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Substituent Effects on Electrocyclic Reactions: Ultrafast Ring-Opening of α -Phellandrene Stimulated by Impulsively Excited Molecular Vibrations

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ABSTRACT

The ring-opening reaction of 1,3-cyclohexadiene (CHD), involving a concerted electrocyclic process with simultaneous electronic and structural rearrangement, has been widely studied for its ability to modulate molecular functionality and confer specific biological activity. In this study, we investigate how substituents influence the ring-opening dynamics of (–)- α -phellandrene (α PH), a naturally occurring CHD derivative, following two-photon photoexcitation to Rydberg states using 3.1 eV pump pulses. The dynamics are probed by time-resolved photoelectron spectroscopy (TRPES) with extreme ultraviolet light (29.5 eV) in combination with quantum chemical calculations. Unlike CHD, which undergoes ballistic ring opening, α PH exhibits a stepwise reaction pathway in the ground state. This difference arises from the steric and mass effects of the isopropyl substituent, which elevate the energy of the first transition state and create a potential barrier. Ultrafast excitation to Rydberg states impulsively triggers coherent intramolecular vibrations, resulting in periodic isomerization between equatorial (eq) and axial (ax) conformers in the ground state of α PH at intervals of 436 fs. These oscillations facilitate the gradual accumulation of the ring-opened product. Intrinsic reaction coordinate (IRC) analyses further reveal that substitution on the CHD moiety substantially alters the potential energy surface, thereby modulating the reaction mechanism. These findings highlight the crucial role of structural substituents in governing ultrafast ring-opening dynamics in conjugated cyclic molecules.

1. INTRODUCTION

An electrocyclic reaction is a pericyclic rearrangement in which π bonds are concertedly converted into σ bonds or vice versa in a conjugated π -electron system within a ring structure. These reactions are intimately involved in various biological activities, such as β -amyrin synthesis in plants, squalene to lanosterol conversion in the human body, and carotenoid biosynthesis.¹⁻⁴ The most representative example is the transformation of 7-dehydrocholesterol (7-DHC) into the precursor of vitamin D₃ (previtamin D₃) in human skin, which occurs when ultraviolet B (UVB) rays induce ring-opening of the 1,3-cyclohexadiene (CHD) moiety (Figs. 1a and 1b).⁵⁻⁷ Owing to their biological significance, the electronic dynamics involved in ultrafast ring-opening reactions of hydrocarbon rings have garnered considerable attention among researchers.

Although the ring-opening dynamics of CHD have been extensively studied,⁸⁻⁴⁰ its simple structure lacks substituents that impose steric hindrance and restrict atomic motion during isomerization. Therefore, the CHD reaction process does not necessarily reflect biologically relevant behavior. Several studies have attempted to investigate the influence of substituents on ring-opening reactions through theoretical analysis.⁴¹⁻⁴³ Although the position and type of substituents influence the potential energy surfaces, all these molecules follow the same universal ballistic ring-opening dynamics without exception.

Herein, we focus on (-)- α -phellandrene (α PH), a CHD derivative that features an isopropyl substituent attached to the bond-breaking carbon atom. This substitution gives rise to two conformers, with the isopropyl group adopting an axial (ax- α PH) or equatorial (eq- α PH) orientation approximately perpendicular or parallel to the ring plane, respectively (Fig. 1c). The structural complexity of α PH lies between CHD and biomacromolecules, making it an ideal model for bridging studies of simple molecules and complex biological systems. The steric hindrance imposed by the large isopropyl substituent is expected to modify its ring-opening dynamics, more closely resembling those observed during biological processes. We anticipate that investigating the ring-opening dynamics of α PH will reveal a new reaction mechanism, advancing our understanding of the ring-opening dynamics of more complex molecular structures. By studying isolated molecules in the gas phase, we gain insights into intrinsic reaction dynamics free from the influence of external factors, which provides a baseline for understanding the reactivity and dynamics of molecules with similar structural units and serves as a valuable reference for future investigations of molecular behavior in solutions or complex biological systems.

