Attosecond-resolved photoionization of chiral molecules

S. Beaulieu, A. Comby, A. Clergerie, J. Caillat, D. Descamps, N. Dudovich, B. Fabre, R. Géneaux, F. Légaré, S. Petit, B. Fons, G. Porat, T. Ruchon, V. Blanche, Y. Mailresse

Chiral light-matter interactions have been investigated for two centuries, leading to the discovery of many chiroptical processes used for discrimination of enantiomers. Whereas most chiroptical effects result from a response of bound electrons, photoionization can produce much stronger chiral signals that manifest as asymmetries in the angular distribution of the photoelectrons along the light-propagation axis. We implemented self-referenced attosecond photoelectron interferometry to measure the temporal profile of the forward and backward electron wave packets emitted upon photoionization of camphor by circularly polarized laser pulses. We measured a delay between electrons ejected forward and backward, which depends on the ejection angle and reaches 24 attoseconds. The asymmetric temporal shape of electron wave packets emitted through an autoionizing state further reveals the chiral character of strongly correlated electronic dynamics.

Bolts and nuts are among the most common chiral objects in our macroscopic world. Their chiral nature is used to convert rotation to directional translation: Rotating the nut on a bolt induces its translation forward or backward, depending on the rotation direction. A very similar effect occurs in the microscopic world when enantiopure chiral molecules are photoionized by circularly polarized radiation [1]. The ejected photoelectrons tend to go forward or backward relative to the light-propagation axis, depending on the helicity of the ionizing light and the handedness of the molecules [2, 3]. As a result, the photoelectron angular distribution shows an asymmetry, called photoelectron circular dichroism (PECD). PECD is one of the most sensitive probes of static [4] and dynamical [5, 6] molecular chirality, producing signals that are up to two orders of magnitude larger than most circular dichroisms. From a classical point of view, PECD can be seen as the result of the combined action of the chiral molecular potential and the circular ionizing electric field on the outgoing electron trajectories [7]. Quantum mechanically, it arises from the interference between partial waves of different parity constituting the outgoing photoelectron wave packet [1]. Both interpretations show that subtle differences in the ionization dynamics can have substantial consequences. Thus, PECD has been proposed as a possible hypothesis to explain the homochirality of terrestrial life [8]: The asymmetric electron ejection induces an asymmetric recoil of the ions, which can lead to enantiomeric separation when accumulated over hundreds of millions of years [9].

Photoionization was considered to be instantaneous from an experimental point of view until attosecond technology made it possible to measure the underlying ultrafast electron dynamics. Delays of a few attoseconds were measured between electrons originating from different atomic orbitals [10], from distinct bands of a solid [11], associated with different vibrational states of a molecular ion [12], or from differing spin-orbit states [13]. The direction of the electron emission also influences the photoionization dynamics: Delays have been observed between electrons ejected at different angles [14–16] or from different sides of an asymmetric molecule [17, 18]. The photoionization process involves more complicated dynamics when autoionization occurs. In that case, the photoabsorption promotes the system into a metastable bound state coupled to equienergetic continuum states through configuration interaction. This coupling leads to autoionization of the metastable state. The interference of direct and indirect photoionization channels produces characteristic (Fano) spectral profiles [19] associated with complex temporal dynamics. Recent pioneering attosecond experiments in rare gases have shown the possibility of measuring the buildup of Fano lineshapes in the temporal domain [20] as well as the spectral phase across the resonance [21, 22], allowing the reconstruction of the temporal profile of the electron wave packet [22].

In this study, we aimed to determine whether or not the electrons ejected forward and backward from a sample of randomly oriented enantiopure chiral molecules were temporally synchronized. Answering this question, for both direct (Fig. 1, A and C) and indirect (Fig. 1, B and D) photoionization pathways, is a challenging task. Up to now, attosecond-delay measurements in the gas phase have been conducted on rare gas atoms or di- and triatomic molecules, which were used as benchmark systems. These experiments have revealed a strong influence of the weak probe field on the outcome of the measurement. It is thus necessary to perform accurate theoretical calculations to calibrate these measurement-induced delays [20, 23]. Such theoretical calculations for large and low-symmetry chiral molecules

---

**Fig. 1. Schematic view of the two time scales of photoionization of two camphor enantiomers.** (1S)−(−)-camphor is shown in (A) and (B); (1R)+(+) camphor in (C) and (D). In direct photoionization [(A) and (C)], the forward (f) and backward (b) electron wave packets may be delayed by a few attoseconds because of the asymmetric scattering of the outgoing electron in the chiral molecular potential. In the case of autoionization [(B) and (D)], the dynamics of the autoionizing state can lead to different temporal structures of photoelectron wave packets in the forward and backward directions, on the femtosecond time scale.

