

Properties of matter can be revealed through its interaction with light. In particular, X-ray based spectroscopies are widely used to gain insight into the local electronic structure of isolated elements or atoms or molecules embedded in an environment, and are element specific. Such capabilities evidence their potential as tools for chemical analysis. The recent development of X-ray free electron laser (XFEL) allows to probe matter with spatial (ångström) and temporal (femtosecond) resolutions out of reach so far with optical lasers or third generation synchrotron sources. The unique characteristics of XFEL radiation are exploited in several areas, such as chemistry, physics and biology. In particular, double core hole spectroscopy, whose sensitivity is considerably enhanced compared to conventional X-ray spectroscopies, is on the rise. Double core hole states, also referred as hollow states, are characterized by two electron vacancies in the inner shell(s). In the XFEL regime, the dominant pathway to produce them is the sequential absorption of two x-ray photons, where a singly core ionized species is produced in the intermediate step. In the present thesis, we tackle the study of double core hole state formation induced by the sequential absorption of two x-ray photons from an intense femtosecond laser pulse. On one hand, we bring forward the influence of the nuclear dynamics on core photoionization processes. On the other hand, we demonstrate that an active control over the competition between photoabsorption and Auger decay in the intermediate single core hole state is possible by varying the laser pulse duration. In pursuing these goals, we develop for the first time a time-dependent full quantum model treating both the photon absorption and the nuclear dynamics explicitly as well as the Auger decay phenomenologically. This purely theoretical work paves the road for a complete description of molecular double core hole state formation in the XFEL regime.