

MFM



A theoretical study on the mechanisms of formation of primal carbon clusters and nanoparticles in space

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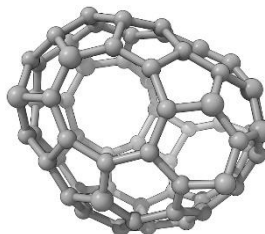
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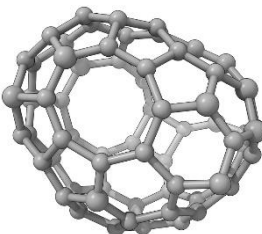


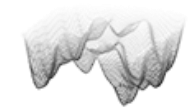
Introduction

- The very first carbon clusters and nanoparticles to originate in the Universe
 - Pre-reaction atomic aggregations
 - Size
 - Orientation
 - Density
 - Cluster characterization
 - Prevalence of structural motifs
 - Prevalence of hybridization
 - Formation of nanoparticles
 - Mechanisms
 - IR spectra and resemblance to known nanoparticles



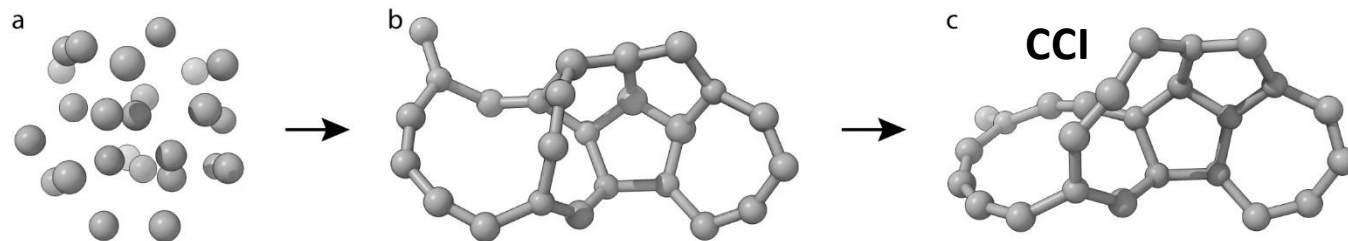
- Methods
 - DFTB2
 - Dynamics
 - Metadynamics
- Computational steps
 - Clusters
 1. Optimization
 2. Dynamics, NVT, 400K, 20ps
 3. Optimization
 4. Metadynamics
 - Nanoparticles
 - Sequential Metadynamics





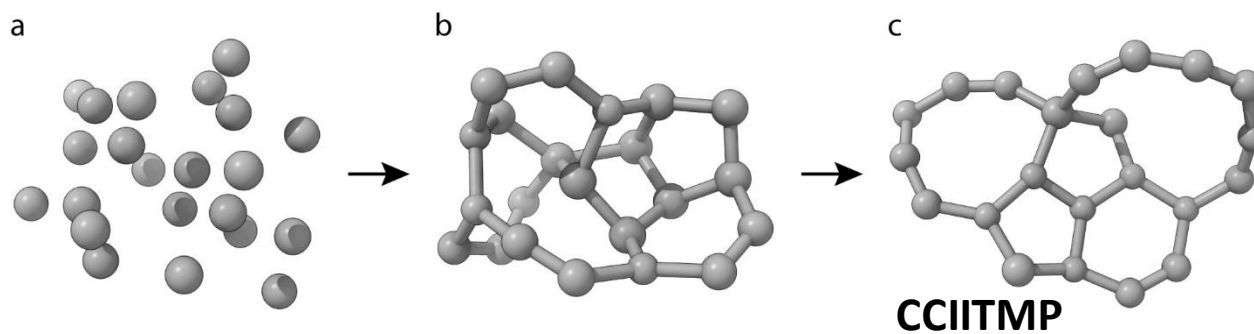
Clusters

High density
Random orientation



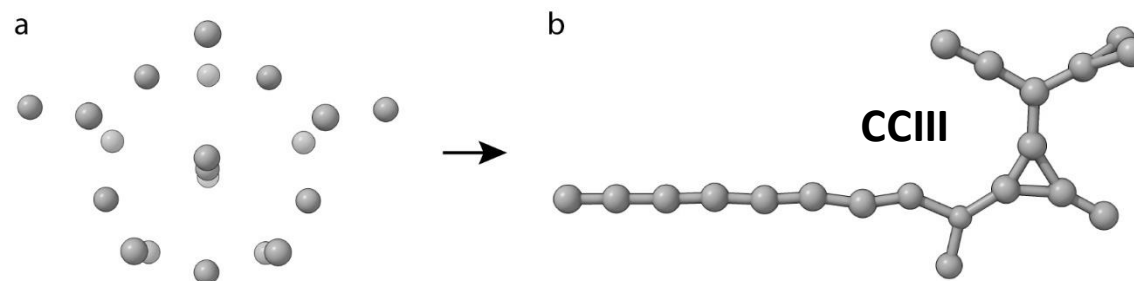
Tangled polycyclic
Mostly sp^2
Closed-cage building block

