Observation of Attosecond Electron Wavepacket of Nitrogen Molecules by XUV Pump-probe with Nonlinear Fourier Transformation Spectroscopy

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Abstract: Multiple electronic states of nitrogen molecules are coherently excited by sub-5 fs harmonics. The generated electron wavepackets between neutral electronic states and singly-charged electronic states are probed by sub-5 fs harmonics by detecting fragment ions.

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1. Introduction

Observation of coupled nuclear and electron motion in molecules is one of the essential steps for understanding chemical reactions [1]. Multiple electronic states of molecules can be coherently excited by attoseond pulse, thanks to its broad spectral bandwith and coherence, to form an electron wavepacket (EWP). So far, the time-evolution of EWPs have been mainly probed by detecting photoelectron with an intense NIR few-cycle pulse.

In the present work, we launched vibrational wavepackets (VWPs) and EWPs of nitrogen molecules using a-few-pulse attosecond pulse train (APT) and the time-evolution was monitored by exciting these wavepackets to the electronic states of N_2^+ leading to the dissociation into N^+ + N.

2. Experimental setup

The intense a-few-pulse APT was generated by focusing the output of sub-15 fs Ti:S femtosecond laser system onto a Xe gas cell. The temporal duration of APT envelope was about 4 fs, which was short enough to observe VWPs. The temporal duration of the attosecond pulses within the APT was shorter than 400 as. The generated APT was spatially divided into two with two Si plates and the reflected harmonic beams are introduced into a velocity-map imaging (VMI) ion spectrometer. The replica of APT pulses was focused onto a molecular beam of N_2 introduced into a vacuum chamber by a piezo valve. The momentum images of N^+ was recorded with a MCP/Phosphor assembly.

3. Results and discussion

First, the pump-probe measuremnt was performed with the long-range coarse scanning mode. The delay Δt was scanned every 2 fs from 0 fs to 400 fs to reveal the VWPs with a period longer than 10 fs. The adiabatic potentials of the excited electronic states relavant to yield N^+ fragments were assigned by comparing the observed vibrational periods with the simulated vibrational periods using spectroscopic constants [3].

Second, the pump-probe measuremnt was performed with the short-range fine scanning mode. The delay Δt was scanned every 35.6 as from -7 fs to + 7 fs for resolving the beat signals of attosecond EWPs with the synthesis of the electronic states assigned by the coarse scanning. Note that the VWPs motions appear in whole the kinetic energy release (KER) regions higher than 0.2 eV, while the beat signals of attosecond EWPs was observed in only around the KER of 0.4 eV. This is due to the characteristics of rhe repulsive electronic states concerned with the probe process by excitation/ionization with one-photon absorption of the APT.

The fragment ion intensities (KER at 0.4 eV) for the coarse and fine scans in accordance with the delay Δt in Figs. 1(a) and 1(c), respectively. The frequency spectra obtained from the intensity variations shown in Figs. 1(a) and 1(c) are depicted in Fig. 1(b) and Fig. 1(d), respectively. In Fig. 1(d), the frequency is normalized by the angular frequency of fundamental light (ω_0).

The observed oscillatory periods of 14-18 fs shown in Fig. 1(b) are ascribed to the time-evolution of VWPs in the electronic states of N_2 ($T_{vib} = 15.6, 18.0, 14.4$ fs for $X^2\Sigma_g^+, A^2\Pi_u, B^2\Sigma_u^+$) launched by harmonics whose order is greater

than or equal to 11 for $X^2\Sigma_g^+$ and $A^2\Pi_u$ states and 13 for $B^2\Sigma_u^+$ state. On the other hand, the slow oscillatory period of 50-80 fs is ascribed to the time-evolution of VWPs in the electronic excited states of neutral manifold ($T_{vib} = 55, 70$ fs for $b^1\Pi_u$, $b'^1\Sigma_u^+$) launched mainly by 9th order harmonic. The peak around 28 fs is ascribed to the overtone beat frequency of VWP in the electronic state $b^1\Pi_u$. The coexistence of these frequency compoents are prerequisite for observing EWPs launched by simultaneous excitation of multiple electornic states spanning between neutral manifold and singly-charged manifold.

