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Probing Ultrafast Solution-Phase Chemistry in the X-ray Water Window and beyond via Soft X-ray Spectroscopy[1]

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A prerequisite for a microscopic understanding of chemical reactions is knowledge of the ultrafast interplay of valence charge distributions, spin states, and nuclear degrees of freedom. These degrees of freedom are often intricately coupled, leading to very complex dynamics. Femtosecond core-level spectroscopy is very well suited to study such dynamics via x-ray absorption near-edge structure (for information on changes in valence charge distribution / spin-state) and via the extended x-ray absorption fine structure (for information in nuclear arrangements) due to the very localized nature of the initial states of well-defined symmetry and the high chemical specificity of core-level excitations. We have employed femtosecond core-level spectroscopy to study metal-ligand interactions in solvated transition metal complexes as an important class of model systems to demonstrate the feasibility and merit of ultrafast solution-phase soft X-ray spectroscopy.[3,4] Laser-induced charge transfer reactions on sub-100 fs time scales trigger structural dynamics in first-row transition-metal complexes that display multiple spin-state changes within 300 fs upon photo-excitation. The combined analysis of vibrational, optical, and core-level spectroscopy reveals a complex interplay of nuclear, electronic, and spin degrees of freedom in these systems that leads to detailed insights into the underlying reaction mechanisms. These are prototypical in nature for a variety of organometallic systems. The chemical specificity of core-level spectroscopy is exploited by probing metal-centered transitions to elucidate the "metallic view." We have very recently succeeded in also following the "ligand view" via soft X-ray spectroscopy in the X-ray water window. The later experiment has far-reaching consequences as it demonstrates the feasibility of studying ultrafast processes and short-lived species of solvated organic compounds via Nitrogen K-edge spectroscopy to deliver a detailed picture of the evolving valence charge density in chemical reactions.

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