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 \( \text{Hg}_n^- \), and its closure was extrapolated to occur at \( n \approx 400 \) atoms. 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 characteristic tails in the photoelectron spectra as a fingerprint of the preceding relaxation dynamics.

We have directly measured the dynamics of electronic relaxation following \( s \) to \( p \) interband excitation of mass selected mercury cluster anions \( \text{Hg}_n^- \) (with \( n = 9 - 22 \)) using ultrafast time-resolved pump/probe photoelectron spectroscopy. 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 \( \text{Hg}_n^- \). 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.

---

