Attosecond Probing of Nuclear Dynamics with Trajectory-Resolved High-Harmonic Spectroscopy

Pengfei Lan,1 Marc Ruhmann,2 Lixin He,1 Chunyang Zhai,1 Feng Wang,1 Xiaosong Zhu,1 Qingbin Zhang,1 Yueming Zhou,1 Min Li,1 Manfred Lein,2* and Peixiang Lu1,3,†

1University of Science and Technology, Wuhan 430074, China
2Institute for Theoretical Physics and Centre for Quantum Engineering and Space-Time Research (QUEST), Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover, Germany
3Laboratory of Optical Information Technology, Wuhan Institute of Technology, Wuhan 430205, China

We report attosecond-scale probing of the laser-induced dynamics in molecules. We apply the method of high-harmonic spectroscopy, where laser-driven recolliding electrons on various trajectories record the motion of their parent ion. Based on the transient phase-matching mechanism of high-order harmonic generation, short and long trajectories contributing to the same harmonic order are distinguishable in both the spatial and frequency domains, giving rise to a one-to-one map between time and photon energy for each trajectory. The short and long trajectories in H2 and D2 are used simultaneously to retrieve the nuclear dynamics on the attosecond and ångström scale. Compared to using only short trajectories, this extends the temporal range of the measurement to one optical cycle. The experiment is also applied to methane and ammonia molecules.

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There is a continuous desire to develop methods with ever-better resolution in ultrafast science. Generally, time-resolved methods rely on ultrashort laser pulses. Therefore, in the past decades, substantial effort has been made to produce attosecond pulses based on high-order harmonic generation (HHG) [1–4]. Since the duration of attosecond pulses is comparable to the time scale of bound electrons, such sources provide an important tool for detecting the ultrafast electron dynamics inside atoms or molecules [5–8], inaugurating a new domain for time-resolved metrology and spectroscopy [9].

One popular method of attosecond probing is the pump-probe measurement [2,8]. In this scheme, a physical process is first triggered by an attosecond pump pulse and subsequently probed by a near-infrared pulse (or vice versa). Then the time-dependent information can be decoded from the streaked photoelectron spectra recorded at different pump-probe delays. On the other hand, HHG itself is a subfemtosecond nonlinear process arising from laser induced electron-ion recollisions [10]. Rich information about the electron-ion system at the time of recollision is encoded in the harmonic spectra. Extracting this information systematically is known as high-harmonic spectroscopy (HHS). HHS has been exploited to image molecular structure with ångström resolution [11–16], e.g., by molecular orbital tomography [11–13]. Moreover, for each high-harmonic order, the freed electron spends a specific time in the continuum before recollision, resulting in the temporal chirp of HHG [17]. The ionization-recollision delay is analogous to a pump-probe delay, providing an alternative way to map the photon energy to time. Based on this property, HHS has been developed into an emerging tool for studying nuclear dynamics [18–23] and charge migration [24–27] with attosecond temporal resolution. However, according to the recollision model [10], there are two trajectories per optical half cycle contributing to each individual harmonic order. The two trajectories are referred to as the “short” and “long” trajectories. Therefore, to guarantee a one-to-one map between the photon energy and time, one trajectory has to be selected by adjusting the pulse energy and time, one trajectory has to be selected by adjusting the phase matching of HHG. For instance, in [19], only the short one is relevant. Since HHG from the long trajectory shows a different chirp property [17] compared to the short trajectory, HHS becomes more powerful if both can be utilized simultaneously.

In this Letter, we demonstrate a trajectory-resolved HHS method. Based on the time-dependent phase matching of HHG, the short and long trajectories are successfully separated in both the spatial and frequency domains, which enables us to build the one-to-one map for each trajectory. Then the short and long trajectories are simultaneously employed to retrieve the laser-induced proton dynamics of hydrogen molecules. This effectively extends the temporal range and enriches the information of the measurement. On the theory side, the present work resorts to complex-time phase matching of HHG, where the attosecond wave packet launched by strong-field ionization differs from the vibrational ground state of the neutral molecule [30].
Compared to [22,23], where this effect was included by using $R$-dependent or vibrational-level dependent tunneling ionization rates, the complex-time approach is not limited to the tunneling (low-frequency) regime.

