



Spin-polarized and site-selective X-ray absorption. Demonstration with Fe porphyrins and $K\beta$ detection

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Abstract

High-spin and low-spin Fe(III) porphyrins were studied by high resolution X-ray fluorescence and fluorescence-detected X-ray absorption spectroscopy using synchrotron radiation. The high-spin $K\beta$ spectrum is split into a main peak ($K\beta_{1,3}$) and a satellite ($K\beta'$) at 15 eV lower energy. The low-spin $K\beta_{1,3}$ peak shifted ≈ 0.7 eV to lower energy, and the $K\beta'$ feature is almost unobservable. Ligand field multiplet calculations show that spin-up (5A_1) and spin-down (7A_1) states are separated for the high-spin spectrum. Spin polarization of the $K\beta$ -detected absorption was demonstrated by enhancement or elimination of the $1s \rightarrow 3d$ transition, depending on the $K\beta$ region used for detection.

1. Introduction

X-ray absorption is now a popular tool for structure determination [1]. A strength and limitation of this technique is that it is sensitive to all different species of the same element in a sample; this makes characterization of mixtures difficult. An ideal detection method would allow the spectra for different chemical species to be recorded separately. One approach that appears promising is to use chemical shifts in X-ray emission during fluorescence-detected X-ray absorption [2] as the means to gain this selectivity [3].

The chemical sensitivity of $K\beta$ X-ray emission spectra has been known for many years [4], and the advantages of using synchrotron radiation as an excitation source have been demonstrated [5–8]. Typical

shifts are on the order of 1 eV per oxidation state change. The final state after $K\beta$ X-ray emission has a 3p core hole for a first transition series metal. Coulomb and exchange interactions between the partially filled 3p and 3d shells make the overall shape of these spectra sensitive to the number and configuration of 3d electrons, hence to the spin state and oxidation state [4–7].

In favorable cases, $K\beta$ emission multiplet splittings can be separated into spin-up and spin-down regions [5–7]. $K\beta$ detection can then be used to record spin-polarized excitation spectra, without the need for circularly-polarized X-rays or spin-polarized samples. This internally referenced spin-polarized X-ray absorption can provide some information comparable to X-ray magnetic circular dichroism (XMCD) [9] and spin-polarized extended X-ray ab-

sorption fine structure (SPEXAFS) measurements [10].

In this Letter, we report $K\beta$ emission and spin-selective excitation spectra of high-spin and low-spin Fe porphyrins [11]. Fe porphyrins serve as electron transfer agents in various cytochromes, in oxygen transport in hemoglobin, as well as in critical enzymes such as cytochrome c oxidase [12] and cytochrome P-450 [13]. The $K\beta$ emission spectra are compared with ligand field multiplet calculations, which predict regions of spin-up and spin-down selectivity. These predictions were then confirmed by recording $K\beta_{1,3}$ and $K\beta'$ X-ray excitation spectra for a high-spin porphyrin. The potential for site-selective spectroscopy of high-spin and low-spin mixtures is discussed.

2. Experimental

Fe $K\beta$ high resolution fluorescence spectra were recorded on a SSRL beamline 6-2 with a set of 3 spherically bent Si (440) crystal spectrometers [14]. Each bent crystal was separately aligned on the Rowland circle, and the beams were all diffracted vertically onto a common spot. A NaI detector was used for initial alignment and for fluorescence detection. The fluorescence emission spectra were recorded by scanning the detector and a slit vertically as the diffraction angle was changed by rotating the Si (440) crystals. The synchrotron radiation excitation beam was focused with a toroidal mirror to a 1×7 mm spot then monochromated using a pair of Si (111) crystals. Finely powdered samples were packed into a sample cell about 2 mm thick. The typical count rates at $k\beta$ peak is around 800 c/s. The emission spectrum takes about 2 h (4 scans) and the excitation spectrum takes around 5 h (10 scans). All of the spectra were taken with samples at room temperatures. The excitation energy was calibrated by reference to the first inflection point of Fe metal as 7111.2 eV [15].

High-spin 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine iron(III) chloride (FeOEP)Cl was used as received from Aldrich. Low-spin 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine iron(III) bis-imidazole, chloride salt (FeOEPIm₂Cl) was prepared by a published method [16].

