

Electronic-vibrational dynamics and coherence in x-ray transient absorption of N_2^+ induced by strong-field ionization

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(Received 21 September 2023; revised 28 August 2024; accepted 7 February 2025; published 14 March 2025)

Attosecond transient absorption spectroscopy (ATAS) is becoming an indispensable and powerful tool in the emerging field of attochemistry, while the interpretation of measurements often requires full considerations of the coupling among various freedoms of motion. Here we develop the ionization-coupling model to incorporate the transient absorption and explore the coupled electronic-vibrational dynamics of nitrogen ions induced by strong-field ionization. It is found the coherent vibrational wave packet on the involved electronic state is created with a broad distribution of vibrational levels, which leads to the spectral overlap on the K -edge absorption. By identifying the contributions of each electronic state, the study reveals the significant role of the excited state $A^2\Pi_u$, differing from previous work by K -edge absorption measurements [Phys. Rev. Lett. **129**, 123002 (2022)]. We uncover features of absorption from forbidden transitions within the laser pulse duration and confirm the vibronic coherence-induced quantum beating of absorption. A scheme is proposed to avoid the spectral overlap and determine the population distribution among the states, which is crucial to resolve the debate on nitrogen air lasing. This work lays down the framework to research the ionic coherence in ATAS and offers valuable insights into the intricate interplay between electronic and vibrational dynamics.

DOI: [10.1103/PhysRevResearch.7.L012070](https://doi.org/10.1103/PhysRevResearch.7.L012070)

Strong-field ionization (SFI) of molecules creates extremely nonstationary ionic states that evolve coherently under the remaining laser field. The SFI-induced electronic, vibrational, and rotational excitation, as well as the quantum coherence, make the molecular ions a unique platform for investigating and manipulating chemical reactions [1–6], and extraordinary radiations such as air lasing and supercontinuum generation [7–9]. Determining the intricate multiple-freedom coupled subcycle ionic dynamics upon SFI is challenging both theoretically and experimentally [10–17], and key questions such as the mechanism of lasing from SFI-created nitrogen molecular ions remain unaddressed since the discovery [8].

Subjecting nitrogen molecules to strong laser fields, the N_2^+ can be created in the electronic states $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$. Laser-like emissions from N_2^+ are observed in the forward direction at wavelengths of 391 and 428 nm, corresponding to transitions from the upper excited state $B^2\Sigma_u^+(\nu=0)$ to the lower ground state $X^2\Sigma_g^+(\nu=0,1)$. Population inversion between $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states is the most straightforward explanation for the lasing effect [18,19].

But how is the population inversion formed? The tunneling ionization theory predicts a lower ionization rate into $B^2\Sigma_u^+$ state due to its larger ionization energy. One possible explanation is that the recollision of photoelectrons with the cation might lead to population transfer from $X^2\Sigma_g^+$ to $B^2\Sigma_u^+$ states [20]. However, other experiments show lasing persists even with circularly polarized driving pulses, which argues against the recollision picture [21]. Later it was realized that the electronic-vibrational coupling is crucial because the single-photon transition from $X^2\Sigma_g^+$ to $A^2\Pi_u$ states can significantly deplete the population in the ionic ground state, leading to possible population inversion between relevant X-B vibrational states [18,19,22]. It is further demonstrated that the upper $B^2\Sigma_u^+$ state could be effectively populated through instantaneous polarization of the new born cation in the field [16] and multiphoton resonant transitions facilitated by the dynamic Stark shift [9]. On the other hand, SFI could create ions in partial coherence [10–12], which might lead to lasing without inversion, as the electronic-vibrational levels of $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ form V-type configurations [23]. It is also possible that rotational coherence comes into play, which causes transient population inversion due to the different rotational constants of $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states [24–27]. However, this interpretation seems to have difficulty explaining the lasing efficiency at a pump wavelength of 800 nm, as demonstrated in Refs. [18,19,28,29]. Nevertheless, uncovering the underlying mechanism of lasing in N_2^+ relies on state-resolved population and coherence measurements with attosecond temporal resolution.