High density
Tetrahedral orientation

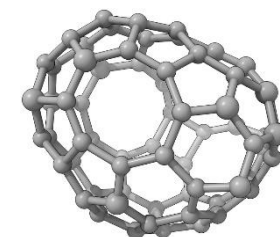


Tangled polycyclic
Mostly sp^2
Closed-cage building block

High density
Tetrahedral orientation

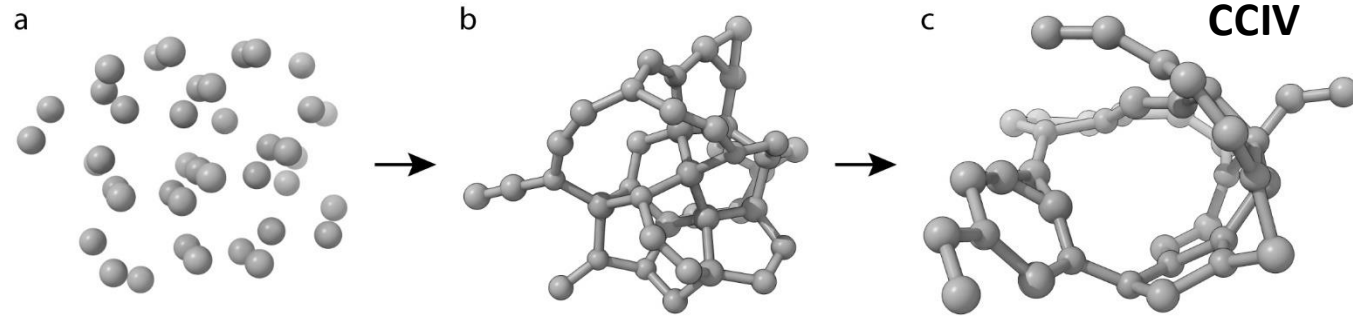


Branched linear
3-atomic rings
Even sp and sp^2

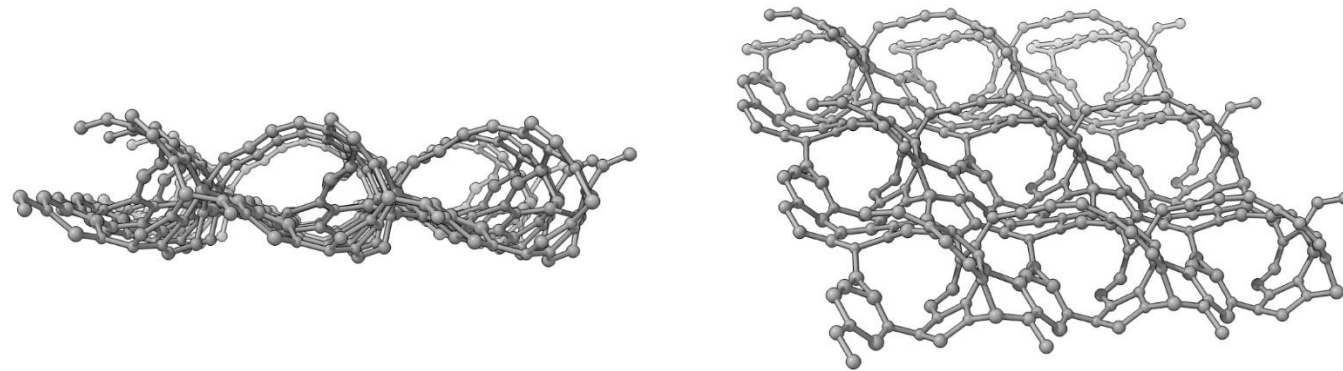


Polymer

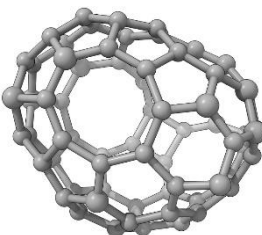
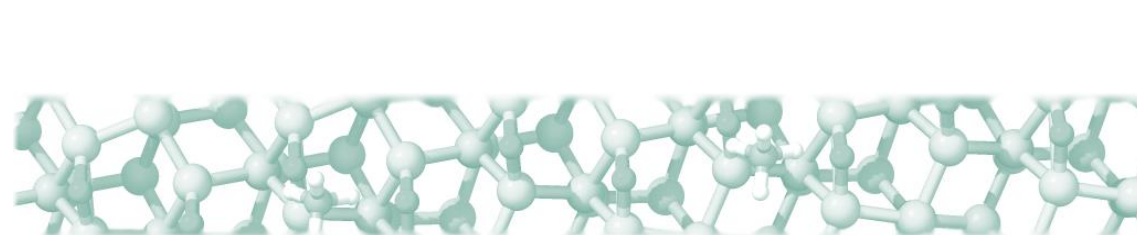