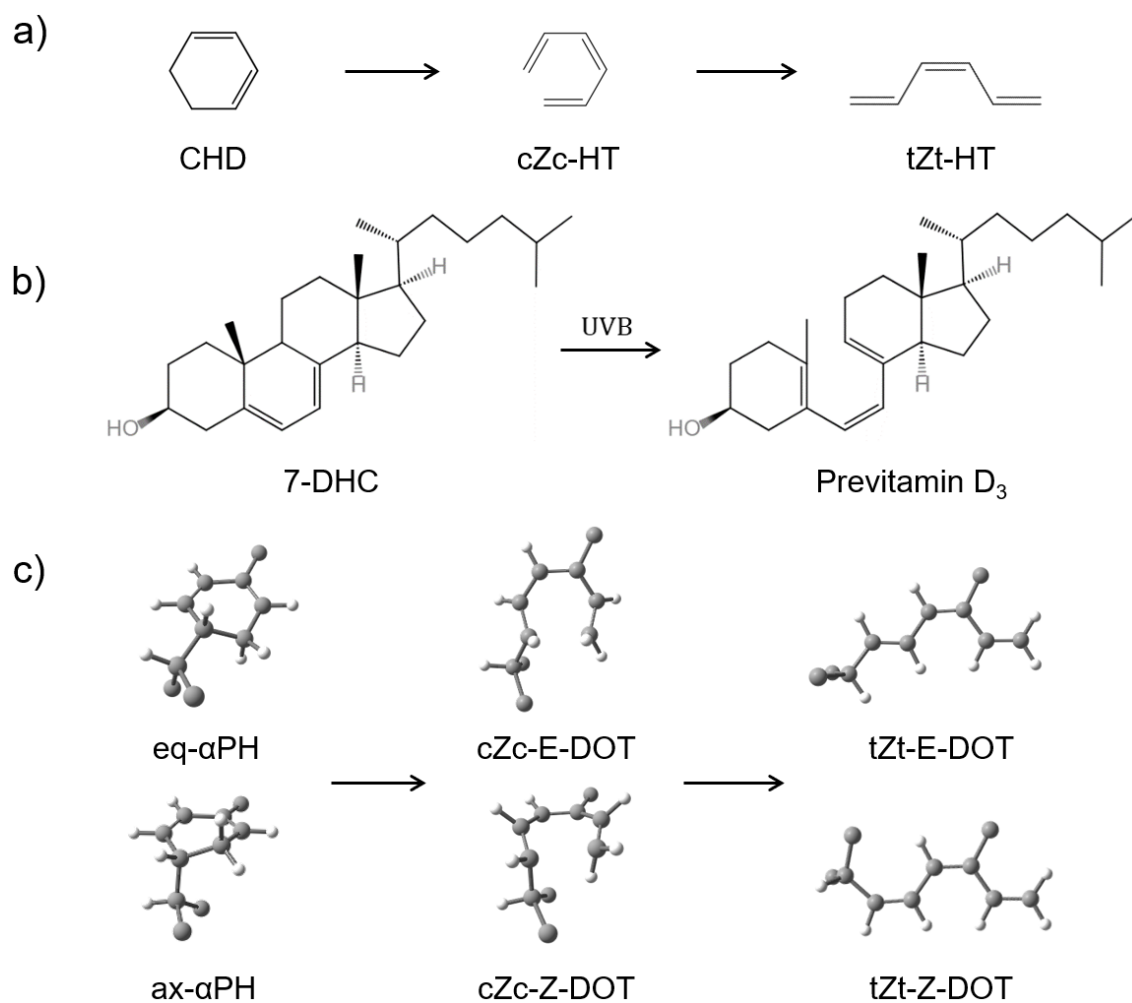


Figure 1. The ring-opening reactions of (a) CHD to hexatriene (HT), (b) 7-DHC to previtamin D₃, and (c) eq- and ax- α PH to cis-trans (E-Z) isomers tZt-E-DOT and tZt-Z-DOT, respectively.