An important ingredient of our scheme is provided by transient phase matching. To explain the idea, let us revisit the Lewenstein model of HHG [28,29]: HHG can be described by the coherent sum over all different quantum trajectories. Each trajectory carries a dipole phase $q \phi_d$. It can be approximately written as $q \phi_d = \alpha^j_d I(t)$, where $I(t)$ is the driving laser intensity and $\alpha^j_d$ is the coefficient of qth harmonic with $j = S$ or $j = L$ representing the short and long trajectories, respectively. In a short laser pulse, the intensity varies with time so that the dipole phase $q \phi_d$ is time dependent. This leads to an instantaneous frequency of each harmonic, which can be expressed by [31–34]

$$\omega_q = q \omega_0 + \alpha^j_d \frac{\partial I(t)}{\partial t}.$$ 

Hence, the harmonic emission in the leading $\frac{\partial I(t)}{\partial t} > 0$/falling $\frac{\partial I(t)}{\partial t} < 0$ edge of a pulse implies a blue/red shift in the harmonic spectrum [see Fig. 1(a)]. On the other hand, the HHG process involves macroscopic propagation effects in the gas medium. The phase mismatch is

$$\Delta k = \Delta k_g + \Delta k_d + \Delta k_e + \Delta k_a [33,34].$$ 

Here $\Delta k_g = q \{2/b[1 + (2z/b)^2]\}$ is due to the spatial phase variations arising from the focusing geometry of the driving laser, $q$ is the harmonic order, $b$ is the confocal parameter, and $z$ is the position of the medium. $\Delta k_d = \alpha^j_d (dI/dz)$ is the phase mismatch due to the intensity-dependent dipole phase. $\Delta k_e = (\omega/c) \Delta n_{el}(\omega)$ and $\Delta k_a = (\alpha/c) \Delta n_{ar}(\omega)$ are due to the dispersions of the free electrons and neutrals. $\Delta n(\omega)$ is the difference between the refractive indices at the harmonic and at the driving laser frequency. It depends on the densities of free electrons and neutrals. The time-dependent intensity of an ultrashort pulse leads to variations of the dipole phase and ionization probability and thus to time-dependent $\Delta k_d, \Delta k_e, \Delta k_a$, and $\Delta k$. In Figs. 1(b) and 1(c), we show the values of $|\Delta k|$ of the 17th harmonic for the long and short trajectories driven by a 30-fs, 800-nm laser field with intensity $1.5 \times 10^{14}$ W/cm². The long trajectory is better phase matched on the leading edge, while the short trajectory is favored on the falling edge. Therefore, HHG from the long trajectory is blue shifted and that of the short trajectory is red shifted. This enables us to clearly separate these two trajectories in the frequency domain. Moreover, since the coefficient $\alpha^j_d$ of the long trajectory is larger than $\alpha^j_d$ of the short trajectory, the phase-matching angle for the long trajectory is larger. Thus the short and long trajectories can also be distinguished in the spatial domain. In short, it is possible to separate the short and long trajectories by recording the spatial profile and spectral properties of high harmonic spectra. The trajectory-resolved HHS enables us to build the one-to-one map between the photon energy and time for both the short and long trajectories, which can be effectively used for ultrafast measurements using the method of [18,19].

A Ti-sapphire driving laser with a central wavelength of 800 nm and pulse duration of 30 fs is employed in our experiment. The incident laser beam is focused to a 2-mm-long gas cell with a pressure of 20 torr by a 600-mm focal-length lens. To evaluate the gas density in the gas cell, we measure the gas pressure with a species-independent vacuum gauge. As in [32], the phase matching of different trajectories is adjusted by carefully changing the beam size, laser power, and gas position. Figures 2(a) and 2(b) show the typical spatially resolved high harmonic spectra for D² and H₂. The laser intensity is estimated to be $1.5 \times 10^{14}$ W/cm². Each harmonic is split into two peaks, marked as $P_L$ and $P_S$ for the 17th harmonic in Fig. 2(a). Moreover, the spatial profile of $P_L$ shows a larger divergence angle than that of $P_S$. Following the above discussion, $P_L$ is due to the long trajectory and $P_S$ is due to the short trajectory. Figure 2(c) shows the spatially integrated signals for the spectra of D² (full-filled) and H₂ (green solid line). The short and long trajectories appear as separated peaks. Unlike [35],

FIG. 1. (a) Normalized envelope of the laser pulse. [(b) and (c)] Time-dependent phase mismatch of 17th harmonic for the long and short trajectories. In the simulation, a 30-fs, 800-nm laser field with intensity $1.5 \times 10^{14}$ W/cm² is adopted.

