Attosecond molecular Coulomb explosion

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Abstract

Molecular Coulomb explosion has been utilized as a precise temporal clock for probing ultrafast motion of nucleus and electrons during chemical reactions. With an intense attosecond pulse train in the extreme ultraviolet region, we were able to image attosecond molecular Coulomb explosion via two photon double ionization process. The present autocorrelation measurement, from which the duration of the attosecond pulse train was determined to be 300 as, serves as the first step toward a pump-and-probe measurement of molecular dynamics with attosecond temporal resolution.

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1. Introduction

In chemistry and molecular physics, ultrafast phenomena have been probed with the temporal resolution of the order of tens of femtoseconds (1 fs = 10^{-15} s) by a pump-and-probe experiment using femtosecond laser light [1]. For probing phenomena occurring in a much shorter time scale associated with rapid motion of electrons within atoms and molecules, it is required to improve the temporal resolution further by more than two orders of magnitude.

Along with the rapid progress in the technique of generation of high-order harmonics in the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) region using intense ultrashort pulse laser light, researchers have begun generating an attosecond (1 attosecond = as = 10^{-18} s) [2–4] pulse train [5–8] as well as an isolated attosecond pulse [9–11]. We are now entering into a new stage beyond femtochemistry [1]. In this extremely short time scale, we will be able to finally ‘see’ how electrons within an atoms or a molecule move in real time [12]. One of the ultimate goals for physicists and chemists are now in the reachable distance.

For applying the new light sources in the attosecond time domain for pump–probe type measurements, we need to characterize generated attosecond pulses. For the characterization, we will naturally use responses of atoms and molecules to attosecond pulses. However, such responses themselves are expected to be highly nonadiabatic as well as nonlinear, and have not been well understood. Indeed, establishing the metrology of attosecond pulses has been one of the central issues in the field of ultrafast optics.

The simplest and direct approach to measure the temporal duration of an ultrashort laser pulse is, of course, to measure an autocorrelation function. So far, two-photon ionization processes of gaseous atoms have been used for the autocorrelation measurement of an attosecond pulse train [7,8] as well as an isolated attosecond pulse [11]. However, as far as photoelectron signals are used, weak signals originated from the nonlinear process tend to be covered by strong signals from one-photon ionization. This is because the wavelength span of an attosecond pulse generated as high-order harmonic(s) exceeds one octave covering the wide VUV–XUV range, and hence, one-photon ionization is a primary process.
Furthermore, the shorter is the pulse duration in the attosecond domain, the wider is the kinetic energy distribution of photoelectrons. This will lead to an unavoidable overlap of one- and two-photon contributions and cause difficulties in extracting autocorrelation signals [8]. In order to overcome the intrinsic difficulties in characterization of attosecond pulses in the VUV–XUV wavelength range by the autocorrelation measurement, development of a new metrology has been awaited.

We have recently observed two-photon above-threshold ionization (ATI) of hydrogen molecules, H$_2$, using the intense 27th harmonic (≈30 nm, ≈15 fs, ≈10$^{13}$ W/cm$^2$) of Ti-sapphire laser light, by detecting H$^+$ fragment ions ejected through the ATI process [13]. Furthermore, the ATI cross-section of H$_2$ was found to be one order of magnitude larger than the corresponding process of He [14]. It was shown for the first time that rich dynamical information on molecular dissociation in the XUV wavelength region was extracted through a nonlinear absorption process and that the nonlinear photo-absorption of XUV photons occurred more efficiently in molecules than in atoms. This indicates that molecules are best suited for characterizing ultrashort laser pulses in the VUV–XUV range by the autocorrelation measurement.

In the present study, we take advantage of the ideal nature of nitrogen molecule N$_2$, which has a much larger nonlinear ionization cross-section than atoms, and measure a train of attosecond bursts lasting for ≈300 as with autocorrelation signals of the atomic fragment ions, N$^+$, ejected through Coulomb explosion [15,16] of N$_2^{2+}$ or dissociation from highly excited N$_2^+$. This is the first demonstration that the molecular Coulomb explosion is induced by a coherent two-photon absorption process of attosecond laser pulses. The present observation also assures a technological achievement for the pump-and-probe measurement of Coulomb explosion imaging of ultrafast phenomena in atoms and molecules with the ultimate temporal resolution in attoseconds.

