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

To cite this article: M Yoshida et al 2017 J. Phys.: Conf. Ser. 875 012017

View the article online for updates and enhancements.
Detection of recurrent fluorescence photons emitted from $C_4^-$

M Yoshida$^1$, T Furukawa$^1$, J Matsumoto$^1$, H Tanuma$^1$, T Azuma$^{1,2}$, H Shiromaru$^1$ and K Hansen$^{3,4}$

$^1$ Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
$^2$ AMO Physics Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
$^3$ Department of Physics, University of Gothenburg 41296 Gothenburg, Sweden
$^4$ Tianjin International Center of Nanoparticles and Nanosystems, Tianjin University, China

E-mail: takeshi@tmu.ac.jp

Abstract. We detected recurrent fluorescence photons from vibrationally hot $C_4^-$ ions stored in an electrostatic ion storage ring. By virtue of the mass-independent storage condition, various anions produced in the laser ablation ion source were simultaneously stored with their own velocities, and ionic species emitting photons were identified from the temporal profile of the detected photons. The fluorescence synchronized with revolution of $C_4^-$, through the bandpass filter for the known absorption band, were clearly observed.

1. Introduction

De-excitation processes of vibrationally highly excited molecules play a critical role for the stabilization of interstellar molecules. Such molecules are often excited to, or formed as hot molecules inherently, either in production by two-body association or in UV irradiation, above decomposition (i.e., dissociation and electron detachment) threshold, and they need to be cooled down to survive. In the interstellar environment, collisional cooling does not work and radiative cooling is an exclusive process for stabilization [1]. Vibrational radiative cooling, in which IR photons are sequentially emitted, is a slow process, typically in an order of milliseconds, and often slower than competing decomposition processes. To study such slow vibrational cooling, hot molecules should be kept in vacuum for a longer time.

Electrostatic ion storage devices of the rings and linear beam traps enable us to isolate molecular ions in vacuum during the period long enough to observe the slow radiative cooling processes [2, 3]. Extensive ion storage studies were dedicated to observe vibrational radiative cooling by measuring dissociation or detachment yield as a function of the storage time or the time after photoexcitation in the ring. In many cases, the cooling of molecular ions is well described solely by the vibrational cooling [4], while some are cooled much faster. To explain this, fast-cooling electronic transitions must be considered [5].

Recurrent fluorescence (RF), an electronic transition from the thermally populated electronic excited states, had long been an undetectable process in a sense that it is essentially indistinguishable from the normal fluorescence. By a series of ion storage experiments, nowadays
the RF processes become recognized to be a not very unusual phenomenon for the molecules in highly isolated environment for example in space.

In most of RF studies, a contribution of the RF process is estimated by observing the delayed dissociation or electron detachment after thermalization. Direct detection of RF photons has been reported only for $C_6^-$ so far [6]. It was enabled by the careful reduction of the background and the accumulation for several tens of hours. The required condition for the RF process is that molecules have low-lying electronic states from a view point of state densities in statistical equilibrium. Among negative carbon clusters, $C_4^-$ also satisfies this condition, and the internal conversion of $C_4^-$ was reported to be very fast [7]. Indeed, signatures of an RF process in $C_4^-$ have already been seen when measuring laser induced delayed detachment [8]. In the present study, we succeeded in direct detection of the RF photons emitted from $C_4^-$.

2. Experiments
The experiments were conducted using an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring) [9]. The circumference of the ring is 7.74 m, and 15 keV $C_4^-$ took about 31.6 $\mu$s for one revolution. The pressure of an order of $10^{-9}$ Pa allowed us to store the ions for more than several seconds. Carbon cluster anions were produced in a laser ablation ion source, of which a schematic is shown in Fig. 1(a). The high-temperature anions produced in the source were extracted without using cooling gases. The anions with high kinetic energy escaped immediately from the ion extraction region, whereas those with relatively low kinetic energies were extracted by the delayed pulse and further accelerated by the bias voltage. Using the two-step acceleration, the anions were accelerated with relatively small kinetic energy spread. Then, the ion beam was directed to the ring by a $90^\circ$ deflection electrode and additional ion beam optics. A close-up schematic view of the motion of the sample disk in the ion source is shown in Fig. 1(b). To stabilize ablation conditions during the long-term continuous operation, the sample disk was driven along the internal gear so as to make irradiated spots of a few mm in diameter shows a cycloid as shown in Fig. 1(c). By this configuration, formation of a trench structure on the target, which may cause instability of the ion beam, was highly suppressed.

![Figure 1](image_url)

**Figure 1.** Schematic drawing of the ion source. (a) Whole view. The second harmonic of a pulsed Nd:YAG laser (Continuum, Minilite II, 10 Hz, 532 nm, 3.6 mJ/pulse) was irradiated on a slowly rotating graphite disk (diameter: approximately 10 mm). A pulsed high voltage of -0.92 kV (HV1) was applied a few $\mu$s after laser irradiation. The extracted anions were further accelerated to 15 keV by the bias voltage (HV2). (b) Motion of the target disk. The target holder (inner circle) rotates and moves along the wall of the outer circle while the ablation laser hits a fixed position. (c) a photograph of the irradiated sample (thermal paper). The cycloid is the trace of the ablation spot.

