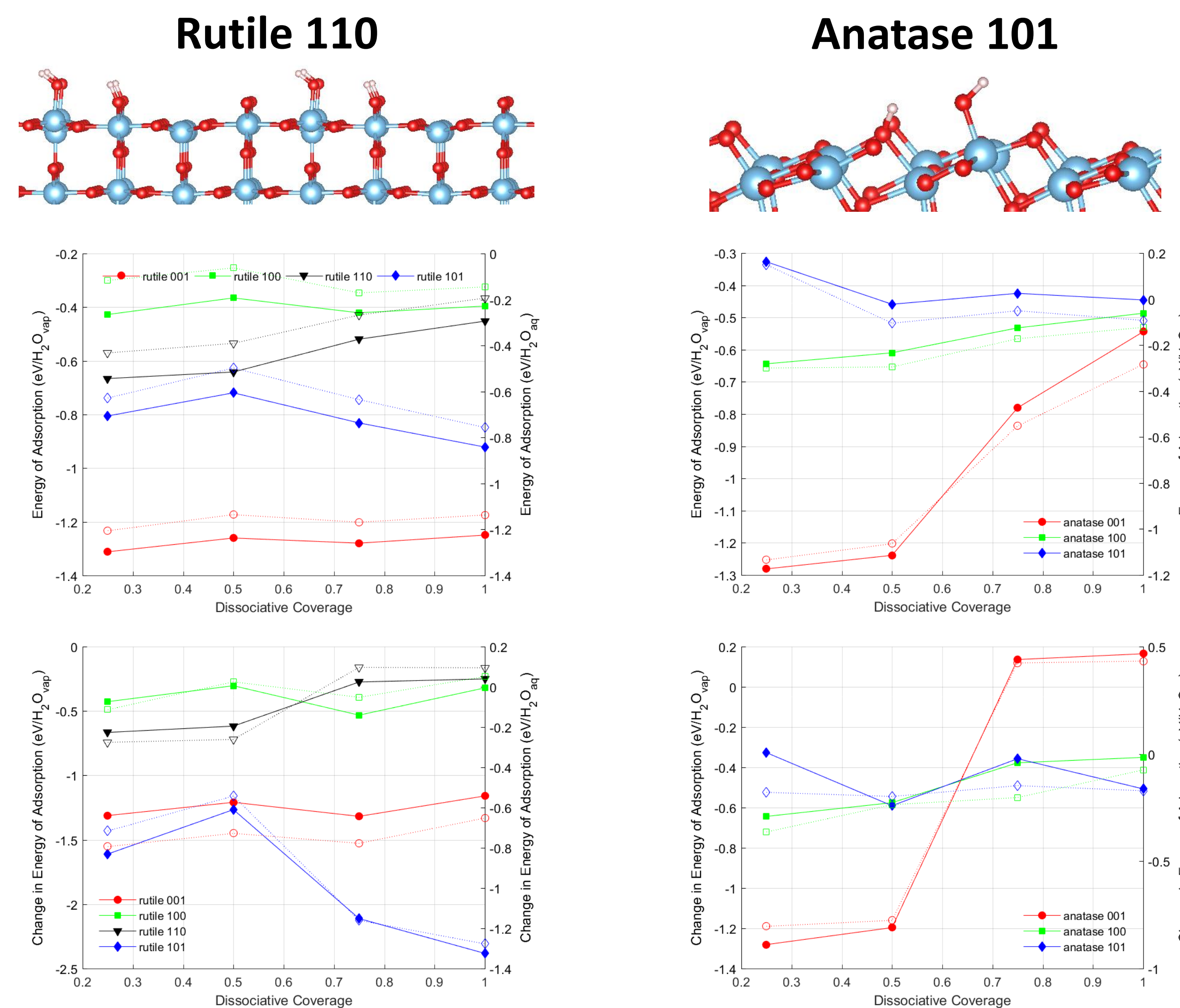
$$dE_{H_2O,ads} = E_n - (E_{n-1} - E_{H_2O})$$