PBC for polymerization
High density
Tetrahedral orientation



1D porous polymer
Mostly sp^2
Reminds of CNTs

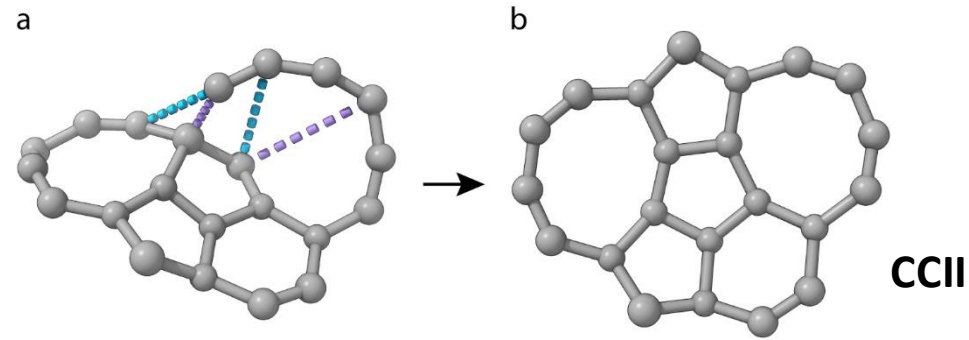


Multicell views

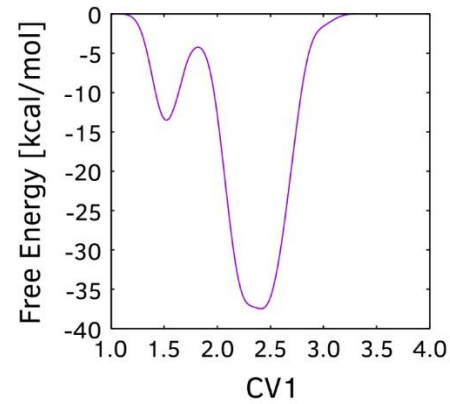


Biased reformation: CCIITMP -> CCII

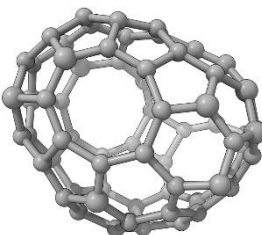
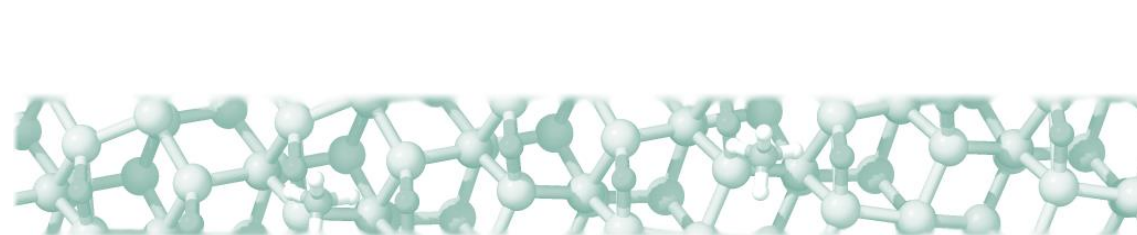
CV distances
Reactive distances



