EPJ Web of Conferences 41, 05017 (2013)
DOI: 10.1051/epjconf/20134105017

(OHFWURQLF ([FLWHG 6WDWH DQG 9LEUD 6ROXWLRQ RI &\WRVLQH 2EVHUYHG E\ 7UD $EVRUSWLRQ 6SHFWURVFRS\ 'HHS 8OWUD /DVHU 3XOVH

-XQ 0L\D]DNL &KLKLUR .DQGD 7DND\RVKL .RED\DVKL

$GYDQFHG 8OWUDIDVW /DVHU 5HVHDUFK &HQWHU 7KH 8QLYHUV &KRIX JDRND &KRIX 7RN\R
-67 &5(67 6DQEDQFKR 7RN\R -DSDQ
'HSDUWPHQW RI (OHFWURSK\VLFV 1DWLRQDO &KLDR 7XQJ 8QLYHUVLW\ 7DLZDQ
,QVWLWXWH RI /DVHU (QJLQHHULQJ 2VDND 8QLYHUVLW\

$EVWUDFW 7LPH UHVROYHG WUDQVLHQW DEVRUSWLRQ F\WRVLQH ZLWK GHHS XOWUDYLROHW ODVHU SXOVH LV U H[FLWHG VWDWH G\QDPLFV DQG FRKHUHQW PROHFXODU Y REVHUYHG DQG WKHLU UHOD[DWLRQ PHFKDQLVPV DUH GLVFXVV

,QWURGXFWLRQ

'1$ DQG 51$ H[KLELW XOWUDIDVW UHOD[DWLRQ XQGHU GHHS ZKLFK HQVXUHV WKDW WKH PROHFXOHV UHOD[WR WKH JUR VWDWH UHDFWLRQV FDQ RFFXU 7KLV LV EHOLHYHG WR EH LP PXWDJHQLF DQG FDUFLQRJHQLF HIIHFWV LQ OLYLQJ V\VW ELRORJLFDOO\ UHOHYDQW PROHFXOHV VXFK DV '1$ EDVHV FRQWH[W RI SKRWR VWDELOLW\ WKHUH KDYH EHHQ PDQ\ PHDQV RI WLPH UHVROYHG DEVRUSWLRQ DQG IOXRUHVFHQFH PHD G\QDPLFV KDYH QRW EHHQ IXOO\ XQGHUVWRRG \HW GXH SXOVHV LQ WKH '89 UDQJH

,Q WKLV VWXG\ '89 SXOVH LV VXFFHVVIXOO\ DSSOLHG IRU W RI ZDWHU VROXWLRQ RI F\WRVLQH '89 SXOVH ZLWK QH JHQHUDWHG E\ D SXOVH IRXU ZDYH PL[LQJ WHFKQLTXH ZLWKRXW H[7UDQVLHQW DEVRUSWLRQ PHDVXUHPHQW XVLQJ WKLV XO XOWUDIDVW HOHFWURQLF H[FLWHG VWDWH G\QDPLFV DQG

([SHULPHQWDO VHWXS

6XE IV GHHS '89 SXOVH ZDV REVHUYHG [IRU LPSXOVH $ SDUW RI IURP D 7L 6DSSKLUH DPSOLILHU ZDV XVHG WR JHQHUDWH ILODPHQW RQ KR.O ORZ IL

