Electronic Supporting Information

The Interaction of Molecular Oxygen on LaO Terminated Surfaces of La_2NiO_4

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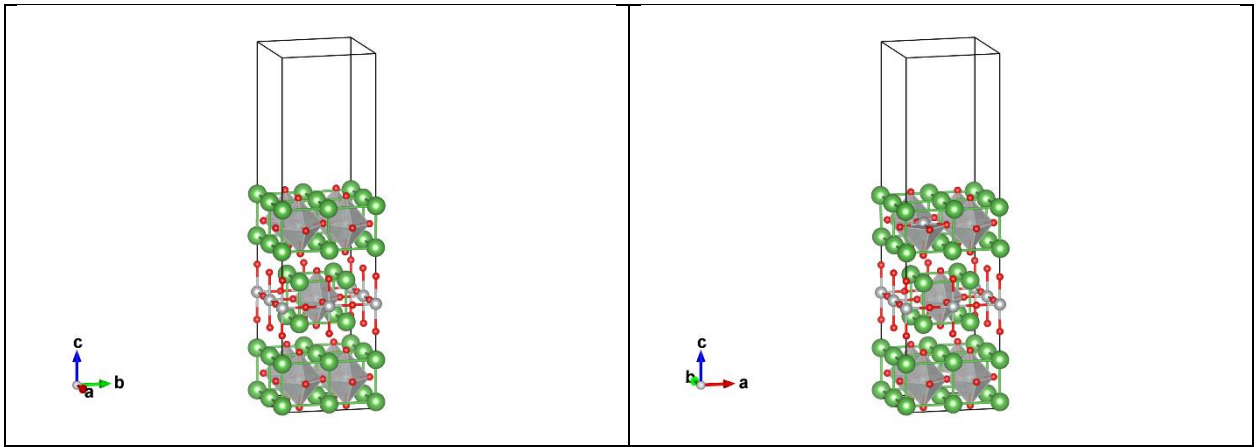
Possible Configurations for Oxygen Surface Interaction

Both defect free and defective LaO terminated surfaces are obtained by cleaving the bulk crystal along the <001> direction. The slab models, shown in Figure 1, are created as a type 2 Tasker surfaces with 9 alternating layers composed of 3 LaO double layers and 3 NiO_2 layers.



a) b)

Figure 1. Nine atomic layer slab representations of a) defect-free, and b) defective 2 x 2 surfaces. La is depicted green, Ni is depicted grey and O is depicted red.

All possible approach configurations for the oxygen molecule with respect to the surface species are considered for the first principle calculations in the Density Functional Theory (DFT) formalism. The following figures depict close-up views of the top perovskite layer of the defect free (left hand column) and the defective surfaces (right hand column) before (a, b) and after (c, d) the relaxation of 9 atomic layer La_2NiO_4 slab. Electron charge density difference plots (e, f) are also shown in each figure. Positive and negative electron density differences are denoted by blue and yellow respectively.