2. Experimental

Our experimental setup for the autocorrelation measurements of the attosecond pulse train is shown in Fig. 1a. Intense high-order harmonics are generated by focusing a fundamental output of intense ultrashort Ti-sapphire laser light (800 nm, 40 fs, 10 mJ, 10 Hz) into a static gas cell (0.10–0.14 kPa) of 10 cm filled with a Xe gas using a positive lens with a focal length of 5 m [17–19]. The generated high-order harmonics and the remaining fundamental light are propagated collinearly into a harmonic beam splitter. The beam splitter composed of closely placed upper and lower Si plates is used both for reducing the intense fundamental laser light copropagating with the harmonics and for making two replicas of an incident attosecond pulse train for the autocorrelation measurement. The fundamental light is absorbed almost

Fig. 1. (a) Schematic drawing of the experimental setup for the autocorrelation measurement of attosecond pulses. (b) Relative intensity of the high-order harmonics.
completely by the plates arranged at the Brewster angles, while \(~\sim60\%\) of the pulse energy of the harmonics is reflected. The remaining portion of the fundamental light, which is typically \(10^{-4}\) of the incident pulse energy, is further reduced by inserting an aperture (2 mmφ) after the Si beam splitter. A lower half of the incident light is delayed by \(\Delta t\) by the adjustment of the translation of a high precision transition stage. Conventionally, a thin metal filter has been employed for eliminating intense fundamental laser light. In our experiment, such a metal filter that inevitably causes significant reduction of the intensities of high-order harmonics and modifies their spatio-temporal structure is not introduced. It is confirmed that the remnant of the fundamental laser light is so weak (~50 GW/cm\(^2\) at the focal region) that it could not induce any sideband signals in a photoelectron spectrum of Ar [20].

The high-order harmonics are focused by a SiC mirror into a molecular beam of \(\text{N}_2\) introduced through a skimmer from a pulsed valve, and the light field intensity of the 11th order harmonic at the focal region is estimated to be \(\sim5\times10^{14}\text{ W/cm}^2\). The atomic and molecular ions generated at the focus are accelerated by two-stage electric fields of a Wiley-McLaren type time-of-flight (TOF) mass spectrometer. The polarization direction of the high-order harmonics is set to be parallel to the TOF tube axis. The relative intensities of the high-order harmonics are determined from the measured photoelectron spectrum of Ar. The intensities of the observed peaks in the photoelectron spectrum originated from the harmonics ranging between 11th and 19th harmonics are regarded as the relative intensities of these high-order harmonics after the correction using the ionization cross-sections of Ar. As for the 9th and 17th harmonics, their intensities were estimated by measuring the intensity spectrum of the generated high-order harmonics using a VUV–XUV imaging spectrometer. This is because the photon energy of the 9th harmonics is below the ionization energy of Ar and the photoionization cross-section drops suddenly at \(\sim26.7\text{ eV}\), which is the photon energy of the 17th harmonic [21]. The intensity distribution of the generated high-order harmonics is shown in Fig. 1b. Their relative intensities are 0.22:1.08:0.16:0.030:0.025, in the increasing order of the odd-order harmonics from the 9th order. The intensities of the harmonics lower than the 9th order at the interaction point are even weaker. In addition, the lower-order harmonics could not contribute to generate \(\text{N}_2^+\) and \(\text{N}_2^{2+}\), as described in Section 3.1.

3. Results and discussion

3.1. Momentum distribution of \(\text{N}^+\) ions

An enlarged view of the momentum distribution of fragment ions \(\text{N}^+\) generated from \(\text{N}_2\) at \(\Delta t = 0\) is shown in Fig. 2a. The central peak with the smaller kinetic energy release can be assigned to \(\text{N}^+\) ions generated through a dissociation process of singly charged nitrogen atoms, \(\text{N}_2^+\), via one-photon dissociative ionization and/or via two-photon ATI (see Fig. 2b [22,23]).

In particular, the broad momentum distribution of the fragment ions indicates that \(\text{N}^+\) ions are prepared sequentially. It can be regarded as the direct evidence that coherent two-photon processes are induced for generating \(\text{N}^+\) ions. Doubly charged parent molecules, \(\text{N}_2^{2+}\), prepared in the quasi-bound well, can also contribute to the central signals, but the fraction is probably small, since the Franck-Condon overlap with the shallow quasi-bound well is expected to be small. The side peaks with the larger kinetic energy release on both sides of the central peak are assigned to the \(\text{N}^+\) generated through Coulomb explosion of \(\text{N}_2^{2+}\).

