Dynamic Jahn–Teller Effect in the Metastable High-Spin State of Solvated [Fe(terpy)$_2$]$^{2+}$

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ABSTRACT: Characterizing structural distortions in the metastable spin states of d$^4$–d$^7$ transition metal ion complexes is crucial to understand the nature of their bistability and eventually control their switching dynamics. In particular, the impact of the Jahn–Teller effect needs to be assessed for any electronic configuration that could be effectively degenerate, as in e.g. the high-spin (HS) manifold of highly symmetric homoleptic Fe$^{II}$ complexes. However, capturing its manifestations remains challenging since crystallization generally alters the molecular conformations and their interconversion. With the rapid progress of ultrafast X-ray absorption spectroscopy, it is now possible to collect data with unprecedented signal-to-noise ratio, opening up for detailed structural characterization of transient species in the homogeneous solution phase. By combining the analysis of picosecond X-ray absorption spectra with DFT simulations, the structure of the photoinduced HS state is elucidated for solvated [Fe(terpy)$_2$]$_2^+$ (terpy = 2,2$'$,6$'$,2$''$-terpyridine). This species can be viewed as the average $^{1}B$ structure in $D_4h$ symmetry that originates from a dynamic Jahn–Teller effect in the HS manifold. These results evidence the active role played by this particular instance of vibronic coupling in the formation of the HS state for this benchmark molecule. Ultimately, correlating the interplay between intramolecular and intermolecular degrees of freedom to conformational strain and distortions in real time should contribute to the development of advanced functionalities in transition metal ion complexes.

INTRODUCTION

Spin crossover (SCO) materials based on d$^4$–d$^7$ transition metal ion complexes are enabling novel strategies to perform sensing,$^{1–3}$ switching,$^{4–10}$ and information storage$^{11}$ in nanodevices. Tailoring the mesoscopic properties of these advanced materials for specific applications requires understanding the bistability displayed by their building blocks at the molecular level.$^{17–21}$ For the quasi-octahedral (O$_6$) [Fe$^{II}$N$_6$] compounds, the ligand field (LF) splits the atomic-like 3d levels into t$_{2g}$ and e$_g$ orbitals. The relative strength of the LF splitting energy compared to the mean spin pairing energy determines the orbital populations and the energetics of the system.$^{22,23}$ A strong LF stabilizes the (t$_{2g}$)$^6$1$^A_g$ low-spin (LS) state over the (t$_{2g}$)$^4$(e$_g$)$^2$3$^T_{2g}$ high-spin (HS) state, leading to an increase of the HS–LS zero-point energy difference $\Delta E_0$.$^{22–24}$ The promotion of two electrons from the non- or weakly-bonding t$_{2g}$ orbitals to the antibonding e$_g$ orbitals causes an average elongation $\Delta R$ of all the metal–ligand (M–L) bonds.$^{22–24}$ The interdependence between $\Delta E_0$ and $\Delta R$ is experimentally evidenced by the alterations in spin-state distributions that result from modifying the M–L bonds through e.g. chemical addition of bulky substituents,$^{25,26}$ encapsulation,$^{27,28}$ or applied external pressure.$^{29,30}$ The parameters $\Delta E_0$ and $\Delta R$ also occur in the formulation of the HS $\rightarrow$ LS intersystem crossing as a nonadiabatic radiationless multiphonon process in the strong coupling limit.$^{31}$ When the HS population is impulsively triggered (e.g., photoinduced), the electronic and structural dynamics of the relaxation can be interpreted with kinetic models where $\Delta R$, which identifies to the totally symmetric Fe–N breathing mode, enters as the single effective reaction coordinate.$^{32–35}$ The lifetime of the metastable HS state follows then the inverse energy gap law; i.e., it increases with decreasing $\Delta E_0$.$^{32–35}$ Although a simple description of the static and dynamic properties in terms of $\Delta E_0$ and $\Delta R$ explains numerous physicochemical trends, it is generally challenged whenever the structural changes undergone by the complex across the spin-state transition amount to significant anisotropic distortions of the first coordination sphere.$^{36–49}$ Among the phenomena leading to such deformations, the Jahn–Teller (JT) effect needs to be explicitly considered for any electronic configuration that could be effectively degenerate,$^{50,51}$ as in e.g. the HS manifold of highly symmetric homoleptic Fe$^{II}$.
complexes. This distortion mediated by vibronic coupling enforces a symmetry lowering, which has a profound impact on the electronic and geometric structure of the HS state. As a mechanism for electron–phonon coupling, the JT effect promotes the synergy between the molecular attributes (e.g., optical and magnetic properties) and the response of the crystalline lattice during e.g. light-induced excited spin state trapping (LIESST) or cooperative phase transitions. Connecting the characteristics of the JT distortion with the emergence of particular mesoscopic properties would allow manipulating this effect through chemical design in order to further develop the bottom-up multifunctionality of SCO materials. A crucial step consists in describing the structural reorganization beyond an overall isotropic expansion of the metal coordination sphere. This in turn requires establishing the multimodal reaction coordinate that drives the anisotropic structural dynamics of the HS → LS transition. However, accessing the intrinsic JT distortion can seldom be achieved through crystallography because the molecular conformations are strongly perturbed by hydrogen bonding and packing forces. As such, delineating the respective role of intra- and intermolecular factors in shaping a given structure is not straightforward. X-ray absorption spectroscopy (XAS) is a technique able to probe the local bonding environment around a specific element without relying on long-range order. Having reached the picosecond and femtosecond regimes, this analytical tool has been successfully employed to track the manifold for this benchmark complex. The Journal of Physical Chemistry C

