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# Structure Prediction of Alumina (Al<sub>2</sub>O<sub>3</sub>)<sub>n=1-4</sub> and Spinel (MgAl<sub>2</sub>O<sub>4</sub>)<sub>n=1,2</sub> Nanoclusters

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David Gobrecht<sup>1</sup>, Dr. Stefan T. Bromley<sup>2</sup>, and Dr. Isabelle  
Cherchneff<sup>1</sup>

<sup>1</sup>Department of Physics, University of Basel

<sup>2</sup>IQTCUB, University of Barcelona

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## Introduction

Classical nucleations theory (CNT) lacks in predicting structures and properties of chemical compounds with sizes below 50Å. In this regime, strong deviations are expected (and found) from bulk-like coordination and properties ([1], [2]). Quantum confinement strongly effects the characteristics of the so called nanoparticles. Hence it is reasonable and appropriate to concern this problem by a bottom-up approach.

Atomic and molecular electronic structure configurations are given by the solution of the time-independent Schroedinger equation which only yields exact solutions for the hydrogen atom with a well-defined  $\frac{1}{r}$ -potential. For more complex, many body quantum systems the ground-state wave function and energy is determined numerically. In this framework I focused on polymers of alumina (Al<sub>2</sub>O<sub>3</sub>) and

spinel ( $\text{MgAl}_2\text{O}_4$ ) which have been spectroscopically detected around oxygen-rich stars and hence are of astronomical importance.

## Initial candidate structures

The finding of the ground-state for a given cluster size and composition is a global optimisation problem. As the number of possible structures grows exponentially with the number of atoms a cluster of ten atoms would have millions of distinct isomers, a polymer of 20 atoms. Hence a complete quantum-mechanical DFT investigation of all possible structures is nowadays computationally limited to small cluster sizes. To efficiently explore the increasingly complex parameter space we generate initial structures by applying simple interatomic potentials:

$$V(r_{ij}) = \frac{q_i q_j}{r} + A \exp\left(-\frac{r_{ij}}{B}\right) - \frac{C}{r^6}, \quad (1)$$

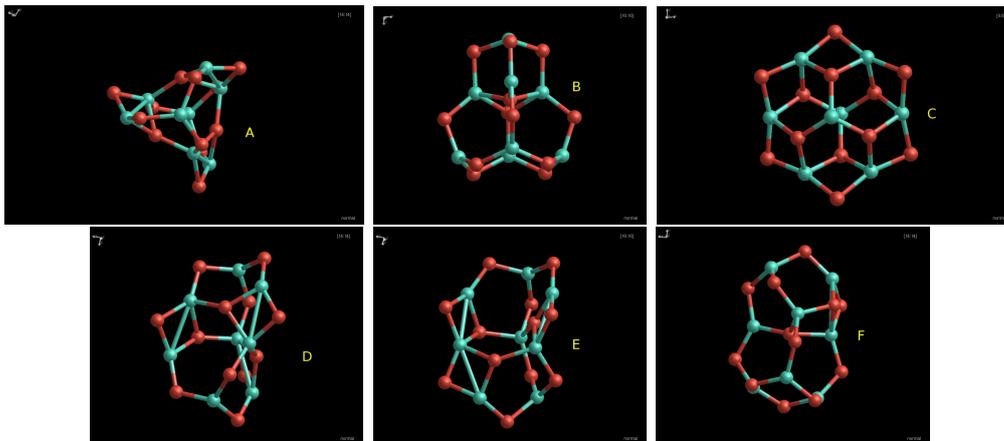
where  $r_{ij}$  is the relative distance between point charge  $i$  and  $j$ . The first term is the Coulomb interaction between cations (Al and Mg) and anion (O) and is hence attractive. The last term counts for the van-der-Waals interaction which is also attractive. To prevent a collapse/fusion of the two point charges into a singularity another, so called Born-Mayer, term is included. This term acts on short relative distances ( $r_{ij} \leq B$ ) and is repulsive. The second and third term in the above equation are also referred to as the Buckingham potential. The values for A, B and C for the Al-O, O-O and Mg-O interaction are derived from bulk material and can be extensively found in the literature [3].

Electric polarization is characterised by a non point-like charge distribution and affects the above potential. To account for polarisation anion and cation their point charges are reduced by a factor of 0-20 % or, the more realistic shell model in which each point charge is divided into two charges, one for the nucleus and electrons of the 'inner' shells and the other for the outer electrons, is applied.

The Monte-Carlo Basin-Hopping (MCBH) global optimisation method with interatomic/-ionic pair potentials (see equation 1) and varying initial geometries, bonding lengths and container radii is employed to generate initial structures. Millions of possible configurations have been reduced to hundreds. On average the 50 most promising (low lying and recurrent) clusters are further optimized with DFT at the B3LYP/6-311+G\* level.