Entirely sp^2
Closed-cage building block

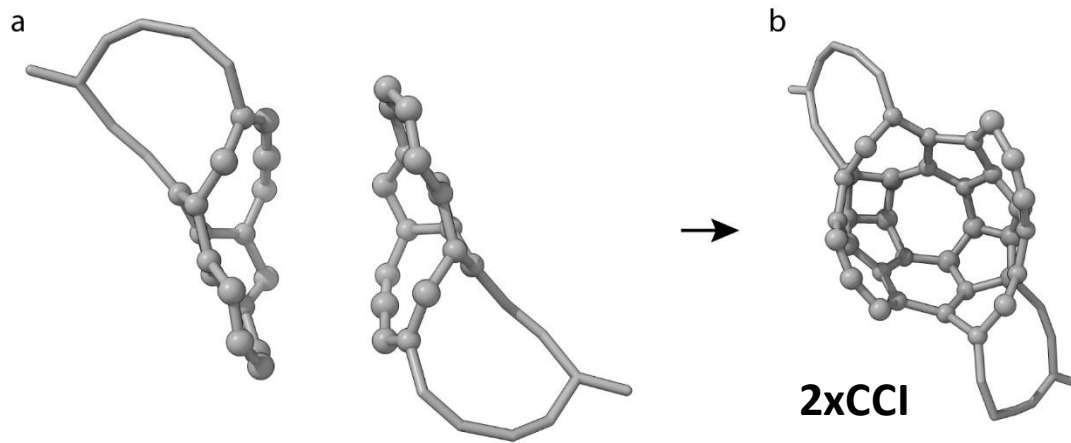


FE Profile
Significantly exothermic



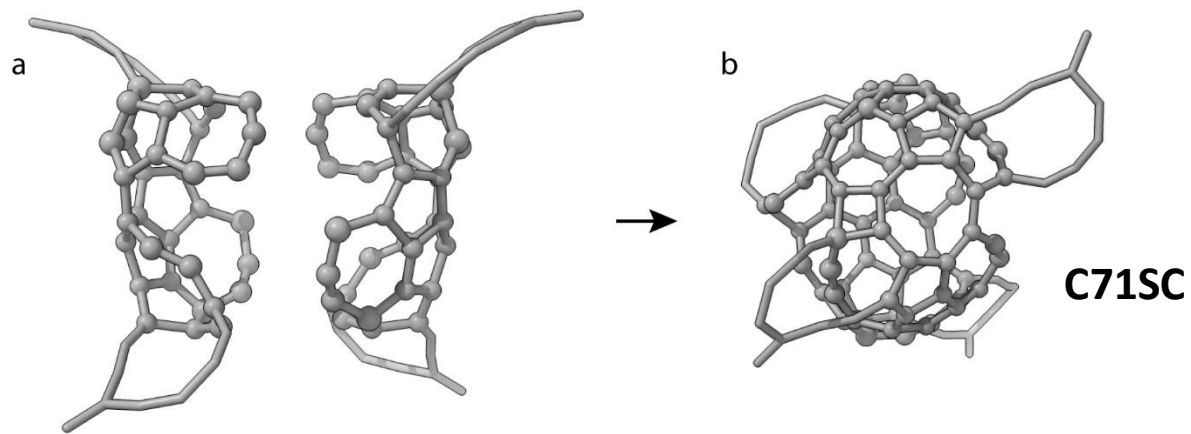
Biased cluster-coupling simulations

2 x CCI

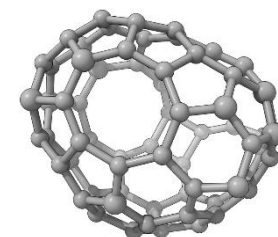


Half-spherical

2 x 2xCCI

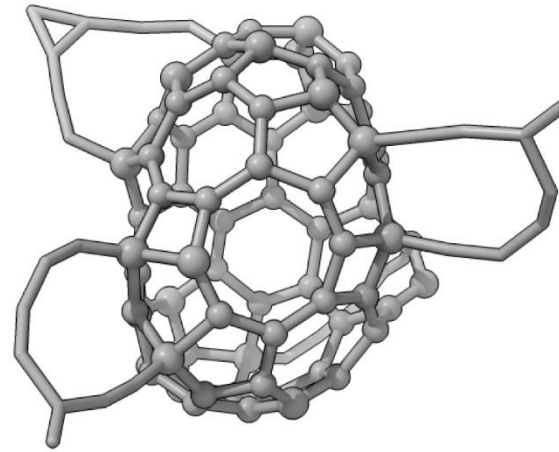


Semi-spherical /