The photoreaction processes of α PH have been investigated using various methods. For example, de Kock et al. employed UV and infrared spectroscopy to demonstrate that irradiation of α PH in a mixture of ether, isopentane, and ethanol solution with a broadband UV light source leads to ring-opening of the CHD moiety, forming 3,7-dimethylocta-1,3,5-triene (DOT) as a triene derivative.⁸ This result is consistent with the conclusions

drawn from time-resolved UV resonance Raman spectroscopy by Reid et al., performed in cyclohexane solution with 275 nm pump and 284 nm probe pulses,^{10, 44} and from matrix isolation infrared spectroscopy conducted by Marzec et al. on α PH isolated in an argon matrix at 13 K, irradiated with UV light generated by a 300 W Hg/Xe lamp.⁴⁵ Recent developments in MeV ultrafast electron diffraction (UED) technology enable observations of the temporal evolution of molecular structure dynamics, revealing that the earliest ring-opening of gas-phase α PH is completed within 200 fs upon single-photon excitation to S_1 .⁴⁶ Although the ring-opening of eq- and ax- α PH follows conformer-specific pathways, their reaction rates are similar. This finding aligns with the result from nonresonant multiphoton ionization of gaseous α PH at 267 nm excitation, which shows an indistinguishable ring-opening time constant of 205 fs for both conformers with a traveling time of 10 ± 5 fs in the Franck–Condon (FC) region.¹⁴ This indicates that α PH can rapidly relax out of this region following photoexcitation, which was also confirmed for solution-phase α PH in heptane, hexadecane, methanol, and 1-butanol using ultrafast broadband UV–visible transient absorption spectroscopy with a 266 nm pump beam.⁵

Given these revealed dynamics, how do the substituents of α PH affect the ring-opening reaction? Some studies have addressed this question by comparing the ring-opening dynamics of α PH with those of unsubstituted CHD.¹⁴ While all molecules under investigation are proposed to follow specific ring-opening pathways, the CHD moiety consistently undergoes the same ring-opening process in the excited state upon S_1

photoexcitation, evolving along the potential energy surfaces and transitioning between electronic states via conical intersections (CIs).^{34, 46} The reported excited-state lifetime of S₁-excited CHD is typically between 68 and 140 fs,^{19, 20, 27, 28, 34, 37} which is shorter than that of α PH (~200 fs).^{14, 46} Except for extended time constants at certain stages of the reaction, Garavelli et al. observed no substantial differences between the ring-opening processes of CHD and α PH, including S₁-state photoexcitation and subsequent rotamer interconversion.¹⁴ This finding was further corroborated by Arruda et al.⁵ Despite our expectations, a new type of ring-opening reaction—distinct from the ballistically driven one in the excited states —has yet to be reported.

The preceding studies have revealed that the ring-opening pathway of gas-phase CHD upon photoexcitation to Rydberg states, located between the S₁ and S₂ states,¹² differs from that induced by direct excitation to the S₁ state.^{21, 30, 32, 38} In the former case, CHD directly relaxes to its ground state without entering the reactive channel, and the subsequent ring-opening reaction proceeds via thermal activation.⁴⁰ According to the Woodward–Hoffmann (WH) rules⁴⁷ and the extensions proposed by van der Lugt and Oosterhoff,^{48, 49} the rotational motion associated with bond cleavage in CHD takes opposite directions in photochemical (conrotatory) and thermal (disrotatory) processes. Consequently, steric hindrance from substituents is expected to influence the thermal ring-opening dynamics differently from the photochemical cases reported so far.^{14, 46}

Motivated by this, we triggered the ring-opening reaction of α PH via excitation to the Rydberg states. In this study, we investigate how Rydberg-state excitations and molecular structure alter the ring-opening dynamics of α PH compared to those of CHD using time-resolved photoelectron spectroscopy (TRPES) with high-harmonic pulses at a photon energy of 29.5 eV. Probing with high-energy photons enables the observation not only of the highest occupied molecular orbital (HOMO) but also of lower-lying molecular orbitals (MOs), thereby providing comprehensive information on the electronic states of α PH over a broad energy range and allowing its chemical reactions to be traced.^{30, 38, 50-}
⁵³ We report for the first time that excitation of α PH to Rydberg states (approximately 0.7–1.3 eV above the S_1 state) leads to distinct stepwise ring-opening dynamics, in contrast to the ballistic dynamics observed in CHD.^{30, 32, 38} The ring opening of α PH occurs intermittently, because only a fraction of the vibrational wavepacket, stimulated by photoexcitation, can overcome the high energy barrier along the intrinsic reaction coordinate (IRC).

