Probing time-dependent structure of the attosecond electron wave packet using shaped re-collision trajectories

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Using orthogonally polarized, 800 nm and 400 nm laser pulses, we generated high harmonics from C\textsubscript{2}H\textsubscript{6} and measured the spectra as a function of the delay between the two laser pulses. We observed that the intensity of each harmonics modulates with the delay. The modulation period of the 14\textsuperscript{th} and 16\textsuperscript{th} harmonics is twice as the period of the modulation of other harmonics. By comparing theoretical calculation, we indentify that the double periodicity is a result of the electron wave packet motion in the valence shell of C\textsubscript{2}H\textsubscript{6} with attosecond time-scale. Our method can be an approach to measure internal electron dynamics and does not require molecular alignment, making it applicable to complex molecules.

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Attosecond electron wave packets moving in a valence shell maybe an unexplored but common feature of chemical reactions, photoionization and charge transfer in molecules [1-5]. When we shine intense, infrared laser pulses to a molecule whose electronic state is close to each other, tunnel ionization will occur from the several electronic states [6-8]. In 2009, it was suggested that this process can create an electron wave packet or electron-hole dynamics in the valence shell of a molecule by utilizing the high harmonic generation from aligned CO_2 [6]. However, there are several difficulties to apply this method directly to other molecules. First, although they identified that the intensity minimum observed on the high harmonic spectra is caused as a result of the interference between the two ionization channels, the interference minimum will appear if two harmonics are emitted from independent two species [9]. It doesn’t guarantee existing of the internal electron wave packet directly. Second, because one linearly polarized laser pulse is responsible for both tunnel ionization and electron re-collision processes, the spatial structure of the internal and continuum electron wave packets are influenced by the molecular alignment angle with respect to the filed direction. That makes observation to be complex and requires extensive theoretical calculation for analysis. Third, it is difficult to trace dynamical change in the electron wave packet as a function of time.

Using C_2H_6, we demonstrate that electron wave packet motion in a valence shell is observed with attosecond time-resolution as it changes. To measure the dynamics, we employ a two-color laser field approach with unaligned molecules [10-11]. This approach allows us to indentify the symmetry of an electron wavefunction (or orbital) in a molecule which is responsible for the high harmonic generation process. It has advantageous over the alignment method employed in Ref. [6] in terms of measuring electron wave packet motion. First, tunnelling and valence electron wave packets produced at a time of ionization should be essentially unchanged for the parameter of measurement, such as the delay between the two laser pulses, except that the tunnelling wave packet will initially move along the direction given by the field. This can be possible because this approach permits disentangling the ionization process from the probing process with re-collision by combing two-color laser fields. That minimizes complexity of the analysis. Second, we can determine key times when the structure as seen by the continuum electron changes drastically since dynamical changes in the wave packet can be explored directly from the measurement by observing the changes in the polarization direction of harmonics as a function of the re-collision angle.
Fig. 1a shows a scheme of the measurement. We combine an 800 nm laser pulse with its second harmonic spatially and temporally. The polarization direction of the 800 nm is set to orthogonal to that of the second harmonic. At the peak of the combined laser fields, tunnel ionization of molecules can form the correlated electron wave packet pair. One moves in the valence and the other moves in the ionization continuum. With unaligned molecules, if tunnel ionization probability is directional to a specific range of angles with respect to the molecular principal axis, the ionized molecular ensemble is distributed in space directionally to the specific angle range. Within one optical period after the ionization, the continuum electron re-collides with the other electron wave packet, leading high harmonic emission. When we change the relative delay between the two laser pulses, the amplitude and the direction of sum of the laser fields change instantaneously. It controls continuum electron trajectory and re-collision angle, $\theta_c$, with respect to the molecular axis. As $\theta_c$ changes, the direction of the induced dipole moment, i.e., the polarization angle of harmonics ($\phi_{HHG}$) varies. The variation of $\phi_{HHG}$ with $\theta_c$ depends on characteristically the alignment and the spatial symmetry of the valence state electron wave packet [10]. Therefore, if dynamical motion occurs in the valence state, then the dependence of $\phi_{HHG}$ on $\theta_c$ follows its motion. Because the harmonic number corresponds to the re-collision time, $t_c$, the dynamical motion is traced along the harmonic number when we choose an appropriate phase matching condition to yield only a short trajectory [12].