Closed-cage



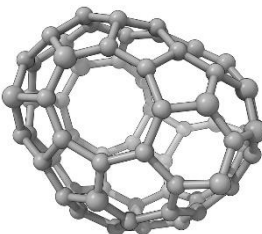


Biased gap-closing simulation



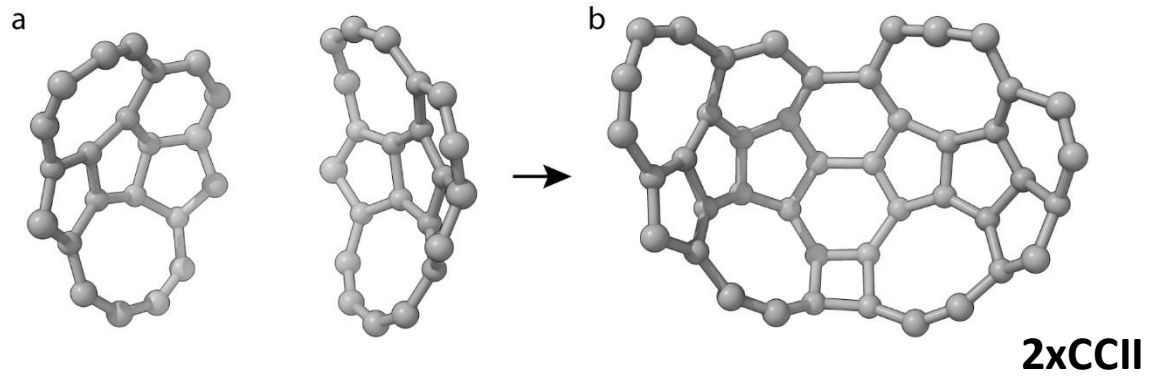
C72SC

C72[4,5,6,7,8,10]fullerene



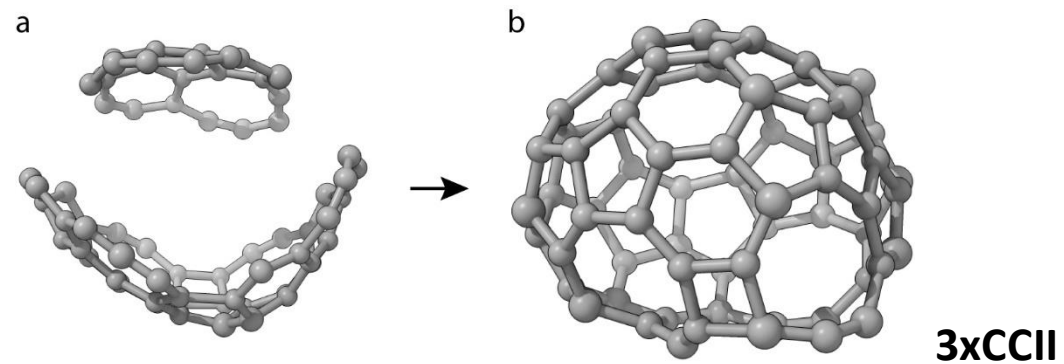
Biased cluster-coupling simulations

2 x CCII

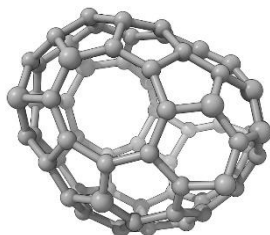


2/3 spherical

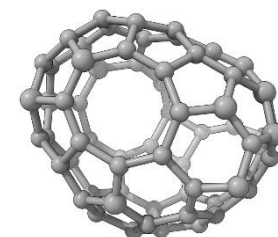
