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Multi-Particle Coincidence Studies of Molecular Single-Photon Ionization Processes

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Akademisk avhandling för filosofie doktorsexamen i Fysik, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 11 april 2025 kl. 13:15 i PJ-salen, Institutionen för fysik, Fysikgården 2, Göteborg.

ISBN: 978-91-8115-158-9 (print)
ISBN: 978-91-8115-159-6 (pdf)
Tillgänglig via http://hdl.handle.net/2077/85036

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Abstract

In this thesis, single photon ionization processes are investigated by means of multi-particle coincidence measurements. The experimental method combines a magnetic bottle time of flight electron spectrometer with ion spectrometry, to efficiently measure the charged particles emerging from the ionization of a molecule in the gas phase. The excellent collection efficiency of the magnetic bottle-type electron spectrometer is vital for these kinds of experiments.

In Papers I-IV of this thesis, the valence double ionization electron spectra and fragmentation of several doubly charged molecules are studied. Here, the multi-coincidence technique extracts ion specific final state ionization spectra revealing the dissociation mechanics for the molecules S_2, CSe_2, $Fe(CO)_5$ and SF_6. For S_2 and CSe_2, the valence double ionization electron spectra are characterized for the first time, and their dicationic state selected fragmentation pathways are identified. Both the double ionization spectra and fragmentation pathways show good agreement between experiment and theory, and provide a benchmark for quantum chemical computations. For the two latter molecules, $Fe(CO)_5$ and SF_6, the investigations focus on the fragmentation pattern and underlying dissociation mechanisms and energetics, for instance scrutinizing the applicability of pure statistical theory.

In Paper V, the focus is on electron-only coincidences of the core-valence ionization of C_3O_2, where one electron is emitted from an innermost core shell of the molecule, and one from the valence shell. C_3O_2 has a cumulative double bond structure with one oxygen at each end, resulting in two chemically different carbon species in the molecule, each contributing differently to the electron spectra. Core-valence double ionization above the C 1s edge reveals several sharp features, which are described well by theoretical modelling. Upon core hole ionization, Auger decay is expected, and for C_3O_2 the Auger spectra from both core-valence and core ionization reveal an unusual energy relation, namely that the lower binding energy carbon core site is associated with higher energy Auger electrons. This suggests a strong selectivity in the final states for the different carbon core ionization sites.

Paper VI considers the spatial distributions of fragments from two-body dissociations. The probability of ionization depends on the molecular orientation relative the polarization of the light, described by the anisotropy parameter β, and for two-body dissociations this is reflected in the fragment distribution. By measuring the ion flight time differences and applying the fit function derived in Paper VI, the anisotropy parameter can be estimated, without the need of a position sensitive detector or simulations of fragment distributions.

The findings of this thesis are of importance for a basic understanding of ionization processes and mechanisms leading to fragmentation, to benchmark theoretical models which describe the electronic structure and the molecular dynamics following single photon ionization, and, for instance, in astrophysical context and plasma research.