

論文の内容の要旨

Ultrafast transient absorption spectroscopy using attosecond soft X-ray pulses in the water window

(「水の窓」領域のアト秒軟X線パルスを用いた
超高速過渡吸収分光)

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Eighteen years have passed since the birth of attosecond spectroscopy in 2001, and its technology has made significant progress. One notable advance is the development of soft X-ray (SX, 200-2000 eV) attosecond science. The first attosecond pulse was generated by high-harmonic generation (HHG) with a femtosecond Ti:sapphire (Ti:Sa) laser, and its photon energy was around 100 eV, in the extreme ultraviolet (XUV) region (10-200 eV). Recently, by using infrared (IR, 1-3 μm) or mid-infrared (MIR, 3-10 μm) optical parametric amplifiers (OPAs) and optical parametric chirped-pulse amplifiers (OPCPAs) as drive sources, the photon energy of high harmonics (HHs) has been significantly extended. So far, the highest photon energy of 1.6 keV was demonstrated in 2012. Such attosecond pulses can be utilized for element-specific X-ray spectroscopy at various absorption edges in the SX region. Especially, HHG-based X-ray absorption spectroscopy (XAS) in the “water window” region, which ranges from the C *K*-edge (284 eV) to the O *K*-edge (543 eV), is intensively investigated. The water window region contains the *K*-edges of C, N, and O. If attosecond spectroscopy at these edges becomes possible, fundamental dynamics of various important materials such as biomolecules, organic solar cells, and photocatalysis are expected to be revealed. However, until now, HHG-based time-resolved XAS, or X-ray transient absorption spectroscopy, has only been established up to the C *K*-edge. Compared to the highest photon energy of 1.6 keV, this photon energy

(284 eV) is much lower. This is because transient absorption spectroscopy requires much more SX photons than a static XAS measurement; in a transient absorption measurement, many absorption spectra have to be measured for many pump-probe delays. Since the photon flux of IR- or MIR-driven HHG is more than ~ 3 orders of magnitude lower than that of Ti:Sa-driven HHG, it is not easy to obtain sufficient photons for transient absorption spectroscopy.

In this dissertation, the realization of HHG-based transient absorption spectroscopy at the N K -edge (400 eV) in the water window is presented. This is achieved by the combination of a powerful IR light source, an efficient HHG scheme, and a robust and stable transient absorption beamline. From the measured transient absorption spectra of nitric oxide (NO) and nitrous oxide (N_2O), electronic, vibrational, and rotational dynamics is successfully extracted, which demonstrates the versatility of HHG-based transient absorption in the SX region. Moreover, novel ultrafast phenomena such as intramolecular position-specific electronic dynamics and molecular alignment of cations are revealed. We believe that these results will deepen the understandings of photoinduced molecular dynamics, and will be a base to apply transient absorption measurements to more complex systems such as liquids or solids.

The dissertation comprises eight chapters. In Chapter 1, a general introduction is given to clarify the motivation and the purpose of the research. In Chapter 2, a detailed theoretical and experimental background is described. In Chapter 3, the IR light source employed in the research is presented. It is a BiB_3O_6 -based OPCPA system, which delivers intense, phase-stable, 10-fs pulses at 1.6 μm . In addition to the description of the light source, a new waveform characterization method of IR pulses is presented. In Chapter 4, the details of the HHG and the transient absorption beamline are described. The HHG setup consists of a semi-infinite HHG gas cell and a two-stage differential pumping system, which enables efficient SX generation. The transient absorption beamline is equipped with an attosecond delay stabilization system to achieve high delay controllability required for transient absorption spectroscopy using attosecond pulses. In Chapter 5, measured properties of the generated SX HHs are presented. Figure 1 plots the measured HH spectra from He and Ne. It is visible that the HH spectrum from He reaches 500 eV, covering a large part of the water window region. In Chapters 6 and 7, the results of transient absorption experiments at the N K -edge are presented. First, in Chapter 6, NO is used as the target of transient absorption. Figure 2 shows the measured transient absorption trace. From the measured transient absorption spectra, signatures of electronic dynamics, vibrational dynamics, and rotational dynamics is extracted. Second, in Chapter 7, N_2O is used as the target. Different from NO, N_2O has two absorption edges at

the N K -edge which originate from two nitrogen atoms in the molecule. In the measured transient absorption spectra, different absorption changes in the two edges are found, implying the existence of intramolecular position-specific electronic dynamics. Moreover, rotational dynamics of both neutral N_2O and N_2O^+ cation is simultaneously observed. The rotational dynamics of the cation is found to be largely dependent on the anisotropy in the strong-field ionization process, which manifests the importance of the coupling between electron and nuclear dynamics. Chapter 8 states the conclusion of the research as well as the future prospect.

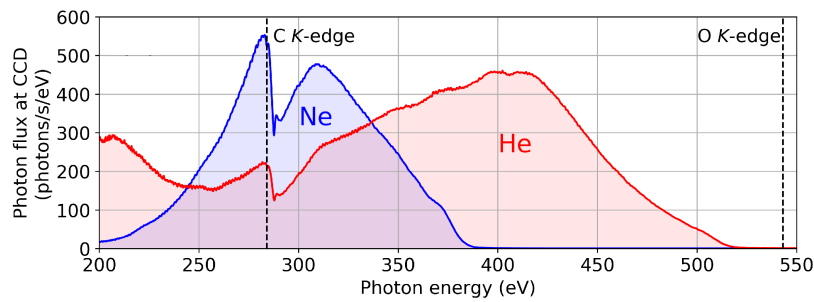


Figure 1: Measured HH spectra from Ne (blue curve) and He (red curve).

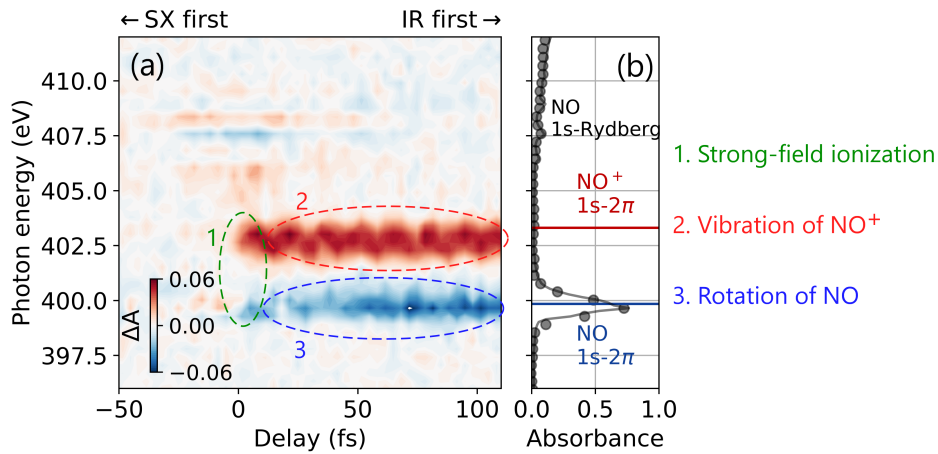


Figure 2: (a) Measured transient absorption trace of NO. The dashed ellipses indicate the regions where three different kinds of dynamics are imprinted. (b) Static absorbance spectrum of NO measured in our beamline (circles) and in a synchrotron facility (solid curve).