

VINYLDENE-ACETYLENE ISOMERIZATION PROBED WITH HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF COLD ANIONS UPON SELECTIVE VIBRATIONAL EXCITATION

MARTIN DeWITT, *Chemistry, University of California, Berkeley, Berkeley, CA, USA*; JASCHA LAU, *Department of Chemistry, University of California, Berkeley, Berkeley, CA, USA*; DANIEL NEUMARK, *Department of Chemistry, The University of California, Berkeley, CA, USA*.

Vinylidene (H_2CC) has been shown to have a complex vibronic structure, with strong coupling between the ground and excited electronic states as well as vibrational wavefunction mixing between vinylidene and its isomeric counterpart, acetylene (HCCH). Our group has previously used slow photoelectron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) to probe such dynamics. However, the vibrational states of neutral vinylidene that exhibit the strongest coupling between electronic states are nominally inaccessible from the vibrational ground state of the anion, making them difficult or even impossible to observe with the cryo-SEVI technique. Here, we use the recently developed technique of infrared-pump, cryo-SEVI-probe (IR-cryo-SEVI) to further uncover vinylidene's complexities by vibrationally exciting the anion along the antisymmetric CH_2 stretch (ν_5) and CH_2 in-plane rocking (ν_6) modes prior to photodetachment. Vibrational pre-excitation along these antisymmetric modes gives access to vibrational states in the neutral that are otherwise inaccessible to cryo-SEVI. Additionally, IR-cryo-SEVI is used as an action technique, able to measure the infrared absorption spectrum of the bare anion without perturbations from tagged atoms or matrices, giving the true vibrational frequencies of these modes.