1-1-2009

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Recommended Citation

N. Dimakis, et. al., (2009) XAFS Debye-Waller factors for deformed hemes and metal substituted hemes.Journal of Physics: Conference Series190:. DOI: http://doi.org/10.1088/1742-6596/190/1/012198

Journal of Physics: Conference Series **190** (2009) 012198 doi:10.1088/1742-6596/190/1/012198

XAFS Debye-Waller factors for deformed hemes and metal substituted hemes

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Abstract. We present an efficient and accurate method for calculating XAFS Debye-Waller factors for deformed active sites of hemoproteins and metal substituted hemes. Based on the Normal Coordinate Structural Decomposition scheme, the deformation of the porphyrin macrocycle is expressed as a linear combination of the normal modes of the planar species. In our approach, we identify the modes that contribute most to the deformation. Small metal-porphyrin structures which match the macrocycle structural deformation of the deformed hemoprotein site are used to calculate the Debye-Waller parameters at sample's temperature. The Debye-Waller factors are directly obtained by calculating the normal mode spectrum of the corresponding metal-porphyrin structure using Density Functional Theory. Our method is tested on Ni-tetraadamantyl porphyrin and cytochrome c structures with more than 500 available scattering paths.

1. Introduction

The active sites of hemoproteins and metal substituted hemes consist of a metal ion located at the centre of the porphyrin ring. The metal choice, its axial ligation, redox potential, and symmetrical porphyrin substitution with tetrahedrally bonded atoms at the four meso bridging carbons results in porphyrin deformation [1,2]. This deformation appears only in the protein environment; outside of this environment the porphyrin is planar [3]. Jenzen *et al.* [4] have developed a computational procedure to obtain the macrocyclic structure in terms of the porphyrin lowest in-plane and out-of-plane normal mode displacements (Normal Coordinate Structural Decomposition-NCSD). For Ni-porphyrins the deformation is expressed by a single mode, the B_{1u} ruffling distortion [5], whereas for Fe-porphyrins multiple modes may be used.

The local region of the metal ion in the macrocyclic structure may be probed by the X-ray Absorption Fine Structure (XAFS) [6,7]. XAFS structural information is typically obtained by fitting experimental extended XAFS (EXAFS) spectra with corresponding simulated FEFF8 [8] spectra of a hypothetical structure. XAFS suffers of high fitting parameter correlation and multiple scattering (MS) [9]. The latter appears in the EXAFS amplitude equation in the form of $e^{-2k^2\sigma_j^2}$, where k is the photoelectron x-ray wavenumber and σ_j^2 is the mean square variation of the j^{th} scattering path. These

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exponential terms are called the EXAFS Debye-Waller factors (DWFs). The σ_j^2 terms are direct functions of the sample's vibrational normal mode spectrum properties (eigenfrequencies and eigenvectors) and temperature. In case of active sites of metalloenzymes, such as active sites of hemoproteins, MS is at the order of several hundred, thus exceeding the maximum number of parameters data may support ($2\Delta k\Delta R/\pi + 2 \cong 20 - 30, \Delta$k and ΔR are the effective k-space and R-space EXAFS spectra ranges, respectively [10]). The correlated Debye model (DM) [11,12] was used in the past for DWF calculation; however, it is insufficient for use in anisotropic materials.

MS DWF calculations were reported by Poiarkova and Rehr using the force–field equation of motion method [13] and by Dimakis and Bunker on active sites of Zn metalloproteins [14] and hemes [15] using Density Functional Theory (DFT) [16,17]. The purpose of this work is to calculate DWFs of large Ni^{+2} and Fe^{+2} porphyrin structures with extensive MS at an acceptable accuracy for EXAFS data analysis. This is achieved by calculating the DWFs of corresponding small metal (Me) porphyrin structures (MeP), which themselves are deformed following the particular normal mode distortion as indicated by the NCSD program.

2. Method

The Ni^{+2}-tetraadamantyl porphyrin and Fe^{+2} cytochrome c large structures (figure 1) serve as reference

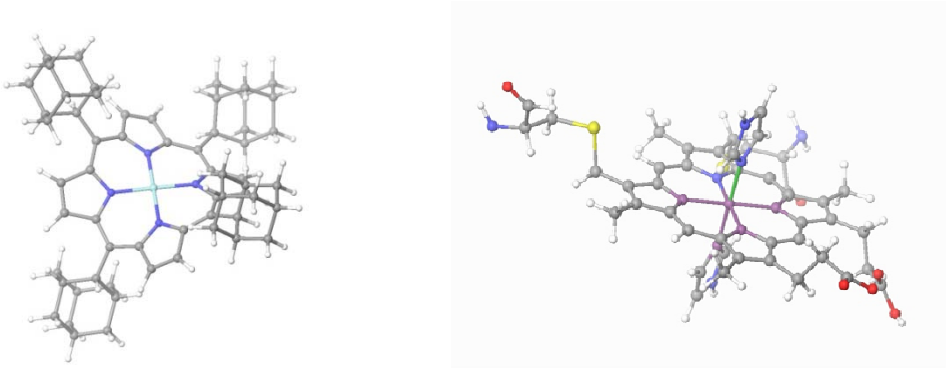

Figure 1. The DFT-optimized structures of Ni^{+2}-tetraadamantyl porphyrin (left) and Fe^{+2} cytochrome c with axial histidine ligation (right).