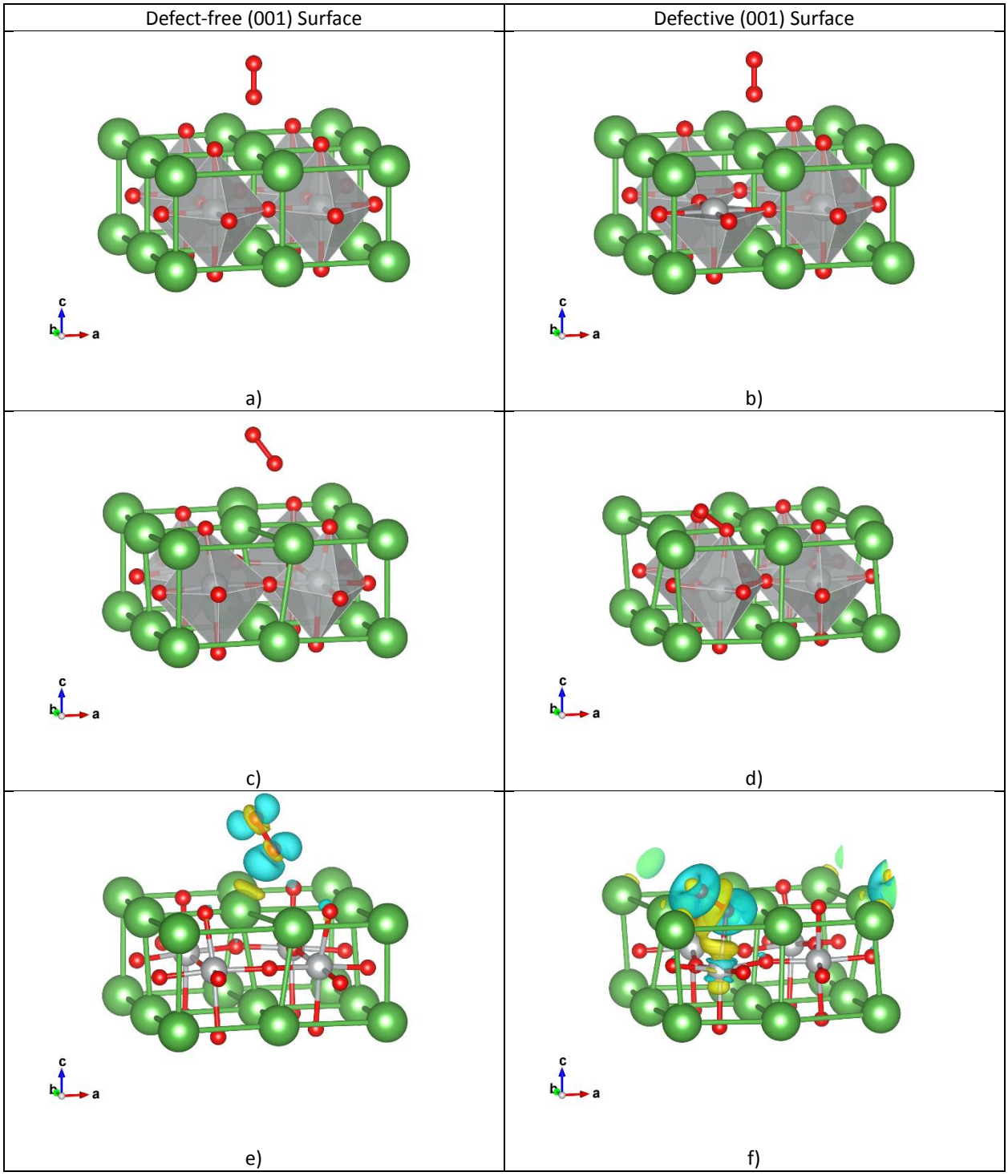


Figure 2. Triplet oxygen molecule is placed end-on top of a La atom.

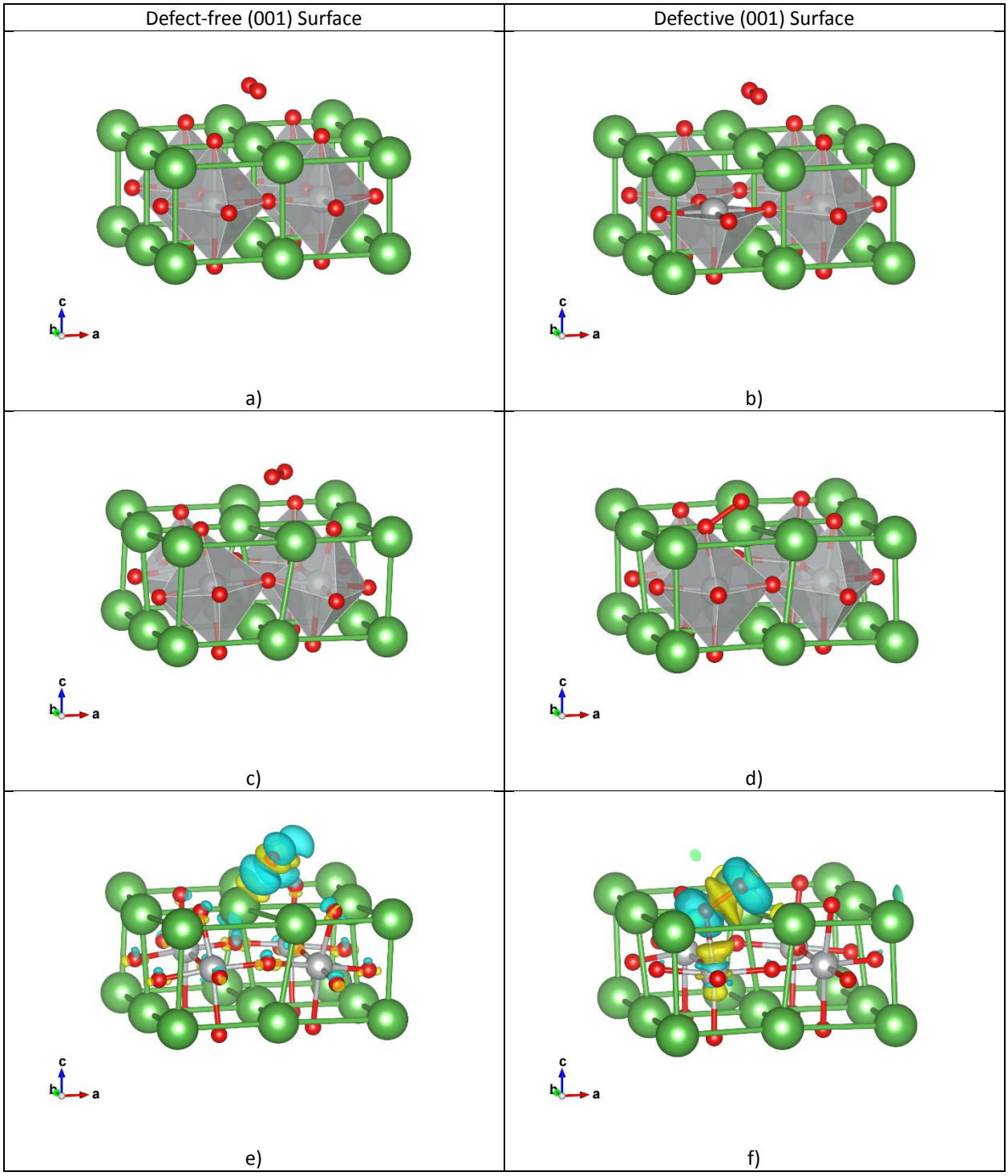


Figure 3. Triplet oxygen molecule is placed side-on top of a La atom.

