Treatement by DFT-D2 of great molecular systems

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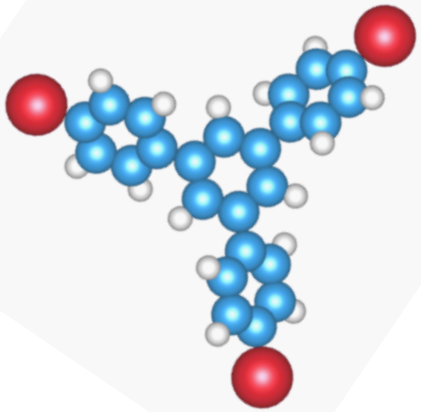
Equipe Minano FEMTO-ST / Dpt MN2S-UFC

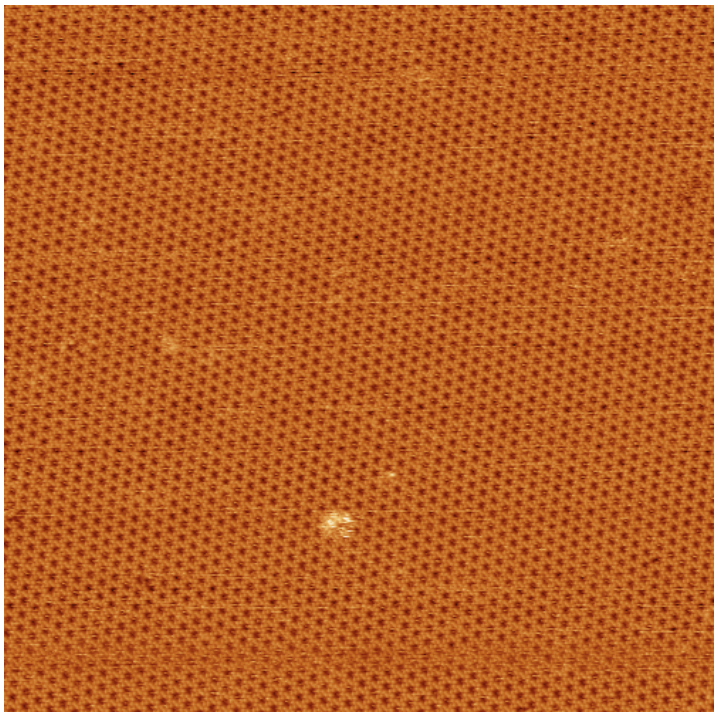
Great HPC challenge
First results Nanospider

Size of systems currently observe today ?

Network TBB/SiB: 1,3,5-tri(4'-bromophenyl)benzene

FEMTO-ST
ANR MISS

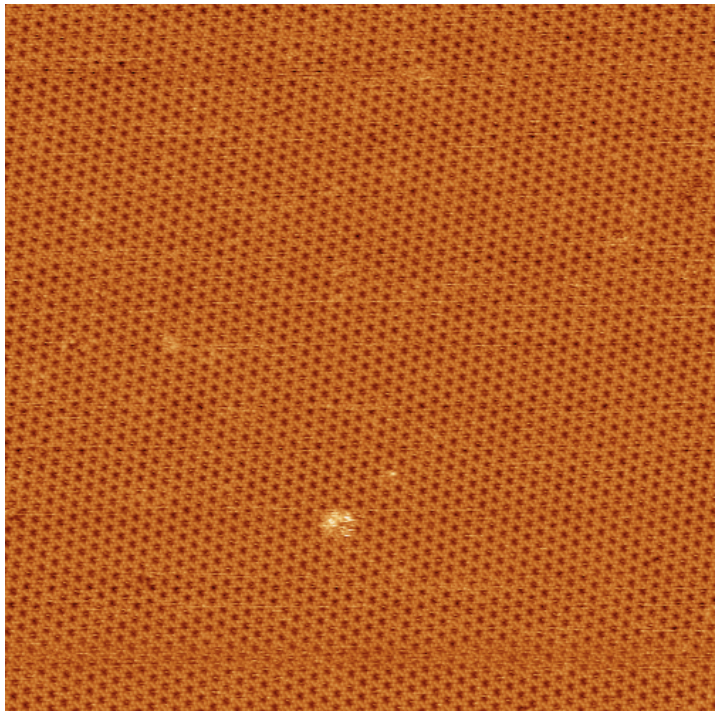




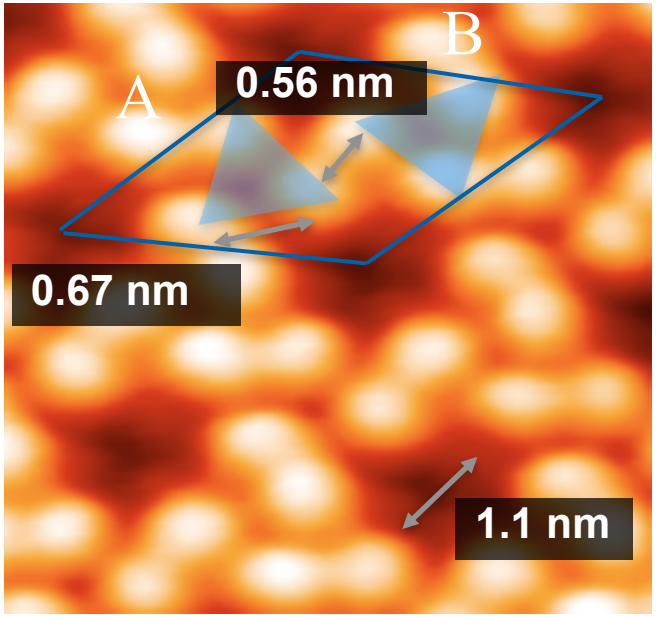
120x120 nm^2, Vs = 2.5 V, It = 0.034 nA, RT

- Nanoporous network
- Large Islands (> 800x800 nm^2), stable until 400 K

Network TBB/SiB: 1,3,5-tri(4'-bromophenyl)benzene



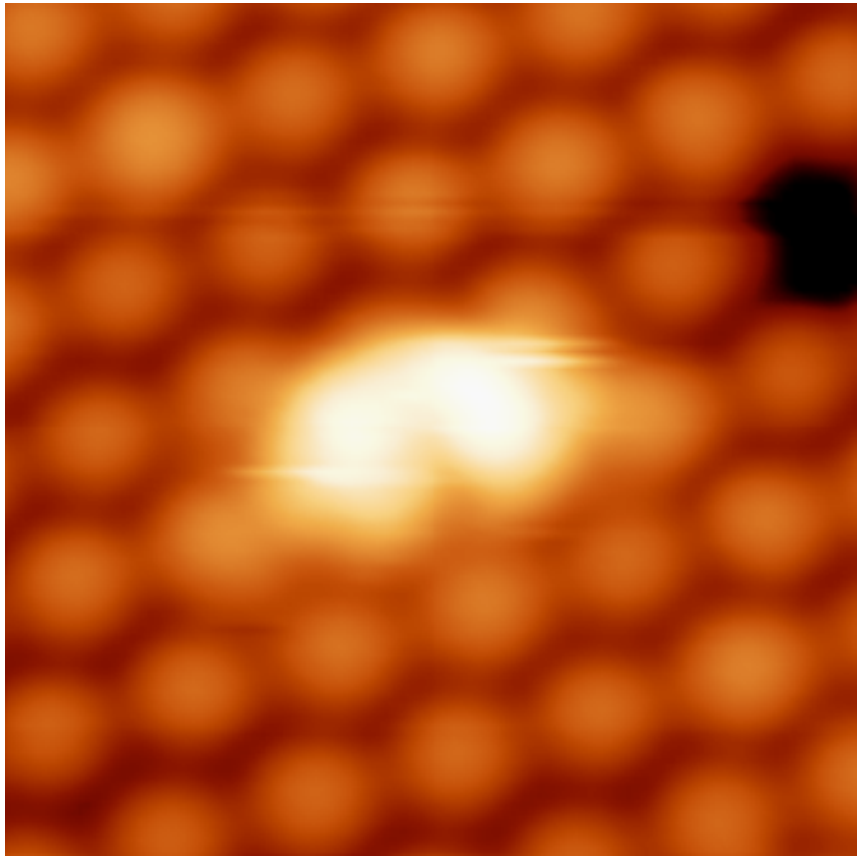
120x120 nm^2, Vs = 2.5 V, It = 0.034 nA, RT



- Lattice commensurate with SiB
- Primitive cell: six protrusions

What we observe experimentally ?

Molecule isolated: PTCDI/SiC(0001) 3x3

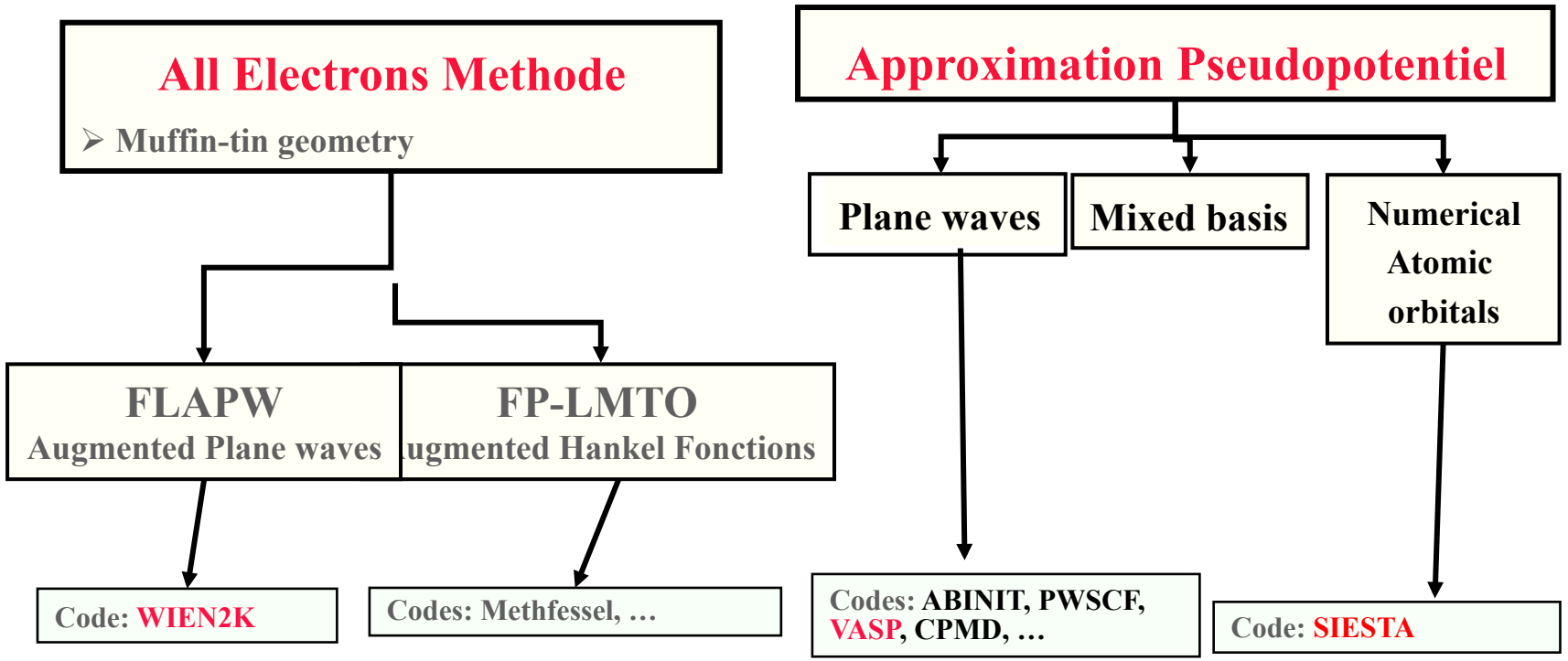


ISMO Orsay

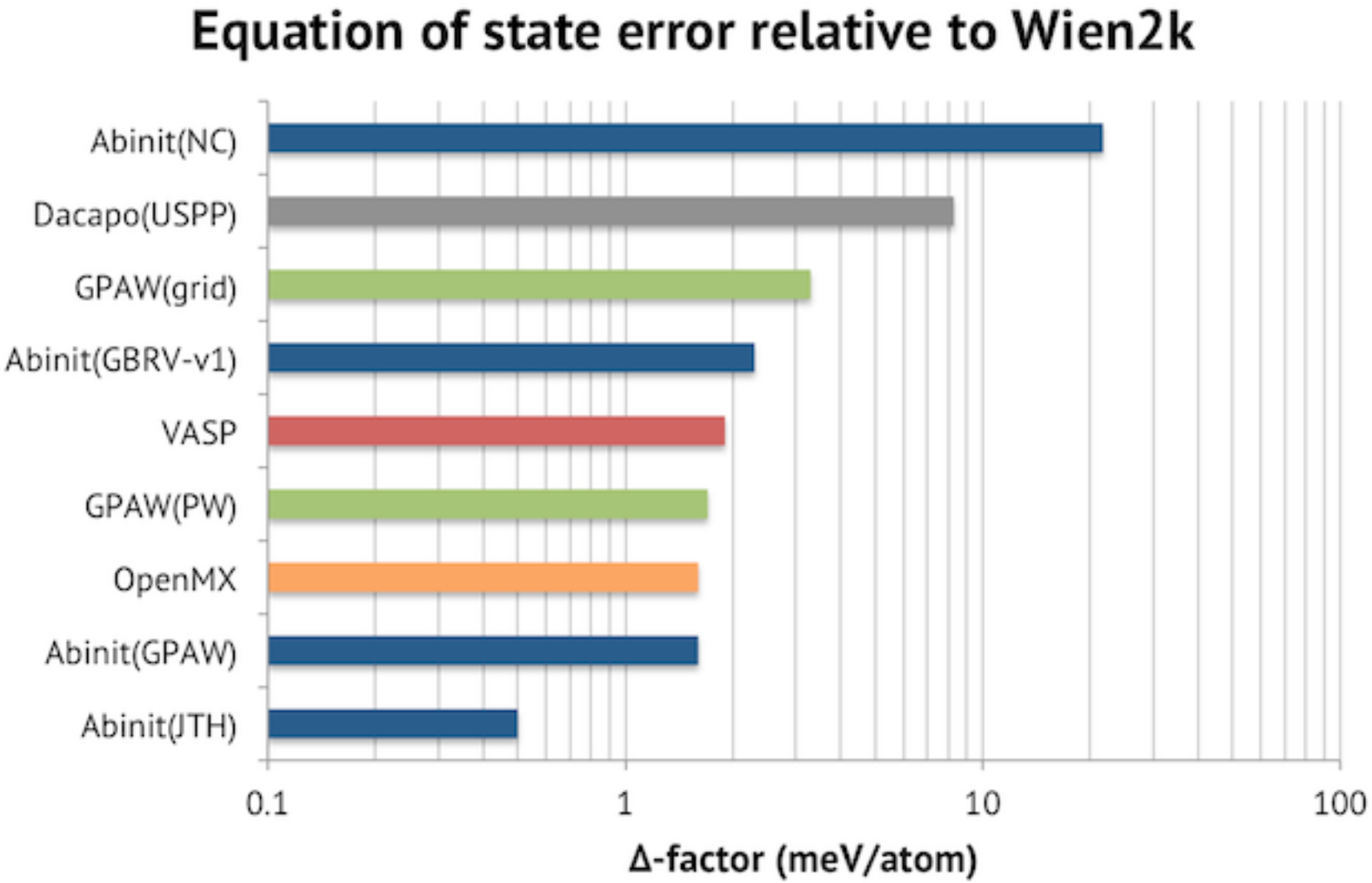
ANR MOLSIC

What we observe experimentally?

What DFT-code to solve Kohn-Sham equation ?



Accuracy ?


