

Vibrational dynamics resolved with sub-10-fs deep-ultraviolet pulses

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Abstract. Time-resolved ultrafast spectroscopy with sub-10-fs deep ultraviolet pulses was demonstrated for the first time. For the spectroscopy, the sub-10-fs pulses with smooth temporal and spectral profiles, which were suitable for spectroscopy, were prepared via the method of the broadband chirped-pulse four-wave mixing. The vibrational and electronically excited state dynamics in the aqueous solution of thymine were investigated with a sub-10-fs resolution. Vibrational wavepackets originating from the electronically excited state and ground state were observed simultaneously. Through this research, it was shown that the sub-10-fs pulses were successfully applied to the ultrafast spectroscopy, opening the door to the new research activity of ultrafast spectroscopy with a sub-10-fs time resolution in the deep ultraviolet.

1 Introduction

Many basic aromatic molecules absorb deep-ultraviolet (DUV) radiation and sometimes undergo photochemical reaction. One of the most important examples is the biologically significant molecule DNA. The photochemical dynamics in DNA and nucleobases have been investigated extensively by transient absorption spectroscopy, time-resolved fluorescence spectroscopy, and time resolved infrared (IR) spectroscopy. However, the dynamics have not been fully understood. Investigation via other spectroscopic approach may be necessary for leading to deeper insight into the dynamics. In the visible spectral range, sub-10-fs optical pulses have been routinely obtained and applied in the transient absorption spectroscopy. This allows one to probe the vibrational dynamics taking place simultaneously with the electronic-excited-state dynamics. Demonstration of this spectroscopy in the DUV wavelength range should lead to a powerful way to investigate the photochemical dynamics of biologically relevant molecules.

In this report, we have applied sub-10-fs DUV pulses generated by the recently developed technique of the broadband chirped-pulse four-wave mixing. The sub-10-fs DUV source is specially designed for use in ultrafast spectroscopy [1,2]. The electronic excited state and vibrational dynamics of an aqueous solution of a nucleobase, thymine were simultaneously probed with a sub-10-fs time resolution. This allows us to observe wavepackets corresponding to several vibrational modes in both the electronic excited states and ground state simultaneously.

2 Experimental

Sub-10-fs DUV pulses were generated by the technique of the broadband chirped-pulse four-wave mixing which is described elsewhere [1,2]. A vertically polarized sub-10-fs DUV pulse was spatially split into two beams using the edge of an aluminium mirror. One of the two beams was sent to an optical delay line composed of an aluminium mirror and a fused-silica prism. By Fresnel transmission loss on the prism surface, the pulse energy was reduced by a factor of about ten and used as a probe pulse. The other beam was used as a pump pulse. The pump and probe pulses were focused into a flow cell (0.2-mm CaF₂ windows, 0.2-mm optical path length) filled with an aqueous solution of thymine. The transmitted probe pulse from the flow cell was sent to a multi-channel spectrometer coupled to a 128-channel multi-channel lock-in amplifier. The intensity of the pump pulse was modulated by an optical chopper for the lock-in detection. The difference absorption spectra were measured over a range of pump-probe delay times from -200 fs to 1800 fs with a step size of 0.2 fs. The pulse energies of the input pump and probe pulses were 40 nJ and 5 nJ, respectively, and the spectrum of the pulses extended from 260-290 nm (4.3-4.8 eV) without missing any spectral component within this range. It had a good spectral overlap with the absorption spectrum of the thymine sample peaking at 4.7 eV. The thymine solution in a flow cell was used to prevent the effect of photodamage.

3 Results and Discussion

Prior to the pump-probe measurement, the propagation distance of the DUV pulse in air was optimized such that the pulse duration became shortest at the position of the sample [1]. The pulse shape of the DUV pulses at the thymine sample was characterized by the technique of self-diffraction-frequency-resolved-optical gating prior to the pump-probe measurements. The temporal intensity profile was a single pulse with a full-width at half maximum of 8.7 fs.

Figure 1 shows the two dimensional (2D) difference absorption spectra of the aqueous thymine solution obtained by the pump-probe measurement. In the positive delay time range, the thymine spectra exhibit positive difference absorption (ΔA) signals at photon energies below 4.42 eV while negative ΔA signals at higher photon energies. The 2D difference absorption spectrum $\Delta A(\omega, t)$ was fitted by global fitting using the sum of exponential decay functions with two time constants, τ_1 and τ_2 (where $\tau_1 < \tau_2$) for extracting the decay process information of the electronic excited states. The fitted time constants were $\tau_1 = 140$ fs and $\tau_2 = 1220$ fs. The former can be assigned to the lifetime of the ¹($\pi\pi^*$) state while the latter to relaxation of the ¹($n\pi^*$) state. The time constant τ_2 may also be assigned to a vibrational cooling process, in which the vibrational energy in the thymine is transferred to the surrounding water molecules.

