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

Supporting Information for:

Spin-state dependence of the structural and vibrational properties of solvated iron(II) polypyridyl complexes from AIMD simulations: II. aqueous $[Fe(tpy)_2]Cl_2$

Latévi M. Lawson Daku

Département de chimie physique, Université de Genève, Quai E. Ansermet 30, CH-1211 Genève 4, Switzerland. E-mail: max.lawson@unige.ch

Contents

List of Figures

1 Structural properties of the aqueous solution

1.1 Structure of $[Fe(tpy)_2]^{2+}$

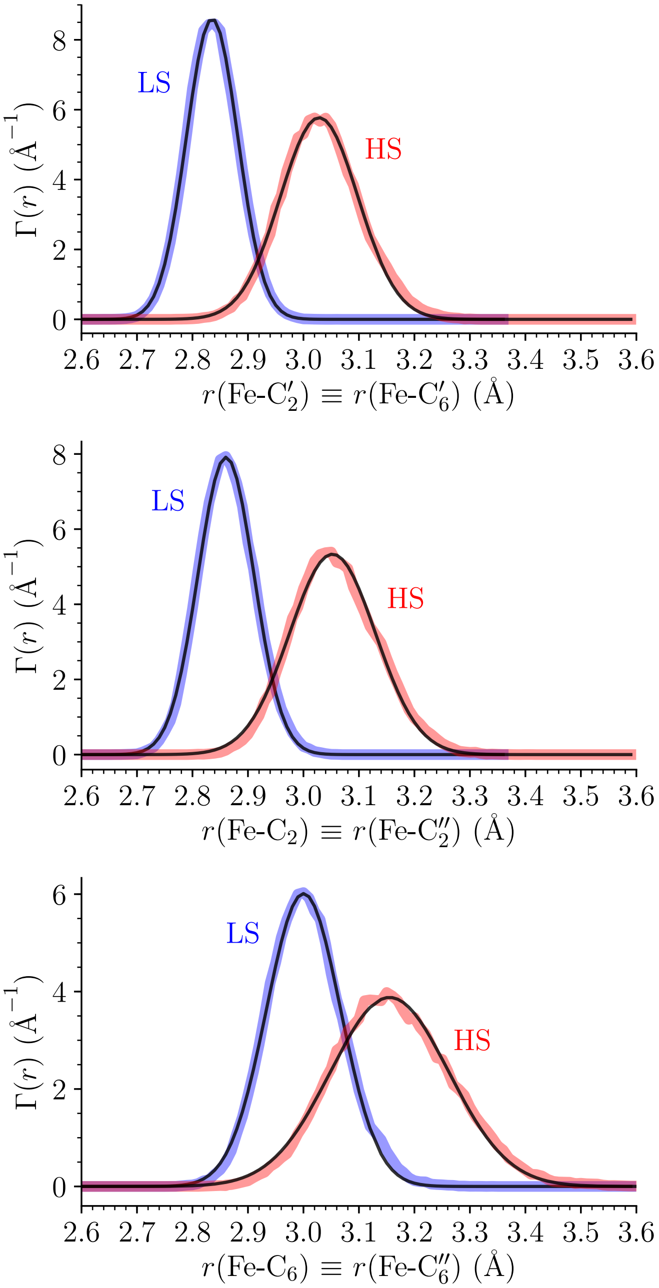

Figure S1 Distribution functions of the Fe-C$'_2$ ≡ Fe-C$'_6$, Fe-C$_2$ ≡ Fe-C$''_2$ and Fe-C$_6$ ≡ Fe-C$''_6$ bond lengths for aqueous $[Fe(tpy)_2]^{2+}$ in the LS and HS states (thick solid or dashed lines). The fits of the data assuming Gaussian distribution functions are also shown (black lines).