Equation of state error relative to Wien2k
Abinit(NC)
Dacapo(USPP)
GPAW(grid)
Abinit(GBRV-v1)
VASP
GPAW(PW)
OpenMX
Abinit(GPAW)
Abinit(JTH)
0.1
1
10
100
Δ-factor (meV/atom)

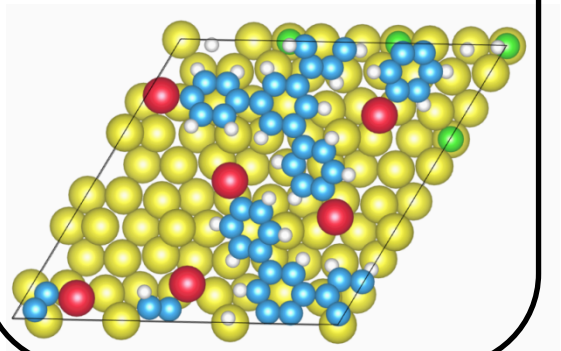
Code used

VASP

b-initio VASP ackage
lenna imulation

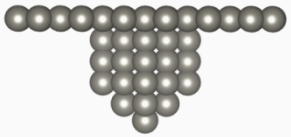
- DFT-D : GGA + correction of Grimme *(Grimme, J. Comp. Chem. 27, 1787 (2006))*

