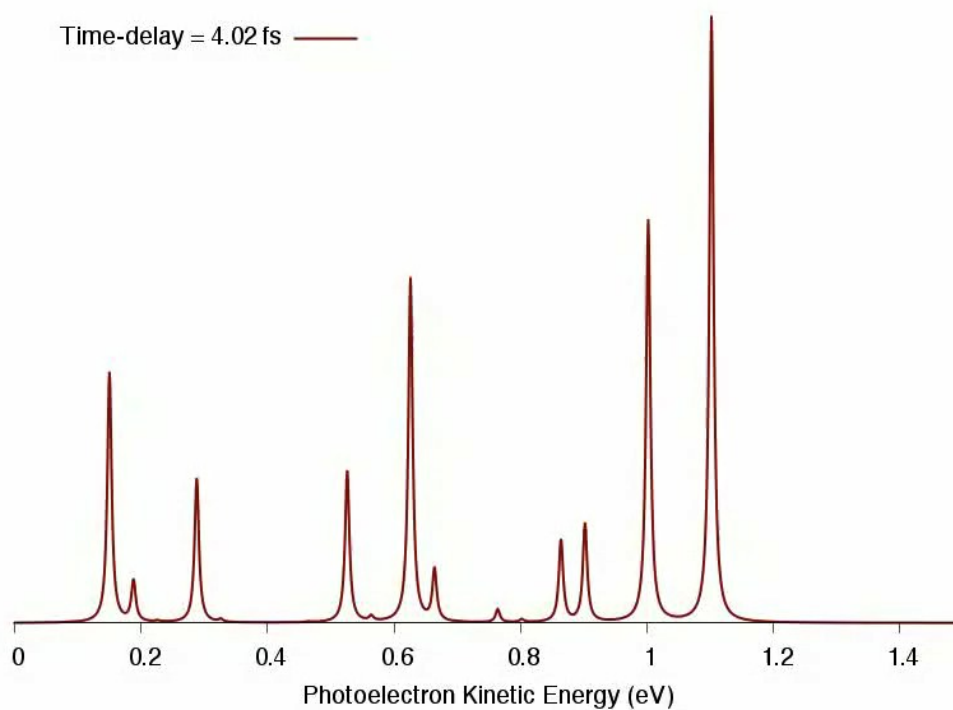
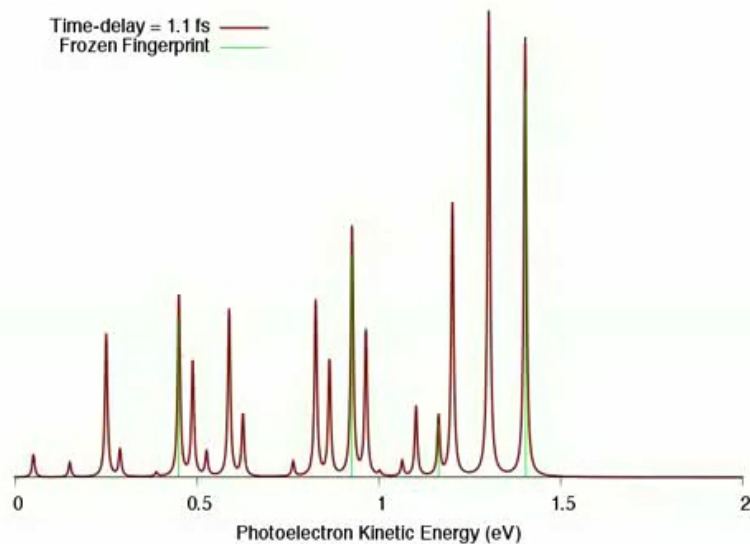


Supplementary Information (A15.05.0073)

A proposed new scheme for vibronically resolved time-dependent photoelectron spectroscopy: pump-repump-continuous wave-photoelectron spectroscopy (prp-cw-pes)



Movie 1: Rapidly varying snapshots as a function of pump-repump time-delay, as a result of fast oscillations of populations in excited state when the pump and repump lasers are in phase, as discussed in section III of the manuscript

