Supplementary information

Table of content

- 1- Materials
- 2- Data analysis framework for the TR-WAXS signal
- **3-** Numerical simulations
- **3a-DFT geometry optimizations and AIMD simulations 3b-Classical MD simulations**
- 4- Calculation of scattering S(q) from the radial distribution functions
- 5- Isochoric solvent response
- 6- Statistical evaluation of various structural models for the TR-WAXS analysis
- 7- Effective reduced numbers of degrees of freedom
- 8- Evaluating the correlation between the fitting parameters
- 9- Sine-Fourier Transform for real-space visualization

10- Highlighting the photoinduced structural changes in the HS excited state of the solvated $[Fe^{II}(bpy)_3]^{2+}$ molecular complex

11- Global structural sensitivity: rigid model selection and thermal disordering

12- DFT optimized geometries : cartesian coordinates

1-Materials

 $[Fe^{II}(bpy)_3](CI)_2$ Was synthesized according to the published protocol [1]. All reagents were used as received from commercial sources without further purification.

[1] Varvara V. Avdeeva Anna V. Vologzhanina Lyudmila V. Goeva Elena A. Malinina Nikolay T. Kuznetsov, Z. Anorg. Allg. Chem. 2014, 2149–2160

2- Data analysis framework for the TR-WAXS measurement

The difference scattering signal from a solution $\Delta S(q,t)$ can be partitioned into three contributions, namely, the bulk solvent difference signal $\Delta S_{solvent}(q,t)$, the solute-only term $\Delta S_{solute}(q,t)$ and the term describing the solute-solvent interactions, $\Delta S_{cage}(q,t)$, also called the cage term. The total difference scattering signal is then expressed as follows:

$$\Delta S(q,t) = \Delta S_{solvent}(q,t) + \Delta S_{solute}(q,t) + \Delta S_{cage}(q,t)$$
(E1)

Within the framework of the established methodology for solution scattering, the solvent term $\Delta S_{solvent}$ is given as the sum of two contributions [1]:

$$\Delta S_{solvent}(q,t) = \Delta T(t) \cdot \frac{\partial S(q)}{\partial T} \Big|_{V = const} + \Delta \rho(t) \cdot \frac{\partial S(q)}{\partial \rho} \Big|_{T = const}$$
(E2)

The two differential profiles on the right side are acquired in separate experiments, where the first term corresponds to isochoric heating and the second term corresponds to adiabatic expansion. However, it should be emphasized that acquiring these profiles under similar experimental conditions is critical for achieving high accuracy of the data fitting. In this experiment the two differentials were obtained by collecting difference scattering from pure water excited with 1490 nm IR radiation and extracted as described elsewhere [1, 2]. Additionally, pure water was excited with the 475 nm radiation at the excitation conditions identical to the experiment with $[Fe^{II}(bpy)_3]^{2+}$

solution, but no difference scattering was detected within the uncertainty of the measurement (see SI.5). This allows ruling out direct multiphoton excitation of the solvent itself.

The solute-only differential profile ΔS_{solute} (q,t) can be calculated based on the optimized structures delivered by the DFT and AIMD optimizations. If the solute structure is relaxed in both the ground state (GS) and the excited state (ES), the atomic positions can be approximated as precisely defined, i.e. the atomic pair distribution functions within the solute can be represented as δ -functions, leading to the finite sum called the Debye equation:

$$S_{solute}^{theor}(q) = \sum_{n} f_n^2(q) + \sum_{n} \sum_{m \neq n} \left(f_n(q) \cdot f_m(q) \cdot \frac{sin^{[m]}(q \cdot r_{nm})}{q \cdot r_{nm}} \right), \tag{E3}$$

The difference scattering signal is calculated as the difference of the $\Delta S_{solute}^{theor}(q)$ for ES and GS having respectively various sets of interatomic distances, r_{nm} . When a single excited state species is photoinduced, the computed difference is scaled by the time-dependent excited state fraction, $\gamma(t)$, which is taken as a fitting parameter in the analysis of the experimental data with:

$$\Delta S_{solute}^{theor}(q,t) = \gamma(t) \cdot (S_{solute}^{theor}(q)|_{ES} - S_{solute}^{theor}(q)|_{GS})$$
(E4)

The cage-term, or the contribution from the solute-solvent interactions $\Delta S_{cage}(q,t)$ is similarly modeled as a difference between respective cage signals of GS and the ES scaled by the excited state fraction. The scattering signals $\Delta S_{cage}^{theor}(q)$ are calculated from the corresponding radial distribution functions, g(r), of all pairs of solvent and solute atoms as obtained from the molecular dynamics simulations, AIMD or classical MD.

$$S_{cage}^{theor}(q) = \sum_{n} N_{n} f_{n}^{2}(q) + \sum_{n} \sum_{m \neq n} \left(\frac{N_{n} N_{m}}{V} f_{n}(q) \cdot f_{m}(q) \int_{0}^{\infty} (g_{nm}(r) - 1) \cdot \frac{\sin[m](q \cdot r)}{q \cdot r} 4\pi r^{2} dr \right)$$
(E5)

where n and m refer to different pairs of solute and solvent atoms. The integration is limited in r by the size of molecular dynamics simulation box. Constructing the difference cage term from the GS and the ES results in the equation (5) of the main text.

Finally, the theoretically predicted difference scattering was corrected for the relatively small but finite polychromaticity of the X-ray beam (1.4% bandwidth). The experimental data, $\Delta S^{exp}(q,t)$, was fitted by the linear combination of the respective difference scattering contributions (E2) by minimizing the χ^2 estimator:

$$\chi^{2} = \sum_{q,t} \left(\frac{\Delta S^{theor}(q,t) - \Delta S^{exp}(q,t)}{\sigma(q,t)} \right)^{2}$$
(E6)

M. Cammarata J. Chem. Phys., 2006, **124**, 124504
 K. S. Kjaer, T. B. van Driel, J. Kehres, K. Haldrup, D. Khakhulin, K. Bechgaard, M. Cammarata, M. Wulff, T. J. Sorensen and M. M. Nielsen, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15003

3-Numerical simulations

3a-DFT geometry optimizations and AIMD simulations

The LS and HS geometries of aqueous $[Fe^{II}(bpy)_3]^{2+}$ have been optimized with the ADF program package [1], using the COSMO (conductor like screening model) implicit model of solvation for water [2] and the dispersion-corrected BLYP-D3 functional [3] combined with the Slater- TZP basis set of triple-zeta polarized quality from the ADF basis set database [4]. The optimizations were performed with the molecular symmetry constrained to D₃ or C₂. The Cartesian coordinates are given in S.I. 12.

