

A theoretical study of the L₃ pre-edge XAS in Cu(II) complexes

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Supporting Information

Computational Details

Numerical experiments have been run by employing the latest version of the Amsterdam Density Functional (ADF) package.¹ SO-ZORA TDDFT-TDA calculations have been carried out by using all-electron QZ4P ZORA basis sets for all the atoms.² The adiabatic local density approximation has been employed to approximate the XC kernel,^{3,4} while for the XC potential applied in the self-consistent field calculations, the LB94 approximate functional with the ground state electronic configuration has been adopted.⁵ Scaled ZORA orbital energies⁶ instead of the ZORA orbital energies in the TDDFT equations have been throughout employed to improve deep core excitation energies.

SO-ZORA TDDFT-TDA calculations pertaining to **I** have been run by assuming the same geometrical parameters adopted by Gewirth *et al.*,⁷ while the plastocyanin blue copper active site has been modeled by using the same cluster ([Cu(S(CH₃)₂)(SCH₃)(NH₃)₂]⁺) proposed by Solomon and coworkers in ref. 8. Two distinct sets of calculations have been run on it. In the former set, the SO-ZORA TDDFT-TDA Cu 2p *f* distribution has been obtained by using Cartesian coordinates reported in Table I of ref. 8 without any optimization. Differently from that, the *f* distribution pertaining to the latter set has been attained for optimized coordinates evaluated by running non-relativistic spin-unrestricted calculations with generalized gradient corrections self-consistently included through the Becke-Perdew formula,⁹ by adopting a TZP Slater-type basis set for all the atoms and by maintaining frozen the (1s-2p)^{Cu}, (1s-2p)^S, 1s^C and 1s^N cores throughout the calculations. Both sets of numerical experiments have been run by assuming a C_s symmetry. Non-Optimized- and Optimized-Structures (NOS and OS, respectively) are quite different. In particular, the OS Cu(II) ion lies at 1.114 Å above the plane defined by the N and S_{cys} species (the NOS Cu(II) ion is almost coplanar with N and S_{cys} atoms, lying 0.349 Å above the corresponding plane); moreover, the long Cu-S_{met} bond shortens from 2.903 to 2.547 Å, while the S_{cys}-Cu-S_{met} (N-Cu-N) angle widens from 110° (96°) to 124° (101°) on passing from NOS to OS.

As far as the *f* distribution of **II** is concerned, it has been evaluated by using the geometrical parameters optimized in ref. 10.

The energy difference between Cu $2p_{3/2}$ and $2p_{1/2}$ spinors should be large enough (~ 20 eV)¹⁰ to avoid, in transitions starting from them, any coupling with each other; nevertheless, the whole Cu $2p_{3/2}/2p_{1/2}$ set has been considered as initial state. No coupling has been revealed.

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Cartesian coordinates (Å) of III^{OS}

Element	x	y	z
Cu	0.034133	-0.243602	0.000000
S	-0.380615	-2.756510	0.000000
S	2.013025	0.666055	0.000000
C	3.326612	-0.607373	0.000000
H	2.926252	-1.624599	0.000000
H	3.952073	-0.440640	0.887399
N	-1.250947	0.168086	1.636259
H	-0.754157	0.027118	2.520582
H	-1.566243	1.142648	1.648226
H	-2.094872	-0.411186	1.681437
C	0.414827	-3.621964	1.404784
H	-0.017191	-3.216197	2.326835
H	0.179195	-4.691098	1.343337
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