

Picosecond Time-Resolved X-Ray Emission Spectroscopy: Ultrafast Spin-State Determination in an Iron Complex**

György Vankó,* Pieter Glatzel,* Van-Thai Pham, Rafael Abela, Daniel Grolimund, Camelia N. Borca, Steven L. Johnson, Christopher J. Milne, and Christian Bressler*

Molecular systems with switchable electronic states have fascinated scientists for decades, in part due to their potential as ultrasmall magnetic devices. Among them, transition-metal-based spin-crossover (SCO) compounds exhibit strikingly different properties, both structural and electronic, between their isoelectronic low-spin (LS) and high-spin (HS) states. Previous research resulted in a rich knowledge of the involved electronic states and key factors that affect the spin-transition conditions.^[1] At low temperature ($T < 50$ K) many different excitations, including visible light, hard and soft X rays, and even nuclear decay, can leave an Fe^{2+} SCO system in a very long-lived HS state.^[2,3] Studies of the temperature and ligand dependence of the lifetime of this HS state led to valuable insights into the electronic structure of SCO complexes.^[4] Nevertheless, these mostly indirect tools left many details about the switching process and the involved electronic states in ambiguity.^[5]

Ultrafast laser techniques offer direct real-time insight into the elementary steps of photoinduced spin transitions.^[6–8]

Applying X-ray absorption spectroscopy (XAS) in combination with laser pumping has proven to be very successful; for example, the structure of the putative HS $^5\text{T}_2$ excited state of $[\text{Fe}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) was directly determined by picosecond-resolved XAS at the Fe K-edge.^[9] A recent structural dynamics study exploiting X radiation in the femtosecond range^[10] delivered a surprisingly simple picture of the photoinduced spin-state switching of aqueous $[\text{Fe}(\text{bpy})_3]^{2+}$: Following laser excitation into the singlet metal-to-ligand charge-transfer ($^1\text{MLCT}$) manifold, prompt (within about 30 fs) intersystem crossing to the $^3\text{MLCT}$ states occurs, and backtransfer of the excited electron to the central atom (with a lifetime of 130 fs) goes straight into the HS $^5\text{T}_2$ state, and thus all of the metal-centered ligand-field states that lie between are bypassed.

However, to unravel the elementary steps in this spin transition one needs observe both the geometric and electronic changes in real time. While X-ray absorption and scattering experiments often emphasize the geometric structure, optical spectroscopic methods address a mixture of vibrational and electronic levels within the entire molecule. Element-sensitive detection of the spin state itself has not been achieved on the subnanosecond timescale. Application of a technique that can unambiguously identify the spin state in bulk media under ambient conditions is thus of great interest for distinguishing electronic from structural variations.

Here we report on direct detection of the spin state of aqueous $[\text{Fe}(\text{bpy})_3]^{2+}$ molecules 60 ps after an ultrashort laser pulse excitation by time-resolved X-ray emission spectroscopy for the first time. Hereby, the laser induces a low-spin to high-spin conversion, which switches back to the LS state on a subnanosecond timescale. We detect the variation of the iron $\text{K}\alpha$ line shape, which unambiguously determines the actual spin state. The interpretation of the time-resolved data is supported by theoretical crystal-field multiplet calculations and experimental $\text{K}\alpha$ spectra of related HS and LS Fe^{2+} reference compounds.

1s X-ray emission spectroscopy (XES) represents a direct probe of the spin state of 3d transition metals, due to the exchange interaction of the core hole with the 3d electrons in the final state.^[11] Hereby, both $\text{K}\alpha$ and $\text{K}\beta$ lines have proved useful as sensitive probes of the spin state.^[12] The $\text{K}\beta$ emission line has been the typical choice for spin-state studies, since the number of unpaired electrons is reflected in the intensity of the $\text{K}\beta'$ satellite peak, which is well separated from the main line due to the large 3p3d exchange interaction.^[13] However, it has been shown both theoretically and experimentally that the $\text{K}\alpha$ lines provide similar information.^[12,14]