The full details of the AIMD simulations performed for aqueous $[Fe^{II}(bpy)_3]Cl_2$ in the LS and HS states are given in Ref [5]. Here, we only report those relevant to the present study. The system used for the AIMD simulations consists of one $[Fe^{II}(bpy)_3]^{2+}$ complex, 2 Cl⁻ counterions and 298 water molecules put in a cubic box of 21 Å on each side. Periodic boundary conditions were used during the simulations carried out at 310 K using the CP2K program package [6] and the BLYP-D3 functional [3]. The core electrons of the atoms were described with Goedecker–Teter–Hutter pseudopotentials [7], and their valence states with the Gaussian-type MOLOPT [8] DZVP-MOLOPT-SR-GTH basis set of double-zeta polarized quality from the CP2K package. A timestep of 0.5 fs was employed and trajectories were recorded every 5 steps. The durations of the recorded LS and HS trajectories are ~76.6 ps and 67.2 ps, respectively.

For both the geometry optimizations and the AIMD simulations, the calculations were run restricted (resp., unrestricted) for the complex in the LS (resp., HS) state.

[1] (a) G.te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders and T. Ziegler, Chemistry with ADF, Journal of Computational Chemistry 22, 931 (2001). DOI: 10.1002/jcc.1056. (b) C.Fonseca Guerra, J.G. Snijders, G. te Velde and E.J. Baerends, Towards an order-N DFT method, Theoretical Chemistry Accounts 99, 391 (1998). DOI: 10.1007/s002140050353. (c) ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. Optionally, you may add the following list of authors and contributors: E.J. Baerends, T. Ziegler, A.J. Atkins, J. Autschbach, O. Baseggio, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, C. Daul, D.P. Chong, D.V. Chulhai, L. Deng, R.M. Dickson, J.M. Dieterich, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A. Goez, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, Z. Hu, C.R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J.W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, M. Pavanello, C.A. Peeples, P.H.T. Philipsen, D. Post, C.C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, J.I. Rodríguez, P. Ros, R. Rüger, P.R.T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Stener, M. Swart, D. Swerhone, V. Tognetti, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev.

[2] (a) A. Klamt and G. Schüürmann, COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient, Journal of the Chemical Society: Perkin Transactions 2, 799 (1993). DOI: 10.1039/P29930000799

(b) A. Klamt, Conductor-like Screening Model for real solvents: A new approach to the quantitative calculation of solvation phenomena, Journal of Physical Chemistry 99, 2224 (1995). DOI: : 10.1021/j100007a062. (c) A. Klamt and V. Jones, Treatment of the outlying charge in continuum solvation models, Journal of Chemical Physics 105, 9972 (1996). DOI: 10.1063/1.472829. (d) C.C. Pye and T. Ziegler, An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package, Theoretical Chemistry Accounts 101, 396 (1999). DOI: 10.1007/s002140050457.[BLYP-D3]

[3] (a) A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Physical Review A 38, 3098 (1988). DOI: 10.1103/PhysRevA.38.3098. (b) C. Lee, W. Yang and R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Physical Review B 37, 785 (1988). DOI: 10.1103/PhysRevB.37.785. (c) S. Grimme, J.

Anthony, S. Ehrlich, and H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, Journal of Chemical Physics 132, 154104 (2010). DOI: 10.1063/1.3382344.

[4] E. van Lenthe and E.J. Baerends, Optimized Slater-type basis sets for the elements 1-118, Journal of Computational Chemistry 24, 1142 (2003). DOI: 10.1002/jcc.10255.

[5] L. M. Lawson Daku, Spin-state dependence of the structural and vibrational properties of solvated iron(II) polypyridyl complexes from AIMD simulations: aqueous $[Fe^{II}(bpy)_3]Cl_2$, a case study, Phys.Chem.Chem.Phys., 2018, 20, 6236. DOI: 10.1039/c7cp07862e.

[6] J. VandeVondele, M. Krack, M. Fawzi, M. Parrinello, T. Chassaing and J. Hutter, Comput. Phys. Commun., 2005, 167, 103.

[7] (a) S. Goedecker, M. Teter and J. Hutter, Phys. Rev. B: Condens. Matter Mater. Phys., 1996, 54, 1703. (b) C. Hartwigsen, S. Goedecker and J. Hutter, Phys. Rev. B: Condens. Matter Mater. Phys., 1998, 58, 3641. (c) M. Krack, Theor. Chem. Acc., 2005, 114, 145.

[8] J. VandeVondele and J. Hutter, J. Chem. Phys., 2007, 127, 114105.

3b-Classical MD

The classical MD simulations were performed in a box of 768 water molecules and one solute molecule using periodic boundary conditions, the flexible TIP3P water model and the COMPAS-II *abinitio* force field (from Material Studio[®] software package). The system was equilibrated in a Nose-Hoover thermostat at temperature of 297 K and density of 1 g/cm³. The solute molecule was kept rigid in the LS and HS states and the charge distributions obtained from DFT using the ESP atomic charge partitioning were kept fixed. This particular charge partitioning was used as suggested for [Fe^{II}(CN)₆] in aqueous environment. The simulations were run for 5 ns with 1 fs step in the canonical NVT ensemble for all the geometries ⁵A-D₃, ⁵B-D₃, ⁵A-C₂, ⁵B-C₂ and AIMD. Figure S1a presents a trajectory snapshot (left) and the respective $g_{nm}(r)$ for the LS and ⁵A-D₃ HS states (right).