As estimated from the photon energies, \(\text{N}^+\) from \(\text{N}_2^{2+}\) can be generated by the absorption of one photon of either the 17th (26.4 eV) or the 19th (29.5 eV) order harmonic, but \(\text{N}^+\) in the side peaks originated from \(\text{N}_2^+\), \(\text{N}^+\) in the central peak from the neutral dissociation pathway (\(\text{N}^+ + \text{N}\)), and the metastable \(\text{N}_2^{2+}\) in the central peak can probably be generated only when two (or more) photons of the harmonics are absorbed. In order that \(\text{N}^+\) is generated from \(\text{N}_2^+\) after a two-photon absorption process, the sum of the orders of the two harmonics should exceed 30th (46.5 eV). When the harmonics are lower than the 9th order, the counterpart harmonic in the cutoff region should be significantly weaker, and therefore, the contribution
from the lower-order harmonics to generate \( N^+ \) and \( N_2^+ \) are expected to be negligible.

### 3.2. Autocorrelation measurement of attosecond pulse train

The autocorrelation function is measured by recording the momentum distribution of \( N^+ \) and \( N_2^+ \) ions as a function of the delay \( \Delta t \). The lower half of the Si beam splitter is fixed to the piezo actuator, whose absolute position accuracy is higher than 10 nm, is moved every 0.1 \( \mu m \) corresponding to sampling at every 170 as, and the delay is scanned from \(-10\) to \(10\) fs. The signals at each delay time are those obtained by accumulating signals for \(2 \times 10^3\) laser shots. The resultant autocorrelation trace is shown in Fig. 3a. The signal changes periodically depending on \( \Delta t \) both in the side-peak and central-peak regions. The modulation in the sum of the intensities within the two side-peak regions marked with ‘C’ is drawn in Fig. 3c. The signal changes periodically depending on \( \Delta t \), the fluctuation in a burst. In the present measurement, the ratios of the intensities within APT, the distribution, half-maximum (FWHM) of respective attosecond pulses could be obtained. However, even at this sampling interval, the least-squares fit to Eq. (1) can securely be done using the fact that the interval of the pulse train is 1.33 fs. The present autocorrelation measurements, the sampling was done at every 170 as. If the resolution is raised by decreasing the sampling intervals below 148–70 as, which are the Nyquist limit of the higher-order harmonics of the orders of 9th–19th, the interferometric fringe could be obtained. However, even at this sampling interval, the least-squares fit to Eq. (1) can securely be done using the fact that the interval of the pulse train is 1.33 fs.

The least-squares fit of Eq. (1) to the observed autocorrelation traces is performed, and the best-fit curves are drawn with red curves in Fig. 3b and c. As optimized parameters, \( \tau_p = 460(50) \) as and \( \tau_e = 15(2) \) fs are determined for the side peaks in Fig. 3b, and \( \tau_p = 330(50) \) as and \( \tau_e = 16(3) \) fs are determined for the central peaks in Fig. 3c.

For calibration of the period of the observed modulations, the autocorrelation measurement is also performed on the fundamental light at 800 nm. As shown in Fig. 3d, the period of the smooth sinusoidal modulation is exactly twice that of the sharper peaks appearing in the autocorrelation traces in Fig. 3b and c. Since the sinusoidal modulation represents the optical cycle of the fundamental light, the sharper peaks clearly shows that high-order harmonics are generated as a train of attosecond bursts occurring with a half cycle of the fundamental light \([24]\). In Fig. 3b and c, the intensities of the sharp peaks decrease gradually as the absolute value of the delay \( \Delta t \) increases. This intensity variation is considered to trace that of the attosecond pulse train (APT).

