

***Ab Initio* Molecular Dynamics Study of an Aqueous Solution of $[\text{Fe}(\text{bpy})_3](\text{Cl})_2$ in the Low-Spin and in the High-Spin State**

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Computational details

The AIMD simulations were performed within the Car-Parrinello scheme,¹ with the CPMD code,^{2,3} using the BLYP functional,^{4,5} a fictitious electron mass of 400 a.u. and a timestep of 4 a.u. (*i.e.*, ≈ 0.097 fs).

Pseudopotentials and planewave basis set. Fully separable⁶ norm-conserving Troullier-Martins pseudopotentials⁷ were used to describe the nuclei and the core electrons of all atoms, while the wavefunctions of the valence electrons were expanded in a planewave basis set (\mathcal{P}) with the kinetic energy cutoff of $E_{cut} = 70$ Ry. For the description of the N, Cl, C, O and H atoms, we used the N_MT_BLYP.psp, Cl_MT_BLYP.psp, C_MT_GIA_BLYP.psp, O_SPRIK_BLYP.psp and H_MT_BLYP.psp pseudopotentials, respectively, from the CPMD pseudo_extlib library. The pseudopotential of the Fe atom was generated with the semicore 3s and 3p states included in the valence shell, using the ld1.x program from the Quantum Espresso program suite⁸. In order to assess the performance of the pseudopotentials and of the planewave basis sets, we used the CPMD code for characterizing at the BLYP level the gas-phase structural and energetic properties of the $\text{Cl}^- - \text{H}_2\text{O}$ dimer and of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the LS and HS states, and compared these results with those obtained with the G03 program package⁹ at the MP2 or BLYP level. The results obtained for the $\text{Cl}^- - \text{H}_2\text{O}$ are summarised in Table 1, whose inspection shows that there is a satisfactory agreement between the all-electron and the combined pseudopotential/planewave description of the dimer. One indeed notes in Table 1 that the structural parameters and interaction energy obtained at the BLYP/ \mathcal{P} agree quite well with those obtained at the MP2/6-311++G(d,p) level.

Table 1: Test calculations performed at the BLYP and MP2 level on the $\text{Cl}^- - \text{H}_2\text{O}$ dimer: selected optimised structural parameters and calculated interaction energy E_{int} .

	Cl ⁻ -H (Å)	O-H (Å)	∠ClHO (deg)	E_{int} (cm ⁻¹)
CPMD: BLYP/ \mathcal{P} ^a	2.124	1.015, 0.978	169.6	-4904
G03: MP2/6-311++G(d,p) ^{a,b}	2.150	0.984, 0.959	165.3	-5488
G03: MP2/6-311++G(d,p) ^c	2.15	0.98, 0.96	165.4	-4792

^aThis work. ^bNo BSSE correction. ^cWith BSSE correction.¹⁰

This agreement is also observed for the results reported in Table 2 for the description of the isolated $[\text{Fe}(\text{bpy})_3]^{2+}$ complex. The LS and HS geometries determined for the complex at the BLYP/ \mathcal{P} level indeed compare quite well with previously reported LS and HS structures (see for instance, Ref.¹¹), and agree with those obtained here with the G03 program. Furthermore, one notes in Table 2 that the BLYP HS-LS energy difference is well reproduced with the CPMD program.

Table 2: Test calculations performed at the BLYP level on the D_3 $[\text{Fe}(\text{bpy})_3]^{2+}$ complex in the LS and HS states: selected optimized structural parameters and calculated HS-LS electronic energy difference $\Delta E_{\text{HL}}^{\text{el}}$.

	CPMD: BLYP/ \mathcal{P} ^a	X-ray ^b	G03: BLYP/ \mathcal{G} ^{a,c}
<i>LS $^1\text{A}_1$ geometries</i>			
Fe-N (Å)	1.997	1.967	2.009
C ₂ -C' ₂ (Å)	1.468	1.471	1.491
β (deg)	81.0	81.8	81.5
γ (deg)	3.0	6.4	2.9
<i>HS $^5\text{A}_1$ geometries</i>			
Fe-N (Å)	2.208	—	2.227
C ₂ -C' ₂ (Å)	1.471	—	1.510
β (deg)	75.1	—	74.9
γ (deg)	−0.4	—	4.9
<i>HS-LS electronic energy differences</i>			
$\Delta E_{\text{HL}}^{\text{el}}$ (cm ^{−1})	7534	—	8083

