



Contribution ID: 102

Type: Contributed poster

## Theoretical simulations of ultra-fast dynamics in solution probed with X-ray spectroscopies

Monday, June 25, 2018 6:45 PM (15 minutes)

Inter-molecular interactions (in particular hydrogen bonding) influence solvation and reaction pathways, and investigations of electronic structure and dynamics on the molecular level are important for a detailed understanding of chemical processes in solution.

In this presentation of a few case studies, I discuss how multi-configuration quantum chemistry (particularly RASPT2), density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations can be used to study hydrogen bonding and excited state dynamics in solution and for simulations of X-ray spectra.

The performance of DFT methods for simulations of nitrogen K-edge X-ray absorption spectra is discussed in relation to the pH dependence in the hydrogen bond environment and electronic structure of aqueous ammonia/ammonium [1]. Furthermore, the influence of hydrogen bonding and core-excited state dynamics on resonant inelastic X-ray scattering (RIXS) is established [2].

To conclude, I will discuss our contributions to rationalize time-resolved iron L-edge and N K-edge RIXS and get insight into valence excited state dynamics in iron complexes and chromophores in solution [3]. The interpretation of L-edge spectra is complicated and relies on accurate theoretical modeling and spectrum simulations to take into account effects of multiplet effects, spin-orbit coupling, chemical interactions, dynamics in the spectroscopic process [4]. The multi-configurational restricted active space method (RASPT2) is an efficient well-targeted approach for the purpose of simulating X-ray spectra, in particular for following distorted geometries along chemical pathways.

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[2] L. Weinhardt, E. Ertan, M. Iannuzzi, M. Weigand, O. Fuchs, M. Bär, M. Blum, J. D. Denlinger, W. Yang, M. Odelius E. Umbach, and C. Heske. Probing hydrogen bonding orbitals: resonant inelastic soft x-ray scattering of aqueous  $\text{NH}_3$ . *Phys. Chem. Chem. Phys.*, 17:27145–27153, (2015).

[3] Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Gröbel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, and A. Föhlisch. Orbital-specific mapping of the ligand exchange dynamics of  $\text{Fe}(\text{CO})_5$  in solution. *Nature*, 520:78–81 (2015).

[4] I. Josefsson, K. Kunnus, S. Schreck, A. Föhlisch, F. de Groot, Ph. Wernet, and M. Odelius. Ab initio calculations of x-ray spectra: Atomic multiplet and molecular orbital effects in a multi-configurational scf approach to the L-edge spectra of transition metal complexes. *J. Phys. Chem. Lett.*, 3:3565–3570 (2012).

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**Session Classification:** Poster session