We obtain the relative value of $\phi_{HHG}$ from the measured high harmonic generation spectra by comparing the intensity ratio between the adjacent odd and even harmonics [10-11]. This is based on the fact that even (odd) harmonics are polarized parallel to the 400 nm (800 nm) polarization axis, respectively. We utilize H$_2$ as a reference molecule to obtain $\theta_c$ as a function of the harmonic number. With unaligned molecules, $\phi_{HHG}$ of H$_2$ is approximately equal to $\theta_c$ because the angular dependence of the tunnel ionization probability is approximately spherical [13]. Therefore, comparison of $\phi_{HHG}$ of H$_2$ with that of C$_2$H$_6$ tells us how the polarization angle changes as a function of the re-collision angle.

In Fig. 1b, we present the structure of the several electronic states of C$_2$H$_6$ obtained by ab-initio calculation and the vertical ionization energy [14]. We also plot the calculated angular dependence of the tunnel ionization probability for the $E_g$ and $A_g$ state at the total laser intensity of $2.0 \times 10^{14}$W/cm$^2$. The dotted line shows the incoherent sum of both tunnel ionization probabilities. It has maximum values at around angles of $\sim 45 \pm$
90 and 225 degrees. The ionization occurs preferentially from these angles. The mechanism to prepare internal electron wave packet replies on ref [6]. The electron wavefunction after the tunnel ionization is given by

\[ \Psi(t) \propto \Psi_b \cdot \Psi_c, \]

\[ \Psi_b = a(1) \cdot \Psi_b(E_{g}) + a(2) \cdot \Psi_b(A_{g}) \exp(-i\varphi(t)) \]  

(1)

where \( a(1) \) and \( a(2) \) is the coefficient and \( \varphi(t) \) is the phase difference between the two states. \( \Psi_b(E_{g}) \) and \( \Psi_b(A_{g}) \) are the electron wavefunctions of the singly-charged ion or Dyson orbital of each ionization channel, where one electron is removed from the most and the second most loosely bound state of \( \text{C}_2\text{H}_6 \), respectively. The coherent superposition between the two wavefunctions generates dynamical motion of the electron vacancy, \textit{i.e.}, hole dynamics or electron wave packet motion in the molecule. Phase matching requires that the continuum electron is returned to its original ground state, forcing the electron to recombine to a new location and a changed hole distribution.

We generate an intense, 35 fs pulse duration, 800 nm laser pulse by a Ti:Sapphire laser system (KMLabs). We double the frequency of the 800 nm pulse by a 300 micrometer thickness \( \beta \)-\( \text{BaB}_2\text{O}_4 \) crystal. We pass both laser beams coaxially through a 0.65 mm calcite plate. By rotating the calcite plate to accumulate an extra optical path, we adjust the phase delay between the two laser pulses \[10\]. We focus the laser pulses to downstream of a pulsed gas jet with a 50 cm focal length spherical mirror. The generated harmonics are dispersed by a flat-field grating (Hitachi, 001-226). The dispersed spectrum is imaged onto a two-dimensional microchannel plate and a phosphor screen. We capture the image by a CCD camera and transfer to a computer. We integrate the signal counts vertical to the dispersed axis.

In Fig. 2, we show the measured high harmonic emission spectra of \( \text{C}_2\text{H}_6 \) vs relative delay between the two laser pulses at the total laser intensity of \( 2.0 \times 10^{14} \text{W/cm}^2 \). For reference, we measure the spectra of high harmonics generated from \( \text{H}_2 \) and \( \text{N}_2 \) as well using the same laser field (not shown). Except for \( 14^{\text{th}} \) and \( 16^{\text{th}} \) harmonics, the intensity of each harmonic emission of \( \text{C}_2\text{H}_6 \) modulates with half of the 400 nm optical period, \( \sim 0.66 \text{ fs} \). This modulation period is caused by the fact that the same amplitude of the laser field is repeated with the period \[10, 11\]. For \( 14^{\text{th}} \) and \( 16^{\text{th}} \), two intensity peaks are observed at every half of the 400 nm optical period. One peak appears at approximately the same delay as the adjacent odd harmonic has a peak \( \sim 0.33 \) and \( \sim 0.99 \).
fs), while the other peak shifts by $\pi$ in the delay (~0.66 and ~1.33 fs). These two peaks converge to one peak in the harmonic range higher than 18$^{th}$. In case of H$_2$ and N$_2$, all harmonics are modulated with half of the 400 nm optical period.

