



GÖTEBORGS UNIVERSITET

Formation and Decay of Multiply-Charged Molecules upon Single-Photon Excitation

Måns Wallner

Institutionen för fysik
Naturvetenskapliga fakulteten

Akademisk avhandling för filosofie doktorexamen i Fysik, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 26 april 2024 kl. 13:15 i PJ-salen, Institutionen för fysik, Fysikgården 2, Göteborg.

ISBN: 978-91-8069-669-2 (print)

ISBN: 978-91-8069-670-8 (pdf)

Tillgänglig via <http://hdl.handle.net/2077/80060>

Abstract

This thesis presents the investigation of dissociative multi-ionisation processes in gas-phase molecules through single photon absorption, employing a combination of ion spectrometry and electron spectroscopy, relying on a magnetic bottle time-of-flight principle. This method is pivotal for capturing all electrons emitted during ionisation, enabled by its unique electric and magnetic field configuration.

The initial part of the thesis (Paper I) explores Coulomb explosion in CD_3I , induced by deep inner-shell ionisation with hard X-rays. The study examines core vacancy relaxation through Auger-Meitner cascades. Using a comparatively simple model, the relaxation and subsequent dynamics of Coulomb explosions are simulated, yielding results that align well with experimental data for medium charge states, although limitations are noted for higher charge states. The research provides insights into the distribution of final charge states following L-shell ionisation, including the involvement of rapid Coster-Kronig transitions.

Papers II-V focus on the dissociation mechanisms of small molecules (SO_2 , OCS , and HNCS) upon single photon double valence ionisation, employing the same experimental approach. Paper II discusses an unconventional dissociation mechanism in SO_2 leading to the unexpected charge retaining SO^{2+} species via autoionisation of the super-excited 2h-1p Rydberg state of SO_2^{+*} at long bond distances. Paper III reports on the production of molecular oxygen, O_2 , in an ionic pathway via a newly revealed metastable state of O-O-S^{2+} . Paper IV examines bond rearrangement upon double ionisation in OCS , establishing a newly identified metastable isomer COS^{++} . Paper V details the dissociation pathways of the main fragmentation channels of HNCS . Each paper contributes to a broader understanding of molecular behaviour under double ionisation.

Paper VI focuses on the sequential three-body dissociation mechanisms leading to unusual shapes, that also deviate from the expected limiting slope of $-\text{m}_\text{B}/\text{m}_\text{BC}$. Two isomers of perfluoro-propyl iodide are found to sequentially break into three fragments, $\text{ABC}^{++} \rightarrow \text{A}^+ + \text{BC}^+$ followed by $\text{BC}^+ \rightarrow \text{B}^+ + \text{C}$, where simulations suggest that the bow-tie and twisted shapes arise from femtosecond secondary lifetimes. At these short time scales the BC^+ is placed well within the effective Coulomb range of A^+ .

Overall, this thesis sheds light on the complex dynamics of dissociative multi-ionisation in several molecules, paving the way for future research in molecular dynamics and chemical reactions in more complex environments.

Keywords: Molecule, electrons, ions, dissociation, fragmentation, coincidence, time of flight, VUV, X-radiation.