

CHEMICAL BOND REFORMATION SUBSEQUENT TO RESONANT AUGER DECAY

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Chlorinated hydrocarbons have large importance in industrial applications due to their diverse properties that the high reactivity of the C-Cl bond induces. The study of high energy reactions in these molecules is an active research area especially in the field of physical chemistry. [1]

In this work we explore the chemical bond reformation process after an X-ray induced core-shell excitation. In the chloromethane (CH₃Cl) molecule, a Cl 2*p* electron was initially excited to an unoccupied antibonding σ^* orbital, which causes a resonant Auger decay to occur. Multiple fragmentation pathways are opened for the system after the Auger decay, with their relative probability depending on the exact Auger final state that is reached. Few specific Auger final states leads to a new chemical bond formation between one hydrogen and the chlorine atom, forming stable HCl⁺ ion.

This phenomenon was experimentally and computationally explored. The experiments involved an electron-energy-resolved fragment-ion coincidence measurement. The coincidence technique allows to measure the various fragmentation pathways by attempting to link the exact Auger final states to the produced ion fragments. In the technique utilized by the coincidence setup at University of Oulu (further information in refs [2, 3] and references therein), the measurement of the kinetic energy of the Auger electron initiates the measurement of the masses of the leftover ions. In this instance, the resonant Auger final states after the Cl 2*p* \rightarrow σ^* excitation were monitored. Several fragmentation pathways are found, while specific interest was in the underlying mechanism of the reformation of HCl⁺ ion. Photon energy dependence of HCl⁺ appearance was further studied by detuning the resonance over a large energy range. The HCl⁺ appearance was confirmed to occur at the σ^* resonance [4]. This dependence and the appearance with respect to the Auger phenomenon was additionally studied using quantum chemical calculations.

[1] G. W. Gribble, [Pure and applied chemistry, 68\(9\), 1699 \(1996\)](#)

[2] E. Kokkonen, *et al.*, [Journal of Chemical Physics, 143, 074037 \(2015\)](#)

[3] E. Kokkonen, *et al.*, [Journal of Chemical Physics, 140, 184304 \(2014\)](#)

[4] C. Miron, *et al.* [Journal of Chemical Physics, 128, 154314 \(2008\)](#)