Real-time observation of electronic, vibrational, and rotational dynamics in nitric oxide with attosecond soft X-ray pulses

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Abstract

Photoinduced quantum dynamics in molecules have hierarchical temporal structures with entangled electronic and nuclear motions. Femtosecond-to-attosecond transient absorption spectroscopy (TAS) using high-harmonic generation (HHG) in the extreme ultraviolet region with a photon energy below 100 eV has been a powerful method for observing such dynamics [1-9]. However, complete measurements of the electronic, vibrational, and rotational molecular dynamics have not yet been achieved. Recent progress of attosecond HHG in the soft X-ray (SX) region around the water window (284-543 eV) [10-13] has opened a new possibility of TAS [14-17] with element specificity by using well-defined core electronic states. Here, we show that TAS in the SX region, around 400 eV, can probe multi-time-scale dynamics of the electronic, vibrational, and rotational degrees of freedom in a nitric oxide molecule at attosecond to sub-picosecond time scales, which provides a complete view of the phototriggered dynamics. This method of employing a photon-in/photon-out measurement using broadband attosecond SX pulses offers a unified approach to understand complete molecular dynamics with element specificity.

Main

The observation of electronic and nuclear dynamics in molecules initiated by light is critical for understanding fundamental mechanisms in photoinduced chemical and physical processes [1]. Pump-probe spectroscopy using high harmonics (HHs) has enabled direct measurements of ultrafast dynamics with femtosecond-to-attosecond temporal resolution through photoelectron/ion spectroscopy [18-20], high-harmonic spectroscopy [21, 22], and transient absorption spectroscopy (TAS) [2-9]. In particular, TAS has unique advantages over other techniques: it is unaffected by the existence of strong laser fields, state-specific even if the probe pulse has a broadband spectrum, and free of the space charge problem. Because of these characteristics, TAS is one of the most ideal techniques for laser-based pump-probe experiments for a wide range of atoms and molecules. To date, by using TAS in the extreme ultraviolet (XUV) region below ~100 eV, real-time observations of electronic processes such as autoionization [2], tunnel ionization [3] or the emergence of laser-dressed states [4] and nuclear dynamics [5-7] have been demonstrated. Couplings between the electronic and nuclear degrees of freedom have also been observed [8, 9]. Recently, due to advances in the development of high-harmonic generation (HHG) driven by long-
wavelength, intense infrared (IR) light sources [10-13], TAS in the soft X-ray (SX) region around the water window (from 284 eV to 543 eV) has become possible [14-17]. Short-wavelength SX pulses are expected to enable element-specific TAS in complex molecules in various environments such as in solvents.

However, until now, there has been no TAS measurement that resolves all the electronic, vibrational, and rotational dynamics in molecules simultaneously. In particular, it has been unclear if molecular rotation can be measured in TAS in the XUV or SX region. Moreover, the maximum photon energy in TAS is mostly limited below 300 eV for molecular targets, which hinders the use of important absorption edges in the higher photon energy range.

Here, we demonstrate that electronic, vibrational, and rotational dynamics at attosecond to sub-picosecond time scales can be simultaneously observed by TAS in the SX region. As a target molecule, we choose nitric oxide (NO). NO is not only a good prototype for understanding fundamental dynamics because of its simple structure, but also important in photochemical reactions in the atmosphere or in laser filaments [23]. TAS is conducted with attosecond SX HHs around 400 eV (nitrogen K-edge). Our results pave the way for the realization of complete measurements of entangled electronic and nuclear dynamics with element specificity.