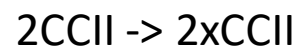
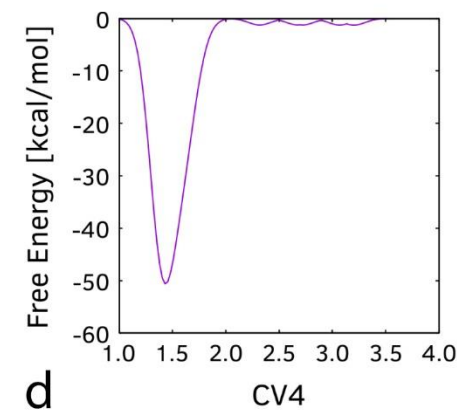
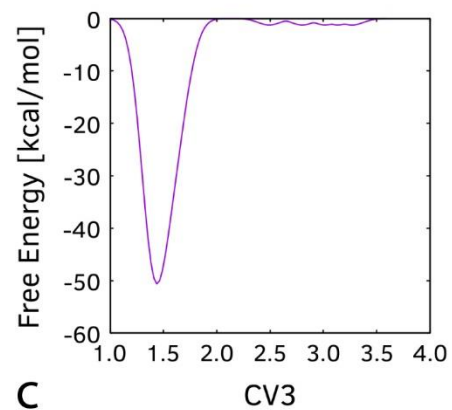
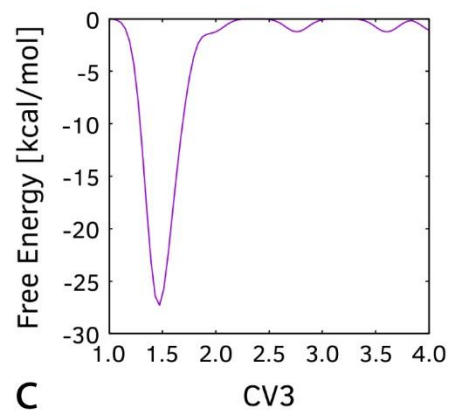
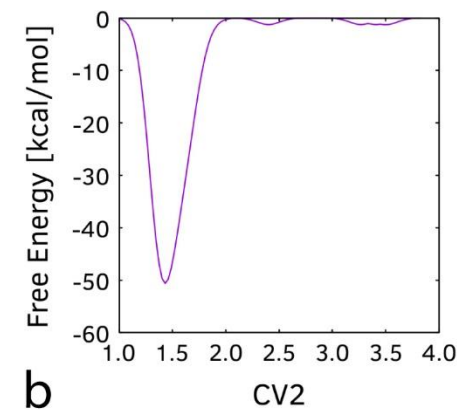
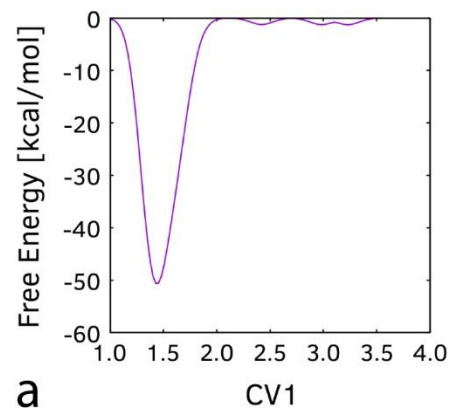
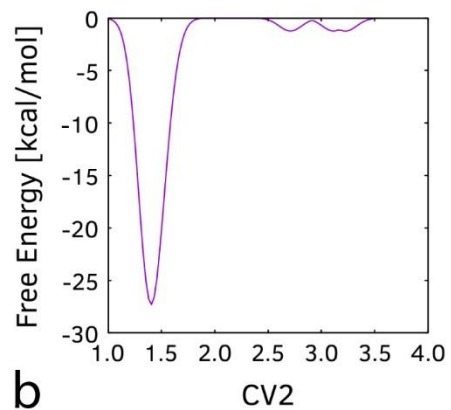
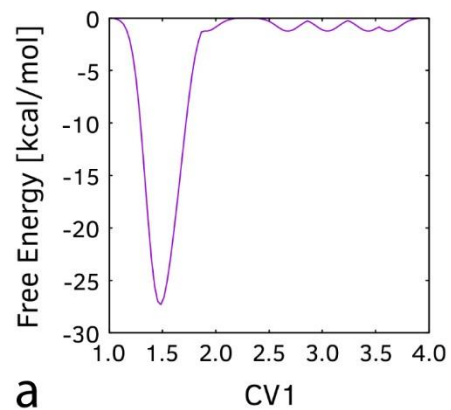
2 x 2xCCII