Figure S1a. (left) A snapshot of the classical MD simulation of $[Fe^{II}(bpy)_3]^{2+}$ in aqueous solution. The water molecules of the first solvation shell are highlighted. (right) Radial distribution functions g r_{Fe-Ow} (r) and $g_{C-Ow}(r)$ for the Fe, C atoms of $[Fe^{II}(bpy)_3]^{2+}$ and the Ow atom of water as simulated by the classical MD for the DFT-optimized structures of the LS ground and the ${}^{5}A-D_{3}$ excited states.

As benchmark, the results obtained for the water radial distribution functions of the water oxygens $g_{OwOw}(r)$ from the present classical MD and AIMD simulations (see section 3a) are compared to previously published experimental [1] (pink squares) and theoretical [2,3] (green dots and blue trace)studies in Figure S1b. The slight deviations between the $g_{OwOw}(r)$ simulated with classical MD

(green trace) and the experimental trace are related to the use of different water models and force fields. The AIMD $g_{OwOw}(r)$ (black trace) agrees will the measurement [1].



Figure S1b. Experimental [1], theoretical [2,3] radial distribution for the oxygen atoms of water $g_{owow}(r)$ compared to classical MD and AIMD simulations used in this work.

- [1] G. Hura et al., Phys. Chem. Chem. Phys. 2003, 5, 1981
- [2] J. S. Medina et al., Chem. Phys. 2011, 388, 9
- [3] A. V. Egorov et al., J. Phys. Chem. B 2011, 115, 14572

4- Calculation of scattering S(q) from radial distribution functions.

Using equation (E5) and the pairwise radial distribution functions of Ow-Ow, Ow-Hw and Hw-Hw from MD simulations it is possible to calculate the static scattering signal that solely arises from the solvent molecules in the liquid phase [1]. Figure S2 shows experimental [2] and simulated scattering profiles for bulk water at room temperature. The apparent mismatch, between the bulk water signal and the AIMD result on Figure S2 may partly come from the fact that the measurements were made at 300 K and the simulations at 310K. Furthermore, the accurate description of water remains a challenging problem, both from the experimental and theoretical viewpoints [3,4]. The good agreement nevertheless brings confidence in the validity of methodology applied further on to calculate the solute-solvent cage term.



Figure S2. Wide angle X-ray scattering for bulk water: experimental (blue, from [2]) and simulated using the g(r) functions from AIMD (red) and for the gas-phase using the Debye equation (green).

- [1] A. Dohn, et al, J. Phys. B: Atom. Molec. Phys. 2015, 48, 24410
- [2] G. Hura J. Phys. Chem. 2000, **113**, 9140

[3] H-S Lee et al, J. Chem. Phys. 2006, 125, 154507

[4] I-C. Lin et al, J. Chem. Theory Comput, 2012, 8, 3902

5- Isochoric solvent response

For the accuracy of the analysis described in section 2, the water solvent response to impulsive heating needs to be obtained under experimental conditions that are similar to those of the actual measurement on the $[Fe^{II}(bpy)_3]^{2+}$ sample. Systematic measurements of the temperature derivative $\partial S(q)|$

 $\frac{dT}{\partial T}|_{V=const}$ were performed at various excitation and probing conditions as summarized in Figure S3



Figure S2 S3. Difference scattering response $\frac{\partial U(q)}{\partial T}|_{V=const}$ for isochoric impulsive heating of bulk water.

This signal was acquired with 1490 nm IR excitation for a monochromatic beam at 25.2 keV (1.4% bandwidth) (black trace) This component was then used as isochoric solvent response during the analysis of the TR-WAXS measurement on $[Fe^{II}(bpy)_3]^{2+}$ In addition, a measurement through dyemediated solvent heating [1] was conducted with 18 keV "pink" (3% bandwidth) beam (blue circles). For quantitative comparison, the monochromatic black traces was convoluted with the experimental "pink" undulator spectrum at 18 keV (3% bandwidth) and 25.2 keV (3% bandwidth) to yield the green and red traces.

[1] K. S. Kjaer, T. B. van Driel, J. Kehres, K. Haldrup, D. Khakhulin, K. Bechgaard, M. Cammarata, M. Wulff, T. J. Sorensen and M. M. Nielsen, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15003

6- Statistical evaluation of various structural models for the TR-WAXS analysis

$$\chi^2_{red} = \chi^2 / (N-(p-1)-1) = \chi^2 / (N-p)$$

(E7)

where N is the number of data points and p the number of fitting parameters. When the error bars have been correctly estimated (i.e. free from systematic errors), χ^2_{red} is not much larger than 1.

In order to provide evidence for various structural and linear combination fit models, the Akaike's Information Criterion (AIC) [1] was used.

Following this approach, the model selection metric is defined as:

$$AIC = -2\log\left(L(\alpha)\right) + 2K$$

where *K* is the number of estimated parameters and *L* is the likelihood function of the fit for a parameter set α , which can be constructed from the χ^2 (E6):

$$L(\alpha) = C \cdot exp(-\chi^2(\alpha)/2)$$
(E9)

Here *C* is a constant independent of α .

Once the AIC is calculated, it is convenient to compare competing models according to their Akaike's evidence ratios R_i with respect to the best model, which are defined as ratios of respective Akaike weights w_i :

$$w_i = \frac{L(\alpha_i)}{\sum_{N} L(\alpha)}$$

where the sum is performed over all evaluated models. The ones that result in evidence ratios of 8 or smaller are typically considered to be within the confidence set of models and are considerably supported by the criterion as best models from the evaluated set.

(E10)

In order to determine a set of best structural models representing the high resolution scattering data for a large q-range, the difference signals $\Delta S(q,t)$ at q > 4.5 Å⁻¹ was fitted with several models M₂ including only the solute and the solvent contributions. The respective χ^2 values and Akaike evidence ratios are given in Table S4. As can be seen, only the model based on the LS and HS structures obtained from the AIMD simulations finds considerable support based on the AIC.

[1] Burham, K.P. & Anderson, D.R. 2002. Model selection and multimodel inference: A practical information-theoretic approach, 2nd Ed. Springer, New York.