3. Results and discussion

3.1. $K\beta$ emission spectra

The $K\beta$ emission spectra for both high-spin Fe(OEP)Cl and low-spin Fe(OEP)Im₂Cl, excited at 7200 eV, are shown in Fig. 1. For the high-spin complex, the spectrum is split into two regions. The main peak (known as $K\beta_{1,3}$) is found at around 7058 eV, while the satellite ($K\beta'$) is at 15 eV lower energy side. For the low-spin complex, the centroid of the $K\beta_{1,3}$ peak is shifted ≈ 0.7 eV to lower energy as compared to the high-spin Fe(III) complex, and there is also very little $K\beta'$ intensity. Similar results, although with lower resolution, have been reported by Koster [17].

The differences between high-spin and low-spin Fe(III) spectra can be explained primarily in terms of different final states for X-ray fluorescence, using an interpretation developed by Tsutsumi [18]. Neglecting charge transfer effects [19], the initial state configuration for excitation far above threshold before $K\beta$ fluorescence is $1s^13d^5$, and the final state is

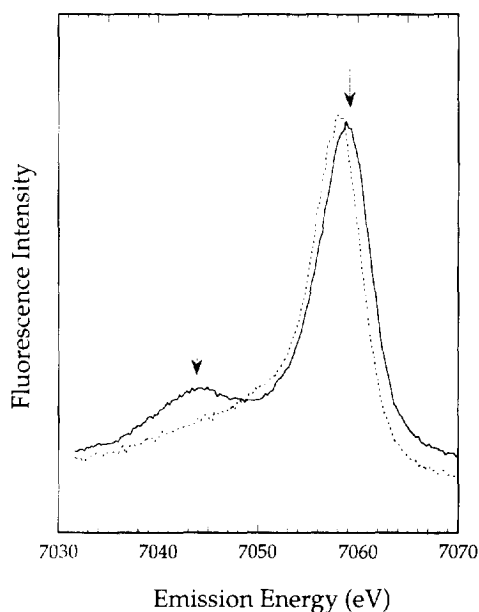


Fig. 1. Experimental $K\beta$ emission spectra of high-spin FeOEP)Cl (solid line) and low-spin FeOEP)Im₂Cl (dotted line) porphyrins. The spin-polarized X-ray excitation spectra were taken monitoring the energy positions indicated by arrows.

$3p^5 3d^5$. In an octahedral environment, the 3d orbitals are split into e_g and t_{2g} orbitals with an energy difference $10 Dq$. Two extreme situations can occur when there are five d electrons. When the ligand field strength is small, Fe(III) adopts a $(t_{2g}^+)^3(e_g^+)^2$ configuration with five parallel spins and 6A_1 ground state. A $(t_{2g}^+)^3(t_{2g}^-)^2$ configuration with 2T_2 symmetry occurs when the ligand field is large. In the final state, the 3p hole interacts very strongly with the partly filled 3d shell, thus the energy splitting in $K\beta$ spectra is caused by the exchange interaction between 3p and 3d levels. In the crystal field multiplet model [20], Coulomb repulsion terms, spin-orbit interactions, and ligand field splittings are also included.

The initial state symmetry determines which final states can be reached by dipole transitions. As seen before, the low-spin $K\beta_{1,3}$ peaks occur at lower energy than fluorescence from the high-spin species¹. Also, a smaller $K\beta'$ feature is predicted in the low-spin case [18]. This chemical sensitivity of fluorescence $K\beta$ spectra allows selective measurement of high-spin or low-spin Fe absorption in a mixed system, by monitoring at appropriate $K\beta$ energies for each species.

In Fig. 2, the calculated spectra are compared with experimental spectra for both high-spin and low-spin Fe porphyrins. The $K\beta_{1,3}$ peak comes primarily from transitions where a 1s spin down hole is created, the $K\beta'$ peak is derived exclusively from spin-up transitions. This separation between spin-down and spin-up transitions makes $K\beta$ fluorescence a good spin-polarized probe of high-spin Fe(III). In the low-spin case, transitions to 3T_2 and 1T_2 states unfortunately overlap and spin-polarized studies would be more difficult.

Fig. 3 illustrates the theoretical site selectivity that can be achieved for high-spin versus low-spin ferric by this technique. The ratio of high-spin intensity over the sum of high-spin and low-spin is given as a function of emission energy. There are three regions.

