Supplementary Information for:

Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy of Adenine, Adenosine and Adenosine Monophosphate in a Liquid

Flat Jet

Masafumi Koga, ¹ Do Hyung Kang,¹ Zachary N. Heim,¹ Philipp Meyer,² Blake A. Erickson,¹ Neal Haldar,¹ Negar Baradaran,¹ Martina Havenith² and Daniel M. Neumark^{1,3*}

¹Department of Chemistry, University of California, Berkeley, California 94720, USA ²Lehrstuhl fur Physikalische Chemie II, Ruhr-Universitat Bochum, 44801, Germany ³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

* Corresponding author. Email: dneumark@berkeley.edu



Figure S1. (a) Contour plot of TRPE spectrum of H₂O background (NaCl 25 mM) under the irradiation of 266-nm pump pulse at 2 μ J/pulse. The feature at 5-7 eV at t=0 is LAPE of the liquid water. (b) Time profile averaged over 5-7 eV. The fitting result with the Gaussian function is also shown as a red solid line.



Figure S2. Correcting for space charge effects. (a) Example of the double-Gaussian fit to $1b_1$ water peak from Ado solution under 400- μ W pump intensity. (b) Shift of the $1b_{1(1)}$ peak position as a function of the delay time.



Figure S3. Contour plot of the TRPE spectrum of AMP without spectral and temporal smoothing.



Figure S4. Contour plot of the TRPE spectrum of Ade at (a) short and (b) long time delay without smoothing.

Temporal boxcar smoothing for AMP



Figure S5. Temporal profiles of AMP at several eBEs with a 3-point boxcar averaging (blue) and without any smoothing (red).

Evaluation of the GLA analyses



Figure S6. (a) Residual of the GLA analysis of Ado obtained under (a) the monoexponential functions and (b) the biexponential functions. (c,d) Time evolution at (c) 3.7 eV and (d) 6.7 eV with the two different GLA results.



Figure S7. Residual plots of GLAs for AMP under (a) the monoexponential functions and (b) the biexponential functions. (c,d) Time evolution at (c) 3.6 eV and (d) 5.8 eV with the two different GLA results.



Figure S8. Residual plots of GLAs for Ade in (a) monoexponential decays and (b) biexponential decays out to 2 ps. Residuals out to 12 ps are shown in (c) and (d).



Figure S9. Time evolutions of Ade at (a,b) 5.7 eV and (c,d) 3.7 eV. The GLA result under mono- and biexponential functions are also shown.



Figure S10. DAS for Ado obtained after GLA under monoexponential function.

Ultrafast Decay Analysis for AMP



Figure S11. Contour plot for AMP without smoothing around t = 0.

Method	$\lambda_{ex}(nm)$	Ado	AMP	Ade	Ref.
XUV-TRPES	266	0.11, 0.47	0.10, 0.56	0.09, 0.48,	
(This work)				9.0	
ТА	263	0.29			Pecourt (2001) ^{1, 2}
FU	270	0.53	0.52		Peon (2001) ³
FU	267	<0.1, 0.5 ^a	<0.1, 0.5 ^b	0.23, 8.0	Gustavsson (2002) ⁴
FU	255	<0.1, 0.42 ^a	<0.1 0.52 ^b		Onidas (2002) ⁵
ТА	263			0.18, 8.8	Cohen (2003) ⁶
FU	265°	0.32		0.55, 8.1	Pancur (2005) ⁷
TA, KTRF	267	0.13, 0.45			Kwok (2006) ⁸
UV-TRPES ^d	266	0.21		0.064, 8.5	Buchner (2013) ⁹
FU	267	0.11-0.27 ^e			Gustavsson (2013) ¹⁰
FU	260		0.32 ^b		Stuhldreier (2013) ¹¹
ТА	266			0.20, 5.4	Roberts (2014) ¹²
UV-TRPES ^f	250-264	0.21-0.24	0.22-0.25		Williams (2018) ¹³

Table S1. Lifetimes of the excited state signals (in ps) in different time-resolved measurements in aqueous solution near-266-nm excitation

^adA. ^bdAMP. ^c They reported lifetimes under various λ_{ex} around 245-280 nm and λ_{pr} around 300-330 nm. ^d λ_{pr} = 5.2 eV. ^e Obtained at various λ_{pr} : 310-380 nm. ^f λ_{pr} = 6.2 eV.