Model	χ^{2} red	X ²	ΔΑΙϹ	Akaike weights	Evidence ratio
M ₂ (⁵ A-D ₃)	0.6293	278.80	10.22	0.00599	165.67006
M ₂ (⁵ E-D ₃)	0.6367	282.06	13.48	0.00117	845.55924
M ₂ (⁵ A-C ₂)	0.6737	298.46	29.88	3.2249E-7	3.07864E6
M ₂ (⁵ B-C ₂)	0.6827	302.44	33.86	4.40829E-8	2.25219E7
M ₂ (AIMD)	0.6063	268.58	0	0.99283	1

Table S4. Statistical measures for comparing various structura	al models M ₂ over 4.5 Å ⁻¹ < <i>q</i> < 11.5 Å ⁻¹
--	---

7- Effective reduced numbers of degrees of freedom

In some WAXS [1] and SAXS studies, the number of independent data points in the TR-WAXS signals is estimated as the number of Shannon channels, which is defined as $N_s = (q_{max}-q_{min})^* D_{max}/\pi$ in [1].

The extra factor of 2 comes from adapting directly the EXAFS case without noting that the photoelectron wavevector is $k^{2}\pi/\lambda$ while the scattering momentum transfer is $q^{4}\pi/\lambda$. However, in this context, the number of independent points (or maximum degrees of freedom) is rather considered as an order of magnitude estimate for the maximum number of optimization (structural) parameters or as a measure of the highest reasonable model complexity. At the same time, it is recognized that increasing the signal to noise ratio, oversampling the signal in q-space and constraining the models allows increasing the information content and the fitting confidence. For example, a linear dependence, i.e. 2 fitting parameters, can be concluded with a minimum of 3 independent data points. However, increasing the number of points and lowering their uncertainties clearly enhances the fit confidence. In our case, the model also contains only 2 (or 3) free "structural" (in terms of functional shape) parameters in the linear combination fit and strong oversampling increases the confidence in the model selection.

We nevertheless acknowledge the possibility of intrinsic systematic correlation between neighboring points as a detection artifact due to for example the broad point spread function of the scintillatorbased FReLoN-4M area detector. Such instrumental correlation would of course compromise the validity of the χ^2 approach to the model evaluation. The original data are reduced binning 2 pixels in the radial direction of the image to each 2θ (or q) bin, which of course does not reduce the possible correlation. We additionally down-sampled (not a binning) the difference scattering curves with a factor of 2, 4 and 6 still keeping the sample experimental errors in the data points of the downsampled curve as in the original data. Such down-sampling affects the χ^2 value due to fewer points and thus reduce the model selection capability based on the Akaike information criterion. Table S5 present the difference in Akaike criterion value and the respective Akaike evidence ratios (also see Figure S6) for the structural models as a function of down-sampling factor (N_{ds}) for scattering data in the range 4.5 Å⁻¹<q<11.5 Å⁻¹, i.e. in the structurally sensitive region. As expected, the evidence ratio of all models decreases with growing N_{ds} , leading to increased model selection uncertainty. However, the general conclusion on the preference of the AIMD structure still holds. For $N_{ds} = 6$, two more models based on the ⁵A-D₃ and ⁵E-D₃ structures are within the confidence set and can be considered as a good representation of the experimental data, which is caused by information loss due to artificial down sampling of data by factor of 6.

[1] K. Haldrup, M. Christensen, M. Meedom Nielsen Acta Cryst. (2010). A66, 261-269

Model	χ², N _{ds} =2 (DF=220)	Evidence ratio	χ², N _{ds} =4 (DF=108)	Evidence ratio	χ², N _{ds} =6 (DF=71)	Evidence ratio
M ₂ (⁵ A-D ₃)	138.96	26.97748	77.70	6.45592	44.55	2.77321
M ₂ (⁵ E-D ₃)	140.01	45.60431	78.52	9.72789	45.46	4.37107
M ₂ (⁵ A-C ₂)	147.65	2079.7486	82.41	68.0333	48.01	15.64275
M ₂ (⁵ B-C ₂)	149.66	5681.68033	83.38	110.49799	48.86	23.92699

Table S5: Comparison of χ^2 values and Akaike evidence ratios for various models M₂ over 4.5 Å⁻1 < q < 11.5 Å⁻¹ using down sampling factors N_{ds} of 2, 4 and 8.

M ₂ (AIMD)	132.37	1	73.97	1	42.51	1



Figure S6. Akaike evidence ratio for various structural models M_2 as a function of down sampling constant N_{ds} . The evidence ratio for the AIMD model with the smallest χ^2 is always 1 and thus represents the best model.

In addition, we note the irregular sensitivity of the χ^2 metric in the various q-ranges of the difference scattering signal $\Delta S(q,t)$. The signal is intrinsically much stronger in the lower q range due to the larger number of solvent-related scatterers and to the quick decay of the atomic form factors with increasing q. This introduces a bias of χ^2 towards the cage- and solvent-related components of $\Delta S(q,t)$, which is partially compensated by the growing sampling density of the signal and larger number of pixels contributing to individual q-bins with increasing q value.

8- Evaluating correlation between the fitting parameters

q range	Covariance	Correlation coeff.	Excited state fraction	Temperature [K]
1.4 <q<11.5 (m<sub="">2)</q<11.5>	-1.687	-0.328	0.4757 +/- 0.02	1.11 +/- 0.01
0.7 <q<11.5 (m₃)<="" td=""><td>0.061</td><td>0.015</td><td>0.408 +/-0.01</td><td>1.1516 +/- 0.01</td></q<11.5>	0.061	0.015	0.408 +/-0.01	1.1516 +/- 0.01
1.4 <q<4.5 (m<sub="">2)</q<4.5>	-14.99	-0.605	0.5080 +/- 0.1	1.1031 +/- 0.02
4.5 <q<11.5 (m<sub="">2)</q<11.5>	-54.545	-0.719	0.41 +/- 0.03	1.42 +/- 0.11

Table S7: The values of covariance and the correlation coefficient for the AIMD structural fits in various q-ranges.