¹ Octahedral symmetry was used for both calculations. The $10 Dq$ value used for high-spin and low-spin is 1.2 and 3.3 eV, respectively. In the high-spin case, the fluorescence initial state could have 7A_1 or 5A_1 symmetry when the escaping 1s electron is spin-down or spin-up with respect to 3d electrons.

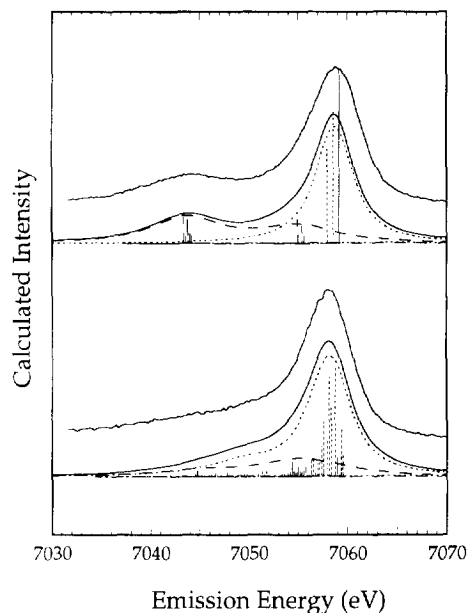


Fig. 2. Experimental spectra with ligand field multiplet simulations of high-spin Fe porphyrin FeOEPCl (top) and low-spin FeOEPIIm₂Cl porphyrin (bottom). Dotted line for the 7A_1 and 3T_2 spin-down transitions, dashed line for the 5A_1 and 1T_2 spin-up transitions, and solid line for total spectra. The stick diagrams show the strengths of individual transitions before linewidth broadening.

Below 7043 eV and above 7061 eV, around 60% of the emission from a 50:50 high-spin:low-spin mixture comes from the high-spin component. Between these two energies, the fluorescence is mostly from the low-spin component. Although the selectivity is

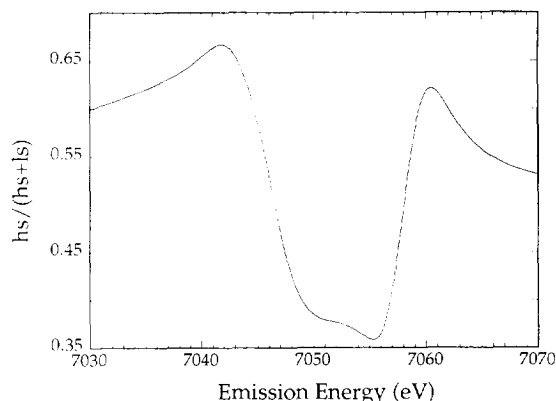


Fig. 3. Calculated intensity ratio of high-spin ferric over the sum of high-spin and low-spin ferric as a function of emission energy.

highest at 7043 eV, the counting rate would be relatively low; detecting at 7061 eV gives much better statistics with almost the same selectivity. The selectivity of low-spin is just the opposite.

3.2. $K\beta$ excitation spectra

Spin-polarized X-ray excitation of the high-spin Fe porphyrin FeOEPCI are shown in Fig. 4. The spin-down absorption spectrum was taken by setting the analyzer crystal at 7059 eV, the peak centroid of $K\beta_{1,3}$, while the spin-up spectrum was selected at 7044 eV. The spin-down spectrum has a clear pre-edge peak around 7112 eV, which is assigned as $1s \rightarrow 3d$ transition. This dipole forbidden transition becomes allowed by mixing Fe 4p character with the predominantly 3d orbitals [21]. There is also a small quadrupole component. Despite the complicated nature of the $1s \rightarrow 3d$ transition, the spin selection rule still holds. When mainly spin-down transitions are monitored at 7059 eV, only the spin-down 3d orbitals can be reached. When probing at 7044 eV, only spin-up transitions are monitored; no $1s \rightarrow 3d$ transitions are possible since all five spin-up orbitals are occupied, therefore very little pre-edge features are observed. This confirms the spin dependence of

