

# Detection of recurrent fluorescence photons emitted from $C_4^-$

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**Synopsis** We detected recurrent fluorescence (RF) photons in the region of visible light emitted from small carbon cluster anions  $C_4^-$  and  $C_6^-$  stored in an electrostatic ion storage ring. The observed RF decay profile for  $C_4^-$  is consistent with our simulation under the assignment that the RF is associated with the  $C^2\Pi_g-X^2\Pi_u$  transition. In addition, observation of the RF at two different wavelengths suggests that the RF band is rather broad.

Cooling dynamics of isolated molecules plays an important role in molecular physics, photochemistry and molecular evolution in the universe. The major cooling process of isolated molecules has been considered to be infrared radiation associated with vibrational transition. It is usually slow with time scales on the order of ms or longer.

For the last few years, a much faster pathway of radiative cooling associated with electronic transition has been confirmed experimentally for some isolated molecules, for example, the small, linear carbon cluster anions  $C_4^-$  and  $C_6^-$  [1,2] and polycyclic hydrocarbon (PAH) cations [3]. It is the visible-photon emission process via the electronic transitions after inverse internal conversion, converting the vibrational energy to the electronic energy. This process is referred to as recurrent fluorescence (RF) or Poincaré fluorescence. At first, the RF process has been studied not by detecting the emitted photon, but instead by observing the statistical delayed detachment or dissociation process of the molecular ions, which provides the information on the evolution of the internal energy and the cooling rate: the unusually fast cooling is a signature of the RF [1-3].

Recently we have succeeded in direct measurements of the RF photons from the  $C_6^-$  stored in an ion storage ring [4]. We observed energy-resolved photons by employing a photomultiplier tube combined with a bandpass filter-I (CWL: 607 nm ( $h\nu = 2.04$  eV), FWHM: 35nm) suitable for 2.04eV photons corresponding to the  $C^2\Pi_g - X^2\Pi_u$  electronic transition of  $C_6^-$ .

In this report, we show new results of the RF photons from  $C_4^-$ . Hot anions produced in the

ion source, from  $C_2^-$  to  $C_6^-$ , were simultaneously stored in the ring. The time profile of the photon intensities detected by the photomultiplier tube, i.e., the synchronized periodic structure to the ion revolution, contributed to exclude uncorrelated background signals.

As is the case for the  $C_6^-$  anions, we detected a significant number of 2.72 eV RF photons associated with the  $C^2\Pi_u - X^2\Pi_g$  electronic transition of  $C_4^-$  anions by using a bandpass filter-II (CWL: 460 nm ( $h\nu = 2.69$  eV), FWHM: 7 nm), and confirmed that the decay profile of the fluorescence is consistent with the simulated evolution of the level population based on the detailed balance theory. However, to our surprise, we found that a substantial amount of the RF photons for the  $C_4^-$  anions are detected with a bandpass filter-I.

The obtained experimental evidence is so far limited, however, this observation suggests that the RF band may be equipped with a non-negligible tail component to the longer wavelength side. This behavior is expected to be a crucial clue to clarify vibrational structures both on the high- and low-energy sides of the band origin of the RF spectrum, and they may imply transitions from the initial vibronic state to other states accompanying the vibrational excitation or deexcitation for several modes.

## References

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