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Femtosecond photoelectron circular dichroism of chemical reactions

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Understanding the chirality of molecular reaction pathways is essential for a broad range of fundamental and applied sciences. However, the current ability to probe chirality on the time scale of primary processes underlying chemical reactions remains very limited. Here, we demonstrate time-resolved photoelectron circular dichroism (TRPECD) with ultrashort circularly polarized vacuum-ultraviolet (VUV) pulses from a tabletop source. We demonstrate the capabilities of VUV-TRPECD by resolving the chirality changes in time during the photodissociation of atomic iodine from two chiral molecules. We identify several general key features of TRPECD, which include the ability to probe dynamical chirality along the complete photochemical reaction path, the sensitivity to the local chirality of the evolving scattering potential, and the influence of electron scattering off dissociating photofragments. Our results are interpreted by comparison with high-level *ab-initio* calculations of transient PECDs from molecular photoionization calculations. Our experimental and theoretical techniques define a general approach to femtochirality.

INTRODUCTION

Most molecules of biochemical relevance are chiral. The mechanisms controlling the chiral selectivity of chemical reactions have therefore been intensively studied over many decades. Despite fundamental advances, our ability to track the dynamically evolving chirality of reacting molecules remains unexpectedly limited.

The most mature techniques of chiral recognition rely on tiny differences in the absorption of circularly polarized light by the enantiomers of a chiral molecule, an effect known as circular dichroism (CD), which arises from the interference of electric and magnetic dipole transitions. Considerable efforts have been invested in the development of time-resolved CD methods, which have been successfully applied to liquid-phase systems (1, 2).

The weakness of the traditional CD effect and the resulting experimental challenges have motivated a recent surge of research activity to find more sensitive methods for chiral discrimination. These recent developments include microwave three-wave mixing (3, 4), Coulomb-explosion imaging (5, 6), high-harmonic generation (HHG) in weakly elliptical (7) and bicircular laser pulses (8, 9), and photoelectron CD (PECD) (10–12). Among these, PECD has been applied to probe the photophysical relaxation dynamics in highly electronically excited (Rydberg) states (13, 14), and HHG in bicircular fields has been used to probe a photochemical reaction (15). Most recently, the Coulomb explosion of a core-ionized chiral molecule has been observed at LCLS (Linac Coherent Light Source) (16), but the PECD measured at three pump-probe delays did not display any clear variations, in agreement with theory.

Here, we report the realization of TRPECD with vacuum-ultraviolet (VUV) pulses, demonstrating a general probe of the chirality of photochemical dynamics. This technique combines the benefits of

VUV time-resolved photoelectron spectroscopy (17–20) with the chiral sensitivity of PECD. The photon energy is sufficiently high for ionization along the entire reaction pathway from the excited state through all intermediate configurations to the final photoproducts. In addition, depending on the ionization energy of the unexcited molecules, the photon energy of the probe may be sufficiently low to prevent their ionization, yielding a background-free technique. Our technique transposes the remarkable chiral sensitivity of PECD from probing static molecules in their electronic ground or excited states (21–35) to probing chiral light-induced dynamics in electronically excited states. This extension opens many promising avenues since PECD effects have been reported for valence orbitals all the way down to core orbitals (11, 21, 27, 36, 37), they have been shown to be sensitive to molecular conformation and chemical substitution (25, 38–40) and capable of identifying absolute configurations by comparison with theoretical calculations (41). These properties originate from the fact that PECD mainly arises from the scattering of photoelectrons in the chiral molecular potential.

We interpret our experimental results by additionally advancing the theoretical methodology for PECD calculations. Whereas these calculations have previously mainly been performed for static molecules in the electronic ground state, we have developed the methods to calculate transient PECDs along photochemical reaction pathways. Whereas previous single-photon-PECD calculations relied on the continuum multiple scattering model using the X-alpha local-exchange potential (21, 22) and density functional theory (42) methods, here, we use accurate quantum calculations of electron-molecular scattering to predict the PECD effects based on single-center partial wave expansion and the Schwinger iterative variational method (43, 44). We have additionally developed the formalism to include photo-selection and molecular alignment into the calculations of PECD. The good agreement between calculated and observed PECDs deepens the understanding of the molecular quantum scattering mechanisms underlying the observed PECD effects.