2. EXPERIMENTAL METHODS

A Ti:sapphire laser system delivered 1.4 mJ, 35 fs pulses at 1 kHz with a central wavelength of 800 nm. The fundamental beam was first frequency-doubled by a β -BaB₂O₄ (BBO) crystal (300 μ m thickness) to generate second-order harmonics (400 nm, 3.1 eV), which served as the pump pulses (5 mm diameter, 15.1 μ J pulse energy). The

residual fundamental beam was then separated from the second harmonic pulses by a harmonic splitter (HS) and focused into a Kr gas jet for high-harmonic generation (HHG). After filtering out the remaining fundamental pulses with an aluminum filter, a time-delay-compensated monochromator was used to select the 19th harmonic (42.1 nm, 29.5 eV) as the probe pulses, ensuring single-harmonic selection while preserving the temporal duration.^{54, 55}

α PH, purchased from Kanto Chemical Co., Inc., was provided as the (–)-enantiomer with an enantiomeric purity exceeding ~80% and used without further purification. The sample was evaporated from the liquid phase at room temperature and transported into a magnetic bottle photoelectron spectrometer via an effusive helium gas flow in a high-vacuum environment. It was then photoexcited to Rydberg states via two-photon absorption of the pump pulses and subsequently ionized by the EUV probe in a non-collinear configuration. This excitation scheme was employed instead of one-photon excitation with 200 nm pulses to maintain consistency with the experimental conditions used for CHD.³⁰ The polarization angle between the pump and probe pulses was set at 55° to minimize polarization effects. A computer-controlled translation stage varied the optical time delay between –0.4 and 1.4 ps, and transient photoelectron spectra were recorded at each delay. The instrument response function (IRF) of the system and the zero-delay time were determined via cross-correlation measurement based on two-photon ionization of Kr by

the pump and probe pulses, yielding an IRF with a full width at half maximum (FWHM) of 101 ± 3 fs. (See Section S3.1 in Supporting Information (SI))

3. COMPUTATIONAL METHODS

The minimum energy structures of α PH and DOT in the ground state (S_0 -MINs) were identified by density functional theory (DFT) calculations at the ω B97XD/cc-pVDZ level, using the single-component artificial force induced reaction (SC-AFIR) method. The transition state (TS) geometry connecting these minima, as well as the IRCs, was subsequently refined using the double-sphere artificial force induced reaction (DS-AFIR) method. DFT calculations were performed with the Gaussian16 program package,⁵⁶ while SC-AFIR and DS-AFIR calculations were conducted using the GRRM17 program.⁵⁷ α PH possesses a chiral center and the (–)-enantiomer corresponds to the R configuration.

To investigate the valence excited states of ax- α PH at its equilibrium structure (S_0 -MIN), we employed the multi-state complete active space second-order perturbation theory (MS-CASPT2) method⁵⁸ with the cc-pVDZ basis set. The reference wavefunctions were generated using the state-averaged complete active space self-consistent field (SA-CASSCF) method with an active space of six electrons in six orbitals (6e, 6o). The lowest three singlet states (S_0 , S_1 , and S_2) were averaged with equal weights and then mixed using the effective Hamiltonian approach in the subsequent MS-CASPT2 calculations. In

these calculations, the carbon 1s orbitals were frozen, and a level shift parameter of 0.2 was applied. The ground and excited cationic states (D_0 , D_1 , and D_2) were computed using the same methodology, except with a (5e, 6o) active space in the SA-CASSCF wavefunctions. All excited-state calculations were performed using the MOLPRO 2012.1 program package.⁵⁹

The Rydberg excited states of ax- α PH at its equilibrium structure (S_0 -MIN) were investigated using time-dependent density functional theory (TD-DFT) with the ω B97XD functional, as implemented in the Gaussian16 program package.⁵⁶ The aug-cc-pVDZ basis set was employed, supplemented with Dunning-Hay (s,p) Rydberg basis functions⁶⁰ on all carbon atoms.