EURDGHQLQJ SKHQRPHQD WKH\ DWWULEXWHG $ QHDU 89 189 SXOVH LV
GRXEOLQJ RI WKH IXQGDPHQWDO SXOVH ZKLFK LV SULQJHG
7KH EURDGEDQG QHDU LQIUDUHG 1,5 DQG 189 SXOVHV ZHUH
ILOOHG JODVV ZLWK $U KHUH D EURDGEDQG '89 SXOVH ZDV JHQHUDWHG
ZDYH PL[LQJ SURFHVV)RU WUDQVLHQW DEVRUSWLRQ PHD
SXOVH ZDV VSDWLDOO\ VSOLW LQWR WZR EHDPV RI WKH HTXDO
WR DQ RSWLFDO GHOD\ OLQH FRPSRVHG RI D VWHSSLQJ P
EHDP ZDV XVHG IRU SXPS SXOVH 7KH SXPS DQG SUREH
XVLQJ D FRQFDYH PLUURU 7KH GLIIHUHQFH DEVRUEDQFH DW
UDQJH IURP WR H9 ZDV PHDVXUHG VLPXOWDQHRXVO\
FRXSOHG WR D SRO\FKURPHWHU 7KH DTXHRXV VROXWLRQ
KRPHPDGH IORZ FHOO E\ XVLQJ D SHULVWDOWLF SXPS WR DY

5HVXOWV DQG GLVFXVVLRQ

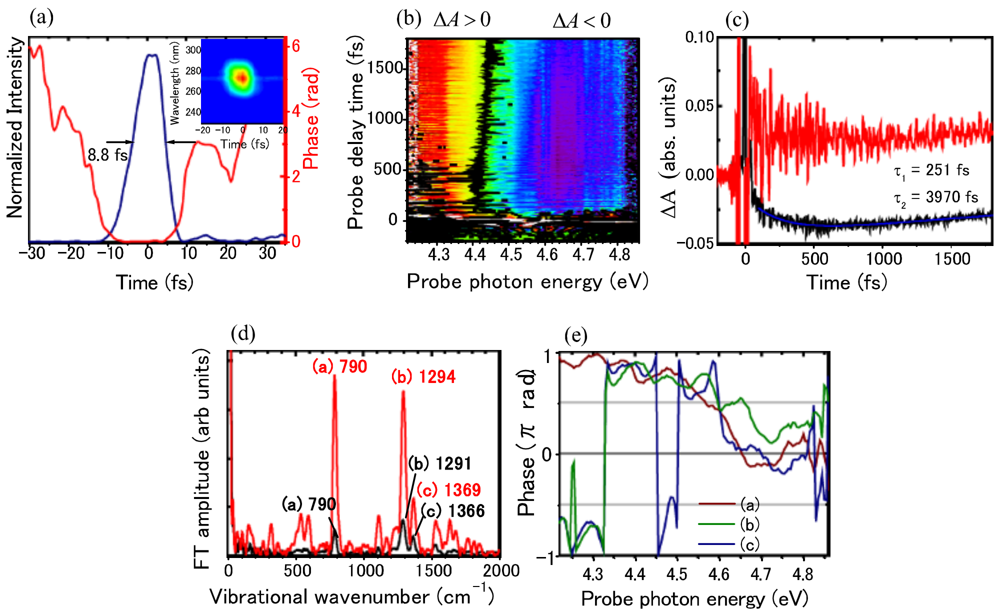

Fig. 1. (a) Retrieved intensity and phase of the DUV pulse. The pulse duration is 8.8 fs in the full-width at half maximum. The inset shows the measured SD-FROG trace. (b) 2D difference transient absorption spectrum ΔA of aqueous solution of cytosine. ΔA is positive when the probe photon energy is below ~4.45 eV, while that is negative above ~4.45 eV. (c) Typical time traces of the difference absorbance in the low- (red line) and high-energy side (black line) in (b). ΔA is spectrally averaged between 4.30 and 4. 36 eV (4.65 and 4. 75 eV) for the low- (high-)energy side. The blue line denotes two-exponential fitting curve for ΔA in the high-energy side with the time constants of 251 and 3970 fs. (d) Fourier amplitude spectra of the time trace in (c). (e) The phases of the observed molecular vibrations corresponding to the three modes in (d).

