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Microjoule-level 20 fs UV pulses for the investigation of molecular dynamics via attosecond transient absorption spectroscopy

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Abstract: A method for generating 20 fs UV pump pulses for attosecond transient absorption spectroscopy is presented. An application of the setup to the real-time mapping of conical intersection dynamics and coherent nuclear motion in CH_3I is demonstrated.
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1. Introduction

Ultrafast spectroscopy based on attosecond (as) probe pulses in the extreme ultraviolet (XUV) is a powerful approach to mapping electronic-nuclear dynamics in molecular systems [1–3]. Since excited-state molecular dynamics are widely accessed in the UV, the incorporation of high-flux femtosecond (fs) UV pump pulses is a major goal in the advancement of ultrafast XUV spectroscopies [4,5]. Here, we report the generation of microjoule-level, 20 fs UV pump pulses with a tunable center wavelength between 256 and 280 nm for attosecond XUV transient absorption spectroscopy. In the setup, UV pulses are obtained through sum-frequency mixing in a barium borate (BBO) crystal between 400 nm pulses and broadband near-infrared (NIR) pulses and as XUV probe pulses are simultaneously obtained through high-harmonic generation (HHG). The fs UV pump - as XUV probe apparatus is applied to the investigation a prototype molecule, methyl iodide (CH_3I) [6]. Due to the fast temporal resolution of the setup, rapid conical intersection dynamics and coherent vibrational motions are readily observed.

2. Experimental Setup and Results

The setup employs the 1.9 mJ output of a carrier-envelope phase stable Ti:Sapphire amplifier delivering 27 fs, NIR centered at 780 nm with a 1 kHz repetition rate. The amplifier output is first split by a 20:80 beamsplitter into two arms. On the first arm, the output is passed through a 200 μm thick Type-I BBO for second-harmonic generation (SHG) producing 20 fs 400 nm pulses. On the second arm, the amplifier output is spectrally broadened in a hollow-core fiber (HCF) and compressed in time to afford 3.8 fs NIR pulses. The HCF-NIR output is then divided by a 50:50 beamsplitter toward pump and probe generation.

A schematic of pump-probe generation and the transient absorption setup is shown in Fig. 1a. On the probe arm, the HCF-NIR pulses are focused into an argon-filled gas cell, producing XUV pulses (40-70 eV, 170 as) via amplitude gating [7]. The XUV is filtered through an aluminum foil, focused by a toroidal mirror into a sample gas cell, and measured by a concave grating and x-ray CCD spectrometer. On the pump arm, the HCF-NIR pulses are filtered through a dichroic, isolating 10 fs NIR pulses. The 10 fs NIR pulses and the 20 fs 400 nm pulses are then collinearly recombined on a second dichroic, steered through a delay stage, and focused into a vacuum chamber containing a 50 μm thick Type-I BBO for sum-frequency mixing. The generated UV is focused and recombined with the XUV arm using three reflective dielectric mirrors which simultaneously remove 400 nm and NIR light from the beam path. The UV beam is focused into the sample gas cell at a crossing angle of 0.7° with respect to the XUV, and blocked before the XUV spectrometer by an aluminum foil.

As shown in Fig. 1b, frequency-tunable UV pulses delivering 1.5-8.9 μJ per pulse are achieved. The transform-limited duration of the UV pulses ranges between 16 and 27 fs. A cross-correlation of the UV-XUV setup is performed using transient absorption measurements in xenon (Fig. 1c). An instrument response function of 21 $\pm$ 6 fs is estimated, confirming that the UV pump pulses are near transform-limited at the sample target.

The setup is applied to the *A*-band photodissociation of CH_3I through a conical intersection (Fig. 2a). Experimentally, a UV pump pulse initiates *A*-band fragmentation along the C-I bond and a time-delayed XUV probe pulse measures absorption transitions from the iodine I(4*d*) core orbital into valence orbitals of the dissociating

molecule. In the transient absorption results shown in Fig. 2b, UV-triggered conical intersection dynamics are observed as well as coherent nuclear motion in the ground state corresponding to C-I stretch vibrations.