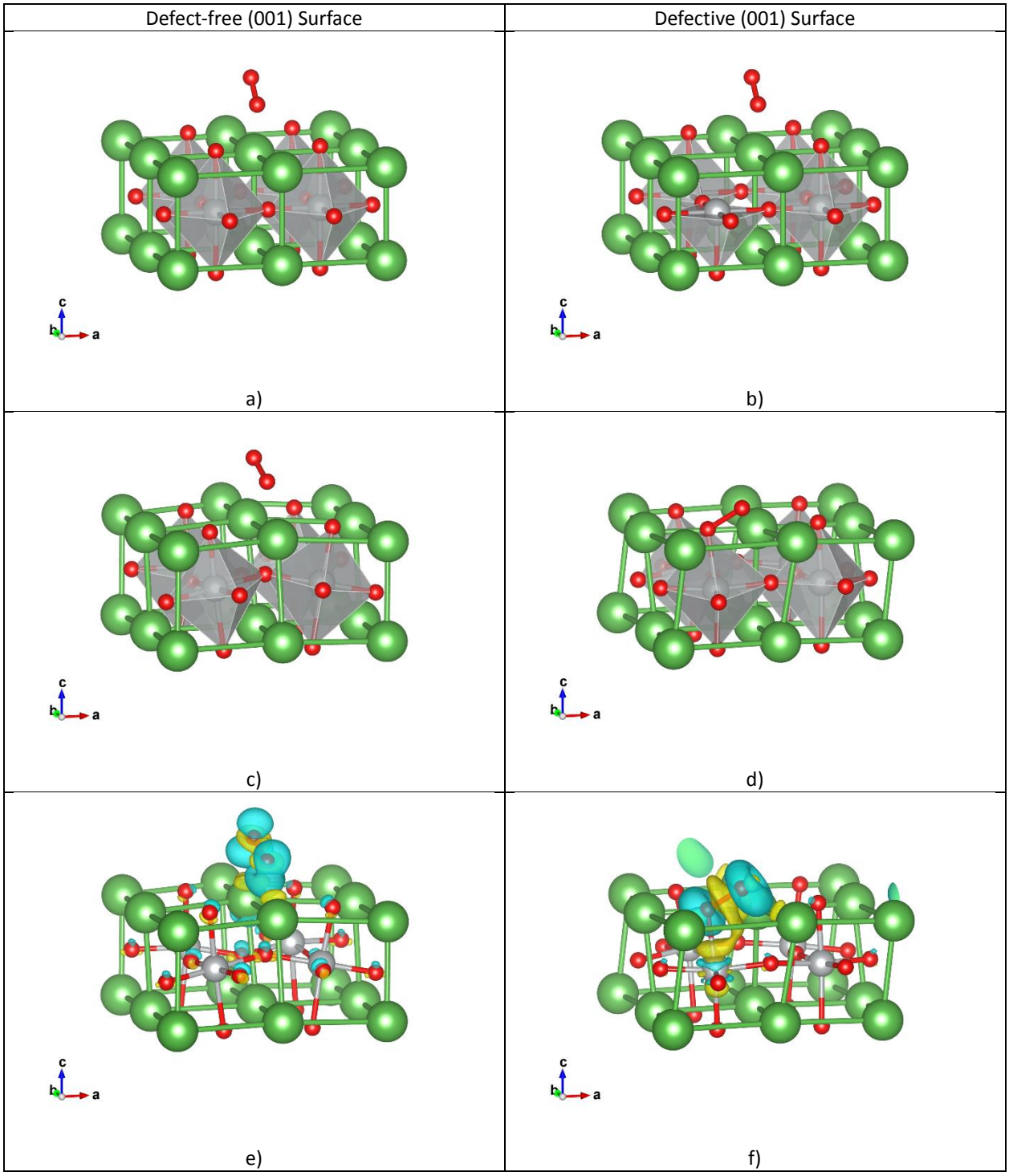


Figure 4. Triplet oxygen molecule is placed 45° inclined on top of a La atom.