1.2 Structure of water

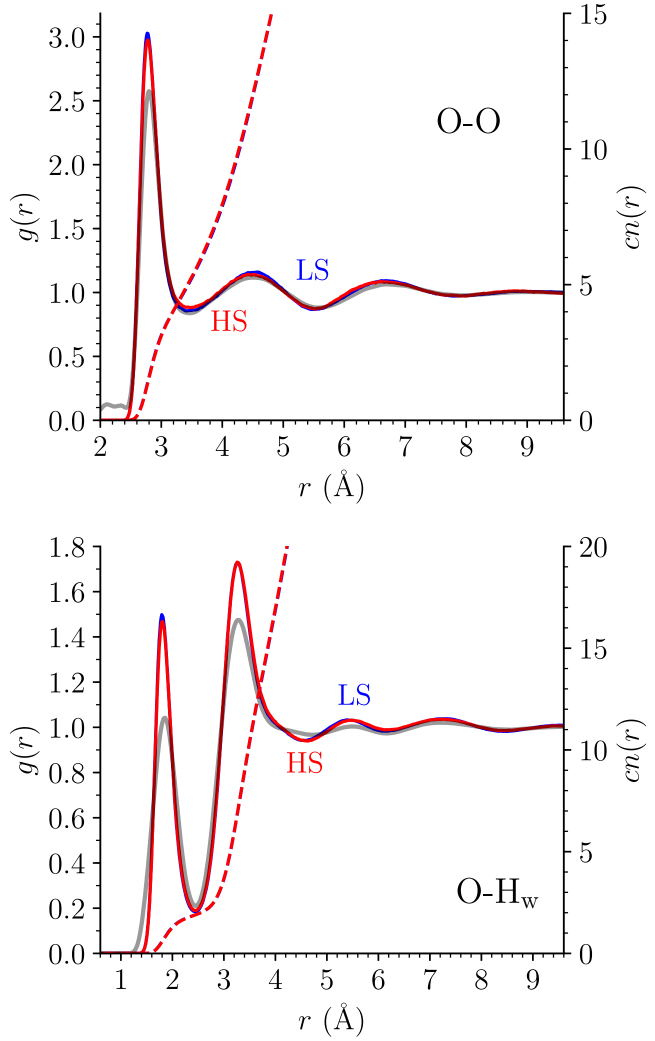

Figure S2 Structure of the water solvent for $[Fe(tpy)_2]^{2+}$ in the LS and in the HS state: intermolecular radial distribution functions of the water oxygen (Top, $g_{OO}(r)$) and hydrogen (Bottom, $g_{OH_w}(r)$) atoms with respect to the O atoms (solid lines, left y-axis), and running coordination numbers $cn(r)$ (dashed lines, right y-axis). The solid gray curves correspond (Top) to the $g_{OO}(r)$[1] and (Bottom) to the $g_{OH_w}(r)$[2] determined experimentally for ambient water.