Figure 1(a) shows a schematic of the experimental setup. We employ a BiB₃O₆-based optical parametric chirped pulse amplifier operating at 1.6 µm with a pulse duration of 10 fs as an HHG driver [24]. Attosecond SX pulses obtained by HHG in helium are used as probe pulses while the IR fundamental pulses are used as pump pulses. The two pulses are collinearly focused into an NO gas cell with piezo-controlled delays. The transmitted SX spectra are measured by a spectrometer consisting of a slit, an aluminium filter, a flat-field grating, and an X-ray charge-coupled device (CCD) camera (for details of the experimental conditions, see Supplementary Section 1). A typical SX spectrum without the NO gas cell is shown in Fig. 1(b). The maximum photon energy reaches above 450 eV, sufficiently covering the nitrogen K-edge. The energy levels of NO relevant to our experiment are depicted in Fig. 1(c). The SX pulse excites an electron in the N 1s core level to the 2π valence level or the Rydberg levels. The measured transient absorption spectrum around 400 eV with a pump intensity of ~1x10¹⁴ W/cm² is shown in Fig. 1(d). Here, the transient absorbance at a delay of τ is defined as ΔA(τ) = -log₁₀(I(τ)/I₀), where I(τ) and I₀ are the transmitted SX intensities at a delay of τ and at a sufficiently large negative delay (typically, ~100 fs), respectively. The measured static absorbance spectrum of NO is shown as black circles in
Fig. 1(e). The black curve in Fig. 1(e) is a reference absorbance measured by a synchrotron source [24], which agrees well with our measurement. The assignments of the absorption peaks are obtained by *ab initio* calculations (for details, see Supplementary Section 2). The strong peak at 399.8 eV and the weak peaks around 407.5 eV are the 1s-2π and 1s-Rydberg peaks of neutral NO, respectively. In the calculation, the position of the 1s-2π peak of NO⁺ is also determined to be 403.3 eV. The main feature in Fig. 1(d) is the suppression of the NO 1s-2π peak and the emergence of the NO⁺ 1s-2π peak when the IR pulse precedes the SX pulse. This indicates the generation of NO⁺ by tunnel ionization. Moreover, around the delay origin, the NO 1s-Rydberg peaks are modulated in the presence of a strong IR field. This is due to the AC Stark shift and the emergence of laser-dressed states, which are similar to those observed in previous TAS studies of atoms and molecules [4, 8, 9, 16]. Here, we focus on the NO and NO⁺ 1s-2π peaks and discuss the dynamics of tunnel ionization and the subsequent nuclear motions.

First, we describe the attosecond tunnel ionization dynamics. Figure 2 shows the transient absorbance at 403.1 eV with a pump intensity of ~2×10¹⁴ W/cm². This photon energy is associated with the NO⁺ 1s-2π peak, and the increase in the absorbance corresponds to tunnel ionization. Around the delay origin, a step-like structure with a period of a half cycle of the pump IR pulse (2.7 fs) is observed. This structure is characteristic of tunnel ionization, reflecting the fact that tunnel ionization is a highly nonlinear process and that ionization dominantly occurs at the peaks of the oscillating laser electric field [3, 19].

Second, we discuss the vibrational dynamics of NO⁺ following ionization. Figure 3(a) shows the delay-dependent central energies of the NO⁺ 1s-2π peak extracted by Gaussian fitting with a pump intensity of ~1×10¹⁴ W/cm². A clear oscillation with a period of 14.5±0.1 fs is observed. The obtained oscillation period agrees well with the value from the literature for the vibration period of NO⁺ (14.23 fs) [26]. The initial phase of the vibration is determined to be (0.17±0.08) π rad, where 0π and 0.5π mean perfect “cosine-like” and “sine-like” phases, respectively. This implies that the observed oscillation is close to “cosine-like.” The mechanism of the observed oscillation in the 1s-2π peak energy, as well as its initial phase, can be explained by the potential energy curves of NO and NO⁺ obtained by the *ab initio* calculation (Fig. 3(b)). Upon ionization, a vibrational wave packet is created on the electronic ground state of NO⁺. Because the equilibrium internuclear distance of NO⁺ is smaller than that of NO, the created vibrational wave packet in NO⁺ is displaced from the bottom of the potential energy curve and
thus starts vibrating. The oscillation of the internuclear distance is directly mapped to the transition energy between the 1s and 2π levels, as the transition energy monotonically decreases with the internuclear distance. This mechanism [6, 7] is consistent with the experimentally observed “cosine-like” initial phase. In addition to the coherent vibration, the observed central energy of the NO+ 1s-2π peak contains a unidirectional upper shift around the delay origin. This shift might be due to the laser-field-induced distortion of the potential curve [27].

