ULTRAVIOLET AND INFRARED SPECTROSCOPY OF DIPHENYLMETHANE IN A SUPERSONIC JET COMBINED WITH QUANTUM CHEMICAL CALCULATIONS

ALOKE DAS , TALITHA M. SELBY, AND TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University West Lafayette, IN 47907*.

Diphenylmethane is a simple bichromophore in which two phenyl rings are attached to the same methylene carbon. The phenyl torsional degrees of freedom are very floppy, and have been the subject of past theoretical and condensed phase studies. This talk will describe our studies of the electronic and infrared spectroscopy of this molecule cooled in a supersonic jet. The resonantly enhanced two photon ionization (R2PI) spectrum of diphenylmethane shows transitions due to only one conformation. There is a strong Franck-Condon progression in a low frequency vibration of 28 cm^{-1} built off the origin transition due to torsional motion of the phenyl rings which indicates that the equilibrium geometry of the molecule in the ground state is displaced in the excited state along the torsional coordinate. Though the high frequency ring modes (560, 962 cm^{-1}) after electronic excitation show similar torsional progressions, a vibration at 123 cm^{-1} has no Franck-Condon progression built on it, indicating a strong coupling between these two motions. The infrared spectra of the 123 cm^{-1} vibration in the C-H stretch region (2850-3150 cm^{-1}) for both ground and excited electronic state are identical. The potential energy surface along the torsional coordinates shows eight equivalent minima with C_{2v} and C_s transition states that are computed to be only 170 and 150 cm^{-1} above the minima, respectively. A model calculation for coupling between the low frequency torsional mode and the 123 cm^{-1} mode has been performed to explain the dependence of the torsional progression on excitation of this mode. The intriguing possibility that the degree of electronic delocalization in the near-degenerate excited state(s) will depend on the vibronic level will also be discussed.