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Double Inner-Shell Vacancies in Molecules

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Double Inner-Shell Vacancies in Molecules

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Molecular electronic states possessing a double core-vacancy, referred to as double-core-hole (DCH) states, were predicted more than thirty years ago, to have interesting properties, which would allow one to probe matter in a much more detailed way compared to conventional single core-vacancy techniques. Though DCH states are characterized by low cross-sections compared to the dominant single-core-hole (SCH) states, which implies experimental challenges, the development of third generation synchrotron radiation (SR) facilities and X-ray free electron lasers (XFEL), in combination with advanced spectroscopy techniques, resulted recently in a significant number of scientific works reporting on the observation of different types of DCH states.

Within the framework of this thesis, experimental work in terms of high resolution single channel electron spectroscopy was carried out, detecting DCH states of the form $K^{-1}L^{-1}V$, where one core electron has been ionized and the second has been excited to an unoccupied orbital V . One example concerns the case of HCl, where the experimental spectrum has been reproduced by a fit model taking into account Rydberg series within different spin-orbit multiplicities. From this analysis, the thresholds for the double ionization continua and the quantum defects for different Rydberg electrons have been extrapolated. Furthermore, electron spectra reflecting the formation of $K^{-2}V$ DCH states, which involve the K shells of the N and C atoms in CH_3CN , have also been recorded and interpreted based on a theoretical model considering the direct (dipolar ionization - monopolar excitation) or the conjugate (dipolar excitation - monopolar ionization) nature of each observed transition. In addition, the initial and final state effects contributing to the chemical shift between the two non-equivalent C atoms have been discussed and visualized by employing a Wagner plot.

Related results are reported on the formation of $K^{-2}V$ DCH states in SF_6 and CS_2 . The influence of the slope of the potential energy curve on the broadening of the spectral features is discussed along with the appearance of a pronounced background. Fingerprints of nuclear dynamics upon the decay of several types of DCH states in H_2O have been identified by recording the related hyper-satellite Auger spectrum.

Complementary, the technique of multi-electron coincidence spectroscopy was used for the study of the formation of $K^{-2}V$ and K^{-2} DCH states in C_4H_{10} , where the latter type of DCHs with both core electrons being ejected to the continuum, has been measured directly and in the same experiment as the $K^{-2}V$ states.