---

1Université de Bordeaux, CNRS, Commissariat à l’Energie Atomique et aux Energies Alternatives (CEA), Centre Lasers Intenses et Applications (CELIUM), UMR5607, F33405 Talence, France. 2Institut National de la Recherche Scientifique, Varennes, Quebec, Canada. 3Sorbonne Universités, UPMC Université Paris 6, CNRS-UMR 7614, Laboratoire de Chimie Physique Matière et Rayonnement, 75252 Paris, France. 4Department of Physics of Complex Systems, Weizmann Institute of Science, 76100 Rehovot, Israel. 5Laboratoire Interactions, Dynamiques et Lasers (LIDYL), CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91919 Gif-sur-Yvette, France.

*Corresponding author. Email: beaulieu@emt.irs.ca
[e.g., camphor (C_{10}H_{16}O)] are currently far from reach.

To directly access the delays between forward and backward electron emission, without any measurement-induced effects, we implemented a self-referenced photoelectron interferometry technique using photoionization by two phase-locked laser fields to detect differential autoionizing photoionization delays with a resolution of 2 as.

By independently controlling the chirality of the ionizing and probe light pulses, we fully decoupled the intrinsic photoionization delays from the measurement-induced delays.

**Photoelectron interferometry**

When an intense femtosecond laser pulse ionizes an atom or a molecule, multiple photons can be absorbed above the ionization threshold [above-threshold ionization (ATI)]. In the spectral domain, ATI produces a comb of photoelectron peaks separated by the laser photon energy \(E_0\). Each peak is characterized by a spectral width \(\delta\omega\), and the overall ATI spectrum extends over a width \(\Delta\omega\). In the time domain, the ATI process leads to the emission of attosecond electron bursts (Fig. 1, A to C) of duration \(\delta t\), which form a train. The overall duration of the train \(\Delta t\) is set by the laser pulse duration, typically a few tens of femtoseconds. The ATI emission can last longer if an autoionizing state is populated: The lifetime of the autoionizing state is encoded in the spectral structure of each ATI peak: \(\Delta t\) is related to \(\gamma\omega\). On the other hand, the autoionization substructures are encoded in the relative amplitude and phase between the different ATI peaks: \(\Delta t\) is associated with \(\Delta\omega\). Thus, to obtain a complete picture of the temporal dynamics of the ionization process, it is necessary to measure the spectral phase of the ATI peaks, both within their bandwidth \(\delta\omega\) and from one peak to the next \(\Delta\omega\). This is possible with the use of photoelectron interferometry (22, 25, 26).

We first present the basic concepts of photoelectron interferometry and highlight the rich spectroscopic information that it provides about the ionized target. For now, we are leaving aside the chiral character of the experiment [by integrating over the photoelectron ejection angles]. The principle of the measurement is described in Fig. 2. The target molecule we chose was camphor, a bicyclic ketone which has been extensively studied in PECD experiments performed in single-photon (1, 27), multiphoton (28, 29), and ATI regimes (30).

Camphor has a first ionization potential of 8.76 eV and Rydberg states starting around 6.2 eV: It is ionized by 2 + \(n\) resonance-enhanced multiphoton transitions when using a 400-nm ultraviolet (UV) field, with \(n\) being the order of the ATI peak. In the presence of a weak infrared (IR) 800-nm field (frequency \(\omega\)), new peaks, called sidebands, appear. The phase difference between the two neighboring ATI peaks and, thus, the temporal properties of the photoelectron emission process.

The photoelectrons were collected by a velocity-map imaging (VMI) spectrometer, which records the angle-resolved photoelectron spectrum (Fig. 2, A and B). The superposition of 800- and 400-nm pulses produces an electric field that is stronger in the upper or lower direction, depending on the relative delay between the two fields. As a consequence, the electrons ejected up and down are modulated in opposite phases (26, 33).

To directly access the delays between forward and backward electron emission, without any measurement-induced effects, we implemented a self-referenced photoelectron interferometry technique using photoionization by two phase-locked laser fields to detect differential autoionizing photoionization delays with a resolution of 2 as.

