Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure and electronic properties of organo-halide lead perovskites: a combined IR-spectroscopy and ab-initio molecular dynamics investigation

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SUPPLEMENTARY INFORMATION

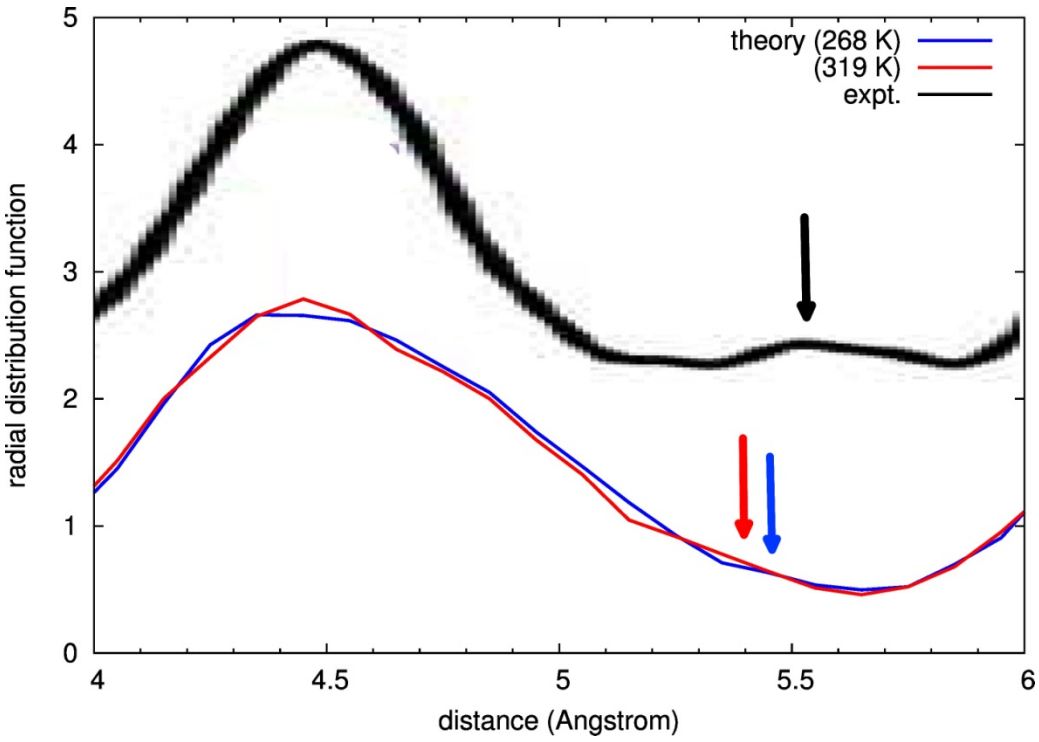


Figure SI1. Theoretical and experimental RDF of the inorganic framework of the $MAPbI_3$ in the region between 4 and 6 Å. Theoretical RDF are obtained from the CPMD simulations at 268 K and at 319 K. Arrows indicate the peaks discussed within the paper in relation with the present region.

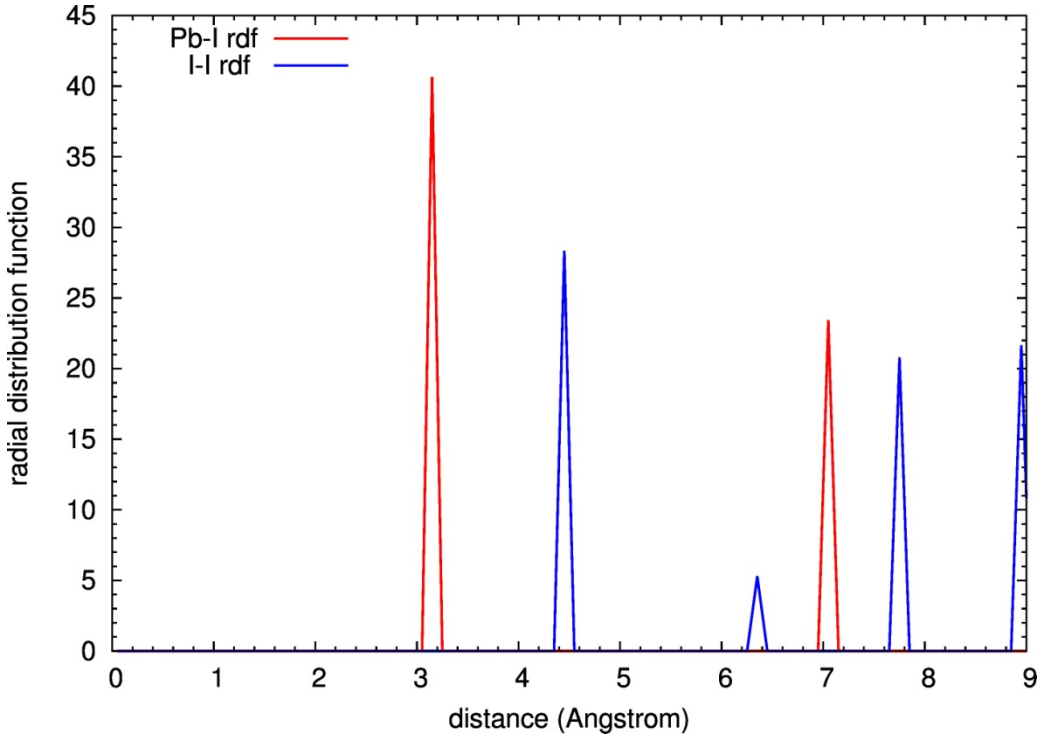
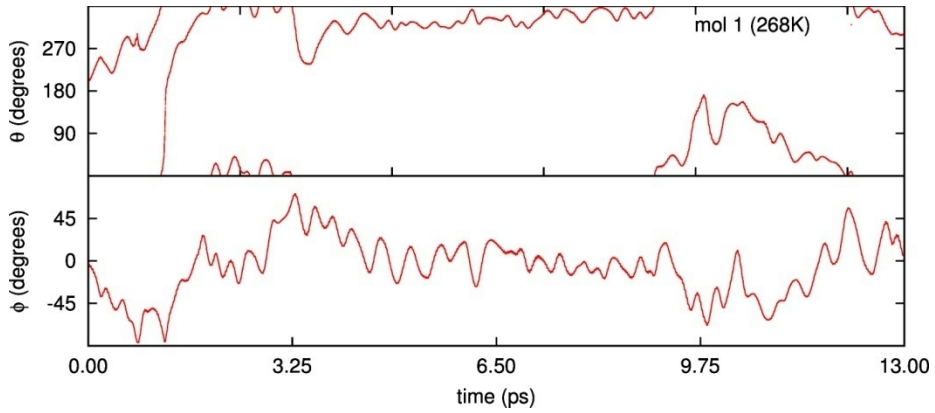