Finally, we describe the rotational dynamics. Figure 4(a) shows the transient absorbance of the NO 1s-2π peak, averaged from 398.7 to 400.6 eV with a pump intensity of ~1×10^{14} W/cm^2. The circles are the measured data, and the solid curves are the calculation results. The calculation contains two signals: tunnel ionization and molecular rotation. The tunnel ionization signal is the abrupt decrease in the absorbance around the time origin, whose shape is determined from sigmoid fitting of the transient absorbance of the NO+ 1s-2π peak. The molecular rotation signal is the slow increase or decrease in the absorbance, which is simulated by the time-dependent Schrödinger equation for the rotational states of NO with a pump intensity of 1.3×10^{14} W/cm^2 (for details, see Supplementary Section 4). The experiment and calculation are in good agreement. The mechanism of the molecular rotation and its effect on the SX absorption are depicted in Fig. 4(b). When an NO molecule is irradiated by a linearly polarized strong IR pulse, it begins to align with the polarization of the IR pulse via the interaction between the induced dipole moment and the laser electric field [28]. Meanwhile, the transition dipole moment between the 1s and 2π orbitals is perpendicular to the molecular axis. Therefore, if the polarization of the SX pulse is perpendicular to that of the IR pulse, the inner product between the SX polarization and the 1s-2π transition dipole moment increases as the NO molecule aligns, resulting in an increase in the SX absorption. Conversely, if the polarization of the SX pulse is parallel to that of the IR pulse, the SX absorption decreases. In Fig. 4(a), a bump structure with a peak at approximately 80 fs is observed. This reflects the fact that the molecular alignment occurs at ~80 fs; subsequently, the alignment is lost due to the dephasing of the rotational states. Note that the rotational dynamics observed in our experiment are difficult to access by conventional TAS in the XUV region using d or p inner shells. The reason is that the d or p inner shells are usually energetically degenerate and the transition dipole moment vector for each degenerate state is oriented differently.

In summary, we demonstrate that electronic and nuclear dynamics of diatomic molecules at attosecond to sub-picosecond time scales can simultaneously be observed by TAS in the SX
region, around 400 eV. The target sample in our experiment is a prototypical diatomic molecule, NO, but the same technique can be applied to more complex molecules in the gas phase or in solvents, where the element specificity of SX absorption can be fully utilized to understand the molecular dynamics that occur in multiple degrees of freedom at different time scales. Such a technique is generally applicable to measure the couplings among electronic, vibrational, and rotational dynamics, which are quite common in strong field-induced molecular dynamics [27, 29] and in photo-induced phase-transition dynamics in charge-transfer complexes [30]. Attosecond TAS in the SX region can possibly resolve these couplings in transient states during chemical reactions or phase transitions, which is difficult to access with other techniques.
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Author contributions

N.S. and J.I. conceived the study. N.S., H.S, and N.I. constructed the TAS beam line. N.S and H.S. performed the experiment. N.S. analysed the data. Y.W., A. C., S. H., and Z.C. developed the HHG scheme. N.I., T.K. and J.I. built the laser source. N.K. conducted the ab initio calculations of the ground states and the core-excited states of NO. All authors discussed the results and wrote the manuscript.

Competing interests

The authors declare no competing financial interests.
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Figure 1. TAS of NO in the SX region. (a) Schematic of the experimental setup. (b) Typical SX spectrum obtained by HHG in helium. (c) Energy levels of NO that are relevant to TAS (right) and the shapes of the N 1s and 2π orbitals (left). (d) Measured transient absorption spectra. The colour scale represents the transient absorbance ΔA (the definition is described in the main text). (e) Static absorbance of NO without the IR pump pulses measured in our experiment (black circles) and in a synchrotron (black curve). The calculated positions of the NO and NO⁺ 1s-2π peaks are indicated by the blue and red lines, respectively.
Figure 2. Attosecond tunnel ionization dynamics. The red circles are the measured transient absorbance data at 403.1 eV. The red curve is their 3-point rolling average, and the shaded area indicates the error.