By independently controlling the chirality of the ionizing and probe light pulses, we fully decoupled the intrinsic photoionization delays from the measurement-induced delays.

**Fig. 2. Principle and implementation of photoelectron interferometry.** (A) Schematic experimental setup. Two phase-locked femtosecond laser pulses with linear or circular polarization are focused into a jet of enantiopure camphor molecules in the interaction zone of a velocity-map imaging (VMI) spectrometer. The photoelectrons are accelerated by a set of electrodes onto microchannel plates imaged by a phosphor screen and a charge-coupled device camera, which records the two-dimensional (2D) projection of the 3D angular distribution of the photoelectron spectrum with an energy resolution around 0.2 eV at 2 eV. (B) Typical measured photoelectron angular distribution and evolution of the second sideband as a function of delay between the two fields. The oscillations in the upper and lower half of the distribution are out of phase, reflecting the up-down asymmetry of the total ionizing electric field. PE, photoelectron energy; \(E_0\), electron ejection angle. (C) Ionization scheme. The 400-nm pulse (duration: 40 fs; intensity: \(\sim 5 \times 10^{12}\) W/cm\(^2\)) induces multiphoton above-threshold ionization (ATI) of the molecules. The first ionizing transition lies in the vicinity of an autoionizing resonance. The 800-nm pulse (duration: 30 fs; intensity: \(\sim 5 \times 10^{11}\) W/cm\(^2\)) produces additional transitions, leading to the creation of sidebands (SB1 and SB2) between the ATI peaks. \(V\), configuration interaction; Ryd, Rydberg states. (D) Angle-integrated photoelectron spectrum composed of ATI peaks and n-th-order sidebands (SBn). The blue lines represent the angularly integrated spectrally resolved \(2\omega\)-oscillation phases for each sideband, and the red dots denote the spectrally averaged \(2\omega\)-oscillation phases for nonresonant SB2 and SB3. \(\varphi_{2\omega}(E)\), energy-resolved sideband oscillation phase; \(\varphi_{2\omega}(\bar{E})\), energy-integrated sideband oscillation phase; PES, photoelectron spectrum.
and three and peaks three and four; have a smooth phase variation across their bandwidth (i.e., without any trace of resonance). We can thus conclude that the resonance occurs in the formation of the first ATI peak (ATI1) and does not propagate to the higher ATI peaks, as confirmed by theoretical calculations of resonant photoelectron interferometry presented in the SM.

We proceeded to investigate the chiral (enantiospecific) photoionization dynamics in the two different regimes identified above: direct attosecond ionization (SB2 and SB3) and indirect femtosecond ionization in the vicinity of an autolocalizing resonance (SB1).

**Attosecond delays in nonresonant photoionization**

We started by analyzing the direct photoionization dynamics, which occur on the attosecond time scale and are encoded in the relative phase between the different ATI peaks. These relative phases can be obtained by extracting the oscillation phases of the signals averaged over the bandwidth of each sidestand, $\varphi_{\text{sidestand}}(\tilde{E})$. Neglecting the variations over the spectral width is equivalent to assuming that the photoionization process is strictly periodic from one laser cycle to the next. The spectral homogeneity of the sidestand phases shown in Fig. 2D indicates that this assumption is reasonable for SB2 and SB3, but not for the resonant SB1, which is discussed later. This scheme is similar to the conventional RABBIT analysis (reconstruction of attosecond beatings by interference of two-photon transitions) (25), here extended to the case of above-threshold ionization (26, 32). Simulations presented in the SM validate the analogy between the two techniques.

Measuring the phase $\varphi_{\text{sidestand}}(\tilde{E})$ is equivalent to measuring the time delay $\tau$ that maximizes the signal of each sideband. This delay can be decomposed as the sum of three contributions that reflect the three steps of the sideband creation (35)

$$\tau = \tau_{\text{light}} + \tau_{\text{W}} + \tau_{\text{ce}}$$

(1)

The ionization is triggered by absorption of light at a well-defined time ($\tau_{\text{light}}$). Next, the electron scatters in the molecular potential and acquires a delay $\tau_{\text{W}}$—the Wigner delay (36). The electron also interacts with the weak IR field, which induces continuum-continuum transitions from the main ATI peaks to the sidestands, introducing an additional delay $\tau_{\text{ce}}$. Whereas $\tau_{\text{light}}$ and $\tau_{\text{ce}}$ are induced by the measurement, $\tau_{\text{W}}$ is intrinsic to the probing system and is the physical quantity of interest. It represents the delay between an electron scattering in a given potential and in a reference potential, as introduced by Wigner in 1955 (36).