In order to clarify the dynamics, in Fig. 3 a and b we plot $\phi_{HHG}$ of H$_2$ and C$_2$H$_6$ obtained from the measured high harmonic spectra. One $\phi_{HHG}$ peak is found in H$_2$ while two $\phi_{HHG}$ peaks are found in C$_2$H$_6$ at every half of the 400 nm period. In the range from 13$^{th}$ to 15$^{th}$ at the delay of ~0.33 fs and ~1.00 fs, $\phi_{HHG}$ of C$_2$H$_6$ is approximately proportional to $\phi_{HHG}$ ($= \theta_c$) of H$_2$. This indicates that dipole moment responsible for high harmonic emission is induced approximately parallel to the re-collision angle. It is consistent with $\sigma$ symmetry character [10]. In the range from the 16$^{th}$ to 21$^{st}$ at the delay of ~0, 0.66 and 1.33 fs, $\phi_{HHG}$ of C$_2$H$_6$ has a peak up ~45 degrees while $\phi_{HHG}$ of H$_2$ is ~0 degree. This indicates that the dipole moment is induced to the angle different from the re-collision angle. Thus, the spatial structure of $\Psi_b$ must be changed during from the re-collision time which yields the low harmonics (~13$^{th}$) to the time which yields the high harmonics (~18$^{th}$). To exhibit the relationship of the re-collision time with the harmonic number, we plot the re-collision time obtained by classical electron trajectory calculation [16] in the right axis of Fig. 3. The range between 13$^{th}$ and 18$^{th}$ corresponds to the re-collision time from 0.8 fs to 1.2 fs.

We have repeated the same measurement at four different driving laser intensities in the range from 1.1 x 10$^{14}$ W/cm$^2$ to 1.7 x 10$^{14}$ W/cm$^2$. From the observed spectra, we obtain the $\phi_{HHG}$ distribution for each laser intensity as shown in the online material [15]. The highest harmonic number where the double intensity peak appears shifts from 16$^{th}$ to 14$^{th}$ and the $\phi_{HHG}$ distribution pattern shifts to low harmonic number as the laser intensity decreases. Thus, the possibilities of interference specific to the molecular structure and the electron wavefunction can be excluded. This is because in case of the structural interference, the characteristic intensity minimum must be independent of the driving laser intensity [6, 17]. When we convert the harmonic number to the re-collision time at each laser intensity using classical electron trajectory calculation, we found that the $\phi_{HHG}$ peak appearing at the delay of 0, ~0.66, and ~1.33 fs stays at the same re-collision time of ~1.2 fs regardless of the laser intensity. Therefore, the experimental result is consistent with the prediction that the tunnel ionization prepares the electron wave packet moving in the molecule [6].

Next, we identify the dynamics of $\Psi_b$ by simulating $\phi_{HHG}$ as a function of the high
harmonic number and the two-color laser delay using a semi-classical, strong-field approximation [16]. First, we calculate electron trajectories and \( \theta_c \) under the two-color laser fields. Then we calculate \( \phi_{HHG} \) from the high harmonic intensity induced parallel to the 800 nm axis and the 400 nm axis [14]. We use Eq. 1 to generate the valence state wave packet, \( \Psi_b \). We neglect the Stark shift between the two states and non-adiabatic population transfer because the transition dipole moment between them is zero since they have the same parity. In this case, the phase evolution in Eq. 1 is given by

\[
\phi(t) = \frac{\Delta E}{\hbar} \cdot \tau_c + \phi(0)
\]

where \( \Delta E \) is the energy separation between the \( E_g \) and \( A_g \) states, and \( \phi(0) \) is the initial phase shift which is determined at the time of tunnel ionization. For characterizing the wave packet, \( \Delta E \) and \( \phi(0) \) are the parameters to be adjusted. We rely on \( \Delta E \sim 2 \text{eV} \) from a result of ab-initio calculation and measured photoelectron spectrum [18]. At fixed \( \Delta E = 2 \text{eV} \), we adjust \( \phi(0) \) over \( 2\pi \) range to fit the observed \( \phi_{HHG} \) with the calculate \( \phi_{HHG} \) distribution. We found that \( \phi(0) = 0.4 \pi \) is a well-fitted value. In Fig. 4 a and b, we show the calculated \( \phi_{HHG} \) at \( \phi(0) = -0.4 \pi \) and \( \phi(0) = 0.4 \pi \), respectively. We choose \( \phi(0) = -0.4 \pi \) to demonstrate how the \( \phi_{HHG} \) distribution is sensitive to the initial phase difference. As we change \( \phi(0) \) from -0.4 \pi to 0.4 \pi, the two \( \phi_{HHG} \) peaks shift from small to large re-collision time. In order to show the relationship between \( \phi_{HHG} \) and \( |\Psi_b|^2 \), we present the calculated \( |\Psi_b|^2 \) at selected re-collision times of \( t_c = 0.8 \text{fs}, 1.0 \text{fs} \) and 1.2 \text{fs} in case of \( \phi(0) = 0.4 \pi \) in Fig. 4.