The concept of VUV-TRPECD is illustrated in Fig. 1. We investigate the time evolution of molecular chirality on the natural,

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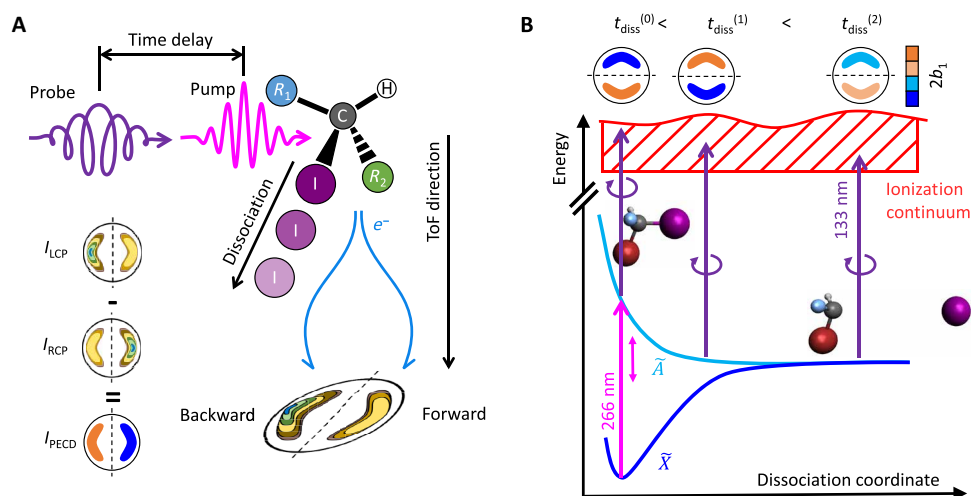


Fig. 1. Concept of VUV-TRPECD. (A) A pump pulse excites the system of interest and thereby initiates a photochemical reaction. A circularly polarized VUV probe pulse ionizes the photoexcited molecule and maps its time-dependent chirality onto a forward-backward asymmetry of the emitted photoelectrons with respect to the probe-pulse propagation direction. ToF, time-of-flight. (B) Illustration of time-resolved PECD in the photodissociation of CHBrFI.

femtosecond time scale of photochemical reactions by combining a source of ultrashort circularly polarized VUV pulses with photoelectron velocity-map imaging in a pump-probe scheme. To showcase the potential of the method, we study the photodissociation reaction of chiral molecules excited by an ultrashort linearly polarized laser pulse and follow changes in the forward-backward asymmetry of the photoelectron angular distribution (PAD) represented by the sign and magnitude of the $2b_1$ coefficient (see section S2), which is a measure of the chirality, via a femtosecond circularly polarized laser pulse in the VUV range. For this purpose, we selected two molecules with complementary characteristics, bromofluoroiodomethane (CHBrFI) and 2-iodobutane (C_4H_9I). In both cases, the C–I bond is selectively dissociated following one-photon absorption at 266 nm. The subsequent dynamics is tracked by a circularly polarized laser pulse centered at 133 nm generated with a new tabletop source described in section S1 and in (45). Our measurements reveal intriguing changes in the PECD signal on the time scale of the bond-breaking dynamics and additionally reveal the chirality of the molecular-radical products. A particular property of this scheme is the selectivity of the probe, which discriminates between the fragments, revealing the chirality changes in the nascent molecular radical.

RESULTS

The time-resolved photoelectron spectrum (TRPES) of the photodissociation of CHBrFI (vertical ionization energy is 9.86 eV) (46) is presented in Fig. 2A. The dynamics on the positive-delay side (Fig. 1B) corresponds to the CHBrFI molecule photodissociating on the \bar{A} -state potential-energy surface into a CHBrF \cdot radical and an iodine atom. The observed spectra are dominated by a time-zero feature corresponding to resonance-enhanced ($1 + 1'$) two-photon ionization. On the positive delay side, the photoelectron signal decays rapidly within the first 300 fs and remains constant afterward. This constant signal forms a broad spectral feature spanning a kinetic energy range from 0 to ~ 1 eV, which is assigned to the CHBrF \cdot radical based on its calculated adiabatic ionization energy of 8.32 eV (47). The iodine atom cannot be ionized by one photon of 133 nm

(9.3 eV) because its ionization energy is too high (10.45 eV) (48). The time-resolved map of the associated asymmetry parameters β_2 is shown in the Supplementary Materials (fig. S2).

The dissociation time is obtained from the signal in the photoelectron kinetic energy range between 0 and 1.5 eV using a monoexponential fit of the form $A \cdot \exp(-t/\tau_{\text{diss}}) + B$ convoluted with a Gaussian cross-correlation (cc; Fig. 2B). The extracted dissociation time is $\tau_{\text{diss}} = (70 \pm 20)$ fs (see Fig. 2B). This value agrees well with a theoretical estimate of $\tau_{\text{diss}}^{\text{(calc)}} = 77$ fs, obtained using a classical propagation on a nonrelativistic ab initio potential-energy surface, and assuming that the dissociation is completed at $r(\text{C} - \text{I}) = 4.5$ Å.