Figure SI2. Radial distribution functions of the Pb to I distances (Pb-I rdf) and of the I to I distances (I-I rdf) obtained from the CPMD simulations on the *Pb-I-fixed* model.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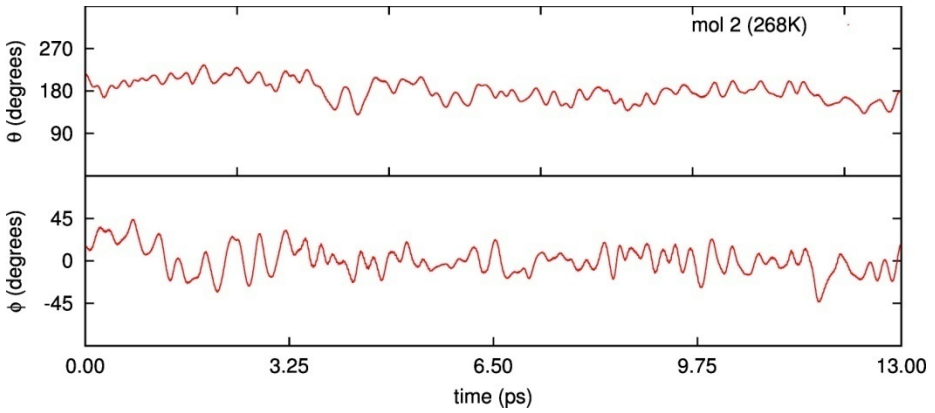
θ (degrees)
270
180
90
ϕ (degrees)
45
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
270
180
90
ϕ (degrees)
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3.25
6.50
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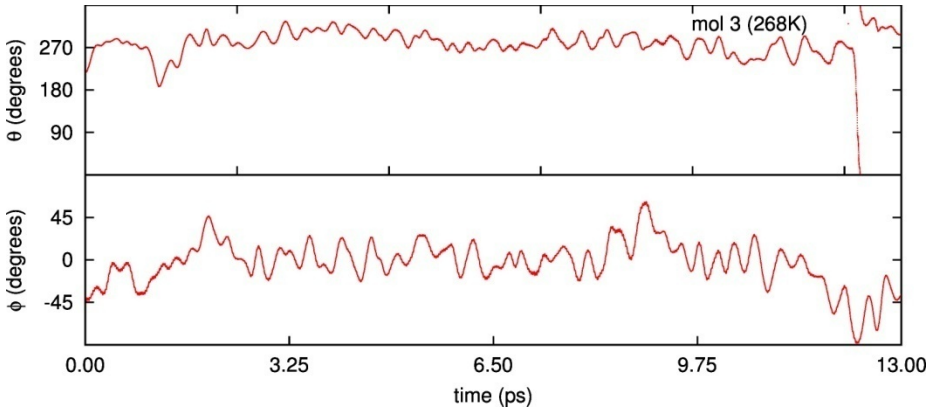
13.00
time (ps)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θ (degrees)
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180
90
ϕ (degrees)
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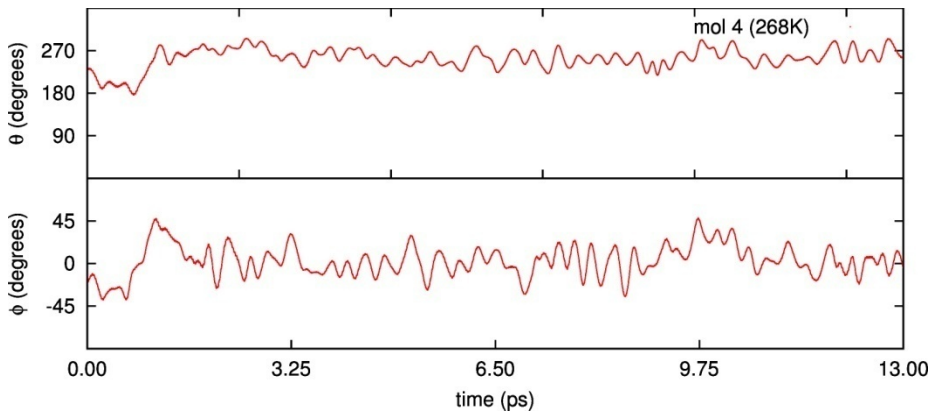
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
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180
90
ϕ (degrees)
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-45
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3.25
6.50
9.75
13.00
time (ps)

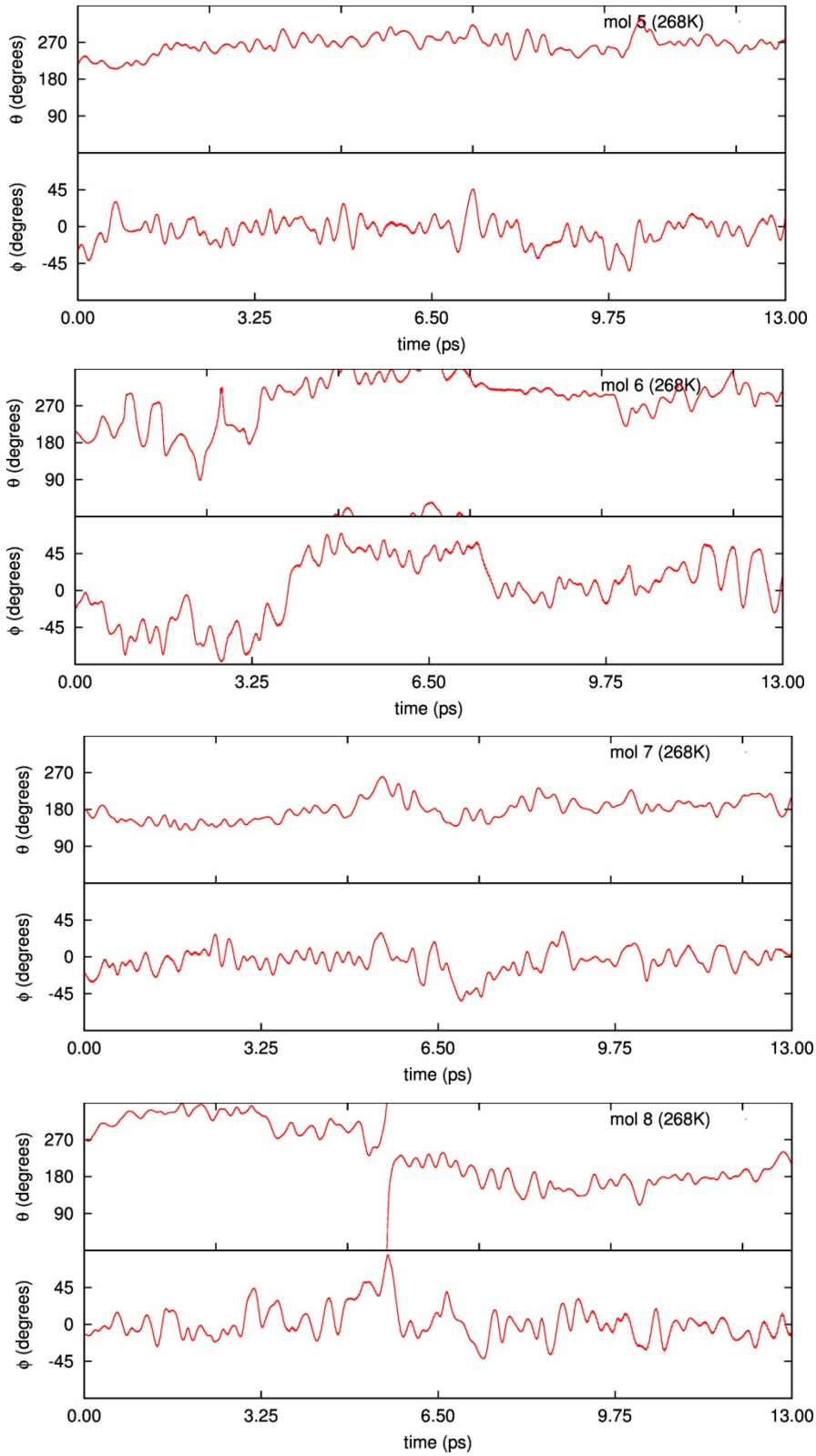
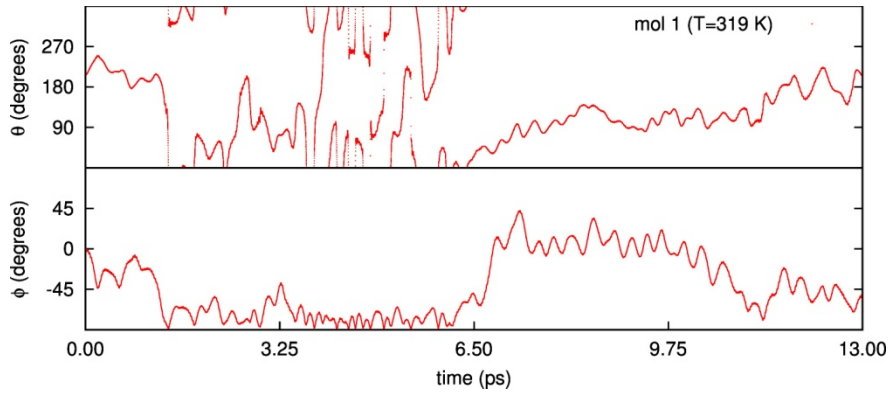


Figure SI3. Orientation of the eight molecule (mol1 – mol8) of the model in the CPMD simulation on the Pb-fixed model at 268 K. θ and φ are the Tait-Bryan angles, where θ and φ are respectively the orientation of the C-N axis in the *xy* plane and the tilt angle with respect to the same plane.