Attosecond transient absorption spectroscopy (ATAS) offers unique advantages for measuring the transient ionic

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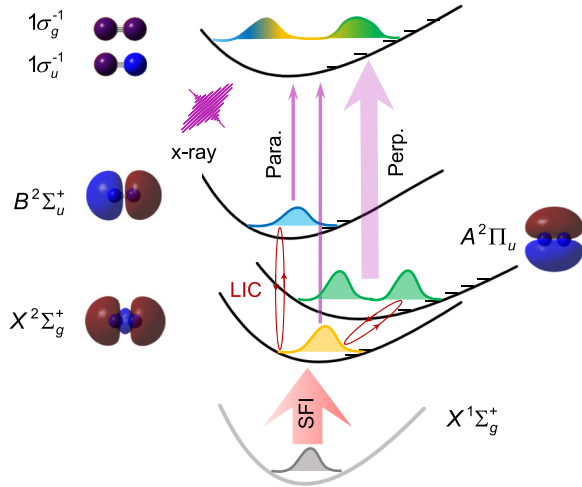


FIG. 1. Overview of the pump-probe scheme for N_2 : SFI creates electronic populations in the first three electronic states of N_2^+ , namely, X, A, and B, each with its respective vibrational wave packets. The laser-induced coupling (LIC, indicated by circles with arrows) leads to the redistribution of electronic population among these ionic states. The electronic-vibrational dynamics and coherence are probed by XAS through parallel or perpendicular transitions from the nitrogen K edge.

dynamics induced by SFI [10–12,17,30,31]. In ATAS, strong laser pulses create nonstationary ionic states, and the time-delayed attosecond pulses probe the transient population and coherence through one-photon absorption from the inner shell to the valence shell. Especially, ultrafast x-ray absorption spectra (XAS) were measured to inspect N_2^+ population distributions [32]. However, in the presence of a strong laser field, the SFI-induced electronic, vibrational, and rotational states are strongly coupled, leading to blurred and extremely complicated absorption spectra. To interpret the observations regarding the N_2^+ lasing mechanism, and more importantly, to fully explore the capabilities of ATAS involving SFI, a comprehensive theory is both indispensable and urgently needed [33–35], which requires full consideration of the coupling among various degrees of freedoms.

In this Letter, we develop the ionization-coupling model [16] to incorporate transient absorption and explore the coupled electronic-vibrational dynamics induced by SFI. The relevant processes are illustrated in Fig. 1, where SFI creates ions in electronic states $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$, each accompanied by its respective vibrational wave packet. The laser-induced electronic-vibrational coupling redistributes the population among the electronic and vibrational states in N_2^+ . The ionic population and coherence are probed by ATAS via transitions from the nitrogen K edge. The calculations reproduce the measured absorption spectra of N_2^+ in Ref. [32]. It is found that the laser-induced electronic-vibrational coupling leads to the coherent vibrational wave packet with broad distribution of vibrational levels, resulting in spectral overlap in the K -edge absorbance. By identifying the contributions of each electronic state, we verify a remarkably high population of the $A^2\Pi_u$ state. This study emphasizes the importance of electronic-vibrational coupling in strong laser field [30].

Moreover, we discover absorption features resulting from the forbidden transitions that occur during the laser pulse, and confirm the existence of quantum beating of absorption induced by vibronic coherence.

We have observed both forbidden transitions during the laser pulse and absorbance modulation after the laser pulse, which are induced by vibronic coherence. A scheme is proposed to avoid the spectral overlap and determine the population among the states, which is crucial for resolving the debate on nitrogen air lasing.

The evolution of the ionic density matrix under strong laser field is given by

$$\frac{d\rho_{iv}^+}{dt} = -\frac{i}{\hbar}[H(t), \rho_{iv}^+] + \left(\frac{d\rho_{iv}^+}{dt}\right)_{\text{ion}} + \left(\frac{d\rho_{iv}^+}{dt}\right)_{\text{decay}}, \quad (1)$$