Top view



bSKAN

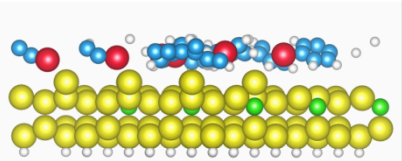
STM tip



DFT
vasp

Bias voltage

Surface



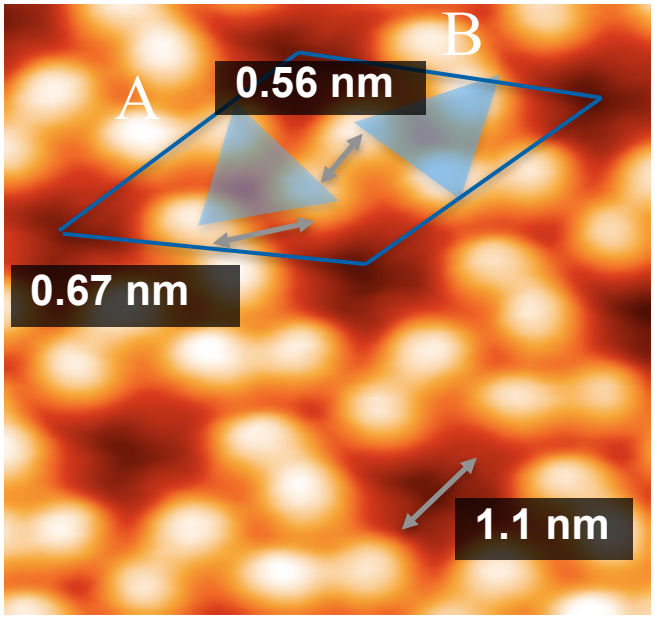
DFT
vasp

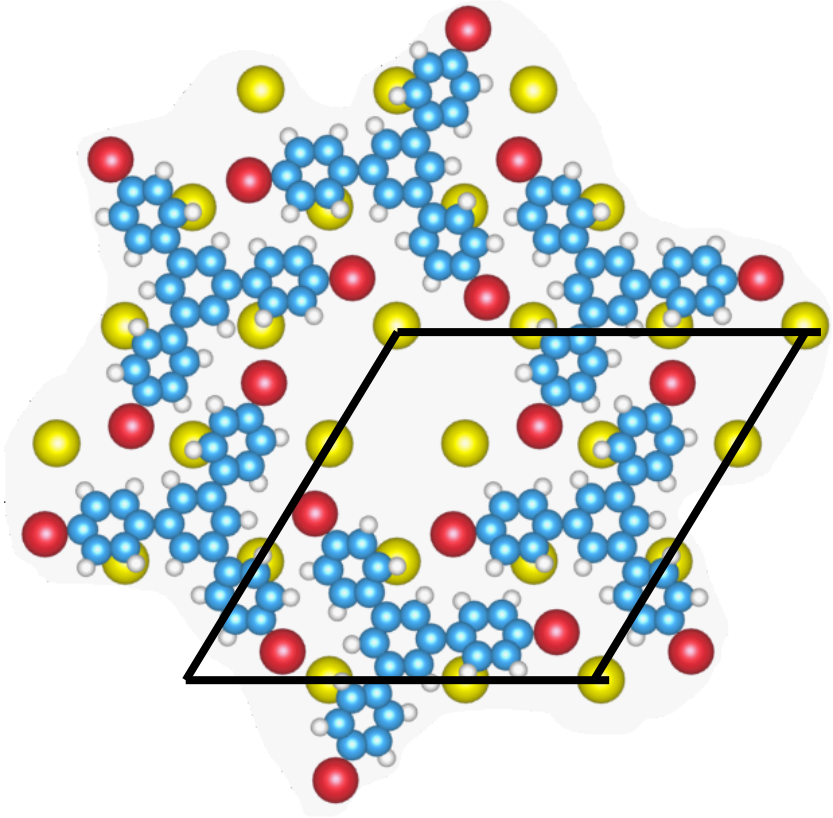
χ ⇒ BSKAN ⇐ ψ

Current tunnelling is calculated

Materials Modelling, DL, March 20,2007

8





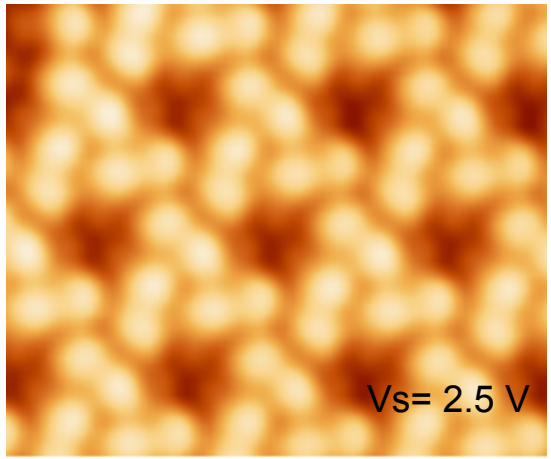
540 Atoms

64 nodes / 4Go/nodes

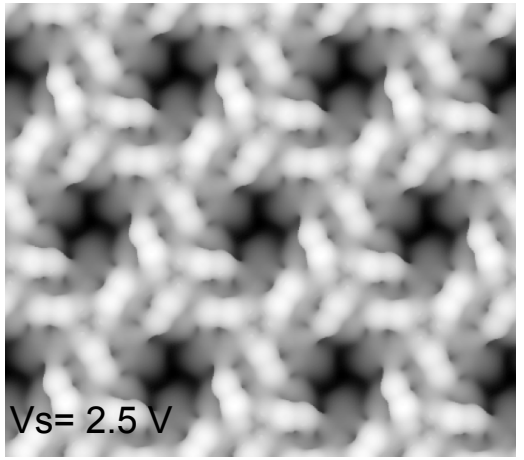
20x20x70 Ang

STM / bSKAN image

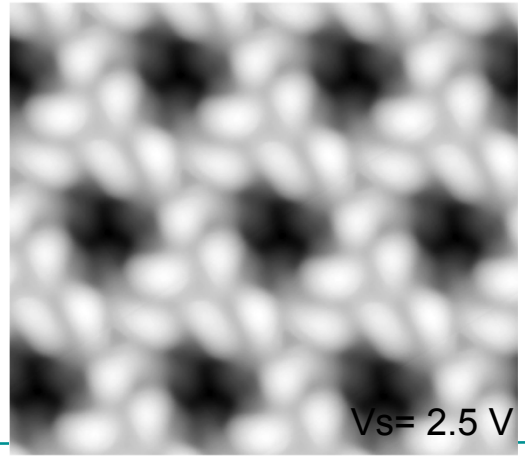
STM Image



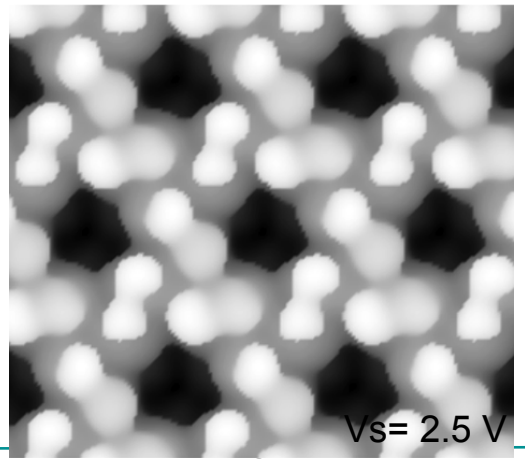
LDOS Image without smoothing



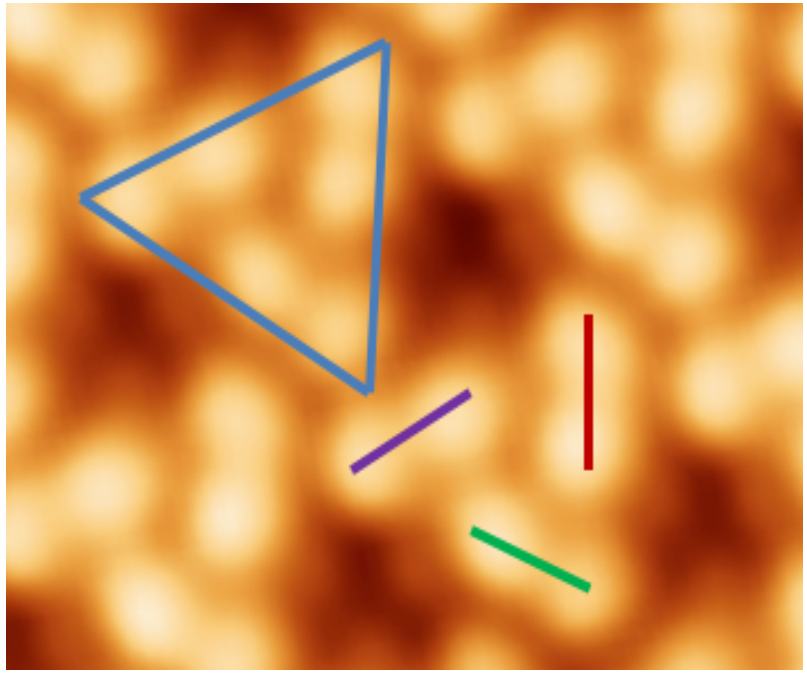
LDOS Image with smoothing

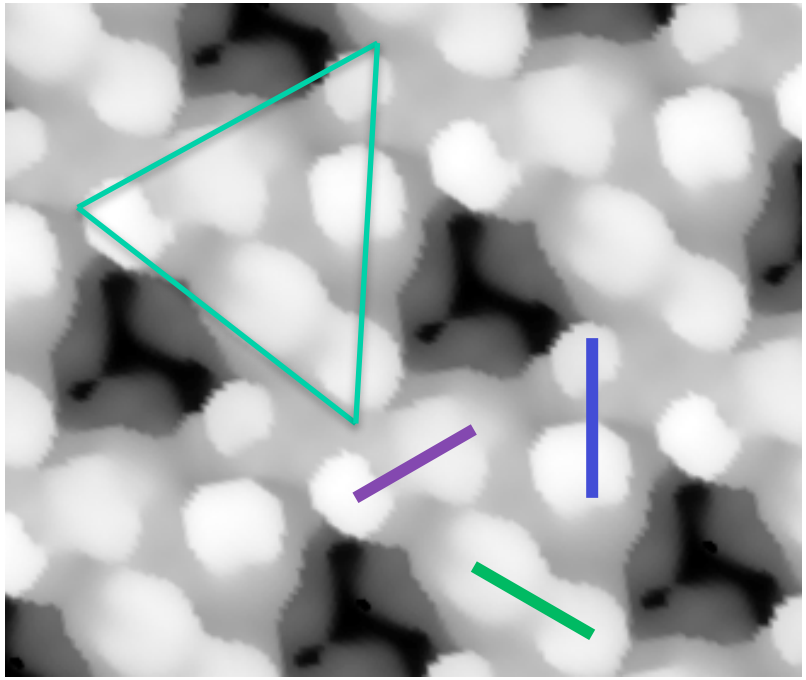


STM image simulated with bSKAN



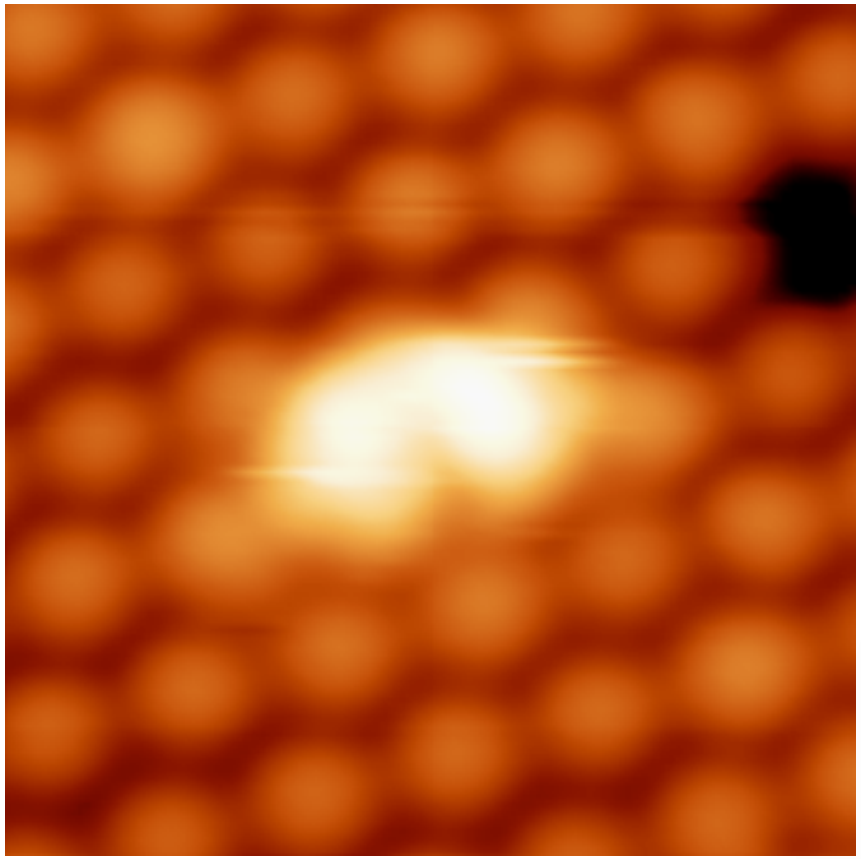
STM / bSKAN image

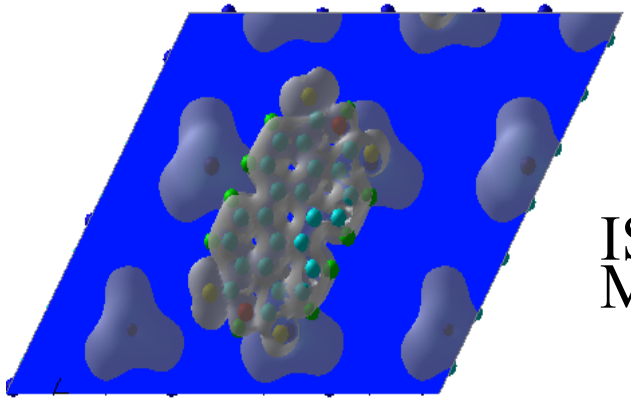




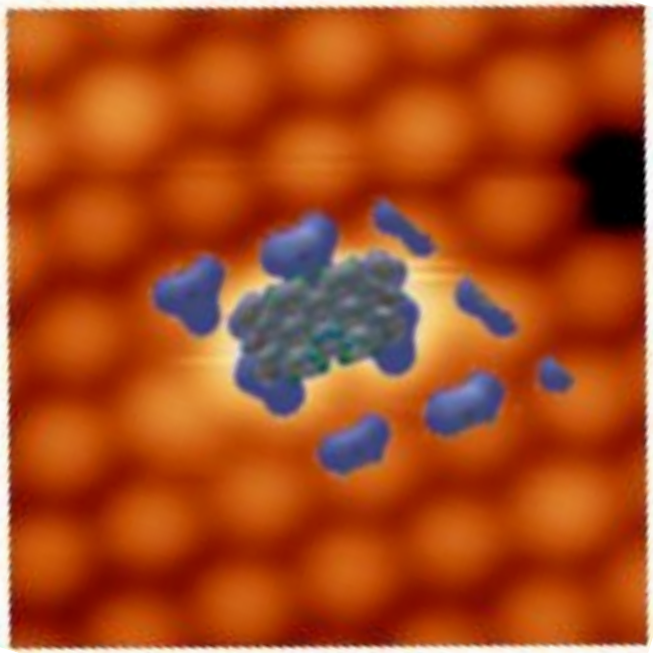
Molecule isolated : PTCDI/SiC(0001) 3X3

ISMO Orsay





IS2M
Mulhouse



Molecule isolated: PTCDI/SiC(0001) 3X3

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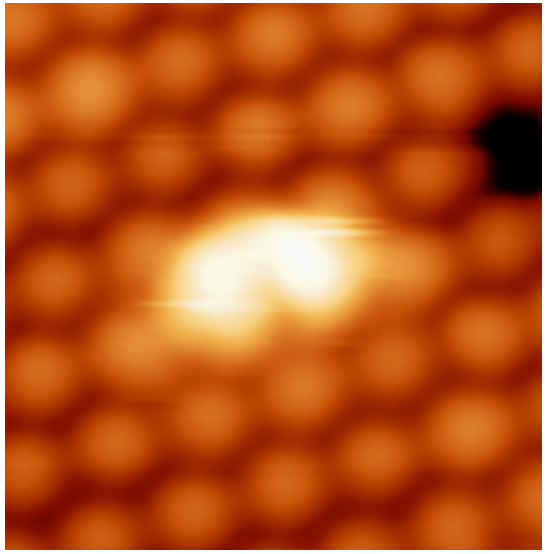
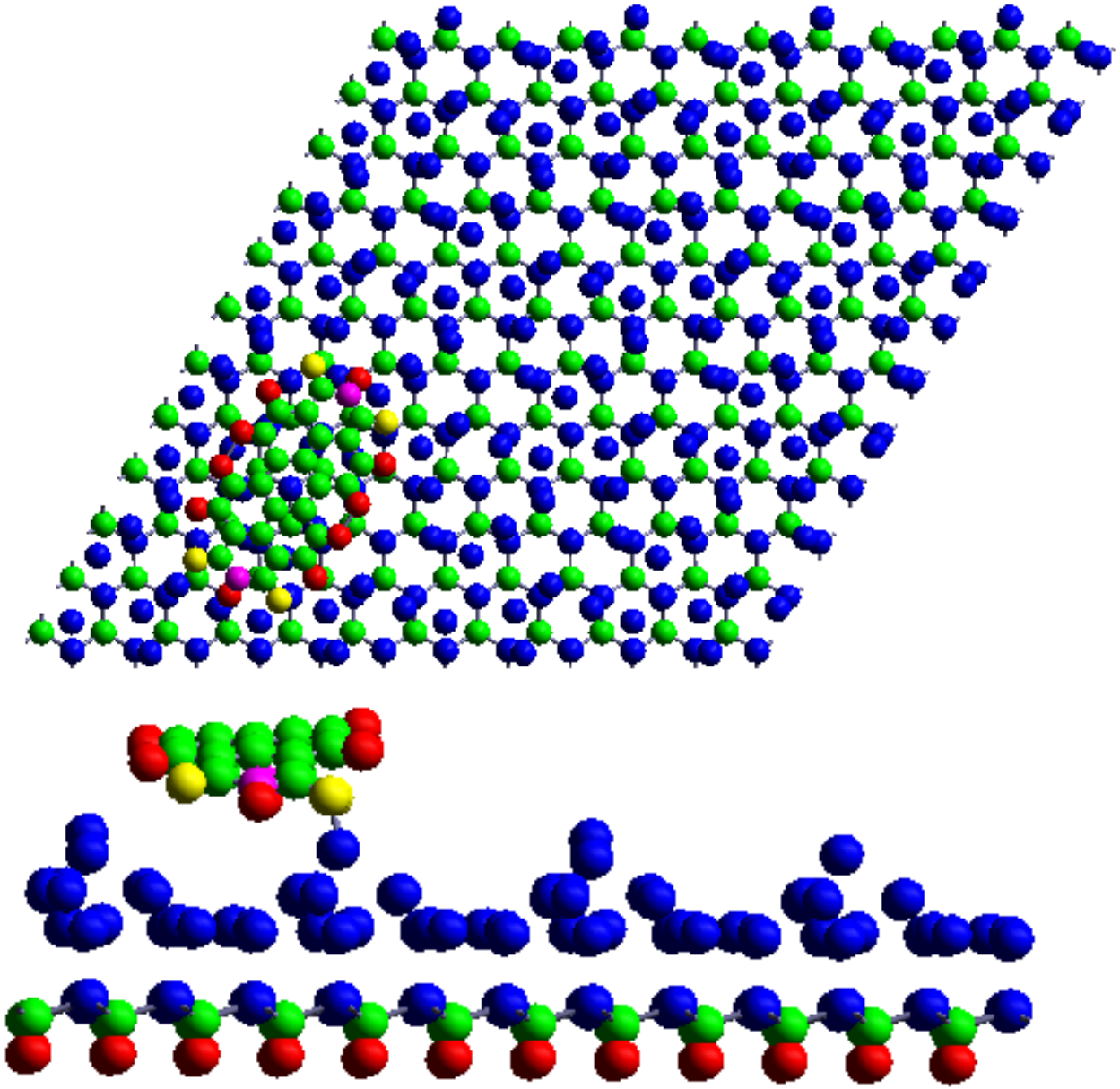
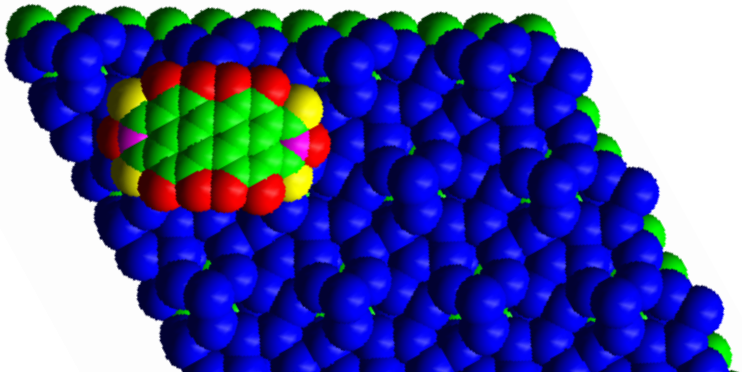
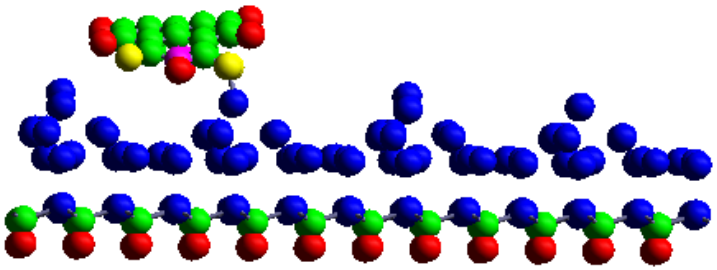


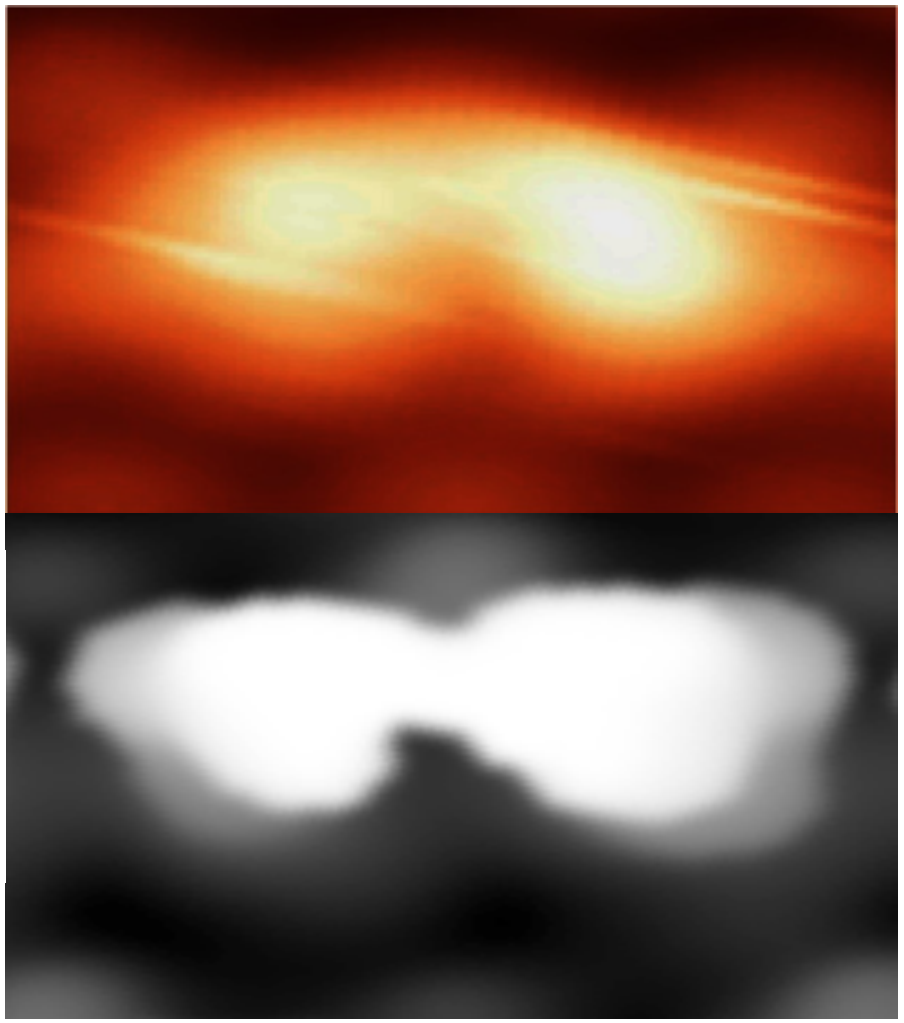
680 Atoms
80 cores /3 Go
38x38x50 Ang



Results Obtained by Bskan



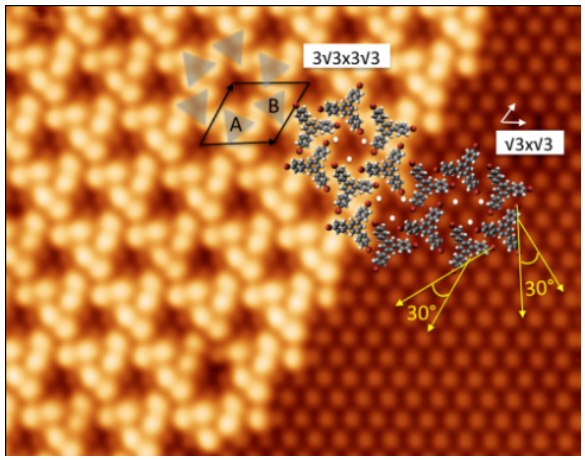


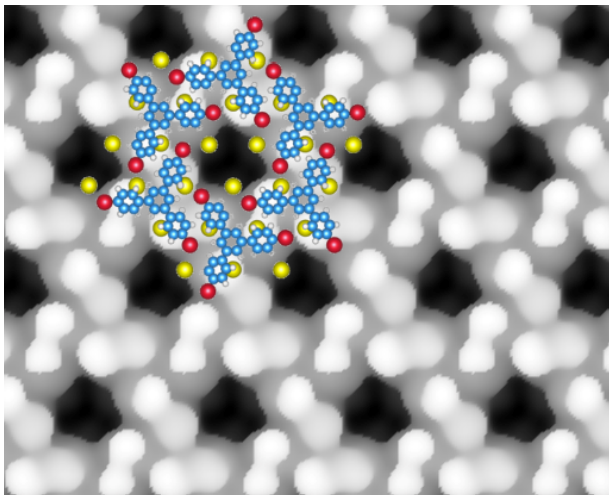


In standard

TBB network

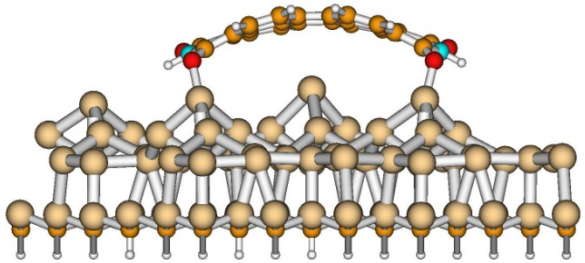
540 Atoms



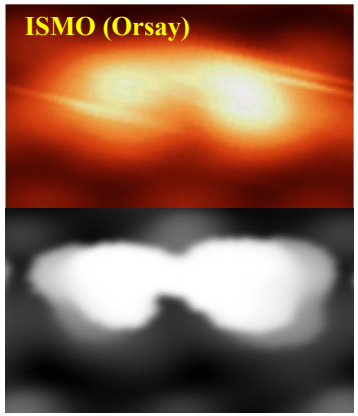


PTCDI on SiC(0001)3x3

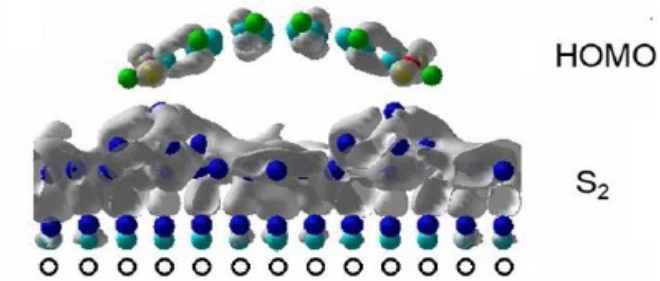
Structural properties



Comparison Experimental STM image And simulated



Electronic properties



680 Atoms

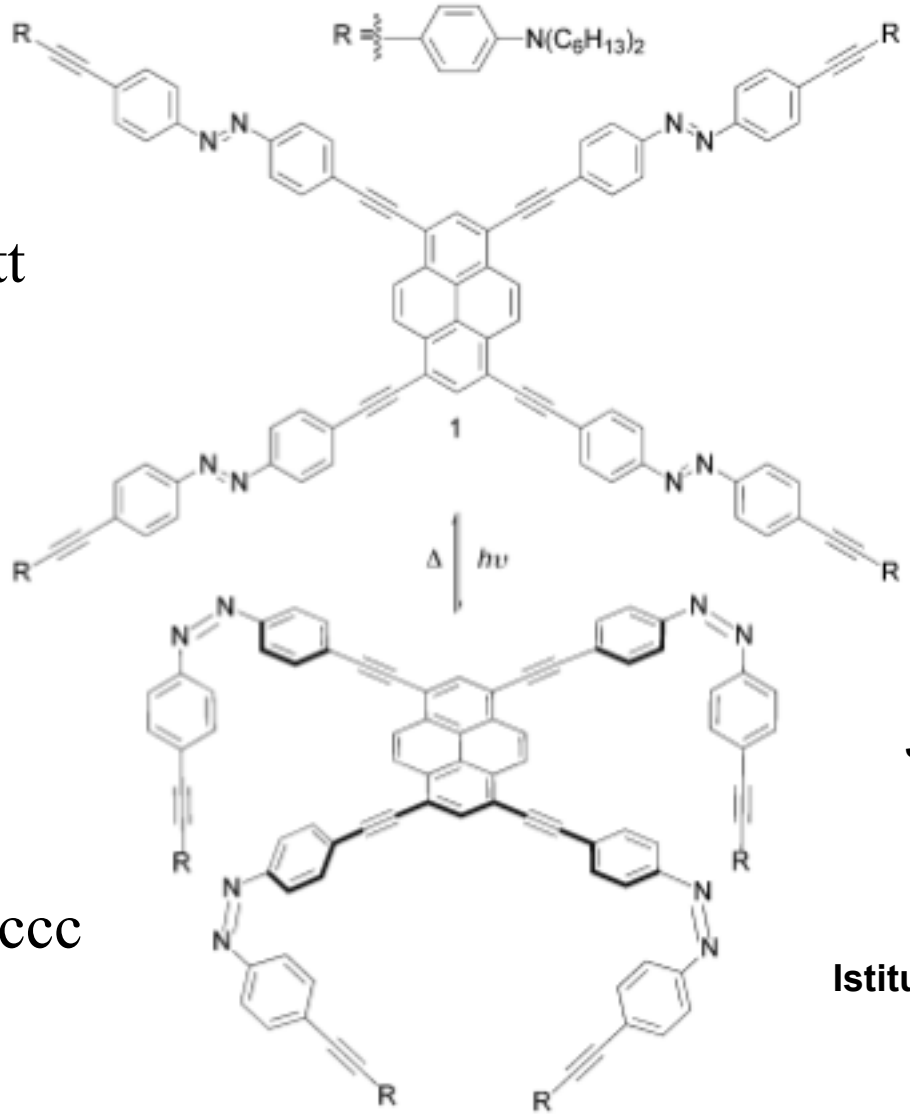
Application : Molecule isolated on surface