H   H   H       H   H   H       H   H   H
H   H   H       H   H   H
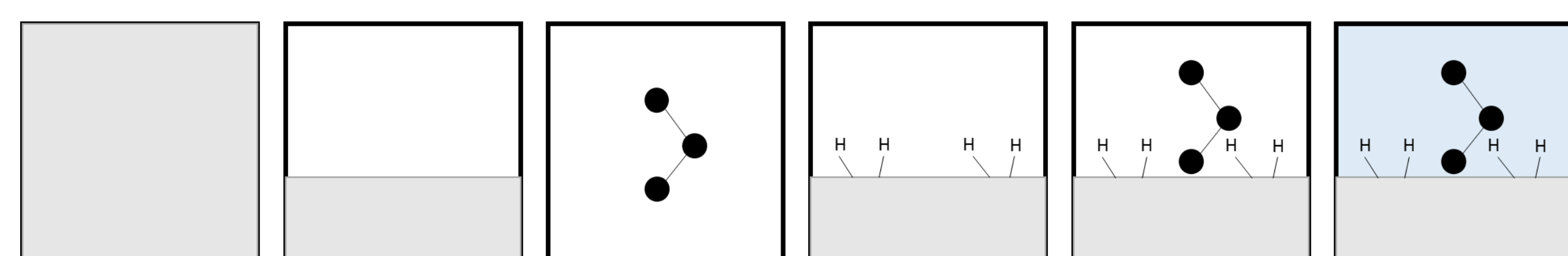
$$E_{PAA,ads} = E_{total} - n_{TiO_2}E_{TiO_2} - A_{hkl}\gamma_{hkl} - n_{H_2O}(E_{H_2O} - E_{H_2O,ads}) - E_{PAA}$$

## Hydroxyl Adsorption

Results are very similar to previous results for anatase [5]. New to this research is a encompassing description of rutile surfaces and the use of implicit solvation as a representative for an aqueous environment.

### Rutile 110

### Anatase 101

## PAA Adsorption Energy

Literature [6] suggests at least 3 different attachment geometries for carboxylic acids on titania. BB had the lowest adsorption energy, but may or may not have a large kinetic barrier to dissociation. M1 was chosen as the attachment geometry for tests.

BB   >   M2B   >   M1

| Type | Energy of Adsorption (eV) |
| --- | --- |
| M1 | -0.502 eV |
| BB | -1.878 eV |
| M2B | -0.714 eV |

Larger molecules can distribute changes in charge better, but also run the risk of having molecule-molecule self interactions. Coverage can be correlated to pH in future tests.

PAA5 (M1):

| | Energy of Adsorption (eV) | |
| --- | --- | --- |
| | 25% H$_2$O Coverage | 100% H$_2$O Coverage |
| PAA1 | -0.490 | -0.430 |
| PAA2 | -0.534 | -0.441 |
| PAA3 | -0.729 | --- |
| PAA4 | -0.698 | -0.598 |
| PAA5 | -0.665 | -0.596 |