where ρ_{iv}^+ is the ionic density-matrix element, with i and v denoting the electronic states and vibrational levels. At every instant, SFI injects coherent vibrational wave packets into the electronic states $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$. The injection rate is calculated using the molecular Ammosov-Delone-Krainov (MO-ADK) theory [36] with the SLIMP package [37]. The vibrational wave packets injected into different electronic states are assumed to be incoherent since the SFI destroys the electronic coherence [10]. The subsequent laser-ion interaction establishes coherence among different vibrational wave packets by laser-induced coupling. The ionic Hamiltonian $H(t)$ includes the interaction between the ion and the pump-probe field, described with the electric dipole approximation. The tensor transition dipole moment is constructed by weighting the electronic transition dipole moment $a_{i,j}$ with their respective Franck-Condon factors $\mu_{iv,jv'} = \langle \phi_{i,v} | a_{i,j} | \phi_{j,v'} \rangle$, describing the field-induced coupling among different states [for details, see the Supplemental Material (SM), Sec. 1.1 [38]]. By solving Eq. (1) numerically, we obtain the time-dependent dipole moment at the pump-probe time delay t_d ,

$$\mathbf{d}(\theta, t, t_d) = \sum_{i,j} \sum_{v,v'} \rho_{iv,jv'}^+(\theta, t, t_d) \mu_{iv,jv'}, \quad (2)$$

at the alignment angle θ between the molecular axis and the polarization direction of the laser field. The density-matrix element $\rho_{iv,jv'}^+(\theta, t, t_d)$ represents the coherence between different states. The XAS are calculated as in Refs. [39,40],

$$\sigma(\theta, \omega, t_d) = \frac{4\pi\alpha\omega}{|\mathbf{e}(\omega)|^2} \text{Im}[\mathbf{d}(\theta, \omega, t_d) \cdot \mathbf{e}^*(\omega)], \quad (3)$$

where $\mathbf{e}(\omega)$ and $\mathbf{d}(\theta, \omega, t_d)$ represent the Fourier transforms of the electric field and the time-dependent dipole moment, respectively. In our calculations, we use an 800 nm, 4.5×10^{14} W/cm² infrared laser pulse with duration of 50 fs and the x-ray pulse centered at 393 eV, with 10^{11} W/cm² intensity and 200 as duration. Both pump and probe pulses are linearly polarized and parallel. The XAS are independent of the x-ray pulse duration as long as the spectra remain continuous (for details, see Sec. 2.2 in the SM [38]). We calculate the absorption spectra for various molecular alignments and integrate over all angles to account for alignment dynamics (for details, see the SM, Sec. 3 [38]).

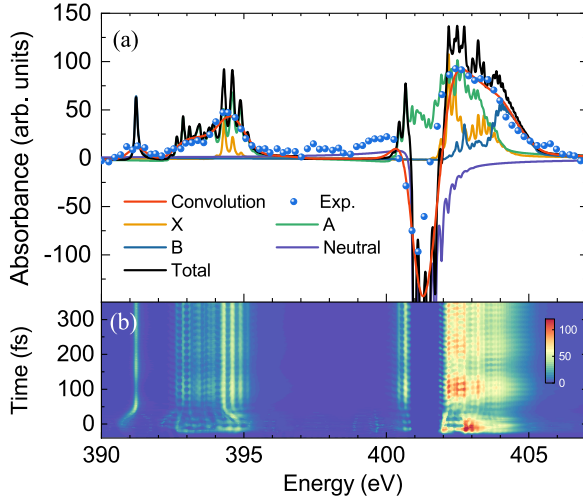


FIG. 2. (a) The calculated time-integrated XAS of N_2^+ (red line) is compared with the experimental results from Ref. [32] (blue dots). Contributions from the three electronic state are also shown separately: $X^2\Sigma_g^+$ (orange line), $A^2\Pi_u$ (green line), and $B^2\Sigma_u^+$ (blue line). (b) The transient XAS of nitrogen molecules exposed to strong laser pulses.

