

(OHFWURQLF ([FLWHG 6WDWH DQG 9LEUDV
6ROXWLRQ RI &\WRVLQH ZLWGHV
\$EVRUSWLRQ 6SHFWURV FIRS\HZLSW KOVXUJ
/DVHUBXO

-XQ 0L\D]BMLFKLURD.QGD7DND\RVKL .RED\DVKL

\$GYDQFHG 8OWUDIDVW /DVHU 5HVHBBPRXQHLQFDMMLRQQLYHUV
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-67 &5(67 6DQERQFKR7RNLRRGDSQ
'HSDUWPHQW RI (OHFWURSKQWBQLYHIDWLWRQDO &KLDLFXHK
7DLZDQ
,QVWLWXWH RI /DVHU (QJLQHBIPIRQOD 28\LNWD 8QLVMDSDQLW\

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F\WRVLQH ZLWGHVSEXOWUDYLROHW ODVHU SXOVH LV UH
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REVHDDGSGWKHLU UHOD\DWLRQ PHFKDQLVPV DUH GLVFXVVH

,QWURGXFWRQ

'1\$ DQG 51\$ H[KLELW XOWWDHIDWVDDH[[FWWRIG XQGHU GHHS
ZKLFK HQVXUV WKDW WKH PROFXOHV UHOD\ WR WKH JUR
VWDWH UHDFWLRQV FDQ QRFIXUHU7K LWRVEKHSPURAMDFORLRQ S
PXWDJHQLF DQG FDUFLQRJHQLF HIIHFV LQ OLYLQJ V\WV
ELRORJLFDOO\ UHOHYDQW PROFXOHV VXFK DV '1\$ EDVHV
FRQWHVWHRU SKRWR VWDELOLW\ WKHUH KDYH EHHQ PDQ\
PHDQV RUHWBPHHG DEVRUSWLRQ DQG IOXRUVFHQFH PHD
G\QDPLFV KDYH QRW EHHQ IXOO\ XQGHUVWRQG XEWDGXX
SXOVHV LQ WKH '89 UDQJH
,Q WKLW VMXG'89VXEOVH LV VXFFHVVIXOO\ DSSOLHG IRU W
RI ZDWHU VROXWLRQ RI F\WRVLQH '89 SXOVH ZLWK QHD
JHQHUDWFKLUSHG SZDWHPIRXXQJ WHFKQLTXH ZLWKRXQV H[
7UDQVLHQW DEVRUSWLRQ PHDVXUHPHQW XVLQJ WKLW XO
XOWUDIDVW HOHFWRQLF H[FLWHG VWDWH G\QDPLFV DQG

([SHULPHQWDO VHWXS

6XE IV GHHS '89 SXOVH ZDURXVHG[SRIULSPXPSW \$SDUW RI
IURP D 7L 6DSSKIHUBIPISOLLUSHIG ZDXOJDFXMLHQRG DRQORZ IL

EURDGHQLQJSEKDPFHGXVDFVLRQ \$ QHDU 89 189 SXOVH LV
 GRXEOLQJ RI WKH IXQGDPHQWDO SXOVH ZKSDKVLVQLHJFDV
 7KH EURDGEDQG QHDU LQIUUDHG 1,5 DQG 1.89 SXOVH ZH
 ILOOHG ZLWKZSHUH D EURDGEDQG '89 SXOVH ZDVTXHQFUDP
 ZDYH PL[LQJ SURFHVV)RU WUDQVLHQW DEVRUSWLRQ PHD
 SXOVH ZDV VSDWLDODV SOLW LQWRUWZQHDRIWKH HJZRH EF
 WR DQ RSWLFDG GHOD\ OLQH FRPSRVHG RI D VWHSSLQJ P
 EHDP ZDV XVHG IRU SXPS SXOVH 7KH SXPS DQG SUREH
 XVLQJ D FRQFDYHWHOLPHUGGLIHPHQFH DEVRUEDQFH DW
 UDQJH IURP WR H9 ZDV PHDVXUH VLPXODWDESRXVL
 FRXSOHG WR D SRO\FKURPHWHU 7KH DTXHRXV VROXWLR
 KRPHD IORZ FHOE\ XVLQJ D SHULVWDOWLF SXPS WR DY

