HIGH-RESOLUTION EXCITED-STATE PHOTOELECTRON SPECTROSCOPY OF JET-COOLED TETRAMETHYLETHYLENE AND 1,1′-BICYCLOHEXYLIDENE

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The spectroscopy and photophysics of tetramethylethylene and 1,1′-bicyclohexylidene have been investigated using excited-state photoelectron spectroscopy in combination with multiphoton excitation. Vibronic coupling within the full manifold of the excited singlet states is shown to play a dominant role in determining the spectroscopic properties of these compounds. Although this vibronic coupling inhibits the determination of excited state excitation energies by excitation spectroscopy, it enables at the same time their observation in the photoelectron spectra. As a result, a large number of previously unobserved Rydberg states could be located and assigned. For both molecules ionization from the Rydberg states is observed to be heavily perturbed by ionization from the underlying quasi-continuum of the (π,π^*) valence state. The photoelectron spectra of 1,1′-bicyclohexylidene reveal that the state around 55000 cm^{-1} (6.82 eV), which has previously been assigned as a second valence state, does not show the ionization pattern expected on the basis of previous suggestions made for the character of this state. Based on this observation and on the result of ab initio calculations on various alkylated mono-olefins, configuration mixing between the (π,π^*) valence state and the (π,3d) Rydberg manifold is offered as a possible explanation.