■ MATERIALS AND METHODS

Synthesis. [Fe(terpy)$_2$]$_2$(PF$_6$)$_2$ and the reference compound [Fe(bpy)$_3$](PF$_6$)$_2$ were prepared according to the published protocols. The commercial reagents were used without further purification.

Picosecond X-ray Absorption Spectroscopy. The time-resolved X-ray absorption spectroscopy (XAS) measurements were carried out at beamline 11ID-D of the APS, Argonne National Laboratory. The molecules were dissolved in acetonitrile (MeCN) to a 2 mM concentration. The solution was flown through a stainless steel tube forming a free jet of 550 μm in diameter. The sample was pumped with the second harmonic output of a Nd:YLF regenerative amplified laser at 527 nm (5 ps fwhm, 1.6 kHz repetition rate). The diameter of the laser spot size was 0.6 mm at the sample position, yielding a fluence of 1 mJ/mm². The X-ray probe pulses were delivered by the APS storage ring during the 24-bunch operation mode, which is characterized by a 80 ps fwhm and a 6.5 MHz repetition rate. The X-ray spot size was 0.45 mm (horizontal) by 0.15 mm (vertical) at the sample position. Two avalanche photodiodes (APDs) positioned at a 90° angle on both sides of the incident X-ray beam collected the X-ray fluorescence signal. A soller slits/Mn filter combination, which was custom-designed for the specific sample chamber configuration and the corresponding sample–detector distance, was inserted between the jet and the APDs. The outputs of the APDs were sent to two fast analyzer cards (Agilent) that were triggered at the optical pump frequency by a signal from scattered laser light collected by a photodiode. The card digitized the X-ray fluorescence signal as a function of time at 1 ns/point after each trigger and averaged repeated measurements at a given integration time, typically 4 s. A third APD identical to the two sample detectors collected the X-ray photons from air scattering before the sample and was used as normalization signal. Each X-ray pulse between two laser triggers was recorded. The fluorescence signal from the synchronized X-ray pulse was collected at chosen time delay t after excitation by the optical pump pulse in order to construct the laser$_{OFF}$(t) trace. Each individual X-ray bunch between two laser pulses was divided by the signal from the normalization detector corresponding to the same bunch. The fluorescence signal from the same X-ray pulse was averaged over 20 round trips in the storage ring prior to the laser pulse in order to construct the laser$_{OFF}$(t) trace, which provided the spectrum of the ground state species μ$_{GS}$. The fitting of the difference signal Δμ(t) = [laser$_{ON}$(t) − laser$_{OFF}$(t)] is described in the next section. The steady-state XAS spectrum of the reference powder sample was obtained in transmission mode at beamline 1811 of the MAXlab swedish synchrotron facility.