The calculated transient K -edge XAS of N_2^+ is presented in Fig. 2(b) as a function of the pump-probe time delay, with positive delays indicating that the laser pulse precedes the x-ray pulse. After the time delay of 75 fs, N_2^+ evolves freely. The slow oscillations in the transient absorption spectra with a period of hundreds of femtoseconds, originate from the laser-induced molecular alignment effects. By integrating the absorption spectra over a 140 fs time interval within the free evolution period, we present the time-integrated absorption spectra in Fig. 2(a). The narrow peak around 391.2 eV results from the resonant transition from $1\sigma_g$ state to $B^2\Sigma_u^+$ state. The transition from the $1\sigma_g$ state to $A^2\Pi_u$ state contributes to the absorption spectra in the energy range from 392.5 to 395.5 eV, spectrally overlapping with the transition from the $1\sigma_u$ state to the $X^2\Sigma_g^+$ state. Specifically, the peak at 394.4 eV, attributed to the transition $1\sigma_u \rightarrow X^2\Sigma_g^+$ as described in Ref. [32], is also significantly contributed to by the vibrational-progressed transitions of $1\sigma_g \rightarrow A^2\Pi_u$. Additionally, for the satellite transitions from $1\sigma_u$ to the lowest unoccupied $1\pi_g$ with vacancies remaining in the $X^2\Sigma_g^+$ or $A^2\Pi_u$ states, spectral overlap is observed in the energy range of 402–404 eV.

The discrete peaks observed in the calculated XAS suggest contributions from multiple vibrational levels, which are not resolved in the experiments due to the limited spectral resolution. To simulate the spectral broadening, we convolute the total absorption spectra with the energy width of 0.3 eV (red curve). The calculations reproduce well the measurements (blue dots) across the entire absorption spectra of N_2^+ . This agreement between our calculations and measurements validates the precision of our theoretical approach and highlights its potential for exploring the intricate interplay between electronic and vibrational dynamics.

To explain the spectral extension in the K -edge absorption from the $A^2\Pi_u$ state, we present the relevant potential-energy curves (PECs) in Fig. 3(a). Calculation details and

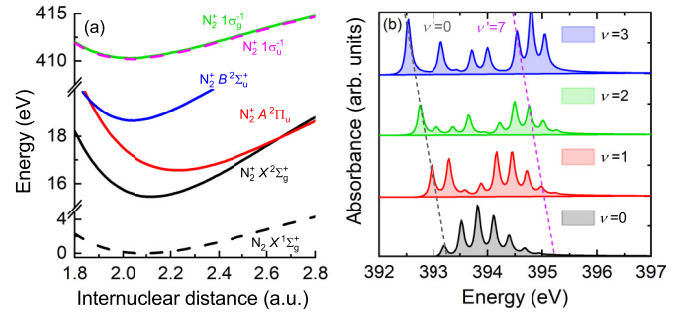


FIG. 3. (a) The relevant potential-energy curves for N_2 and N_2^+ . (b) Time-integrated XAS with transitions between $A^2\Pi_u$ state and $1\sigma_g^{-1}$ core-hole state with vibrational levels $\nu = 0-3$. The dashed lines indicate transition energies to $1\sigma_g^{-1}$ core-hole state with vibrational levels $\nu' = 0$ and $\nu' = 7$.

comparison with previous results are provided in Sec. 1.2 of the SM [41–43]. In the presence of strong laser fields, the $A^2\Pi_u$ state can be efficiently populated through electronic-vibrational coupling with one-photon resonant transition from the ionic ground state $X^2\Sigma_g^+$ [9,16]. The significant enlargement of the equilibrium nuclear distance from the $X^2\Sigma_g^+$ to $A^2\Pi_u$ states causes a broad distribution of vibrational levels in the latter. Interestingly, the electronic-vibrational coupling redistributes the population toward higher vibrational levels, leading to a deviation from the Franck-Condon distribution (see in Sec. 2.4 of the SM [38]). Additionally, for the K -edge absorption from $A^2\Pi_u$ state to $1\sigma_g^{-1}$ core-hole state, the bond length is shorten again, and thus much more vibrational levels of the K shell are involved. The combination of these effects results in the final spectral extension in the K -edge XAS from the $A^2\Pi_u$ state, which is overlooked in Ref. [32]. As shown in Fig. 3(b), the K -edge XAS from the $A^2\Pi_u$ state exhibit an absorption energy range spanning from 392.5 to 395.5 eV, confirming the crucial role of laser-induced electronic-vibrational coupling in exploring the dynamics from the K -edge XAS [4,44], which strongly relies on the accuracy of the PECs. This study reveals the significant role of the state $A^2\Pi_u$ in the XAS measurements, which was underestimated in previous work [32].

