

# Ultrafast Laser Science

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Speed of ultrafast energy transfer from light to molecules (*i.e.* primary processes of photosynthesis, photoisomerization in visual pigments, *etc.*) is on the order of femtosecond ( $10^{-15}$  s). In our laboratory, we develop cutting edge lasers for such ultrafast molecular science, namely, femtosecond or attosecond ( $10^{-18}$  s) ultrashort pulse lasers.

For example, arbitrary waveform synthesis can be performed with simultaneous generation of femtosecond light pulses in various wavelength regions and superimposition of them with precisely controlled phases.

We would like to develop such advanced light control technology, which can push forward the research on ultrafast photochemical reactions.

I have just joined IMS since February 2010. Currently I am setting up my laboratory. In this review article, I introduce my previous works in RIKEN where I was working until the end of January 2010.

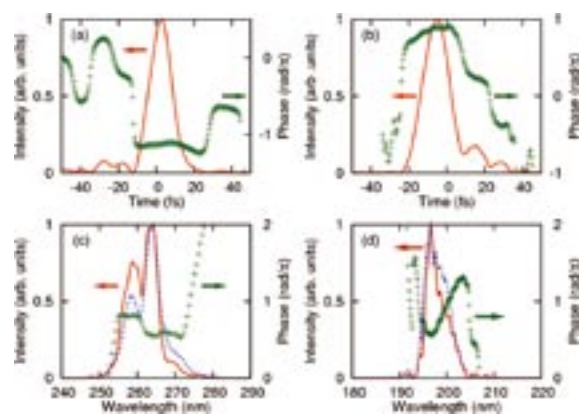
## 1. Experimental and Theoretical Investigation of a Multicolor Filament<sup>1)</sup>

Gas media, which are transparent and low dispersion in much wider range than solid media, are useful for frequency conversion of femtosecond pulses beyond the wavelength region from 0.4 to 2  $\mu\text{m}$  with keeping the pulse width short ( $<30$  fs). However, efficient frequency conversion was difficult since the nonlinearity of gas media is much smaller than that of solid media.

Recently, we have developed nonlinear frequency conversion scheme with the use of self-guiding effect of intense ultrashort pulses, namely, filamentation. By gently focusing second harmonic (400 nm,  $\omega_{\text{SHG}}$ , 0.5 mJ) and fundamental (800 nm,  $\omega_{\text{FUN}}$ , 0.5 mJ) of Ti:Sapphire laser pulses into gases, nondegenerate four-wave mixing  $\omega_{\text{SHG}} + \omega_{\text{SHG}} - \omega_{\text{FUN}} \rightarrow \omega_{\text{fwm}}$  and cascading  $\omega_{\text{fwm}} + \omega_{\text{SHG}} - \omega_{\text{FUN}} \rightarrow \omega_{\text{cas}}$  through filamentation occurred and resulted in an efficient frequency conversion to 260 nm ( $\omega_{\text{fwm}}$ , 16  $\mu\text{J}$ ) and 200 nm ( $\omega_{\text{cas}}$ , 4  $\mu\text{J}$ ). The pressure dependence of the conversion efficiency cannot be explained by a one-dimensional model, but calculation of multicolor filament by a three-dimensional model was suc-

cessful. The simulation result indicates a broad scalability of the scheme for frequency conversion of ultrashort pulses.

These two pulses were compressed by grating-based compressors sharing the same grating. The pulse widths were characterized to be 14 fs (260 nm, 4.7 eV) and 17 fs (200 nm, 6.3 eV) using a dispersion-free transient-grating frequency-resolved optical gating (TG-FROG). The results are shown in Figure 1. The energies of 260 and 200 nm pulses after the compression were 2.5  $\mu\text{J}$  and 0.5  $\mu\text{J}$ , respectively.



**Figure 1.** The retrieved 260 nm and 200 nm pulses obtained with TG-FROG. (a) 260 nm; time domain. (b) 200 nm; time domain. (c) 260 nm; frequency domain. (d) 200 nm; frequency domain. Solid lines show intensities and cross dots show phases. Dotted lines in the frequency-domain figures are the spectra measured by a spectrometer directly.

## 2. Time-Resolved Photoelectron Imaging of Ultrafast Internal Conversion through Conical Intersection in Pyrazine<sup>2)</sup>

The ultrashort UV pulses generated by using four-wave mixing through filamentation were used for time-resolved photoelectron imaging spectroscopy. The experimental setup is shown in Figure 2. The time resolution of the experiment was determined to be 22 fs by cross correlation of the pump and probe pulses in situ. By using the pump-probe photoelectron

imaging apparatus, a nonadiabatic electronic transition through a conical intersection in the benchmark polyatomic molecule of pyrazine was studied. The lifetimes of the  $S_2$  and  $S_3$  states of pyrazine were determined to be  $22 \pm 3$  fs and  $41 \pm 2$  fs, respectively, by the global fitting of the time-energy maps of photoelectron kinetic energy (PKE) distributions. Quantum beat with an approximately 50 fs period was observed after the  $S_2 \rightarrow S_1$  internal conversion, which was attributed to the totally symmetric vibration  $\nu_{6a}$  in  $S_1$  (see Figure 3).