XAS Data Analysis and Fitting Procedure. The analysis of the XAS data was performed with the Athena and Artemis programs interfaced to FEFF$^{73–75}$ and IFEFFIT.$^{76,77}$ Athena was used for pre-edge background removal, post-edge normalization, and atomic background subtraction. A $R_{bg}$ of 1 was chosen as upper limit of the low-R region. This parameter fixes the number of knots for the spline employed in the atomic background simulation through the equation

$$R_{\text{knots}} = \frac{2R_{\text{bg}} \Delta k}{\pi}$$

$\Delta k$ is the spline range in $k$ space, where $k$ is the photoelectron wavenumber defined as

$$k = \frac{2m(E - E_0)}{\hbar^2}$$

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with \( E_0 \) being the absorption edge energy. The remaining oscillatory modulation \( \chi(k) \) is due to constructive and destructive interferences between the wave of the outgoing photoelectron directly ionized from the core orbital and the wave of the photoelectron backscattered off the surrounding atoms. Therefore, the function \( \chi(k) \) contains element-specific structural information. It can be expressed as

\[
\chi(k) = \sum_i \frac{S_0 N \mu(k)}{kR_i^2} e^{-2k^2 \sigma^2} e^{\frac{-2kR_i}{\lambda}} \sin[2kR_i + \delta_i(k)]
\]

where \( \lambda(k) \) is the photoelectron mean free path and \( S_0 \) is the amplitude reduction factor. For each neighboring shell \( i \) around the absorbing atom, \( \mu(k) \) is the scattering amplitude, \( \sigma^2 \) is the Debye–Waller factor, \( R_i \) is the average distance of \( i \)th shell atom to the absorbing atom, and \( \delta_i(k) \) is the corresponding phase shift. The DFT structure of the LS ground state was entered in Artemis in order to determine the scattering paths necessary to evaluate the \( \mu(k) \). Figure 1 shows the geometric structure of \([\text{Fe(terpy)}_2]^2+\) and the atom labeling used in the EXAFS fitting procedure.

![Figure 1. Schematic of the molecular structure of \([\text{Fe(terpy)}_2]^2+\) with the atom labeling used in the EXAFS fitting procedure.](image)

DFT Optimization. Density functional theory (DFT)\(^{79,80}\) has been applied to the determination of the geometry adopted by the \([\text{Fe(terpy)}_2]^2+\) complex in the LS and in the HS state. The calculations have been performed with the ADF program package\(^{81}\) using the PBE\(^{82}\) and RPBE functional,\(^{83}\) with the Slater-type TZP basis set of triple-\(\zeta\) polarized quality from the ADF basis set database.\(^{84,85}\) The calculations have been first performed for the complex in the gas phase. The influence of the acetonitrile solvent has then been taken into account using the conductor-like screening model (COSMO).\(^{86-89}\)

RESULTS AND DISCUSSION

Photoinduced HS State of \([\text{Fe(terpy)}_2]^2+\) from Transient XAS Experiment. The ground state of \([\text{Fe(terpy)}_2]^2+\) corresponds to a \((t_2g)^6\) LS configuration, for both the crystalline and the solution phase. The mer-tridentate coordination of the terpy ligand enforces a marked \(D_{2d}\) distortion of the first coordination sphere (FCS) away from ideal \(O_6\) symmetry, with the axial Fe–N\(_a\) bond length being shorter than the distal Fe–N\(_b\) one.\(^{90-92}\) Upon pulsed laser excitation at \(\lambda_{exc} = 527\) nm, a fraction \(\alpha\) of the molecules is promoted to the HS state on the subpicosecond time scale.\(^{46}\) Figure 2a shows the \(\mu_{\text{laser ON}}(t)\) (blue) and \(\mu_{\text{laser OFF}}\) (black) normalized XAS spectra at the Fe K-edge \((E_0 = 7109\) keV) for a pump–probe delay of \(t = 120\) ps. The inset shows the optical density for these two molecules. The red arrow indicates the excitation wavelength \(\lambda_{exc}\).

