

Abstract

The studies presented in this Thesis are focused on the role that nuclear dynamics plays in the formation of X-ray absorption (XAS) and resonant inelastic X-ray scattering spectra (RIXS) of multimode free molecules. A combined approach based on *ab initio* electronic structure methods and quantum nuclear wave packet dynamics is applied to two systems – water and methanol in gas phase. An IR-pump X-ray probe scheme is employed to explore the XAS and RIXS spectra of a vibrationally excited water molecule and its isotope substitutions using a two-dimensional wave packet technique. A selection of different initial vibrational states makes it possible to explore different vibrational progressions of the final electronic state due to a spatial filtration of vibrations in the core-excited state and because of selection rules. We demonstrate the possibility to use RIXS as a tool to study X-ray absorption from a selected vibrational level of the ground state. IR-pump X-ray-probe spectroscopy of the HDO molecule sheds light on the old classical problem of the wave function collapse. The collapse of the wave function takes time, as it is demonstrated by the gradual evolution of the ground electronic state vibrational wave function localized on an OH or OD bond to a delocalized vibrational wave function of the $2b_2$ core-excited state of HDO. We describe in detail the dynamical nature of the splitting of the $1b_1$ peak in the RIXS spectrum of H_2O and of the isotope substituted HDO and D_2O molecules. It is shown that this splitting is referred to close-lying molecular and atomic-like peaks. A special attention is paid on the polarization dependence of RIXS.

In order to study X-ray spectra of multimode molecules we developed a special theoretical tool, the so-called mixed representation, where m modes are described using the time-dependent wave packet technique while the remaining n modes are treated using the stationary method of Franck-Condon (FC) amplitudes. This approach combines the advantages of the quantum wave packet technique for simulations of the dynamics in dissociative states with the efficiency of the FC method for computing transitions between bound states. It is shown that the multimode nuclear dynamics plays an important role in the formation of the XAS and RIXS spectra of methanol. The main reason for this is different vibrational broadening and dynamics in the core-excited states with different potential energy surfaces. The nuclear dynamics in the core-excited states is crucial for the formation of the long multimode vibrational progression in the RIXS spectra which are sensitive to the value of the detuning of the exciting X-rays from the XAS resonance. It is found that the soft modes fade faster than the high frequency modes when the value of the detuning is increased and thus when the scattering duration becomes shorter. The entanglement of vibrational modes by anharmonicity and by the life-time vibrational interference makes the formation of the RIXS spectra in polyatomic molecules more complex in comparison with diatomic molecules.