1.3 Hydration structure of $[Fe(tpy)_2]^{2+}$

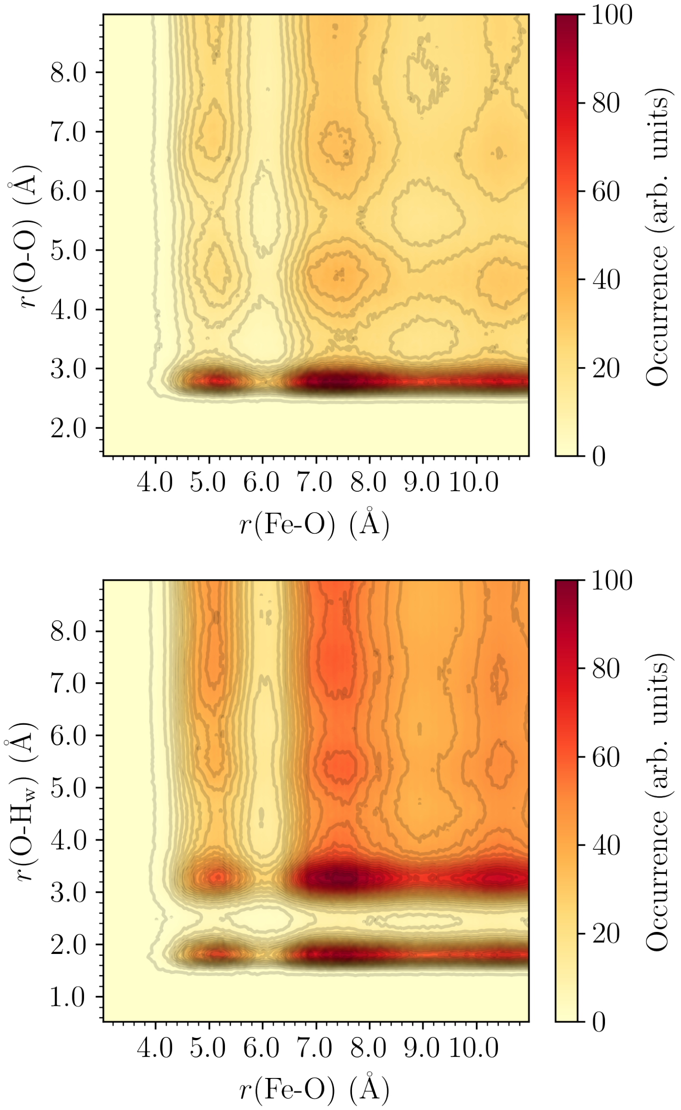

Figure S3 Hydration structure of $[Fe(tpy)_2]^{2+}$ in the LS state: Combined Fe-O/O-O (Top) and Fe-O/O-H_w (Bottom) radial/radial distribution functions.

1.4 Hydration structure of Cl^-

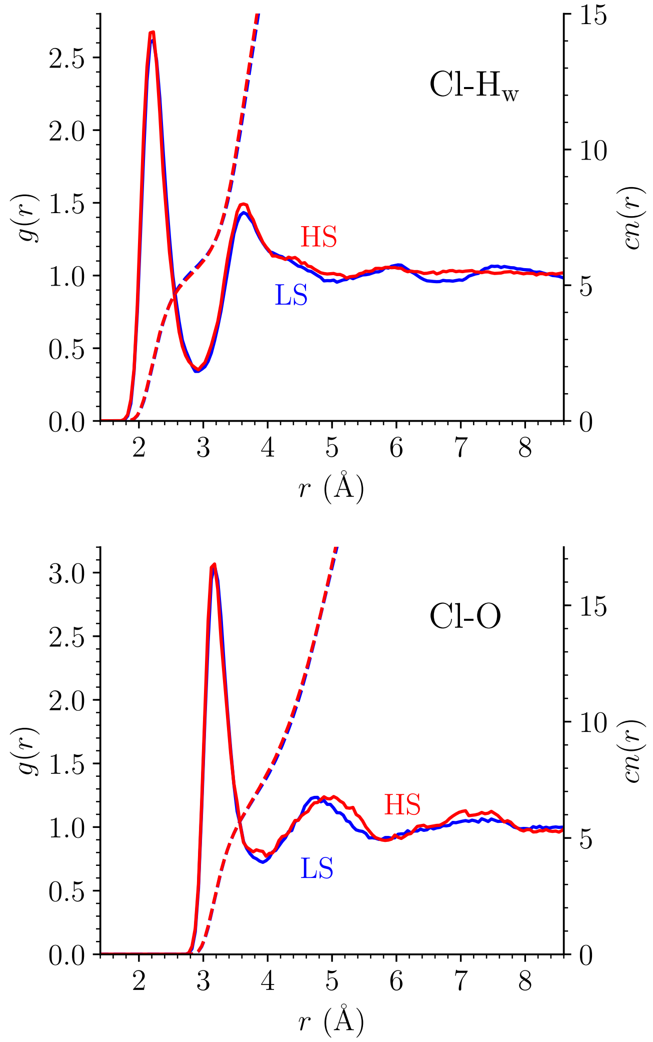

Figure S4 Hydration structure of Cl^- for $[Fe(tpy)_2]^{2+}$ in the LS and in the HS state: radial distribution functions $g(r)$ of the water hydrogen (Top) and oxygen (Bottom) atoms with respect to the Cl atoms (solid lines, left y-axis) for $[Fe(bpy)_3]^{2+}$ in the LS and in the HS state, and running coordination numbers $cn(r)$ (solid lines, left y-axis).