![Figure 2. (a) \(\mu_{\text{laser OFF}}\) and \(\mu_{\text{laser ON}}\) traces at \(t = 120\) ps for \([\text{Fe(terpy)}_2]^2+\). The inset zooms on the near-edge region. (b) Comparison between the difference traces \(\Delta \mu(t) = (\mu_{\text{laser ON}}(t) - \mu_{\text{laser OFF}})\) for \([\text{Fe(terpy)}_2]^2+\) (blue) and \([\text{Fe(bpy)}_3]^2+\) (red) at \(t = 120\) ps. The inset shows the optical density for these two molecules. The red arrow indicates the excitation wavelength \(\lambda_{exc}\).](image)
two $\Delta \mu(t)$ traces were obtained under the exact same experimental conditions (i.e., concentration, laser and X-ray focus, jet speed). The comparison with calibrated difference spectra of $[\text{Fe(bpy)}_3]^2$ allows estimating an $\alpha$ of $80 \pm 5\%$ for this experiment. The modifications of the spectral line shapes in the near-edge region reflect the bond elongation in the FCS, common to all the HS states of $[\text{Fe}^{II}\text{N}_6]$ complexes.

Figure 3a displays the $k^2$ weighted EXAFS function $\chi(k)$ extracted from $\mu_{\text{laser,OFF}}$ and $\mu_{\text{laser,ON}}(t)$ spectra for the solvated $[\text{Fe(terpy)}_2]^2$. Along with the one obtained for a static XAS spectrum of solid $[\text{Fe(terpy)}_2]_2[PF_6]_2$ (gray). It should be noted that the $\mu_{\text{laser,OFF}}$ spectrum is identical to the one of the powder sample, ruling out any influence of solution on this profile. On a $k$ scale, the slight alterations in oscillation amplitudes and the slow relative dephasing away from the edge energy can be traced back to the anisotropic expansion in $[\text{Fe(terpy)}_2]^2$ over $[\text{Fe(bpy)}_3]^2$ (Figure 3b).

Figures 4a and 4b contain respectively the amplitude and the phase for the Fourier transform of $k^2 \chi(k)$ in real ($R$) space directly extracted from the $\mu_{\text{laser,OFF}}$ and $\mu_{\text{laser,ON}}(t)$ spectra. The fit parameters for the LS and HS states are summarized in Table 1. The value of $82 \pm 8\%$ obtained for $\alpha$ (Figure 4c) from the $\chi^2$ minimization procedure is in excellent agreement with the reference measurements described above. Figure 4d shows the reconstructed $k^2 \chi(k)$ of the corresponding excited state spectrum. The structural parameters obtained for the LS state are in accord with previous crystallographic measurements, which report an average axial bond length Fe–N$_a$ of 1.885 Å and an average distal bond length Fe–N$_b$ of 1.981 Å. For the HS state, the bond lengths extracted from the XAS analysis can be compared to the results from DFT optimizations outlined in the next section.