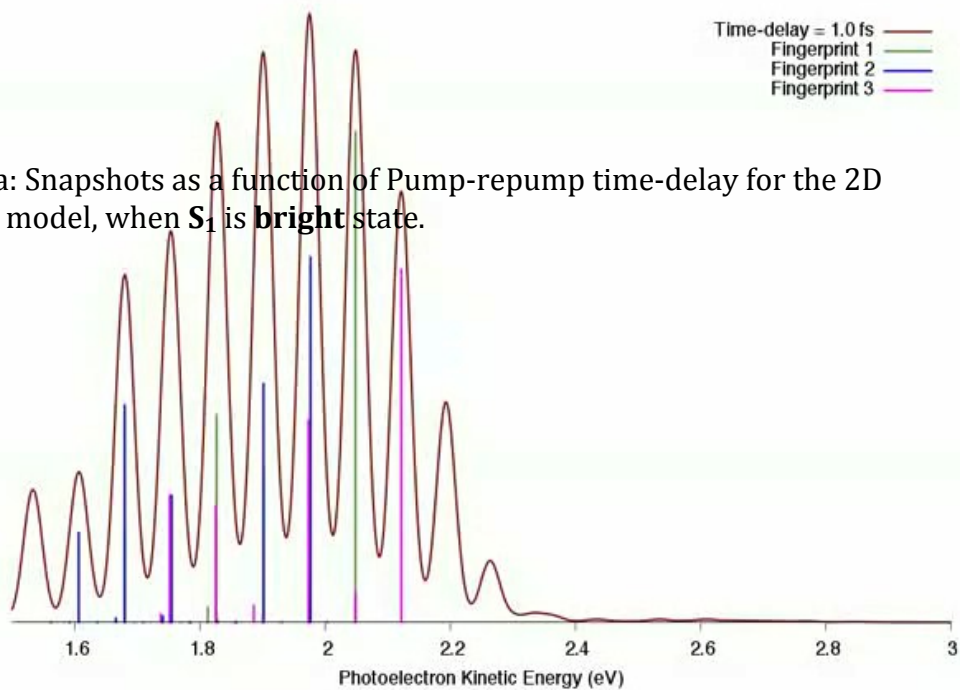
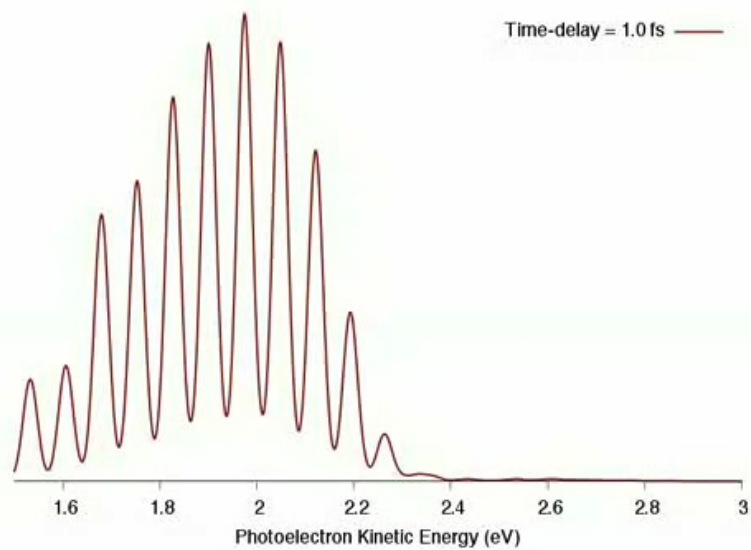


Time-delay = 1.1 fs —
Frozen Fingerprint —

Movie 2: Some features of snapshots become independent of time-delay, by choosing suitable phase relation, as described in section III of the text