7KH '89 ODVHU SXOVH DQG VWDWLRQDU\ DEVRUSWLRQ

7KH SXOVH GXUDWLRQ RI WKH '89 SXOVH ZDV PHDVXUHG E\
JDWLQJ)52* WHFKQLTXH 7KH FRPPHUFLDO VRIWZDUH)52*
ZDV HPSOR\HG IRU WKH DQDO\VLV)LJXUH D VKRZV WKH '89 ODV
DQG WKH UHWULHYHG WHPSRUDO LQWHQVLW\ 7KH UHWULH

IV LQ WKH WRWDO KDOI PD[LPXP The inset shows the measured SD-FROG trace. 7KH VSHFWU SHDN RI WKH '89 SXOVH LV VKLIWHG WR WKH EOXH VLGH RI WKH DEVRUSWLRQ VSHFWUXP HGJH

'\QDPLFV RI HOHFWURQLF H[FLWHG VWDWH

)LJXUH E VKRZV WKH WLPH UHVROYHG DEVRUSWLRQ VSHFWUXP 7KH H[SHULPHQWV ZHUH SHUIRUPHG DW WKH LQWHQVLWLHV UHVSHFWLYHO\ ΔA ...)LJXUH F VKRZ WKH ΔA ... ORZ HQHUJ\ VLGH respectively. The intense oscillatory structures in the delay time between -100 fs and 100 fs is attributed to electronic coherence induced by the two pulses. It is noteworthy that the observed signal is periodically modulated due to coherent molecular vibration. At the delay time longer than 100 fs, ΔA in the high-energy side decreases initially and then recovers slowly. The time trace of ΔA can be fitted by two exponentials with the time constants of ~250 fs and ~4 ps. Such multi-exponential decay dynamics has been observed in the previous transient absorption and fluorescence up conversion measurements [3,4], and considered to be attributed to the excited state relaxation from $\pi\pi$ and $n\pi$ states, although vibrational population relaxation may also contribute. On the other hand, it is difficult to characterize the electronic excited state in the low-energy side because the signal is strongly modulated due to the molecular vibration even after 100 fs.

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We calculated Fourier transform (FT) amplitude spectra of the time trace of ΔA to examine the origin of the measured molecular vibrational dynamic. Here, we analyzed ΔA after 100 fs to exclude the initial contamination of the coherent artifact. Figure 1(d) shows FT amplitude of ΔA in the high- and low-energy side. Three intense vibrational peaks are observed, and peak positions in the high-energy side agree with that of the Raman frequency (789, 1289, and 1364 cm^{-1})[5] , while that in high-energy side seems to be slightly blue-shifted. Figure 1(e) shows the phase of the observed molecular vibrations of three intense peaks as a function of probe photon energy. It appears that all three phases in the low-energy side are close to π. From this together with the sign of ΔA suggest that the signal in the low-energy side is mainly attributed to the excited state dynamics; the pump pulse excites cytosine to the electronic excited state, which is detected by the probe pulse predominantly as a transition to a higher excited state. The difference in the electronic configuration between the ground state and excited state may results in the difference in the measured vibrational frequencies.

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Using sub-10 fs DUV pulses, the electronic excited state and vibrational dynamics of water solution of cytosine are simultaneously observed. The present study is expected to provide further understanding of relevant biological molecules such as DAN and gives some insight on the ultrafast photochemical dynamics induced by DUV irradiation.

< .LGD DQG 7 .RED\DVKL -2SW 6RF $P % 28
7 .RED\DVKL DQG < .LGD 3K\V &KHP &KHP 3K\V 14
$ 6KDUR 7 *XVWDYVVRQ DQG & (-Q 5HQDXOG DQG % .RKOHU 3K\V /HWW 380
3 0 +DUH & 7 0LGGOHWRQ .- 0HUWHO - 0 +HUEHUW DQG % .RKOHU &KHP 3K\V /HWW 104 $FDG 6FL
%(%LOOLQJKXUVW 6$ 2ODWXQGH DQG 3 /RSS 3K\V &KHP % 113