ISOMER-SPECIFIC SPECTROSCOPY AND CONFORMATIONAL DYNAMICS OF ORTHO-, META-, AND PARA-ETHYNYLSTYRENES

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The infrared and ultraviolet spectroscopy of ortho-, meta-, and para-ethynylstyrene isomers (oES, mES, and pES) were studied by a combination of methods, including resonant two photon ionization (R2PI), UV-UV hole-burning spectroscopy (UVHB), resonant ion-dip infrared spectroscopy (RIDIRS), and rotationally resolved fluorescence excitation spectroscopy. In addition, the newly-developed method of stimulated emission pumping-population transfer spectroscopy (SEP-PTS) was used to place direct experimental bounds on the barrier to conformational isomerization in meta-ethynylstyrene. $S_1 \leftarrow S_0$ origin transitions of oES and pES occur at 32369 and 33407 cm^{-1}, respectively. In mES, the cis and trans conformations are calculated to be close in energy. In the R2PI spectrum of mES, the two most prominent peaks (32672 and 32926 cm^{-1}) were confirmed by UVHB spectroscopy to be $S_1 \leftarrow S_0$ origins of these two conformers. The red-shifted conformer was identified as the cis structure by least squares fitting of the rotationally resolved fluorescence excitation spectrum of the origin band. There are also two possible conformations in oES, but transitions due to only one were observed experimentally, as confirmed by hole-burning spectroscopy. Density functional theory calculations (B3LYP/6-31+G*) predict that the cis-ortho conformer, in which the substituents point towards each other, is about 2 kcal/mol higher in energy, and should only be about 5% of the room temperature population of oES. The barrier to cis $\rightarrow$ trans isomerization in mES was determined to be in the range 990-1070 cm^{-1} using SEP-PT spectroscopy. The analogous trans $\rightarrow$ cis barrier was in the same range (989-1065 cm^{-1}), indicating that the relative energies of the zero-point levels of the two isomers are (EZPL(cis) $-$ EZPL(trans))= -75 - $+81$ cm^{-1}. Both the barrier heights and relative energies of the minima are close to those determined by DFT Becke3LYP/6-31+G* calculations.