**Photoinduced HS State of $[\text{Fe(terpy)}_2]^2$ from DFT Optimization.** To date, modeling simultaneously the structures and the energetics of open-shell transition metal complexes with good accuracy remains theoretically challenging. In DFT, most modern exchange-correlation functionals adequately predict the geometry adopted by the complexes in the different spin states and the relative energies of the states within the spin manifolds. However, the results obtained for the energy difference between the states of different spin multiplicities strongly depend on the selected functional, and so far, no functional has emerged as the one of choice. In this study, we have therefore used the PBE GGA functional, which exhibits the tendency of GGA functionals to strongly overestimate the HS–LS energy difference, along with the RPBE GGA functional, which was shown to give satisfactory estimates of this energy difference for $[\text{Fe(bpy)}_3]^2$ and $[\text{Fe(terpy)}_2]^2$. The improved performance of RPBE over PBE was ascribed to its larger gradient exchange correction, and because correlation turns off relative to exchange with an increase of the latter, RPBE tends to give slightly longer M–L bond than PBE. Both functionals have been employed to optimize first the $D_{sd}$ geometries of the LS and HS states for $[\text{Fe(terpy)}_2]^2$ in the gas phase and in MeCN using the COSMO solvation model. All the energetic and structural parameters are reported in the Supporting Information. In a $D_{sd}$ symmetry, the $^1A_1g$ (O$_g$) LS state becomes the $^1A_1$ (D$_{sd}$), state, while the $^3T_{2g}$ (O$_{2g}$) HS state splits into the two tetragonal components $^3E$ (D$_{sd}$) and $^3B_1$ (D$_{sd}$). As expected, the values of the Fe–N bond lengths obtained with RPBE are systematically larger than with PBE (by about $\sim 0.03 \text{ Å}$) due to the enhanced exchange interaction. Considering first the LS state, passing from the gas phase to the solution phase mainly translates into a minor shortening of the Fe–N bonds, which can be viewed as a means of reducing the exposure of the ligand aromatic rings to the polar solvent. Overall, the solvated $^1A_1$ (D$_{sd}$) geometries of the LS species are in very good agreement with the reported crystallographic structures and the present XAS measurements. Considering then the HS state, the $^3B_2$ (D$_{sd}$) state is found to lie lower in energy than the $^3E$ (D$_{sd}$) state with both functionals. Inclusion of solvation effects leads to a slight decrease of the Fe–N distances and destabilizes the $^3B_2$ (D$_{sd}$) and $^3E$ (D$_{sd}$) with respect to $^3A_1$ (D$_{sd}$) by about 700 cm$^{-1}$. Selected geometrical parameters for $^3E$ (D$_{sd}$) and $^3B_1$ (D$_{sd}$) are given in Table 2.

Comparison with the selected structural parameters returned by the present picosecond XAS analysis (Table 2) corroborates the earlier finding that the first coordination shell of the photoinduced HS state matches the one of the $^3E$ (D$_{sd}$) geometry better than the one of the $^3B_2$ (D$_{sd}$) geometry, especially when considering the difference $R_{\text{Fe–N}_{\text{a}}}$–$R_{\text{Fe–N}_{\text{b}}}$ for which most of the systematic errors cancel out. However, such a result cannot be readily rationalized, since $^3B_1$ (D$_{sd}$) is actually the state of lowest energy. It should be pointed out that it is not possible to strictly conclude about the equilibrated HS geometry from the $D_{sd}$ calculations due to vibronic instability. According to the JT theorem, any nonlinear system presenting an electronic degeneracy is further distorted by the coupling to some specific molecular vibrations (i.e., the JT-active modes), so as to lower the symmetry and the total energy. Since the direct product $E \otimes E$ in $D_{sd}$ contains the irreducible representations $A_1 + A_2 + B_1 + B_2$, the symmetries...
Transient XAS Measurement and DFT Calculations in probably arises from the vibronic coupling between the 5B2 e modes with imaginary frequencies of large modules. This vibrational instability, which is characterized by the presence of the photoinduced HS state. (c) Fitted excited state fraction $\alpha$. The value for $\alpha$ employed to build the traces in (b) and (d) was 82%.

Table 1. Fit Parameters for the LS and HS States of Solvated $[\text{Fe(terpy)}_2]^{2+}$

<table>
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<th></th>
<th>$\Delta E$ (eV)</th>
<th>$S^2$</th>
<th>$R_{Fe-N} (\text{axial})$ (Å)</th>
<th>$R_{Fe-N} (\text{distal})$ (Å)</th>
<th>$R_{Fe-C_A} (\text{C_A})$ (Å)</th>
<th>$R_{Fe-C_B} (\text{C_B})$ (Å)</th>
<th>$R_{Fe-C_C} (\text{C_C})$ (Å)</th>
<th>$\sigma^0_{Fe-C_{A,B}}$</th>
<th>$\sigma^0_{Fe-N_{A-B,C}}$</th>
<th>$\sigma^0_{Fe-N_{A-B,C}}$</th>
<th>$\alpha$ (%)</th>
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<td>LS</td>
<td>$-1.9 \pm 0.4$</td>
<td>0.97</td>
<td>1.86 ± 0.02</td>
<td>1.97 ± 0.02</td>
<td>2.80 ± 0.03</td>
<td>2.83 ± 0.03</td>
<td>2.99 ± 0.03</td>
<td>0.004 ± 0.003</td>
<td>0.004 ± 0.003</td>
<td>0.004 ± 0.003</td>
<td>82 ± 8</td>
</tr>
<tr>
<td>HS</td>
<td>0 ± 1</td>
<td>0.97</td>
<td>2.09 ± 0.02</td>
<td>2.18 ± 0.02</td>
<td>2.98 ± 0.02</td>
<td>3.02 ± 0.02</td>
<td>3.18 ± 0.02</td>
<td>0.004 ± 0.004</td>
<td>0.004 ± 0.004</td>
<td>0.004 ± 0.004</td>
<td>82 ± 8</td>
</tr>
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</table>