The negative time-delay side represents the photoexcitation to Rydberg states by the 133-nm pulse. The evolution on this Rydberg-state manifold is followed by one-photon ionization with the 266-nm pulse. On the negative-delay side, the signal decays to zero in about 0.5 ps. This decay is much faster than the expected lifetime of the Rydberg states and is therefore attributed to the photoexcited wave packet leaving the configurational space from where one-photon ionization by the 266-nm pulse is possible. The signal in the energy range between 2.5 and 5.0 eV (see Fig. 2A) is well represented by a monoexponential decay with a lifetime of $\tau_{\text{Rydberg}} = (97 \pm 6)$ fs.

After discussion of the TRPES results, we now turn to the TRPECD results. Enantiomerically pure ($\sim 90\%$ enantiomeric excess) samples of CHBrFI have been obtained by chiral chromatographic separation of racemic samples as described in section S4. The pump-probe measurements were performed by using circularly polarized 133-nm pulses to ionize the molecule following excitation by a linearly polarized 266-nm pulse. The PECD images were formed by subtracting inverted photoelectron images measured with left- and right-circularly polarized 133-nm pulses. These images were inverted using a modified version of the onion-peeling method; see section S2 for more details. The resulting difference image contains only the chiral contribution to the PAD. The chiral signal integrated over the photoelectron kinetic energy range corresponding to the nascent CHBrF fragment (0 to 1.5 eV) is determined by a fit of the form $2b_1 \cos \theta$ to the PECD image, where θ is the photoelectron emission angle with respect to the propagation direction of the circularly polarized light.

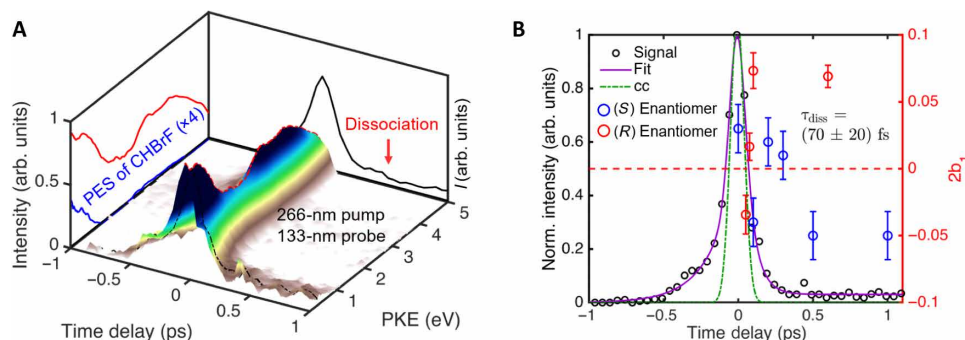


Fig. 2. Probing time-dependent chirality in the photodissociation of CHBrFI. (A) Time-resolved photoelectron spectra obtained with pump and probe laser pulses centered at 266 and 133 nm, respectively (positive delays) and vice versa (negative delays). Photoelectron spectrum of CHBrFI radical (blue solid line) is obtained by averaging the time-resolved spectra between 0.3 and 1 ps. (B) Photoelectron signal integrated over kinetic energy from 0 to 1.5 eV (left y axis, black) and time-dependent PECD of the photodissociation of both enantiomers of CHBrFI (right y axis, red). cc stands for the cross-correlation signal (green dash-dotted line).

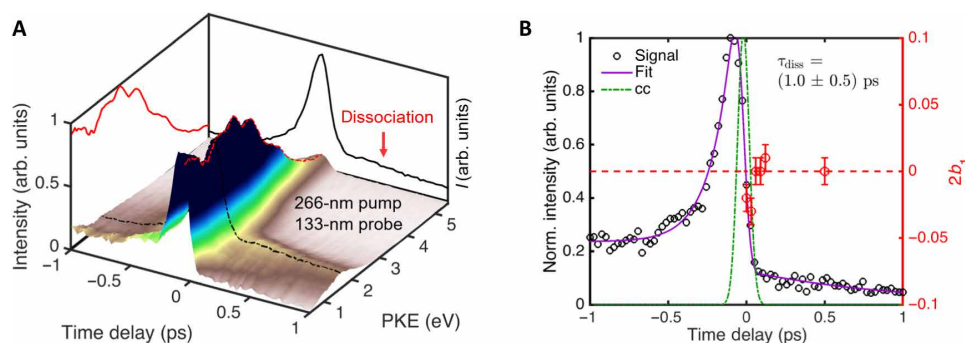


Fig. 3. Probing time-dependent chirality in the photodissociation of 2-iodobutane. (A) Time-resolved photoelectron spectra obtained with pump and probe laser pulses centered at 266 and 133 nm, respectively (positive delays) and vice versa (negative delays). (B) Photoelectron signal integrated from 0.7 to 2.5 eV kinetic energy (left y axis, black) and time-dependent PECD of the photodissociation of 2-iodobutane (right y axis, red).

