AUGER RECOMBINATION DYNAMICS IN ISOLATED MERCURY CLUSTER ANIONS Hg_n^- ($n = 9 - 22$) FOLLOWING $S \rightarrow P$ INTERBAND EXCITATION AT 4.65 eV

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The electronic structure of mercury clusters follows the Bloch-Wilson model over a wide size range. As the number of atoms increases, the s/p-hybridisation is enhanced, accompanied by a widening of the filled valence s band and the empty p-band. This leads to a reduction of the gap between those bands, which will eventually merge. The band-gap can be readily observed by photoelectron spectroscopy of mercury cluster anions Hg_n^-, and its closure was extrapolated to occur at $n \approx 400$ atoms.[a] At sufficiently high photon energies, absorption competes the photodetachment promoting a second electron into the p-band and leaving a hole of s-character. The excitation can interact both with nuclear and electronic degrees of freedom before recombining and emitting the remaining electron from the p-band. This leads to characterstic tails in the photoelectron spectra as a fingerprint of the preceeding relaxation dynamics.[b]

We have directly measured the dynamics of electronic relaxation following *s* to *p* interband excitation of mass selected mercury cluster anions Hg_n^- (with $n = 9 - 22$) using ultrafast time-resolved pump/probe photoelectron spectroscopy.[c] Auger decay of the excited clusters was found to occur on a timescale of $300 - 500$ fs, changing abruptly between $n = 12$ and 13. These dynamics also define an upper limit of the non-adiabatic coupling and are an order of magnitude faster than results previously reported on such electronic relaxation in Hg_n. This difference is interpreted as the result of correlated electron dynamics, and mechanisms are posited for relaxation of both the excited electrons in the *p*-band and the hole in the *s*-band.

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[a] B. v. Issendorff, and O. Cheshnovsky, *Annu. Rev. Phys. Chem.* **56**, 549 (2005).

[b] R. Busani, R. Giniger, T. Hippler, and O. Cheshnovsky, *Phys. Rev. Lett.* **90**, 083401 (2003).

[c] G. B. Griffin, A. Kammrath, O. T. Ehrler, R. M. Young, O. Cheshnovsky, and D. M. Neumark *Chem. Phys.* (2007) **doi:**10.1016/j.chemphys.2007.12.005.