Supplementary information for the PCCP article "Ultrafast dynamics of uracil and thymine studied with a sub-10-fs deep ultraviolet laser"

B. Xue,^{a,b} A. Yabushita^c and T. Kobayashi^{a,b,c,d}

^a-Advanced Ultrafast Laser Research Center and Department of Engineering Science, Faculty of Informatics and Engineering, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan.

^{b.}CREST, Japan Science and Technology Agency, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan.

^c Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan.

^{d.} Institute of Laser Engineering, Osaka University, 2-6 Yamada-Oka, Suita, Osaka 565-0871, Japan.

Sample preparation

Uracil and thymine (5-methyluracil) powder are purchased from Sigma Aldrich and used without further purification. Uracil and thymine are dissolved in distilled water to prepare an aqueous solution with molar concentrations of 4 mM and 2 mM, respectively. The aqueous solution is continuously circulated around a home-made flow cell using a peristaltic pump. The cell is composed of 0.2-mm-thick CaF₂ windows with the optical path length of 0.2 mm.

Sub-10-fs DUV pump-probe spectroscopy setup

The technique of broadband chirped-pulse four-wave mixing (FWM) used for generating a sub-10-fs DUV pulse has been described elsewhere.^{1,2} Briefly, a near-infrared (NIR) pulse from a Ti: sapphire chirped-pulse amplifier is transmitted through glass blocks (10-mm fused silica and 5-mm BK7) and positively chirped. The pulse is then focused into a krypton-gas-filled hollow fiber for spectral broadening by selfphase modulation. A near-UV pulse generated by frequency doubling of a NIR pulse is negatively chirped with a double-pass prism pair. The broadband NIR pulse and NUV pulse are spatially and temporally synthesized in another hollow-core fiber filled with argon gas. By the FWM process in the hollow-core fiber, a broadband and negatively chirped DUV pulse is generated. After collimation of the DUV pulse with a concave mirror, the NIR and NUV pulses transmitted through the hollow-core fiber and co-propagated with the DUV pulse are carefully eliminated using harmonic separators. For this process, the following setup is used: two low-dispersion harmonic separators reflect the DUV wavelength component while transmitting the NIR wavelength component and the broadband NUV component, and then two low-dispersion dielectric mirrors are used for the s-polarized pulse in the wavelength range of 250-290 nm. After these separators, the pulse energy of the residual NUV and NIR pulses co-propagating with the DUV pulse (200 nJ) is less than 1 nJ, or less than 1% of the energy of the DUV pulse. The polarization of the horizontally polarized DUV pulse is changed to vertical polarization with a periscope consisting of aluminum mirrors. The beam is split into two beams, which are focused noncollinearly onto a 0.2-mm-thick CaF₂ plate. By detecting the self-diffraction (SD) signal generated in the plate with a multichannel spectrometer (USB2000, Ocean Optics) while scanning the optical delay line, a SD-frequencyresolved optical gating trace is measured for characterization of the pulse shape. By optimizing the distance between the harmonic separators in air via path length tuning, the pulse duration of the DUV pulse is compressed to the shortest pulse duration possible (details are shown in Fig. S1).

After characterization of the pulse duration, the two CaF₂ plates are replaced with the home-made flow cell. The transmitted probe pulse from the flow cell is focused into a multimode fiber that is connected to a multichannel spectrometer coupled to a 128-channel multichannel lock-in amplifier.³⁻⁵ The intensity of the pump pulse is modulated with a frequency of 500 Hz by an optical chopper for the lock-in detection. The difference absorption spectra are measured over a range of pump-probe delay times from -200 fs to 1800 fs with a step size of 0.2 fs. These features allow for application of the pulse in ultrafast spectroscopy without undue complications. The DUV pulse broadband chirpedpulse FWM is easily compressed down to a sub-10-fs pulse duration without the use of an external pulse compressor.^{1,2} The pulse is spatially split into two beams¹ using the edge of an aluminum mirror. One of the two beams is sent to an optical delay line composed of a stepping motor stage (FS-1020PX, Sigma-Tech), an aluminum mirror, and a fused-silica prism. The pulse energies of the input pump and probe pulses are 100 nJ and 12 nJ, respectively. All of the experiments are performed at room temperature (293 K).



Fig. S1. The spectrum and measured pulse duration of the DUV pulse

Assignment of data analysis

The signals in uracil and thymine at delay times of around 0 fs are also seen for the water sample, which can be seen more clearly in a difference absorbance trace obtained after averaging in the range between 4.70 eV and 4.75 eV (see Fig. 4(b) in Ref. 6). Specifically, there are intense oscillatory structures in the delay time range between -100 fs and 60 fs, with similar structures apparent for both samples in this delay range. Therefore, the intense oscillatory structure is not attributable to molecules of uracil and thymine but is considered to be mainly due to a coherent artefact, perturbed free induction decay, and interference between the scattered pump light and probe diffracted in the direction of the probe. The small differences in the strength of the artefact in the range of $4.6 \sim 4.8$ eV are explained by the knowledge that the coherent artefact appears in the same direction as the incoherent signals.⁵

The traces of the time-dependent difference absorbance change (example shown in Fig. S2 for uracil sample) are analysed by a global fitting procedure using the fitting function Eq.(1) described in the main text, which allows for three separate species, $\Delta A_1(\omega)$, $\Delta A_2(\omega)$, and $\Delta A_3(\omega)$, and two corresponding time constants, $\tau_1(\omega)$ and $\tau_2(\omega)$. ω is the angular frequency of the spectral component of the probe pulse. Fitting is performed in the photon energy range between 4.35 eV and 4.76 eV, for which the relative intensity of the laser is higher than 1% of the peak of the laser spectrum. In this equation, the meanings of the coefficients $\Delta A_1(\omega)$, $\Delta A_2(\omega)$, and $\Delta A_3(\omega)$ of the corresponding exponential functions are considered to be $\Delta A_1(\omega) = A_1(\omega) - A_2(\omega)$, $\Delta A_2(\omega) = A_2(\omega) - A_3(\omega)$, and $\Delta A_3(\omega) = A_3(\omega)$. The coefficients include the effect due to bleaching of the ground state. Then, $A_i(\omega)$ must be replaced with $A_i(\omega) - A_0(\omega)$ (i = 1 ~ 3) as the relevant parameters.

In the lowest photon energy regions for both cases of uracil and thymine, the values of τ_1 and τ_2 are very close to each other or in similar spectral regions as in 4.37 ~ 4.39 eV for uracil and in 4.35 ~ 4.39 eV for thymine; it is not possible to separate them clearly. This means that there is no substantial component in the spectral regions because of spectral cancellation of the positive (induced absorption) and negative (bleaching and stimulated emission) difference absorbance change corresponding to second shortest lifetime $\tau_2(\omega)$ component. To discuss non-constant decay time, the $\tau_2(\omega)$ component in uracil, which has the highest reliability due to its large $\Delta A(\omega, t)$ and no contribution of coherent artifact, is used.



Fig. S2. The traces of the time-dependent difference absorbance change for uracil.

References

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