Supporting Material for

Ab Initio Molecular Dynamics Study of the Hydration of Li^+, Na^+ and K^+ Montmorillonite. Influence of isomorphic substitution.

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Figure S1: Trajectories of the cations (black lines) for Li^+, Na^+, K^+ for each substitution type. View from above the surface. The surface atoms: Si, O and Al are shown as yellow, red and magenta circles, respectively.

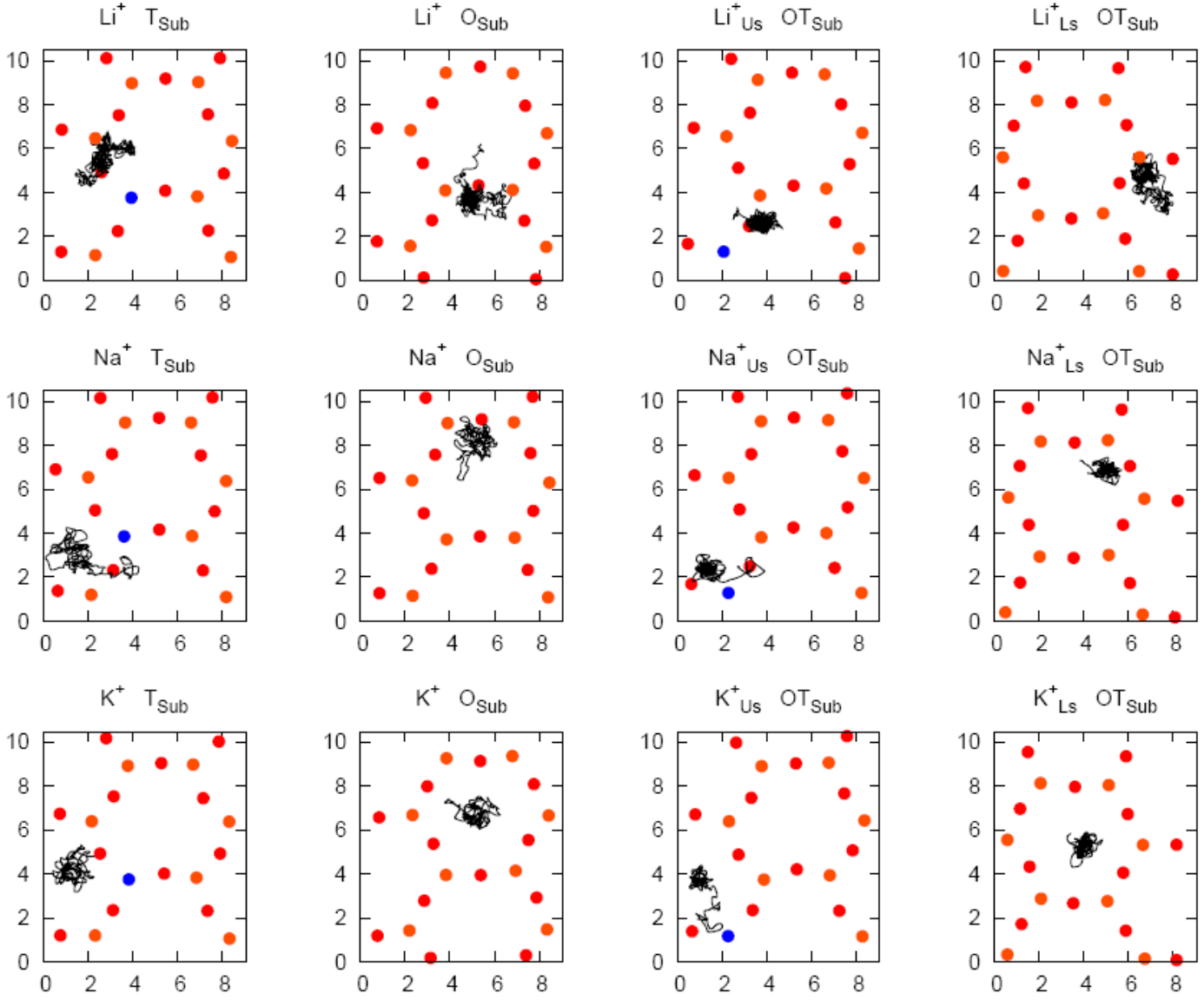

Figure S2: Trajectories of the cations (black lines) for Li^+, Na^+, K^+ for each substitution type. Evolution of atoms along the Oc cell parameter as a function of the time. The central red and blue represents the water interlayers oxygen and hydrogen atoms. The above and below yellow and brow represent the Si and Al atoms, while the red the O atoms.