^aThis work. ^bTaken from the X-ray structure of $[\text{Fe}(\text{bpy})_3](\text{PF}_6)_2$.¹² ^cIn the \mathcal{G} basis set of Gaussian-type orbital (GTO) functions, the H atoms are described by the Pople double- ζ polarized 6-31G** basis set,^{13,14} whereas for the heavy atoms, the compact effective potentials (CEPs) of Stevens *et al.* are used to describe the atomic core electrons while the valence electrons are described with associated GTO basis sets of double- ζ polarized quality, for the C, Si, O and N atoms, (CEP-31G* basis set), and of triple- ζ quality for the Fe atom, (CEP-121G basis set).^{15,16}

Details of the simulation in the LS state. A preliminary classical MD simulation of 1 ns duration was first run at 300 K with the Gromacs package.¹⁷ In this simulation, the OPLS-AA force field¹⁸ was employed, using for water the TIP4P model,¹⁹ keeping the geometry of $[\text{Fe}(\text{bpy})_3]^{2+}$ fixed to its optimized LS geometry and providing an approximate model of the complex based on

charges derived from a Mulliken population analysis. The AIMD simulation was started with the CPMD code from the final configuration of the classical simulation. The simulation temperature of 300 K were adjusted during a first run of ~ 0.1 ps by velocity scaling, then by putting a Nosé-Hoover chain on each ionic degree of freedom (massive thermostating) during a run of ~ 2.7 ps. Massive thermostating was kept on during the AIMD production run of 24.479 ps during which the LS trajectory was recorded every 10 steps.

Details of the simulation in the HS state. The simulation in the HS state was started from a snapshot of the LS trajectory taken at $t \approx 3.251$ ps. The system was first quenched onto the HS Born-Oppenheimer (BO) surface. The temperature was then adjusted by velocity scaling in a ~ 0.6 ps run followed by a run of ~ 3.3 ps wherein massive thermostating was activated. During these two equilibration runs, the system was quenched several times back onto the HS BO surface. At the end of the second run, the system was again quenched back onto the HS BO surface before putting an other Nosé-Hoover chain on the electronic degrees of freedom, and let it evolve during ~ 0.2 ps. The HS trajectory was then recorded each 10 steps during the production run of 3.950 ps.

Visualization and analysis. The results of the calculations were visualized and analyzed using the VMD software^{20,21} and tools from the Gromacs program suite.

Solvation structure of the chloride anions in the LS and HS states.

Figure 1 shows the radial distribution functions (RDFs) of the water oxygen (O) and hydrogen (H_w) atoms with respect to the Cl atoms, $g(r)$, calculated using a radial grid of 0.1 \AA . They do not noticeably evolve upon the LS \rightarrow HS change of states, and they actually compare very well with those recently reported by Heuft and Meijer.²²

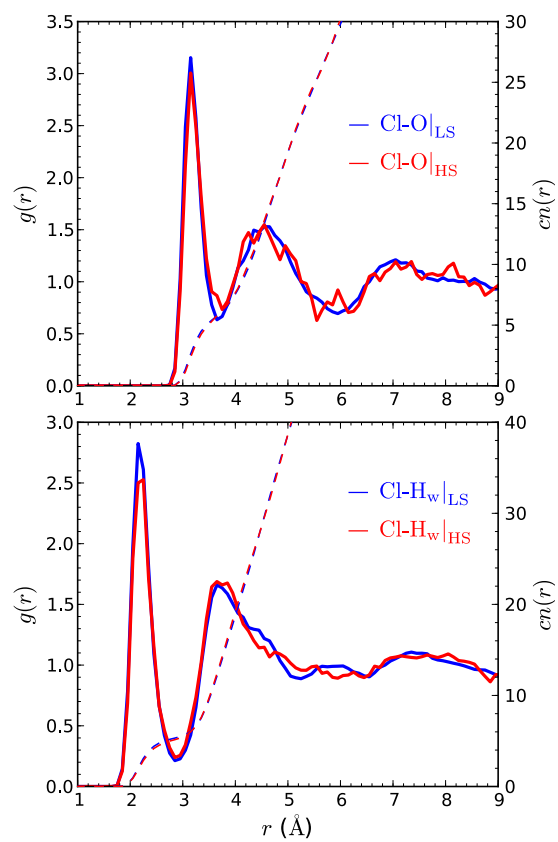


Figure 1: LS and HS RDFs $g(r)$ of the water oxygen and hydrogen atoms with respect to the Cl atom (solid lines, left y-axis), and running coordination numbers $cn(r)$ (dashed lines, right y-axis).

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