Revisiting fundamental properties of TiO2 nanoclusters as condensation seeds in hot Jupiter atmospheres

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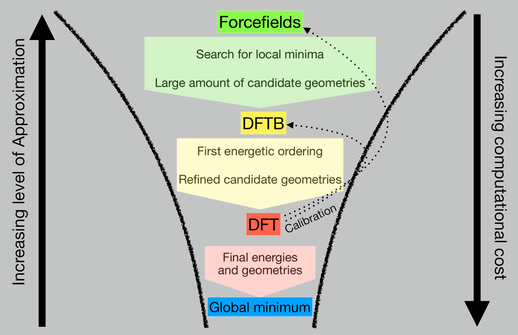
Motivation

- Clouds in hot Jupiter atmospheres form through the condensation of gas species on small solid particles called cloud condensation nuclei (CCN)
- These CCN are created from the gas phacse through nucleation of molecular clusters of species like TiO_2
- To accurately calculate nucleation rates, we need to accurately determine thermochemical properties of these molecular clusters.
- **GOAL:** Find the minimum energy cluster geometry and thermochemical properties for TiO_2 molecular clusters of size $N = 3 - 15$.

Methods

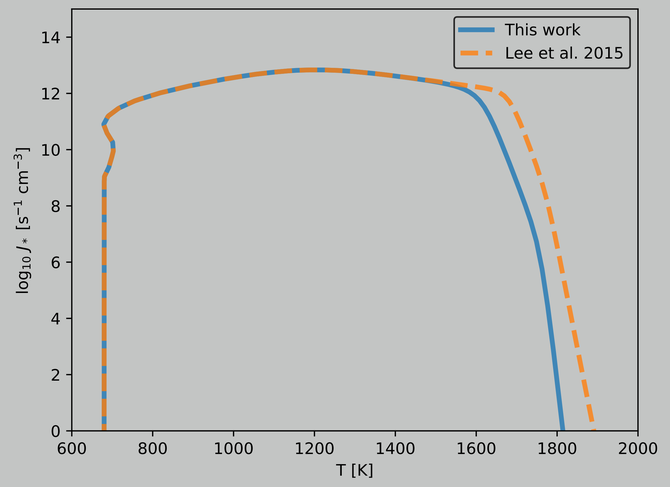


- We employ a funnel approach to explore the geometry parameter-space for cluster candidates
- Three different levels of approximation are employed to calculate binding energies:
  - Force field
  - Density-Functional based tight binding (DFTB)
  - Density functional theory (DFT)
- **Steps in the Funnel**
  1. Determine the best parameterisation for DFT calculations from experimental results for the monomer
  2. Optimise known small cluster isomers with DFT parameterisation
  3. Use optimised small cluster isomers to calibrate force-field and DFTB parameterisations (dashed arrows)
  4. Generate candidate geometries
  5. Optimise candidate geometries to find a global minimum

Summary and Outlook

- **Developed a self-consistent method to establish energetic global minima for small molecular clusters**
- **New cluster data to calculate nucleation rates, impacting cloud formation**
- **Updated cluster data shows nucleation stops being efficient at lower temperatures**

Nucleation rates



- Comparison of TiO_2 nucleation rates for the morning terminator of a hot Jupiter pressure-temperature profile ($T_{eff} = 1600K$, $\log(g) = 3$) for cluster data from this work (blue) and Lee et al. (2015) (orange).
- Calculated with non-classical nucleation theory, allowing only for homogeneous, homo-molecular nucleation
- Nucleation stops being efficient at lower temperatures when compared to older cluster data (Lee et al. 2015; Jeong et al. 2000)

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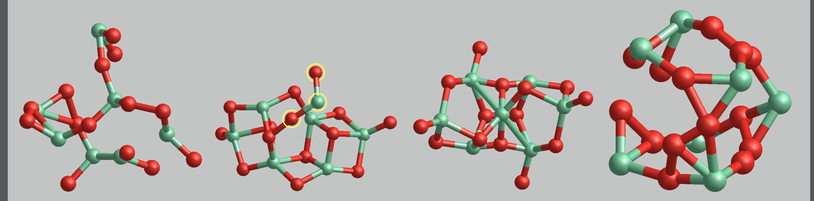
Generation of candidate geometries



- Four different approaches for creation of candidate geometries of size N (from left to right for $N = 7$):
  1. N monomers are iteratively randomly attached
  2. A monomer (yellow circles) is randomly attached to a known isomer of size $N - 1$
  3. A known isomer of size $\frac{N}{2}$ is mirrored about a random axis, an additional monomer is added in the center if N is uneven
  4. N equidistant points are calculated on a sphere and a monomer is placed at each point

Density functional theory (DFT)

- Quantum-chemical method used to determine the properties of the cluster
- Parameterisation through functionals and basis-sets
- Choice of functional and basis-sets strongly impacts resulting cluster data and therefore nucleation rates
- 129 parameterisations tested against laboratory data for the TiO_2 monomer
- Best paremeterisation: B3LYP functional with cc-pVTZ basis-set and GD3BJ empirical dispersion
- Used to optimise calibration isomers and final candidates

References

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