To confirm the double \( \phi_{HHG} \) structure is due to the dynamics, we calculate \( \phi_{HHG} \) vs the harmonic number and the delay using the single \( E_g \) or \( A_g \) state, respectively. The sum of \( \phi_{HHG} \) peaks calculated from only the \( E_g \) or \( A_g \) state doesn’t fit the observed \( \phi_{HHG} \) distribution. We also calculate the angular distribution of the tunnel ionization probability from the coherent superposition of the two states at \( \phi(0) \) of 0.4. The distribution is approximately the same as the incoherent sum case, shown in Fig. 1b.

Before concluding, we present possibilities how the phase shift between two states, \( \phi(0) \), can be caused at the time of tunnel ionization. The re-colliding electron wave packet (\( \Psi_c \)) generated from different electronic states must constructively interfere with each other in order to lead to efficient high harmonic generation. This requirement may select ensembles of the bound state electron wavefunctions with a particular phase difference so that the \( \Psi_c \) can constructively interfere. Other possibilities include the effect of the
laser fields which can change the time-evolution of the wavefunction, or the effect of different electrostatic potentials of the two channels on the outgoing electron.

In summary, we have demonstrated that dynamical motion of the valence electron wave packet can be mapped on the high harmonic emission spectra generated by the two-color laser pulses. For further applications, our approach can be extended to measuring dynamics associated with changes in the dipole moment such as internal electron motion induced by intense laser fields, core-level ionization, chemical reaction, external atom or molecular migration, and so on [19-20]. If we use an infrared laser pulse such as 2000 nm and its second harmonic, then we can increase $\theta_c$ over 90 degrees and extend the harmonic number because the continuum electron achieves a higher re-collision energy. If the amplitude of the dipole moment vector as well as $\phi_{\text{HHG}}$ can be obtained, then we expect to re-construct a 3D orbital image as it changes by combining with molecular orientation technique [21].

References
[15] See the supplementary material for the data and analysis.
Figure caption

Figure 1

a. Tunnel ionization creates wave packet pairs in the ionization continuum ($\Psi_c$) and in the valence state ($\Psi_b$). Upon re-collision between two wave packets, the high harmonics are emitted. At each re-collision time, we scan the re-collision angle ($\theta_c$) with respect to the molecule by scanning the phase delay between an 800 nm and a 400 nm laser pulses. The time of re-collision is determined by the observed photon energy of the high harmonic emission. We read the structure of the valence electron wave packet from the relationship between the polarization angle of the high harmonics and the re-collision angle (see text).

b. (left) Schematic diagram of the calculated, selected valence-shell electronic structure of C$_2$H$_6$. (right) The calculated angular distribution of the tunnel ionization probability for the most loosely bound energy level ($E_g$ state, magenta line) and the second most loosely bound energy level ($A_g$, red line) of C$_2$H$_6$ at the laser intensity of $2.0 \times 10^{14}$ W/cm$^2$. We show only one of the $E_g$ degenerated wave function. The dotted line is the incoherent sum of these two lines. The ionization probability of the other states can be neglected.

Figure 2

High-harmonic generation spectra from C$_2$H$_6$ vs the delay between the two laser pulses. We choose the zero-delay at an arbitrary phase. The total harmonic intensity modulates with the period of $\sim 0.66$ fs while the intensity of 14$^{th}$ and 16$^{th}$ harmonics modulates with the period of $\sim 0.33$ fs.

Figure 3

$\phi_{HHG}$ vs the delay between the two laser pulses for a H$_2$ and b C$_2$H$_6$. We interpolate $\phi_{HHG}$ along the two axis. In the right axis, we plot the re-collision time which is calculated from the harmonic number.

Figure 4

Calculated $\phi_{HHG}$ (degrees) vs the harmonic number and the phase delay at an initial phase ($\varphi(0)$) of (a) $-0.4 \pi$ and (b) $0.4 \pi$. We use the energy difference between the most and the second most loosely bound state of C$_2$H$_6$, $\Delta E = 2.0$ eV. The right panel shows the calculated $|\Psi_b|^2$ and the total phase $\varphi$ in Eq. 2 at selected re-collision time.
Figure 1 (Niikura et al.)

(a) A diagram illustrating the evolution of wave functions $\Psi_c$ and $\Psi_b$ over time from $t = 0$ to $t_c$ and $t'_c$.

(b) A graph showing ionization energy $E_g$, $A_g$, and $E_u$ with a polar plot indicating the ionization rate at various angles.

Ionization rate $\times 10^{14}$
Figure 2 (Niikura et al.)
Figure 3 (Niikura et al.)
Figure 4 (Niikura et al.)