X-ray Raman scattering of liquids

Faris Gel'mukhanov

Theoretical Chemistry and Biology, KTH Royal Institute of Technology S-106 91 Stockholm, Sweden
faris@kth.se

Local probes of the electronic ground and valence excited states are essential for understanding hydrogen bonding in aqueous environments. Vibrational infra-red (IR) spectroscopy is an established technique for investigations of hydrogen bonding. High-resolution X-ray absorption spectroscopy [1] and resonant inelastic X-ray scattering (RIXS) [2] offers a complement to IR vibrational spectroscopy. The propagation of the nuclear wave packet in dissociative core-excited state results in the long vibrational progression seen in both theory and experiment. This gives great advantage of RIXS in comparison with IR spectroscopy which probes mainly the first OH excitation. We show how different resonant inelastic X-ray scattering (RIXS) channels deliver separate information; about the local structure via long-range dynamics in quasi-elastic RIXS and about short-range dynamics, which is much less sensitive to the structure, in the electronically inelastic 1b1 and 4a'' channel in water and methanol, respectively. Our theoretical framework is composed of classical ab initio molecular dynamics (MD) simulations, calculation of local potential energy surfaces from the sampled configurations, and quantum wave packet modeling of the nuclear motion in relevant degrees of freedom. Thereby, we reach insights into the variations in the local HB environment, which strongly affects the long-range part of the OH potential energy curves (PEC). For enhanced insight, we derive the distribution of PECs of OH bonds with intact and broken HBs as reconstructed from experimental RIXS data of liquid water. In contrast by analysis of the dynamic mechanisms, we show that the splitting, emerging for pre-edge core-excitation, has a purely dynamical origin and is primarily sensitive to the short-range part of the PEC since the splitting of the 1b1 and 4a'' peaks is formed at short time-scales before fragmentation.

References

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