We present applications of extreme ultraviolet (XUV) single-order laser harmonics to gas-phase ultrafast photoelectron spectroscopy. Ultrashort XUV pulses at 80 nm are obtained as the 5th order harmonics of the fundamental laser at 400 nm by using Xe or Kr as the nonlinear medium and separated from other harmonic orders by using an indium foil. The single-order laser harmonics is applied for real-time probing of vibrational wavepacket dynamics of I$_2$ molecules in the bound and dissociating low-lying electronic states and electronic-vibrational wavepacket dynamics of highly excited Rydberg N$_2$ molecules.

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this case, which results in a spectrum with a frequency comb consisting of odd order harmonics.

The cut-off energy of high-order harmonics can reach the soft X-ray or higher energy region, depending on the wavelength and intensity of the fundamental pulse. Considerable attention has been drawn to laser high-order harmonics especially in the so-called water window region (2–4 nm) in recent years, for time-resolved imaging of biological molecules in solution. Compared to the soft X-ray (0.1–10 nm), larger photon flux can be obtained in the vacuum ultraviolet (VUV, 10–200 nm) and XUV (10–121 nm), where most of the atoms/molecules exhibit large absorption cross-sections by valence or inner-core electron transitions. By applying high-order harmonics as a pump pulse in time-resolved spectroscopy, one can interrogate extremely ultrafast dynamics in highly excited states, such as cascaded Auger processes of Xe,11 coherent dynamics of autoionizing states of Xe,12 and charge migration in phenylalanine.23 Alternatively, harmonics can be used as a probe of ultrafast dynamics triggered by other pump pulses, as demonstrated in transient absorption spectroscopy of valence-shell electron dynamics in Kr+24 and two-electron dynamics of He,25 and in photoelectron spectroscopy of dissociation dynamics of molecules.26–29

Some of these applications favor single-order harmonics. Photoelectron spectroscopy is powerful in studying ultrafast molecular dynamics as electron kinetic energy can directly specify intermediate and/or terminal electronic states involved in the wavepacket motion. When many order harmonics are employed in photoelectron spectroscopy, photoelectron signals (reflecting a dynamical process of interest) can be obscured by spectral overlaps with other photoelectron peaks associated with adjacent harmonic orders. It is therefore preferred to use a single-order harmonic pulse as a probe to prevent spectral congestion. One straightforward approach is to select a particular harmonic order of interest in the frequency domain. There are several approaches proposed for this purpose, using grating pair,28 zone-plate,30 and dielectric multilayer mirrors,31–33 as well as spectral filters.22,34,35 The spectral width thus selected determines the shortest pulse duration at the Fourier transformed limit.

For instance, multilayer mirrors coated with SiC/Mg were used for obtaining XUV pulses at 32 nm (hv = 42 eV) generated as the 27th order harmonics of the fundamental at 800 nm.32 The reflectance of the SiC/Mg mirror is optimized for the photon energy region of the 27th order harmonics while that for the neighboring order harmonics is suppressed more than an order of magnitude. The 27th order harmonic pulses (~30 fs) thus obtained were successfully applied to time-resolved photoelectron spectroscopy of unimolecular dissociation of Br2 molecules in the C1Πu state with a temporal resolution of 85 fs.32

Alternatively, metal thin foils have been used as band-pass filters for laser high-order harmonics in XUV.18,22,24,34,35 Although optical properties such as transmission photon energies and bandwidths are determined by materials of thin foils, they offer a simple and robust way for the single harmonics order selection. In this contribution, we describe our recent work on the single-order harmonics generation in XUV by using an indium foil35 and its applications to ultrafast photoelectron spectroscopy.