Figure 3. Coherent molecular vibration. (a) Measured central energy of the NO+ 1s-2π peak as a function of the delay (circles). The solid curve is the fitting result with a cosine function plus a Gaussian function around the time origin. The dashed curve is the cosine component of the fitting result. (b) Potential energy curves of the relevant states obtained by the ab initio calculation and a schematic of the mechanism of the molecular vibration.
Figure 4. Coherent molecular rotation. (a) Measured (circles) and calculated (solid curves) transient absorbance of the NO 1s-2\(\pi\) peak averaged from 398.7 to 400.6 eV. The blue and red data are measured when the polarizations of the SX and IR pulses are perpendicular and parallel, respectively. (b) Schematic of the mechanism of the SX absorption change upon molecular alignment.
Supplementary Information for
Real-time observation of electronic, vibrational, and rotational dynamics in nitric oxide with attosecond soft X-ray pulses

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1. Details on the TAS beamline

A detailed schematic of the TAS beamline is presented in Fig. S1. The IR pulses obtained from the BiB$_3$O$_6$-based optical parametric chirped-pulse amplifier (1.6 µm, 10 fs, 1.5 mJ, 1 kHz) are split into pump and probe arms by a beam splitter. In attosecond TAS (Fig. 2 in the main text), the pump and probe arms contain 20% and 80% of the total pulse energy, respectively. In the other measurements, the percentages are 10% and 90%, respectively. In the probe arm, the IR pulses are focused by a lens (f = 50 cm) into a semi-infinite helium gas cell (2.3 bar for attosecond TAS and 2.4 bar for the other measurements) to generate SX HHs. A two-stage differential pumping system after the gas cell using two dry pumps (500 l/min.) reduces the gas pressure in the subsequent vacuum chambers in the beamline. The SX pulses are passed through an aluminium filter (150 nm) to remove the fundamental IR component and focused into an NO gas cell (0.1 bar, 1.5 mm thick) by a toroidal mirror (f = 2 m). The pump IR pulses are recombined with the probe SX pulses by a hole-drilled mirror and collinearly focused into the NO gas cell by a lens (f = 25 cm). The delay between the SX and IR pulses is scanned by a piezo stage. In the attosecond measurement (Fig. 2), the delay is controlled to a precision of ~30 as with a feedback system using a HeNe laser which propagates collinearly with the SX and IR pulses [S1]. The SX spectra are recorded by a spectrometer consisting of a slit (50 µm), a flat-field grating (Shimadzu, 2400 l/mm), and a back-illuminated X-ray CCD camera (Andor, Newton SO).

The carrier-envelope phase (CEP) of the IR pulses is passively stabilized during attosecond TAS. The CEP-dependence of the HH spectra is shown in Fig. S2(a), showing clear half-cycle cutoff structures [S2]. In attosecond TAS, an HH spectrum at a CEP of 0.7π in Fig. S2(a) is employed (Fig. S2(b)). The nitrogen K-edge (400 eV) is covered by only one half-cycle cutoff, indicating that we use isolated attosecond SX pulses. In the other measurements, the CEP is rapidly scanned from shot to shot with a step of 0.1π by using an acousto-optic programmable dispersive filter in the laser system. Practically, this corresponds to a “randomization” of the CEP. The HH spectrum shown in Fig. 1(b) in the main text is measured under such a condition. The randomization of CEP reduces the fine spectral structures in the HH spectrum, resulting in a better signal-to-noise ratio in TAS.
Figure S1. Detailed schematic of the TAS beamline. The splitting ratio of the beam splitter is R:T = 20:80 for attosecond TAS (Fig. 2 in the main text) and 10:90 for the other measurements, respectively. The delay feedback system is employed only in attosecond TAS.