mol 1 (T=319 K)
θ (degrees)
270
180
90
ϕ (degrees)
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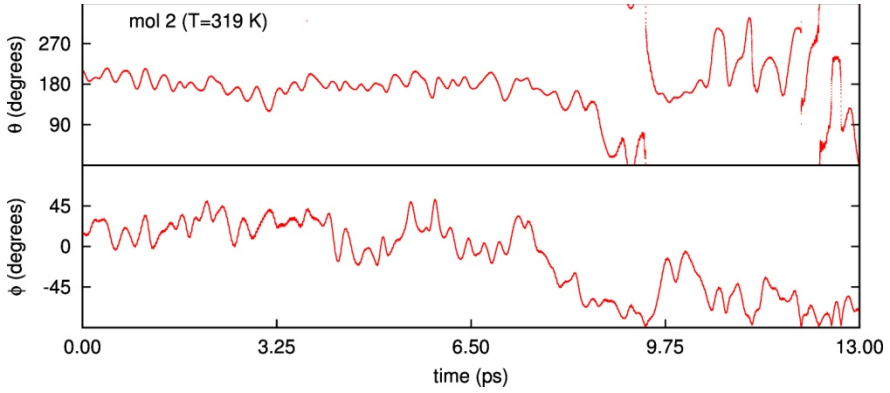
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
270
180
90
ϕ (degrees)
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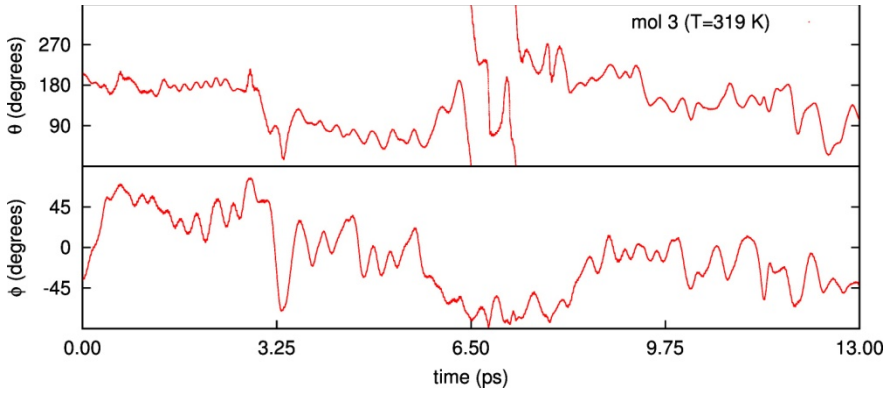
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
270
180
90
ϕ (degrees)
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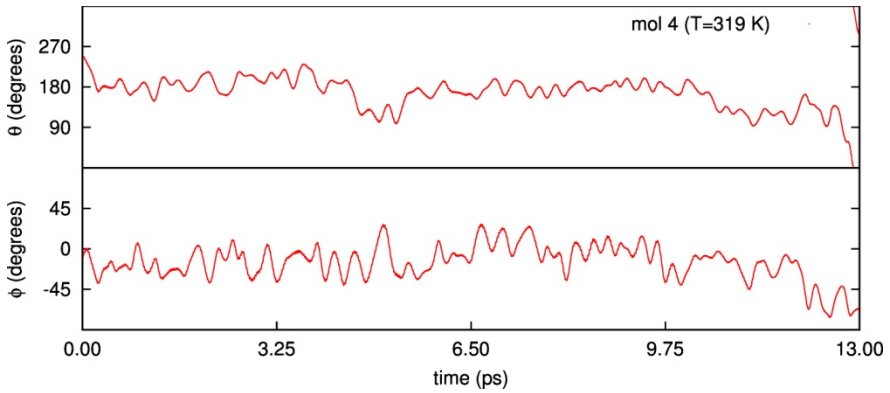
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)


mol 4 (T=319 K)
θ (degrees)
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180
90
ϕ (degrees)
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-45
0.00
3.25
6.50
9.75
13.00
time (ps)

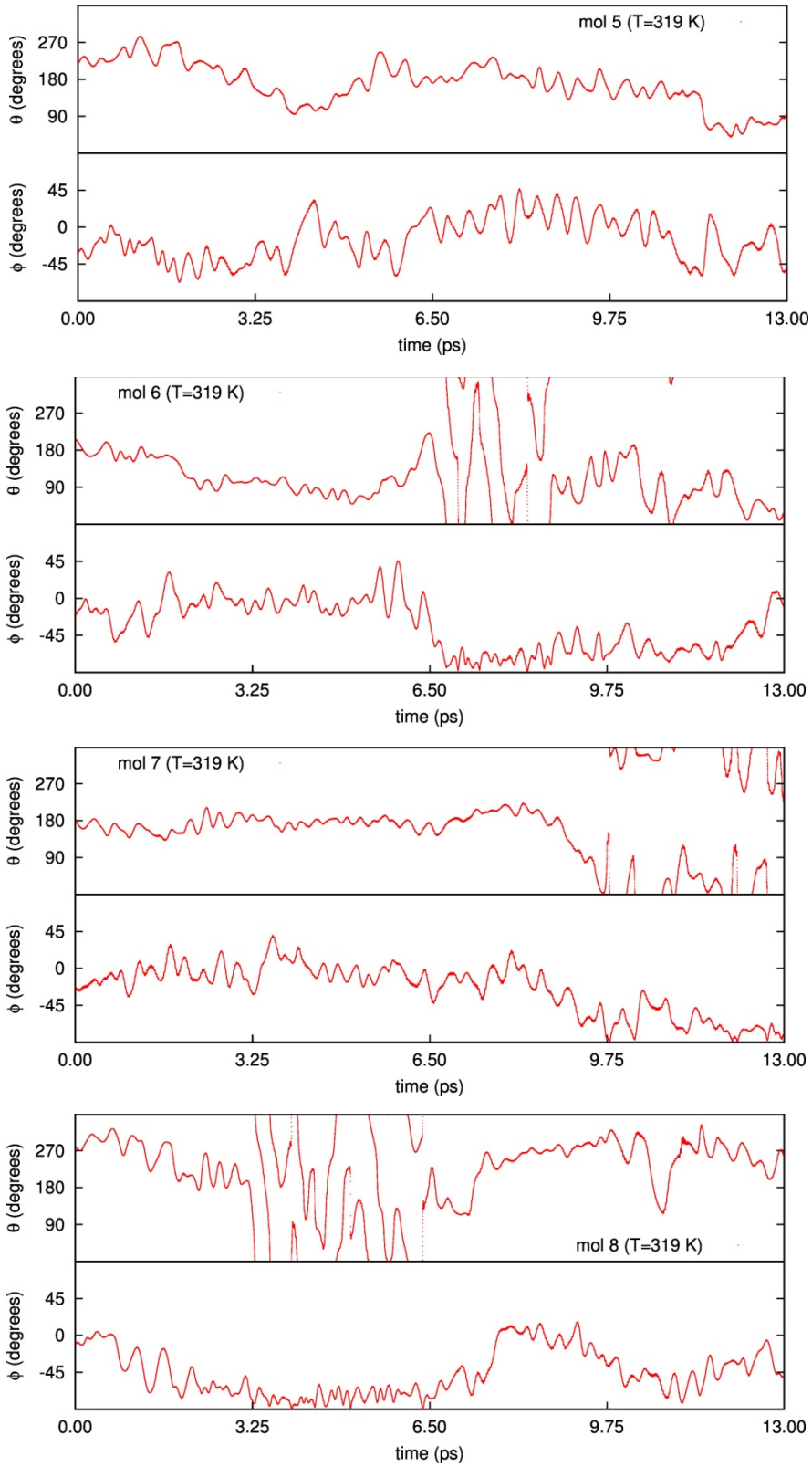
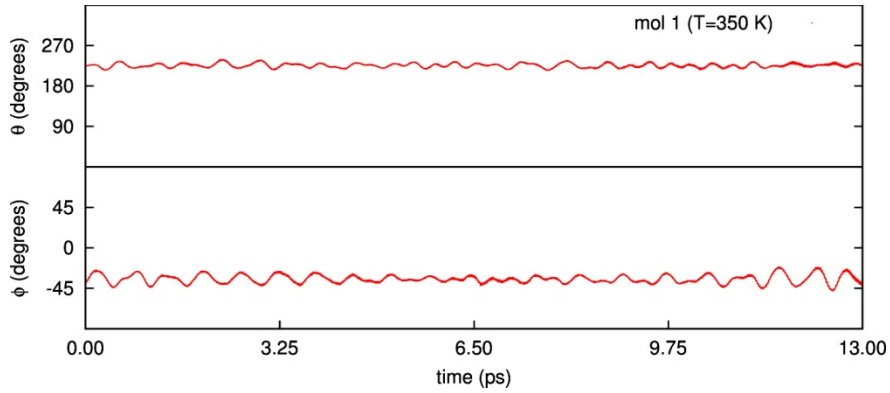