II. EXPERIMENTAL

Figure 1(a) shows a schematic diagram of our experimental setup for ultrafast photoelectron spectroscopy. The output of the Ti:Sapphire laser system (800 nm, <40 fs, 2 mJ/pulse) was divided into two parts. One was frequency-doubled by a BBO crystal and focused by a plano-convex lens (f = 500 mm) to a cylindrical cell containing rare gas (Kr, Xe) in a high vacuum chamber. Generated high-order harmonic pulses were transmitted through a thin metal filter and focused by a concave mirror (f = 1000 mm) to a gaseous target in the interaction region of a magnetic bottle spectrometer. The other laser output in near-infrared (NIR) was used to generate ultrashort visible (VIS) pulses by an optical parametric amplifier (TOPAS-C, Light Conversion Ltd.) to pump iodine molecules or directly used as a probe for the Rydberg wave-packets of N2 without wavelength conversion. The VIS/NIR laser beam was introduced into the spectrometer with a small angle (0.25°) to the high-order harmonics. Electrons from the target
molecules were guided to a micro-channel plate (MCP) detector by an inhomogeneous magnetic field of a cone-shape permanent magnet as well as a homogeneous magnetic field from a solenoid. Electron signals were counted by using an amplifier-and-timing discriminator (9327, Ortec) and a time-to-digital converter (TDC8, RoentDek). A typical resolution ($\Delta E_{\text{kin}}$) at an electron energy ($E_{\text{kin}}$) was $E_{\text{kin}}/\Delta E_{\text{kin}} \approx 50$ with a 1.5 m-long time-of-flight tube.

To select single-order harmonics from the nonlinear media, we employed an indium filter (0.1 μm thickness, Ni-mesh support, Lebow Co.) having transmittance in the XUV region of $h\nu = 13–16$ eV (Fig. 1(b)). In our approach, laser pulses at 400 nm, instead of 800 nm, are employed as the driving laser. Since the 5th order harmonics at 80 nm (15.5 eV) falls within the transmittance band of an indium filter, it can be selected from other harmonics. It should be noted that when an 800 nm pulse is used, both the 9th and 11th order harmonics are transmitted (see Fig. 1(b)). Instead, for the 400 nm pulse, care should be taken to pre-compensate the spectral dispersion by chirp mirrors, because dispersion introduced by optical windows, lens, and air during the propagation is more significant in the UV range than in NIR. To demonstrate the single-order harmonics selection by using an indium filter, photoelectron spectroscopy of iodine molecules was carried out. Without indium filters, photoelectron peaks associated with the single 5th and 7th order harmonics as well as the combination of the 3rd and 5th order harmonics with the fundamental were identified in the spectrum. On the other hand, by inserting an indium filter, these peaks disappeared except for the peaks corresponding to the 5th order harmonics.

### III. APPLICATION TO ULTRAFAST PHOTOELECTRON SPECTROSCOPY

#### A. Vibrational wavepacket dynamics of I$_2$

Molecular iodine in the low-lying electronic states has been subjected to a variety of time-resolved studies based on light-induced fluorescence, $^{16–38}$ four-wave mixing, $^{39,40}$ ion mass spectrometry, $^{41,42}$ and zero-kinetic energy (ZEKE) photoelectron spectroscopy. $^{33}$ In addition to periodic vibrational motions, coherent phenomena such as fractional revivals $^{43}$ and quantum ripples due to wavepacket interference $^{36}$ have been identified in the $B^3\Sigma^+_u \rightarrow \Pi^+_u$ state. In most experimental observations, however, wavepacket motion is probed in a confined region around turning points where optical transition dominantly takes place because of the Franck-Condon principle. This limitation could be removed when wavepacket is projected onto (dissociative) ionic state where spatial information on wavepacket motion can be reflected to a change of photoelectron or ion kinetic energy. Such measurements with ultrashort pulses are of significant importance to identify how molecular coherence collapses spatiotemporally during the wavepacket evolution. Here, we perform ultrafast photoelectron spectroscopy of I$_2$ molecules as a prototype system by using single-order harmonics in XUV in order to demonstrate real-time probing of the wavepacket dynamics over a wide range of the internuclear coordinate.