Semi-spherical /
Closed-cage

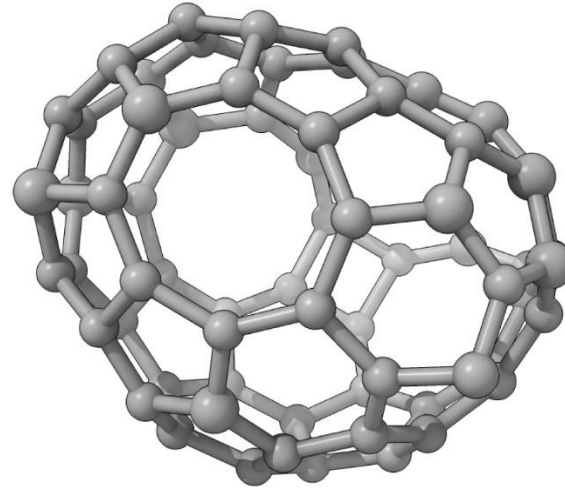


FE Profile of the simulations



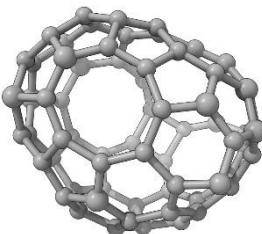


Biased gap-closing simulation

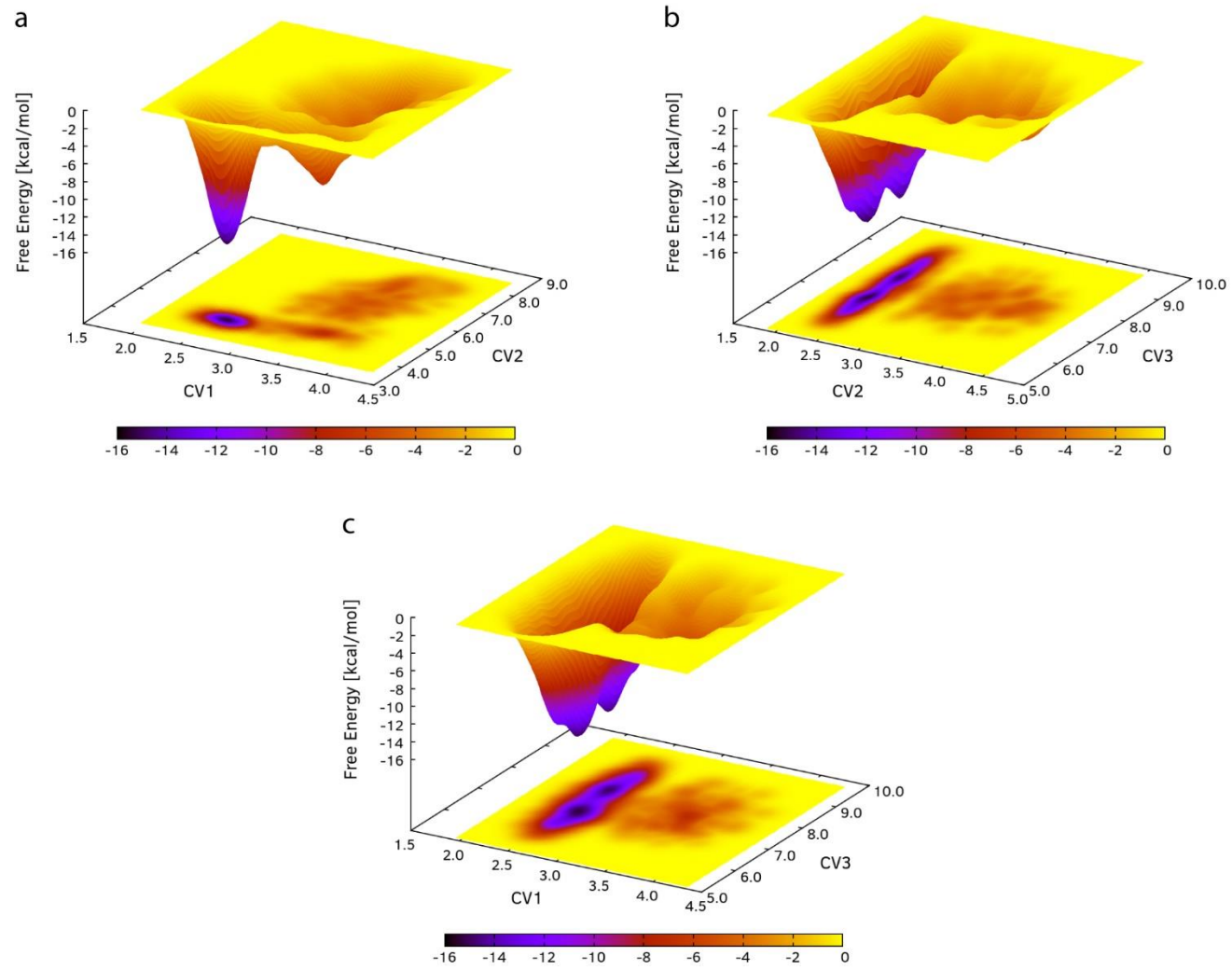


C66

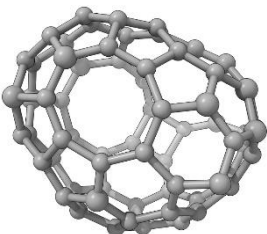
C66[4,5,6,7,8,13]fullerene



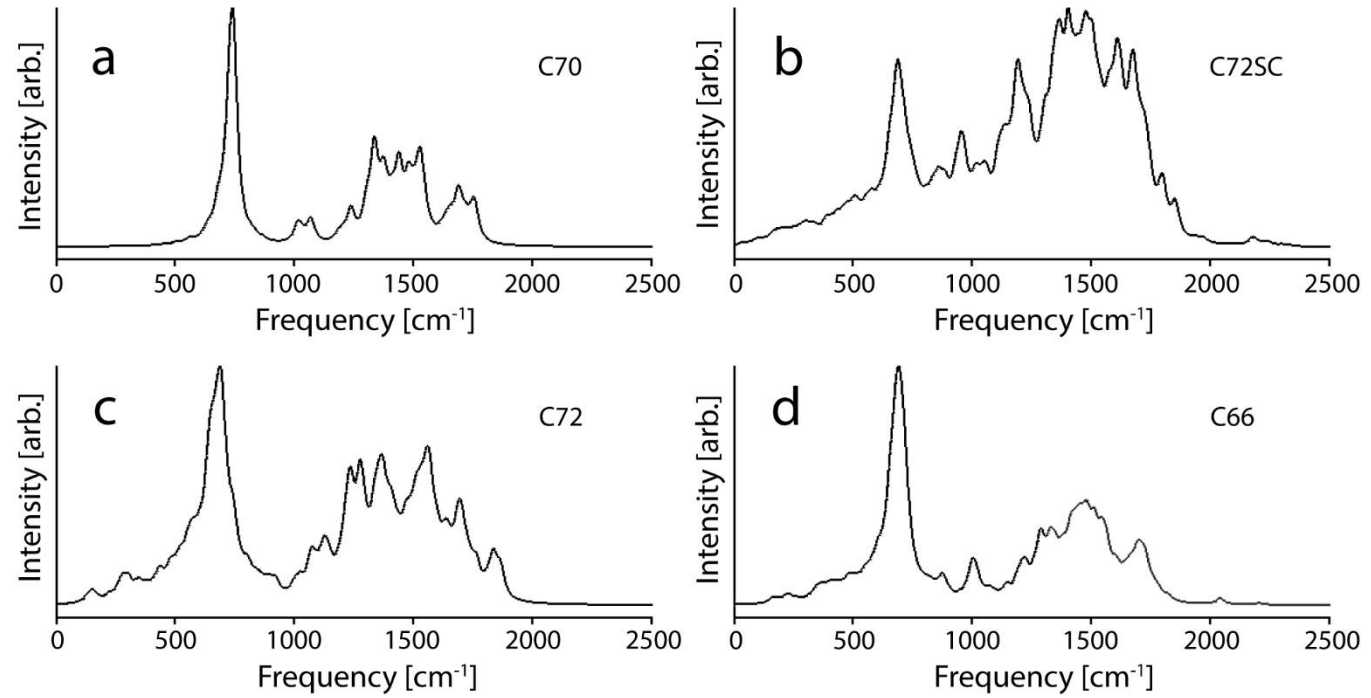
FES of the simulation



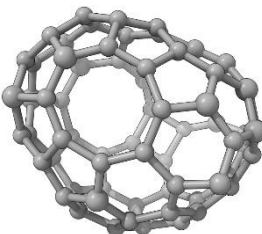
2 x 2 CV FESs of the biased gap-closing reactions



IR spectra



C72 and C66 can be mistaken for C70



Conclusions

- Orientation in initial aggregation – largely irrelevant
- Higher initial density -> tangled polycyclic, no sp , sp^2 dominant, low sp^3
- Lower initial density -> branched linear + rings of low atom count, sp and sp^2 dominant, no sp^3
- High initial atom count -> porous polymers
- Small clusters readily couple to nanoparticles
- Alternative explanation for experimental detection of fullerenes or fullerene-like structures in space
- The very first “bottom-up” theoretical model of closed-cage nanoparticle formation