Non-integer frequency peaks in the frequency spectrum in Fig. 1(d) exihibits electonic responses since these peaks cannot be explained by the frequency components appearing in the interferometric autocorrelation measurement of APT [2]. The origin of these peaks can be explained by the formation of EWPs between neutral electronic states and singly-charged electronic states. The relevant potential energy curves of N_2 and N_2^+ are shown in Fig. 2.

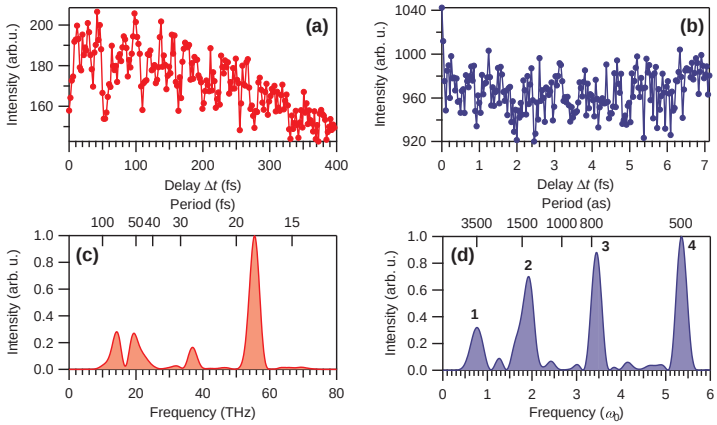

Fig. 1. The delay dependent fragment ion N^+ ($E = 0.4$ eV) intensities and frequency spectra. (a) Fragment ion intensity in the long-range scan. (b) Fragment ion intensity in the short-range scan. (c) Frequency spectrum of (a). (d) Frequncy spectrum of (b). ω_0 is the frequency of fundamental pulse.

Table 1. Observed electron wavepackets.

	1	2	3	4
T_{osc} (as)	3500	1400	770	500
ΔE (eV)	1.2	3.1	5.4	8.3
Assigment	$A^2\Pi_u$-$X^2\Sigma_g^+$	$B^2\Sigma_u^+$-$X^2\Sigma_g^+$ or $X^2\Sigma_g^+$-$b^1\Pi_u$	$B^2\Sigma_u^+$-$b^1\Pi_u$	$D^2\Pi_g$-$b^1\Pi_u$

The peak 1 is assinged to be the beat frequency of the EWP composed of $X^2\Sigma_g^+$ and $A^2\Pi_u$ states because the energy difference of these two states (1.2 eV) coincides with the measured frequency. In addition, both two bound states should yield N^+ fragments with the similar KER at 0.4 eV by the excitation to the coherent superposition of the $C^2\Sigma_u^+$ (from $X^2\Sigma_g^+$) and $D^2\Sigma_g^+$ (from $A^2\Pi_u$) repulsive states with one-photon absorption of the 7th or 5th order harmonic. The orgin of observed other peaks 2-4 are determined with the similar manner as summerized in Table 1.

In summary, we have succeeded in observing electron wavepacket of nitrogen molecules with XUV-pump and XUV-probe method by detecting the kinetic energy distribution of fragment ion as a function of delay XUV pulses.

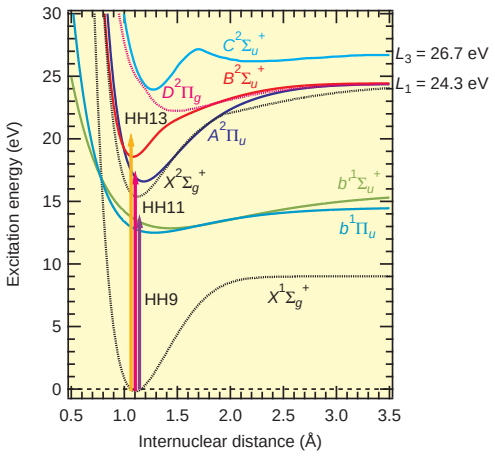

Fig. 2. Potential energy curves of N_2 / N_2^+ [3, 4].

References

1. P.A. Carpeggiani *et al.*, Phys. Rev. A **89**, 023420 (2014).
2. T. Okino *et al.*, J. Phys. B. **47**, 124007 (2014).
3. A. Lofthus *et al.*, J. Phys. Chem. Ref. Data **6**, 113 (1977).
4. T. Aoto *et al.*, J. Chem. Phys. **124**, 234306 (2006).