The TRPECD observed during the photodissociation of CHBrFI is shown in Fig. 2B. Higher-order Legendre contributions to the PECD (49) are found to be negligible [$b_3 = (0.00 \pm 0.01)$] for both enantiomers and all measured time delays. In the case of the (*S*)-enantiomer, the PECD value at 0-fs time delay amounts to $2b_1 = (0.03 \pm 0.01)$, followed by a sign inversion to $2b_1 = (-0.04 \pm 0.01)$ at 100-fs delay, another sign inversion to delays of 200 and 300 fs, and a third inversion of the PECD up to delays of 500 fs. Because of limitations in the quantity of enantiopure samples, the measurements on the (*R*)-enantiomer were focused on the early time delays, which confirmed the inversion of the PECD to lie between 50 and 80 fs, and a late time delay, which confirmed the chirality of the photoproduct radical. Overall, the measured PECD values display the antisymmetry that is expected upon exchange of the enantiomers.

The generality of our VUV-TRPECD method is demonstrated through its application to another molecule, 2-iodobutane. This molecule is structurally more complex because the atomic substituents (Br and F) at the chiral center are replaced with methyl and ethyl groups that have many internal degrees of freedom (internal rotations and vibrations). As in the case of CHBrFI, we study the selective C–I bond dissociation induced by a pump pulse centered at 266 nm.

The TRPES is shown in Fig. 3A. Positive time delays correspond to the dissociation of the C–I bond. The dissociation produces a 2-butyl radical and an iodine atom, whereby the latter does not contribute to the photoelectron spectrum for the same energetic reasons

as stated above. Since the vertical ionization energy of the 2-butyl radical amounts to 7.6 eV (50), the corresponding photoelectron band should lie at photoelectron kinetic energy of PKE = 1.7 eV. This value agrees well with the measured transient spectrum. The signal at negative time delays corresponds to an excitation to high-lying Rydberg states (51). The time-resolved map of the associated asymmetry β_2 parameters is shown in the Supplementary Materials (fig. S2).

The observed dynamics are analyzed by a fit to the spectrum in the energy range between 0.7 and 2.5 eV. The fitting results are shown in Fig. 3B, where a monoexponential decay of the form $A \cdot \exp(-t/\tau_{\text{diss}})$, convoluted with a Gaussian cc, is fitted to the positive delay side of the TRPES. The dissociation is completed within the temporal overlap of the pump and probe pulses. The photoelectron signal originating from the 2-butyl radical then further decays with a time constant $\tau_{\text{diss}} = (1.0 \pm 0.5)$ ps, which is assigned to vibrational relaxation (52). A fit to the signal on the negative delay side yields a time constant $\tau_{\text{Rydberg}} = (140 \pm 20)$ fs for the wave packet dynamics created in the Rydberg states.

A distinctive feature of 2-iodobutane is that the ground state can be one-photon ionized by 133-nm radiation. This allowed us to measure both a static PECD from the unexcited molecule and a transient PECD from the dissociating state of the molecule. The static PECD for the ground state amounts to $2b_1 = (-0.11 \pm 0.02)$, represented by a green diamond in Fig. 4B, which additionally shows the PECD image. The PECD at the temporal overlap of the pump and probe