To resolve the enantiosensitivity of Wigner delays, we turned to chiroptical measurements comparing the sideband oscillation phases for electrons emitted in the forward (f) versus backward (b) directions and extracting the difference $\Delta \tau_{\text{sb}} = \tau_{\text{fb}} - \tau_{\text{cc}}$. This procedure naturally eliminates $\tau_{\text{light}}$, which is strictly common to the forward and backward electrons. Further decoupling is achieved by using different combinations of linearly and circularly polarized light. The forward/backward (f/b) symmetry can be broken only by the chiral nature of the interaction—that is, if a circularly polarized light pulse is used. We can thus selectively break the f/b symmetry only in the ionization step by using a circularly polarized UV field and a linear IR field. In that case, $\Delta \tau_{\text{fb}} = 0$ and $\Delta \tau_{\text{cc}} = \Delta \tau_{\text{W}}$. Alternatively, we can render the Wigner delay f/b symmetric by using a linearly polarized UV field for ionization and a circularly polarized IR field probing photons to obtain $\Delta \tau_{\text{fb}} = 0$ and $\Delta \tau_{\text{cc}} = \Delta \tau_{\text{W}}$.

The photoelectron images were separated in four quadrants, and the signal was angularly averaged in each quadrant. A Fourier analysis of the 2o oscillations was conducted to determine the delay that maximized each sideband, in each quadrant. We calculated the difference between the delays measured in the forward and backward directions ($\Delta \tau_{\text{fb}}$). This procedure was repeated for left and right helicities, as well as for five consecutive measurements of each enantiomer. The delays measured from opposite helicities or opposite enantiomers have opposite signs, revealing that the differential f/b ionization delay is a genuine chiral observable. To extract the most accurate value of the differential delay, we averaged the results obtained from the (+) and (-) enantiomers: $\Delta \tau_{\text{fb}} = [\Delta \tau_{\text{fb}}^+ - \Delta \tau_{\text{fb}}^-]/2$ (see SM).

First, we used a linearly polarized UV ionizing field and a circularly polarized IR measurement field. The Wigner component $\tau_{\text{W}}$ of the sideband delay was thus f/b symmetric ($\Delta \tau_{\text{fb}} = \Delta \tau_{\text{cc}}$). The results shown in Fig. 3A reveal that the differential f/b continuum-continuum induced delay is zero (within the 2-as accuracy of the present measurement). This means that the laser-induced transitions produce essentially the same delay on electrons emitted in the forward and backward directions, without any substantial sensitivity to the chiral character of the ionic potential. However, a weak influence of the chiral potential is still noticeable in this polarization configuration: The intensity of SB2 averaged over all UV-IR delays shows a f/b asymmetry (PCED) on the order of 0.5% (two times smaller than when the UV is circularly polarized).

To find signatures of chirality in the photoionization delays, we resolved the angular dependence of the photoionization dynamics (14, 37, 38). We integrated the photoelectron signal in slices of $10^\circ$ around different ejection angles $\alpha$ from the polarization plane of the light and then measured the associated delays ($\Delta \tau_{\text{cc}}$). The results for SB2 are shown in Fig. 3B. For electrons emitted beyond $70^\circ$, the signal was too low to extract reliable values. A weak but nonzero $\Delta \tau_{\text{cc}}$ is measured when electrons are ejected close to the polarization plane of the IR laser, reaching $5 \pm 2\text{ as}$ at $\alpha = 25^\circ$. This delay tends to vanish for higher ejection angles, but the error bars become larger because of the lower level of signal. Measurements on SB3 show a zero delay, regardless of the ejection angle (see SM). In the commonly accepted intuitive picture of multicolor photoionization, the linear UV field induces bound-free transitions starting...
from the molecular core region, and the IR field subsequently drives continuum-continuum transitions while the electron is escaping from the core region. The continuum-continuum transitions are thus rather insensitive to the details of the molecular potential. This interpretation was recently confirmed by the observation of a zero continuum-continuum delay between electrons escaping the two sides of an oriented asymmetric molecule in theoretical calculations (17). The zero overall delay we measured between forward and backward electrons on SB2 and SB3 is consistent with this picture. Nevertheless, the angle-resolved measurements demonstrate that the continuum-continuum transitions can be slightly influenced by the core (chiral) region of the potential.