[*] Dr. G. Vankó
KFKI Research Institute for Particle and Nuclear Physics
P.O.B. 49, 1525 Budapest (Hungary)
E-mail: vanko@rmki.kfki.hu

Dr. P. Glatzel
European Synchrotron Radiation Facility
Boîte Postale 220, 38043 Grenoble Cedex 9 (France)
E-mail: pieter.glatzel@esrf.fr

Dr. C. Bressler
European XFEL GmbH
Albert Einstein Ring 19, 22 607 Hamburg (Germany)
Fax: (+49) 40-8998-1904
E-mail: christian.bressler@xfel.eu

V.-T. Pham, Dr. C. J. Milne
Laboratoire de Spectroscopie Ultrarapide
Ecole Polytechnique Fédérale de Lausanne
1015 Lausanne (Switzerland)

Dr. R. Abela, Dr. D. Grolimund, Dr. C. N. Borca, Dr. S. L. Johnson
Swiss Light Source, Paul-Scherrer Institut
5232 Villigen PSI (Switzerland)

[**] This work was funded by the Swiss National Science Foundation via contracts no. PP002-110464, 2000-059146.99, 200021-107956, and 620-66145.01, by the Hungarian Scientific Research Fund (OTKA) under contract No. K 72597, and by the Swiss Light Source (SLS). G.V. acknowledges support from the Bolyai János Fellowship. The ESRF support groups and the staff of ID26 are gratefully acknowledged. We thank A. Hauser (University of Geneva) for providing us with the $[\text{Fe}(\text{bpy})_3]\text{Cl}_2$ sample, and M. Willmann and B. Meyer (PSI) for their technical expertise in setting up the XES spectrometer.



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201000844>.

The $K\alpha$ emission after photoionization can be treated as a second-order process in which initially a hole in the 1s shell is created and subsequently refilled by an electron from the 2p level (Figure 1 a). The final state electron configuration in

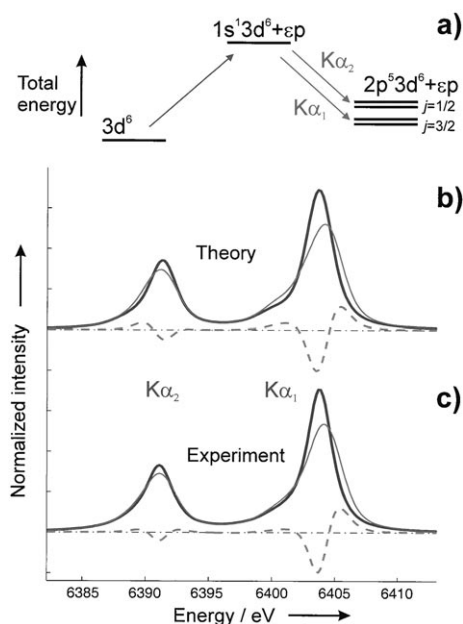


Figure 1. a) Energy scheme for $K\alpha$ emission in Fe^{2+} . Only open shells are considered and the photoexcited electron in the continuum is denoted ϵp . b) Calculated $K\alpha$ fluorescence lines for HS (thin line) and LS (thick line) Fe^{2+} in an octahedral crystal field. The difference spectrum is also shown (dashed line). c) Experimental $K\alpha$ spectra of HS and LS Fe^{2+} reference compounds ($[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{bpy})_3]\text{Cl}_2$ powders, respectively).