## PAA Charge Distribution

Adding or removing an electron is analogous to a photoexcitation in the ab-initio sense. Changing the total number of charges in the boxes changes the charge distribution in both the molecule and the titania.
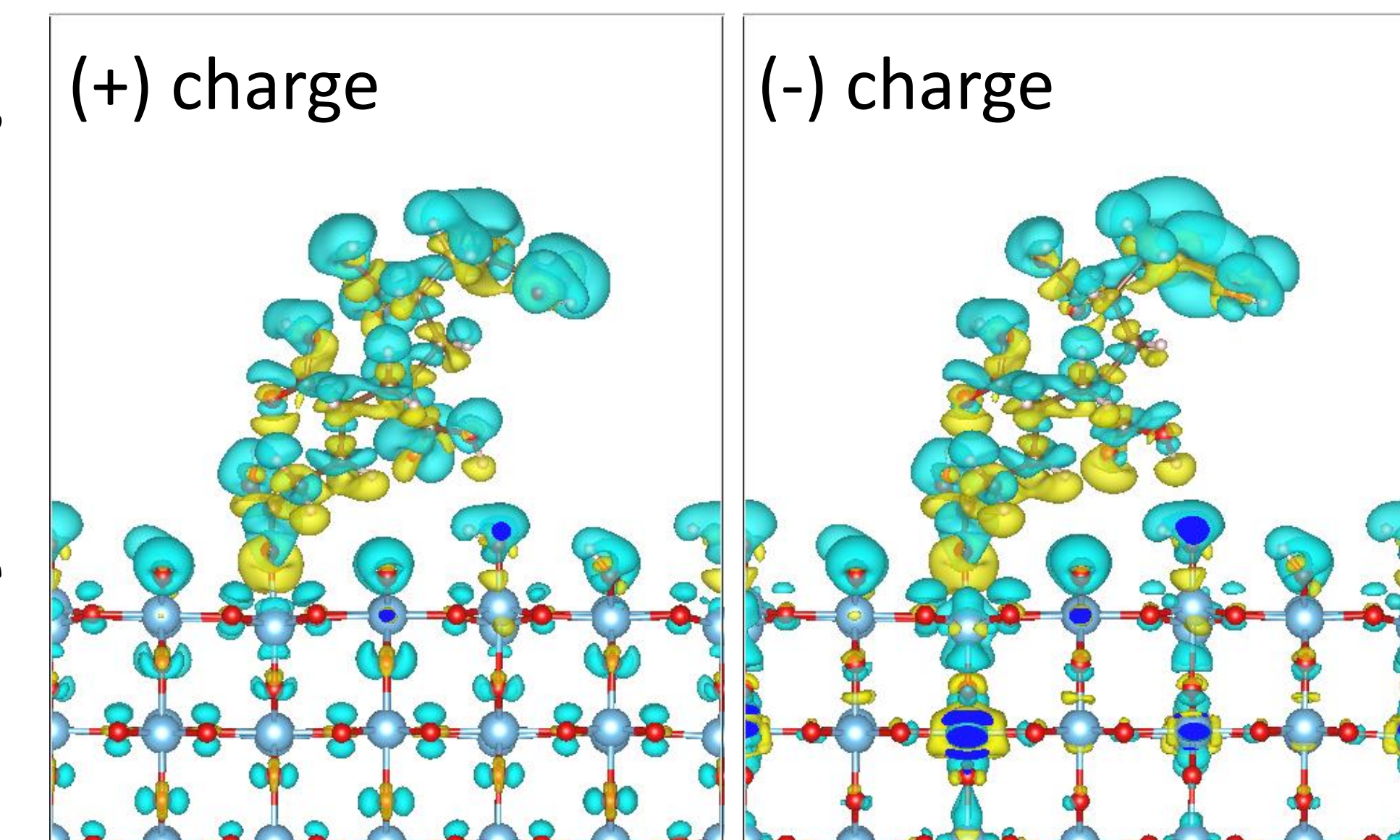
(+) charge

(-) charge

Tests with different charges experience strain effects. Scaled up to hundreds of monomers it will have a huge steric effect. Relaxation tests cannot be performed in solvation.

| | (+) charge | (-) charge | -H | -OH | -2H | -2OH |
| --- | --- | --- | --- | --- | --- | --- |
| Strain | 0.00112 | -0.00163 | -0.00056 | 0.00292 | -9e-5 | 0.00400 |