References

- J.-M. L. Pecourt, J. Peon and B. Kohler, Ultrafast Internal Conversion of Electronically Excited RNA and DNA Nucleosides in Water, *J. Am. Chem. Soc.*, 2000, 122, 9348-9349.
- J. -M. L. Pecourt, J. Peon and B. Kohler, DNA excited-state dynamics: Ultrafast internal conversion and vibrational cooling in a series of nucleosides, *J. Am. Chem. Soc.*, 2001, **123**, 10370-10378.
- J. Peon and A. H. Zewail, DNA/RNA nucleotides and nucleosides: direct measurement of excited-state lifetimes by femtosecond fluorescence upconversion, *Chem. Phys. Lett.*, 2001, 348, 255-262.
- T. Gustavsson, A. Sharonov, D. Onidas and D. Markovitsi, Adenine, deoxyadenosine and deoxyadenosine 5'-monophosphate studied by femtosecond fluorescence upconversion spectroscopy, *Chem. Phys. Lett.*, 2002, 356, 49-54.
- 5. D. Onidas, D. Markovitsi, S. Marguet, A. Sharonov and T. Gustavsson, Fluorescence properties of DNA nucleosides and nucleotides: a refined steady-state and femtosecond investigation, *J. Phys. Chem. B*, 2002, **106**, 11367-11374.
- 6. B. Cohen, P. M. Hare and B. Kohler, Ultrafast excited-state dynamics of adenine and monomethylated adenines in solution: Implications for the nonradiative decay mechanism, *J. Am. Chem. Soc.*, 2003, **125**, 13594-13601.
- 7. T. Pancur, N. K. Schwalb, F. Renth and F. Temps, Femtosecond fluorescence upconversion spectroscopy of adenine and adenosine: Experimental evidence for the $\pi\sigma^*$ state?, *Chem. Phys.*, 2005, **313**, 199-212.
- 8. W. M. Kwok, C. Ma and D. L. Phillips, Femtosecond time- and wavelengthresolved fluorescence and absorption spectroscopic study of the excited states of

adenosine and an adenine oligomer, J. Am. Chem. Soc., 2006, 128, 11894-11905.

- F. Buchner, H. H. Ritze, J. Lahl and A. Lübcke, Time-resolved photoelectron spectroscopy of adenine and adenosine in aqueous solution, *Phys. Chem. Chem. Phys.*, 2013, 15, 11402-11408.
- T. Gustavsson, N. Sarkar, I. Vayá, M. C. Jiménez, D. Markovitsi and R. Improta, A joint experimental/theoretical study of the ultrafast excited state deactivation of deoxyadenosine and 9-methyladenine in water and acetonitrile, *Photochem. Photobiol. Sci.*, 2013, **12**, 1375-1386.
- 11. M. C. Stuhldreier and F. Temps, Ultrafast photo-initiated molecular quantum dynamics in the DNA dinucleotide d(ApG) revealed by broadband transient absorption spectroscopy, *Faraday Discuss.*, 2013, **163**, 173-188.
- G. M. Roberts, H. J. Marroux, M. P. Grubb, M. N. Ashfold and A. J. Orr-Ewing, On the participation of photoinduced N–H bond fission in aqueous adenine at 266 and 220 nm: a combined ultrafast transient electronic and vibrational absorption spectroscopy study, *J. Phys. Chem. A*, 2014, **118**, 11211-11225.
- H. L. Williams, B. A. Erickson and D. M. Neumark, Time-resolved photoelectron spectroscopy of adenosine and adenosine monophosphate photodeactivation dynamics in water microjets, *J. Chem. Phys.*, 2018, **148**, 194303.