Figure S2. (a) CEP dependence of the HH spectra (the splitting ratio of the beam splitter is R:T = 20:80). (b) HH spectrum employed in attosecond TAS (CEP = 0.7π in (a)).
2. *Ab initio* calculation of the ground states and the core-excited states of NO

The neutral and cationic ground states, NO ($^2\Pi$) and NO⁺ ($^1\Sigma^+$), and the lowest N 1s-2π ($\pi^*$) excited states, NO* ($^2\Delta$) and NO⁺* ($^1\Pi$), were obtained by configuration-interaction (CI) calculations including single and double substitutions up to 17 virtual orbitals from the full valence configuration space over 3-6 $\sigma$ and 1-2 $\pi$ orbitals using the self-consistent field (SCF) orbitals for each state, where the core orbitals are frozen and their occupation numbers are fixed in the CI calculations. Primitive basis functions were taken from (73/7) contracted Gaussian-type functions [S3]. They were augmented with two $d$-type polarization functions for each atom: the exponential $\zeta=2.704$ and 0.535 for oxygen, $\zeta=1.986$ and 0.412 for nitrogen. The contraction schemes were (4111111/31111/1*1*). The calculations were performed by using the originally developed quantum chemical computation code GSCF3 [S4, S5]. The results are shown in Table S1. We should note the second and third lowest N 1s-$\pi^*$ states, NO* ($^2\Sigma^-$) and NO⁺* ($^2\Sigma^+$), contribute to the observed N 1s-$\pi^*$ band ([25] in the main text), though we do not use these state energies in the present work.

Table S1. Total energies $E_{\text{total}}$ in a.u. (1 a.u. = 27.2116 eV) obtained from the CI calculations for the neutral and cationic ground states, NO ($^2\Pi$) and NO⁺ ($^1\Sigma^+$), and the lowest N 1s-2π excited states, NO* ($^2\Delta$) and NO⁺* ($^1\Pi$).

| Internuclear distance (Å) | Ground states | Lowest N 1s-2π excited states |
|---------------------------|---------------|-------------------------------|
|                           | NO ($^2\Pi$)  | NO⁺ ($^1\Sigma^+$)            |
|                           |               | NO* ($^2\Delta$)               |
|                           |               | NO⁺* ($^1\Pi$)                |
| 0.95                      | -129.39570    | -129.15443                    |
|                           |               | -114.62817                    |
|                           |               | -114.27827                    |
| 1.05                      | -129.50551    | -129.21200                    |
|                           |               | -114.78051                    |
|                           |               | -114.38051                    |
| 1.15                      | -129.53468    | -129.20075                    |
|                           |               | -114.84218                    |
|                           |               | -114.40611                    |
| 1.25                      | -129.52139    | -129.15826                    |
|                           |               | -114.85510                    |
|                           |               | -114.39525                    |
| 1.35                      | -129.48719    | -129.10403                    |
|                           |               | -114.84357                    |
|                           |               | -114.37220                    |
3. Semi-classical simulation of the molecular vibration