FIG. 2. Spatially resolved harmonic spectra from (a) D₂ and (b) H₂. (c) Spatially integrated HHG signals for the spectra in (a) and (b).
autocorrelation function. Including the dependence of the electron, vibrational dynamics is initiated in the remaining model [28] for HHG [18,19,38]. When the neutral molecule extended to long trajectories and complex-time electron dynamics we use the theory developed in [18,19,38] to obtain similar results within the error bars in Fig. 3(a). Harmonics function of harmonic order. The ratio is calculated by using the mismatch due to ionization are insignificant in our experiment. With the pressure changing from 15 to 35 Torr, the HHG yields of both trajectories exhibit a quadratic increase (the scaling factors are 1.92 and 2.05, respectively). The increasing ratio for the short trajectory is larger than that of the short trajectory. Similar results are obvious interference between them is observed. To explain our experiment and to retrieve the proton trajectory with ionization time \(t\) and recollision time \(\tau\), the harmonic intensity for an electron with excursion time \(\theta\) and recombination time \(t\) is selected by choosing the appropriate saddle-point times (see the text), for the measured and exact field-free Born-Oppenheimer (BO) potentials, respectively. The time-evolution operator \(U^\tau_0\) describes the vibrational motion on the BO potential curve of the ion \(H_2^+ / D_2^+\). According to (1), the probability for electron recombination is sensitive to the overlap between the evolved vibrational state of the ion and the ground vibrational state of the neutral molecule. The recombination matrix element \(d_{\text{rec}}(k, R) = e_E \langle k | \hat{p} | \psi_R \rangle\) in the direction of the laser polarization \(\mathbf{e}_E\) is taken in velocity form [39]. It accounts for two-center interference effects in the recombination step [40–43]. The continuum states \(|k\rangle\) are approximated by plane waves \(e^{ikr}\) and \(\psi_R\) is the electronic Dyson orbital for fixed \(R\). The latter can be approximated by a linear combination of hydrogen ground states [44], yielding \(d_{\text{rec}}(k, R) \propto \cos(kR \cos \theta / 2)\), where \(\theta\) is the angle between the momentum of the returning electron and the internuclear axis.

The times for ionization and recollision are obtained by applying the saddle-point approximation to the HHG amplitude. For a linearly polarized laser field, the relevant equations for harmonic frequency \(\omega\) are [29,45]

\[
\frac{|p(t, t') + A(t')|^2}{2} = -I_p
\]  
\[
\frac{|p(t, t') + A(t)|^2}{2} = \omega - I_p
\]  
with the saddle-point momentum \(p(t, t') = -\int_0^t dt'' A(t'') / (t - t')\). Here, \(A(t) = -\int_0^t dt' E(t')\) is defined in terms of the laser electric field \(E(t)\). The ionization potential is defined as \(I_p = V_{BO}^+(R_0) - E_0\) where \(V_{BO}^+\) is the BO potential of the ion. \(R_0\) is the equilibrium distance of the neutral molecule and \(E_0\) is its ground-state energy. We use the full complex solutions of (2) and (3) for \(t\) and \(\tau\) in the calculations of the autocorrelation function. According to Eq. (3) the momentum of the electron at return is given by \(k_r(\omega) = \sqrt{2(\omega - I_p)}\). The distribution \(\sigma(\theta)\) of alignment angles \(\theta\) is calculated at the pulse peak as in [46], assuming room temperature 293.15 K of the molecules. The summation over angles yields

\[
C(\omega) = \int_0^\infty dR \int_0^{\pi/2} d\theta \sigma(\theta) \cos \left(\frac{kR}{2} \cos \theta\right) \times \chi_0'(R) U^\tau_0(k) \chi_0(R)
\]  
with excursion time \(\tau = \tau(\omega) = t(\omega) - t'(\omega)\). The short or long trajectory is selected by choosing the appropriate solutions of Eqs. (2) and (3). The ratio of harmonic intensities from \(D_2\) versus \(H_2\) is then approximated as

\[
C(t, t') = \int_0^\infty dR d\tau \int_0^{\pi/2} d\theta \sigma(\theta) \cos \left(\frac{kR}{2} \cos \theta\right) \times \chi_0'(R) U^\tau_0(k) \chi_0(R).
\]
that the harmonic ratio decreases for long excursion times, namely in the limit of low harmonic orders for long trajectories; cf., Fig. 2 in [47]. The location of the maximum ratio is also modified by two-center interference [46], which is included in our present model.