### 3.3. Pulse duration of attosecond pulse train

For estimating the pulse duration \( \tau_p \), as the full-width at half-maximum (FWHM) of respective attosecond pulses within APT, the distribution,

\[
I(\Delta t) = a_0 + a_1 \exp \left\{ -\frac{(\Delta t)^2}{\tau_e^2} \right\} \exp \left\{ -\frac{(\Delta t - J T_{\text{APT}})^2}{\tau_p^2} \right\}
\]

is introduced to represent APT, where \( a_0 \) represents a constant shift adjusting the background one-photon contribution, \( a_1 \) the amplitude of the entire envelope of the autocorrelation trace, and \( J T_{\text{APT}} \) the cycle of the attosecond bursts. In the present measurement, the ratios of \( a_1/a_0 \) were 1.5 for the central peak and 1:4 for the side peaks. The smaller ratio at the central peak is originated from the larger contribution from one-photon ionization. Since the data accumulation of \(2 \times 10^3\) laser shots was done at each time delay, the fluctuation in \( a_0 \) is expected to be significantly small. In Eq. (1), it is assumed that the respective pulses within APT are expressed by a Gaussian distribution with an equal width, \( \tau_p \), and that the entire envelope of APT is expressed by a Gaussian distribution with the width \( \tau_e \).

Consequently, the temporal duration of the attosecond pulses within APT, which is \(\sqrt{2}\) of FWHM of the autocorrelation trace, is determined to be \( \tau_p = 320(40) \) as for the side peaks, and that for the central peaks is determined to be \( \tau_p = 240(30) \) as. Though the interval of the sampling is 170 as, the width of a smooth Gaussian function obtained after the least-squares fit can be determined with the precision of 30–40 as. Similarly, FWHMs of the entire envelope of APT are determined to be \( \tau_e = 11(1) \) fs for the side peaks and \( \tau_e = 11(2) \) fs for the central peaks.

In the present case, the observed autocorrelation traces are expected to be composed of the five harmonics for the side peaks (\( N = 5 \) ) and the six harmonics for the central peaks (\( N = 6 \)), by referring to the threshold energies of the \( N_2^+ \) and \( N_2^2+ \) in Fig. 2b. The combinations of two harmonics from 11th to 19th can induce the side peaks originated from \( N^+ \) generated via the Coulomb explosion of \( N_2^+ \). On the other hand, the combinations of two harmonics from 9th to 19th can induce the central peak from \( N^+ \) via dissociative ionization of \( N_2^+ \). The durations of the transform-limited pulse within the attosecond pulse train are estimated from the measured relative intensities of the harmonics to be 270 as for the central peak and 300 as for the side peaks on the assumption that the attosecond pulse train is composed of the harmonics from 9th to 19th.

These values are consistent with the observation above. In the estimation of the pulse duration from the measured autocorrelation trace, the Gaussian waveform is assumed, therefore, the pulse duration from the autocorrelation trace
could become slightly shorter than that estimated from the harmonic intensity distribution.

It can be securely said that a train of pulses whose duration is \( \sim 300 \text{ as} \) is generated by the coherent superposition of high-order harmonics and its temporal structure is measured by the efficient two-photon dissociative ionization of \( \text{N}_2 \) molecules.

4. Summary

We have measured the autocorrelation function of the APT generated as high-order harmonics without using a thin metal filter that would deteriorate spatio-temporal structure of attosecond pulses with its non-uniform thickness. The present achievement enabled by removal of a
metal filter is primarily due to the high efficiency of the two-photon absorption cross-section of N₂, which is one or two-orders of magnitude larger than Ar, whose ionization energy is nearly equal to N₂.

The deterioration of the spatio-temporal profile of attosecond pulses by the Si beam splitter is negligible since the figure tolerance of the Si beam splitter is better than 1/40 \( \lambda \) at 633 nm. The present measurements, combined with our previous study on the two-photon ATI process of H₂ [13], suggest that molecules have a much larger cross-section for two-photon absorption in the VUV–XUV region than atoms, which facilitates autocorrelation measurements of attosecond pulses.

We have demonstrated in the present study that an ensemble of molecules is an efficient nonlinear medium suitable for the characterization of attosecond pulses. This molecular explosion detector for ultrashort pulses (MEDUSA), introduced in the present study, has a wide applicability for measurements of ultimately short pulses in the attosecond time domain.

In addition to the contribution to attosecond metrology, the present study has also extended the potentiality of Coulomb explosion imaging for revealing ultrafast molecular dynamics with unprecedented temporal resolution, which will provide a basis for research on light–matter interaction in the attosecond time domain.

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