The voltage of the 10-degree deflector at the entrance of TMU E-ring was switched on after the specific ions of interest were injected. Various anionic species with smaller masses, $C_n^-$ and $C_nH^- \ (n=2-6)$, were injected to the ring. The heavier ions arriving later were rejected.
Because of the mass independent ion storage condition, which is a characteristic feature of the electrostatic ion storage ring, all of the admitted anions were simultaneously stored in the ring. The ionic species in the ring was identified by their mass-dependent revolution periods. Whenever it is necessary, we dump unwanted ions by applying a kick-out pulsed voltage to one of the deflectors synchronized with the passage of the ion bunch. On the other hand, simultaneous storage has a great advantage in identifying the RF photons because it gives information on the size specificity of the RF photon emission process under the identical conditions. During the ion storage, neutral particles produced by electron detachment were detected by a stack of 40 mm microchannel plates (MCP), placed at the extension of the straight section. The mass of the ions and the temporal profile of the ion bunch were determined by these time-resolved signals.

![Figure 2. Schematic drawing of the photon detection area. The photons emitted from the ion bunch were observed through an UHV-compatible quartz viewport with a diameter of 60 mm. Using four optical plano-convex lenses (diameter: 100 mm for Lens 1 and 2, 50 mm for Lens 3 and 4, focal length: 250 mm for Lens 1 and 2, 70 mm for Lens 3 and 4), the emitted photons were focused on a photocathode of a photomultiplier tube (PMT, Hamamatsu, R943-02).](image)

The single-photon detection system, which is the same as that employed in the previous study on $\text{C}_6^{-}$ except for the badpass filter wavelength, is schematically shown in Fig. 2. We used two bandpass filters; one for 460 ± 7 nm (Semrock, FF01-460/14, hereafter $F_{460}$) and the other for 607 ± 35 nm (Semrock, FF01-607/70, hereafter $F_{607}$), suitable for the expected $\text{C}^2\Pi_u \rightarrow X^2\Pi_g$ transition of $\text{C}_4^-$ and $\text{C}^2\Pi_g \rightarrow X^2\Pi_u$ transition of $\text{C}_6^{-}$, respectively. These filters were set between Lens 3 and 4. To confine the field of view, an aperture (diameter: 10 mm) was placed at the focal plane of Lens 2 between Lens 2 and 3. The solid angle of the lens systems was 0.069 sr, i.e. 0.56% of $4\pi$ sr, defined by the acceptance of the viewport. The length of the photon detection region was approximately 10 mm, whereas the total length of the ion bunch in the direction of propagation was typically 100 - 370 mm during storage. Transmittances of the viewport and lenses were 0.9 and 0.7, respectively. Those of $F_{460}$ and $F_{607}$ in the transmission wavelength region were higher than 0.9. The quantum efficiency of the PMT is 0.19 for 460 nm and 0.15 for 608 nm. By taking account of these parameters, the detection efficiency of the optical system was estimated to be an order of $10^{-4}$ for the RF photons emitted in the photon observation region.

3. Results and Discussion

The temporal profiles of the detected photons obtained using $F_{460}$ and $F_{607}$ are shown in Fig. 3(a) and (b), respectively. Those of the detected neutrals, which give information on the temporal profiles of the stored ions in the runs for $F_{460}$ and $F_{607}$, are also shown in 3(c) and (d), respectively. We assign the peak at 0.016 ms in 3(a) and 3(b) to RF photons emitted from $\text{C}_4^-$ in both cases, because the detection timing of these photons agrees well with the passage of $\text{C}_4^-$. In (b), also the peak of RF photons from $\text{C}_6^-$ appears, as observed in our previous study [6]. The RF photons obtained using $F_{460}$ are naturally expected, however, those for $F_{607}$ are somewhat surprising. At around 607 nm, which is the wavelength of the C-X transition of $\text{C}_6^-$,
the absorption of $C_4^+$ is very weak if it is cold [10]. To confirm the broad or widely-spread feature of the RF spectra, more detailed study using additional filters covering the wide range of wavelengths is now under way.

![Figure 3](image-url)

**Figure 3.** Temporal profiles of detected photon yields obtained using $F_{460}$ (a) and $F_{607}$ (b). The photon intensity is normalized by the accumulation time, the ion intensities, the quantum efficiency of the PMT, and the window width of the bandpass filters. The assignment of the peaks is given in the figures. The most intense peak in (a) and (b) is due to the switching noise. The delay time of the neutrals from the photons, indicated by the horizontal red bars, agrees well with the time of $C_4$ drifting from the photon detection area to the MCP. In (b), the additional peak is synchronized with the peak of $C_6^-$ in (d), of which the delay time indicated by the horizontal blue bar agree well with the flight time of $C_6^-$. The peaks in (c) and (d) represent the neutrals produced along the storage ring orbit and the preceding straight injection line. As these pulse counts are saturated by the high event rate they represent only the timing information.

**Acknowledgment**

We thank Mr. Y. Oda for his contribution in construction of the laser ablation ion source. This work is partly supported by the JSPS KAKENHI Grant No. 17H02937 and 26220607.

**References**

[1] Larsson M et al 2012 *Rep. Prog. Phys.* 75 066901 and references therein
[2] Møller S P 1997 *Nucl. Instr. and Meth.* A 394 281
[3] Strasser D et al 2002 *Phys. Rev. Lett.* 89 283204
[4] For example, Goto M et al 2013 *J. Chem. Phys.* 139 054306
[5] For example, Andersen J U et al 2001 *Eur. Phys. J.* D 17 189
[6] Ebara Y et al 2016 *Phys. Rev. Lett.* 117 133004
[7] Zhao Y et al 1996 *J. Chem. Phys.* 105 4905
[8] Kono N et al 2015 *Phys. Chem. Chem. Phys.* 17 24732
[9] Jinno S et al 2004 *Nucl. Instrum. Methods Phys. Res.* A 532 477
[10] Freivogel P et al 1997 *J. Chem. Phys.* 107 22