*D indicates the degeneracy of the scattering paths fixed in FEFF. The values kept constant during the optimization are indicated in italics.

Table 2. Comparison between Selected Structural Parameters in the HS State of Solvated $[\text{Fe(terpy)}_2]^{2+}$ Obtained from the Transient XAS Measurement and from the DFT Calculations in $D_{2d}$ Symmetry (Ref 46 and This Work)

<table>
<thead>
<tr>
<th></th>
<th>$R_{Fe-N} (\text{axial})$ (Å)</th>
<th>$R_{Fe-N} (\text{distal})$ (Å)</th>
<th>$R_{Fe-N}/R_{Fe-N}$ (Å)</th>
<th>$R_{Fe-C_A} (D = 6)$ (Å)</th>
<th>$R_{Fe-C_B} (D = 6)$ (Å)</th>
<th>$R_{Fe-C_C} (D = 6)$ (Å)</th>
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</thead>
<tbody>
<tr>
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<td>2.18 ± 0.02</td>
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<td>3.036</td>
<td>3.070</td>
<td>3.18 ± 0.03</td>
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<td>0.94</td>
<td>3.036</td>
<td>3.070</td>
<td>3.193</td>
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<tr>
<td>DFT (E):MeCN-D_{2d}</td>
<td>2.180</td>
<td>2.212</td>
<td>0.932</td>
<td>3.081</td>
<td>3.092</td>
<td>3.166</td>
</tr>
<tr>
<td>DFT (B_{2g}):MeCN-D_{2d}</td>
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<td>0.931</td>
<td>3.046</td>
<td>3.056</td>
<td>3.132</td>
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Figure 4. Amplitude and phase for the Fourier transform of the EXAFS function $k^2\chi(k)$ along with the best fit for (a) the LS ground state and for (b) the photoinduced HS state. (c) Fitted excited state fraction $\alpha$. (d) The EXAFS function $k^2\chi(k)$ of the photoinduced HS state for $[\text{Fe(terpy)}_2]^{2+}$. of the non-totally symmetric JT-active modes for the $^3E$ ($D_{2d}$) state are $a_{2g}$, $b_{1u}$, and $b_{2u}$. The $^3B_2$ ($D_{2d}$) geometry also exhibits a vibrational instability, which is characterized by the presence of e modes with imaginary frequencies of large modules. This probably arises from the vibronic coupling between the $^3B_2$ ($D_{2d}$) state and the close-lying $^3E$ ($D_{2d}$) state. In order to account for these effects, the optimizations were undertaken in the reduced $D_3$ symmetry. Upon $D_{2d} \rightarrow D_3$ symmetry lowering, $^3B_2$ ($D_{2d}$) becomes $^3B_1$ ($D_3$) while $^3E$ ($D_{2d}$) splits into $^3B_1$ ($D_3$) and $^3B_1$ ($D_3$), these two extrema of the HS potential energy surface being equivalent when interchanging the x- and y-axes. As expected, the JT effect has an impact on the $^3E$ ($D_{2d}$) configuration. Both in the gas phase and in MeCN, the $^3B_2$ ($D_3$) and $^3B_1$ ($D_3$) states are now predicted with PBE and the RPBE to be quasi-degenerate with $^3B_1$ ($D_3$) within the so-called chemical accuracy of $\pm 350 \text{ cm}^{-1}$ (see Supporting Information). The $^3B_1$ ($D_3$) state is predicted to coincide with the $^3B_2$ ($D_{2d}$) state on the HS potential energy surface. Attempting to localize it invariably returns either the $^3B$ ($D_{2d}$) state or the $^3B_1$ ($D_3$).
component of the excited ligand-field $^3E$ ($O_h$) state originating from the $(t_{2g})^3(t_{2g})^3$ ($O_h$) configuration. The calculations performed in the gas phase and in MeCN led to a $D_2$ $^5B_2$ geometry, which is given as a minimum by the vibrational analysis conducted on the gas-phase geometry. The energetics of the complex in the gas phase and solvated in MeCN for the $D_2$ and $D_2$ symmetries are displayed in Figures 5 and 6. The comparison with the selected structural parameters returned by the present picosecond XAS analysis is outlined in Table 3.

