PROBING COMPETITIVE NONCOVALENT INTERACTIONS: RESONANCE ENHANCED TWO-PHOTON IONIZATION (R2PI) SPECTROSCOPY OF HALOAROMATIC CLUSTERS

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Non-covalent interactions in bromobenzene have been studied here using resonance two-photon ionization (R2PI) spectroscopy combined with a linear TOF-mass spectrometer. Bromobenzene clusters were created in a supersonic expansion with helium as a carrier gas. The molecules were excited and ionized from the ground state in a two stage process. The general trend observed in the R2PI spectra of all the clusters is the broadness and a red-shift relative to the monomer absorption. Optimized dimer and trimer structures were calculated at the M06-2x/aug-cc-pVDZ level, which show that π-stacked and C-H/π interactions are most important in these clusters. TD-DFT calculations of the different cluster conformers have been carried out to assess the geometry changes active upon electronic excitation. The theoretical studies are helpful in explaining trends observed in the R2PI spectra.