Figure SI4. Orientation of the eight molecule (mol1 – mol8) of the model in the CPMD simulation on the Pb-fixed model at 319 K. θ and φ are the Tait-Bryan angles, where θ and φ are respectively the orientation of the C-N axis in the *xy* plane and the tilt angle with respect to the same plane.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θ (degrees)
270
180
90
ϕ (degrees)
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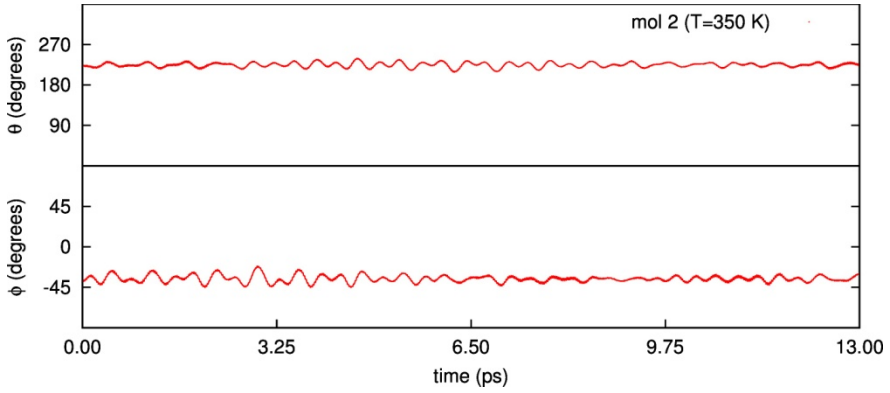
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)


mol 2 (T=350 K)
θ (degrees)
270
180
90
ϕ (degrees)
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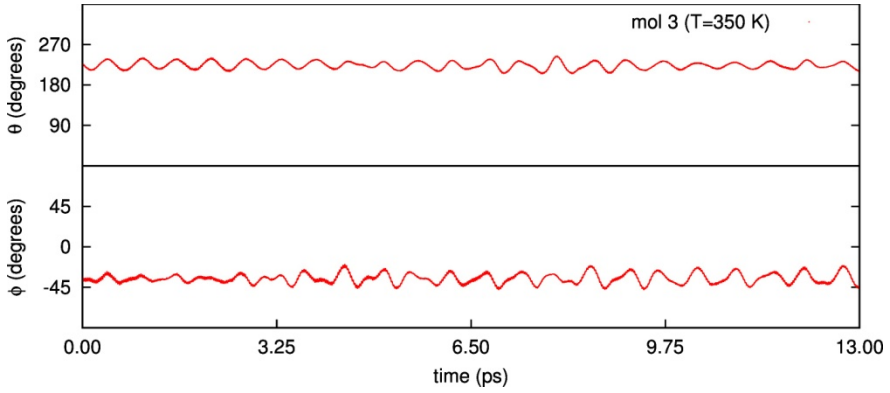
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
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180
90
ϕ (degrees)
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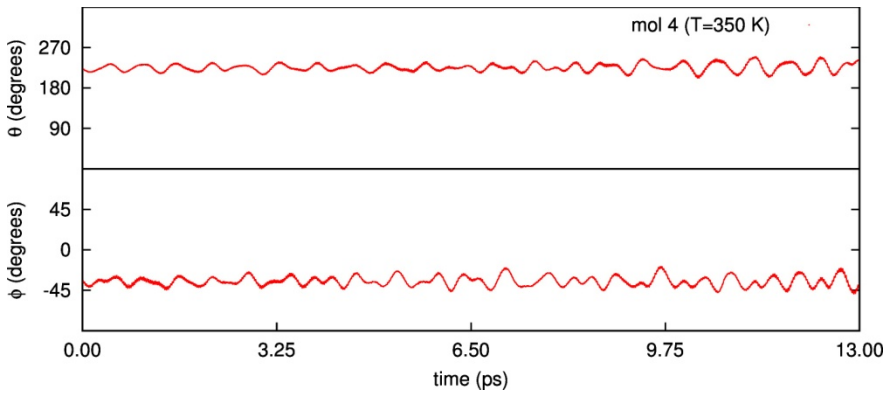
0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)


mol 4 (T=350 K)
θ (degrees)
270
180
90
ϕ (degrees)
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0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)

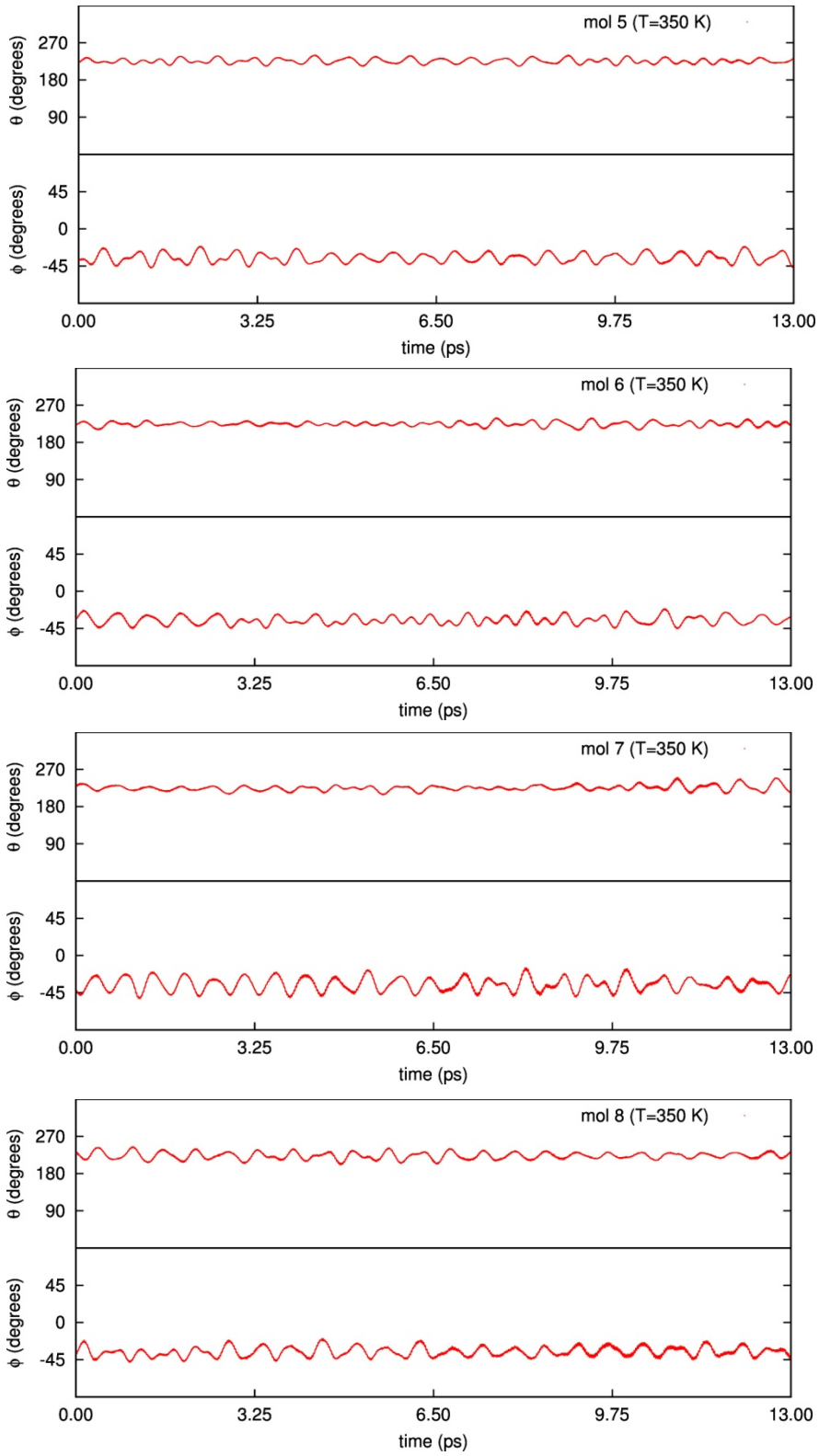
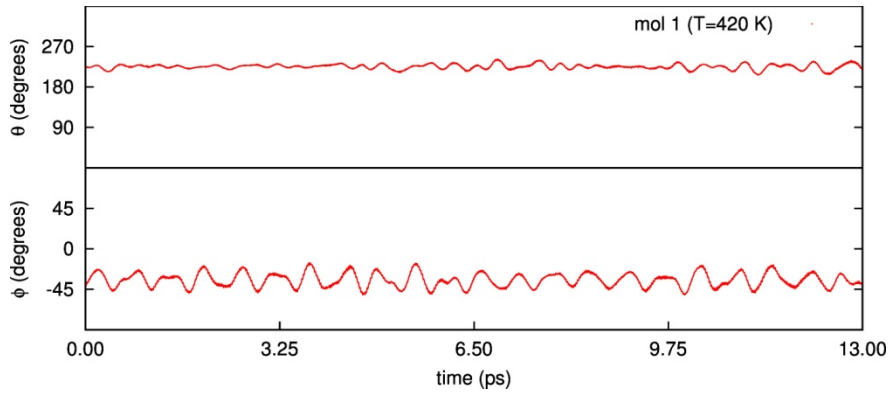