9- Sine Fourier Transform for real-space visualization

The conversion of the curves $\Delta S(q)$ to real space (*r*-space) for both the solute and the cage terms is defined by a sine Fourier transform (FT):

$$r \Delta S(r) = \frac{1}{2\pi^2} \int_0^\infty \frac{1}{F_{sharp}(q)} q \Delta S(q) \sin(qr) exp^{[m]}(-(\alpha q)^2) dq$$
(S7)

where $exp^{[in]}(-(\alpha q)^2)$ is a convertion factor (here α =0.21 Å) to avoid the termination errors due to $F_{sharp}(q) = \sum_{n} \sum_{m \neq n} f_n(q) f_m(q)$ the truncated q-range as suggested by Warren [1], $F_{sharp}(q) = \sum_{n} \sum_{m \neq n} f_n(q) f_m(q)$ is the sharpening function ($f_{i,j}(q)$ are the atomic scattering form factors for n-th and m-th atom in the molecule). For the cage term, the number of solvent atoms contributing to the sharpening function was defined for a maximum oxygen and hydrogen coordination numbers within the MD simulation box.

Figure 4 in the main text presents several sine-FT. The "data" curve (red) corresponds to the sine-FT over 0-11.5 Å⁻¹.for the difference between the TR-WAXS signal and the isochoric solvent contribution fitted with model M₂ over the range 1.4-11.5 Å⁻¹. The two "simulation" curves correspond to the sine-transform over 0 to 4.5 Å⁻¹ (black) and over 0 to 11.5 Å⁻¹ (blue) for the solute contribution to the difference signal calculated from the optimized AIMD. In the first case, the missing data points for q < 0.7 Å⁻¹ ("data" curve) due to the blocking of the direct beam were added through a smooth polynomial extrapolation slowly converging to 0 in order to avoid truncation artifacts.

[1] B.E. Warren, "X-ray diffraction", Dover Publications, inc., New York (1969)

10- Highlighting the photoinduced structural changes in the HS excited state of the solvated $[Fe^{II}(bpy)_3]^{2+}$ molecular complex

According to the kinematic diffraction limit, the correlation term of the X-ray scattering signal for a particular pair of atoms at a certain distance from each other is proportional to both atomic form factors, f(q), which are in turn proportional to the atomic number at least for q->0. Within a simple approximation, the "sensitivity" of the scattering signal to a specific atomic pair at a fixed distance can be thought as being proportional to the multiplication of their atomic numbers. All interatomic distances of the $[Fe^{II}(bpy)_3]^{2+}$ solute can then be gathered as a histogram plot taking into account the multiplicity of bond occurrence and the respective atomic numbers of the pairs. Figure S8 shows the corresponding distribution of sensitivity to the interatomic distances for the $[Fe^{II}(bpy)_3]^{2+}$ in the LS and HS states, along with the difference (same as Figure 4 (bottom) in the main text). Such a construction is not used in the analysis and serves purely for the clarity of visual representation.



Figure S8. Representation of the sensitivity of Thompson scattering to various interatomic distances for the $[Fe^{II}(bpy)_3]^{2+}$ molecule in the LS and HS states. The scattering power of specific atomic pairs is taken into account by multiplying to their atomic numbers i.e. $Z_n \times Z_m$.

11- Global structural sensitivity: rigid model selection and thermal disordering

According to Table S5, the statistical metrics for rigid model selection seem to indicate that the symmetric ⁵A-D₃ DFT structure is a better representation of the thermalized HS state than the less symmetric ⁵B-C₂ structure, despite the fact that the change in average Fe-N bond length (R_{av}) in C₂ symmetry is much closer to the one of the AIMD structure. This can be explained by a careful examination of how bond length changes between GS and ES affect the TR-WAXS solute signal $q.\Delta S_{Solute}(q)$ as a function of q. For example, the net elongation ΔR_{av} produces the dominant oscillatory differential scattering pattern. The quasi-period is directly related to the magnitude of ΔR_{av} . As a finer effect, several concurrent changes in individual bond lengths induce a superposition of quasi-oscillations, all dephased with respect to each other along the q axis depending on their magnitude. As such, the overall excursion around 0 of the TR-WAXS signal tends to reflect the distribution of bond length changes.

Figure S9 shows the q. ΔS_{Solute} (q) terms associated to the various structural models tested in this work scaled by an arbitrary constant for easier comparison for comparison. It is clear that the quasiperiod of the oscillations for the AIMD structure is closer to the one for the C₂ structures than for the D₃ structures. This can be traced back to the respective ΔR_{av} . On the contrary, the amplitude of the oscillation for the ⁵A-D₃ is the most closely distributed around the AIMD signal. With the present noise level, it seems that the contribution to the chi2 from the signals in the q-range 5.5-7 Å⁻¹ is larger than in the q-range above 7 Å⁻¹. In fact if the fit is done for q>7 1 Å⁻¹ the chi2 of the AIMD and ⁵B-C2 structures are extremely close (the AIMD fit remainaining slightly better), while the D₃ structures have larger chi2. However, it should be noted that the reduced data range limits the strict statistical validity of this observation.



Figure S9. Simulated differential signals $q.\Delta S_{solute}$ (q) associated to the ${}^{5}A-D_{3}$ (blue), ${}^{5}E-D_{3}$ (green) ${}^{5}A-C_{2}$ (red) ${}^{5}B-C_{2}$ (cyan) structures optimized with DFT and to the AIMD structure (violet).

Finally, the possible impact of thermal disordering on the structural model selection should be assessed. In the presented analysis, the GS and the ES structures are held rigid when calculating the scattering signals from the solute. This constraint was introduced in order to compare the DFT and AIMD geometries within the same set of approximations. When including a natural distribution of the inter-atomic distances within the solvated solute due to thermal motions, the exact Akaike ranking of the preferred DFT structures may very well change. Although this could be practically achieved for the AIMD structure through the g(r) of the solute, it is not clear how such a disordering could be consistently estimated within the framework of DFT optimization. Moreover, it could be proposed that the AIMD structure could still provide the best fit, since even in the rigid approximation, it already to some extent accounts for the dominant variations in the Fe-N bond lengths.