Fe^{2+} is thus $1s^22p^53d^6$, which is affected by a strong 2p spin-orbit interaction that splits the final states and results in the $K\alpha_1$ ($j = 3/2$) and $K\alpha_2$ ($j = 1/2$) emission lines. The interaction between the unpaired electron in the 2p shell and the 3d electrons splits the final states further. These (2p,3d) Coulomb and exchange interactions give rise to a rich multiplet structure that cannot be resolved individually due to the core-hole lifetime width, but effectively results in an additional broadening of the $K\alpha_1$ and $K\alpha_2$ line shapes. The exchange interaction between unpaired spins renders the $K\alpha$ emission sensitive to the spin state in the 3d shell. No exchange interaction is present in a low-spin $3d^6$ configuration (with $S = 0$) and the $K\alpha_1$ line is sharp compared to that of the high-spin form ($S = 2$) with a strong (2p,3d) exchange interaction (Figure 1 b).

We measured these effects using LS $[\text{Fe}(\text{bpy})_3]\text{Cl}_2$ and the HS form of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (phen = 1,10-phenanthroline) for reference (Figure 1 c, experimental details in Supporting Information); the spectra and their difference compare well with theoretical calculations, which clearly reinforces the use of this technique as a spin probe.

We implemented XES for time-resolved experiments at the microXAS beamline of the Swiss Light Source. Details of the core experimental setup, data collection, and initial data treatment strategies were published elsewhere;^[15] Figure 2 summarizes the new TR-XES setup and data acquisition

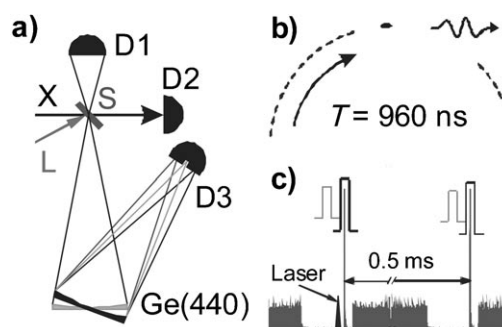


Figure 2. a) Setup for TR-XES (top view). The laser (L) and X-ray (X) beams congruently overlap on the 0.1 mm thick liquid jet (S) tilted at 45° . Fast avalanche photodiodes collect the total fluorescence (D1), transmitted intensity (D2), and XES intensity (D3). b) Schematic of the electron-bunch filling pattern at the Swiss Light Source. Several 2 ns-spaced bunches are followed by an approximately 200 ns long empty section, in which one densely packed electron bunch is placed (round trip time 960 ns). The 1 kHz laser is synchronized to this single pulse with an adjustable time delay. c) The (monochromatized) X-radiation, composed of an approximately 760 ns-long “superbunch” together with the well-separated 100 ps-long isolated pulse, is fed into a gated integrator within its approximately 20 ns-long time window [indicated in c)] at twice the repetition rate of the femtosecond laser, together with two additional measurements within the empty gap for dynamic background correction. Thus, the output signal of the gated integrator consists of alternating laser-on/laser-off X-ray intensities, and pairwise subtraction delivers the photoinduced X-ray intensity change.

applied for the reported experiment (further details in the Supporting Information).

With this setup we measured the difference between the laser-excited and ground-state XES photons at a time delay of 60 ps. At this time delay only the HS 3T_2 state should remain populated. Indeed, the transient spectrum in Figure 3 shows very good agreement with the expected variation shown in Figures 1 b and c. This provides evidence that the 665 ps-lifetime (at 300 K) excited state of $[\text{Fe}(\text{bpy})_3]^{2+}$ is indeed an $S = 2$ HS state. To the best of our knowledge, this is the first direct determination of the spin momentum of a transient species on the ultrafast timescale. We emphasize that previous measurements on $[\text{Fe}(\text{bpy})_3]^{2+}$ were not directly sensitive to the precise number of spin-unpaired valence electrons; this is now achieved by time-resolved XES. While the X-ray absorption fine structure at the edge is shaped by a complex interplay between structural and electronic effects, the rather simple spectral shape and theoretically well understood electron–electron interactions in K-shell emission spectroscopy allow for unambiguous interpretation of spin state. X-ray absorption and emission spectroscopy are thus complementary techniques and their combination allows disentanglement of structural from electronic changes.