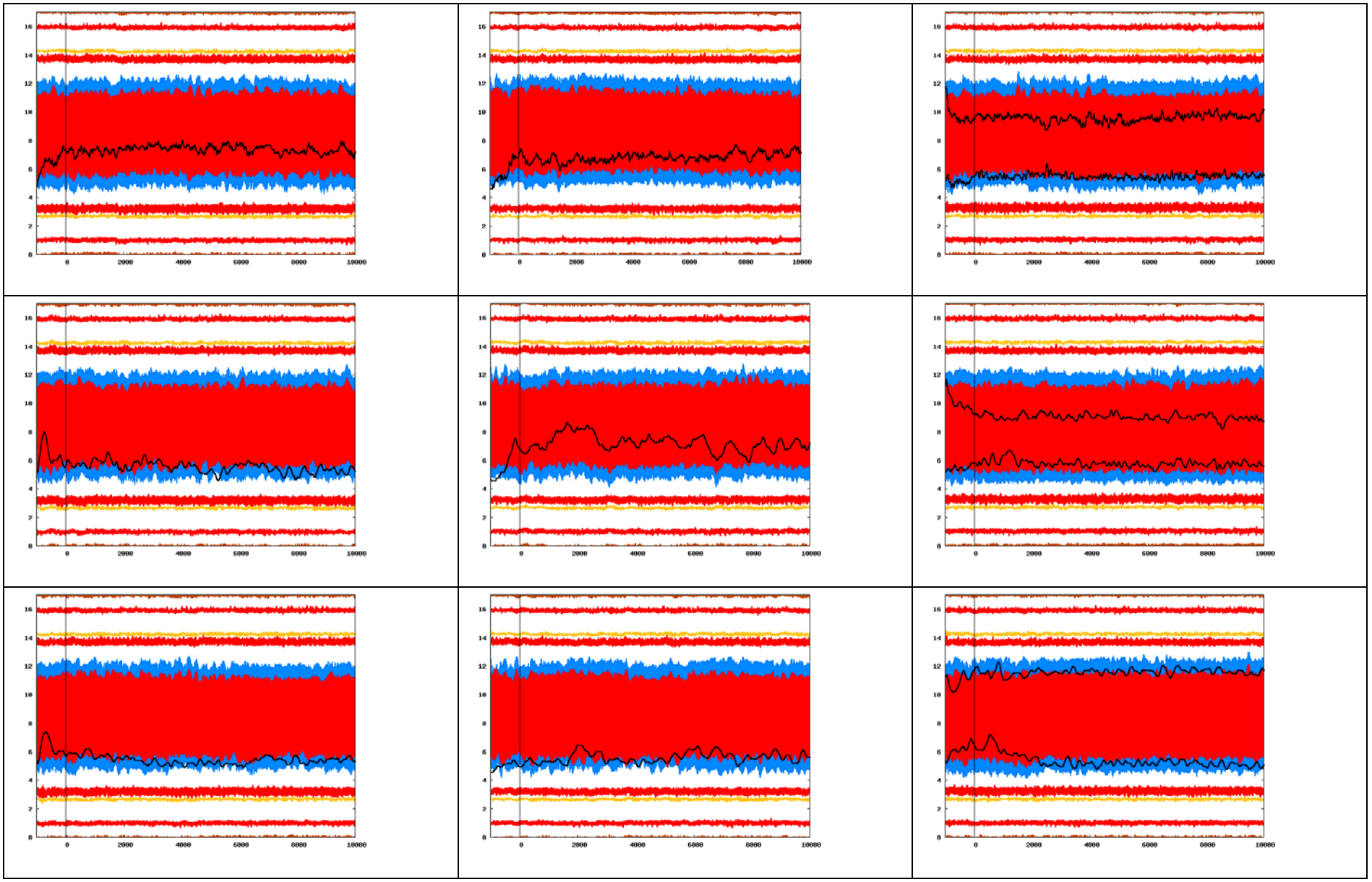

Figure S3. DOS computed and averaged over the 10 ps simulations for the systems with water, for each cation and substitution (in blue). DOS computed for the optimized dry montmorillonite for each cation and substitution (in red). Energy in eV.