To elucidate the periodic dynamics observed in the photoelectron spectra, the Born-Oppenheimer molecular dynamics (BOMD) method was employed to analyze a representative dynamic trajectory, assuming that the electronically excited molecule rapidly relaxes to a highly vibrationally excited state in the electronic ground state. The BOMD trajectory was initiated from the equilibrium structure of eq- α PH, with 6 eV of kinetic energy (corresponding to the Rydberg excitation energy) applied along the lowest-frequency normal mode. This mode involves changes in the dihedral angle of the CHD ring and drives the structural transformation from eq- α PH to ax- α PH. This initial condition was chosen because the IRCs for the ring opening of eq- α PH and ax- α PH to

DOT align with these vibrational modes in the early stages. Moreover, the same mode facilitates the interconversion between eq- α PH and ax- α PH, which proceeds with a very small activation barrier, as confirmed by IRC calculations. The BOMD trajectory was computed using the velocity-Verlet integration scheme with a time step of 1 fs, employing DFT calculations at the ω B97X-D/cc-pVDZ level with the in-house SPPR program.⁶¹

4. RESULTS AND DISCUSSION

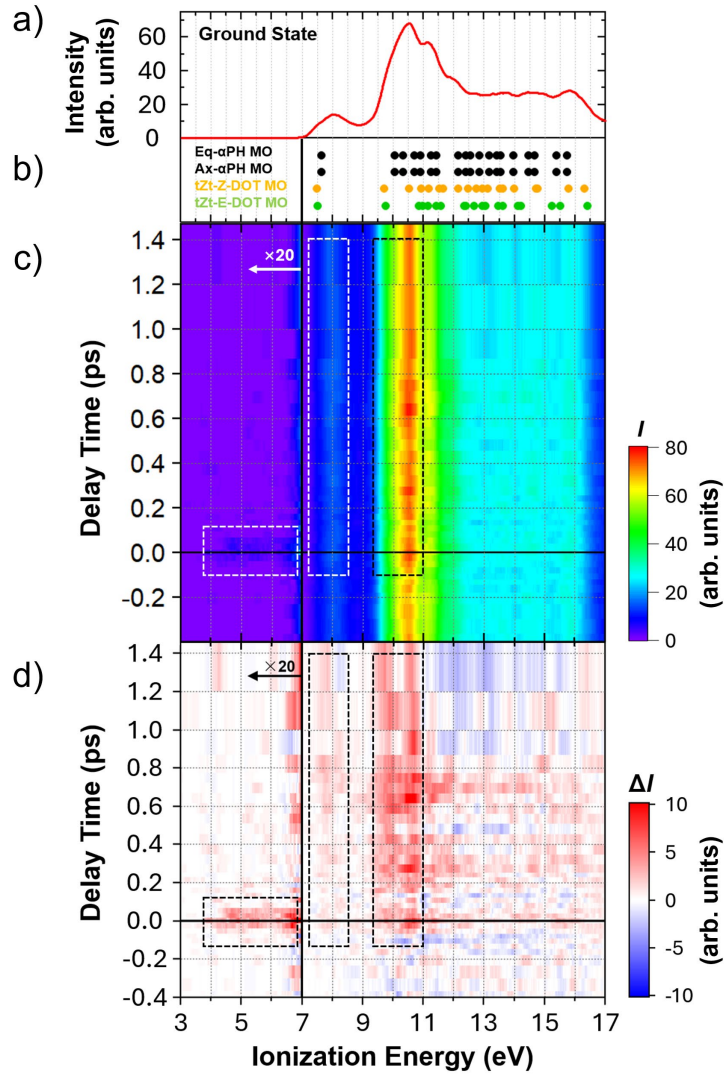


Figure 2. (a) Photoelectron spectrum of α PH in the ground state. (b) Absolute values of MO energies for eq- and ax- α PH (black dots), tZt-Z-DOT (orange dots), and tZt-E-DOT (green dots). (c) Time-resolved photoelectron spectrogram (I) and (d) Difference photoelectron spectrogram (ΔI), with signal intensities of <7.0 eV amplified 20 times. The dotted boxes in panels (c) and (d) indicate specific regions discussed in the following sections.