Figure SI5. Orientation of the eight molecule (mol1 – mol8) of the model in the CPMD simulation on the Pb-I-fixed model at 350 K. θ and φ are the Tait-Bryan angles, where θ and φ are respectively the orientation of the C-N axis in the *xy* plane and the tilt angle with respect to the same plane.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θ (degrees)
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180
90
ϕ (degrees)
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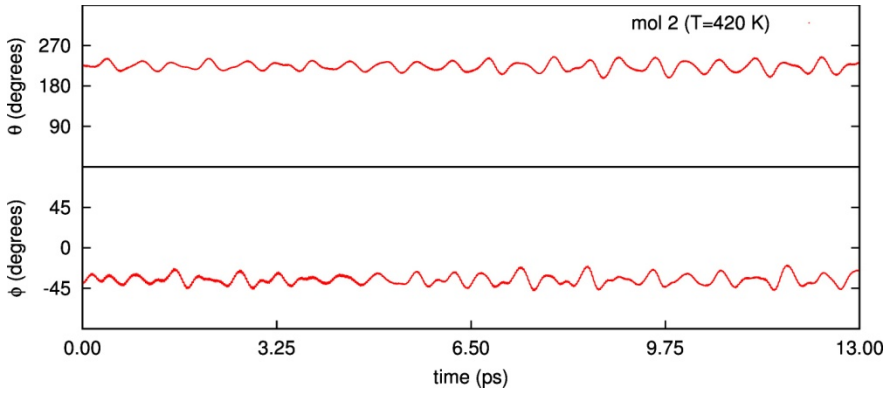
-45
0.00
3.25
6.50
9.75
13.00
time (ps)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θ (degrees)
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180
90
ϕ (degrees)
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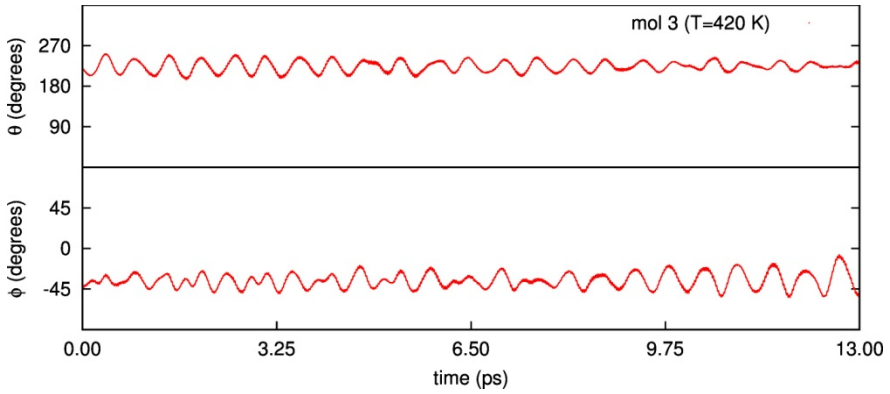
-45
0.00
3.25
6.50
9.75
13.00
time (ps)


mol 3 (T=420 K)
θ (degrees)
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180
90
ϕ (degrees)
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-45
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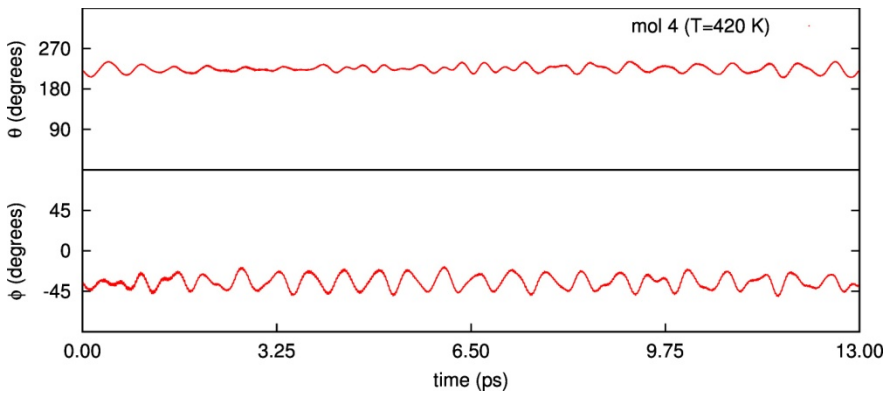
3.25
6.50
9.75
13.00
time (ps)


mol 4 (T=420 K)
θ (degrees)
270
180
90
ϕ (degrees)
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0
-45
0.00
3.25
6.50
9.75
13.00
time (ps)

