HIGH RESOLUTION IONIZATION-BASED SPECTROSCOPY OF BENZONITRILE AND PHENYLACETYLENE CATIONS

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Mass analyzed threshold ionization (MATI) and photoinduced Rydberg ionization (PIRI) spectra of benzonitrile and phenylacetylene have been recorded. The initial excitation used a frequency-doubled, Fourier transform-limited pulse-amplified c.w. laser to pump single rotational lines in the $S_1 - S_0$ band of the parent molecules. Subsequent resonant transitions to high Rydberg levels were detected either by field ionization (MATI) or by autoionization resulting from another resonant laser absorption in the ion core (PIRI). In all cases, the sample was a cold molecular beam of the target molecule seeded in inert gas. The resulting spectra have vibrational resolution and their detailed structure depends on the intermediate ro-vibronic levels used in the excitation steps. The C-X transition studied in phenylacetylene is electronically allowed, and the vibrational structure could be well simulated using the results of electronic structure and Franck-Condon calculations. The B-X transition studied in benzonitrile is electronically forbidden, and a new method of vibronic coupling analysis was developed to calculate the relative intensities of the inducing modes using only electronic transition moment calculations and Franck-Condon factors. With that information, a complete vibrational analysis has been possible.

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