THE INFRARED AND ULTRAVIOLET SPECTROSCOPY OF JET-COOLED *ORTHO*-, *META*-, and *PARA*-ETHYNYLSTYRENE

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Vibronic spectroscopy of *ortho*-, *meta*-, and *para*-ethynylstyrene (OES, MES, and PES) was studied by resonant two photon ionization (R2PI). The origins of the OES and PES are 32369 $cm^{-1}$ and 33417$cm^{-1}$, respectively. In the MES, there are two possible conformations that occur close in energy. In the R2PI spectrum of MES the two most prominent peaks occur at 32683 $cm^{-1}$ and 32936 $cm^{-1}$. UV-UV holeburning (UVHB) spectroscopy confirmed that these transitions are due to the two different conformations of MES. There are also two possible conformations in OES, but calculations suggest that the conformation with the substituents pointing towards each other should only be about 5% of the room temperature population. The UVHB spectrum of OES confirms that only one conformer is present. In the R2PI spectra of each of these isomers there is evidence of vibronic coupling of the $S_1$ state to an excited electronic state. Ground state infrared spectra in the C-H stretch region (3000-3300 $cm^{-1}$) were obtained using resonant ion-dip infrared spectroscopy (RIDIRS). In all three isomers, the acetylenic C-H stretch fundamental was split by Fermi resonance. Infrared spectra were also recorded in the excited electronic state using a UV-IR-UV version of RIDIR spectroscopy. In all three isomers the acetylenic C-H stretch fundamental was unshifted from the ground state, but no Fermi resonance was seen. Experiments designed to measure the barrier to isomerization of the vinyl group will also be discussed.