

# Multidimensional nuclear dynamics studied by resonant X-ray scattering and pump-probe spectroscopy

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# Abstract

This thesis is devoted to theoretical studying of the multidimensional nuclear dynamics in molecules with the help of X-ray and pump-probe spectroscopy. Using an accurate yet computationally cheap mixed approach multimode X-ray absorption spectra (XAS) and resonant inelastic X-ray scattering (RIXS) spectra of water, methanol, and acetic acid were calculated and compared with the available experimental spectra in the gas and liquid phases. Based on a theoretical study of RIXS in a water molecule through the dissociative core-excited state  $|O1s^{-1}4a_1^1\rangle$ , the dynamic origin of the splitting of the lone pair RIXS resonance  $|1b_1^{-1}4a_1^1\rangle$  was proved. This result also explains the dynamic nature of the splitting of this peak in liquid water. The decisive role of multimode nuclear dynamics in explaining the experimental XAS and RIXS spectra of methanol, as well as the splitting of the lone pair peak, was theoretically substantiated. RIXS anisotropy effects were fully considered and discussed. The role of hydrogen bonds on vibrational RIXS in the gas phase and liquid acetic acid was analyzed. In contrast to the gas phase, the quasi-elastic RIXS of oxygen K-edge of liquid acetic acid does not exhibit long vibrational progression, which is qualitatively different from water and methanol. We explained this behavior by the unusually strong influence of the hydrogen bond, which changes the character of the intermediate core-excited state. The combined theoretical-experimental study allowed us to obtain information on the local structure and quantum nuclear dynamics in the liquid system. Besides advanced theory of RIXS, we developed several new pump-probe techniques, where infrared (IR), ultraviolet (UV), or X-ray pump is combined with XAS or X-ray photoemission spectra (XPS) as a probe. Using accurate theoretical simulations for CO molecule, we show strong sensitivity of X-ray spectra to the relative polarization between IR-pulses and X rays, which can be effectively used for extraction of the weak IR-induced signal. In the framework of UV-pump X-ray probe (UVX-PP) spectroscopy for long overlapping pulses we shown qualitative difference of the UVX-PP spectra vibrational structure from that of RIXS, allowing for a complementary study of the potential energy curves of the valence- and core-excited molecular states. In the scheme utilizing two time-delayed X-ray pulses we show theoretically that the phase modulation of the XAS or XPS spectra is shifted with respect to the phase oscillation comb of the X-ray double pulse, reflecting the dynamics of the light interaction with a quantum system.