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## Real-time observation of electronic, vibrational, and rotational dynamics in nitric oxide with attosecond soft X-ray pulses at 400 eV: supplementary material

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#### 1. EXPERIMENTAL SETUP

A detailed schematic of the TAS beamline is presented in Fig. S1. The IR pulses obtained from the BiB<sub>3</sub>O<sub>6</sub>-based optical parametric chirped-pulse amplifier (1.6  $\mu$ m, 10 fs, 1.5 mJ, 1 kHz) are split into pump and probe arms by a beam splitter. The pump and probe arms contain 10% and 90% of the total pulse energy, respectively. In the probe arm, the IR pulses are focused by a lens (f = 50 cm) into a semi-infinite helium gas cell (2.4 bar) 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 (4f = 2 m). The SX pulse

duration is estimated to be ~200 as by SFA calculation. The pump IR pulses are recombined with the probe SX pulses by a holedrilled mirror and collinearly focused into the NO gas cell by a lens (f = 25 cm). The IR intensity is estimated to be ~1×10<sup>14</sup> W/cm<sup>2</sup>. The delay between the SX and IR pulses is scanned by a piezo stage. In the attosecond TAS measurement (Fig. 2 in the main text), 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 photon flux at 400 eV at the CCD is ~80 photons/s/eV.



Fig. S1. Detailed schematic of the TAS beamline. The delay feedback system is employed only in attosecond TAS.

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 cut-off structures [S2]. In attosecond TAS, an HH spectrum at a CEP of  $0.8\pi$  in Fig. S2(a) is employed (Fig. S2(b)). The nitrogen *K*-edge



**Fig. S2.** CEP-dependent HH spectra. (a) Measured HH spectra with the relative CEP scanned from 0 to  $2\pi$ . (b) HH spectrum employed in attosecond TAS (CEP =  $0.8\pi$  in (a)).

(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  $0.1\pi$  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.

### 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<sup>+</sup> ( $^{1}\Sigma^{+}$ ), and the lowest N 1s-2 $\pi$  ( $\pi^*$ ) excited states, NO\*( $^{2}\Delta$ ) and NO<sup>+\*</sup>( $^{1}\Pi$ ), 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 schemes for nitrogen. The contraction were (411111/31111/1\*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 [29], 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 (2II) and NO+ (1 $\Sigma$ +), and the lowest N 1s-2 $\pi$ excited
states, NO*( $^{2}\Delta$ ) and NO+*( $^{1}\Pi$ ).

Internuclear distance (Å)	Ground states		Lowest N 1s-2π excited states	
	NO (2Π)	NO+ (1Σ+)	NO* (²Δ)	NO+* (1Π)
0.95	-129.3957	-129.1544	-114.6281	-114.2782
1.05	-129.5055	-129.2120	-114.7805	-114.3805
1.15	-129.5346	-129.2007	-114.8421	-114.4061
1.25	-129.5213	-129.1582	-114.8551	-114.3952
1.35	-129.4871	-129.1040	-114.8435	-114.3722

## 3. CALCULATION OF MOLECULAR ROTATION AND ITS EFFECT ON SX ABSORPTION

Laser-induced molecular rotation is simulated by solving the timedependent Schödinger equation for the rotational states of NO, as described in [32]. The polarizability and rotational constant required for the calculation are taken from [S6, S7]. As an excitation IR pulse, we use a Gaussian pulse (1.6  $\mu$ m, 10 fs FWHM, 1.3×10<sup>14</sup> W/cm<sup>2</sup>) that is similar to those employed in the experiment.

The degree of molecular alignment can be evaluated by  $\langle \cos^2\theta \rangle$ , where  $\theta$  is the angle between the IR polarization vector and the molecular axis and  $\langle \cdot \rangle$  means a thermally averaged expectation value. The calculated  $\langle \cos^2\theta \rangle$  as a function of time is plotted in Fig. S3 for various temperatures. Note that the temperature of NO is 300 K in the actual measurement because NO 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



**Fig. S3.** Calculated degree of alignment of NO irradiated by a 1.6 µm, 10 fs, 1.3×10<sup>14</sup> W/cm<sup>2</sup> Gaussian pulse for various rotational temperatures.

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,  $<\cos^2\theta >$ .

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