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**FIG. 1.** (a) Schematic diagram of the experimental setup for time-resolved photoelectron spectroscopy with single-order harmonics at 80 nm. (b) Transmittance of an indium filter (0.1 μm thick). Energy positions of the high order harmonics (H3–H7 for 400 nm and H7–H15 for 800 nm) are indicated by bars.
Figure 2 shows relevant potential energy curves of $I_2$ and $I_2^+$ molecules.\textsuperscript{44,45} An ultrashort pump laser pulse (490 nm, $h\nu = 2.53$ eV, $\sim 90$ fs) launches nuclear wavepackets in both the bound $B^3\Pi_{\nu''}$ and the repulsive $B'^{\prime}\Pi_{\nu'}$ states. These vibrational wavepackets propagate independently on the $B^3\Pi_{\nu''}$ and the $B'^{\prime}\Pi_{\nu'}$ potential curves. Since the pump photon energy is above the dissociation threshold of the bound $B^3\Pi_{\nu''}$, both of these wavepackets eventually dissociate as $I_2(B^3\Pi_{\nu''}) \rightarrow I(2P_{3/2}) + I^*(2P_{1/2})$ and $I_2(B'^{\prime}\Pi_{\nu'}) \rightarrow I(2P_{3/2}) + I(2P_{3/2})$, respectively.

The wavepacket dynamics evolving on these two different potential curves is probed by the ultrashort XUV pulses (80 nm, 15.5 eV, 121 fs) introduced with a time delay ($\Delta t$). Figure 3(a) shows the photoelectron spectrum of $I_2$. Since the XUV photon energy exceeds the ionization threshold (9.3 eV) of the $I_2$ molecule, photoelectrons from the ground state (X$^1\Sigma_g^+$) to $X^2\Pi_{1/2g}$ and $X^2\Pi_{3/2g}$ states of $I_2^+\Pi_{1u}$ are observed at 5.5 eV and 6.2 eV in the spectrum, respectively. When the pump pulse is introduced at $\Delta t = 450$ fs, new peaks (i) and (ii) appear at 4.3 eV and 5.1 eV. From the energy conservation, these peaks can be assigned to photoelectrons from iodine atoms in the ground (2P$_{3/2}$) and the excited (2P$_{1/2}$) states.

The evolution of the difference photoelectron spectrum is shown in Fig. 3(b). Both the peak (i) and the peak (ii) show a similar behavior exhibiting a rapid increase after the irradiation of the pump pulse at $\Delta t = 0$. The integrated intensity of peak (ii) is plotted as a function of $\Delta t$ in Fig. 3(c), showing that the signal presents a monotonic increase to reach a plateau at $\Delta t \sim 300$ fs. To understand how the dissociation dynamics in the $I_2^+$ excited states is reflected in the observed photoelectron spectra, vibrational wavepacket simulation was carried out separately for the $B^3\Pi_{\nu''}$ and $B'^{\prime}\Pi_{\nu'}$ states by using the split-operator method.\textsuperscript{46} The wavepacket launched on the $B'^{\prime}\Pi_{\nu'}$ potential curve immediately starts to leave the Franck-Condon region of the $I_2$ ground state to reach the dissociation limits $I(2P_{3/2}) + I^*(2P_{1/2})$ in ~200 fs (Fig. 2). The wavepacket in $B^3\Pi_{\nu''}$ shows slightly slower dissociation dynamics (~300 fs) to $I(2P_{3/2}) + I^*(2P_{1/2})$ due to the bound character of the excited state.

FIG. 2. Potential energy curves represent relevant electronic states of $I_2$ and $I_2^+$.\textsuperscript{45} Dynamics of vibrational wavepackets launched on excited $I_2$ molecules by a visible pump pulse is probed by an XUV ultrashort laser pulse introduced with a time delay $\Delta t$. The nuclear wavepackets at $\Delta t = 0$ and 120 fs are shown for the pump wavelength of 490 nm. The density of wavepacket at internuclear distances larger than 8.1 a.u. is taken as the atomic signal (see text).
To compare with the experimental results of the peak (ii), the atomic photoelectron signals are assumed proportional to the wavepacket density $\psi(R,t)|^2$ integrated over the internuclear distance $R \geq 8.1$ a.u., where the photoelectron energy falls within the observed width (0.24 eV) of the peak at 5.1 eV. The obtained results in Fig. 3(c) show an earlier increase for the $B^0_{3}P^0_1 u$ state (dashed, black) than $B^0_{3}P^0_0 u$ (solid, black) as expected. It should be noted that the experimental results cannot be explained by the contributions from the $B^0_{3}P^0_0 u$ state or that from the $B^0_{0}P^0_1 u$ state alone, because both curves have steeper slopes than the experimental data. Therefore, to reproduce the experimental results, the contributions from these two states should be added with appropriate weights. In our previous study, the peak at 5.1 eV is assigned to photoionization from the atomic ground state, $I(\frac{3}{2}P_{3/2}) \rightarrow I^+ (3P_{2}) + e^-$. The contribution from the excited fragment, $I^*(\frac{3}{2}P_{1/2}) \rightarrow I^+ (3P_{0}) + e^-$, is considered negligible because the corresponding peak to another spin-orbit state, $I^*(\frac{3}{2}P_{1/2}) \rightarrow I^+ (3P_{0}) + e^-$, is missing in the spectra. In such a case, a weight ratio of the two curves can be obtained from the absorption cross-sections (1.1 Mb and 0.65 Mb) of the $B^0_{3}P^0_0 u$ and $B^0_{0}P^0_1 u$ states from the ground state, with the latter multiplied by 2 to account for the yields of the $I(\frac{3}{2}P_{3/2})$ atom. The curve simulated with relative weights of 0.46 and 0.54 thus obtained is plotted in Fig. 3(c), showing a good agreement with the observed data. These results clearly demonstrate that ultrafast molecular dissociation evolving in the two different electronic states is simultaneously monitored in real time by photoelectron spectroscopy with ultrashort XUV pulses.

