Time-Resolved Photoelectron Spectroscopy with a Tuneable Femtosecond VUV Source RUARIDH FORBES, Stanford University, USA; University of Ottawa, Canada, SIMON P. NEVILLE, University of Ottawa, Canada, MARTIN A. B. LARSEN, University of Copenhagen, Denmark, ANDREY E. BOGUSlavskiy, University of Ottawa, Canada, RUNE LAUSTEN, MICHAEL S. SCHUURMAN, NRC, Canada, ALBERT STOLOW, University of Ottawa; NRC, Canada — Time-resolved photoelectron spectroscopy (TRPES) has emerged as the gold standard technique to interrogate non-adiabatic excited state dynamics in isolated molecules but, to date, has been mostly limited by a wavelength coverage limited the UV to IR. We report the construction of a tuneable vacuum-ultraviolet (VUV) femtosecond laser source based on four-wave mixing in rare gases, capable of producing pulses from 145-180nm. The source has been utilized in a VUV/UV TRPES investigation into Rydberg-valence coupling in the polyatomic molecule acetone. The results highlight the complex interplay between internal conversion occurring within the Rydberg manifold and population of a $\pi\pi^*$ valence state, the latter of which has not been previously experimentally observed. The results were compared to Multi-Configurational Time-Dependent Hartree (MCDTH) calculations, which verified our spectroscopic assignments. As acetone is the simplest ketene, we expect these results will have implications in the excited state dynamics for a large set of molecular systems.