Molecule Arachnoïd : nanospider

- **Objective:**
  - Understand experimental observations
- **Solution**
  - Full DFT-D2 simulation with the surface
  - Simulate STM images

Molecule Arachnoïd : nanospider

$C_{152}H_{158}N_{12}$



J. Zeitouny, A. Llanes-Pallas, D. Bonifazi

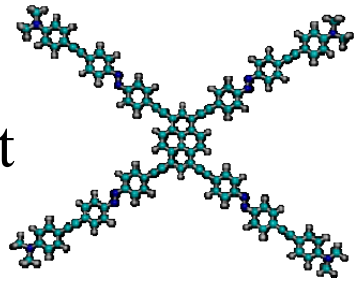
(Universita di Trieste)

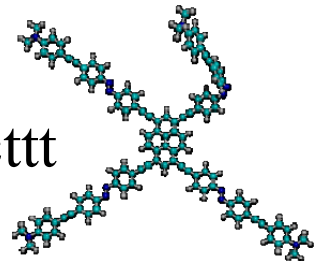
A. Belbakra, A. Barbieri, N. Armaroli

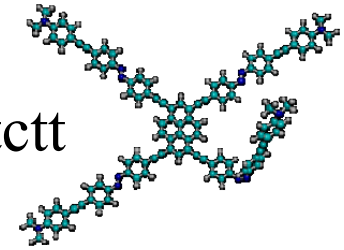
Istituto per la Sintesi Organica e la Fotoreattivita del CNR, Bologne

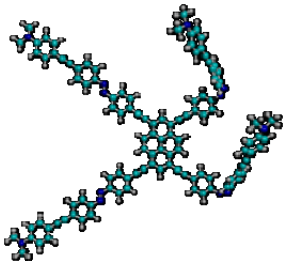
Chem. Commun., 2011, 47, 451–453

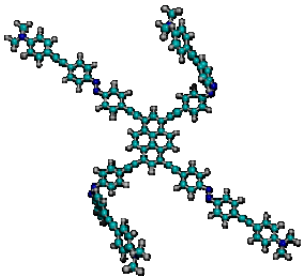
HYPERCHEM results

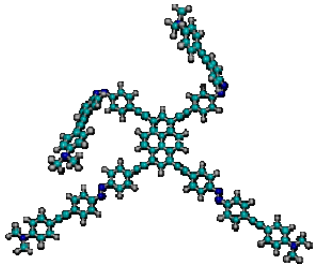
tttt 

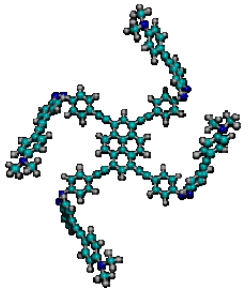
cttt 

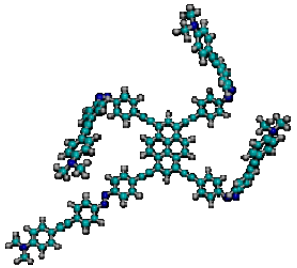
tctt 

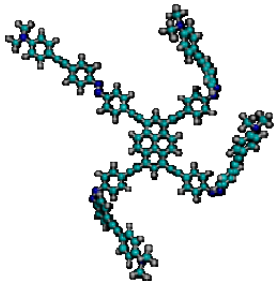
cctt 

ctct 

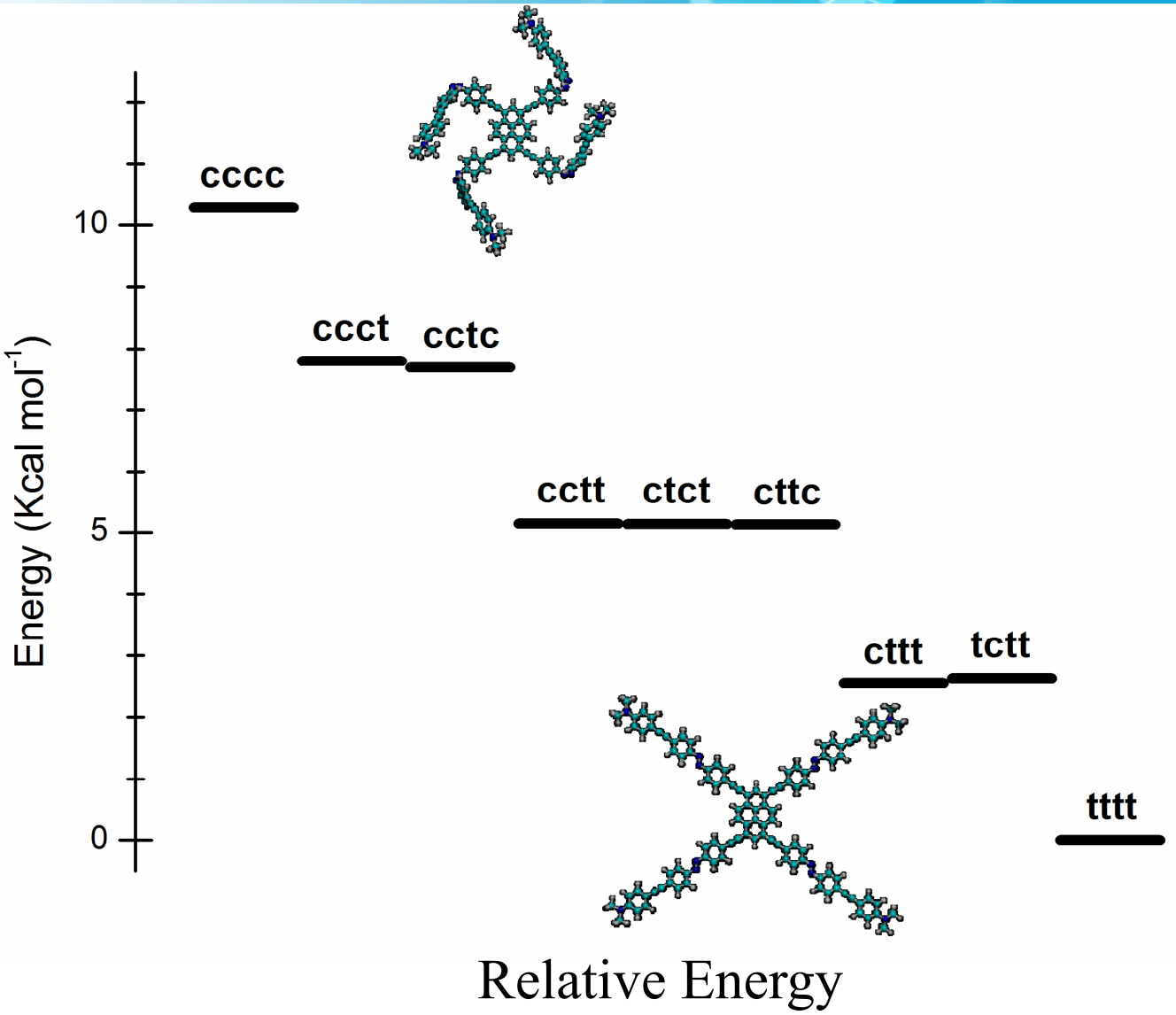
cttc 

cccc 

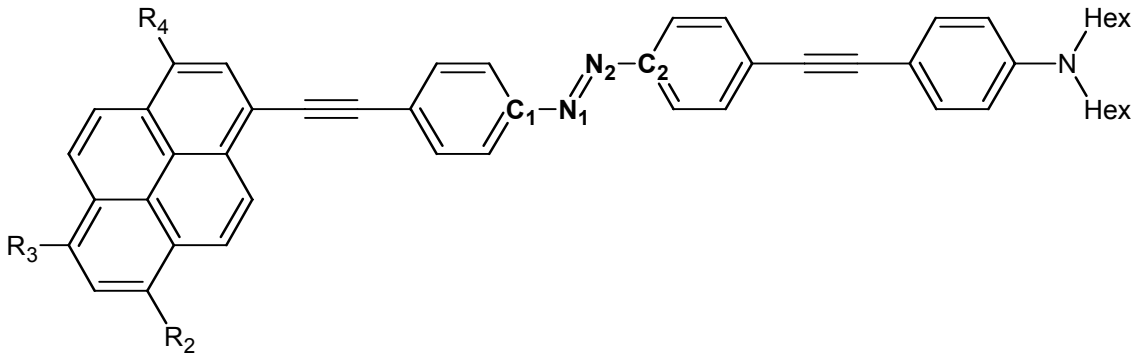
cctc 

ccct 

HYPERCHEM results

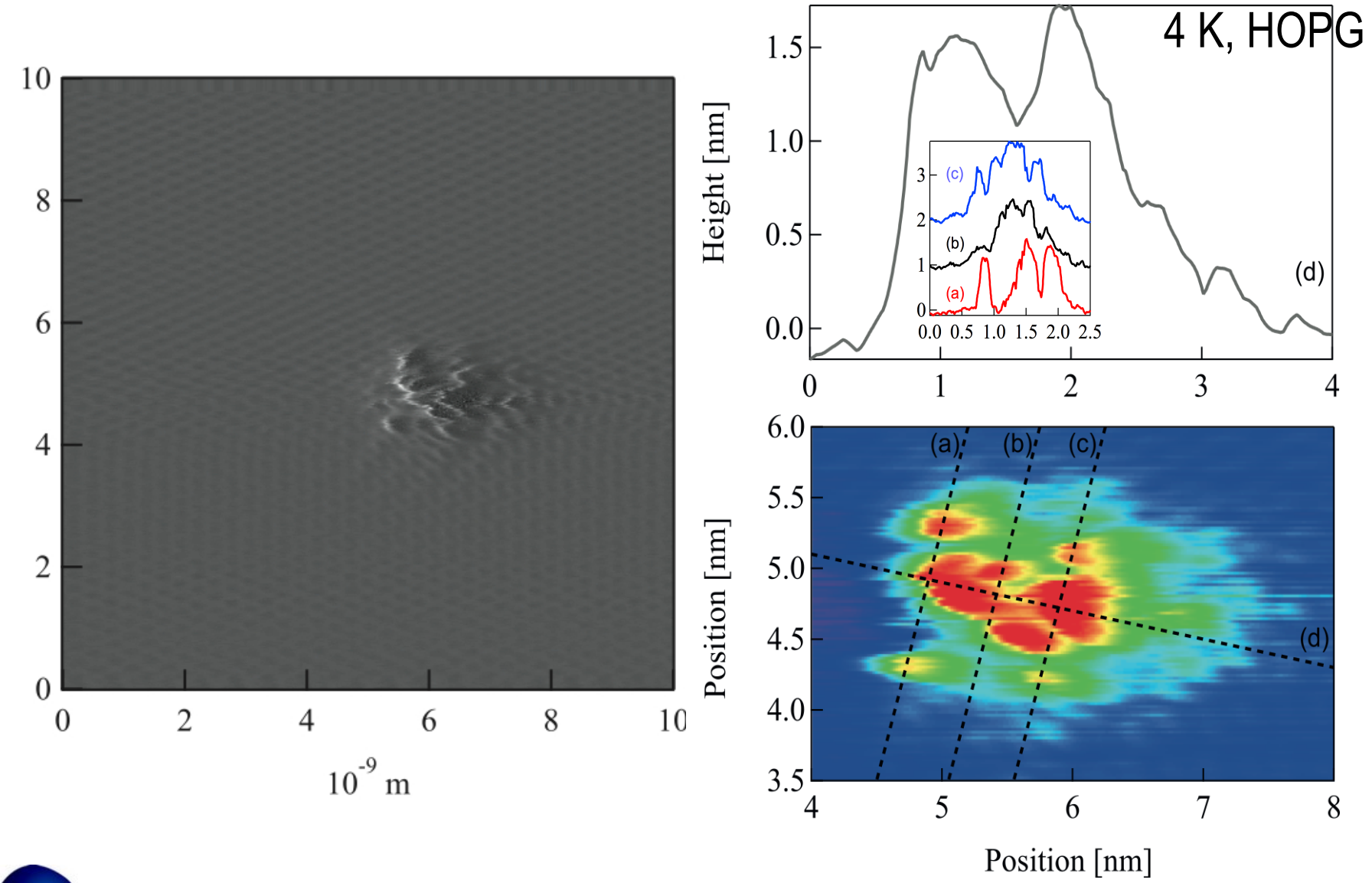


HYPERCHEM results



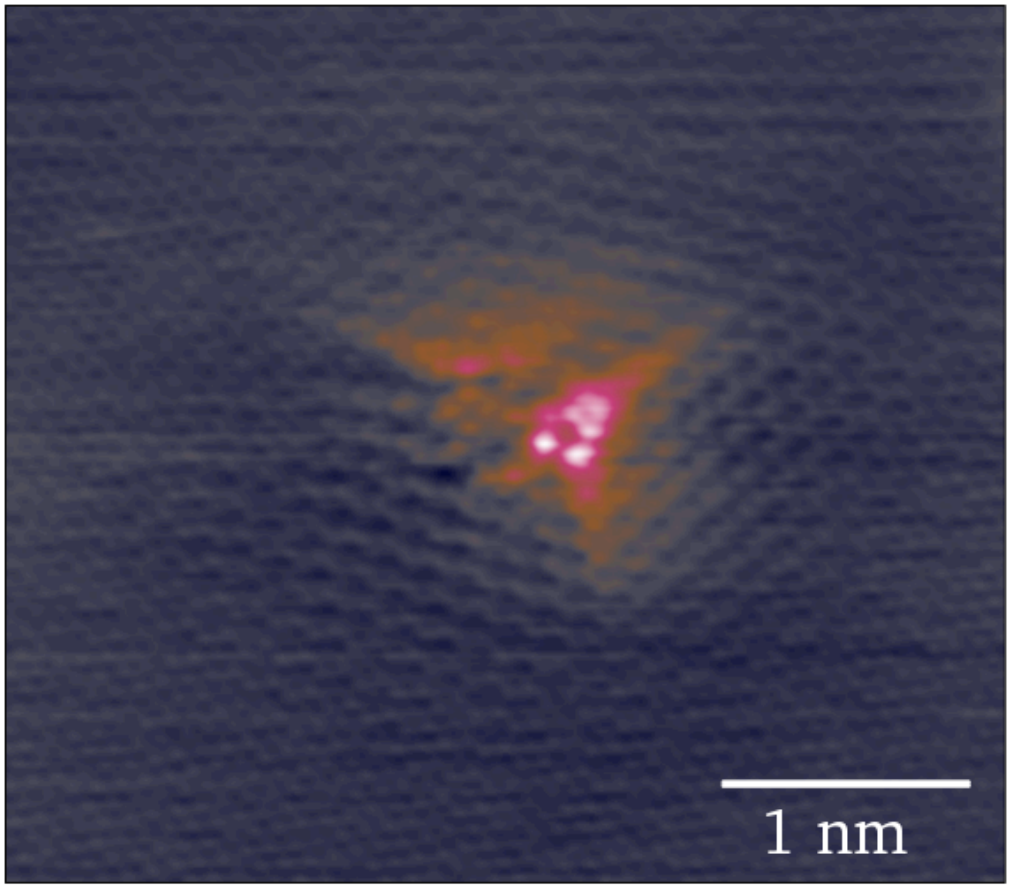
Isomer	Bond length (Å)			Bond angle (°)		Dihedral angle (°)
	C_1-N_1	N_1=N_2	N_2-C_2	C_1-N_1=N_2	N_1=N_2-C_2	C_1-N_1=N_2-C_2
tttt	1.4469	1.2321	1.4461	119.97	120.03	179.94
cttt	1.4522	1.2166	1.4522	126.92	126.83	0.15
tctt	1.4465	1.2318	1.4457	119.87	119.83	179.48
cctt	1.4520	1.2168	1.4517	127.16	127.09	0.23
ctct	1.4523	1.2170	1.4521	126.93	126.80	0.14
cttc	1.4524	1.2167	1.4524	126.87	126.90	0.01
ccct	1.4526	1.2168	1.4522	127.05	126.96	0.10
cctc	1.4522	1.2164	1.4518	127.08	126.85	0.18
cccc	1.4523	1.2167	1.4520	127.04	127.02	0.39

S. Melinte (Institute of Condensed Matter and Nanosciences - Université Catholique de Louvain)



Molecule Arachnoïd : nanospider

STM image onto HOPG at 77K



What we observe ?