Notably, transient K -edge XAS can also explore electronic population dynamics and vibronic coherence, as shown in Fig. 4. The results are strongly dependent on the alignment angle between the molecular axis and the polarization direction of the pump-probe field. For parallel alignment, XAS are primarily contributed by the absorption from $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states, and perpendicular absorption from the $A^2\Pi_u$ state is forbidden. The absorption from $B^2\Sigma_u^+$ state manifests as a narrow absorption peak, which includes the vibrational transitions of 0-0 and 1-1 with the same transition energy of 391.2 eV. Absorption from $X^2\Sigma_g^+$ state, with three peaks, corresponds to transitions from the vibrational level $\nu = 0$ to $\nu' = 0-2$. For perpendicular alignment, XAS are mainly contributed by absorption from $A^2\Pi_u$ state, involving more than ten vibrational levels. Concurrently, the population of the $X^2\Sigma_g^+$ state cannot be probed with the perpendicularly polarized x-ray pulse. At alignment angle of 45° , absorptions from all three electronic states are allowed.

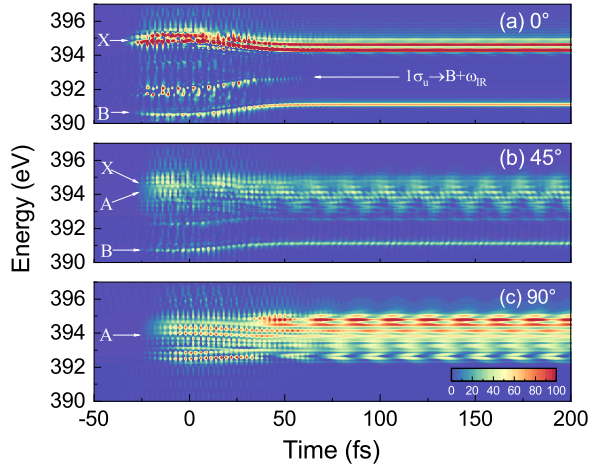


FIG. 4. Transient x-ray absorption spectra are presented for different alignment angles between the molecular axis and the polarization direction of the pump-probe field: (a) 0°, (b) 45°, and (c) 90°.

Within the strong laser pulse, the absorption energies from $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states exhibit significant upward and downward shifts, respectively. This shifts are attributed to the AC Stark effect as a consequence of the coupling induced by the laser field [9,45]. The rapid oscillations with half-period of the laser pulse originate from the transient polarization of the electronic states under the strong laser field, as observed in the attosecond XAS of atoms [10,11,17]. It is noteworthy that absorptions from transitions that are forbidden within the laser pulse [46] also appear in the XAS of N_2^+ . For instance, the $B^2\Sigma_u^+$ state is not accessible from the $1\sigma_u$ state through single-photon absorption. However, in presence of the laser pulse, this transition can occur by absorbing an additional laser photon, i.e., to the laser-dressed state $1\sigma_u \rightarrow B + \omega_{IR}$, as indicated in Fig. 4(a). These features resemble Floquet engineering, which aims to dynamically tailor the electronic properties of solid-state materials [47], underscoring the intricate interplay between the laser field and the x-ray pulse interacting with deep-lying core-shell states.

Quantum beating observed in the transient *K*-edge XAS indicates the existence of vibronic coherence. Figure 5(a) presents the integrated absorption spectra ranging from 393.7 to 396 eV, including transitions from both $X^2\Sigma_g^+$ and $A^2\Pi_u$ states. At alignment angle of 90°, oscillation with period of 18.4 fs is indicative of the coherent vibrational wave packet dynamics within $A^2\Pi_u$ state. At 45°, additional rapid oscillation emerges due to the interference between the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states, which both transition to the $1\sigma_g^{-1}$ core-hole state. The rotational coherence is manifested by a minimum at approximately 50 fs when integrating the transient XAS spectra from 402 to 404 eV. Taking into account the dynamic alignment effects, our calculations reproduce this minimum in the satellite transitions. These transient absorption oscillations reveal the vibronic and rotational coherence induced by the laser-induced coupling after SFI, which plays a pivotal role in charge migration [3] and chemical reactions [44,48,49].