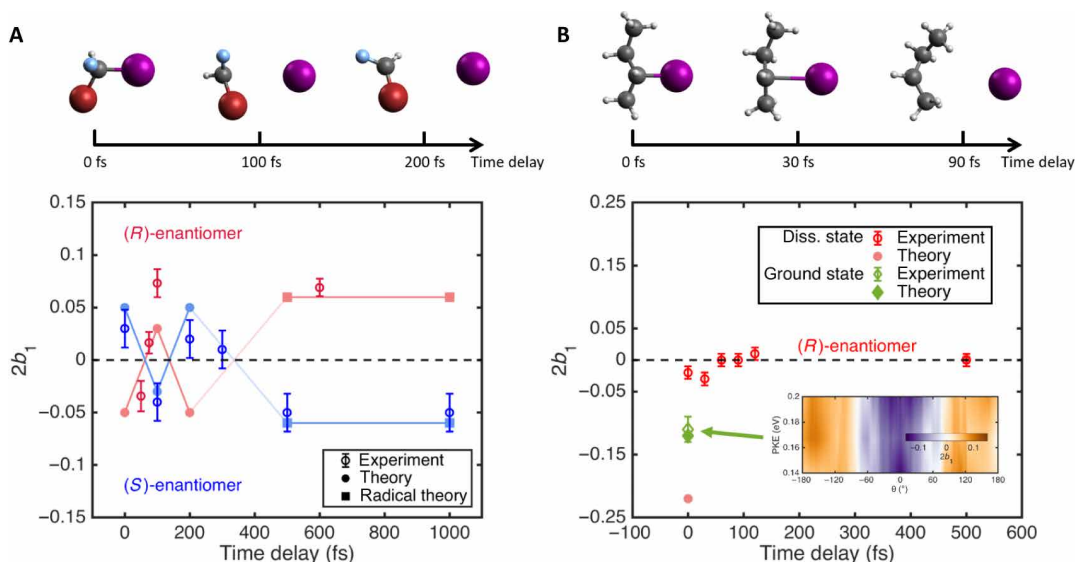


Fig. 4. Comparison of calculated and measured PECDs and their interpretation. (A) TRPECD during the photodissociation of CHBrFI. The lines connecting the calculated points are meant as a guide to the eyes only. (B) TRPECD (circles) of the photodissociation and ground-state PECD (diamonds) of the (*R*)-enantiomer of 2-iodobutane. The inset shows a PECD image in polar coordinates obtained from the ground state of 2-iodobutane. Error bars represent $\pm 2\sigma$ error from the nonlinear fit. Details are given in the main text.

pulses is much smaller in magnitude ($2b_1 = -0.02 \pm 0.01$). Subsequently, the PECD increases to reach a maximum (in magnitude) of $2b_1 = -0.03 \pm 0.01$ at a delay of 30 fs and decays to zero by 60 fs, remaining close to zero for all later time delays.

DISCUSSION

To rationalize the observed TRPECD signals, we have developed a new method to calculate the PECD effect on the basis of accurate electron-molecule scattering methods. Details about this work are described in section S3.

The PECD associated with the electronically excited state of CHBrFI prepared in the experiment was calculated as follows. The excited-state wave function at the equilibrium geometry of the electronic ground state was obtained through a state-specific complete active space self-consistent field (CASSCF) calculation using the MOLPRO package (53, 54). The ePolyScat package (43, 44) was then used to obtain the photoionization matrix elements from which the chiral-sensitive PAD coefficient b_1 was extracted in a subsequent step.

We first discuss the TRPECDs measured in the case of CHBrFI. The experimental data are reproduced in Fig. 4A as open circles, whereas the calculated results are shown as filled circles. The calculations reproduce the sign alternation of the PECD observed in the experiment, as well as the order of magnitude of the transient PECD effects. Specifically, the sign changes from $t = 0$ to 100 fs, observed for both enantiomers, and the additional inversions from $t = 100$ to 200 fs and from $t = 200$ to 500 fs, observed for the (*S*)-enantiomer, are all reproduced. All calculated PECDs shown in this article were obtained for isotropic axis distributions. The effect of photoselection does not change qualitatively the results, as discussed in section S3.

Calculations for delays longer than $t = 200$ fs could not be numerically converged because they correspond to C—I bond lengths larger than 4.65 Å, which cannot be efficiently described within the single-center expansion used in ePolyScat. Instead, the calculated

PECD values given for $t = 500$ and 1000 fs (blue squares) were obtained from a calculation on the equilibrium geometry of the isolated CHBrF* radical in its electronic ground state. At this delay, the CHBrF* radical can be safely assumed to behave as an isolated entity. In this case, we even obtain a quantitative agreement with the measured values obtained from both enantiomers.

The measured TRPECD signals of 2-iodobutane are reproduced in Fig. 4B in red. At time zero, the experimental values of both the ground and the first excited states are shown (green diamond and red circle, respectively). Both measured PECDs are negative, but the ground-state PECD is significantly larger in absolute value. In the case of the electronic ground state, the experimental and calculated PECDs agree well. In the case of the electronically excited state at temporal overlap of pump and probe pulses, the measured PECD is significantly smaller than the calculated value. This discrepancy might be caused by the contribution of a second photoionization channel, in which the 133-nm photon is absorbed first and the 266-nm photon is absorbed second. This channel is not included in our calculations. Attempts to calculate PECDs for longer time delays, i.e., larger C—I separations, were not successful because the ePolyScat calculations did not converge. However, the PECD of the 2-butyl radical in its electronic ground state could be obtained. It is shown as the filled red circle at a delay of 500 fs, which agrees well with the vanishing measured PECD.