5HVXOWV DQG GLVFXVLRQ

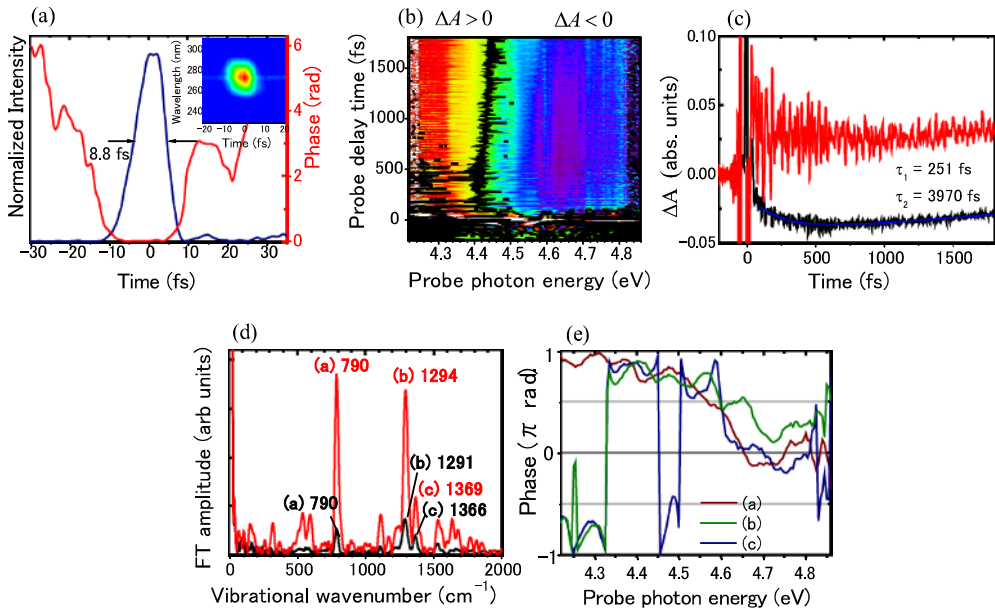


Fig. 1. (a) Retrieved intensity and phase of the DUV pulse. The pulse duration is 8.8 fs in the full-width at half maximum. The inset shows the measured SD-FROG trace. (b) 2D difference transient absorption spectrum ΔA of aqueous solution of cytosine. ΔA is positive when the probe photon energy is below ~ 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 '89GLDIDVDFWLRQPHDVTXHQFUDP
 JDWLQJ526' WHFKQLTXH 7KH FRPPHUFDO VRIWZDUH)52*
 ZDMPSOR\HG IRU WKH DQVORZLVWKLJXSUBWADFHRI '89 ODVH
 DQG WKH UHWULHYHG WHPSRUDO LQWHQVLW\ 7KH UHWULH

IV LQ W K G W K O D W K D I O I n s e r t S h o w s T h e M e a s u r e d S D - F R O G t r a c e . 7 K H V S H F W U
S H R I W K H ' 8 9 S X O V H L V Z K U L R W Q I Q V O D E H R U S W L R Q V S H D W W U W K H
H G J H

' \ Q D P L F W R K H H O H F W U R Q L F H [F L W H G V W D W H

) L J X U H E V K R Z I V H W K G F H D E V R L E S W D L R Q H G S E H F D W U H X U F J L Q J W
7 K H H [S H U L P H Q W V Z H U H S H U I R U P H G D W W K H L Q W H Q V L W L H
U H V S H F W L L Y H O R X Q G W R Z K H O S R U R E M B W R Q L M C E H H O R Z H 9 Z K L O
W K I D W Q H D E V R K H H 9) L J X U H F V K R Z W K H W A S I L E D V O K W D K L O K V
O R Z Q H U J r e s p e c t i v e l y .

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.

9 L E U D W L R Q D O G \ Q D P L F V

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.

& R Q F O X V L R Q

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.

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7 . R E D \ D V K L D Q G < . L G D 3 K \ V & K H P & K H P 3 K \ V
\$ 6 K D U R Q * R X W W D 9 V \ D I Q \ \$ H Q D X C O V D U N R & K W B K \ V / H 3 8 0 W
3 0 + D U H & U B V \$ R I Q i Q D G G % 3 E R O H U D W O 1 0 \$ F D G 6 F L
% (% L O O L G J K X 2 0 D V G H S 5 D R S S Q R Z 3 K \ V & K I B P %