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A linear tandem time-of-flight mass spectrometer was designed and constructed to study unimolecular dissociation and photodissociation dynamics of aniline⁺-(water)_n cluster cations. A part of the metastable aniline⁺-(water)_n (n=1-16) cluster cations produced by photo-ionization of neutral clusters in the first stage dissociates in the field-free region. The parent and daughter ions so produced were separated in the second stage via pulsed acceleration field. The dominant dissociation channel of the metastable aniline⁺-(water)_n cluster ions was aniline⁺-(water)_n --> aniline⁺-(water)_{n-1} + water. The decaying time constants of the ions evaluated by analyzing the TOF spectra ranged from 50 to 520 μs and turned out to be highly dependent on the cluster size. Photodissociation dynamics of aniline⁺-(water)_n cluster cations was investigated by irradiation of the mass-selected cluster cations with a photodissociation laser pulse (266, 355, and 532 nm) in the field-free region of the second stage, ~1 m downstream from the first stage. The photofragment ions were mass-analyzed to examine the photodissociation channels of aniline⁺-(water)_n cluster cations. Figure 1 shows photodissociation mass spectra of aniline⁺-(water)₉ at 266, 355, and 532 nm. DFT calculations were carried out to obtain the optimized geometries of the cluster ions and their binding energies with the *Gaussian* program package at the B3LYP/cc-pVDZ level.

Figure 1. Photodissociation mass spectra of aniline⁺-(water)₉ at (a) 266 nm (b) 355 nm and (c) 532 nm.

