### Title
A single-photon sensitive synchroscan streak camera for room temperature picosecond emission dynamics of adenine and polyadenylic acid

### Author(s)
Kobayashi, Shunsuke; Yamashita, Mikio; Sato, Takuzo; Muramatsu, Shigeru

### Citation

### Issue Date
1984-12

### Doc URL
http://hdl.handle.net/2115/45319

### Rights
© 1984 IEEE. Personal use of this material is permitted. However, permission to reprint/republish this material for advertising or promotional purposes or for creating new collective works for resale or redistribution to servers or lists, or to reuse any copyrighted component of this work in other works must be obtained from the IEEE.

### Type
article

### File Information
JQE20-12_1383-1385.pdf
A Single-Photon Sensitive Synchroscan Streak Camera for Room Temperature Picosecond Emission Dynamics of Adenine and Polyadenylic Acid

SHUNSUKE KOBAYASHI, MIKIO YAMASHITA, TAKUZO SATO, AND SHIGERU MURAMATSU

Abstract—It is experimentally verified that a synchroscan streak camera, incorporating a microchannel plate and synchronizing with UV picosecond pulses generated inside the cavity of a mode-locked CW ring dye laser, has enough sensitivity to detect picosecond emission phenomena in the region of a single-photon event. To demonstrate the usefulness of the synchroscan streak camera, the first measurement of time- and wavelength-resolved emissions in the picosecond region is successfully carried out for adenine and polyadenylic acid aqueous solutions at room temperature, and shows that their shortest lifetimes, due to the monomer fluorescence, are 6 and 8 ps, respectively.

For a study on nucleic acid photochemistry and photobiology, it is essential to make clear the dynamic behavior of the luminescence from nucleic acid bases in monomers, polymers, and higher order structures. Many investigations of the excited state dynamics of nucleic acids and their components have been carried out [1]. However, their emissions at room temperature remain incompletely characterized because of their low quantum yields ($10^{-4} \sim 10^{-3}$) and fast lifetimes ($10^{-11} \sim 10^{-13}$ s) [2]. Room temperature emission spectra, quantum yields, and lifetimes of nucleotides were reported recently by Ballini et al. [3] and Rigler et al. [4] with a single-photon counting method. They found that the emission quantum yields of adenine and polyadenylic acid were $2.4 \times 10^{-4}$ and $3 \times 10^{-3}$, respectively [3]. The lifetime of polyadenylic acid depended on the wavelength of the emission band, and the origin of more than three emission components was discussed [3]. However, the questions still remain because of the instrumental restriction of the time resolution. Therefore, further investigation based on time- and wavelength-resolved emission measurements in the picosecond time region is strongly needed.

An electron-optical streak camera in synchronous operation with a mode-locked CW dye laser has become the most useful instrument that can directly measure the time and wavelength versus the intensity profile of a picosecond optical event for the weak luminescence [5], [6]. Using a highly-sensitive synchroscan streak camera with a mode-locked and internally frequency-doubled CW ring dye laser, we report the first direct measurement of picosecond time- and wavelength-resolved emissions from adenine and polyadenylic acid in aqueous solutions at room temperature.

The experimental configuration used is shown schematically in Fig. 1, which is essentially similar to that previously reported [5], [7] except for the following points. An actively mode-locked Ar ion laser (Spectra-Physics 171) was used to synchronously pump a Rhodamine 6G ring dye laser at the repetition rate of 82 MHz. A high long-term stability of the mode-locked Ar ion laser enabled us to produce continuous trains of 85 ps pulses. A ring synchronous mode locking was chosen for efficient intracavity second-harmonic generation. Continuous trains of UV picosecond pulses at 291 nm had the average power of 0.2 mW per each direction under the pumping power of 1.7 W.

The two-dimensional synchroscan streak camera (Hamamatsu Photonics C1587) in our system had a high sensitivity since a microchannel plate (MCP; gain $5 \times 10^3$ at 900 V) was incorporated [8]. The streak image was monitored by a SIT vidicon of OMA II (Princeton Applied Research 1215/1216) which displayed and analyzed the two dimensional signal of time-resolved spectra or wavelength-resolved decays. When MCP is operated at 700 V to hold the reasonable signal-to-noise ratio, the streak camera amplifies one photon at the photocathode to $10^3$ photons at the phosphor screen. Two percent of these are collected into the SIT cathode and recorded as one count
by OMA II. Therefore, it is deduced that the sensitivity of the present synchroscan system is in the region of a single-photon event. Moreover, the photon utility of the streak camera at each event is far better than that of the time-correlated single-photon counter.

The sensitivity was confirmed by the measurement of the very weak fluorescence from psoralen in ethanol. The UV picosecond pulses used to excite the psoralen solution was focused into a 10 mm square quartz sample cell. The fluorescence was collected at 90° with respect to the incident beam and was focused into the entrance slit of a grating polychromator (Jobin Yvon HR 320). A pyrex plate was used to reduce light scattered from excitation UV pulses. The polychromator has a dispersion of 10 nm/mm and covers the 120 nm spectral width. The results showed that even for the 7.2 × 10⁻⁸ M psoralen solution, time-resolved fluorescence spectra were observed at the S/N of 15 in a few hundred picoseconds time region in the integration time of 15 s. This means that the solution emits only 30 photons per pulse into all solid angles since the fluorescence yield of psoralen is 0.8 × 10⁻² [9]. The optical collection efficiency of the system is estimated to be 10⁻⁴. As a result, 3 × 10⁻³ photons per pulse at the photocathode of the streak tube [8] are enough to measure time-resolved fluorescence spectra. Therefore, it is concluded that the sensitivity of the present two-dimensional synchroscan streak camera system is high enough to detect the emission in the region of a single-photon event. In addition, it was confirmed that the streak camera had a large dynamic range of 5 × 10³ [8].