We can simulate so great system ?

HPC « Grands Challenges »

Cluster HPC :

Mésocentre Université de Franche Comté

(300 cpu)

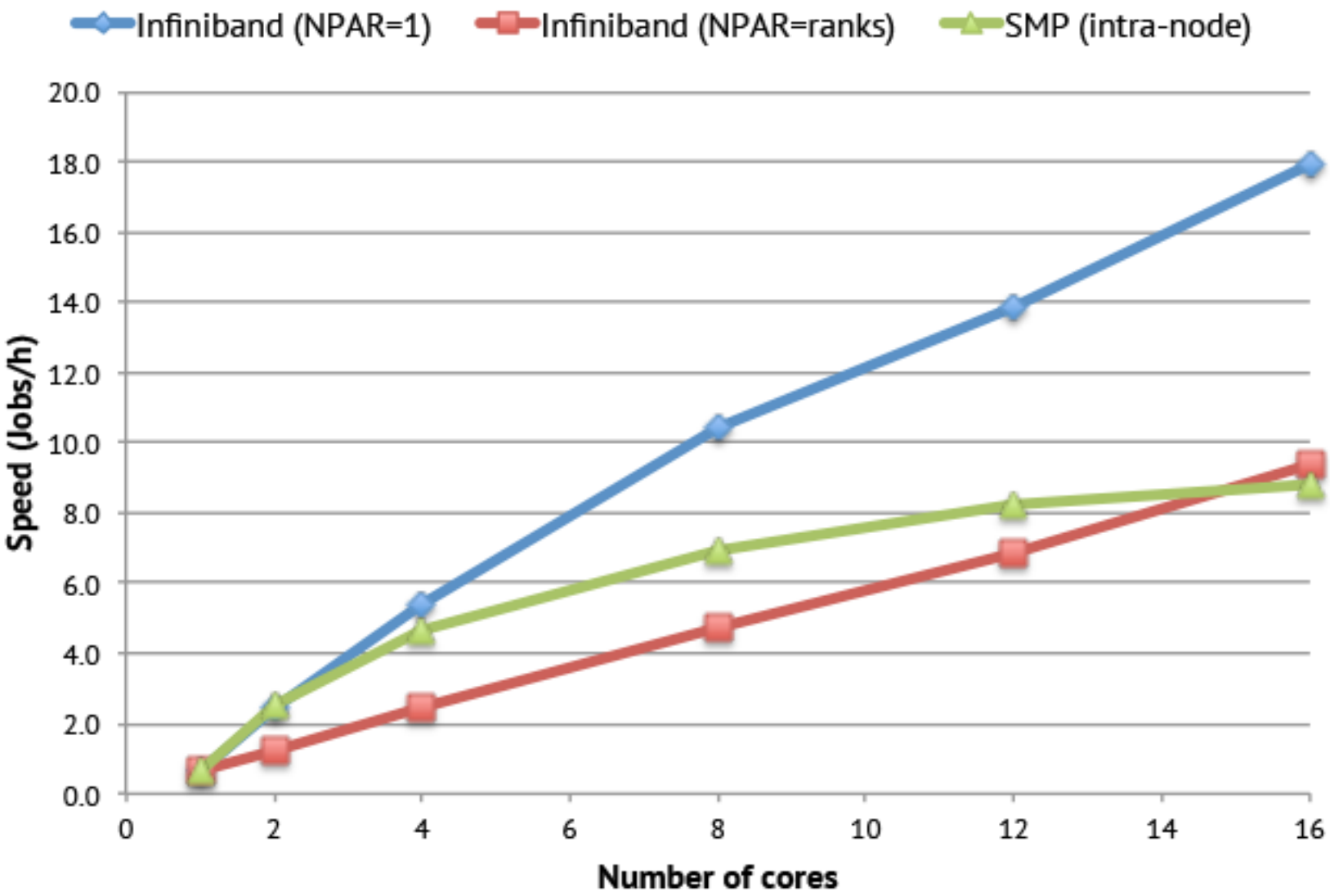
Simulations challenge HPC rules :

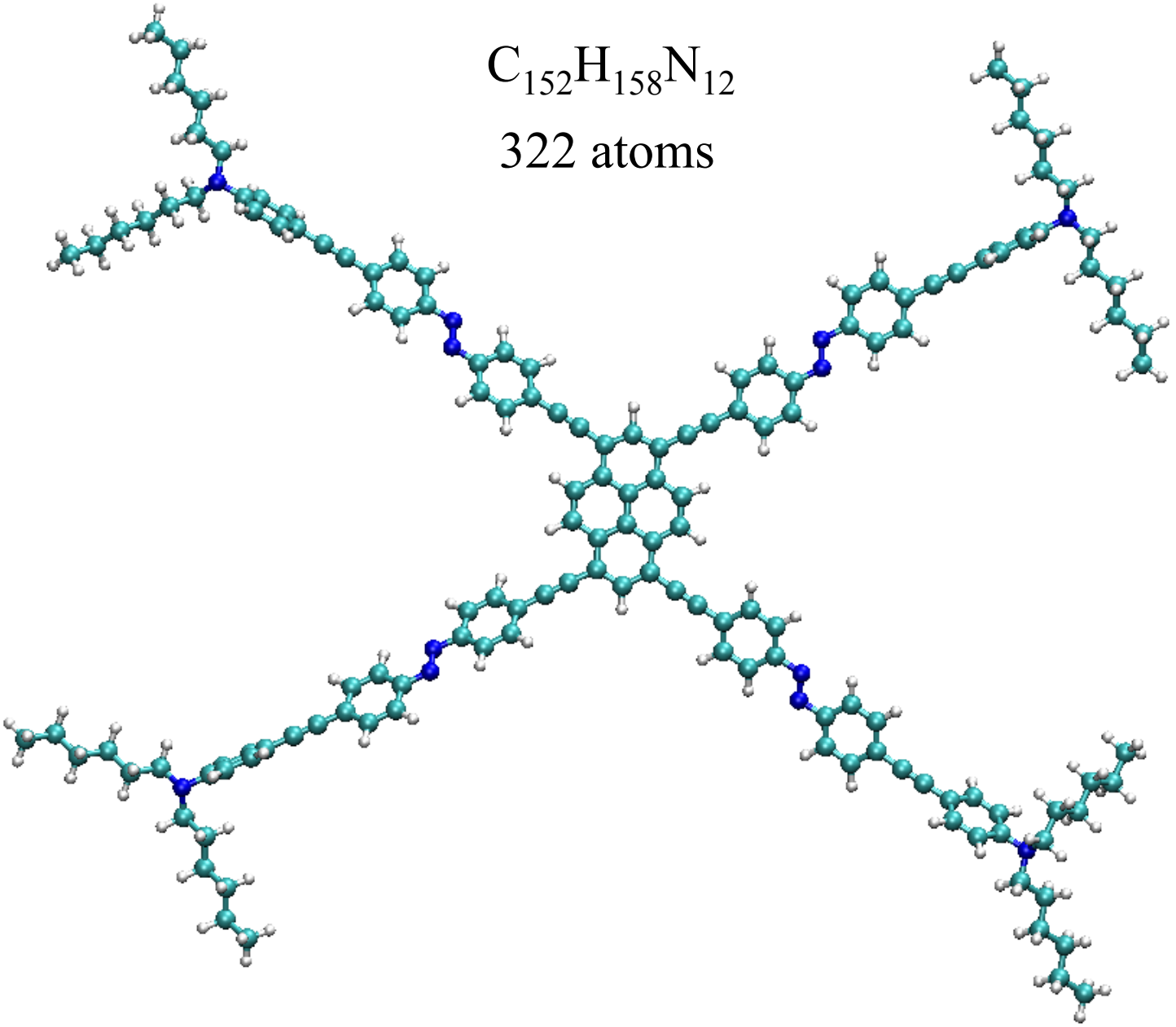
As fast as possible…

Full-DFT

Using vdw-D2

Good precision (Normal)


Infiniband (NPAR=1)
Infiniband (NPAR=ranks)
SMP (intra-node)
Speed (Jobs/h)
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
2
4
6
8
10
12
14
16
Number of cores


$C_{152}H_{158}N_{12}$
322 atoms

NWRITE = 2
IALGO = 38

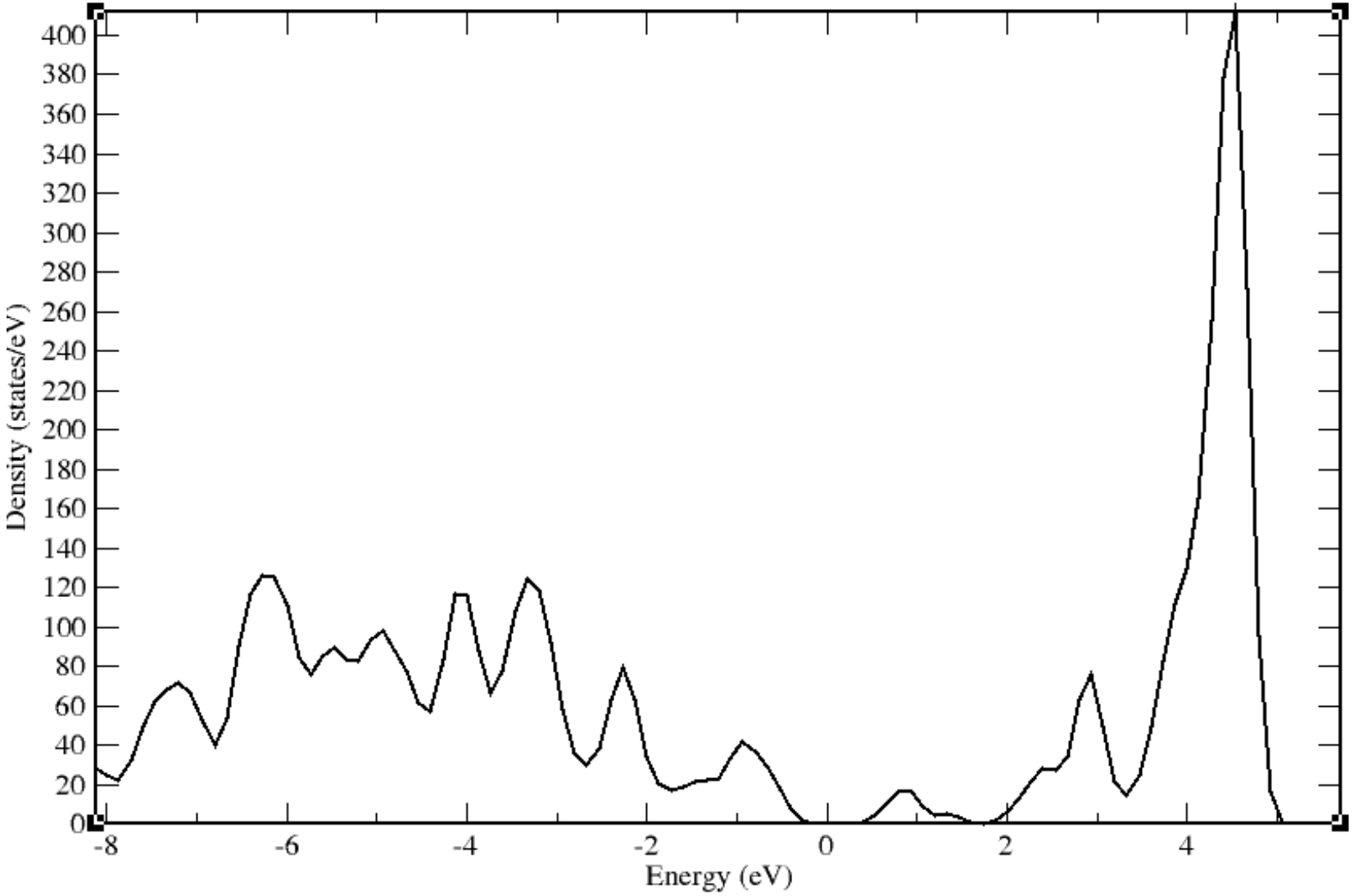
LREAL = A
LWAVE=.TRUE.
AMIN=0.01
ISMEAR=0
ENCUT=400 eV

#ionic relaxation
IBRION=2
 NSW=90
 POTIM =0.1
EDIFFG=-1e-02
TEBEG = 77   temperature
LORBIT=1
RWIGS= 0.866500 0.866500 0.266500
LVDW= .TRUE.
NPAR=1

 32 nodes
 4 Go/node

 70x70x50 Ang

PDOS


Density (states/eV)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-8
-6
-4
-2
0
2
4
Energy (eV)

First test simulation on Au surface

Test #0 806 atoms

64 nodes --→ 6 Go/node

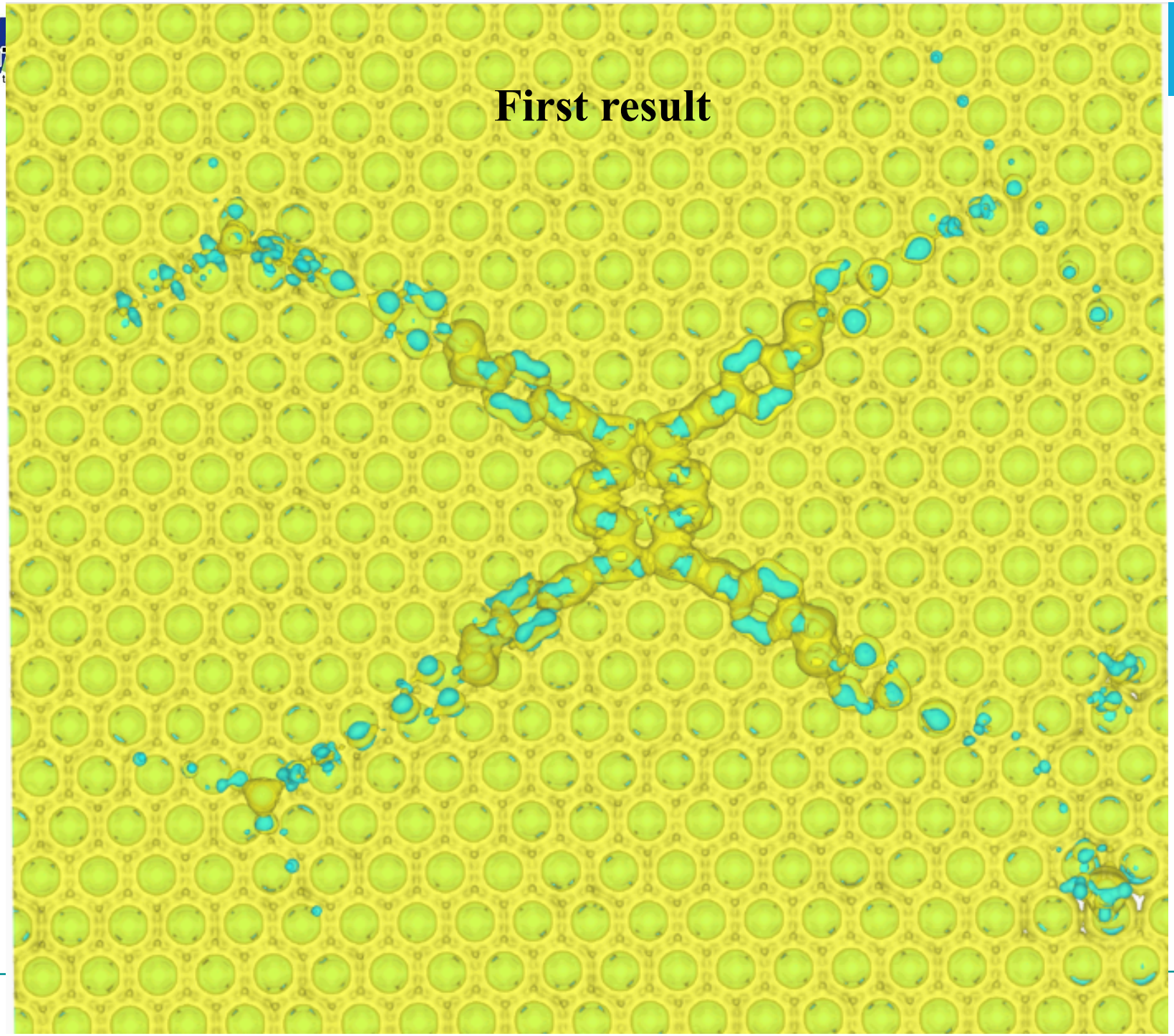
60x60x30 Ang

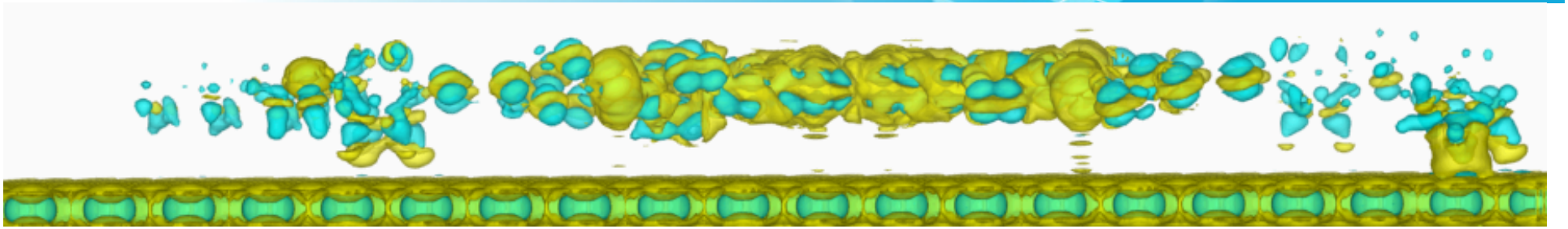
```
NWRITE = 2
IALGO  = 38

#ionic relaxation
IBRION=2
 NSW=2
```