Already a change of oxidation state implies a change in spin state, and the X-ray emission lines are likewise sensitive to electron-transport phenomena in general, for example, redox reactions in photochemistry.^[11] Time-resolved X-ray emission spectroscopy is thus a viable tool for element-selective studies on electronic structure during ultrafast processes. The limit in time resolution is governed by the core-hole lifetime, which is on the order of a few femtoseconds for 3d transition metals. Nonresonant X-ray emission

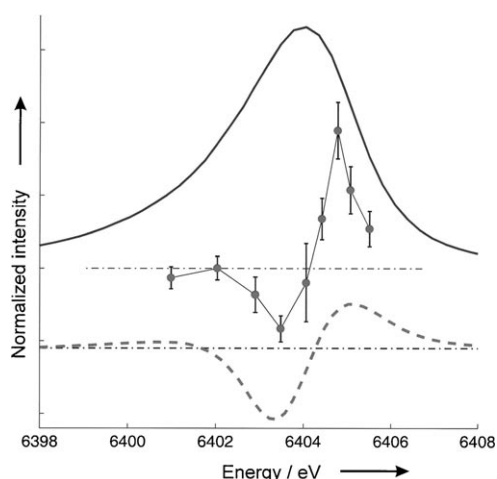


Figure 3. TR-XES results for an aqueous solution of $[\text{Fe}(\text{bpy})_3]^{2+}$. The solid line is the $\text{K}\alpha_1$ emission line measured on the ground state (scaled down by a factor of 9). Circles with error bars (one standard deviation) represent the spectral difference between XES measured at 60 ps after laser excitation and XES of the ground state. The expected effect at 10% excitation yield is shown as a dashed line: this corresponds to the spectral difference for 10% HS content, which was constructed from the HS and LS reference spectra in Figure 1 c).

spectroscopy does not require tunability of the incident energy and is thus an attractive technique for upcoming large-scale X-ray sources with femtosecond time resolution (X-ray free-electron lasers). These will not only provide access to the femtosecond time regime but will also enable the study of fluorescence lines with extremely low yield. The valence-to-core X-ray emission, for example, has been shown to be a sensitive probe of the ligand sphere,^[16] and femtosecond XES can track the ultrafast changes, which reveal the interplay between electronic and nuclear dynamics.

A fascinating prospect for combining X-ray absorption and emission spectroscopies on the femtosecond timescale is the possibility to study the temporal evolution of the geometric structural and electronic changes separately, and thus address the fundamental question of what triggers which kind of response. Thus, the information that now becomes available in time-resolved X-ray emission spectroscopy will help to address the elementary steps of different processes related to physical and chemical transformations in chemistry, materials science, and molecular biology.

Experimental Section

The laser pump/X-ray emission probe experiments were performed at the microXAS beam line of the Swiss Light Source at the Paul Scherrer Institute. The core experimental strategy is described in detail elsewhere,^[15] and for this specific XES experiment (Figure 2) in the Supporting Information.

Received: February 10, 2010
 Revised: May 21, 2010
 Published online: July 7, 2010

Keywords: femtochemistry · iron · spin crossover · time-resolved spectroscopy · X-ray emission spectroscopy