The difference photoelectron spectra in Fig. 3(b) show additional weak peaks (iii) and (iv) at 7.9 eV and 8.6 eV at $\Delta t = 0$ fs, which disappear in a short time scale ($\sim 100$ fs) as shown in Fig. 3(c). Since the difference between photoelectron energies observed at $\Delta t = 0$ fs and the original photoelectron peaks at 5.5 eV and 6.2 eV (to the ground states of $I_2$) agrees with the pump photon energy ($hv = 2.53$ eV), these weak peaks can be assigned to photoelectrons from the excited states of $I_2$. Figure 3(b) shows that the peak (iii) at 7.9 eV is accompanied by a
tail-like feature extending to $\Delta t \sim 150$ fs, which can be attributed to the evolution of the vibrational wavepacket in the excited states.

To illustrate how the propagation of a vibrational wavepacket is mapped to the XUV photoelectron spectrum, we reduced the pump photon energy to 2.34 eV (530 nm) to excite bound vibrational levels in the $B^3\Pi_{0^+}$ state. At this photon energy, a vibrational wavepacket is prepared by a coherent superposition of the vibrational levels ($v \sim 30$). The obtained results are shown in Fig. 4. The bound $B^3\Pi_{0^+}$ state dominates the photoabsorption from the ground state with a large absorption cross-section $\sigma$ of 2.71 Mb, but contributions from the repulsive $B^3\Pi_{1u}$ state ($\sigma = 0.41$ Mb (Ref. 47)) are also visible as the appearance of the atomic peak (ii) at 5.1 eV at a large time delay.

The difference photoelectron spectra in Fig. 4(b) show the appearance of the peak (iii) and the peak (iv) at 7.8 and 8.5 eV around $\Delta t = 0$ fs. The evolution of these peak intensities is plotted in Fig. 4(c), showing that the latter appears only around $\Delta t = 0$ fs. The peak (iv) is therefore attributed to a sideband of the $X^2\Pi_{3/2g}$ photoelectron peak, which appears only when the visible and XUV laser pulses are overlapped in time. The same applies to the peak (iii), assigned to the sideband of the $X^2\Pi_{1/2g}$ peak. However, the latter contains an additional component, which recurs at a longer time delay at $\Delta t \sim 500$ fs. From the energy conservation, this component can be attributed to the photoelectrons from the $B^3\Pi_{0^+}$ state to the $I_2^+ X^2\Pi_{1/2g}$ state. Indeed, the recurrence period is in good agreement with the classical vibrational period (440 fs) for $v = 30$ in the $B^3\Pi_{0^+}$ state. The difference between the $X^2\Pi_{3/2g}$ and $X^2\Pi_{1/2g}$ components is explained as follows. The main electronic configurations are $\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u$ for the $B^3\Pi_{0^+}$ state and

![Diagram](image)

**FIG. 4.** (a) Photoelectron spectra of $I_2$ by using a pump pulse at 530 nm and a probe pulse at 80 nm with a delay of $\Delta t = 100$ fs. Photoelectron spectra obtained without the pump pulse and the difference between pump-on and pump-off spectra are also shown. (b) Time evolution of the difference photoelectron spectrum as a function of $\Delta t$. (c) Photoelectron intensities plotted against the time delay $\Delta t$ for peaks (iii) and (iv). (d) Evolution of photoelectron spectra simulated incorporating the contributions from the $X^2\Pi_{1/2g}$, $A^2\Pi_{3/2u}$, and $A^2\Pi_{1/2u}$ final states of $I_2^+$ (see text for details).
Further developments of tunable ultrashort XUV light sources will be necessary in this respect.