Second, we broke the f/b symmetry in the ionization step by switching the polarization state of the ionizing UV field to circular while using a linearly polarized IR field. In this case, the photoionization process is intrinsically f/b asymmetric, whereas the continuum-continuum coupling is f/b symmetric: Δf/b = Δf/b. The magnitude of the temporally averaged PECD on SB2 was larger than in the previous configuration, reaching 1%. The measurements (Fig. 3C) show a differential delay of Δf/b = 7 ± 2 as for the second sideband (SB2). Our experiment is thus able to reveal a small f/b asymmetry in the Wigner delay in the photoionization of chiral molecules by circularly polarized light. The Δf/b vanishes for SB3 because of the decrease of both the f/b asymmetric character of the photoionization and the absolute Wigner time delay with increasing photoelectron kinetic energy.

The evolution of the differential Wigner delays with photoelectron ejection angle are shown in Fig. 3D. Close to α = 0°, Δf/b is null, which is not surprising because the PECD also vanishes in the laser polarization plane. For electrons emitted in the 60°-to-70° slice, Δf/b reaches 24 as. This angle-resolved analysis shows that although the average difference between forward and backward electron ionization times is only 7 as, it strongly varies with ejection angle and can reach higher values for electrons emitted away from the laser polarization plane. Repeating this analysis for SB3 shows that the differential Wigner time delay remains zero within the error bars for all photoelectron ejection angles (see SM). By accessing the angular dependence of the emission time, our measurements give access to the phase properties of the photoionization matrix elements. The determination of the underlying scattering phase shifts has been a long-standing quest of photoionization experiments, and our results show that their energy derivatives (i.e., the Wigner delays) are accessible with high accuracy through the use of a relatively simple setup.

The differential Wigner delay is a signature of the asymmetric scattering process at the heart of the photoelectron circular dichroism phenomenon. Wigner delays are determined by the energy derivative of the scattering phase. We performed a theoretical analysis of the photoionization of camphor molecules (see SM for details about the theoretical model). Our calculations confirm the existence of asymmetric Wigner delays, even in a randomly oriented ensemble of molecules. The theoretical f/b differential Wigner delay Δf/b is on the order of 5 as for 2-eV electrons, in agreement with the present experimental observation. The evolution of Δf/b with respect to the photoelectron energy, shown in the SM, reveals rich spectroscopic features that are not visible in the photoelectron spectrum and cannot be easily distinguished in the PECD signal. Thus, Δf/b is a sensitive chiral observable, which enables tracking of subtle features of the molecular potential (such as the differential Cooper minima) that survive molecular orientation averaging (see SM). This observation opens prospects for highly sensitive experiments—for instance, through molecular-frame measurements (39) as well as accurate testing of advanced quantum theories of molecular photoionization.

The differential f/b analysis and the control of the chiral symmetry-breaking of the interaction enabled us to fully decouple the different components of the photoionization delays, without the need for any theoretical input, and to reveal a tiny but measurable delay in the direct photoionization. We proceeded to use photoelectron interferometry to extract more complex dynamics occurring when the chiral molecules are photoionized in the vicinity of an autoionizing resonance.

**Resonant photoionization**

Continuum resonances play an essential role in the photoionization of most polyatomic molecules. They can arise from the shape of the molecular potential, in a single-electron picture (shape resonances) (40), or from multi-electron dynamics involving electron correlations and couplings between different channels (41). In both cases, spectrally localized scattering phase jumps are expected, reflecting the modification of the ionization dynamics. For instance, in chiral molecules, the PECD was recently shown to be enhanced in the vicinity of a Fano resonance (41). We used the photoelectron interferometry technique to directly track the asymmetric ionization dynamics of chiral molecules in the vicinity of an autoionization resonance.

As shown in Fig. 2D, SB1 presents a sharp n-phase jump around 1.9 eV, which reflects the presence of a resonance on the first ATI peak. We resolved this phase jump in the forward (blue, φf) and backward (red, φb) directions, using circularly polarized UV (Fig. 4A) or IR (Fig. 4C) light. When the UV light is circularly polarized, the spectral phase exhibits a weak ~0.75-rad bump centered around 2.1 eV. A notable difference was observed between the forward and backward spectral phases. This difference (Δφf/b = φf − φb) (Fig. 4B) shows a good mirroring between the two enantiomers.