Finally, it should be noted that the geometries optimized in the lower $C_2$ symmetry systematically resemble very closely the ones obtained in $D_2$ symmetry. This can be readily traced back to the fact that the various HS states only differ through the occupation of the split $t_{2g}$ nonbonding orbitals.

Dynamic Nature of the Vibronic Coupling in the Photoinduced HS State of [Fe(terpy)$_2$]$^{2+}$. The present experimental and theoretical results clearly demonstrate that including the JT effect is crucial for obtaining a consistent picture of the electronic and geometric structure adopted by the solvated HS state. Since the electron–phonon coupling strength is always finite in solution phase, the fluctuations due to the ionic motions have to be considered in order to understand the dynamic nature of the vibronic coupling across the spin-state transition. Several studies have already suggested that the solvent plays a significant role. For example, the crystal structure of [Fe(terpy)$_2$(ClO$_4$)$_2$]H$_2$O,90 where the complex is in the LS state, reveals that some solvent molecules are nested in the accessible voids between the ligands, reflecting a strong conformational correlation of the complex with its first solvation shell. Upon photoabsorption, the Franck–Condon state is formed instantaneously in the average solvent cage that was accommodating the LS ground state. It then decays via ultrafast intersystem crossing to the HS state, in which the high-frequency Fe–N stretching mode and some of the low-

Table 3. Comparison between Selected Structural Parameters in the HS State of Solvated [Fe(terpy)$_2$]$^{2+}$ Obtained from the Transient XAS Measurement and from the DFT Calculations in $D_2$ Symmetry