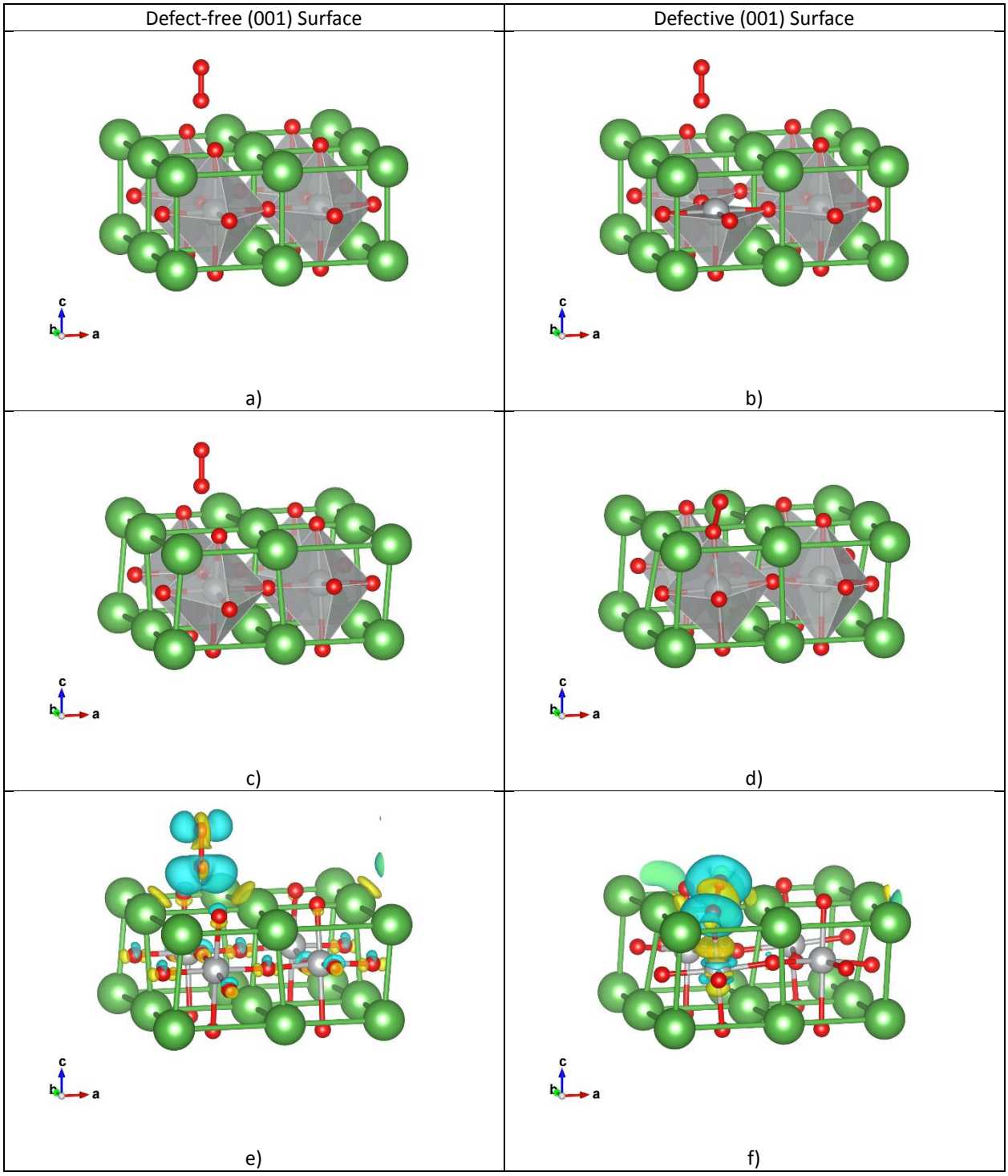


Figure 5. Triplet oxygen molecule is placed end-on top of a La-La bridge.

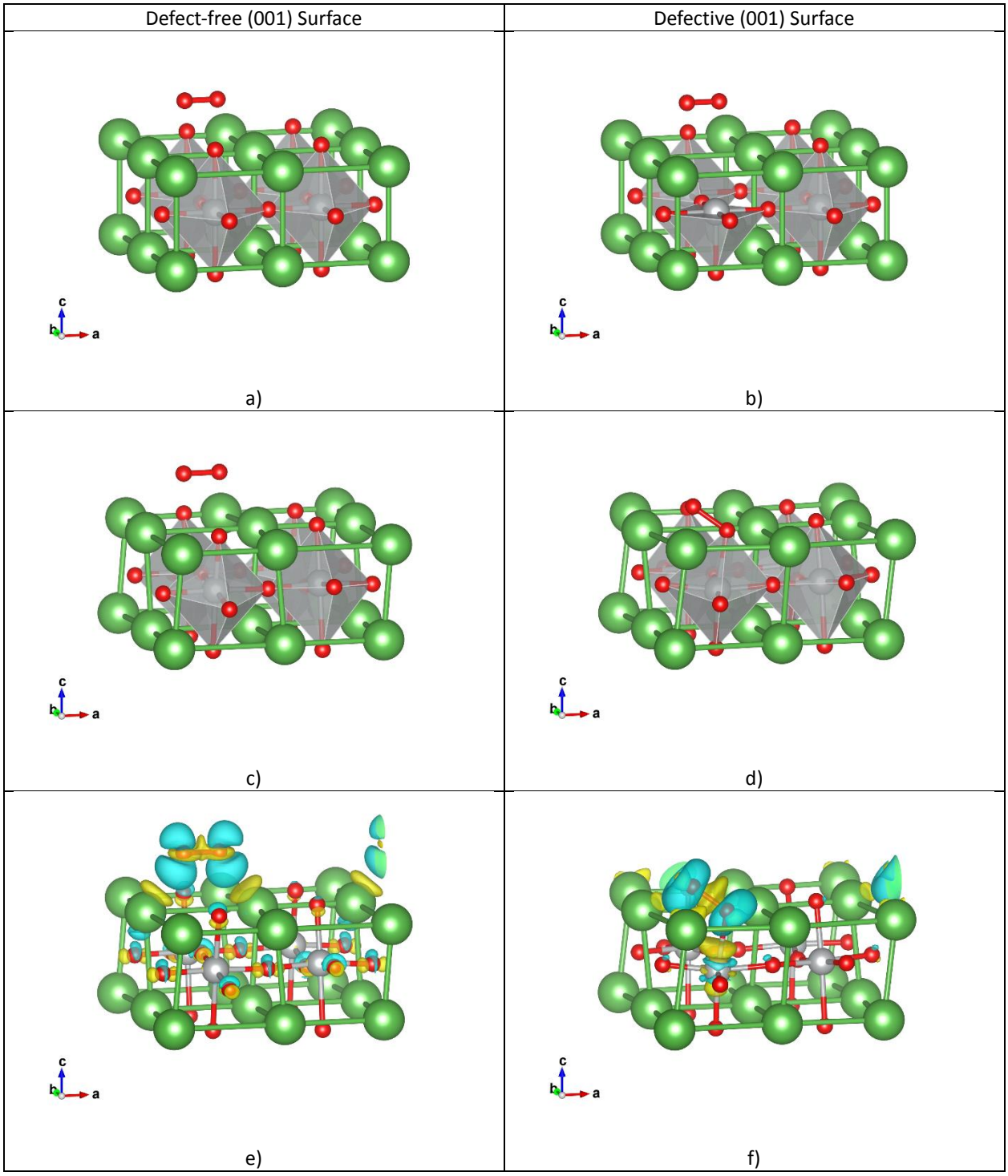


Figure 6. Triplet oxygen molecule is placed side-on top of a La-La bridge.