Finally, we propose a scheme to resolve the population dynamics from XAS by taking advantage of the alignment-dependent transition dipole moments [50]. This approach

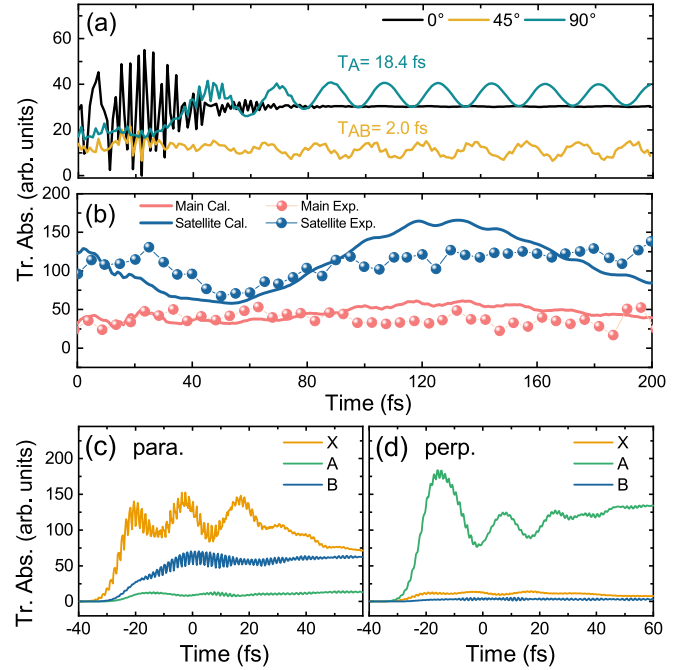


FIG. 5. (a) The temporal evolutions of XAS integrated from 393.7 to 396 eV at alignment angles of 0°, 45°, and 90°. (b) The spectrally integrated absorbance for mainline (red) and satellite line (blue) transitions is compared with experimental results (points) from Ref. [32]. Panels (c) and (d) depict electronic population dynamics for molecules pre-aligned at 45°, probed with x-ray pulses parallel and perpendicular to the molecular axis, respectively.

allows us to separately probe the population dynamics by adjusting the polarization direction of the x-ray pulse. With molecules pre-aligned at $\theta = 45^\circ$ with the degree of alignment given by $\langle \cos^2(\theta) \rangle = 0.8$, all three electronic states are populated. As demonstrated in Figs. 5(c) and 5(d), the $X^2\Sigma_g^+$ state (orange) and $B^2\Sigma_u^+$ state (blue) can be probed using x-rays polarized parallel to the molecular axis, whereas the $A^2\Pi_u$ (green) state is investigated by varying the polarization direction to be perpendicular to the molecular axis. Combining the parallel and perpendicular measurements facilitates clear resolution of the transition from the ionic ground state $X^2\Sigma_g^+$ to the excited state $A^2\Pi_u$ (see Sec. 3 in the SM for detailed calculations [38]). These findings underscore the significance of alignment-dependent transition dipole moments in the field of XAS measurements.

In conclusion, we have investigated theoretically the coupled electronic-vibrational dynamics and coherence of nitrogen ions induced by SFI, in corroborate with previous transient *K*-edge absorption experiment [32]. We establish a theoretical approach to simulate the transient absorption and explore the intricate dynamics induced by SFI, which accurately reproduce the experimental measurements. By identifying the contributions of each electronic state, we found that the excited state $A^2\Pi_u$ can be efficiently populated due to the laser-induced electronic-vibrational coupling. This suggests that electronic population inversion occurs for certain molecular alignments of nitrogen. The theory helps uncover features of absorption from transitions that are forbidden

within the laser pulse duration and confirms that vibronic coherence induces modulations of absorbance after SFI. A scheme is proposed to determine the population transfer at various probing geometries to avoid spectral overlap. This work establishes the theoretical framework for further studies on photoionization-initiated dynamics and coherence in the emerging field of attochemistry.

This work is supported by the National Natural Science Foundation of China (Grants No. 12234020, No. 12474281, and No. 12274461), and the Science and Technology Innovation Program of Hunan Province (Grant No. 2022RC1193). The authors appreciate the fruitful discussions with Dr. Erik T.J. Nibbering.

J.Z., G.B., and Q.Z. contributed equally to this work.

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