Spectroscopy and dynamics of large molecular ions utilizing a liquid nitrogen cooled electrostatic storage ring

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An electrostatic ion storage ring like TMU E-ring allows us to keep molecular ions circulating in vacuum for a long period up to a few minutes to study their slow dynamics. Vibrationally cold ions are available by cooling down the environment to the liquid nitrogen temperature, which suppresses the excited states of stored molecular ions through IR radiation. By introducing a visible tunable laser, we investigated the evolutional change of the absorption intensities and spectrum depending on the ion storage time, and succeeded in extracting the dynamics like the decay process of the metastable-state or the de-excitation process of the hot large molecular ions.

One example is determination of the radiative lifetime of the $a^4\Pi_u$ metastable state of O_2^+. We measured neutral products from metastable decay processes as a function of the ion-storage time. To selectively observe the metastable decay of a specific quantum state, photodissociation of the metastable ion was induced by a 10-Hz tunable laser in a wavelength between 494 and 680 nm. A long-lived component of the lifetime of 3.4 s has been newly found in the decay curves in addition to two shorter lifetime components, which clearly demonstrated the validity of the ring for studying such slow dynamics.

Another typical example is determination of the cooling rate and the internal temperature of hot large polyatomic ions. The cooling rates of hot C_{60}^- have been measured in the time region up to several tens of ms by observing the delayed electron detachment yield with one-photon laser excitation. The absolute energy scale is established by the photon energy and the cooling time interval is derived from the non-exponential decay of the ensemble of hot molecules. Alternative scheme with sequential multi-photon laser excitation was also tried for zinc phthalocyanine anions, when the molecule was not so hot, by observing the change in the laser fluence dependence of the yield.

A recent progress using TMU E-ring is introduction of an electrospray ion source to produce large molecular ions. For instance, microhydrated methylene blue cations, $MB^+(H_2O)_n$, are produced and their size-distributions are measured as a function of the source temperature. A series of $MB^+(H_2O)_n$ ions were observed up to n = 60, while intensities of n = 1 - 3 were extremely suppressed. To store these MB^+ ions in the TMU E-ring, they were captured in a pre-trap first, and extracted and accelerated to 15keV in a 10 Hz pulse mode. The stored ion intensities were directly monitored by evacuating them from the ring. The observed excitation spectra of laser induced reaction yielding the neutral species were compared with those obtained for MB^+ ions produced directly in a laser-desorption ion source.

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