Mem. S.A.It. Vol. 91, 236

Memorie della

Dust in the Universe

S. Cristallo[1] and D. Gobrecht[2]

[1] Istituto Nazionale di Astrofisica – Osservatorio Astronomico d'Abruzzo, Via Mentore Maggini, s.n.c. 64100 Teramo, Italy, e-mail: `sergio.cristallo@inaf.it`
[2] Institute of Astronomy, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

Abstract. Dust is ubiquitous in the Universe and plays a crucial role in astrophysical environments. Dust impacts the synthesis of complex organic molecules in molecular clouds, the wind-driving of evolved stars and the formation of celestial bodies (e.g. asteroids, planets) in proto-planetary discs. The dust formation from a gaseous medium requires several thermodynamic conditions: densities above a certain threshold to ensure sufficient collisions between the constituent particles, moderate temperatures below the stability threshold of the dust component, and sufficient time for the nucleation and growth of molecular clusters into larger grains. Such conditions are found in the circumstellar environments of Asymptotic Giant Branch (AGB) stars. AGB stars thus belong to the major sources of cosmic dust and return the interstellar medium in our galaxy.

1. Introduction

Owing to their large refractories alumina clusters are promising candidates to form the seed particles of dust formation in oxygen-rich Asymptotic Giant Branch (AGB) stars that represent one of the major cosmic dust sources (see e.g. Decin et al 2017). We intend to gain insight whether the alumina cluster are able to trigger the onset of dust synthesis in AGB stars. Hence, the goal of this computational project is to investigate the most favourable stoichiometric alumina $(Al_2O_3)_n$, $n = 1 - 10$, cluster structures by means of quantum-chemical methods such us Density Functional Theory (DFT). We employ two different hybrid functionals, B3LYP (Becke et al. 1993) and PBE0 (Perdew et al. 1996), in combination with a sufficiently large basis set 6-311+G* in order to aluminum oxide clusters. Benchmark calculations show that the B3LYP/6-311+G* method is reliable for Al-O molecular systems and compares well to the higher-level-of-theory method CCSD(T)/aug-cc-pVTZ (Li and Cheng 2012). Moreover, we performed a vibrational analysis of the most stable isomers of each size n. The knowledge about the vibrational modes is required to construct appropriate partition functions and to find real minima (instead of transition states). In addition, a computed vibrational IR spectra allows us to compare our results with observations of stellar spectra.

2. Results

We revisited the minimum structures reported by Li and Cheng 2012 for $n = 1 - 7$ and confirmed the Global Minima (GM) found on the B3LYP/6-311+G* level of theory. However, we note significant differences between the PBE0 and the B3LYP optimized structures for $n > 6$. For $n = 7$, we find different GM for the PBE0 and the B3lYP functionals. The

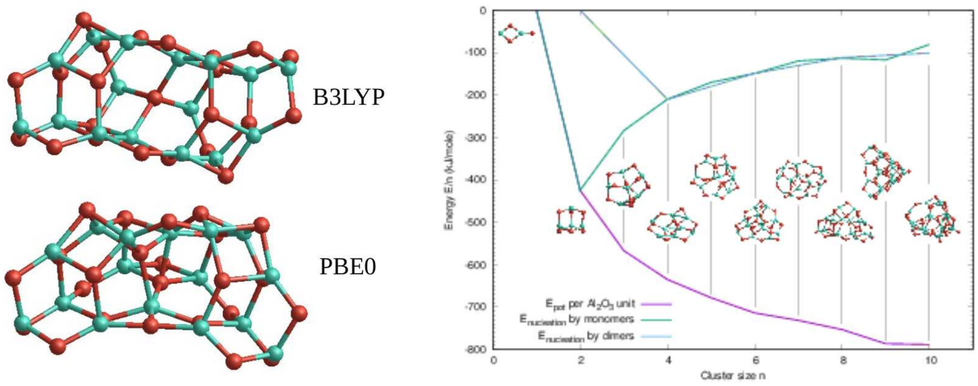

Fig. 1. *Left*: GM structures for cluster size n=8 at the B3LYP and PBE0 level of theory. *Right*: Cluster nucleation energies as function of size n and GM (B3LYP) isomers

GM of the PBE0 is only the 7 th most favourbale structure in the B3LYP. Vice versa, the GM at the B3LYP level of theory lies 0.33 eV above the GM of the PBE0 calculation. Also for sizes $n = 8$ we find different geometries as lowest-energy isomers. Both isomers are unprecedented, new GM structures and are displayed in Figure 1.

On the right hand side of Figure 1, the potential energies (normalized to an Al_2O_3 unit) of the GM clusters is displayed. Also, the nucleation energies for homogeneous cluster growth by monomers, $(E(n) - E(n-1) - E(1))/n$, and by dimers, $(E(n) - E(n-2) - E(2))/n$, respectively. During our global optimisation searches, we found cage-like structures that are hollow in their inner part for every size $n = 1-10$. These structures are characterised by strictly 3-coordinated Al atoms and O atoms that have a coordination number of two corresponding to the number of valence electrons. In the following, we assign them as members of the "bubble" structural family. In Figure 2, their most stable representatives of the structural "bubble" family, and their relative energy to the global minimum are depicted.