The most remarkable feature of the measured TRPECDs is their different behavior in the two molecules. Whereas the TRPECD of CHBrFI shows pronounced variations as a function of time, including at least three inversions of its sign, the TRPECD of 2-iodobutane converges rapidly to zero. These different dynamics can be explained in terms of the structural dynamics of the nascent radicals. Whereas the CHBrF* radical has a single low-frequency vibrational mode, i.e., the umbrella motion, the 2-butyl radical has many soft modes, including internal rotations and the H-wagging mode.

To understand these differences, we discuss the topology of the potential-energy surfaces of the two radicals along the coordinate

that interconverts the two enantiomers, i.e., the umbrella mode in CHBrFI and the H-wagging mode in the 2-butyl radical (see Fig. 5). The one-dimensional cut of the potential-energy surface of the CHBrF[•] radical along the umbrella mode exhibits a double-well structure as shown in Fig. 5A. The two minima correspond to two enantiomeric pyramidal geometries of the radical, whereas the local maximum of the potential corresponds to a planar achiral geometry. The characteristic time scale for the transformation of one enantiomeric structure into the other, which occurs by tunneling when the total energy lies below the barrier, is also known as the stereomutation time $\tau_{\text{stereo}} = h/(2\Delta E_{10})$ (55), where h is the Planck constant, and ΔE_{10} is the energy splitting between the lowest and the first excited vibrational states of the inversion mode. The vibrational energy levels, calculated using a one-dimensional discrete-variable-representation approach (56) along the umbrella-like coordinate, are shown as horizontal lines. The stereomutation time for the CHBrF[•] radical in its lowest pair of eigenstates is $\tau_{\text{stereo}} = 5.29$ ps. Because the dissociation time is much shorter than the stereomutation time, the CHBrF[•] radical may be formed in one of the two possible pyramidal forms, which corresponds to a coherent superposition of at least the two lowest states of the umbrella mode. Our observation of a nonvanishing PECD for pump-probe delays at which dissociation is completed (0.5 to 1.0 ps) is consistent with a long stereomutation time, i.e., the formation of a photoproduct that remains chiral on the time scale of our measurements.

Figure 5B shows a one-dimensional cut of the potential energy surface of the 2-butyl radical along the H-wagging coordinate. This potential also has a double-well structure, but in this case, the barrier height is much lower. This leads to a situation where the lowest vibrational state lies above the barrier and results in an effectively achiral equilibrium structure. This explains both the vanishing calculated PECD for the 2-butyl radical and the rapid decay of the measured PECD to zero.

The most intriguing aspect of our TRPECD results is the observation of multiple sign changes of the PECD effect during the photodissociation of CHBrFI. The time delays $t = 100$ and 200 fs correspond to C–I distances of more than 4 \AA over which the potential energy surfaces are flat. Since the probe pulse cannot ionize atomic iodine, ionization happens exclusively from the CHBrF[•] radical at both delays. The sign changes in the PECD effect could therefore originate from inversions of the CHBrF[•] radical along the umbrella mode. To

verify this hypothesis, we have repeated the PECD calculations shown in Fig. 4A by using the same molecular geometries but removing the iodine atom, repeating the electronic structure and lastly the photoionization calculations to obtain the PECD of the CHBrF[•] fragment. The results, shown as green circles in Fig. 6, are negative for all time delays, in contrast to the PECD calculations including the iodine atom (blue circles). This shows that the sign inversions of the PECD do not originate from the inversions of the CHBrF[•] radical. They must therefore be caused by the presence of the dissociating iodine atom. Since the latter is separated by $>4 \text{ \AA}$ from the CHBrF[•] radical at delays >100 fs and has therefore no effect on the electronic structure of the radical, the inversions of the PECD must originate from scattering of the photoelectrons originating from the CHBrF[•] radical on the neutral iodine atom. The marked effect of electron scattering from the iodine atom on the PECD is particularly apparent by comparing PECD values at pump-probe delays $t = 100$ and 200 fs. At the earlier time delay, the PECD values are very similar, whereas they are almost opposite at the later delay. The sensitivity of this PECD effect extends well beyond that of photoelectron spectroscopy. Whereas the photoelectron spectrum remains essentially unchanged after $t = 100$ fs (Fig. 2) because the dissociating wave packet has reached the flat part of the potential energy surfaces, the PECD is still highly sensitive to the presence of the dissociating atom to the level that it changes sign several times. These results highlight the extreme sensitivity of TRPECD to the structural evolution of the dynamically evolving molecular environment, beyond the simpler energetic aspects probed by TRPES.