2 Dipole moments

2.1 The Cl^- anions

The dipole distribution functions of the Cl^- anions and of the water molecules in and beyond their first solvation shell are plotted in Figure S5. The distributions exhibit a vanishing dependence on the spin state of $[Fe(tpy)_2]^{2+}$. There is a weak coupling between the Cl^- and $[Fe(tpy)_2]^{2+}$ ions in water. The predicted dipole moments are: 0.74 ± 0.31 D for Cl^- , 2.86 ± 0.28 D for the water molecules in its first hydration shell and 2.92 ± 0.28 D for the water molecules belonging to the bulk.

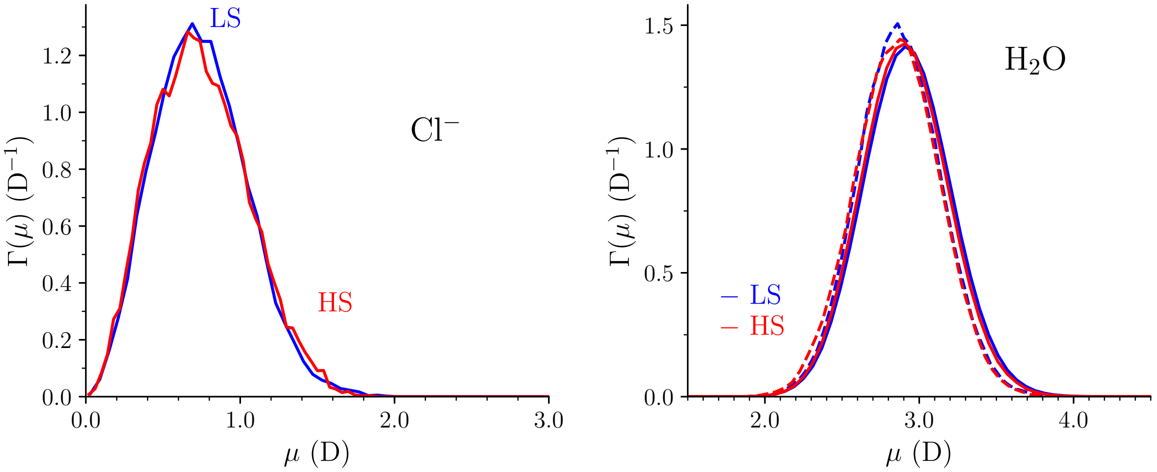

Figure S5 Dipole distribution functions of Cl^-(Left) and of the water molecules in (r(Cl-O) $\leq$ 4.0 Å, dashed lines) and beyond (r(Cl-O) $>$ 4.0 Å, solid lines) the first hydration shell of Cl^- (Right) for $[Fe(tpy)_2]^{2+}$ in the LS and in the HS.