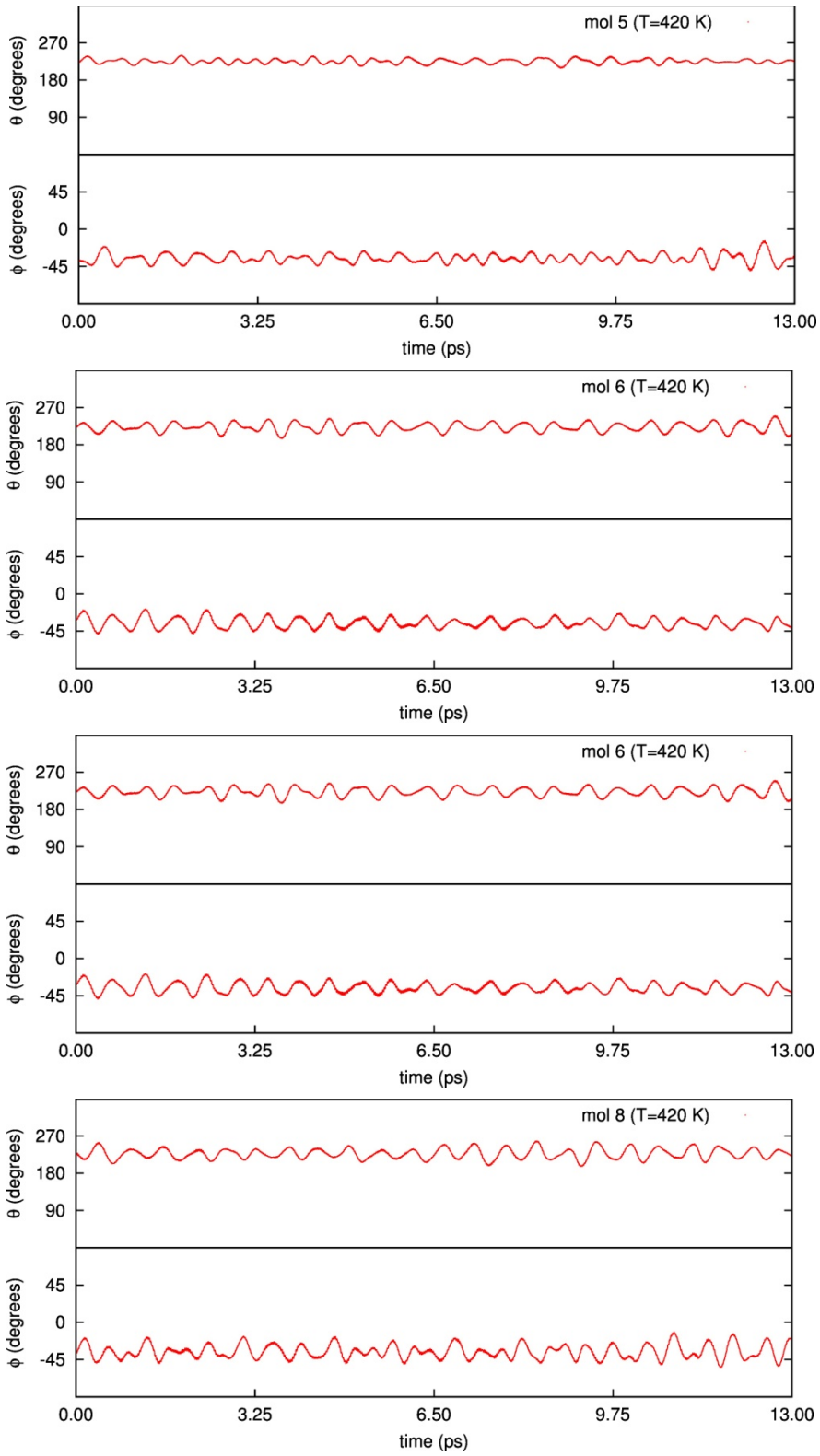

Figure SI6. Orientation of the eight molecule (mol1 – mol8) of the model in the CPMD simulation on the Pb-I-fixed model at 420 K. θ and φ are the Tait-Bryan angles, where θ and φ are respectively the orientation of the C-N axis in the *xy* plane and the tilt angle with respect to the same plane.

Table SI1. Number of rotations of the eight molecules of the model (See Figure SI1) along the *x*, *y* and *z* axis during the CPMD simulation on the Pb-fixed model at 268 K.

	mol 1	mol 2	mol 3	mol 4	mol 5	mol 6	mol 7	mol 8
x axis	1	0	1	0	0	0	0	1
y axis	0	0	1	1	1	0	0	1
z axis	3	2	0	0	0	0	4	3

Table SI2. Number of rotations of the eight molecules of the model (See Figure SI1) along the *x*, *y* and *z* axis during the CPMD simulation on the Pb-fixed model at 319 K.

	mol 1	mol 2	mol 3	mol 4	mol 5	mol 6	mol 7	mol 8
x axis	1	0	1	0	0	0	0	1
y axis	0	0	1	1	1	0	0	1
z axis	3	2	0	0	0	0	4	3

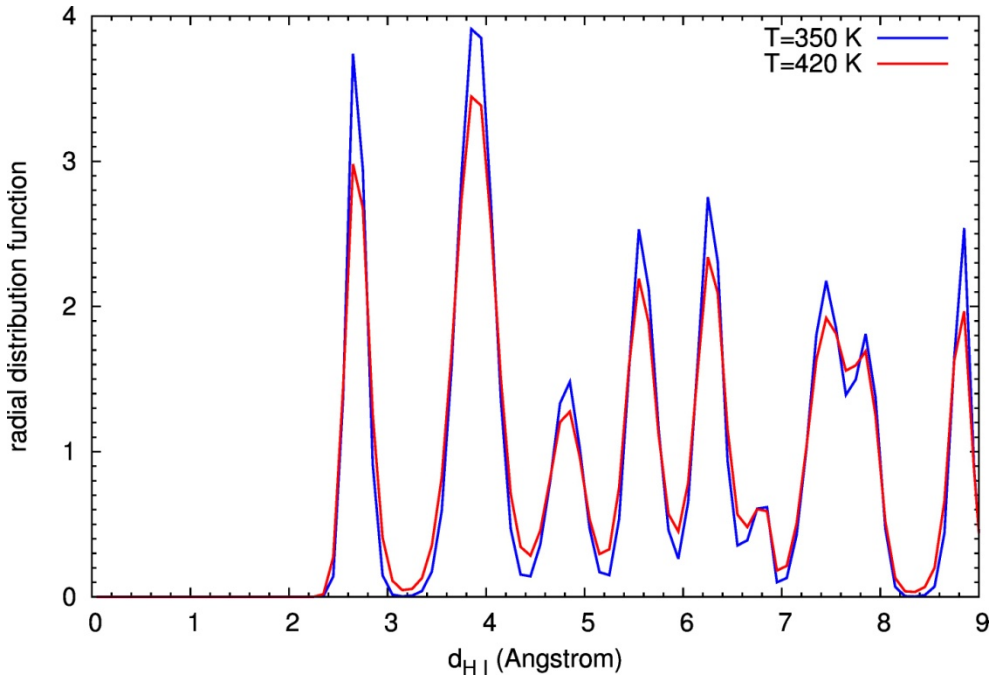

Figure SI7. Radial distribution function of the I to H distance obtained from the CPMD simulations on the Pb-I-fixed model at 350 and 420 K.

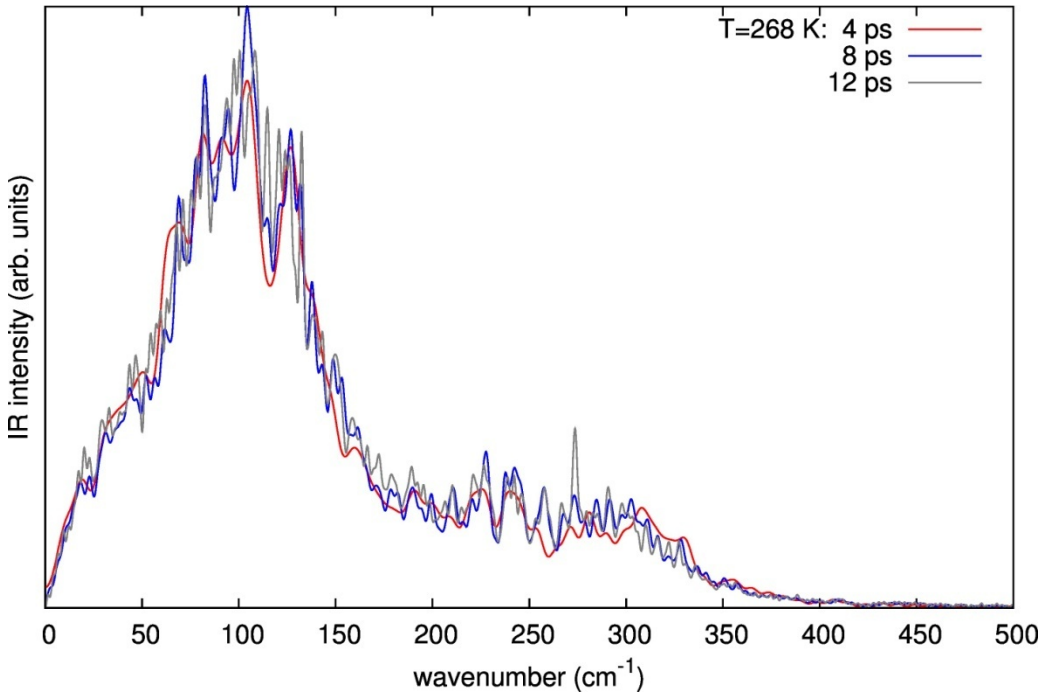

Figure SI8. Convergence of the IR spectrum computed from the CPMD simulation at 268 K with respect to the size of the simulation time.