In this work, we have demonstrated a new general technique for probing chirality changes during a chemical reaction. We have revealed the potential of VUV-TRPECD by time resolving the changes in molecular chirality introduced by the selective C–I bond dissociation of two chiral molecules with complementary characteristics. Our results were interpreted by comparison with a new theoretical method for calculating PECDs based on accurate electron-molecule scattering calculations.

In the case of CHBrFI, we have observed a pronounced variation including sign changes of the PECD during the photodissociation reaction. These inversions of the PECD have been assigned to photoelectron scattering off the dissociating iodine atom on the basis of our calculations. The measured PECD at long time delays differs from zero and agrees with the calculated PECD of the chiral equilibrium

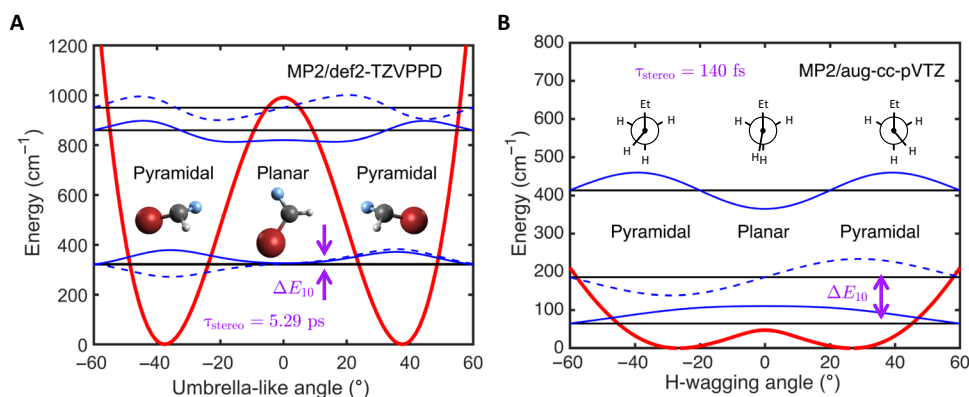


Fig. 5. Illustration of the origin of photoproduct chirality. (A) Potential-energy surface of the CHBrF radical along the umbrella mode and its lowest-lying vibrational eigenstates. (B) Potential-energy surface of the 2-iodobutane radical along the hydrogen-wagging coordinate and its lowest-lying vibrational eigenstates. Blue solid and dashed lines discern vibrational eigenstates, including those of tunneling doublets.

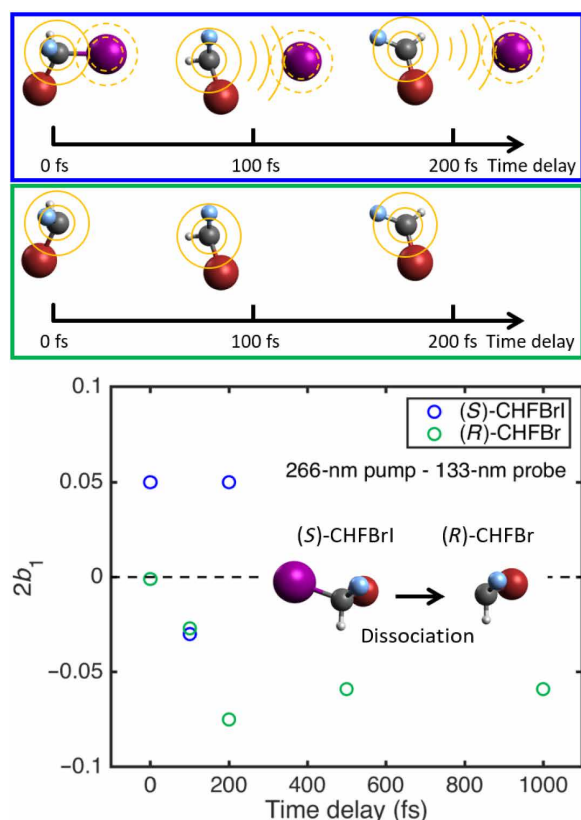


Fig. 6. Effect of photoelectron scattering off the iodine atom (yellow dashed circles) on TRPECD. Calculations of the PECD of the dissociating molecule (blue) and the CHBrF radical using the same atomic coordinates but removing the iodine atom (green).

geometry of the CHBrF[•] radical. In the case of 2-iodobutane, we have measured the PECD of both the excited and the unexcited molecules. Our measurements have revealed a rapid decay of the PECD to zero within 60 fs. This observation is explained in terms of a rapid racemization of the nascent 2-butyl radical rationalized by the achiral equilibrium geometry of the 2-butyl radical.