2.2 The $[\mathrm{Fe(tpy)_2}]^{2+}$ solute

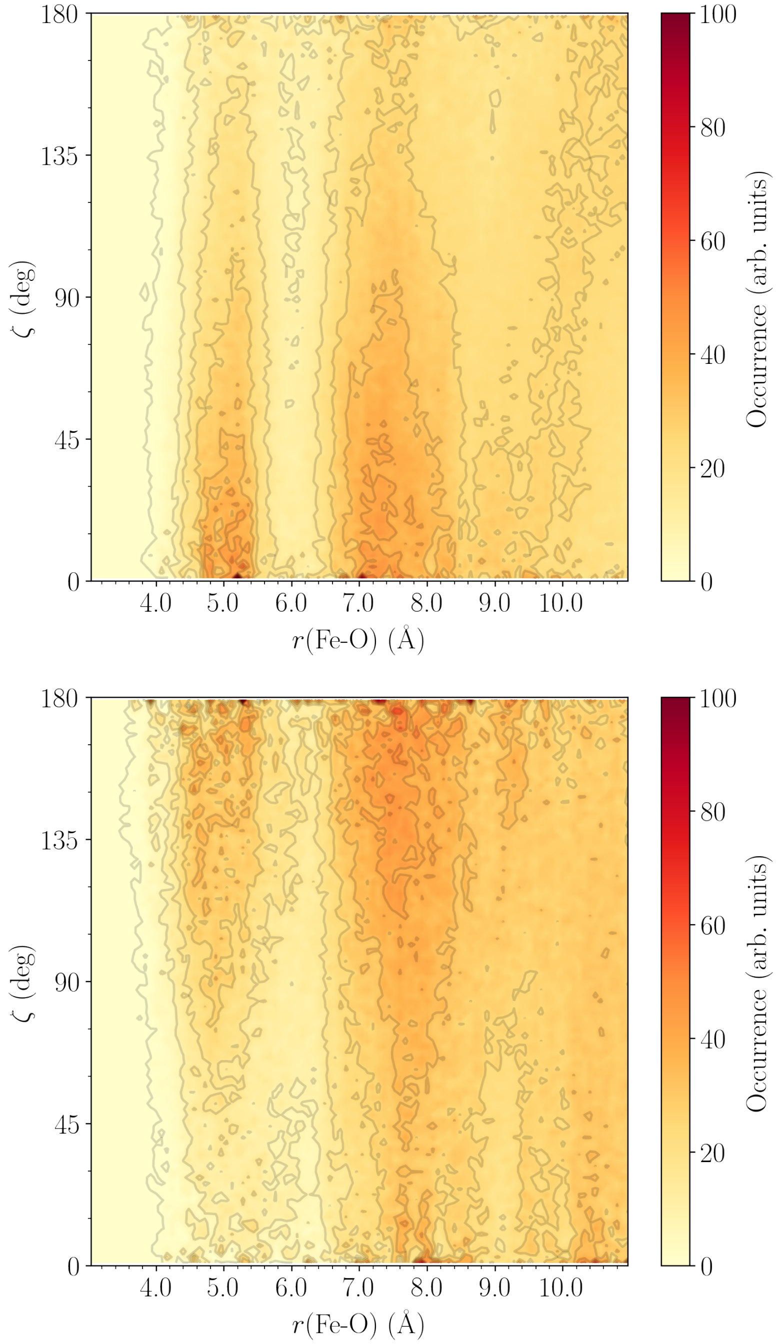

Figure S6 Combined Fe-O/ζ radial/angular distribution function for $[\mathrm{Fe(tpy)_2}]^{2+}$ in the LS (Top) and in the HS (Bottom) state (ζ: angle between the dipole moment of $[\mathrm{Fe(tpy)_2}]^{2+}$ and that of the observed water molecule).

3 Vibrational properties

3.1 LS and HS IR spectra of aqueous $[Fe(tpy)_2]Cl_2$

The IR spectrum of aqueous $[Fe(tpy)_2]Cl_2$ in the LS or HS state has been calculated by subtracting from the IR spectrum of the whole system the contribution of the solvent. These spectra and the associated HS-LS difference spectrum are superimposed in Figure S7 with those determined for $[Fe(tpy)_2]^{2+}$. For the solution in either spin state, the spectrum of $[Fe(tpy)_2]Cl_2$ shows small differences with respect to the one of $[Fe(tpy)_2]^{2+}$. As pointed out in the AIMD study of aqueous $[Fe(bpy)_3](Cl)_2$,[3] these differences are due to the included contributions of the Cl^- anions with their fluctuating charge distributions and the added solute-solute and solute-solvent intermolecular contributions. The nearly perfect match between the HS-LS difference spectra reflects the vanishing spin-state dependence of these additional contributions to the IR spectrum.