## Refinement on the DFT level

Inspection of the initial structures on the DFT level gives electronic, thermal, vibrational, rotational and zero-point energies (quantum mechanical harmonic oscillator) as well as frequencies of vibrational modes and rotational constants. The optical properties, i.e. the spectra of the obtained infrared frequencies and



**Figure 1** – The six lowest-energy alumina tetramers  $Al_8O_{12}$  with relative energies 0.00 (A), 0.12 (B), 0.19 (C), 0.26 (D), 0.27 (E) and 0.29eV (F).

assigned intensities, differ isomer by isomer. In the context of astronomical observations this is marvellous, since the IR spectra not only tells us about the dust species itself but also about its structure and hence, indicates possible formation pathways.

## Thermodynamic characteristics of clusters

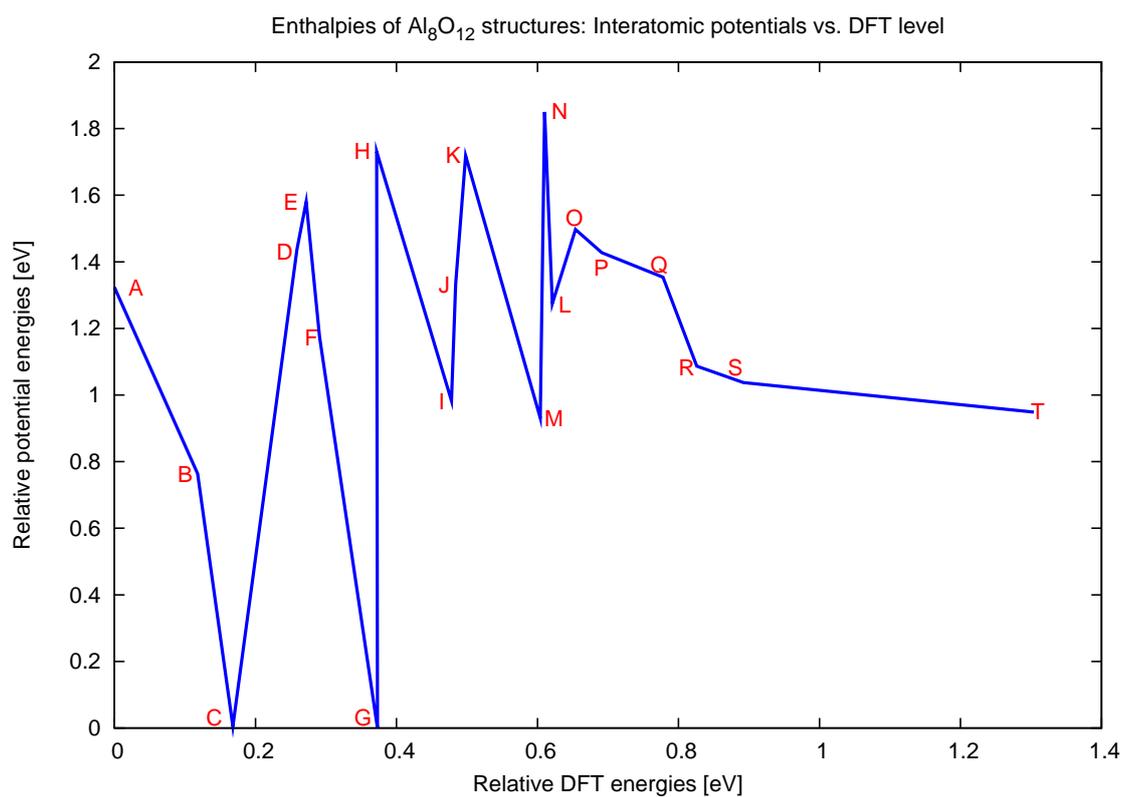
The DFT level computations are performed at standard conditions. In circumstellar environments rather hot ( $\sim 2000K$ ) and dilute conditions prevail and the most substantive thermodynamic energy, the Gibbs Free Energy (GFE), which determines whether a chemical process is energetically favorable or not, differs significantly.

The GFE can be expressed in terms of the partition function (PF) and its derivatives which in turn results from translational, electronic, vibrational and rotational motion contributions. IR frequencies, rotational constants and split up energies are used to calculate the contribution from each component. For a given equilibrium pressure and temperature the GFE of formation is finally determined.

## Results

The 20 lowest-energy alumina clusters reported by [4] have been well reproduced by up to a size of  $n = 4$  (see Figure 1). In addition we found structures not detected by [4].

For Spinel clusters the case is different: In the literature no extensive study on the DFT level has been performed, although some possible ground-state structures have been proposed [3].



**Figure 2** – Comparison of inter-ionic potentials and energies at the B3YLP level for distinct  $Al_8O_{12}$  structures. Obviously the energetic order is not preserved. Nevertheless the MCBH method with pairwise ionic potentials yields a good and complete set of initial structures. The capital letters  $A, B, \dots$  denote distinct structures.

## Acknowledgment

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