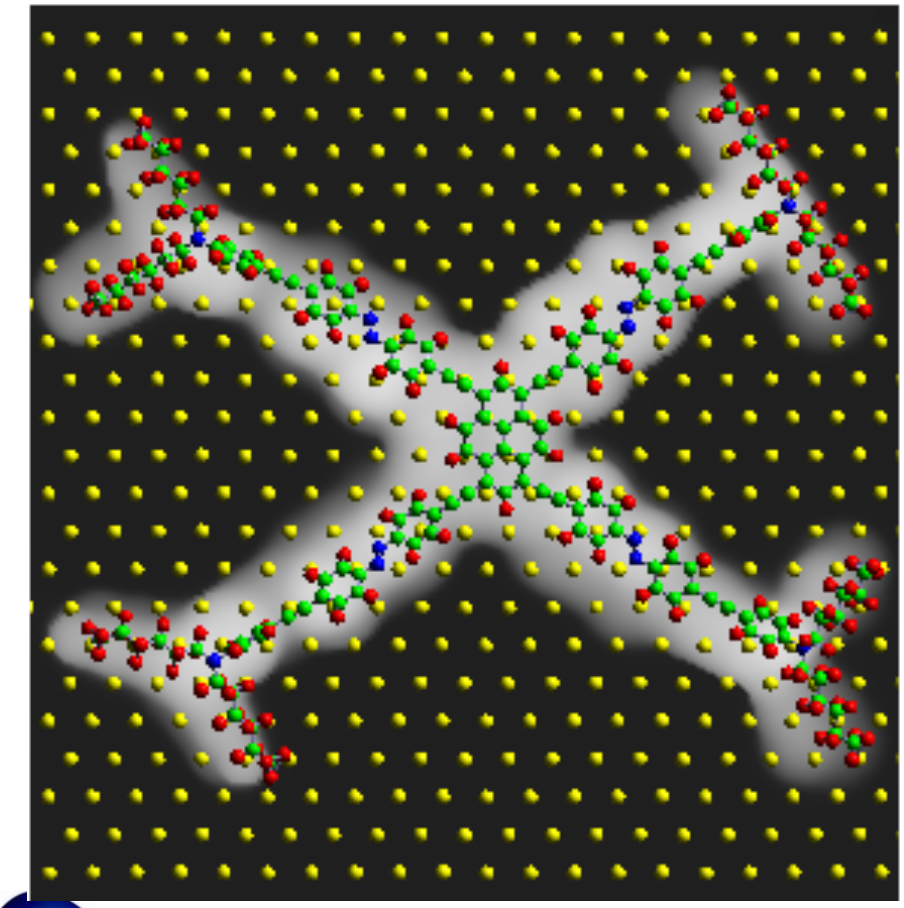
Temps Elapsed time (sec): 165351.328 s (46 h)

i.e. : 2939 h monoprocessor !

First result





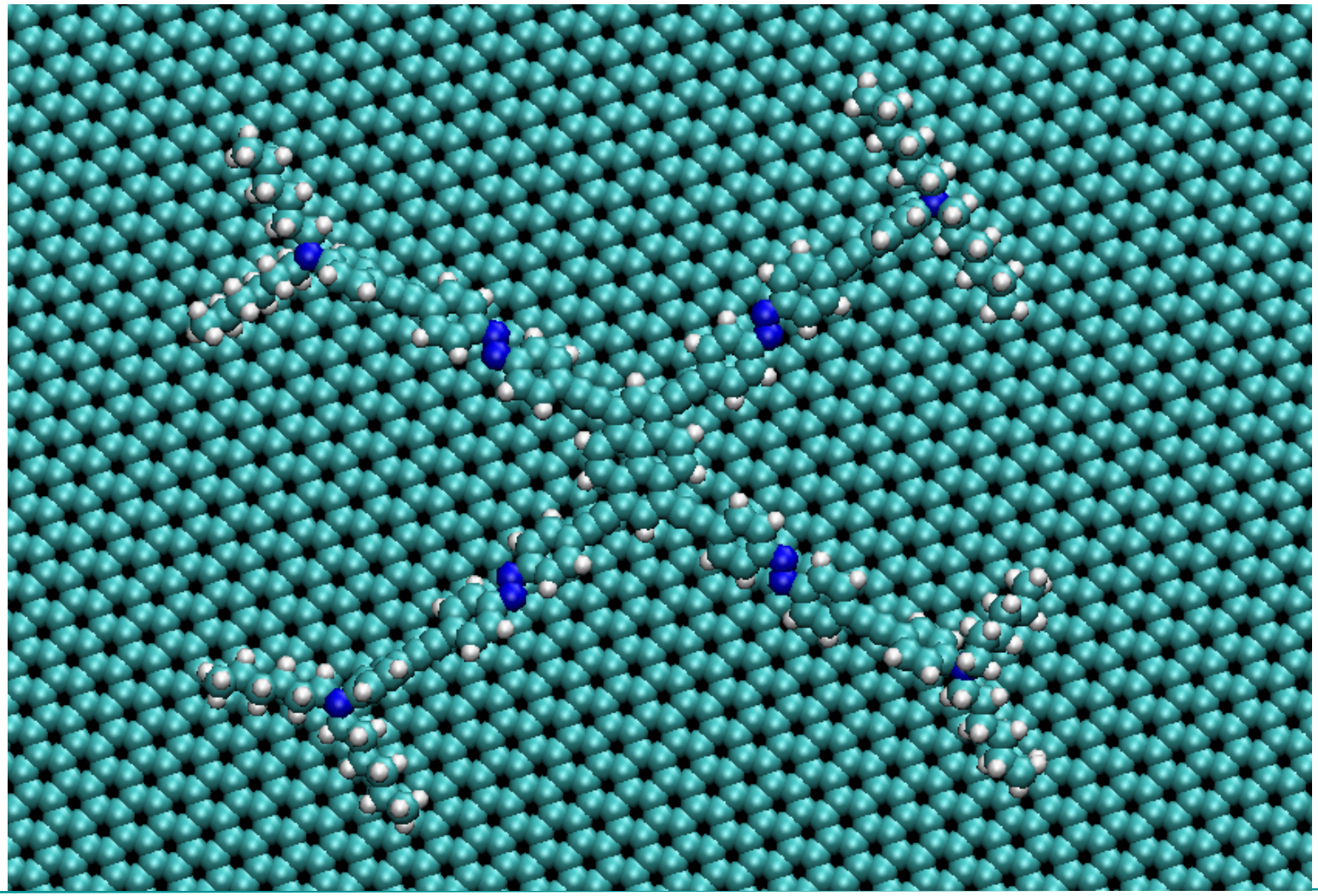


Simulations challenge HPC rules :

Verified

Application::

Great system PAW with 2122 and 3922 atoms



64 nodes --→ 10 Go/node

74x74x50 Ang

NWRITE = 2
IALGO = 38

#ionic relaxation
IBRION=2

Test

Time : 356070.114 for 2 ionic relaxation steps== 6330 h mono

Test

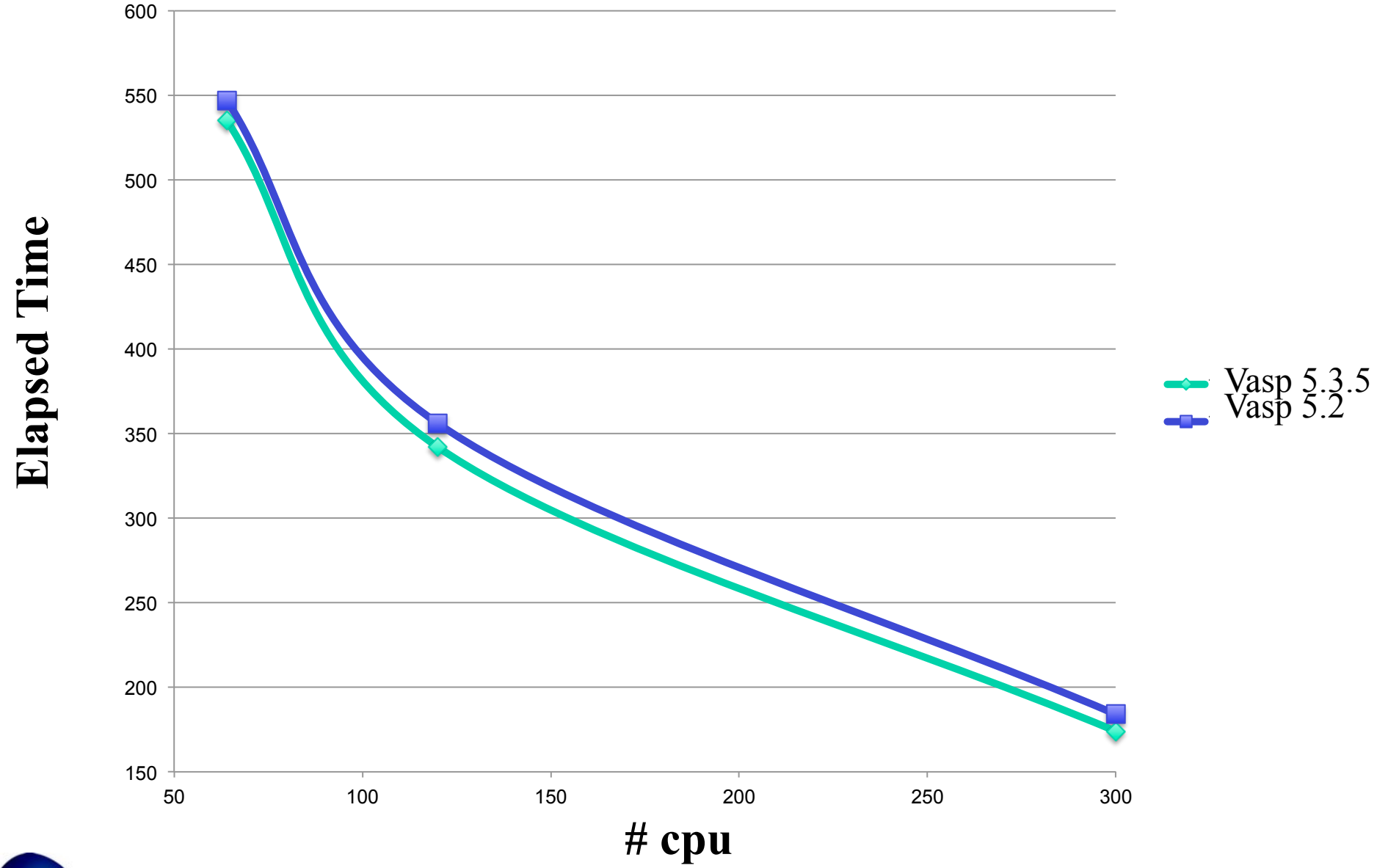
Time : 535. ks (148 h) for 5ionic relaxation steps == 9514 h mono

120 nodes --→ 5 Go/node

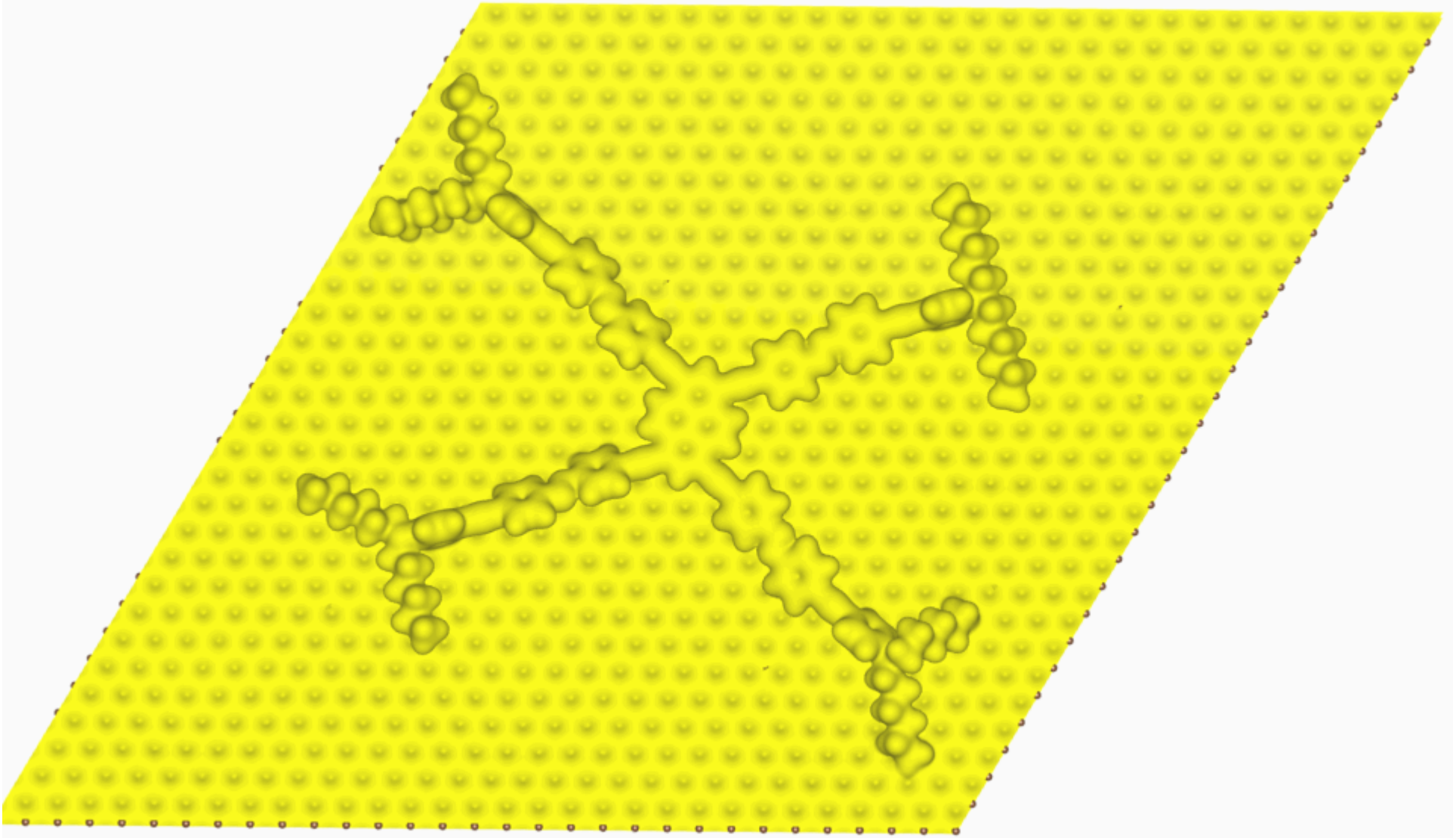
Time : 342 ks (95 h) for 5 ionic relaxation steps== 11421 h mono