To understand the observed vibrational dynamics, wavepacket simulation for the $B^1\Pi_{0^+}$ state was carried out. The time-resolved photoelectron spectra were separately calculated for each final state (Fig. 5) by the time-dependent perturbation theory.\(^ {48}\) Figure 4(c) shows the simulated photoelectron spectra obtained as a weighted sum of the relevant final states, $X^2\Pi_{3/2}$, $A^2\Pi_{3/2}$, and $A^2\Pi_{1/2}$. The contributions from the $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ states are adjusted to reproduce the experimental results and set to 1/10 of the $X^2\Pi_{3/2}$ state rather than the $X^2\Pi_{1/2}$ state.

To understand the observed vibrational dynamics, wavepacket simulation for the $B^1\Pi_{0^+}$ state was carried out. The time-resolved photoelectron spectra were separately calculated for each final state (Fig. 5) by the time-dependent perturbation theory.\(^ {48}\) Figure 4(c) shows the simulated photoelectron spectra obtained as a weighted sum of the relevant final states, $X^2\Pi_{3/2}$, $A^2\Pi_{3/2}$, and $A^2\Pi_{1/2}$. The contributions from the $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ states are adjusted to reproduce the experimental results and set to 1/10 of the $X^2\Pi_{3/2}$ state rather than the $X^2\Pi_{1/2}$ state.

It should be noted that there exist a number of excited states of $I_2$ $^+$ converging to the $\Gamma^+^2(^3P_2)$, $\Gamma^+^2(^3P_0)$, $\Gamma^-^2(^3P_2)$, and $\Gamma^-^2(^3P_1)$ asymptotes, located 0.943 eV, 0.799 eV, and 0.879 eV above the lowest dissociation limit.\(^ {44}\) This implies that contributions from these final states appear at photoelectron energies about $\sim 1$ eV lower than that for the $X^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ final states for the vibrational wavepacket probed near the outer turning points. Indeed, remnants of oscillatory structures are seen in Fig. 4(b) in the photoelectron energy range (5–6 eV) where the contributions from the excited final states are expected.

The present results demonstrate that the single-order harmonics at 80 nm is a powerful probe for time-resolved photoelectron spectroscopy to monitor nuclear wavepacket motion. The high photon energy allows us to trace the dynamics of target molecules all the way from the initial stages of the photo-induced processes to the final products. On the other hand, the photoelectron signals from the target molecules in the ground state can be an obstacle, as it masks the time-dependent components in the photoelectron spectra. In the present case, the vibrational dynamics corresponding to the photoelectron energy regions around 5.5 and 6.2 eV are not clearly visible due to the spectral overlap with the strong $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ peaks (see Figs. 3(b) and 4(b)). Further developments of tunable ultrashort XUV light sources will be necessary in this respect.

**B. Rydberg wavepacket dynamics of $N_2$**

Single-order harmonics can be used as a pump to study ultrafast dynamics in highly excited states. Rydberg wavepackets, formed by coherent superposition of highly excited Rydberg states, exhibit dynamics on a variety of time scales depending on the (effective) principle quantum number ($n$).\(^ {49}\) Since the classical orbiting period of a Rydberg electron scales with $r = n^{-1}$, the time scale of electron dynamics rapidly increases as $n$ increases and reaches the femtosecond to pico-second range at $n \sim 10$.