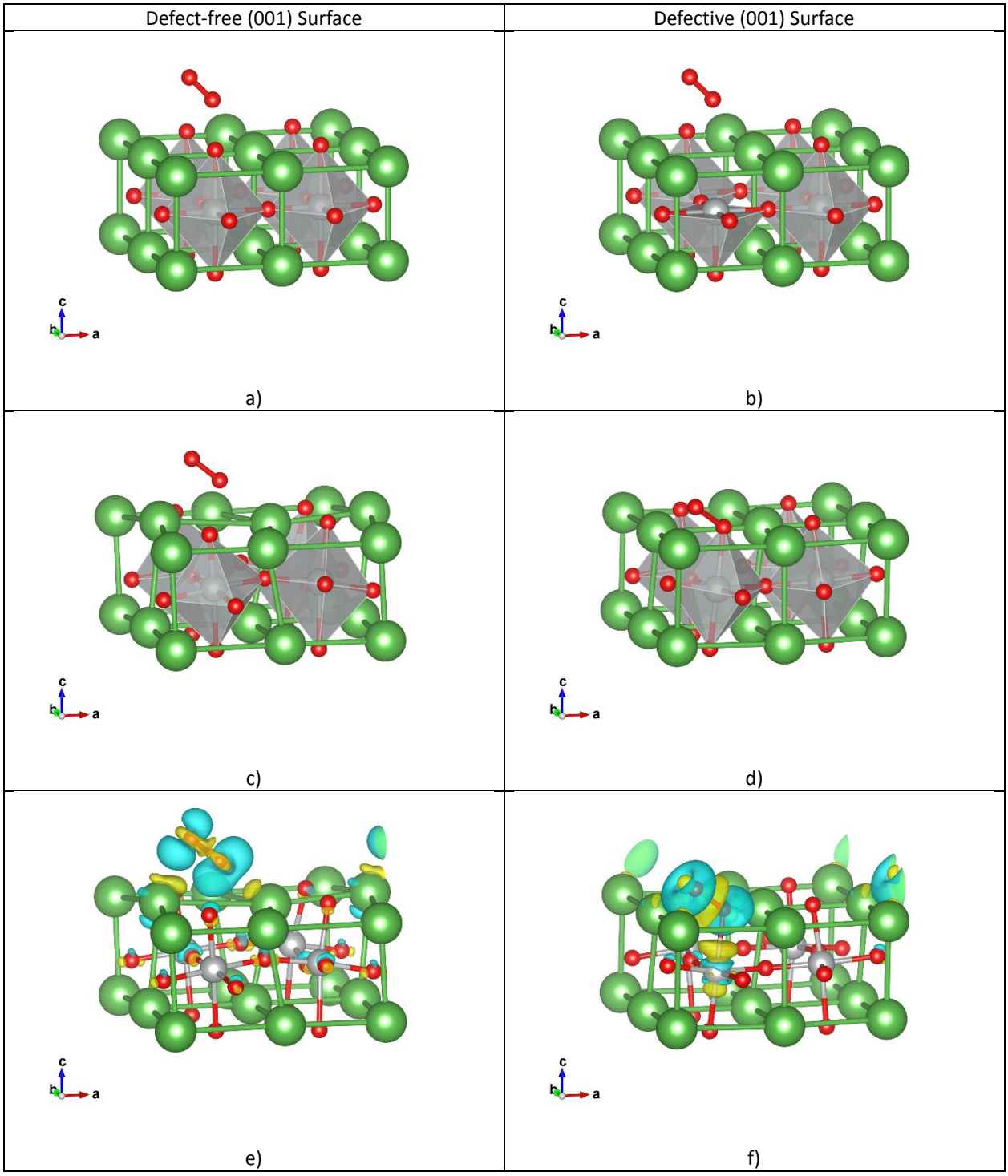


Figure 7. Triplet oxygen molecule is placed 45° inclined on top of a La-La bridge.