Figure 2a shows the photoelectron spectrum of α PH without photoexcitation, while Fig. 2b displays the absolute values of the MO energies for both eq- and ax- α PH along with their respective photolysis products, tZt-E-DOT and tZt-Z-DOT.⁴⁶ These energies were obtained via DFT calculations at the ω B97X-D/cc-pVDZ level and are plotted in different colors. By incorporating long-range and dispersion corrections into the DFT calculations, the application of the extended Koopmans' theorem to the photoelectron spectra is justified.^{62, 63} The black dots in Fig. 2b correspond to the ground-state spectrum of α PH, and the energy difference between eq- α PH and ax- α PH is found to be negligibly smaller than the spectral shifts experimentally observed. In this study, DFT calculations at the ω B97XD/cc-pVDZ level predict that the total energies of ax- and eq- α PH differ by only 3.6 meV, which is consistent with the high-level CCSD(T)-F12/cc-pVDZ-F12 results reported by Champenois et al.⁴⁶ Accordingly, the ax- and eq- α PH conformers are expected to be nearly equally populated at room temperature. However, an UED experiment conducted by the same group indicated that the population of ax- α PH was

less than 20% under the same conditions.⁴⁶ Since a definitive explanation for this discrepancy is currently lacking, our subsequent discussion is based on the computational results. Further investigation is required to resolve this inconsistency.

Figures 2c and 2d show the time-resolved photoelectron spectrogram I and the difference photoelectron spectrogram ΔI , respectively, where ΔI was obtained by subtracting the ground-state spectrum from the measured spectrum at each delay time. Three key experimental features, highlighted by the dashed boxes in Figs. 2c and 2d, were observed: (i) excited-state signals appeared between 3.5 and 6.5 eV upon photoexcitation, (ii) the HOMO energy shifted multiple times over a 1.4 ps timescale, and (iii) the peak at 10.2 eV periodically split into two peaks as the delay time increased. These features will be discussed in the context of the extended Koopmans' theorem,^{62, 63} under which the MO energies approximate the corresponding ionization potentials.

4.1 Excited-State Dynamics

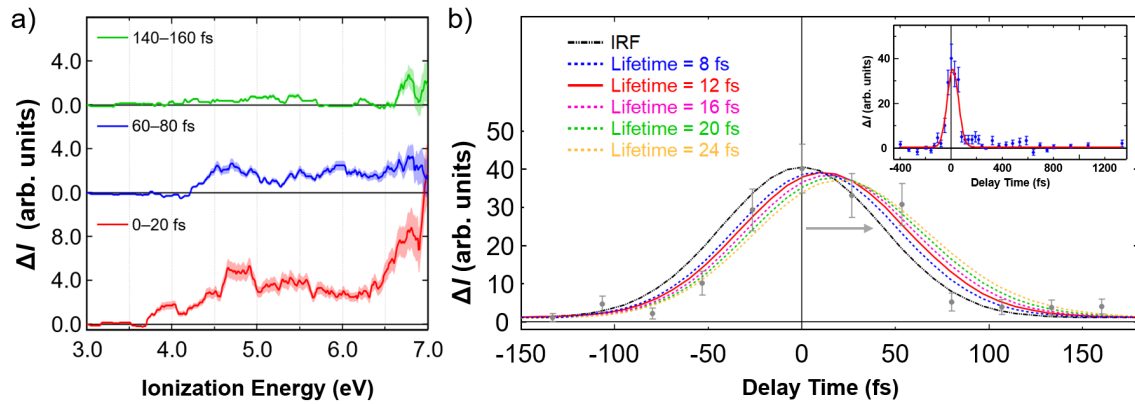


Figure 3. (a) Temporal evolution of ΔI spectra between 3.0 and 7.0 eV, integrated over 0–20, 60–80, and 140–160 fs delay times from top to bottom. Shaded areas represent the errors estimated by Poisson statistics. (b) The time-resolved photoelectron yield of α PH in the 4.2–6.4 eV range. The solid red line corresponds to a fitted lifetime of 12 fs. For comparison, the black dashed line shows the IRF, while the blue, pink, green, and orange dashed lines represent fitting results with a fixed lifetime of 8 fs, 16 fs, 20 fs, and 24 fs, respectively. The inset displays the excited-state photoelectron yield across the whole temporal window of the measurement. Error bars represent uncertainties estimated from Poisson statistics.

First, we focus on the excited states of α PH. Figure 3a presents the time-resolved photoelectron spectra of α PH in the region of the excited states, integrated over 0–20, 60–80, and 140–160 fs delay times. At zero delay time, distinct bands were observed in the energy range of 3.9–6.0 eV, corresponding to ionization transitions from excited to ionic states, including the $S_1 \rightarrow D_0$ (3.88 eV) and $S_1 \rightarrow D_1$ (5.99 eV) transitions, as listed in Table 1. The remaining peaks are attributed to Rydberg states with energies of approximately 5.5–6.1 eV, located between the S_1 and S_2 valence excited states (see Section S2.3 of SI).