![FIG. 5. Time-resolved photoelectron spectra calculated for the vibrational wavepacket in the $B^1\Pi_{0^+}$ state with different final states in $I_2$: (a) $X^2\Pi_{3/2}$, (b) $X^2\Pi_{1/2}$, (c) $A^2\Pi_{3/2}$, and (d) $A^2\Pi_{1/2}$. The pump and probe photon energies are 2.53 eV (530 nm) and 15.5 eV, respectively (see text for details).](image-url)
which is comparable with those of vibrational and rotational degrees of freedom in a molecule. Therefore, unlike atomic systems, molecular Rydberg wavepacket exhibits more complex dynamics due to the interplay between electron and nuclear degrees of freedom.

Rydberg states of molecular nitrogen have been subjected to a number of detailed studies by absorption, ZEKE, and fluorescence spectroscopy, collision experiments, and also by ab initio calculations. Rydberg states of molecular nitrogen have been subjected to a number of detailed studies by absorption, ZEKE, and fluorescence spectroscopy, collision experiments, and also by ab initio calculations. Recently, high-order laser harmonics was applied to study transient Fano resonances on autoionizing states located above the ionization threshold. In the present study, time-resolved photoelectron spectroscopy with single-order harmonics at 80 nm is carried out to investigate ultrafast coherent dynamics of Rydberg states which are converging to the X^2Σ^+ as well as A^2Π states of the N_2^+ ion.

The single-order harmonics at 80.4 nm (15.42 eV) covers several absorption peaks of N_2 in the bandwidth (~0.10 eV) to create a wavepacket consisting of n_πσ(0) (n = 9–13), 9πσ(0), 10πσ(0), 6πσ(1), 5πσ(2), 5πσ(2), 4πσ(4), 8f(0), and 9f(0) Rydberg states converging to X^2Σ^+ and 3dσ(2) and 4σ(1) to A^2Π. Where numbers in the parentheses represent the vibrational quantum numbers. Time evolution of the Rydberg wavepacket is probed by a time-delayed ultrashort NIR pulse (800 nm) ionizing to the N_2 X 2Σ^+ state (see Fig. 6(a)).

The recorded photoelectron spectrum exhibits five peaks corresponding to the \( v' = 0 \text{–} 4 \) final vibrational levels of N_2 X 2Σ^+. Compared with the conventional photoelectron spectrum by using the He II light source, three extra peaks to the \( v' = 2 \text{–} 4 \) levels are identified. The time evolution of the integrated intensity of the \( v' = 2 \) peak is plotted in Fig. 6(b) as a function of the pump-probe time delay up to ~2 ps. The signal shows a steep rise around 0 fs and exhibits a rapid decay characterized by a double exponential function with \( \tau_1 = 290(40) \) fs and \( \tau_2 = 9(7) \) ps lifetime components.

The temporal profile of the \( v' = 2 \) peak recorded with a finer step is shown in Fig. 6(c), which exhibits a clear modulation in intensity with a period of 279(17) fs up to \( \Delta t = 800 \) fs. The oscillation period can be attributed to the coherent dynamics between Rydberg states pumped by the XUV laser pulse at 80.4 nm. In this wavelength region, there are two dominant absorption bands around 80.6 and 80.1 nm. The former exhibits a substructure with two main
peaks, one consisting of 6pσ(1), 8f(0), and 3dδ(1) and the other consisting of 5pσ(2), 9pσ(0), and 4pσ(4). The energy difference between these two peaks is about 110 cm⁻¹, which corresponds to a period of 300 fs in good agreement with the observed period. Since these bands contain Rydberg states with different principal quantum numbers, conversing to different electrons and vibrational states of N₂⁺, the observed coherent dynamics would be understood in terms of a superposition of wavepackets of (i) Rydberg electron motion, (ii) electron motion in the ion core, X³Σg⁺ and A²Πg, and (iii) vibrations of the ion core. Such a Rydberg system exhibiting interplay between different degrees of freedom should be interesting targets for coherent control of molecular dynamics as demonstrated with NO.⁵⁵

IV. SUMMARY

We presented a simple and robust approach for single-order harmonic generation in XUV, by utilizing 400-nm fundamental laser pulses and an indium thin foil filter. The applications to ultrafast photoelectron spectroscopy on (1) vibrational wavepackets of bound and repulsive excited states of I₂ and (2) electronic-vibrational Rydberg wavepackets of N₂ are demonstrated, showing that the unique approach generating XUV single-order laser harmonics is promising for studying ultrafast molecular wavepacket dynamics.

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