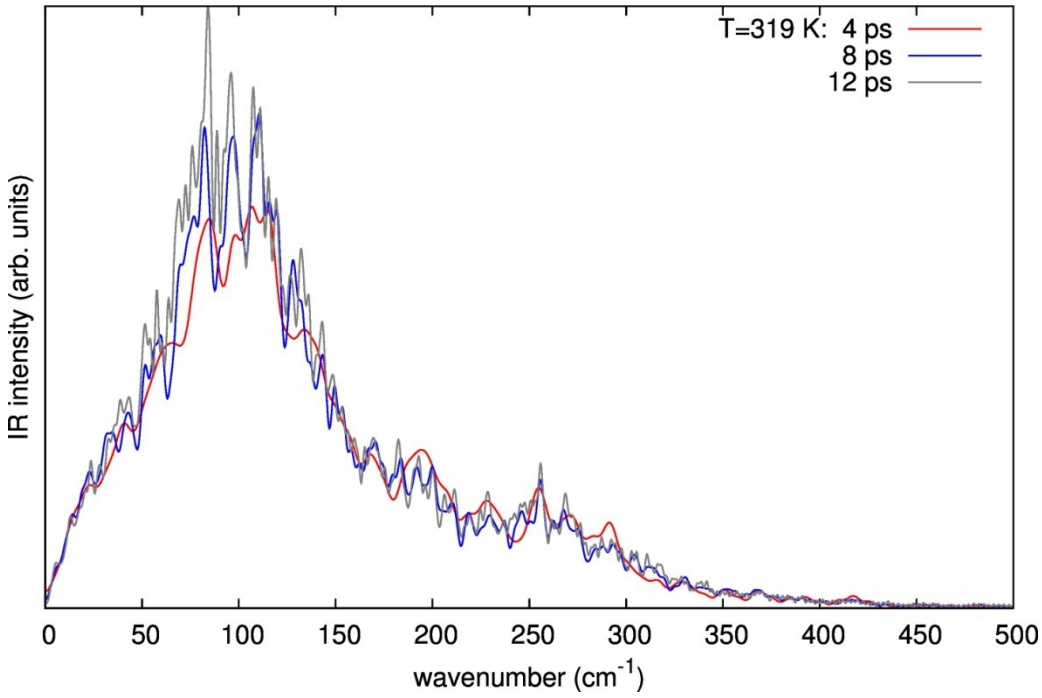

Figure SI9. Convergence of the IR spectrum computed from the CPMD simulation at 268 K with respect to the size of the simulation time.

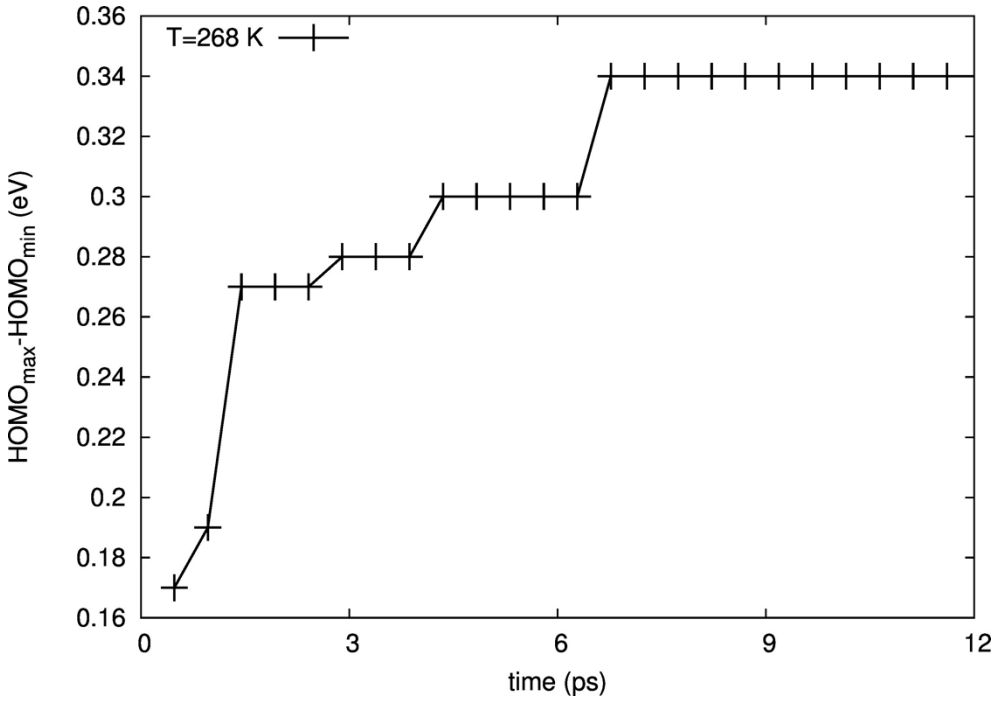

Figure SI10. Convergence of the energy difference between the maximum and the minimum energy of the HOMO level of the CPMD simulation at 268 K with respect to the time of the CPMD simulation.

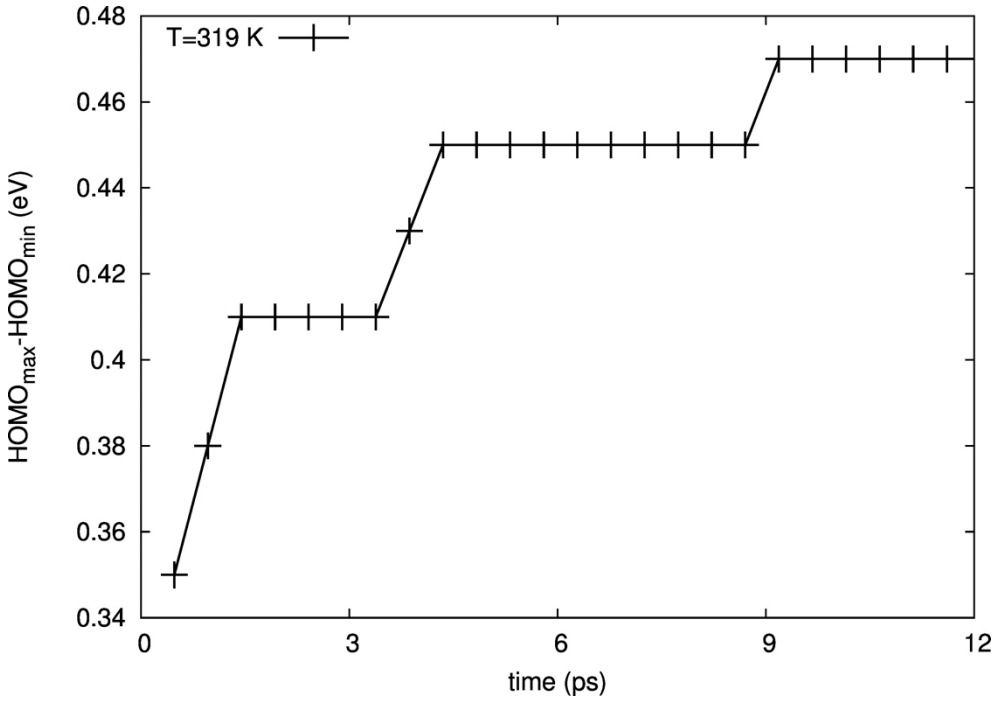

Figure SI11. Convergence of the energy difference between the maximum and the minimum energy of the HOMO level of the CPMD simulation at 319 K with respect to the time of the CPMD simulation.