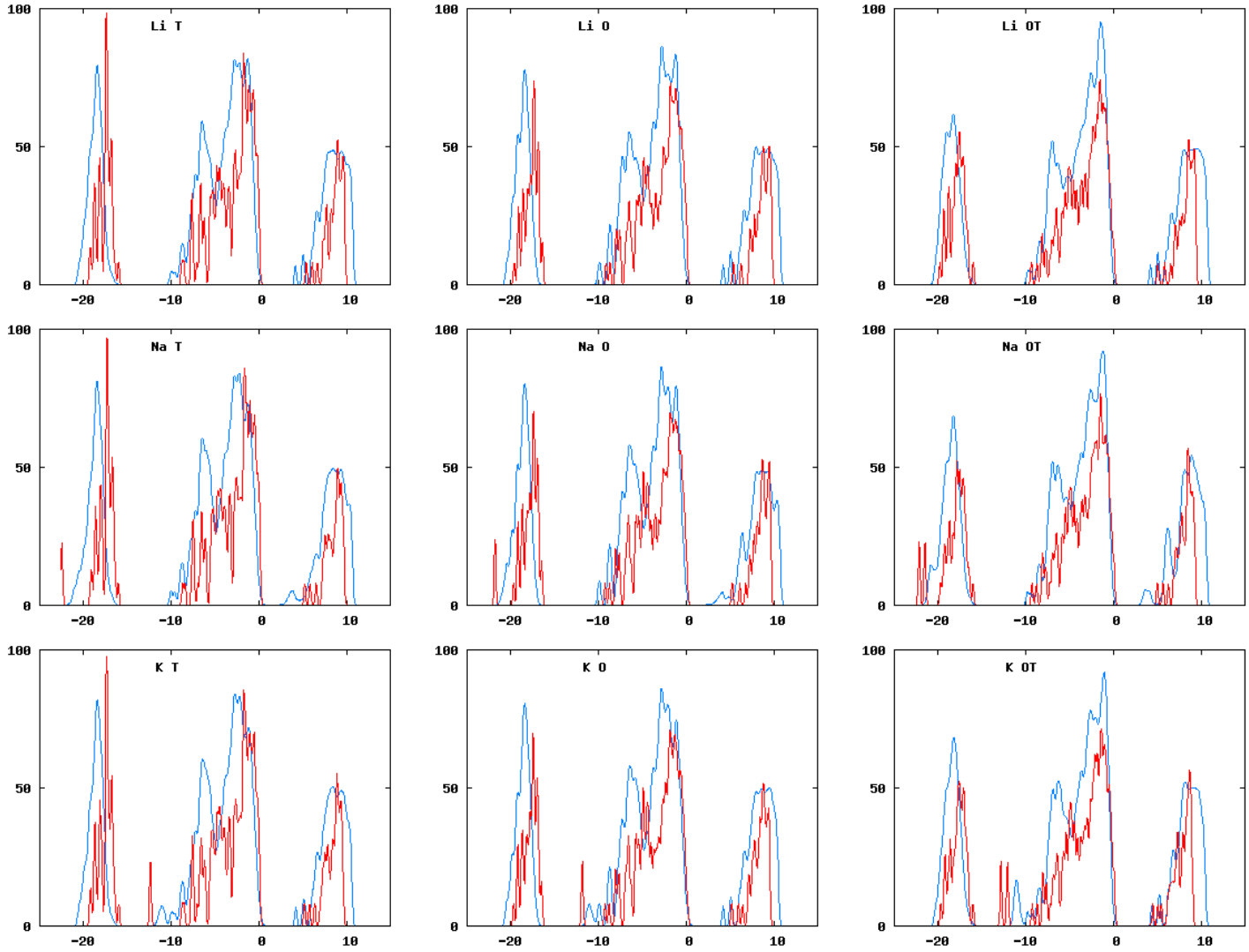

Table S1: Differences between the cell parameters of the monoclinic cell obtained from experimental and theoretical work with the cell parameter of the orthorhombic cell used in the present work.

	Experiment ref 45	Theory ref:31	This work		
			parameters	Err-Exp (%)	Err-Theo. (%)
a	5.17	5.12	5.20	0.01	1.56
b	8.94	9.05	9.06	1.32	0.11
c	9.95	10.01	9.75	2.01	2.6
β	99.9	101.9	90.0	9.91	11.68
Int.Layer Dist.	9.802	9.795	9.745	0.58	0.51
Volume	453.4	453.4	458.9	1.21	1.21

Appendix:

Inclusion of the Kinetic Stress tensor in VASP:

-a- Kinetic Stress Tensor

The pressure computed by VASP does not include the kinetic Stress Tensor. We included it in the VASP code according to:

$$J_{\alpha\beta}=\sum_{i}^{N} m_i v_{i\alpha} v_{i\beta}+\left(\frac{\partial U}{\partial \epsilon_{\alpha\beta}}\right)$$ ->> First Term (kinetic) not included in VASP.

The instantaneous Pressure on the Cell is :

$$P=\frac{Tr(J)}{V}=\frac{J_{xx}+J_{yy}+J_{zz}}{3*V}$$

-- >> To be included in VASP: Kinetic Stress Tensor:

$$P_{kin}=\frac{\sum_{i}^{N} m_i*V_{ix}{}^2+\sum_{i}^{N} m_i*V_{iy}{}^2+\sum_{i}^{N} m_i*V_{iz}{}^2}{3*V}$$

$$P_{kin}=\frac{\sum_{i}^{N} m_i(V_{ix}{}^2+V_{iy}{}^2+V_{iz}{}^2)}{3*V}$$

Procedure used to obtain the a and b parameters:

- 9 points are computed 3 for a and 3 for b. An increment of 1% is added to a or b. For each combination

_ Ions are relaxed
_ Equilibration perdio (500 steps, T maintained at 300K)
_ Production: 1000 steps, using NVE ensemble.

- The mean values for the pressure are:

	a	b	<P>
a0 b0	8.9627	10.3340	20.78
a0 b1	8.9627	10.4374	11.50
a0 b2	8.9627	10.5407	2.87
a1 b0	9.0524	10.3340	10.72
a1 b1	9.0524	10.4374	3.66
a1 b2	9.0524	10.5407	-6.32
a2 b0	9.1420	10.3340	3.90
a2 b1	9.1420	10.4374	1.57
a2 b2	9.1420	10.5407	-16.43

The plot of these vales P as a function of a,b: