Ground state potential energy surfaces and femtosecond dynamics around selected atoms from resonant inelastic x-ray scattering

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Thermally driven chemistry as well as materials' functionality are determined by the potential energy surface of a systems electronic ground state. This makes the potential energy surface a central and powerful concept in physics, chemistry and materials science. However, direct experimental access to the potential energy surface locally around atomic centers and to its long-range structure are lacking. Here we demonstrate how sub-natural linewidth resonant inelastic soft x-ray scattering (RIXS) at vibrational resolution is utilized to determine ground state potential energy surfaces locally and detect long-range changes of the potentials that are driven by local modifications. We show how the general concept is applicable not only to small isolated molecules such as O2 but also to strongly interacting systems such as the hydrogen bond network in liquid water. The weak perturbation to the potential energy surface through hydrogen bond formation is detected and translated into softening of the ground state potential around the coordinating atom[1, 2].

Through the core hole clock concept, RIXS also accesses dynamical information on the timescale of the core hole lifetime. We take sub-femtosecond snapshots of the electronic and structural properties of water molecules in the hydrogen bond network where we derive a strong dominance of nonsymmetric molecules in liquid water in contrast to the gas phase and determine the fraction of highly asymmetrically distorted molecules[3].

The instrumental developments in high resolution resonant inelastic soft x-ray scattering are currently accelerating and will enable broad application of the presented approach. With this multidimensional potential energy surfaces that characterize collective phenomena such as (bio)molecular function or high-temperature superconductivity will become accessible in near future.

References

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