12- DFT optimized geometries : cartesian coordinates

|--|

Fe 0.000000 0.000000 0.00000

- N 1.509294 0.765499 1.045382
- N 1.509294 -0.765499 -1.045382
- C 2.761708 0.438867 0.588215
- C 1.405056 1.574647 2.127380
- C 2.518122 2.075196 2.798964
- C 3.796938 1.738398 2.342183
- C 3.916144 0.913610 1.224147
- C 2.761708 -0.438867 -0.588215
- C 1.405056 -1.574647 -2.127380

С	2.518122	-2.075196	-2.798964

- C 3.796938 -1.738398 -2.342183
- C 3.916144 -0.913610 -1.224147
- H 0.400446 1.809639 2.457852
- H 2.373890 2.715977 3.664999
- H 4.685286 2.111085 2.846163
- H 4.896939 0.640182 0.847879
- H 0.400446 -1.809639 -2.457852
- H 2.373890 -2.715977 -3.664999
- H 4.685286 -2.111085 -2.846163
- H 4.896939 -0.640182 -0.847879
- $N \qquad -0.091706 \ -1.689836 \ \ 1.045382$
- $\mathsf{N} \quad -1.417588 \ -0.924337 \ -1.045382$
- C -1.000784 -2.611143 0.588215
- C 0.661157 -2.004138 2.127380
- C 0.538112 -3.218355 2.798964
- C -0.392972 -4.157444 2.342183
- C -1.166863 -3.848285 1.224147
- C -1.760924 -2.172276 -0.588215
- C -2.066213 -0.429490 -2.127380
- C -3.056233 -1.143159 -2.798964
- C -3.403966 -2.419046 -2.342183
- C -2.749281 -2.934675 -1.224147
- H 1.366971 -1.251616 2.457852
- H 1.165160 -3.413838 3.664999
- H -0.514390 -5.113119 2.846163
- H -1.894055 -4.560965 0.847879
- H -1.767416 0.558024 -2.457852
- H -3.539050 -0.697861 -3.664999
- H -4.170896 -3.002034 -2.846163
- H -3.002884 -3.920783 -0.847879

- $N \qquad -1.417588 \quad 0.924337 \quad 1.045382$
- N -0.091706 1.689836 -1.045382
- C -1.760924 2.172276 0.588215
- C -2.066213 0.429490 2.127380
- C -3.056233 1.143159 2.798964
- C -3.403966 2.419046 2.342183
- C -2.749281 2.934675 1.224147
- $C \quad -1.000784 \quad 2.611143 \quad -0.588215$
- C 0.661157 2.004138 -2.127380
- C 0.538112 3.218355 -2.798964
- C -0.392972 4.157444 -2.342183
- C -1.166863 3.848285 -1.224147
- H -1.767416 -0.558024 2.457852
- H -3.539050 0.697861 3.664999
- H -4.170896 3.002034 2.846163
- H -3.002884 3.920783 0.847879
- H 1.366971 1.251616 -2.457852
- H 1.165160 3.413838 -3.664999
- H -0.514390 5.113119 -2.846163
- H -1.894055 4.560965 -0.847879

Geometry ⁵E-D₃ (HS)

Fe	0.000000	0.000000	0.000000
N	1.723395	0.758693	1.100672
Ν	1.723395	-0.758693	-1.100672
С	2.951756	0.438727	0.598554
С	1.640094	1.558078	2.185727
С	2.765123	2.072641	2.829598
С	4.028593	1.750199	2.321946
С	4.122592	0.929045	1.197207
С	2.951756	-0.438727	-0.598554

С	1.640094	-1.558078	-2.185727

- C 2.765123 -2.072641 -2.829598
- C 4.028593 -1.750199 -2.321946
- C 4.122592 -0.929045 -1.197207
- H 0.635251 1.779756 2.535628
- H 2.646682 2.708134 3.703354
- H 4.930632 2.132793 2.793889
- H 5.097601 0.678356 0.791757
- H 0.635251 -1.779756 -2.535628
- H 2.646682 -2.708134 -3.703354
- H 4.930632 -2.132793 -2.793889
- H 5.097601 -0.678356 -0.791757
- $N \qquad -0.204650 \quad -1.871850 \quad 1.100672$
- N -1.518744 -1.113157 -1.100672
- C -1.095929 -2.775659 0.598554
- C 0.529288 -2.199402 2.185727
- C 0.412398 -3.430987 2.829598
- C -0.498580 -4.363964 2.321946
- C -1.256720 -4.034792 1.197207
- C -1.855827 -2.336932 -0.598554
- C -2.169382 -0.641324 -2.185727
- C -3.177521 -1.358346 -2.829598
- C -3.530014 -2.613765 -2.321946
- C -2.865873 -3.105747 -1.197207
- H 1.223688 -1.440021 2.535628
- H 1.021971 -3.646161 3.703354
- H -0.618263 -5.336449 2.793889
- H -1.961327 -4.753830 0.791757
- H -1.858939 0.339734 -2.535628
- H -3.668653 -0.938027 -3.703354
- H -4.312369 -3.203656 -2.793889

- H -3.136274 -4.075474 -0.791757
- N -1.518744 1.113157 1.100672
- N -0.204650 1.871850 -1.100672
- $C \quad -1.855827 \quad 2.336932 \quad 0.598554$
- C -2.169382 0.641324 2.185727
- C -3.177521 1.358346 2.829598
- C -3.530014 2.613765 2.321946
- C -2.865873 3.105747 1.197207
- C -1.095929 2.775659 -0.598554
- C 0.529288 2.199402 -2.185727
- C 0.412398 3.430987 -2.829598
- $C \qquad -0.498580 \quad 4.363964 \quad -2.321946$
- C -1.256720 4.034792 -1.197207
- H -1.858939 -0.339734 2.535628
- H -3.668653 0.938027 3.703354
- H -4.312369 3.203656 2.793889
- H -3.136274 4.075474 0.791757
- H 1.223688 1.440021 -2.535628
- H 1.021971 3.646161 -3.703354
- H -0.618263 5.336449 -2.793889
- H -1.961327 4.753830 -0.791757

Geometry ⁵A₁-D₃ (HS)