Overall, we have demonstrated that VUV-TRPECD opens a general route to studies of dynamical chirality during chemical reactions. This approach is sufficiently sensitive to be applicable to molecules in the gas phase. This general method gives access to the chirality of complete photochemical reaction pathways from photoexcitation through conical intersections to the final products, without the restrictions that are imposed by photon energies in the visible-ultraviolet range. Hence, this technique has the potential to drive major new developments in the understanding of the dynamic evolution of molecular chirality in chemical reactions and its role in chiral recognition and enantioselective molecular processes in general.

MATERIALS AND METHODS

Experiment

All experiments have been performed using a two-color pump-probe scheme using low-order harmonic generation in a semi-infinite gas cell and a velocity-map imaging (VMI) spectrometer (57). A Ti:Sa regenerative amplifier operating at 1 kHz delivered 2.0-mJ pulses centered at 800 nm with 28-fs pulse duration. The input beam was

divided into two arms using an 80:20 beam splitter. The reflected beam was frequency-doubled using a 300- μm -thick β -barium borate crystal to obtain 570- μJ pulses at 400 nm (~ 35 fs). The second harmonic beam was separated from the fundamental beam by reflections on four dichroic mirrors. The polarization of the beam was controlled by a motorized rotational stage with a quarter-wave plate for 400 nm (45). The beam was focused by a $f = 500$ -mm spherical mirror into a semi-infinite gas cell filled with Xe. The Xe pressure $p_{\text{Xe}} = 10$ mbar was selected such that the third harmonic of 400 nm (133 nm, i.e. 9.3 eV) was optimized. The transmitted beam was used for the third-harmonic generation giving 1.2- μJ pulses of 266 nm (~ 70 fs). Both beams were delivered into a vacuum chamber using their respective dichroic mirrors and then focused noncollinearly (with a crossing angle of less than 1°) by two spherical mirrors ($f = 0.5$ m for the harmonic beam and $f = 1$ m for the 266-nm beam). All in-vacuum mirrors were motorized, allowing for fine adjustment of the spatial overlap.

Samples (racemic or enantiomerically enriched) were evaporated and mixed with Ne as a carrier gas. The mixture was delivered into the vacuum chamber through a pulsed nozzle (orifice 150 μm , 1-kHz repetition rate). The gas jet created by the nozzle was skimmed by a 500- μm skimmer and propagated 10 cm downstream to reach the interaction region where it was ionized by the combined action of the laser beams. A cc between both pulses was determined by nonresonant two-color ionization (133 + 266 nm) of Xe. The cc function was taken into account during data analysis as an instrument-response function. Ejected photoelectrons were imaged using electrostatic lenses fulfilling VMI conditions and a dual micro-channel plate detector in a Chevron configuration, backed with a phosphor screen.

Theory

Ground-state geometries for both molecules were optimized with the Orca program package on the MP2/aug-cc-pVTZ level of theory. All molecular geometries for the first excited state needed for subsequent CASSCF and ePolyScat calculations were obtained from ab-initio molecular-dynamics calculations. The Born-Oppenheimer molecular-dynamics (BOMD) on the first excited singlet state, calculated at the CIS/6-311G* level with four singlet states and no triplet states, was performed using the Q-Chem program package. The time step of the BOMD was 25 atomic units (0.6 fs), and the initial velocities were set to zero.

The electronic-structure calculations were done in the MOLPRO program package. Since ePolyScat only works with Hartree-Fock-type wave functions in which each orbital is either doubly occupied, singly occupied, or empty, we described the first excited state of the molecules using a simple CASSCF-type wave function using an active space consisting of two electrons in two orbitals, CAS(2,2), with only two electronic states with the ground-state weight 0 and the first-excited-state weight 1. We used cc-pVTZ basis set on all atoms except iodine, which was described with the all-electron 6-311G* basis set. As a result, the first excited state was described as $(\dots)^2(\text{HOMO})^1(\text{LUMO})^1$.

Photoionization matrix elements were calculated with ePolyScat program package (43, 44), which calculates the matrix elements by solving the corresponding quantum-mechanical scattering problem in a single-center partial-wave expansion using the Schwinger variational principle. For each time delay, two calculations were done in which either the highest-occupied molecular orbital (HOMO) or the lowest-unoccupied molecular orbital (LUMO) was ionized, and

the other orbital was left singly occupied. From the calculated photoionization matrix elements, b_1 coefficients were calculated in a separate custom-built routine, and HOMO and LUMO contributions were averaged to get the final b_1 coefficient.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <https://science.org/doi/10.1126/sciadv.abq2811>

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Femtosecond photoelectron circular dichroism of chemical reactions

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