International Conference on Ultrafast Phenomena © Optica Publishing Group 2022

Attosecond electronic dynamics of core-excited states of N_2O probed by transient soft X-ray spectroscopy

Nariyuki Saito[1], Nicolas Douguet[2], Nobuhisa Ishii[3], Teruto Kanai[1], Yi Wu[4], Andrew Chew[4] Seunghwoi Han[4,5], Barry I. Schneider[6], Jeppe Olsen[7], Luca Argenti[4], Zenghu Chang[4], and Jiro Itatani[1]

[1] The Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
[2] Kennesaw State University, Marietta, Georgia 30060, USA
[3] Kansai Photon Science Institute, National Institutes for Quantum and Radiological Science and Technology, 8-1-7 Umemidai, Kizugawa, Kyoto 619-0215, Japan
[4] CREOL and Department of Physics, University of Central Florida, 4111 Libra Drive, PS430, Orlando, Florida 32816, USA
[5] School of Mechanical Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South Korea
[6] National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
7 Department of Chemistry, qLEAP Center for Theoretical Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark
Author e-mail address: jitatani@issp.u-tokyo.ac.jp

Abstract: Half-cycle oscillation is observed in transient absorption spectra of N_2O at N *K* edge (400 eV) irradiated by intense IR pulses, which is attributed to tunneling ionization of core excited states by intensive TDSE-based simulation. © 2022 The Author(s)

1. Introduction

Recent advances of intense ultrashort-pulse IR and MIR sources have extended the cutoff energy of the high harmonics into the soft X-ray (SX) region and opened the door to field-driven electron dynamics in solids [1]. With SX high harmonics, femtosecond pump-probe spectroscopy, or transient absorption spectroscopy (TAS), has been demonstrated to trace chemical dynamics [2, 3]. SX TAS also offer new opportunity to trace electron dynamics even on the attosecond time scales, where intramolecular electron dynamics such as creation of core hole states followed by ultrafast relaxation processes are expected to be observed by all optical manner. Time resolved measurement of such extremely fast processes will deepen our understanding of x-ray-matter interactions. Here, we measure the transient absorption spectra of N_2O molecules irradiated by intense IR pulses. The measured transient absorption spectra show two main features: (i) modulation of the SX absorption with a period that is one half-cycle of the IR field, and (ii) monotonic increase and decrease of the SX absorption due to tunnel ionization of N_2O in the ground state. A TDSE-based theoretical model is developed which successfully reproduced these features, and the half cycle oscillation is attributed to the tunnel ionization of the core-excited states [4].

2. Experiments and Simulation

In the experiment, we employ a BiB_3O_6-based optical parametric chirped-pulse amplifier with a center wavelength of 1.6 μm, pulse duration of 10 fs, pulse energy of 1.5 mJ, and repetition rate of 1 kHz [5] as a drive laser for HHG and TAS. The isolated SX pulses are obtained in a gas cell filled with Ne at ~3.1 bar with the selection of the carrier-to-envelop phase by measuring the half-cycle cutoff. The IR pump pulse and the SX probe pulse are linearly polarized in the same direction, and collinearly focused into a gas cell filled with N_2O at ~0.1 bar as shown in Fig.1(a). The transmitted SX spectrum is measured by a grating based SX spectrometer with an X-ray CCD camera. The delay between the pump and probe pulses are interferometrically stabilized and controlled by a piezo stage with the accuracy of <100 as.

Figure 1(b) illustrates the molecular orbital diagram of N_2O, where one can see two major excitations from the N_t 1s or N_c 1s core orbital to the 3π orbital at ~401 and ~405 eV, respectively. Figure 2(a) shows the measured transient absorption spectra of N_2O at the N *K* edge as a function of the pump-probe delay. The location of the time zero is determined by the rapid increase of absorption by N_2O^+ N 1s-3π (~403 eV) with uncertainty of several femtoseconds. The absorbance at the N_2O N_t 1s-3π (~401 eV) and at the N_2O N_c 1s-3π (~405 eV) decreases at positive delays, while the absorbance between 401 and 405 eV increases. Furthermore, the experimental data of Fig. 2(a) exhibit prominent vertical fringes with a half the period of the pump IR pulse (T_{IR}/2~2.7 fs) in both N_2O and N_2O^+ peaks.