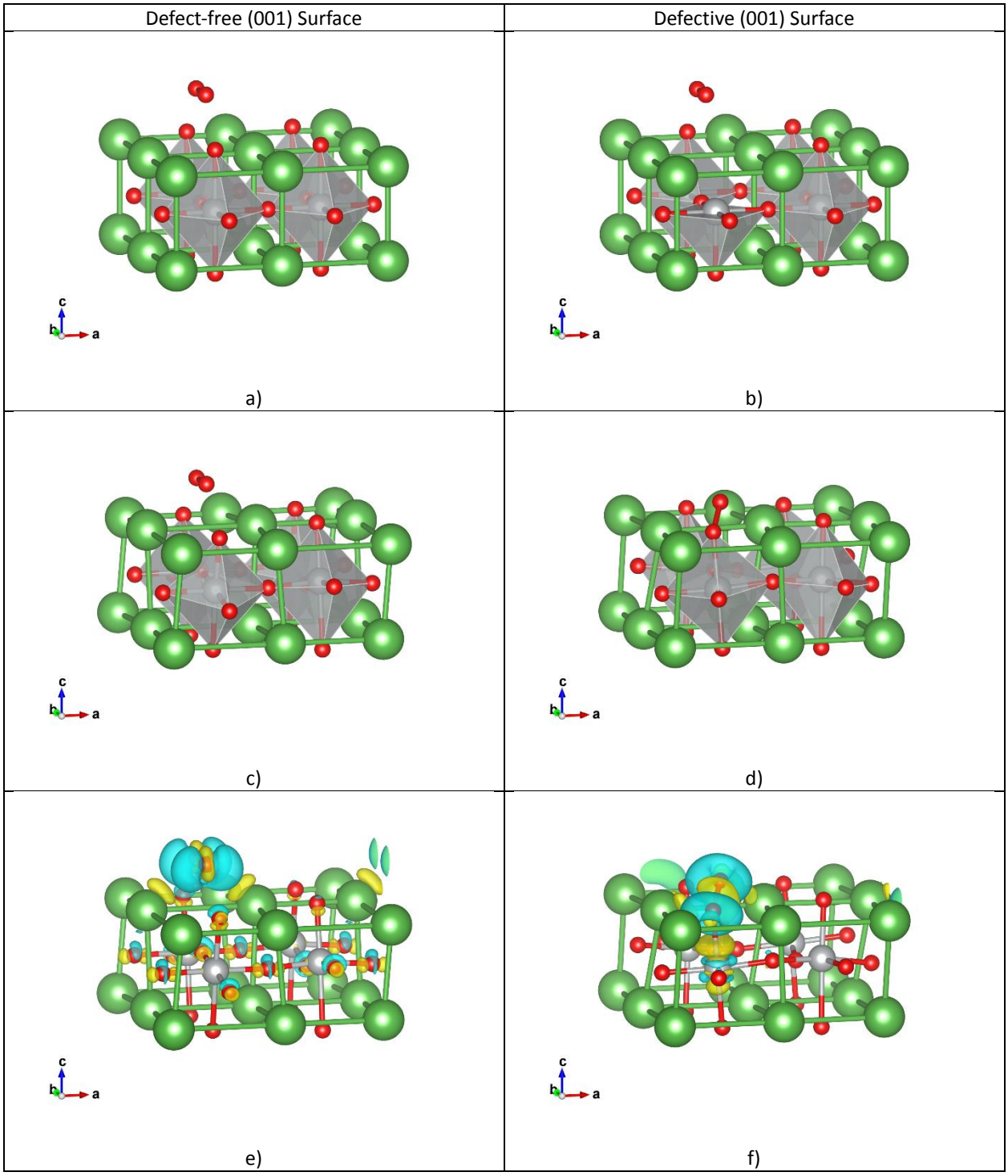


Figure 8. Triplet oxygen molecule is placed side-on cross to a La-La bridge.

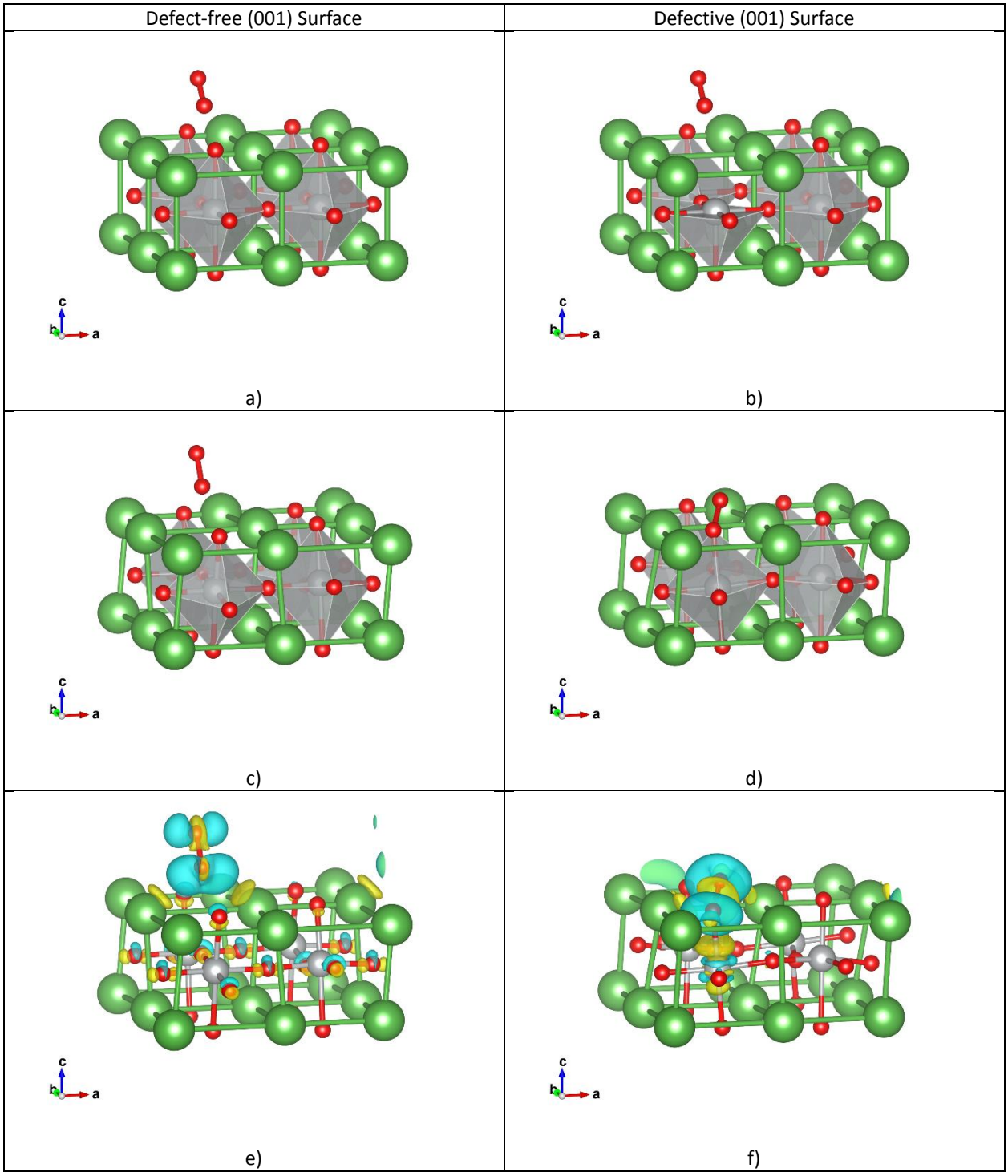


Figure 9. Triplet oxygen molecule is placed 45° inclined on cross to a La-La bridge.

