This dataset includes the Optimized structures in the VASP POSCAR format for our study *'On the Oxidation State of Single-Atom Re/TiO2 Hydrogenation Catalysts: A Computational Study'*. It includes different single-atom Rhenium (Re) surface species and the important intermediates and transition states for CO2 activation for lower energy Re species. We have considered both pristine and defect containing TiO2 surfaces in our calculations. A detailed overview of data compilation is provided below.

**1.** Multiple single-atom Re species formed on both perfect and defect-containing TiO2 surfaces are organized in two directories: Re\_species\_on\_TiO2-p (for perfect surface) and Re\_species\_on\_TiO2-d (for defect containing surface). Each directory contains a TiO2 surface (either perfect or defective) along with various Re species with oxidation states ranging from 0 to +7, as outlined below.

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**2.** Molecular geometries of CO, H2O and H2 were optimized to gain their electronic energies. These files are present in the directories:

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**3.** Geometries of different bulk Re reference species were computed and are provided in:

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**4.** Important intermediates and transition states are calculated for selected Re species on perfect and defect containing TiO2 surfaces. These structures are compiled within the directory Re\_species\_CO2\_activation\_reaction\_path as follows:

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