300 nodes --→ 2 Go/node

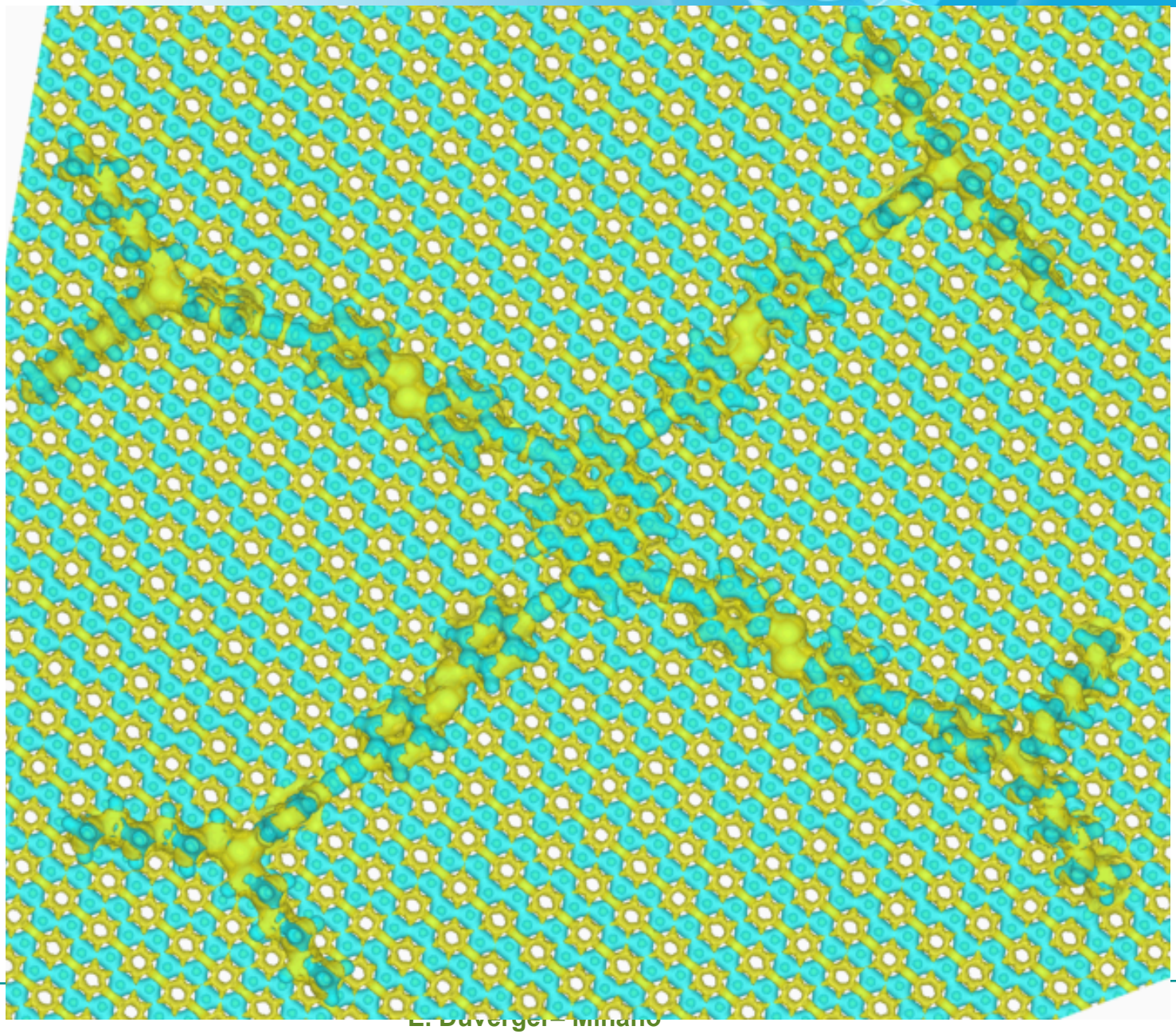
Time : 174 ks (48h) for 5 ionic relaxation steps== 14542 h mono


Elapsed Time
600
550
500
450
400
350
300
250
200
150
50
100
150
200
250
300
cpu
Vasp 5.3.5
Vasp 5.2

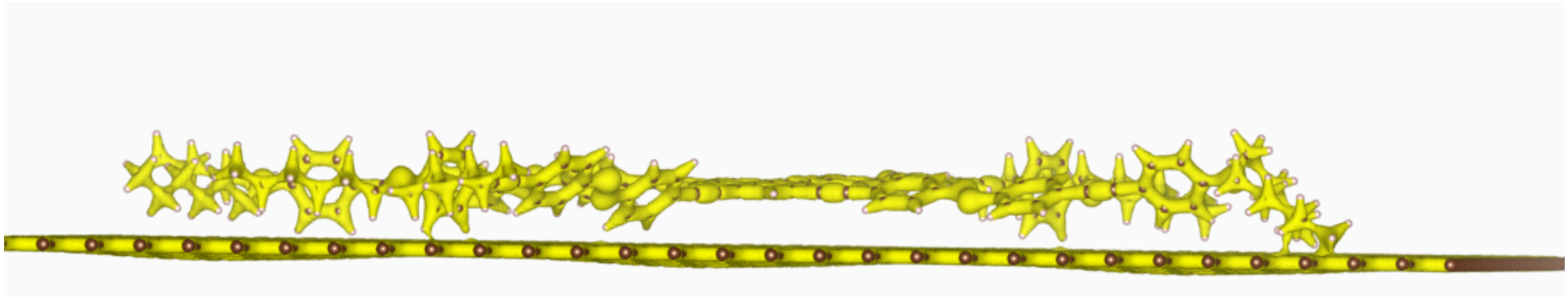
LDOS on HOPG



Laplacian

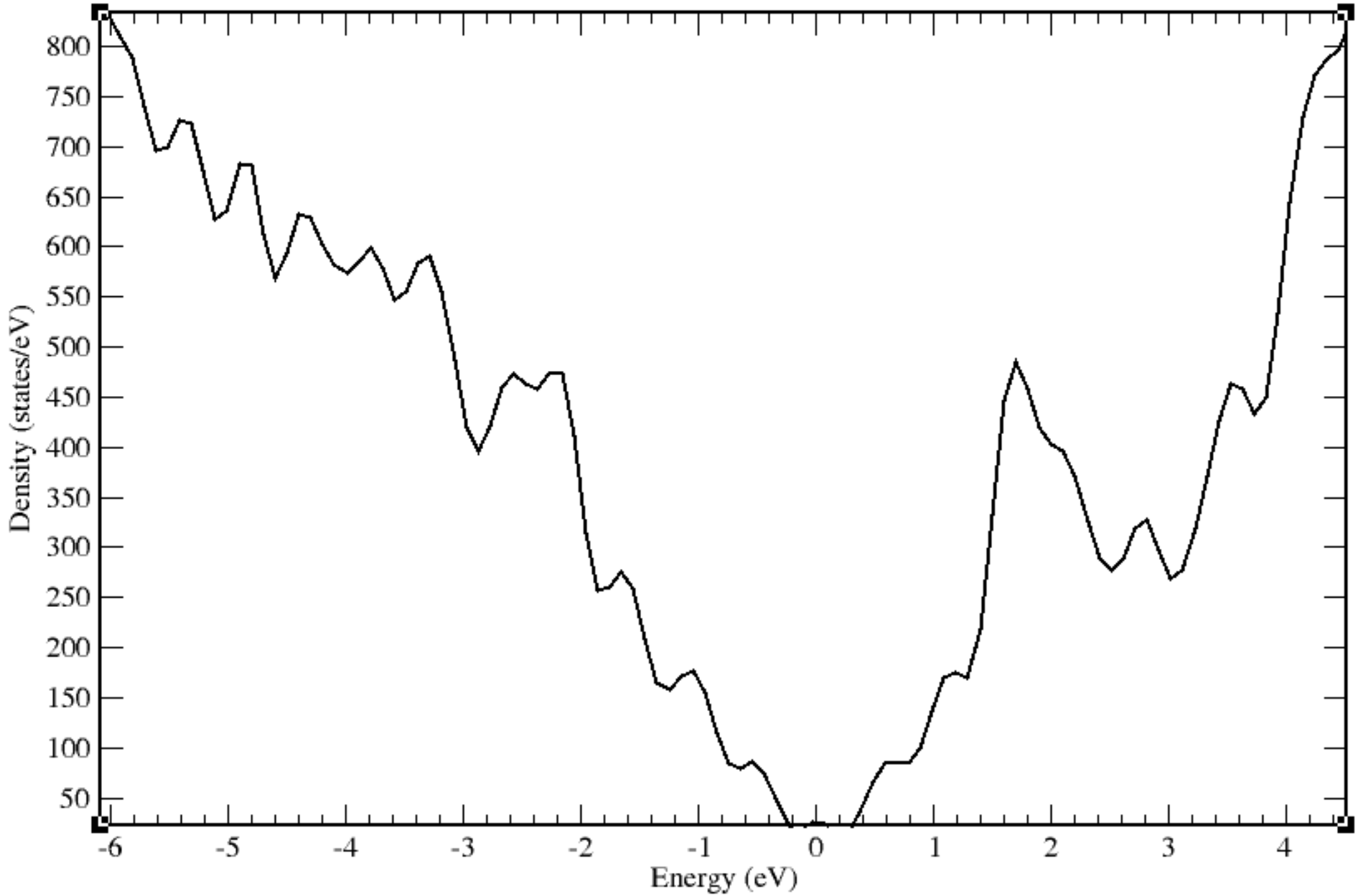


Nanospider arms in interaction with the HOPG substrate

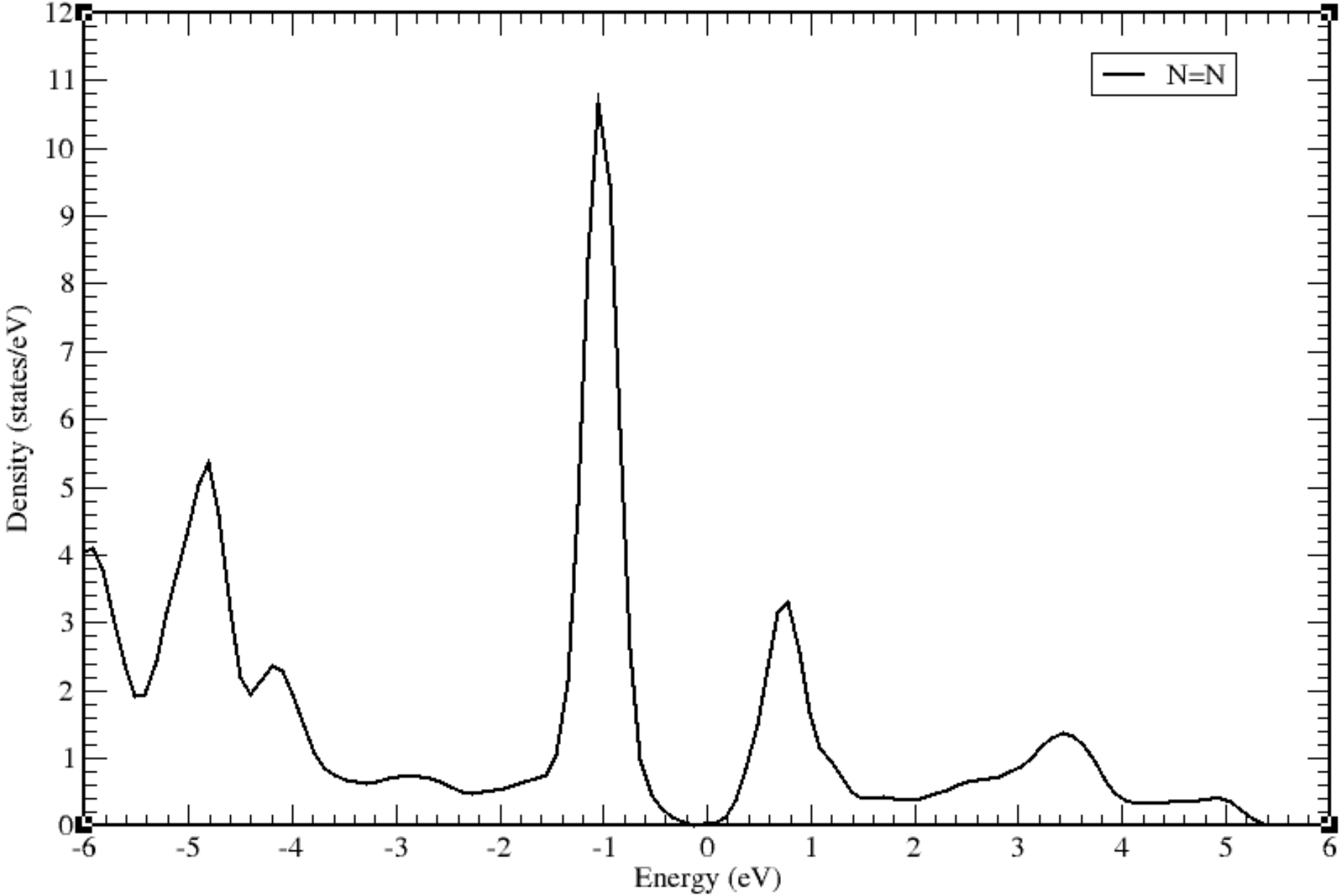


Energy and bias voltage interesting?

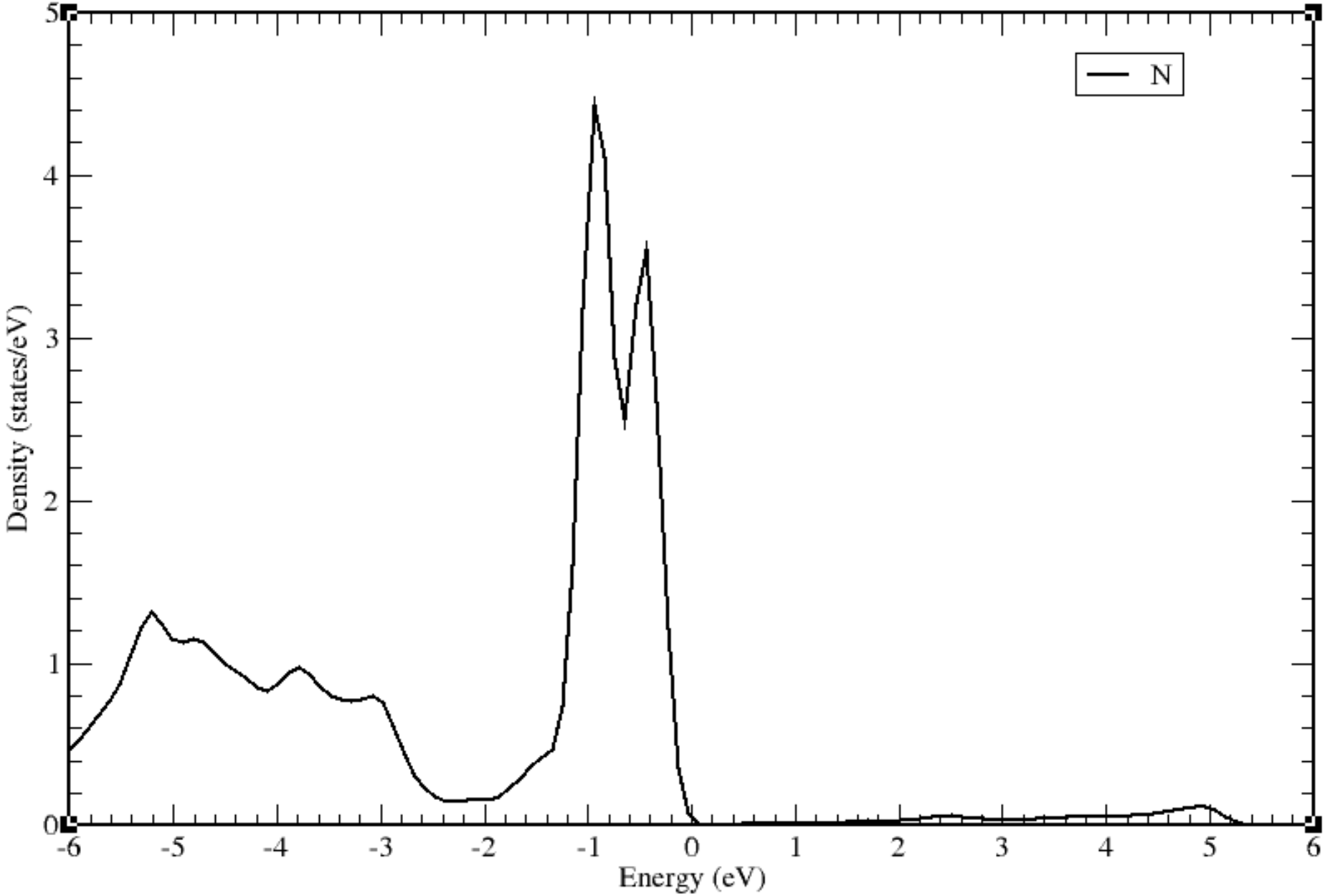
PDOS


Density (states/eV)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
-6
-5
-4
-3
-2
-1
0
1
2
3
4
Energy (eV)