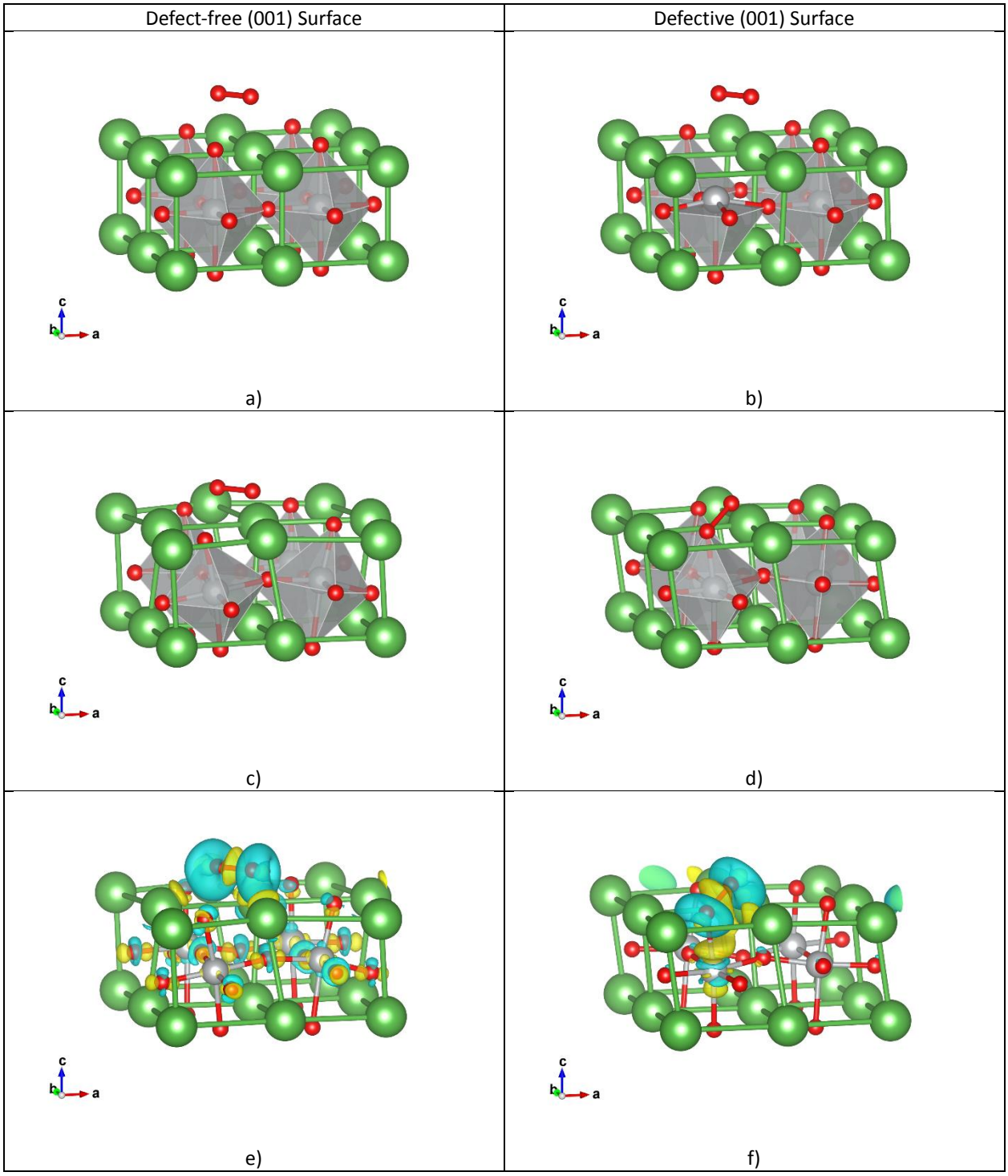


Figure 10. Triplet oxygen molecule is placed slip position on La.