We use an optimization algorithm [48] for finding an ionic BO potential such that the calculated ratios match the experimental ratios. This makes it possible to effectively measure the ionic potential in the range reachable within the time span of the short and long trajectories. For this retrieval, we have neglected the small trajectory-dependent deviation of the harmonic frequencies from integer harmonic orders. The resulting ratios from this fit are shown in Figs. 3(a) and 3(b), reproducing the experimental ratios well both for intensities of 1.5 and $2 \times 10^{14}$ W/cm$^2$. The corresponding nuclear motion for $1.5 \times 10^{14}$ W/cm$^2$ is depicted in Fig. 4. During the initial tunneling ($t' \rightarrow \text{Re}t'$), the internuclear distance increases approximately linearly as Fig. 4(a) shows. Overall, the nuclei separate slightly more quickly than predicted by a calculation using the exact field-free BO potential. Compared to the field-free BO potentials, the equilibrium positions of the measured potentials are shifted to slightly larger distance, e.g., from Re$t'$ to Re$t$, for the short trajectory, for D$_2$ (thick lines) and H$_2$ (thin lines). The origin of the time axis is set to the moment after tunneling, i.e., to Re$t'$. The curves start at different Re$t$ because the tunneling dynamics is dependent on the isotope and BO potential. (c) Same as (b) for the long trajectory.

$$R_C(\omega) = \frac{|C_D(\omega)|^2|\Gamma|^{P_{t'}}}{|C_{H}(\omega)|^2|\Gamma|^{P_{t}}},$$

with the instantaneous ionization rate $\Gamma(I_P,t') = \exp(-2(2I_P)^{3/2} / (3|E(Re't')|)).$

The first section of the temporal path, namely $t' \rightarrow \text{Re}t'$, indicated by the orange arrow in Fig. 4(a), can be identified with the tunneling of the electron. During this time, the vibrational ground state of the neutral molecule undergoes an imaginary-time evolution and yields the initial vibrational state of the ion for the subsequent real time evolution $\text{Re}t' \rightarrow \text{Re}t$. The last section $\text{Re}t \rightarrow t$ is usually small and does not affect the results significantly.

Previous theory [18,19] has already shown that the increasing ratio for short trajectories is explained by a slower decay of the autocorrelation function in the heavier isotope due to the slower motion. Since the dynamics of the cation is bound, it has a turning point and already before reaching it, the autocorrelation functions of the two isotopes approach each other; see Fig. 2 in [39]. This explains

FIG. 4. Vibrational dynamics for the 19th harmonic in the exact field-free (dashed lines) and measured (solid lines) BO potentials. (a) Stepwise time evolution of the internuclear distance $R$ from the ionization time $t'$ to the recombination time $t$, for the short trajectory of H$_2$. (b) Evolution of the internuclear distance after tunneling, i.e., from Re$t'$ to Re$t$, for the short trajectory, for D$_2$ (thick lines) and H$_2$ (thin lines). The origin of the time axis is set to the moment after tunneling, i.e., to Re$t'$. The curves start at different Re$t$ because the tunneling dynamics is dependent on the isotope and BO potential. (c) Same as (b) for the long trajectory.
FIG. 5. (a) Spatially integrated high harmonic spectra from CH$_4$ and CD$_4$, (b) Ratio between harmonic intensities from CD$_4$ and CH$_4$ as a function of harmonic order. Circles and squares are for the long and short trajectories, respectively. The dashed lines show the theoretical ratio from [50].

[50, 51]. Note that the previous experiment [19], using only the short trajectory, did not cover the time range beyond 1.6 fs and hence did not exhibit ratios less than 1. We have also compared harmonics from NH$_3$ and ND$_3$ molecules. Good agreement between our experiment and simulation is found in this case [51].

In summary, we have confirmed that the isotope dependence of molecular high-order harmonic generation persists for long trajectories. Using harmonic generation from both short and long trajectories leads to an improved retrieval of the nuclear motion with attosecond and ångström precision. We have demonstrated trajectory-resolved HHS for H$_2$/D$_2$, CH$_4$/CD$_4$, and NH$_3$/ND$_3$ molecules. This underlines the general validity of the method.

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*Corresponding author.
lein@itp.uni-hannover.de

†Corresponding author.
lupeixiang@mail.hust.edu.cn


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[51] See Supplemental Material http://link.aps.org/supplemental/10.1103/PhysRevLett.119.033201 for more discussions about the HHG with methane and ammonia molecules, which includes Ref. [52].