

## Slow deexcitation dynamics of molecular ions stored in RICE and TMU E-ring

Toshiyuki Azuma

We have studied isolated molecular ions in a vacuum by taking advantage of two electrostatic ion storage rings, RICE in the cryogenic condition and TMU E-ring at room temperature over the years. We have focused on the deexcitation dynamics of laser-excited carbon clusters ( $C_n^-$ ) and understood them based on statistical descriptions. This strategy was successfully applied for larger molecules, i.e., pentacene anions ( $C_{22}H_{14}^-$ ) [1].

Recently, we have started rovibrational state-selective observation of the deexcitation of small molecular ions using a wavelength-tunable pulsed laser. The first example is the vibrational cooling of triatomic molecular ions  $N_2O^+$  in the range of several seconds. We found that the deexcitation dynamics drastically deviate from the statistical description based on a Boltzmann-type distribution [2,3]. We also observed deexcitation of the simple iso-nuclear diatomic negative molecule  $C_2^-$  in the tens of millisecond range. An iso-nuclear diatomic molecule has zero dipole moment, and the vibration transition is prohibited due to its symmetry. However, it is de-excited via spontaneous infrared radiation between electric excited and ground states. The time evolution of the population at specific vibrational states was measured up to 60 milliseconds, providing the first quantitative experimental support for long-standing theoretical predictions [4]. We also tackled  $Si_2^-$  on the microsecond time region. To our surprise, the excitation spectra show well-resolved rovibronic structures exclusively in the delayed time region [5].

### References

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