To understand the behavior of TAS around the time zero, we have developed a model that is based on the time-dependent Schrödinger equation (TDSE). We first consider process I in Fig. 2(b) where the SX pulse excites an electron in the N 1s core orbital to a valence orbital. Then the IR pulse subsequently promotes the electron to another valence orbital. In this case, the transient absorption spectra gradually converge to the SX-only limit as the

time delay increases without half-cycle oscillation. When we introduce process II in Fig. 2(b) in which the weakly bound core-hole states can also be directly ionized by the intense IR field, the core-excites state acquires an instantaneous time-dependent width because of the step-like population decrease by tunneling. The simulation result reproduces the prominent half-cycle oscillation. We then consider process III in Fig. 2(b), in which the valence electron is tunnel ionized by the IR pulse to produce NO+, and subsequently the core electron is excited to the valence orbitals by the SX pulse. Numerically solving the set of TDSEs for N_2O and N_2O^+, weak half-cycle oscillation appear at the positive delay around 402 eV. The overall transient absorption spectra are shown in Fig. 2(c).

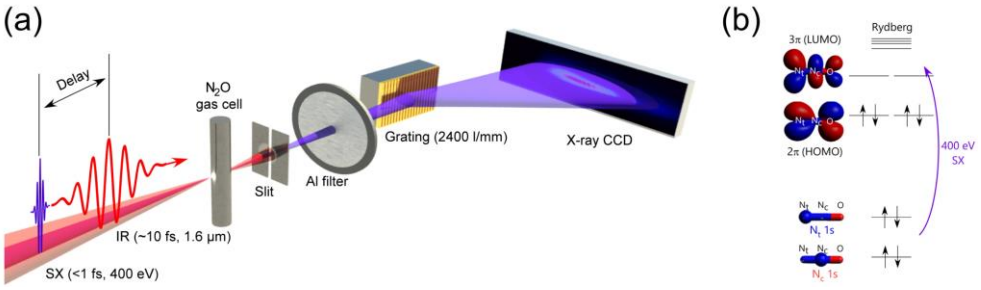

Fig. 1. (a) Schematic of the experimental setup. (b) Molecular orbital diagram of N_2O.

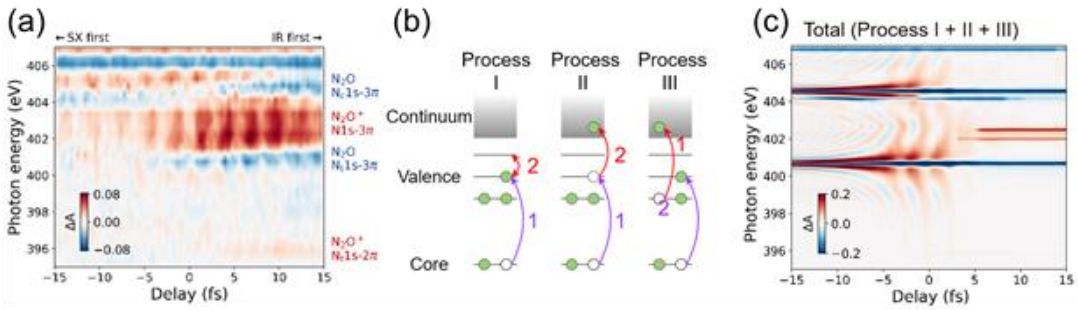

Fig. 2. (a) Measured transient absorption spectra. (b) Relaxation processes considered in the simulation. (c) Simulated transient absorption spectra including the total process (I+II+III).

3. Conclusions

We conduct attosecond TAS of N_2O at the N *K* edge, which exhibits monotonic absorption changes due to the creation of N_2O^+ (process III) as well as half-cycle oscillation at the absorption lines of N_2O and N_2O^+ (process II and III). The TDSE-based simulation reproduces these features by considering three excitation processes. The most dominant process is found to be process II where the weakly bound electrons of core-hole states tunnel ionize at the crest of the optical field, leading to the sub-optical cycle modulation of the electric dipole amplitude between the ground state and the core-excited states. We expect that further improvement of the energy resolution of our SX-TAS will allow us to distinguish the electron dynamics of different core-excited states in molecules which are not fully resolved in the current experimental setup.

3. References

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