<table>
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<th>HS state</th>
<th>$R_{Fe-N_a}$ (axial) (Å)</th>
<th>$R_{Fe-N_b}$ (distal) (Å)</th>
<th>$R_{Fe-N_a} - R_{Fe-N_b}$ (Å)</th>
<th>$R_{Fe-N_a}/R_{Fe-N_b}$</th>
<th>$R_{Fe-C_a}$ (Å) ($D = 6$)</th>
<th>$R_{Fe-C_b}$ (Å) ($D = 6$)</th>
<th>$R_{Fe-C_c}$ (Å) ($D = 6$)</th>
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<tr>
<td>DFT ($^3h_2^2h_1$)-MeCN-$D_2$</td>
<td>2.127</td>
<td>2.224</td>
<td>0.097</td>
<td>0.956</td>
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<td>3.203</td>
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<td>complex solvated in MeCN</td>
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<tr>
<td>DFT ($^3h_2^2h_1$)-MeCN-$D_2$</td>
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<td>2.189</td>
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<td>0.960</td>
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</tbody>
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frequency modes involving ligands and solvent are collectively excited. Whenever the electronic configuration would be degenerate, the JT-active modes also take part to the stabilization of the equilibrated HS state, as reported here for the photoinduced HS state of [Fe(terpy)]$^{2+}$ in MeCN. Concurrently, the solvent molecules reorient around the vibrationally hot HS state as it thermalizes within a few picoseconds by dissipating the excess energy to the surroundings as heat. Overall, the structural changes in the first solvation shell amount to more than 50% of the bulk solvent reorganization energy for [Fe(terpy)]$^{2+}$ in dimethyl sulfoxide.99 Femtosecond transient absorption spectroscopy in the UV−vis region has also shown that the unimolecular rate constants of the HS → LS transition are solvent-dependent for most [Fe$^{16}$N$_6$] complexes.99−101 These findings highlight the necessity of developing further the multiscale description of spin-state transitions. Theoretically, a full vibronic treatment beyond the Born−Oppenheimer approximation has to be performed considering that the internal electronic and the nuclear degrees of freedom are all strongly coupled.102−105 In addition, the solvation models have to be refined in order to account for the specific solute−solvent interactions.102−106 Experimentally, establishing the multimodal reaction coordinate of the spin-state transition requires tracking the ultrafast structural dynamics with spin and element sensitivity on several length scales scale. Although an exhaustive real-time mapping at the molecular level is still currently lacking, the essential tools are rapidly emerging, and some of them have already been applied to the benchmark complex [Fe(bpy)$_3$]$^{2+}$ in aqueous solution. Femtosecond X-ray emission spectroscopy measurements have recently uncovered the intermediate triplet state that mediates the photoinduced formation of its HS state.107 Simultaneous X-ray spectroscopy and scattering experiments reaching the typical ∼100 ps temporal resolution at a storage ring facility have captured the global structural changes in the photoexcited solute, the temperature increase in the bulk solvent, and the density increase associated with the response of the caging solvent.109 This last observation quantitatively agrees with ab initio molecular dynamics (MD) simulations predicting that the Fe−N bond elongation in the HS state triggers on average the expulsion of two water molecules from the first solvation shell.102 An improved model electronic Hamiltonian104,105 has been employed in the MD simulations of the low-lying electronic states of [Fe(bpy)$_3$]$^{2+}$ in aqueous solution. For this complex, the $^2$T$_{2g}$ (O$_h$) HS state is split by the D$_3$ LF into the $^4$E (D$_3$) and $^4$A$_1$ (D$_3$) components. Under the influence of the JT effect, $^3$E (D$_3$) further splits into the $^5$A$_2$ (C$_2$) and $^5$B (C$_2$) states, while $^5$A$_1$ (D$_3$) becomes the $^5$A$_1$ (C$_2$) state. These MD simulations indicate that the $^5$B (C$_2$) component is stabilized compared to $^5$E (D$_3$) but that the $^5$A$_1$ (C$_2$) remains the state of lowest energy, a conclusion, which could be readily tested with picosecond XAS measurements achieving high S/N ratio. Comparing the manifestations of the dynamic JT effect for the bidentate and tridentate coordination in Fe$^{11}$ complexes also awaits similar ab initio MD simulations and complementary ultrafast X-ray scattering measurements for the HS state of solvated [Fe(terpy)$_2$]$^{2+}$.

**CONCLUSION**

In summary, the transient HS state of solvated [Fe(terpy)$_2$]$^{2+}$ has been reinvestigated through the analysis of picosecond X-ray spectra obtained with high S/N ratio. The comparison with DFT calculations performed in $D_{2d}$ and $D_3$ symmetry shows that this species can be viewed as the average $^3$B structure in $D_3$ symmetry that originates from a dynamic Jahn−Teller effect in the HS manifold. These results highlight the importance of accounting for this effect in order to conciliate the energetics and the structural parameters obtained through experiment and theory. More generally, this study suggests that intramolecular vibronic coupling, which is strongly influenced by specific interactions with the solvation shell, plays a crucial role in the formation of the metastable state. Consequently, establishing the complete reaction coordinate that encodes the ultrafast structural dynamics of spin-state transitions in 3d transition metal complexes requires elaborating a refined atomic-scale description for the interplay between intramolecular and intermolecular degrees of freedom. Harnessing the detailed characterization of subtle structural rearrangements should facilitate the tailoring of the anisotropic distortions within this class of complexes in order to tune their electronic and magnetic properties. Since investigations in the homogeneous solution phase are accessing intrinsic deformations, they constitute stepping stones in the design of novel strategies able to translate molecular distortion and conformational strain into advanced functionalities.

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**ASSOCIATED CONTENT**

Supporting information

Results of the optimization calculations performed for [Fe(terpy)$_2$]$^{2+}$ in the gas phase and in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

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