Fe	0.000000	0.000000	0.000000
N	1.753811	0.729782	1.116568
N	1.753811	-0.729782	-1.116568
С	2.982106	0.418858	0.615192
С	1.665678	1.491063	2.226225
С	2.788958	1.979038	2.895536
С	4.053485	1.661119	2.390564
С	4.152027	0.874399	1.240429

- $C \qquad 2.982106 \ -0.418858 \ -0.615192$
- C 1.665678 -1.491063 -2.226225
- C 2.788958 -1.979038 -2.895536
- C 4.053485 -1.661119 -2.390564
- C 4.152027 -0.874399 -1.240429
- H 0.658963 1.704663 2.575687
- H 2.667834 2.587934 3.787863
- H 4.954144 2.020311 2.883226
- H 5.129210 0.626187 0.838840
- H 0.658963 -1.704663 -2.575687
- H 2.667834 -2.587934 -3.787863
- H 4.954144 -2.020311 -2.883226
- H 5.129210 -0.626187 -0.838840
- N -0.244896 -1.883736 1.116568
- N -1.508916 -1.153954 -1.116568
- C -1.128311 -2.792009 0.615192
- C 0.458459 -2.188051 2.226225
- C 0.319418 -3.404827 2.895536
- C -0.588172 -4.340981 2.390564
- C -1.318761 -4.032960 1.240429
- C -1.853795 -2.373151 -0.615192
- C -2.124137 -0.696988 -2.226225
- C -3.108376 -1.425789 -2.895536
- C -3.465314 -2.679862 -2.390564
- C -2.833265 -3.158561 -1.240429
- H 1.146800 -1.423011 2.575687
- H 0.907299 -3.604379 3.787863
- H -0.727432 -5.300570 2.883226
- H -2.022311 -4.755120 0.838840
- H -1.805763 0.281653 -2.575687
- H -3.575134 -1.016445 -3.787863

- H -4.226712 -3.280259 -2.883226
- H -3.106899 -4.128933 -0.838840
- N -1.508916 1.153954 1.116568
- N -0.244896 1.883736 -1.116568
- $C \quad -1.853795 \quad 2.373151 \quad 0.615192$
- C -2.124137 0.696988 2.226225
- $C \quad -3.108376 \quad 1.425789 \quad 2.895536$
- C -3.465314 2.679862 2.390564
- $C \quad -2.833265 \quad 3.158561 \quad 1.240429 \\$
- C -1.128311 2.792009 -0.615192
- C 0.458459 2.188051 -2.226225
- C 0.319418 3.404827 -2.895536
- C -0.588172 4.340981 -2.390564
- $C \qquad -1.318761 \quad 4.032960 \quad -1.240429 \\$
- H -1.805763 -0.281653 2.575687
- H -3.575134 1.016445 3.787863
- H -4.226712 3.280259 2.883226
- H -3.106899 4.128933 0.838840
- H 1.146800 1.423011 -2.575687
- H 0.907299 3.604379 -3.787863
- H -0.727432 5.300570 -2.883226
- H -2.022311 4.755120 -0.838840

Geometry ¹A-C₂ (LS)

Fe	0.000000	0.000000	-0.000866
N	1.291846	-0.059973	1.501057
N	-1.291846	0.059973	1.501057
С	0.732784	-0.042449	2.753648
С	2.640646	-0.136893	1.392786
С	3.480598	-0.188062	2.503316
С	2.916018	-0.164254	3.784807

С	1.527344	-0.091834	3.907263
С	-0.732784	0.042449	2.753648
С	-2.640646	0.136893	1.392786
С	-3.480598	0.188062	2.503316
С	-2.916018	0.164254	3.784807
С	-1.527344	0.091834	3.907263
Н	3.042215	-0.145119	0.387559
Н	4.555084	-0.245459	2.355507
Н	3.543730	-0.202271	4.670987
Н	1.064786	-0.073587	4.887963
Н	-3.042215	0.145119	0.387559
Н	-4.555084	0.245459	2.355507
Н	-3.543730	0.202271	4.670987
Н	-1.064786	0.073587	4.887963
N	-0.056815	1.978815	-0.089460
Ν	-1.376820	0.191696	-1.414003
С	-0.949811	2.497977	-0.992145
С	0.676408	2.834407	0.663722
С	0.565966	4.218598	0.548906
С	-0.340228	4.754487	-0.374802
С	-1.105373	3.881950	-1.150677
С	-1.686642	1.483732	-1.755838
С	-2.000615	-0.819729	-2.065642
С	-2.952274	-0.597837	-3.058921
С	-3.278879	0.719083	-3.406252
С	-2.636340	1.768327	-2.746694
Н	1.372283	2.385429	1.360803
Н	1.183562	4.855093	1.175907
Н	-0.448950	5.829635	-0.488868
н	-1.816620	4.269652	-1.871509
Н	-1.730063	-1.824026	-1.765361

- H -3.422884 -1.448047 -3.544046
- H -4.017990 0.925358 -4.175676
- H -2.867543 2.797500 -2.998596
- N 1.376820 -0.191696 -1.414003
- $\mathsf{N} \qquad 0.056815 \ -1.978815 \ -0.089460$
- C 1.686642 -1.483732 -1.755838
- C 2.000615 0.819729 -2.065642
- $C \qquad 2.952274 \quad 0.597837 \quad -3.058921$
- C 3.278879 -0.719083 -3.406252
- C 2.636340 -1.768327 -2.746694
- C 0.949811 -2.497977 -0.992145
- C -0.676408 -2.834407 0.663722
- C -0.565966 -4.218598 0.548906
- $C \qquad 0.340228 \ -4.754487 \ -0.374802$
- C 1.105373 -3.881950 -1.150677
- H 1.730063 1.824026 -1.765361
- H 3.422884 1.448047 -3.544046
- H 4.017990 -0.925358 -4.175676
- H 2.867543 -2.797500 -2.998596
- H -1.372283 -2.385429 1.360803
- H -1.183562 -4.855093 1.175907
- H 0.448950 -5.829635 -0.488868
- H 1.816620 -4.269652 -1.871509

Geometry ⁵A-C₂ (HS)

