Ultrafast electron dynamics in pump-probe spectroscopies of surfaces: from transient excitonic to quasi-stationary polaronic states

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Rapid development of pump-probe spectroscopies has greatly advanced the studies of electronic excitations in the real time domain. State- and time-resolved two-photon-photoemission (TR2PPE) measurements utilizing ultrashort laser pulses with variable delay have provided unprecendented insight into the dynamics of quasiparticles at metal surfaces. This has enabled detailed investigations of quasiparticle energetics and decay in the intermediate states of 2PPE from quasi-two-dimensional surface bands which are of fundamental interest in many aspects of surface science. In particular, occupied surface state- (SS) and unoccupied image potential-state (IS) bands constitute ideal prototype systems for studying ultrafast quasiparticle dynamics and relaxation phenomena in restricted dimensionality. So far the majority of analyses of 2PPE data from surface bands have invoked pre-existent SS- and IS-states whose many-body properties were assessed *a posteriori* by perturbation methods. However, since IS-bands arise from an interplay of the surface band gap and retarded polarization interaction, the image potential supported IS-states are fully developed only after the completion of screening of excited quasiparticle charges on the time scale of several surface plasmon cycles. Consequently, such states are mainly inaccessible in ultrafast measurements utilizing laser pulses of few femtosecond duration and delay. Instead, the evolution of an optically excited electron with energy below the vacuum level and a SS-band hole in the intermediate state of TR2PPE should be visualized as a transient exciton which with the formation of image charge evolves into a weakly correlated quasiparticle pair (IS-electron+SS-hole). The corresponding many-body scenario maps onto the problem of propagation of an electron-hole pair initially governed by excitonic interactions which in the course of time give way to polaronic interactions of each quasiparticle with the developing screening cloud and thereby to establishment of IS-band states. Temporal stages of these processes will be illustrated and quantified on the paradigmatic example of 2PPE from Cu(111) surfaces.