structures throughout this work. The DWFs of the reference structures macrocycle are estimated by calculating the corresponding parameters from appropriate small Ni^{+2} and Fe^{+2} porphyrins structures (NiP and FeP, respectively). The NiP and FeP serve as model structures. Additionally, DWFs for the Fe-His paths of the Fe^{+2} cytochrome c are calculated from a small H-Fe^{+2}-His complex as previously (Ref. 14). All structures are geometrically optimized using the unrestricted DFT under the X3LYP hybrid functional [18] and the LACV3P**+ [19] atomic basis set. The "**" symbol stands for polarization functions on all atoms but the metal ion, whereas the "+" symbol stands for diffuse basis functions on all atoms but the hydrogens. The X3LYP exchange correlation functional is considered an improvement over the well-known B3LYP [20] functional and provides more accurate heats of formation. The LACV3P**+ basis set includes valence and outermost core electrons for the metal ions, while the remaining core electrons are treated with effective core potentials (ECP). The ECP accounts for mass-velocity relativistic effects. The remaining elements are treated with the all-electron 6-311G**+ Pople basis set. DFT-calculated phonon normal mode spectrum of the optimized reference and modeled structures was in turn used to calculate the SS and MS σ^2s at a given sample temperature. DFT calculations are performed using the Jaguar v7.5 program [21], which incorporates the pseudospectral method to calculate most of the time consuming

integrals with the same accuracy as the fully analytical codes. To save CPU time, the phonon mode of the large structures of figure 1 was obtained using a partial Hessian approach, where hydrogen atoms were not included in the calculation.

3. Results and Discussion

Table 1 shows the σ^2 values of some of the most important SS and MS (at 150 K), as calculated directly from the DFT-optimized structures of figure 1 vs. corresponding values calculated from the MeP structures. For the latter structures, the ruffling angle was set to match the corresponding angle of the reference structure (i.e., 50° and 0° for the NiP and FeP structures, respectively). Disagreements on the σ^2s at R-distances away from the metal absorbing atom (e.g., the Me-C and Me-C-C paths at R > 4 Å) are due to 1) the accuracy of σ^2 as calculated by the partial Hessian approach and 2) additional secondary

Table 1. SS and MS σ^2 values for Ni^{+2}-tetraadamantyl porphyrin and Fe^{+2} cytochrome c structures at 150 K, as directly calculated by their phonon normal mode spectrum and the corresponding spectrum of small MeP.

Path	R(Å)	σ^2 ($\times 10^{-3}$ Å^2)		R(Å)	σ^2 ($\times 10^{-3}$ Å^2)	
		Me=Ni			Me=Fe	
		Reference structure	MeP		Reference structure	MeP
Me-N	1.901	1.93	2.01	2.281	2.27	2.15
Me-C	2.914	2.31	2.68	3.054	2.51	2.69
Me-N-C	3.104	2.25	2.44	3.225	2.46	2.74
Me-C	3.342	2.46	3.07	3.417	2.16	3.12
Me-N-N	3.802	2.73	3.27	4.055	3.10	3.13
Me-C	4.135	2.05	2.79	4.302	2.43	3.04
Me-C-C	4.160	2.03	2.74	4.405	2.49	3.13

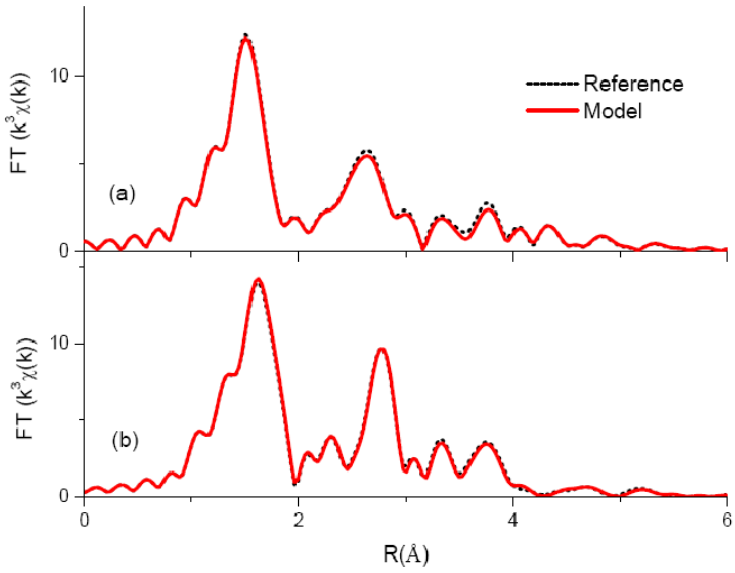

Figure 2. FEFF8 simulated Fourier transformed EXAFS spectra of DFT-optimized a) Ni^{+2}-tetraadamantyl porphyrin and b) Fe^{+2} cytochrome c structures, using DWFs directly calculated from the whole structure (reference) and from the MeP (model) at 150 K.

distortions beyond the one considered here (B_{1u} mode). Figure 2 shows the FEFF8 simulated Fourier transformed EXAFS spectra for the structures of figure 1($\Delta k = 15$ Å^{-1}), using DWFs calculated directly from the whole structures and from the corresponding small MePs as described adobe. Simulated spectra of figure 2, which include more than 500 scattering paths, indicate an excellent agreement between the two calculations.

4. Conclusion

SS and MS DWFs of large DFT-optimized active sites of hemoproteins and metal substituted hemes were directly obtained by calculating their normal mode spectrum at the partial Hessian approximation limit. These factors were compared with corresponding values obtained from small MeP structures by adjusting the MeP model structure ruffling angle to match with the one of the large structure. This method is generic and will be expanded to other metal substituted hemes with and without axial ligation.

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