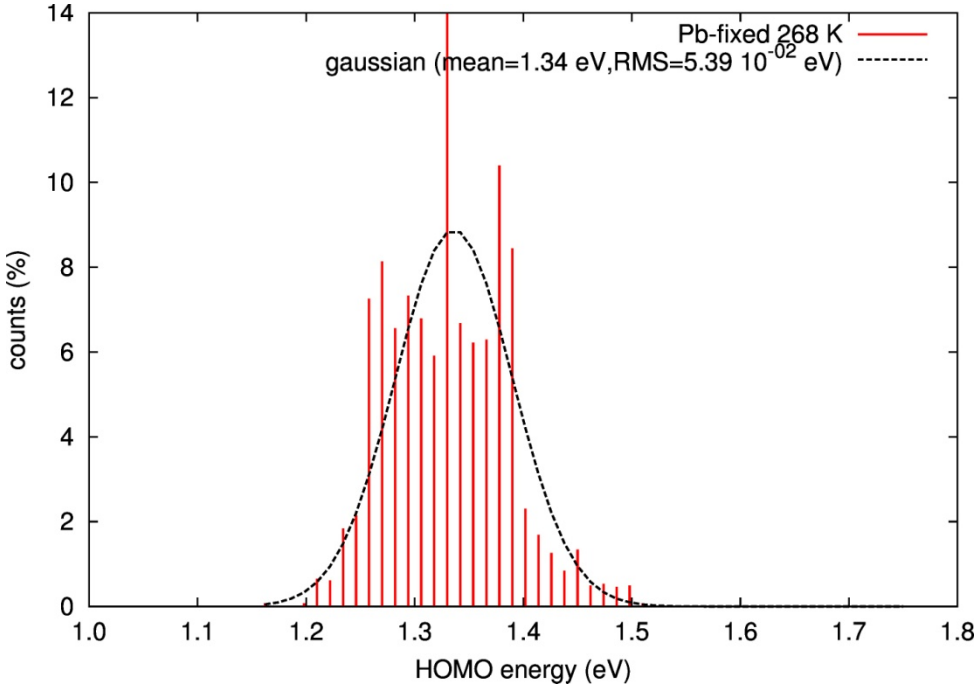

Figure SI12. HOMO energy distribution obtained from the CPMD carried out on the *Pb-fixed* model at 268 K.

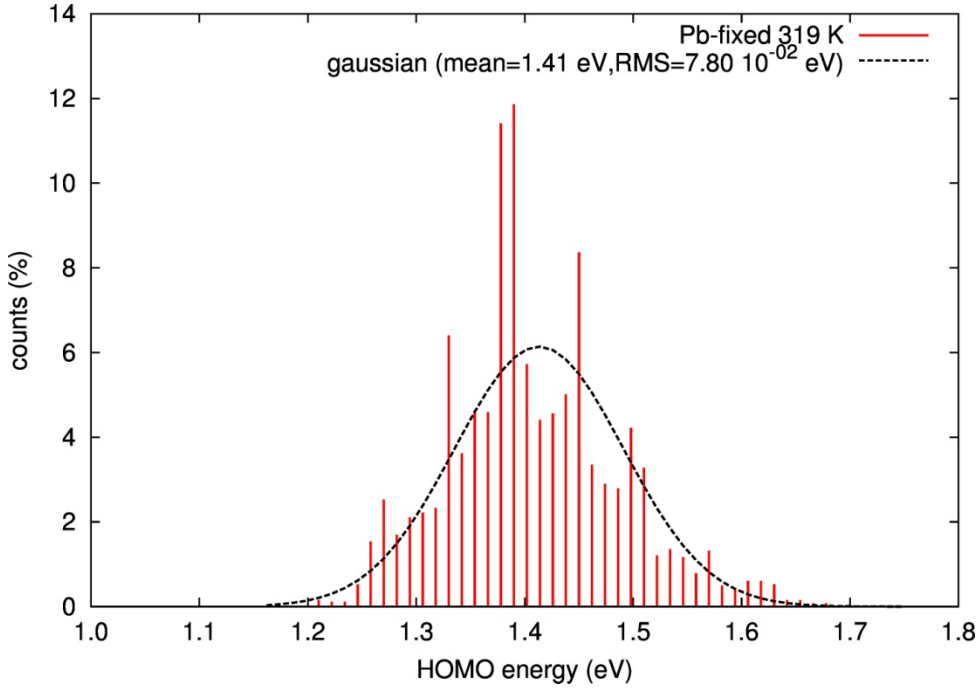

Figure SI13. HOMO energy distribution obtained from the CPMD carried out on the *Pb-fixed* model at 319 K.

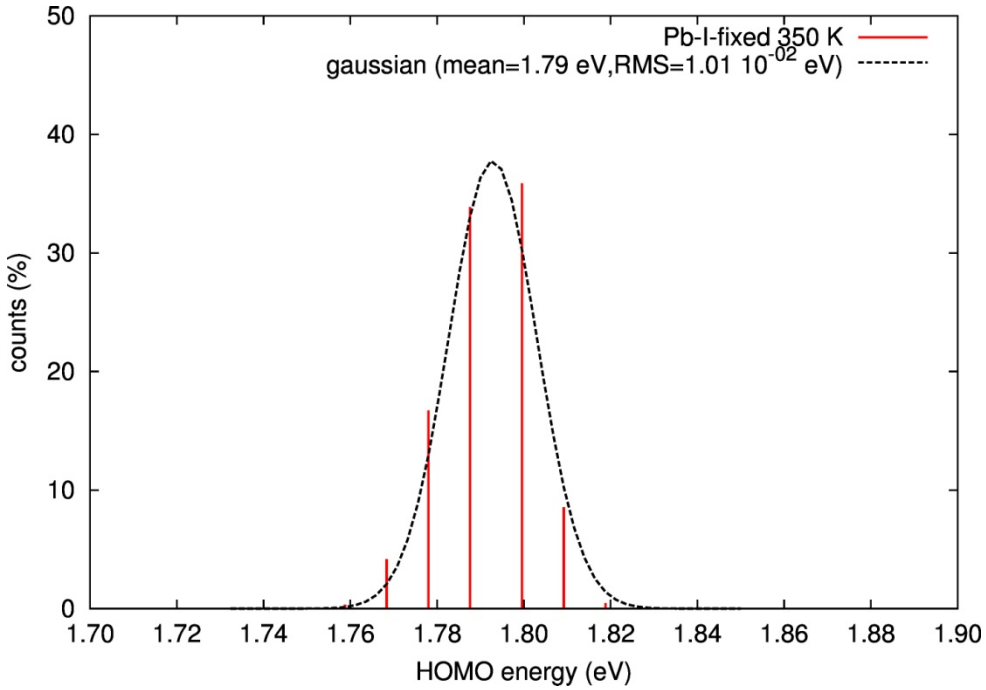

Figure SI14. HOMO energy distribution obtained from the CPMD carried out on the Pb-I-fixed model at 350 K.

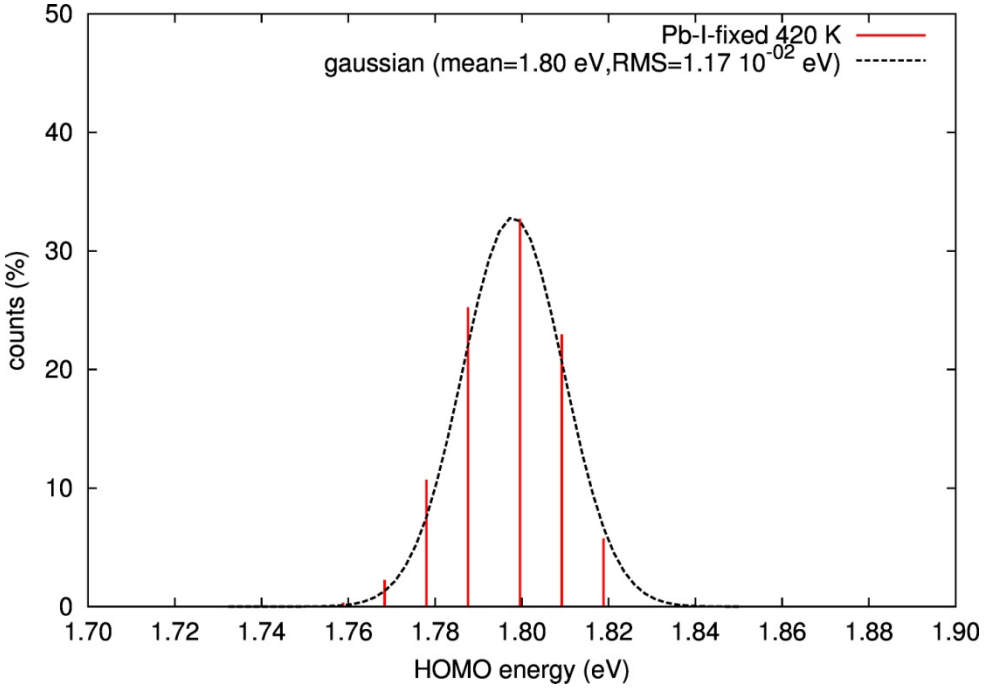

Figure SI15. HOMO energy obtained from the CPMD carried out on the Pb-I-fixed model at 420 K.