The case where the f/b symmetry is broken by the weak IR pulse (linear UV and circular IR) is more intriguing. The spectral phases show a steep ~n jump around 1.9 eV, in opposite directions for forward and backward electrons. After the jump, the phases become nearly identical, as they are separated by ~2π (Fig. 4C). The f/b differential phases (Δφf/b) obtained in the two enantiomers are almost exactly opposite (Fig. 4D). To a first approximation, the presence of this huge asymmetry is unexpected. The circularly polarized field acts during the continuum-continuum transitions, which should be affected mostly by the long-range (nonchiral) part of the molecular potential and should, therefore, be f/b symmetric (27). Our measurement demonstrates that in the vicinity of advanced quantum theories of molecular photoionization.

**Fig. 4. Phase-resolved resonant photoionization in camphor.** (A and C) Spectral amplitudes (black) and forward and backward spectral phases [φf(E), blue; φb(E), red] of SB1 in (+)-camphor, using left-circularly polarized UV field and linearly polarized IR field in (A) and linearly polarized UV field and left-circularly polarized IR field in (C). (B and D) Forward/backward (f/b) asymmetry of the spectral phase (Δφf/b) in camphor, using left-circularly polarized UV field and linearly polarized IR field in (B) and linearly polarized UV field and left-circularly polarized IR field in (D). In (B) and (D), the dots represent the mean values of the f/b asymmetry of the spectral phase, whereas the solid lines show the error bars, which are defined as 95% confidence intervals.
of a resonance, the f/b symmetry can also be broken during the continuum-continuum transitions. This finding is in agreement with a recent theoretical investigation of photoelectron interferometry, which demonstrated that the simple separation of the measured delay (τ), in a sum of the contributions from Wigner (τW) and continuum-continuum (τcc) delays, no longer held in the presence of a resonance (42). Argenti et al. demonstrated that τW and τcc are entangled in resonant photoionization. The measured delay (τ) is representative of the two-color photoionization process, and our results show that the circular polarization of the weak IR field is sufficient to induce a major symmetry-breaking, in the presence of a resonance.

**Asymmetric electron wave packets**

We could retrieve the temporal profiles of the two-color forward and backward wave packets by Fourier-transforming their measured spectral amplitudes and phases. To extract the angular dependence of these temporal profiles, we analyzed the oscillations of SBI as a function of the electron ejection angle (α), as done previously in the nonresonant case (see raw data in SM). Figure 5 shows the resulting angle-resolved wave packets in the temporal domain. In both polarization configurations, the wave packet shows a single temporal peak when the electrons are ejected close to the propagation axis of the light (90°) and a double-peak structure when the electrons are ejected near the laser polarization plane (0°). The latter are signatures of the temporal interference between the direct nonresonant and the resonant components of the autoionizing wave packets (22). The effect of the resonance appears more confined along the laser polarization direction when the UV field is linearly polarized (Fig. 5B), probably because of a stronger anisotropy of the resonant excitation compared with the circularly polarized case.

The chiral nature of the photoionization process can be investigated by comparing cuts of the temporal profile of electrons ejected at positive (forward, blue) and negative (backward, red) angles (α) (Fig. 5). When the UV field is circularly polarized, the two bumps of the forward electron wave packet emitted around 30° maximize ∼400 as after the backward wave packet (Fig. 5A). A similar delay is measured around 60°, where the wave packet shows a single-peak structure. As the ejection angle further increases, the ordering between forward and backward emission reverses, with a ≈ 250–as delay around 80°. These subtle features obey chiral inversion when switching from one enantiomer to the other, as shown in the SM. In the other polarization configuration (Fig. 5B), the two bumps from the forward and backward wave packets are synchronized in time for electrons ejected close to the laser polarization plane (α = 0°). However, their relative yield is strongly f/b asymmetric. This means that in the vicinity of resonances, where τW and τcc are entangled (42), the perturbative IR pulse can be used to break the f/b symmetry and to subsequently tailor asymmetric electronic wave packets, both in time and space. At larger emission angles, where the dynamics are governed by a single nonresonant pathway, the single-peak wave packets become f/b symmetric. This analysis provides a deep insight into the angular dependence of the multielectron dynamics governing autoionization.

