Doping effects on the singlet-triplet gap and bonding of the silicon trimer

Nguyen Minh Tam,[a,b] **Tran Dieu Hang,**[b] **Hung Tan Pham,**[a] **My Phuong Pham-Ho,**[a] **Minh Tho Nguyen**[b]

[a] *Institute for Computational Science and Technology (ICST), Quang Trung Software City, Ho Chi Minh City, Vietnam*

[b] *Department of Chemistry, University of Leuven, B-3001 Leuven, Belgium*

(Abstract) We revisit the singlet-triplet energy gap (ΔE_{ST}) of silicon trimer and evaluate the gaps of its derivatives doped by a cation (H^+, Li^+, Na^+, K^+) and an atom (Be, Mg, Ca) using the composite G4 method, coupled-cluster theory CCSD(T)/CBS and CASPT2 (for Si_3) computations. Both $^1A_1$ and $^3A_2'$ states of Si_3 are determined to be degenerate. An intersystem crossing between both states appears to be possible at a point having an apex bond angle of around $\alpha = 68 \pm 2^o$ which is 16 ± 4 kJ/mol above the ground state. The proton and alkali metal cations tend to favour the low spin state, but do not modify significantly the ΔE_{ST}, whereas a doping of earth-alkali atoms stabilize the singlet and substantially enlarge the ΔE_{ST} of the doped clusters. The proton affinity of silicon trimer is determined as $PA(Si_3) = 827 \pm 4$ kJ/mol. The metal cation affinities and metal atom affinities are also predicted. Electron localization function (ELF) and ring current analysis shows that the singlet trimeric ring Si_3 is non-aromatic, the Li^+ cation renders it anti-aromatic whereas attachment of a Be atom makes the resulting tetramer a σ-aromatic cycle.