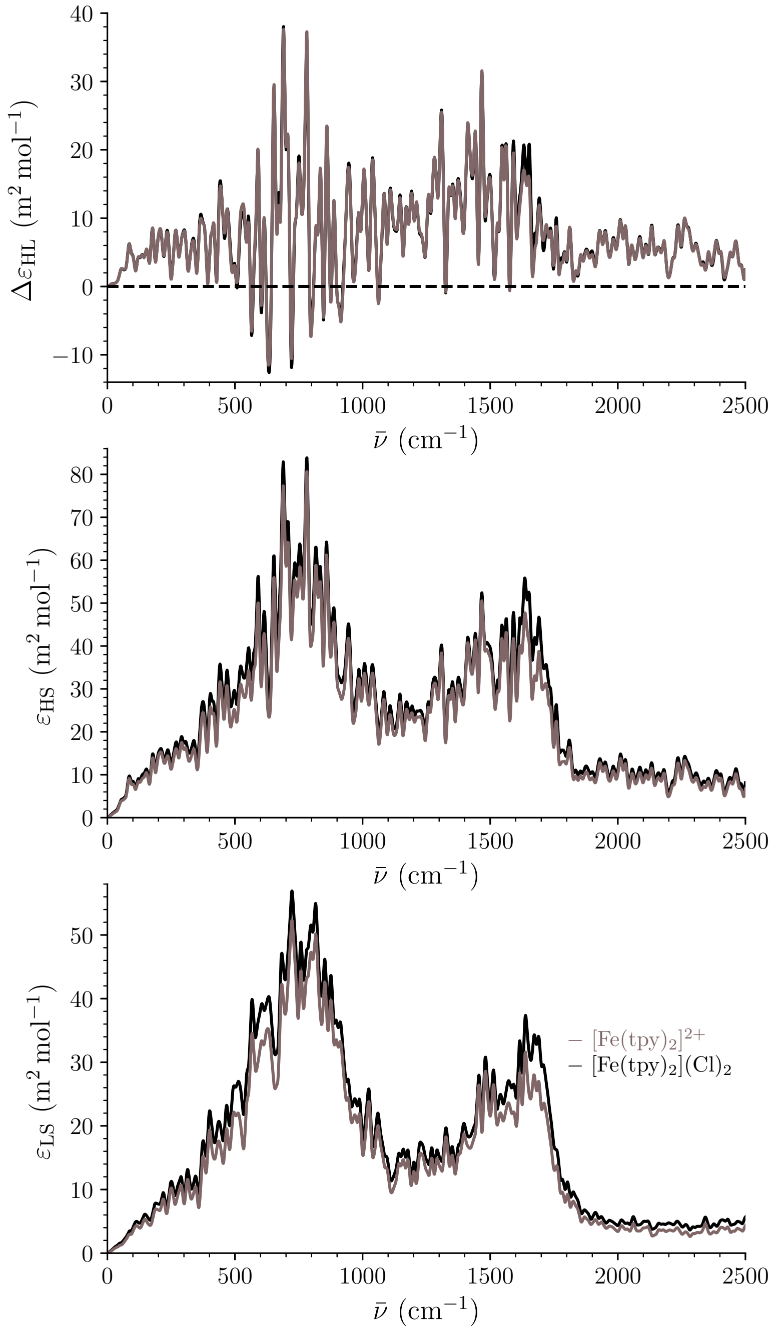

Figure S7 Comparison between the IR spectra of aqueous $[\mathrm{Fe(tpy)_2}]\mathrm{Cl_2}$ and aqueous $[\mathrm{Fe(tpy)_2}]^{2+}$: LS (bottom) and HS (middle) IR spectra, and corresponding HS-LS difference curves (top; resolution of the ACFs: 512 time steps).

References

1 L. B. Skinner, C. Huang, D. Schlesinger, L. G. M. Pettersson, A. Nilsson and C. J. Benmore, *J. Chem. Phys.*, 2013, **138**, 074506.

2 A. K. Soper, *ISRN Phys. Chem.*, 2013, **2013**, 279463.

3 L. M. Lawson Daku, *Phys. Chem. Chem. Phys.*, 2018, **20**, 6236–6253.