Synchronizing the emission signal with the deflection voltage of the streak camera was done by monitoring visible pulses from the dye laser with a p-i-n photodiode. The full width at half maximum (FWHM) of the UV pulses in the integration time of 1 s was 24 ps, while the FWHM was only 5 ps at the 100 ns gate time in which 8 pulses were accumulated. This broadening can be attributed to the arrival time jitter in the synchronously pumped dye laser system.

Adenine and polyadenylic acid (sodium salt) was purchased from Yamasa Shoyu Co., Ltd., and used without further purification. The water used for the fluorescence measurement was a Dotite Luminasole grade and no detectable emission was observed under the experimental conditions.

Fig. 2. Time-resolved emission spectra measured for an adenine aqueous solution (6 × 10⁻⁴ M) at room temperature; (a) 0 ps, (b) 85 ps, (c) 170 ps, and (d) 340 ps.

The time-resolved emission spectra measured for an adenine aqueous solution (6 × 10⁻⁴ M) at room temperature are shown in Fig. 2. Each spectrum was accumulated in the successive 85 ps duration. A narrow Raman line from solvent H₂O was observed at 320 nm, in Fig. 2(a), and was used as a reference of the time profile of UV pulses because the Raman scattering is an instantaneous phenomenon and has the same optical geometry as fluorescence. A short wavelength emission, which corresponds to the reported monomer emission [3], was observed at 340 nm immediately after the excitation. The 340 nm emission disappeared within 42 ps, while a red shifted emission was predominant at 390 nm over several hundred picoseconds. The longer lifetime emission can be attributed to the adenine aggregate compared to the results for polyadenylic acid [3]. The corresponding wavelength-resolved decay curves are shown in Fig. 3 with the Raman scattering profile. The lifetime of the 340 nm emission was calculated to be 6 ps from the deconvolution of curve (a) measured as the response to the excitation pulse and the curve (b) measured as the decay around the 340 nm emission [10]. The fitting was done within ±0.5 ps accuracy. The result is shown in Fig. 3. The temporal broadening Δτ(λ) due to the path difference for a monochromator at the given wavelength λ was discussed by Schiller and Alfano [11] and estimated to be ~10 ps at 300 nm in our system. The pulse broadening inside the monochromator can be neglected, since 25 ps of the FWHM of Raman scattering, in Fig. 3(a), is in agreement with 24 ps of the FWHM of the laser pulse which is little affected by the width of the grating. Using Δτ(320 nm) = 10 ps in our system and Δτ(340 nm)/Δτ(320 nm) = 1.06, one can estimate the difference between Δτ(320 nm) of the reference wavelength and Δτ(340 nm) of the monomer emission to be 0.6 ps. This can be neglected compared to the measured lifetime of 6 ps. The measured value is in agreement with the calculated lifetime of 1.0 ps [2]. Therefore, the origin of the 340 nm emission is assigned to the lowest π-π* state. The lifetime of the 390 nm emission was measured to be 790 ps.

Fig. 3. Wavelength-resolved decay curves measured for an adenine aqueous solution (6 × 10⁻⁴ M) at room temperature; (a) 320 nm (Raman scattering profile), (b) 340 nm, and (c) 380 nm. Closed circles represent the calculated value with the lifetime of 6 ps.
emission. The longer component of the decay curves has been fitted by two time constants of 510 ps and 1.3 ns, since it with forbidden character.

mers. The emitting states of the aggregates may be singlet fluorescence, which was suggested by Ballini [3], shows nonsingle exponential character. These may be assigned to the aggregate fluorescence of different configurations [3] , [4], [12]. The radiative lifetimes of the excited states of aggregates estimated from the measured lifetimes and quantum yield are two-order-of-magnitude longer than those of monomers. The emitting states of the aggregates may be singlet, with forbidden character. A possibility for the delayed excimer fluorescence, which was suggested by Ballini et al. [3], is ruled out because no rise up at 340 and 390 nm was observed.

The red shifted 390 nm emission of adenine is similar to that found in polyadenylic acid, which was not reported by Ballini et al. [3]. The discrepancy may come from the different experimental conditions concerning the concentration and excitation wavelength. The further investigations including this point are in progress.

In summary, we have demonstrated that the two-dimensional synchroscan streak camera, incorporating the microchannel plate and operating synchronously with an efficient UV picosecond pulses at high repetition rates, is sensitive enough to detect the emission in the region of a single-photon event. Using this system, we have first measured picosecond time-dependent emission spectra and wavelength-resolved decays at room temperature for adenine and polyadenylic acid aqueous solutions whose emissions have very low quantum yields and very short lifetimes.

**Acknowledgment**

The authors wish to thank Dr. M. Ishikawa, A. Hirano, and M. Nomura for their experimental assistance.

**References**