- [1] *Spin Crossover in Transition Metal Complexes, Vols. I–III* (Eds.: P. Gütllich, H. A. Goodwin), Springer, Heidelberg, **2004**, *Top. Curr. Chem.*, 233–235.
- [2] S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* **1984**, *105*, 1–4.
- [3] P. Gütllich, A. Hauser, H. Spiering, *Angew. Chem.* **1994**, *106*, 2109–2141; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024–2054; G. Vankó, F. Renz, G. Molnár, T. Neisius, S. Kárpáti, *Angew. Chem.* **2007**, *119*, 5400–5403; *Angew. Chem. Int. Ed.* **2007**, *46*, 5306–5309; D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn, N. A. Young, *J. Chem. Soc. Dalton Trans.* **1997**, 4371–4376.
- [4] A. Hauser, *Top. Curr. Chem.* **2004**, *234*, 155–198.
- [5] C. Brady, J. McGarvey, J. McCusker, H. Toftlund, D. Hendrickson, *Top. Curr. Chem.* **2004**, *235*, 173–184.
- [6] J. K. McCusker, K. N. Walda, R. C. Dunn, J. D. Simon, D. Magde, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 298–307.
- [7] J. E. Monat, J. K. McCusker, *J. Am. Chem. Soc.* **2000**, *122*, 4092–4097.
- [8] W. Gawelda, A. Cannizzo, V.-T. Pham, F. van Mourik, C. Bressler, M. Chergui, *J. Am. Chem. Soc.* **2007**, *129*, 8199–8206.
- [9] W. Gawelda, V.-T. Pham, M. Benfatto, Y. Zauschitsyn, M. Kaiser, D. Grolimund, S. L. Johnson, R. Abela, A. Hauser, C. Bressler, M. Chergui, *Phys. Rev. Lett.* **2007**, *98*, 057401.
- [10] C. Bressler, C. Milne, V.-T. Pham, A. ElNahhas, R. M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser, C. N. Borca, G. Ingold, R. Abela, M. Chergui, *Science* **2009**, *323*, 489–492.
- [11] a) P. Glatzel, U. Bergmann, *Coord. Chem. Rev.* **2005**, *249*, 65–95; b) F. M. F. de Groot, A. Kotani in *Core Level Spectroscopy of Solids*, Taylor and Francis, New York, **2008**.
- [12] G. Vankó, T. Neisius, G. Molnár, F. Renz, S. Kárpáti, A. Shukla, F. M. F. de Groot, *J. Phys. Chem. B* **2006**, *110*, 11647–11653.
- [13] J.-P. Rueff, C.-C. Kao, V. V. Struzhkin, J. Badro, J. Shu, R. J. Hemley, H. K. Mao, *Phys. Rev. Lett.* **1999**, *82*, 3284–3287; J. Badro, J.-P. Rueff, G. Vankó, G. Monaco, G. Fiquet, F. Guyot, *Science* **2004**, *305*, 383–386; J.-P. Rueff, A. Mattila, J. Badro, G. Vankó, A. Shukla, *J. Phys. Condens. Matter* **2005**, *17*, S717–S726; J.-F. Lin, G. Vankó, S. D. Jacobsen, V. Iota, V. V. Struzhkin, V. B. Prakapenka, A. Kuznetsov, C.-S. Yoo, *Science* **2007**, *317*, 1740–1743.
- [14] X. Wang, F. M. F. de Groot, S. P. Cramer, *Phys. Rev. B* **1997**, *56*, 4553–4564; G. Peng, F. M. F. de Groot, K. Hämäläinen, J. A. Moore, X. Wang, M. M. Grush, J. B. Hastings, D. P. Siddons, W. H. Armstrong, O. C. Mullins, S. P. Cramer, *J. Am. Chem. Soc.* **1994**, *116*, 2914–2920.
- [15] W. Gawelda, V. T. Pham, A. El Nahhas, S. L. Johnson, D. Grolimund, M. Kaiser, R. Abela, M. Chergui, C. Bressler, *Proc. SPIE* **2007**, *6727*, 67271P; C. Bressler, R. Abela, M. Chergui, *Z. Kristallogr.* **2008**, *223*, 307–321; W. Gawelda, V. T. Pham, A. El Nahhas, M. Kaiser, Y. Zauschitsyn, S. Johnson, D. Grolimund, R. Abela, A. Hauser, C. Bressler, M. Chergui, *AIP Conf. Proc.* **2007**, *882*, 31–36.
- [16] G. Smolentsev, A. Soldatov, J. Messinger, K. Merz, T. Weyermüller, U. Bergmann, Y. Pushkar, J. Yano, V. K. Yachandra, P. Glatzel, *J. Am. Chem. Soc.* **2009**, *131*, 12451–12457.