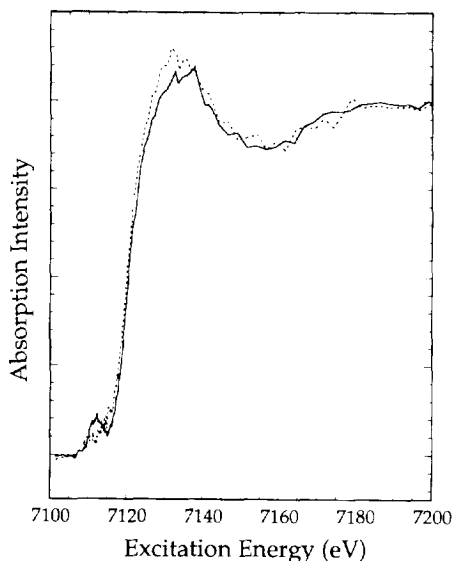


Fig. 4. Spin-polarized X-ray excitation spectra of high-spin FeOEPCI. Solid line for spin-down absorption, monitoring 7059 eV; dotted line for spin-up absorption, detecting at 7044 eV.

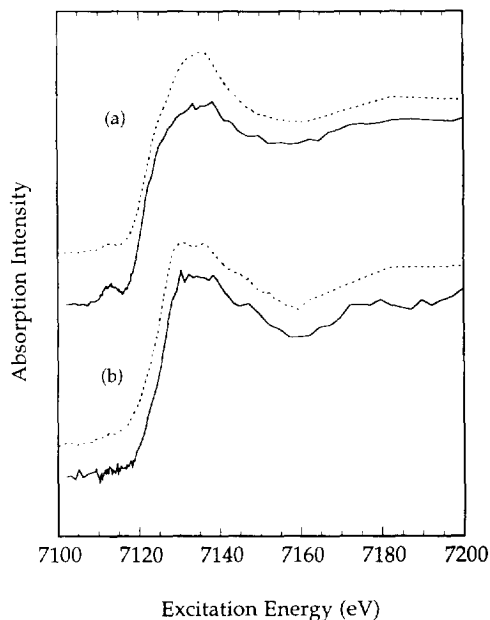


Fig. 5. High resolution $K\beta_{1,3}$ fluorescence excitation spectra (solid line) with conventional transmission spectra (dotted line) for (a) high-spin FeOEPCI and (b) low-spin FeOEPIIm₂Cl porphyrins.

the fluorescence spectrum. However, Lorentzian tail of the main peak will appear in the spin-up spectrum (so called resonant Raman effect) [9], covalency, configuration interaction and spin-orbit coupling will also complicate the simple spin polarization picture, which might explain the nonvanishing pre-edge features in the spin-up spectrum.

In Fig. 5, we compare the high resolution fluorescence excitation spectra with conventional transmission spectra for high-spin and low-spin porphyrins. The excitation spectra were taken monitoring the $K\beta_{1,3}$ centroid, at 7059 eV and 7058.2 eV, and are similar to the transmission spectra in both cases, but with more intense pre-edge features in excitation spectra [22]. This again confirms the spin component assignment in the fluorescence spectrum. In the high resolution fluorescence excitation spectrum, only spin-down transitions are monitored, which have intense $1s \rightarrow 3d$ transition. The conventional transmission spectrum includes both spin-up and spin-down transitions. As shown in Fig. 4, the spin-up transition has small pre-edge features, therefore a much weaker $1s \rightarrow 3d$ is observed in the 'averaged' transmission

spectrum. The edge is also sharper because of the elimination of 1s core hole natural line width in the K β monitored spectrum [22]. The 1s \rightarrow 3d transition in the nearly octahedral low-spin compound is weak since much less 4p character mixing with the 3d orbitals, even in the fluorescence excitation spectra. The absorption edge shifts about 1 eV to higher energy for the low-spin porphyrin. At higher energy (40 eV above the edge), we observed what Oyanagi and coworkers [23] identified as the spin-state marker bands.

4. Summary

Iron K β X-ray fluorescence emission and excitation spectroscopy has been used to study high-spin and low-spin porphyrins. The low-spin Fe K $\beta_{1,3}$ is shifted to lower energy by \approx 0.7 eV from the high-spin Fe, and the K β' almost disappears for low-spin compounds. The ligand field multiplet model successfully explains the shapes and positions of the spectra. We find that the spin state shifts are large enough to select for high-spin or low-spin Fe with a crystal spectrograph. These chemical shifts should make site selective EXAFS experiments possible on mixtures of spin states. Potential applications include systems like prussian blue, with discrete high spin Fe(III) and low spin Fe(II) sites, as well as enzymes like cytochrome c oxidase and sulfite reductase.

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