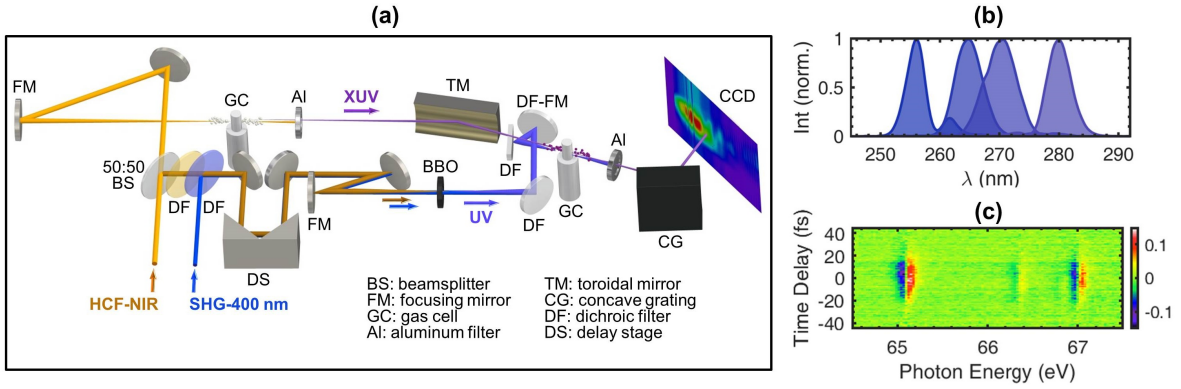

Fig. 1. Experimental setup. (a) UV-XUV generation and transient absorption configuration. (b) Spectrum of the generated UV pulses. (c) Transient absorption cross-correlation in xenon plotted in ΔOD.

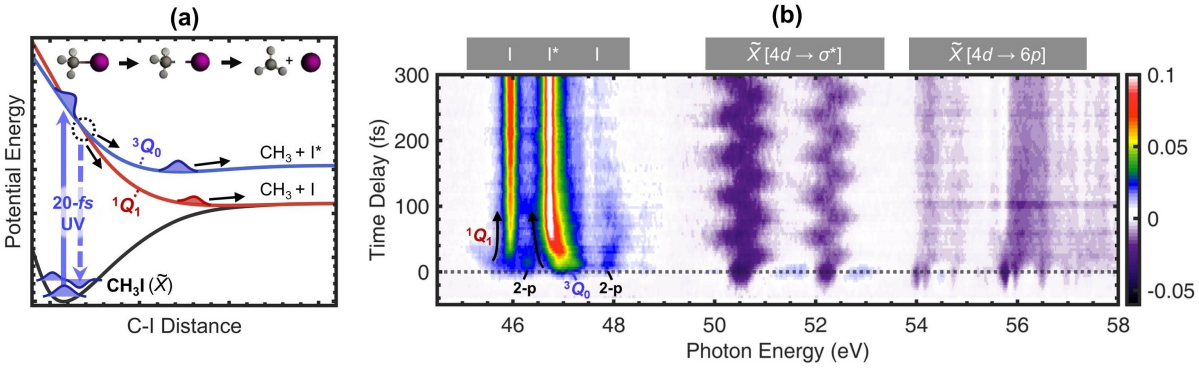

Fig. 2. Dynamics in CH_3I launched by UV pump pulses. (a) Schematic of *A*-band through a conical intersection (dotted circle) and vibrational coherences launched in the ground state. (b) Experimental transient of CH_3I. The evolution of positive ΔOD features (bright blue-red shades) correspond to excited-state dynamics launched by the UV pump. In addition to the *A*-band, Rydberg states accessed via two-photon UV excitation (2-p) are observed. Oscillating negative ΔOD features (purple shades) correspond to the ground state vibrational coherence.

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