To simulate the delay dependence of the central position of the 1s-2\(\pi\) peak (Fig. 3(a) in the main text), we semi-classically calculate the molecular vibration of NO\(^+\) based on the potential energy curves obtained from the \textit{ab initio} calculations. First, the probability density of the vibrational ground state of NO, \(P_{\text{NO}}(R)\) is calculated from its potential energy curve (Fig. S3, blue curve). Here, \(R\) is internuclear distance. Note that the energy spacing of the vibrational levels of NO is sufficiently large (0.23 eV, derived from its vibration frequency [S6]), so only the ground state is populated at room temperature. Then, by using the \(R\)-dependent ionization potential (Fig. S3, black dashed curve) and the molecular ADK model [S7], the \(R\)-dependent ionization rate, \(w(R)\) is obtained at a laser intensity of \(1\times10^{14}\) W/cm\(^2\). The probability density of the vibrational wave packet in NO\(^+\) created by tunnel ionization is calculated as \(P_{\text{NO}^+}(R) = P_{\text{NO}}(R)w(R)\) (Fig. S3, red curve). The vibrational wave packet is then approximated as a classical particle which moves along the potential energy curve of NO\(^+\) and is initially located at the center of mass of \(P_{\text{NO}^+}(R)\). The internuclear distance as a function of time after ionization, \(R_{\text{vib}}(t)\) is calculated by solving the classical equation of motion. \(R_{\text{vib}}(t)\) can be directly mapped to the position of the NO\(^+\) 1s-2\(\pi\) absorption peak, \(E_{1s-2\pi}(t)\). We then consider the instrument response function (IRF) which originates from the temporal duration of the IR and the SX pulses and the timing jitter between them. The IRF is obtained by the Gaussian fitting of the time derivative of the measured total peak area of the NO\(^+\) 1s-2\(\pi\) peak around the delay origin (Fig. S4, gray curve). The convolution of the IRF and \(E_{1s-2\pi}(t)\) gives the delay-dependent central position of the NO\(^+\) 1s-2\(\pi\) peak (Fig. S4, blue curve) which can be compared to the experimental data (Fig. S4, red circles). The calculation qualitatively reproduces the experimental values. However, the vibration amplitude and the phase obtained by the calculation do not qualitatively agree with the measured data. This discrepancy might be reduced by using more strict quantum mechanical models for molecular vibration, or by improving the approximation accuracy of the \textit{ab initio} calculations.
Figure S3. Calculated probability density of the vibrational ground state in NO (blue curve) and the vibrational wave packet in NO$^+$ created by tunnel ionization (red curve). The ionization potential of NO is shown as a black dashed curve.

Figure S4. Calculated (blue curve) and measured (red circles) relative central position of the NO$^+$ 1s-2\pi peak as a function of delay. The IRF is shown as a gray curve.
4. Calculation of molecular rotation and its effect on SX absorption

Laser-induced molecular rotation is simulated by solving the time-dependent Schrödinger equation for the rotational states, as described in [28] in the main text. The polarizability and rotational constant required for the calculation are taken from [S8, S9]. As an excitation IR pulse, we use a Gaussian pulse (1.6 µm, 10 fs FWHM, $1.3 \times 10^{14}$ W/cm$^2$) that is similar to those employed in the experiment. The degree of molecular alignment can be evaluated by $<\cos^2 \theta>$, where $\theta$ is the angle between the IR polarization vector and the molecular axis and $<>$ means a thermally averaged expectation value. The calculated $<\cos^2 \theta>$ as a function of time is plotted in Fig. S5 for various temperatures. Note that the temperature of NO is 300 K in the actual measurement because it is filled in a gas cell.

The relationship between molecular alignment and SX absorption is formulated as follows. We assume that the transition dipole moment between the inner shell and the valence orbital is perpendicular to the molecular axis. If the polarizations of the IR and SX pulses are parallel, the inner product between the transition dipole moment and the SX polarization vector is proportional to $\sin \theta$. Therefore, the SX absorption is proportional to $<\sin^2 \theta> = 1 - <\cos^2 \theta>$. On the other hand, if the polarizations of the IR and SX pulses are perpendicular, the inner product is proportional to $\sqrt{1 - \sin^2 \theta \cos^2 \varphi}$, where $\varphi$ is the polar angle. In this case, the SX absorption is proportional to $<\int (1 - \sin^2 \theta \cos^2 \varphi) d\varphi / 2\pi> = (1 + <\cos^2 \theta >)/2$. By using these expressions, the relative SX absorption change can be evaluated from the calculated degree of alignment, $<\cos^2 \theta>$.

![Figure S5. Calculated degree of alignment of NO irradiated by a 1.6 µm, 10 fs, $1.3 \times 10^{14}$ W/cm$^2$ Gaussian pulse for various rotational temperatures.](image)
Supplementary references

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