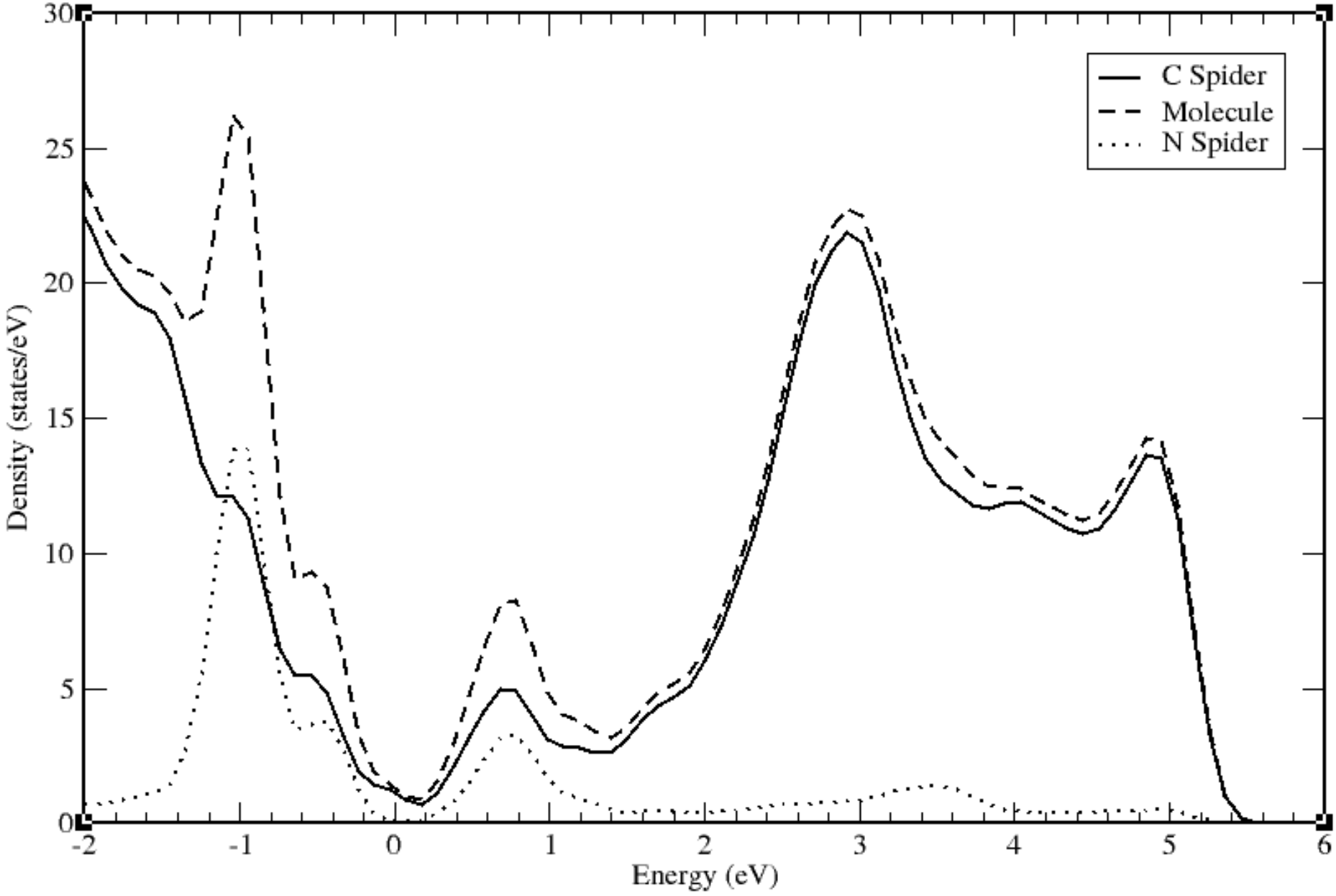
N=N PDOS


N=N
Density (states/eV)
Energy (eV)
12
11
10
9
8
7
6
5
4
3
2
1
0
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6

PDOS N



PDOS different contributions



POST- treatment with Bskan

V=-1V

Resolution

120x120

I=0.1 nA

V=-1V

Resolution

120x120

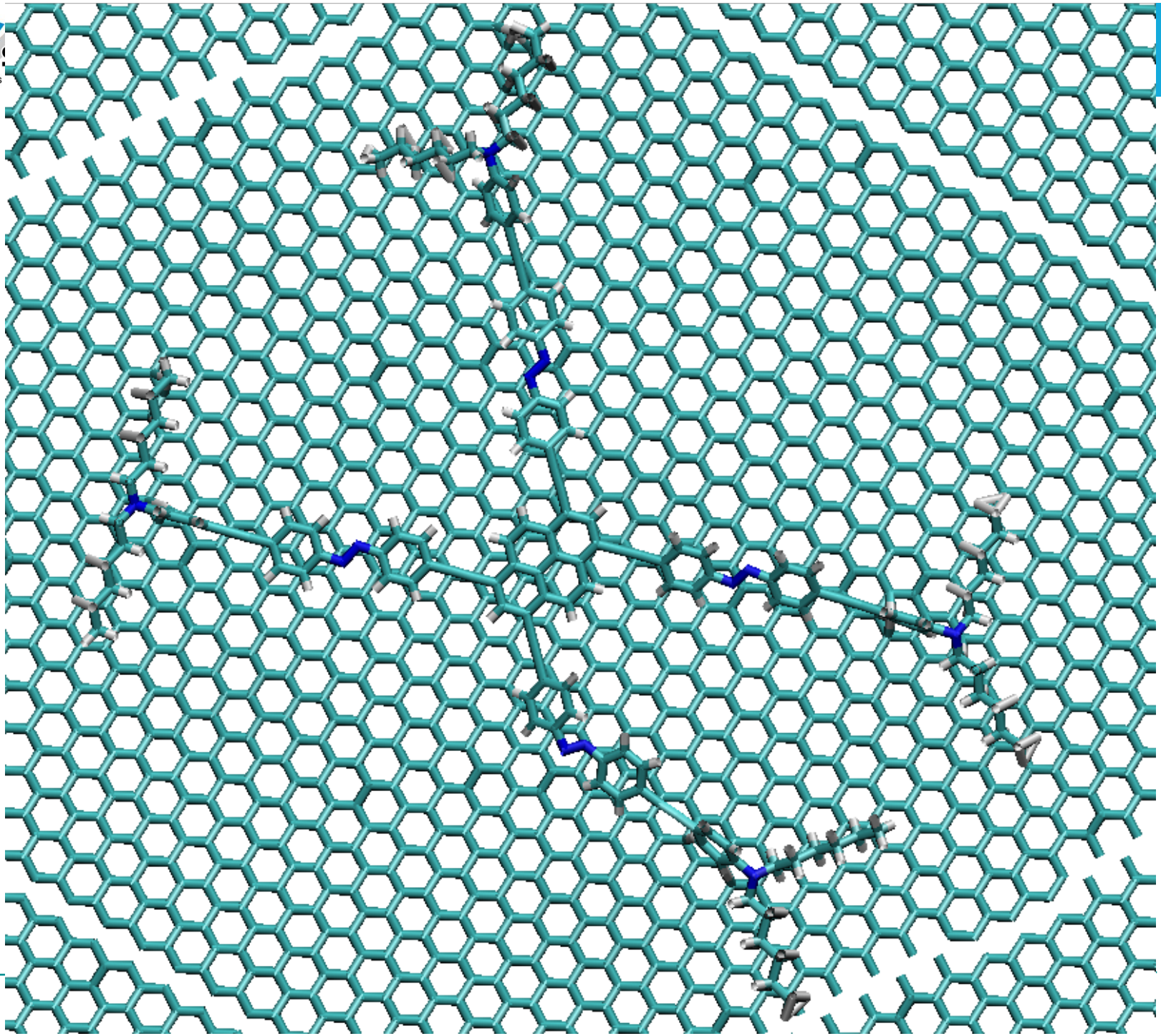
I=0.05 nA

V=-1V
Resolution

120x120

I=0.07 nA

Displacement of one arm

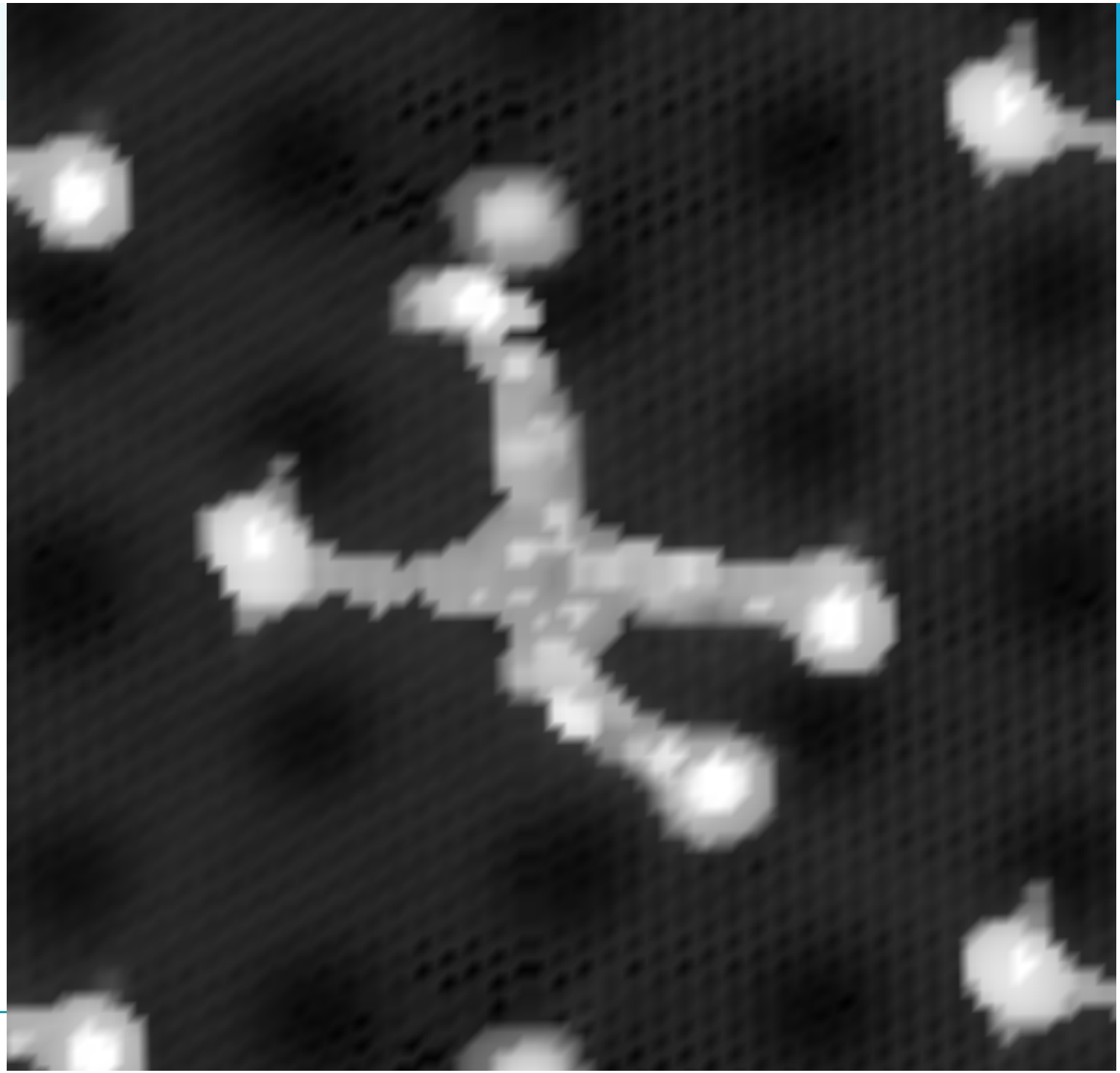


V=-1 V

Resolution

120x120

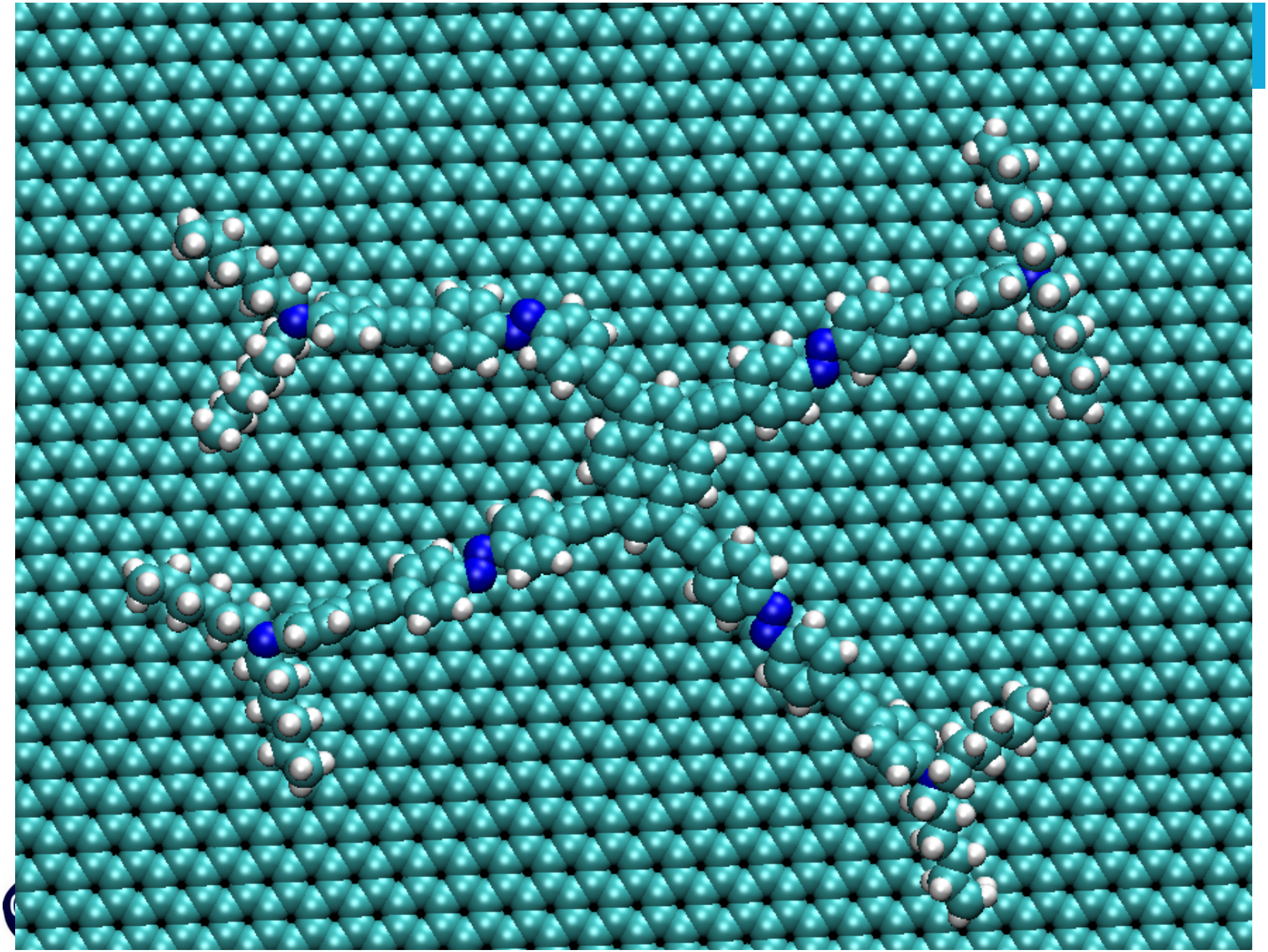
I=0.05 nA



Conclusion

Possibility to simulate great system in PAW

At minima 300 c.p.u in standard !



Thank you for your attention