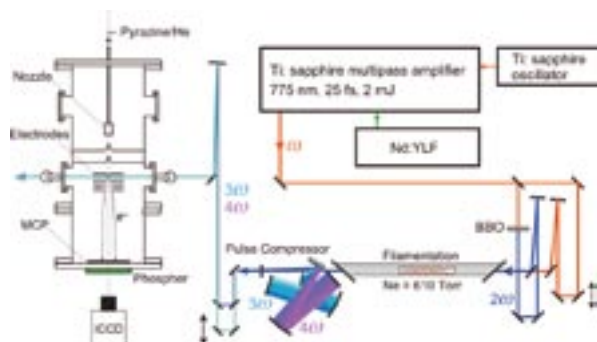


Figure 2. Schematic of the experimental setup.

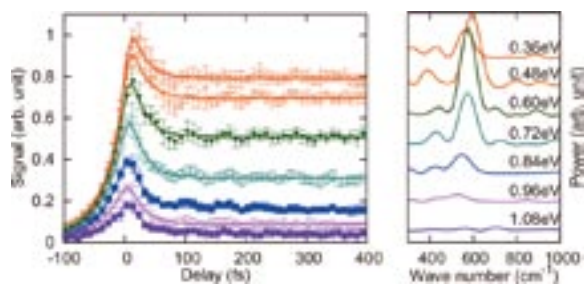


Figure 3. Time evolutions of photoelectron intensities at selected PKE subsections of pyrazine. The oscillatory features are due to the vibrational wave-packet motion along  $Q_{6a}$ . The solid lines show the results of the global fitting. Fourier power spectra of oscillatory components of photoelectron signal intensities after a delay time of 70 fs are also shown on the right panel.

### 3. Spectral Phase Transfer to Ultrashort UV Pulses through Four-Wave Mixing<sup>3)</sup>

It is very meaningful to have ultrashort VUV pulses at photoelectron spectroscopy for molecules since deactivation processes to the ground state can be explored by a probe pulse with high photon energy. Replacing the fundamental pulse in the previous scheme to output of a near infrared optical parametric amplifier, we attempted to generate pulses with shorter wavelength ( $<200$  nm). Second harmonic of Ti:Sapphire laser output (400 nm,  $\omega_{\text{SHG}}$ , 0.35 mJ) and near infrared pulses (1200 nm,  $\omega_{\text{NIR}}$ , 0.2 mJ) from a noncollinear optical parametric amplifier were gently focused into neon gas, and ultrashort pulses with the center wavelengths of 237 nm ( $\omega_{\text{fwm}}$ ) and 167 nm ( $\omega_{\text{cas}}$ ) were produced by four-wave mixing processes,  $\omega_{\text{SHG}} + \omega_{\text{SHG}} - \omega_{\text{NIR}} \rightarrow \omega_{\text{fwm}}$  and  $\omega_{\text{fwm}} + \omega_{\text{SHG}} - \omega_{\text{NIR}} \rightarrow \omega_{\text{cas}}$ , respectively. The spectra of the generated pulses are shown in Figure 4. The energy of the generated 237 nm

pulse was approximately 1.5  $\mu\text{J}$  whereas that of the 167 nm pulse were estimated to be less than 100 nJ. The reason for the lower efficiency than the previous scheme would be mode quality of NOPA output and/or phase matching condition of the nonlinear mixing. Coherence length of the phase matching ( $1/\Delta k$ ) is half of the previous four-wave mixing process.

Transfer of spectral phase from the near infrared ultrashort pulses to the UV pulses through the four-wave mixing process was also demonstrated. Assuming monochromatic second harmonic, the even order spectral phase of the near infrared pulse is transferred to the UV pulse with the opposite sign, whereas the odd order spectral phase is transferred with the same sign in principle. We controlled the spectral phase of the NIR pulses by prism insertion of a SF10 prism compressor, and measured spectral phases of the NIR pulses and the generated UV pulses by using FROG. The experimental results are shown in Figure 5. The convexities (up or down) of the spectral phase at the main part of the spectrum are opposite with each other suggesting chirp directions of the pulses are opposite with each other. Concerning the TOD, high frequency components present larger concavity compared with low frequency components in both cases. Therefore, the sign of the TOD was kept the same. A positively chirped near infrared pulse was used for generating a negatively chirped UV pulse, which was compressed down to 25 fs by a magnesium fluoride window. In principle, the spectral phase transfer scheme can also be applied to the chirp control of the generated VUV pulses.

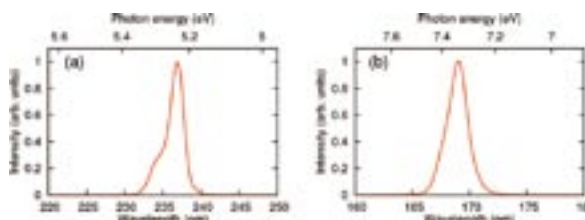


Figure 4. Typical spectra of (a) UV and (b) VUV pulses generated through the four-wave mixing and the cascaded process, respectively.

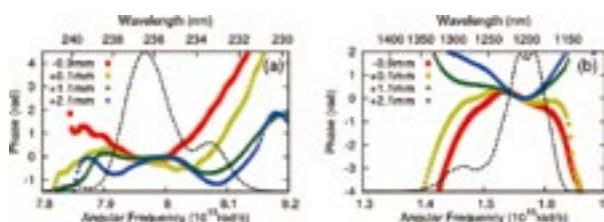


Figure 5. Spectral phases of (a) UV and (b) corresponding NIR pulses at each prism insertion. Intensity of each pulse is also shown as a dashed curve.

### References

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- 2) Y.-I. Suzuki, T. Fuji, T. Horio and T. Suzuki, *J. Chem. Phys.* **132**, 174302 (2010).
- 3) P. Zuo, T. Fuji and T. Suzuki, *Opt. Express* **18**, 16183 (2010).