## Related: Band Structures of H-doped Titania

Titania is commonly tested with oxygen vacancies or N-doping to enhance visible light absorption.
Dr Rankin's group has shown H-doping also enhances visible light absorption.
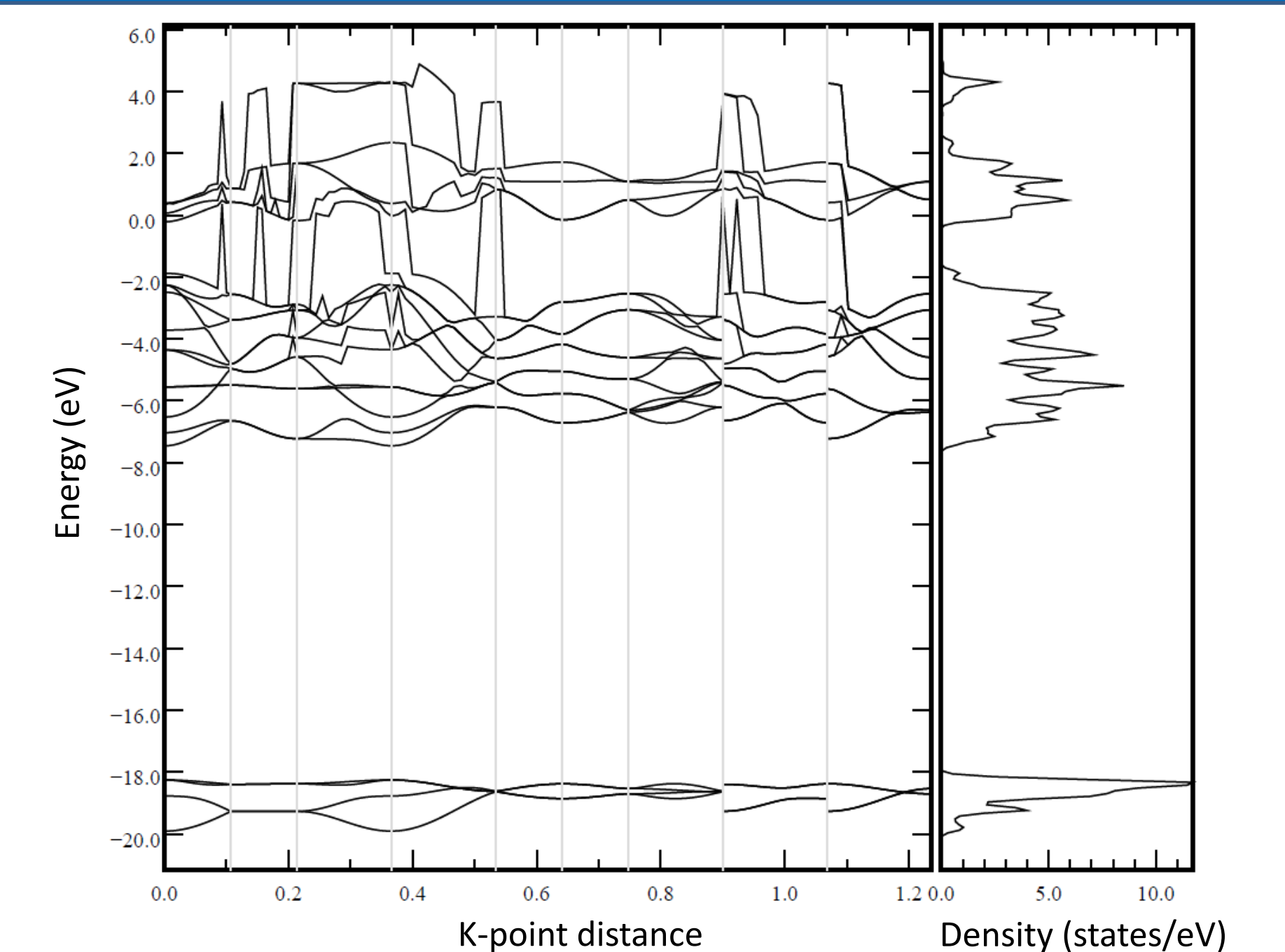
## Conclusions and Future Work

- Comparison of vacuum and solvation calculations suggest as you increase surface coverage, less energy contributions will be made by the solvation tool to passivate the surface.
- PAA adsorption energies are based on volume of charge distribution and molecule self interactions
- Changes in charge distribution affect both TiO$_2$ and PAA, suggesting light mediated charge transfer
- The effects of oxygen vacancies and doping will be investigated
- Specific chemical mechanisms will be investigated

## References

[1] U. Diebold. *Surface Science Reports* 48 (2003) 53-229.
[2] Esch et al. *Applied Surface Science.* 288 (2014): 275-287. Web.
[3] Kister, Cassanas, and Vert. *Polymer* 39(2) (1998): 267-273. Web.
[4] Bohmer et al. *J. of Colloid and Interface Sci.* 164, 126-135 (1994).
[5] C. Arrouvel et al. *Journal of Catalysis 222 (2004) 152–166.*
[6] Manzhos et al. *Molecules.* 2015, 20, 3371-3388.

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