Comparison of the two polarization configurations used in the measurements (Fig. 5) reveals that the wave packet asymmetry is much stronger when the weak IR field is circularly polarized. We attribute this result to the sequential nature of the resonant photoionization process. The linearly polarized UV photons populate a quasi-bound state embedded in the continuum, which can relax by ionization, releasing electrons at the energy of the first ATI peak (autoionization) (Fig. 2C). However, another process could lead to ionization of the quasi-bound state: the absorption of one IR photon releasing an electron with the energy of the first sideband. This can be seen as a classic PEC experiment, starting from a highly excited quasi-bound state. Recent experiments showed that PECD could be observed when bound states excited by linear photons were ionized by circularly polarized photons (5). The present scheme extends this scenario to quasi-bound states. On the other hand, when the UV photons are circularly polarized, they can induce an asymmetric wave packet in the excited states, a phenomenon called photoexcitation circular dichroism (43). The ionization of such a wave packet by linearly polarized light produces f/b asymmetries, but they were observed to be weaker than the PECD from excited states. This could explain why we observe a weaker wave packet asymmetry when the IR photons are linearly polarized.

**Time-frequency analysis**

The temporal profile of the wave packets only provides spectrally integrated information about the rich ongoing dynamics. The spectral origin of temporal asymmetries can be revealed via a time-frequency analysis (44). The Wigner-Ville distribution (WVD) is particularly noteworthy because it encodes the quantum interference between different components of a wave packet.
For a wave function $\Psi(t)$, the WVD $[W\Omega, t]$ is defined as

$$W(\Omega, t) = \int \Psi(t - \tau/2)\Psi^*(t + \tau/2)e^{i\Omega\tau}d\tau \quad (2)$$

where $\Omega$ is the angular frequency, $t$ is the time, and $i$ is the imaginary unit. Figure 6 shows the WVD of the electron wave functions emitted around $\alpha = +10^\circ$ (forward, $\Psi^f(t)$) and $\alpha = -10^\circ$ (backward, $\Psi^b(t)$) from the laser polarization plane. The distributions were calculated by averaging the wave packet from $(1\Sigma^+)\text{camphor}$ and the mirrored wave packet from $(1\Sigma^-)\text{camphor}$. A strong negative lobe is present around time $t = 0$ at the energy of the resonance (1.9 eV), revealing the quantum interference between the direct and indirect ionization components. Hyperbolic fringes converging to the energy of the resonance are observed in the leading or backward wave packets, both in time and space, which is a strongly dominated by a single resonant pathway, which leads to the disappearance of the strongly asymmetric shaping of photoelectron waves, both in time and space, which is a new scheme for multidimensional attosecond quantum control. The high accuracy of the measurements can also be used as a powerful benchmarking tool for quantum theories of molecular photoionization. Finally, our approach could be generalized to a broad variety of systems to shed light on the ultrafast asymmetry-breakings, which are at the heart of very recent technological and scientific breakthroughs, such as in superconducting chiral nanotubes (45) and chiral spintronics devices (46).

