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Supplementary Information: Valence Orbitals and Local Bond Dynamics Around N Atoms of Histidine Under X-ray Irradiation

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The simulation of core excited state dynamics of histidine under basic conditions in Fig. 1 exhibits scattering duration spectral shifts and intensity changes equivalent to the ones of the neutral structure discussed in the main article. This statement holds for the N_π-protonated/N_τ-deprotonated tautomer under neutral conditions in Fig. 2 which exhibits energetically swapped energies for the X-ray absorption resonances of the N_π and N_τ site, which indicates that there is no impact of the coexistence of the two tautomers on the detected spectra. The simulations for the N_π-protonated/N_τ-deprotonated tautomer under basic conditions in Fig. 3 exhibit the same swap in X-ray absorption resonance energies. The overall agreement of the simulated emission spectra with the experimental data is worse than for the simulation of the other tautomer in Fig. 1 which supports the finding of Li and Hong [1] who identify the N_τ-protonated/N_π-deprotonated tautomer as the dominant species at the studied pH.

References

1 S. Li and M. Hong, *J. Am. Chem. Soc.*, 2011, **133**, 1534–1544.

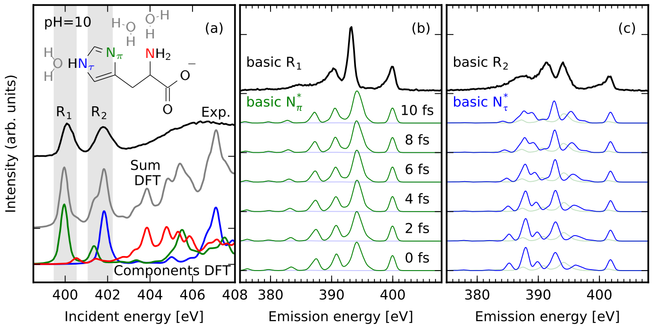

Fig. 1 N 1s core excited state dynamics in histidine under basic conditions. The fingerprint of protonation and dynamics on X-ray absorption (a) and resonant X-ray emission spectra (b) and (c) is equivalent to the one for histidine in a neutral environment.

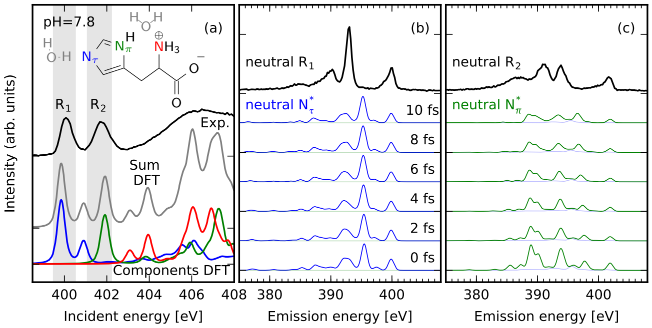

Fig. 2 N 1s core excited state dynamics in histidine under neutral conditions for the N_π-protonated/N_τ-deprotonated tautomer. The change in protonation is reflected in energetically swapped X-ray absorption resonances for the individual N sites. The fingerprint of protonation and dynamics on X-ray absorption (a) and resonant X-ray emission spectra (b) and (c) is equivalent to the one of the tautomer discussed in the article.

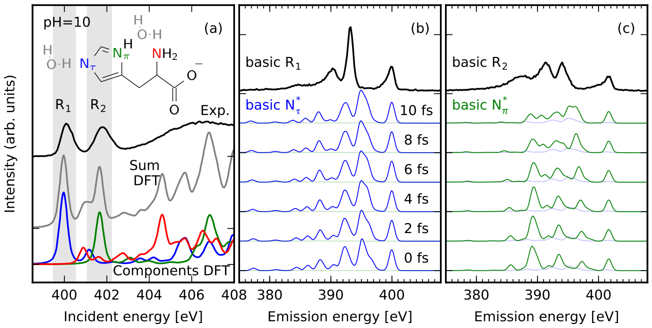

Fig. 3 N 1s core excited state dynamics in histidine under basic conditions for the N_π-protonated/N_τ-deprotonated tautomer. The change in protonation is reflected in energetically swapped X-ray absorption resonances for the individual N sites. The resonant emission spectra in (b) and (c) exhibit changes similar to the ones for the other tautomer (Fig. 1) with an overall worse agreement with the experimental spectrum.

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