Fe	0.000000	0.000000	0.071017
N	1.338293	0.048790	1.784756
N	-1.338293	-0.048790	1.784756
С	0.743974	-0.013793	3.010221
С	2.684164	0.021496	1.695853
С	3.509237	-0.058940	2.817907

С	2.908996	-0.124998	4.080537
С	1.514512	-0.105664	4.178497
С	-0.743974	0.013793	3.010221
С	-2.684164	-0.021496	1.695853
С	-3.509237	0.058940	2.817907
С	-2.908996	0.124998	4.080537
С	-1.514512	0.105664	4.178497
н	3.092901	0.070662	0.691360
н	4.588610	-0.072202	2.698097
н	3.516106	-0.194970	4.979157
н	1.040163	-0.168392	5.151301
н	-3.092901	-0.070662	0.691360
н	-4.588610	0.072202	2.698097
н	-3.516106	0.194970	4.979157
н	-1.040163	0.168392	5.151301
Ν	-0.088776	2.133921	-0.213957
Ν	-1.527003	0.262228	-1.460107
С	-0.937468	2.584532	-1.184088
С	0.636458	3.023657	0.500068
С	0.566361	4.397943	0.282011
С	-0.290865	4.870283	-0.720417
С	-1.049458	3.957556	-1.456131
С	-1.719030	1.543438	-1.892489
С	-2.224357	-0.737559	-2.044031
С	-3.138724	-0.521269	-3.073805
С	-3.332111	0.788509	-3.531295
С	-2.615170	1.828212	-2.935625
н	1.291426	2.602470	1.255893
Н	1.169988	5.073242	0.881204
н	-0.370690	5.934749	-0.924716
Н	-1.721584	4.313903	-2.228336

- H -2.034270 -1.735085 -1.661334
- H -3.676004 -1.361064 -3.505098
- H -4.029138 0.997957 -4.338428
- H -2.754268 2.846335 -3.281182
- N 1.527003 -0.262228 -1.460107
- N 0.088776 -2.133921 -0.213957
- C 1.719030 -1.543438 -1.892489
- C 2.224357 0.737559 -2.044031
- C 3.138724 0.521269 -3.073805
- C 3.332111 -0.788509 -3.531295
- C 2.615170 -1.828212 -2.935625
- C 0.937468 -2.584532 -1.184088
- C -0.636458 -3.023657 0.500068
- $C \qquad -0.566361 \quad -4.397943 \quad 0.282011 \\$
- $C \qquad 0.290865 \ -4.870283 \ -0.720417$
- $C \qquad 1.049458 \ \ \text{-}3.957556 \ \ \text{-}1.456131$
- H 2.034270 1.735085 -1.661334
- H 3.676004 1.361064 -3.505098
- H 4.029138 -0.997957 -4.338428
- H 2.754268 -2.846335 -3.281182
- H -1.291426 -2.602470 1.255893
- H -1.169988 -5.073242 0.881204
- H 0.370690 -5.934749 -0.924716
- H 1.721584 -4.313903 -2.228336

Geometry ⁵B-C₂ (HS)

Fe	0.000000	0.000000	-0.059424
N	1.333302	-0.008297	1.645793
Ν	-1.333302	0.008297	1.645793
С	0.740227	-0.002506	2.876411
С	2.683627	-0.016594	1.567234

С	3.505971	-0.011859	2.691824
С	2.905964	-0.002787	3.957955
С	1.513219	0.000166	4.049315
С	-0.740227	0.002506	2.876411
С	-2.683627	0.016594	1.567234
С	-3.505971	0.011859	2.691824
С	-2.905964	0.002787	3.957955
С	-1.513219	-0.000166	4.049315
Н	3.099858	-0.022730	0.565263
Н	4.585580	-0.016169	2.572466
Н	3.512373	0.000953	4.859908
Н	1.036925	0.005601	5.023138
Н	-3.099858	0.022730	0.565263
Н	-4.585580	0.016169	2.572466
Н	-3.512373	-0.000953	4.859908
Н	-1.036925	-0.005601	5.023138
Ν	-0.054270	2.175847	-0.233917
Ν	-1.576567	0.369277	-1.487606
С	-1.042302	2.679592	-1.028841
С	0.729713	3.027486	0.460829
С	0.577587	4.412680	0.400850
С	-0.443296	4.937154	-0.401120
С	-1.262127	4.062563	-1.120268
С	-1.839243	1.675316	-1.779971
С	-2.229875	-0.608451	-2.151423
С	-3.185476	-0.340292	-3.130433
С	-3.472092	0.997048	-3.430299
С	-2.792571	2.012754	-2.752484
Н	1.497035	2.569263	1.076856
н	1.238865	5.055704	0.974507
н	-0.602667	6.010356	-0.465119

- H -2.060780 4.455729 -1.739231
- H -1.971329 -1.624677 -1.870643
- H -3.687718 -1.158784 -3.637600
- H -4.211201 1.248245 -4.186485
- H -2.997386 3.050765 -2.988627
- N 1.576567 -0.369277 -1.487606
- N 0.054270 -2.175847 -0.233917
- C 1.839243 -1.675316 -1.779971
- $C \qquad 2.229875 \quad 0.608451 \quad \text{-}2.151423$
- C 3.185476 0.340292 -3.130433
- C 3.472092 -0.997048 -3.430299
- C 2.792571 -2.012754 -2.752484
- $C \qquad 1.042302 \ \ \text{-}2.679592 \ \ \text{-}1.028841$
- C -0.729713 -3.027486 0.460829
- C -0.577587 -4.412680 0.400850
- $\mathsf{C} \qquad 0.443296 \ -4.937154 \ -0.401120$
- C 1.262127 -4.062563 -1.120268
- H 1.971329 1.624677 -1.870643
- H 3.687718 1.158784 -3.637600
- H 4.211201 -1.248245 -4.186485
- H 2.997386 -3.050765 -2.988627
- Н -1.497035 -2.569263 1.076856
- H -1.238865 -5.055704 0.974507
- H 0.602667 -6.010356 -0.465119
- H 2.060780 -4.455729 -1.739231