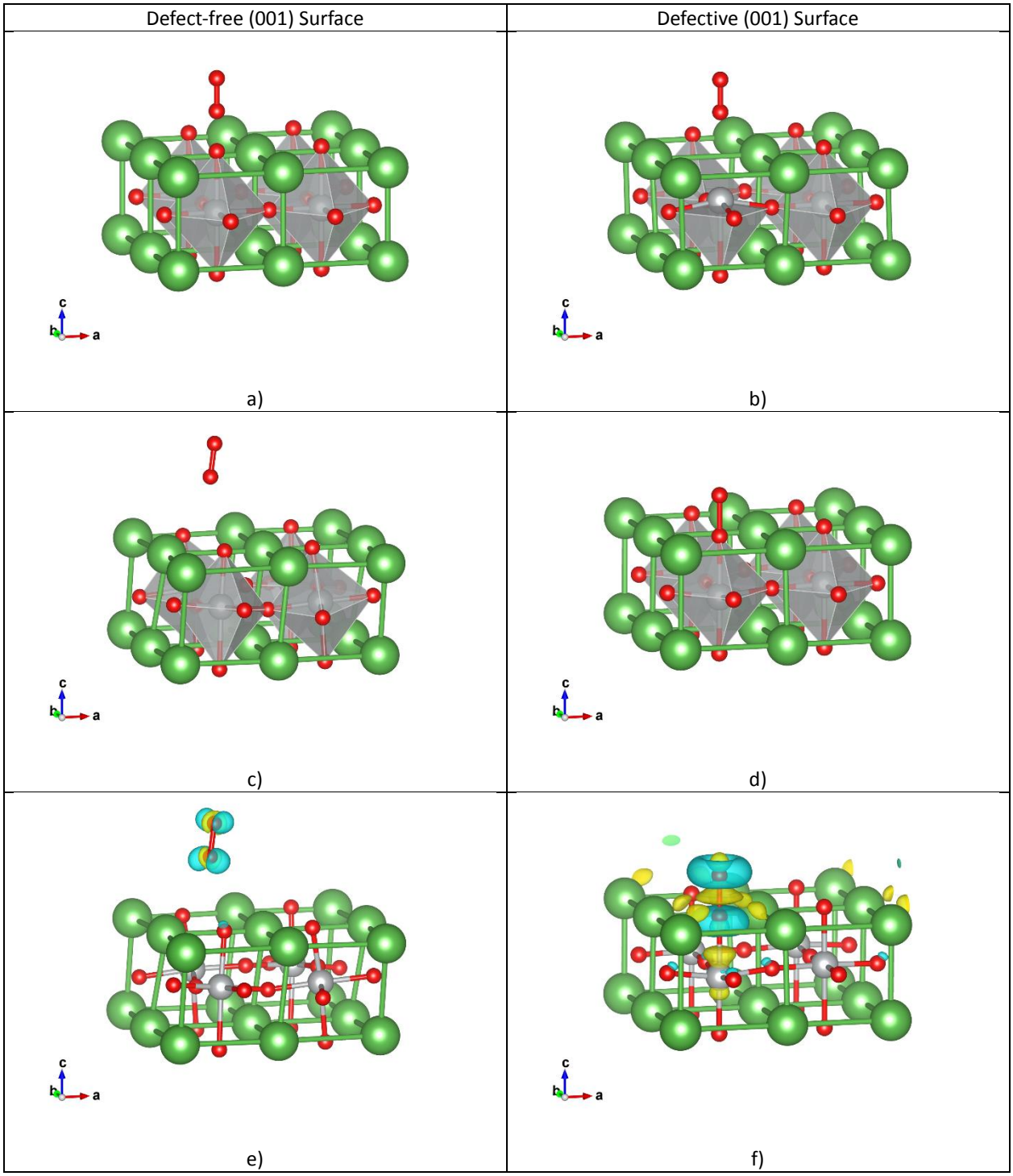


Figure 11. Triplet oxygen molecule is placed end-on to a) an O atom, b) O vacancy on the surface.

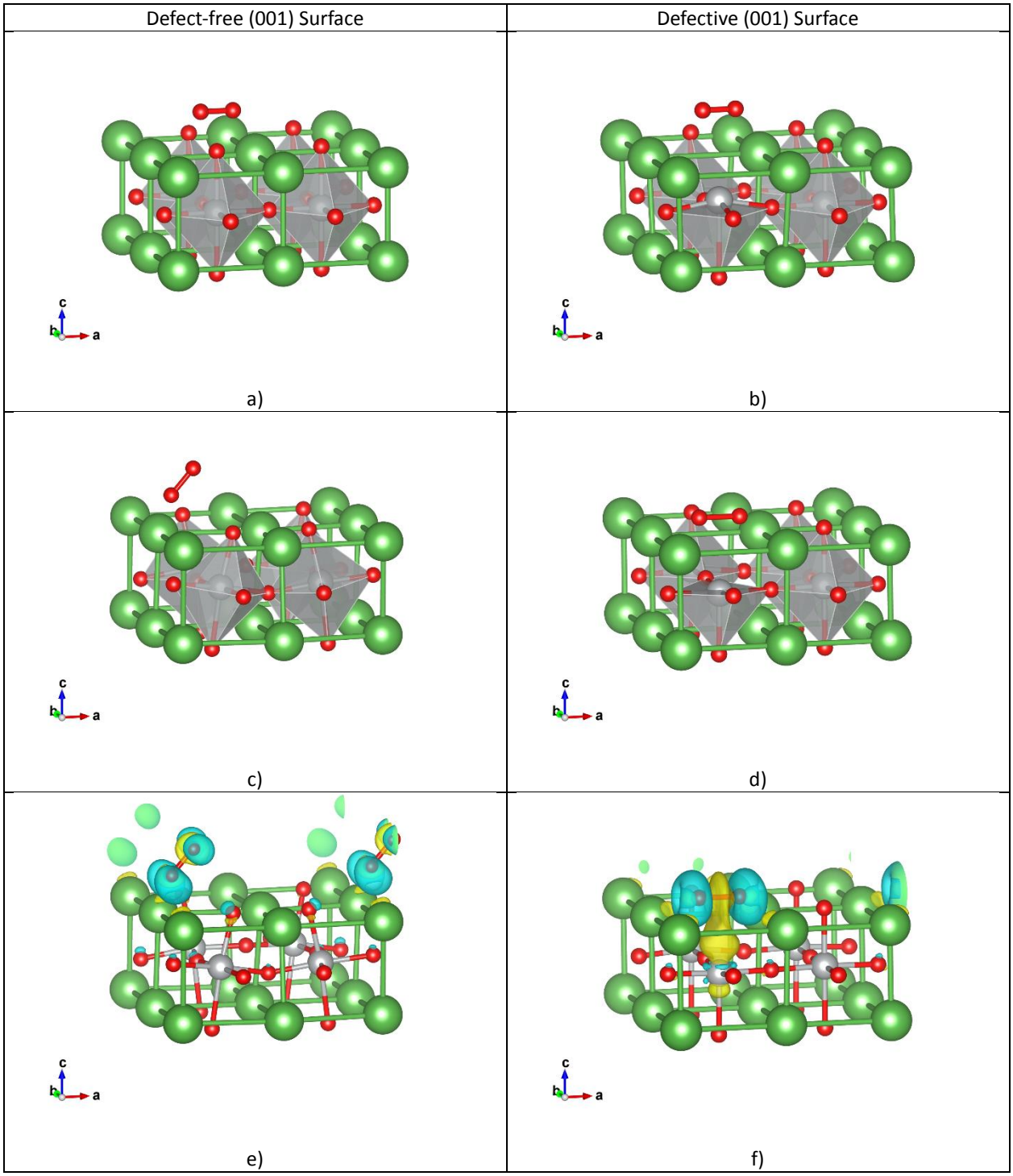


Figure 12. Triplet oxygen molecule is placed side-on to a) an O atom, b) O vacancy on the surface.