

**Resonant Two-Photon Ionization Spectroscopy of Styrene (Methanol)<sub>n</sub> Clusters, *n* = 1–9****H. Mahmoud, I. N. Germanenko, Y. Ibrahim, and M. S. El-Shall\****Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006**Received: February 10, 2003*

Well-resolved spectra of styrene–methanol binary clusters SM<sub>*n*</sub>, with *n* = 1–9, have been obtained by the (one-color) resonant two-photon ionization technique using the 0<sub>0</sub><sup>0</sup> resonance of styrene. The spectra reveal a rapid increase in complexity with the number of methanol molecules in the cluster, associated with van der Waals modes and isomeric forms. Two distinct isomers are identified for each of the clusters studied with the exception of SM<sub>4</sub> and SM<sub>8</sub>. The progressive addition of methanol molecules to the SM complex leads to the formation of stable cyclic and branched cyclic methanol subclusters within the SM<sub>*n*</sub> clusters. The spectral shift of the cluster origin reflects the nature of the intermolecular interactions within the binary cluster. Blue shifts are observed for the SM, SM<sub>2</sub>, and SM<sub>3</sub> clusters and are consistent with hydrogen bonding interactions between the OH groups and the styrene π-system. A remarkable switch in the spectral shift from blue to red is observed at the SM<sub>4</sub> cluster and is consistent with the ring structure of the methanol tetramer. Evidence is provided for intracuster dissociative proton-transfer reactions within the S<sub>2</sub>M<sub>*n*</sub><sup>+</sup> (*n* > 2) clusters that generate protonated methanol clusters. These reactions may explain the strong inhibition effects exerted by small concentrations of methanol on the cationic polymerization of styrene.