In our study, just the dimer ($n = 2$) "bubble" structure corresponds to the GM, the trimer ($n = 3$) is the 7 th most favourable structure . All the other "bubble" clusters have significantly larger potential energies. The latter fact is of great importance for the calculation of the surface tension . If all GM for $n = 1-10$ would belong to the same structural family, a value for the surface tension sigma can be approximated by a fit of the normalized potential energy versus cluster size n 1/3 . As this is clearly not the case for small stoichiometric $(Al_2O_3)_n$ clusters, higher order terms needs to be included to fit the potential/nucleation energies. The "bubble" clusters exhibit either preferentially rings with 6, 8 or 10 members that exhibit with a strict cation-anion ordering. We do not exclude the possibility that the members of the "bubble" cluster family represent the global minimum isomers for larger clusters size $n > 10$ as predicted by Gu et al. 2015. However, our study indicates rather a contrary trend: The larger the cluster size n, the greater is the relative energy between "bubble" cluster and for size $n > 2$.

We were granted 225'000 CPUh on Marconi in total and we have almost entirely consumed our budget (91 %). We might even have used a larger amount of calculation time. The reason were the unexpected differences in the potential energies PBE0 and B3LYP-optimised structures as well as the discovery of a series of unprecedented GM and other low-lying isomers for cluster sizes $n = 8, 9, 10$. We published a letter with the new findings to Chemical Physics Letters (Gobrecht et al. 2018) that focuses on the nucleation of

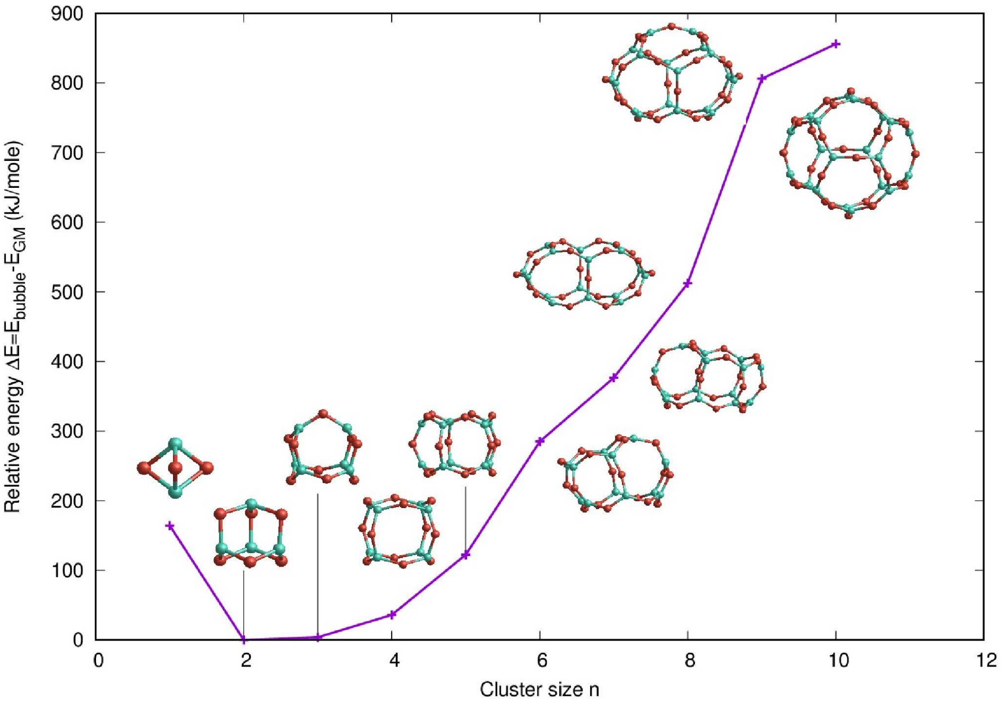

Fig. 2. Representatives of the "bubble" cluster structural family and their relative energies (in kJ/mole) with respect to the GM of each cluster size n

$(Al_2O_3)_n$ clusters in circumstellar conditions. We gratefully thank CINECA for the opportunity to use the Marconi HPC cluster and will acknowledge the support form CINECA in our publications.

Acknowledgements. We acknowledge the computing centre of Cineca and INAF, under the coordination of the "Accordo Quadro MoU per lo svolgimento di attività congiunta di ricerca Nuove frontiere in Astrofisica: HPC e Data Exploration di nuova generazione", for the availability of computing resources and support.

References

Becke, A. 1993, J. Chem. Phys, 98, 1372

Decin, L., et al. 2017, A&A, 608, 55

Gobrecht, D., Decin, L., Cristallo, S., Bromley, S.T. 2018, Chem. Phys. Lett., 711, 138

Gu, Y. B., Xu, N.X., Lin, M.H., Tan, K. 2015, Comput. Theor. Chem., 1063, 29

Li, R., Cheng, A 2012, CTC, 996, 125

Perdew, J. P., et al. 1996, J. Chem. Phys, 105, 9982