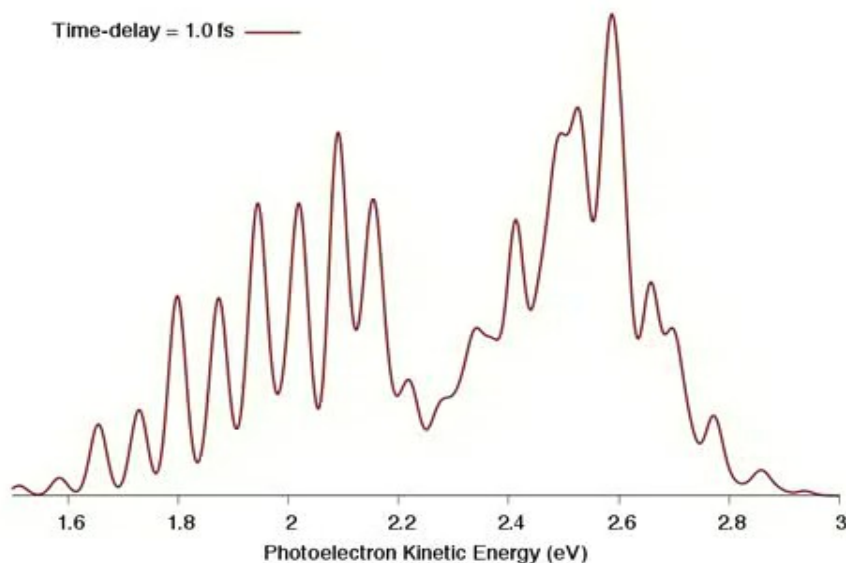
Movie 3: The frequency of oscillations of populations can be made much smaller by choosing the phase on electronic resonance (equal to excitation energy) resulting in slow evolution of snapshots as a function of time-delay, as described in section III of the text

Photoelectron Kinetic Energy (eV)

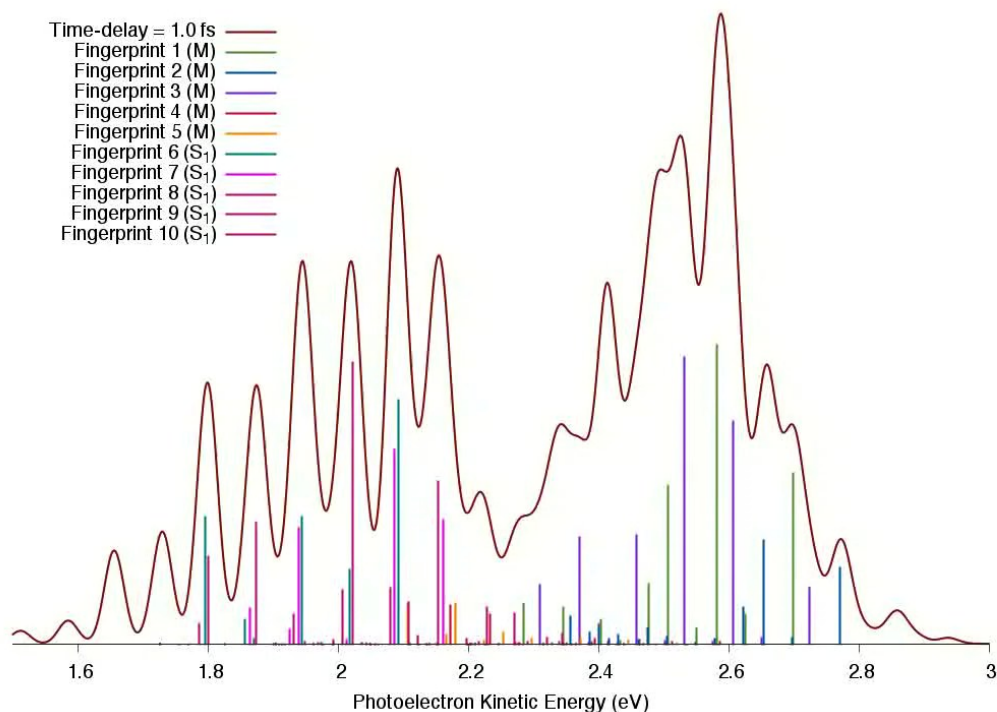


Movie 4a: Snapshots as a function of Pump-repump time-delay for the 2D vibronic model, when S_1 is **bright** state.

Movie 4b(Same as 4a): Fingerprints corresponding to a particular vibronic excited level grow in unison. Monitoring a particular level (colored sticks) shows that these lines move up and down together as a function of time-delay. Only a few fingerprints are needed to capture dominant features of the snapshots.



Movie 5a: Snapshots as a function of Pump-repump time-delay for the 2D vibronic model, when S_2 is **bright** state. [As discussed in Section IV]



Movie 5b (Same as 5a): The right part of the snapshots are captured well by only a few fingerprints (M), while the left part needs many fingerprints of both M and in particular S_1 fingerprints.

M: Excited vibronic eigenstates with “mixed” character (S_1 / S_2)

S_1 : Excited vibronic eigenstates with more than 80% S_1 character