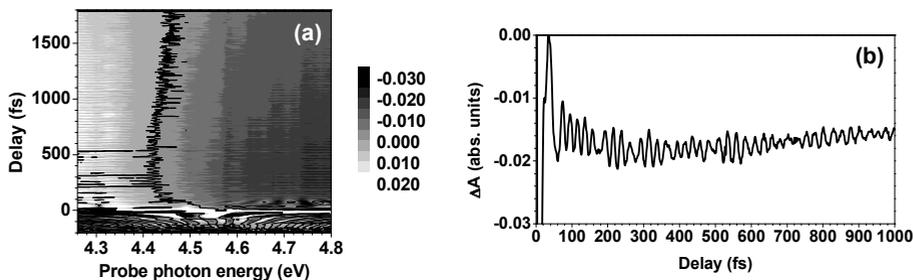


Fig. 1. (a) Two dimensional difference absorption spectra and (b) difference absorbance trace averaged over the photon energy range between 4.70 and 4.75 eV.

The information of the vibrational dynamics was contained in the difference absorption spectra, which appeared as oscillatory structures in the difference absorbance traces, as shown in Figure 1 (b).

The period of the oscillation is about 20 fs and delay-time dependent, indicating that several vibrational motions of thymine were impulsively excited and modulated the difference absorbance. By Fourier analysis of the 2D difference absorption spectra, the frequencies of the vibrational components contained in the difference absorption spectra were estimated to be 110, 616, 748, 816, 989, 1177, 1241, 1362, and 1666 cm^{-1} , all of which correspond to vibrational modes of thymine. Among them, the intensities of the last three modes were much higher than the other modes, and can be assigned to a C-CH₃ stretch + a ring stretch (1241 cm^{-1}), a C-H bend + a C=C stretch (1362 cm^{-1}), and a C=C stretch + C=O stretch (1666 cm^{-1}), respectively [3,4]. The phases of almost all the vibrational modes were at around $\pm\pi/2$, suggesting that they are due to the electronic ground state. On the other hand, the phases of the modes at 816 and 1177 cm^{-1} (at 4.29 eV) were about π and can be attributed to the electronic excited state. The mode at 1177 cm^{-1} can be assigned to a C-N stretch and a C-H bending mode [3,4].

To investigate further the vibrational dynamics, averaged difference absorbance trace obtained in the range 4.28–4.30 eV was analysed by spectrogram analysis. It was observed that at time delays longer than 500 fs, a sideband was generated near the 1240 cm^{-1} component and the frequency of the band continuously red-shifted until it reached 1177 cm^{-1} with a time delay of about 200–300 fs. This results indicate that the mode at 1177 cm^{-1} is generated after the decay of the $^1(\pi\pi^*)$ state. Another explanation is also possible that if the signal at 1177 cm^{-1} is due to the $^1(n\pi^*)$ state, then the frequency reduction taking place before recovery of the ground-state may be due to the process from $^1(\pi\pi^*)$ state to the $^1(n\pi^*)$ state. In this case, the red shift may be due to a reduction in the bond order for the transition process from $^1(\pi\pi^*)$ state to $^1(n\pi^*)$ state. The amount of electrons flowing from the π orbital to the π^* orbital during this transition process is expected to be greater than that from the non-bonding orbital to the π^* orbital. Therefore the bond-order uniformities in $n\pi^*$ excitation is not as strong as those in $\pi\pi^*$ excitation as expected.

4 Summary

In summary, sub-10-fs single DUV laser pulses have been applied to transient absorption spectroscopy for the first time. The electronic excited state decay dynamics as well as vibrational dynamics of an aqueous solution of thymine were probed by the DUV pulses. Two time constants, 140 fs and 1220 fs were extracted by the global fitting of the 2D difference absorption spectra, which can be assigned to the lifetime of the $^1(\pi\pi^*)$ state and relaxation of the $^1(n\pi^*)$ state, respectively. Vibrational modes up to 1666 cm^{-1} were also observed. Among them, the modes at 816 cm^{-1} and 1177 cm^{-1} were assigned to the electronic excited state. For the mode at 1177 cm^{-1} , the vibrational frequency change with time was observed, which indicated that the mode at 1177 cm^{-1} was generated after the decay of the $^1(\pi\pi^*)$ state or the mode was due to the $^1(n\pi^*)$ state. In the latter case the frequency reduction taking place before recovery of the ground-state may be due to the process from $^1(\pi\pi^*)$ state to the $^1(n\pi^*)$ state.

Sub-10-fs DUV pulses are now available, which are applicable to ultrafast spectroscopies. The spectroscopy with the sub-10-fs time resolution provides a powerful tool that discloses detailed insight into vibrational dynamics and electronic-excited state relaxation in important molecules like benzene, amino acids, and DNA bases, thanks to its high time resolution.

References

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