REFERENCES AND NOTES
1. I. Powis, Advances in Chemical Physics, S. A. Rice, Ed. (John Wiley, 2008).
2. B. Ritchie, Phys. Rev. A 13, 1411–1415 (1976).
3. N. Bowring et al., Phys. Rev. Lett. 86, 1187–1190 (2001).
4. I. Nahon, G. A. Garcia, I. Powis, J. Electron Spectrosc. Relat. Phenom. 204, 322–334 (2015).
5. A. Comby et al., J. Phys. Chem. Lett. 7, 4534–4539 (2016).
6. S. Beaulieu et al., Faraday Discuss. 194, 325–348 (2016).
7. S. Beaulieu et al., New J. Phys. 18, 102002 (2016).
8. U. Meierhenrich, Amino Acids and the Asymmetry of Life, Advances in Astrobiology and Biogeophysics (Springer, 2008).
9. M. Tia et al., J. Phys. Chem. Lett. 4, 2698–2704 (2013).
10. K. Klunder et al., Phys. Rev. Lett. 106, 143002 (2011).
11. A. L. Cavalieri et al., Nature 449, 1029–1032 (2007).
12. S. Haessler et al., Phys. Rev. A 80, 01404(R) (2009).
13. I. Jordan et al., Phys. Rev. A 95, 033404 (2017).
14. S. Heuser et al., Phys. Rev. A 94, 063409 (2016).
15. P. Hockett, E. Frumker, D. M. Villeneuve, P. B. Corkum, J. Phys. At. Mol. Opt. Phys. 49, 095602 (2016).
16. D. Baykusheva, H. J. Wörner, J. Chem. Phys. 146, 124306 (2017).
17. A. Chacon, M. Leir, C. Ruiz, Phys. Rev. A 89, 053427 (2014).
18. L. Cattaneo, J. Vos, M. Lucchini, C. Creli, U. Keller, in Proceedings of the International Conference on Ultrashort Phenomena (Optical Society of America, 2016), p. UMB3.3.
19. U. Fano, Phys. Rev. 124, 1866–1878 (1961).
20. A. Kaldun et al., Science 354, 738–741 (2016).
21. M. Kotur et al., Nat. Commun. 7, 10566 (2016).
22. V. Gruzov et al., Science 354, 734–738 (2016).
23. M. Ossiander et al., Nat. Phys. 13, 280–285 (2017).
24. P. Agostini, F. Fabre, G. Mainfray, G. Peticer, N. K. Rahman, Phys. Rev. Lett. 42, 1127–1130 (1979).
25. P. M. Paul et al., Science 292, 1689–1692 (2001).
26. L. J. Zipp, A. Natan, P. H. Bucksbaum, Optica 1, 361 (2014).
27. L. Nahon et al., Phys. Chem. Chem. Phys. 18, 12696–12706 (2016).
28. C. Lux et al., Angew. Chem. Int. Ed. 51, 5001–5005 (2012).
29. C. S. Lehmann, N. B. Ram, I. Powis, M. H. M. Janssen, J. Chem. Phys. 139, 234307 (2013).
30. C. Lux, M. Wollenhaupt, C. Sarpe, T. Baumert, ChemPhysChem 16, 115–137 (2015).
31. D. W. Schumacher, F. Weihe, H. G. Muller, P. H. Bucksbaum, Phys. Rev. Lett. 73, 1344–1347 (1994).
32. X. Gong et al., Phys. Rev. Lett. 118, 134503 (2017).
33. S. Kruszwicz et al., Phys. Rev. Lett. 115, 043001 (2015).
34. G. A. Garcia, I. Nahon, I. Powis, Rev. Sci. Instrum. 75, 4989–4996 (2004).
35. J. M. Dahlström, A. L’Hullier, A. Maquet, J. Phys. At. Mol. Opt. Phys. 45, 183001 (2012).
36. E. Wigner, Phys. Rev. 98, 145–147 (1955).
37. S. A. Assefi, Y. Ni, I. J. Raisinski, H. G. Muller, M. J. Vrakking, Phys. Rev. Lett. 91, 223902 (2003).
38. P. Hockett, J. Phys. At. Mol. Opt. Phys. 50, 154002 (2017).
39. M. Tia et al., J. Phys. Chem. Lett. 8, 2780–2786 (2017).
40. M. Piancastelli, J. Electron Spectrosc. Relat. Phenom. 100, 167–190 (1999).
41. D. Catone et al., Phys. Rev. Lett. 108, 083001 (2012).
42. L. Argenti et al., Phys. Rev. A 95, 043425 (2017).
43. S. Beaulieu et al., arXiv:1612.08764 [physics.atm-clus] (27 Feb 2017).
44. D. Busto et al., arXiv:1709.07639v1 [physics.atom-ph] (22 Sep 2017).
45. F. Qin et al., Nat. Commun. 8, 14465 (2017).
46. R. Naaman, D. H. Waldeck, Annu. Rev. Phys. Chem. 66, 263–281 (2015).

ACKNOWLEDGMENTS
We thank R. Bouillaud and L. Merzeau for technical assistance and A. L’Hullier for fruitful discussions. This project has received funding from the European Research Council under the European Union Horizon 2020 research and innovation program 662978 - EXCITERS and from LASERLAB-EUROPE, grant 284464, the European Commission’s Seventh Framework Programme. We acknowledge the financial support from the French National Research Agency through grants ANR-14-CE32-0013 MISFITS, ANR-14-CE32-0010 XISTASE, and IdEx Bordeaux LAPHIA (ANR-10-IDEX-03-02) and the Conseil Regional de Nouvelle-Aquitaine (21.3.09011502 COLA2 project). J.-C. and R.T. acknowledge financial support from the LABEX PlusPar project, the program “Investissements d’Avenir” under the reference ANR-11-IDEX-0004-02, and the program ANR-15-CE30-0001-01-CIMBAAD. S.B. acknowledges the Natural Sciences and Engineering Research Council of Canada Vanier Scholarship. The data presented in the study are available in the SM.

SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/358/6368/1288/suppl/DC1

Beaulieu et al., Science 358, 1288–1294 (2017) 8 December 2017 6 of 6