Table 1. Energy levels of the ground and excited states of neutral and cationic ax- α PH, calculated at the MS-CASPT2/cc-pVDZ level. All energies are vertical excitation and

ionization energies computed from the optimized α PH geometry in the S_0 state, with its electronic energy defined as zero.

Neutral State	Energy (eV)	Ionic State	Energy (eV)
S_0	0.00	D_0	7.83
S_1	3.95	D_1	9.93
S_2	7.24	D_2	11.82

The excited state dynamics of α PH integrated between 4.2 and 6.4 eV is presented in Fig. 3b. The signal intensity decreased rapidly and dropped below 10% of the peak value at 90 fs. The photoelectron spectrum of α PH reverts to its original profile following the disappearance of the excited states at approximately 110 fs. (See Figs. 2d and 3b) This suggests that all subsequent processes occur after ultrafast relaxation to the ground state.

Figure 3b also shows that the excited state appears slightly later than the IRF, represented by the black dotted line, whose peak is defined as time zero based on the cross-correlation measurement (see S1.1 in SI). This delay can only be reproduced by introducing the lifetime of the excited states τ_{decay} . The excited-state dynamics are characterized using a single exponential function of time t :

$$F(t) = \exp(-t/\tau_{decay}),$$

The experimentally observed photoelectron yield $f(t)$ is expressed by the convolution of $F(t)$ with the cross-correlation function between the pump and probe pulses $X(t)$ as follows:

$$f(t) = \int_{-\infty}^t X(t')F(t - t')dt',$$

where

$$X(t) = A \cdot \exp\{-4\ln 2 \cdot (t/\tau_{\text{FWHM}})^2\},$$

with A denoting the amplitude and τ_{FWHM} representing the full width at half maximum of the Gaussian instrument response function. The measured τ_{FWHM} is 101 ± 3 fs (see Section S1.1 of SI). The decay constant τ_{decay} is determined by fitting $f(t)$ to the experimental data using the least-squares method, yielding an excited-state decay constant of 12 ± 2 fs. The error, arising from experimental noise as well as from uncertainties in τ_{FWHM} and the time-zero determination, is evaluated as the standard deviation of the fitting residuals.

Despite τ_{decay} being shorter than the IRF, the steep temporal gradients in both the rise and decay shown in Fig. 3b ensure a small uncertainty, thereby supporting a reliable determination of τ_{decay} below the IRF limit. This could be visualized by showing not only the fitting result but also the cases with different time constants. The solid red line represents the best-fit lifetime of 12 fs, while the dynamics with lifetimes of 8 fs, 16 fs,

20 fs, and 24 fs are shown by the blue, pink, green, and orange dotted lines, respectively, in Fig. 3b. As the lifetime increases, the central peak of the fitted curve shifts progressively to the right, as shown by the gray arrow in Fig. 3b, while the corresponding coefficient of determination (R^2) exhibits an overall decreasing trend (0.930, 0.932, 0.921, 0.897, and 0.866). Therefore, we adopt 12 ± 2 fs as the best-fit excited-state lifetime. Further investigations with higher temporal resolution are necessary to discuss the excited-state dynamics in detail.

The extremely short excited-state lifetime suggests that relaxation from the Rydberg state proceeds via a highly efficient, nonradiative pathway back to the ground state. The absence of significant variations in the early-stage (approximately <130 fs) spectral signal during the ultrafast relaxation implies that Rydberg-excited α PH does not enter the reactive channel, evolve along the reaction coordinate, or access CIs associated with pronounced structural distortions, as observed upon S_1 -state excitation.⁴⁶ Instead, the energy dissipation appears to involve minor geometrical distortions that enable internal conversion without substantial reorganization of the molecular framework. This behavior is consistent with previous observations reported in Rydberg-excited CHD and other polyatomic molecules,^{19, 21, 64, 65} where excitation to higher-lying Rydberg states leads to bypassing the reactive potential energy surfaces and rapidly returning to the ground state. Nevertheless, the detailed physical mechanism underlying this unique relaxation pathway remains to be further elucidated.

4.2 HOMO Evolution and Periodic Spectral Modulation

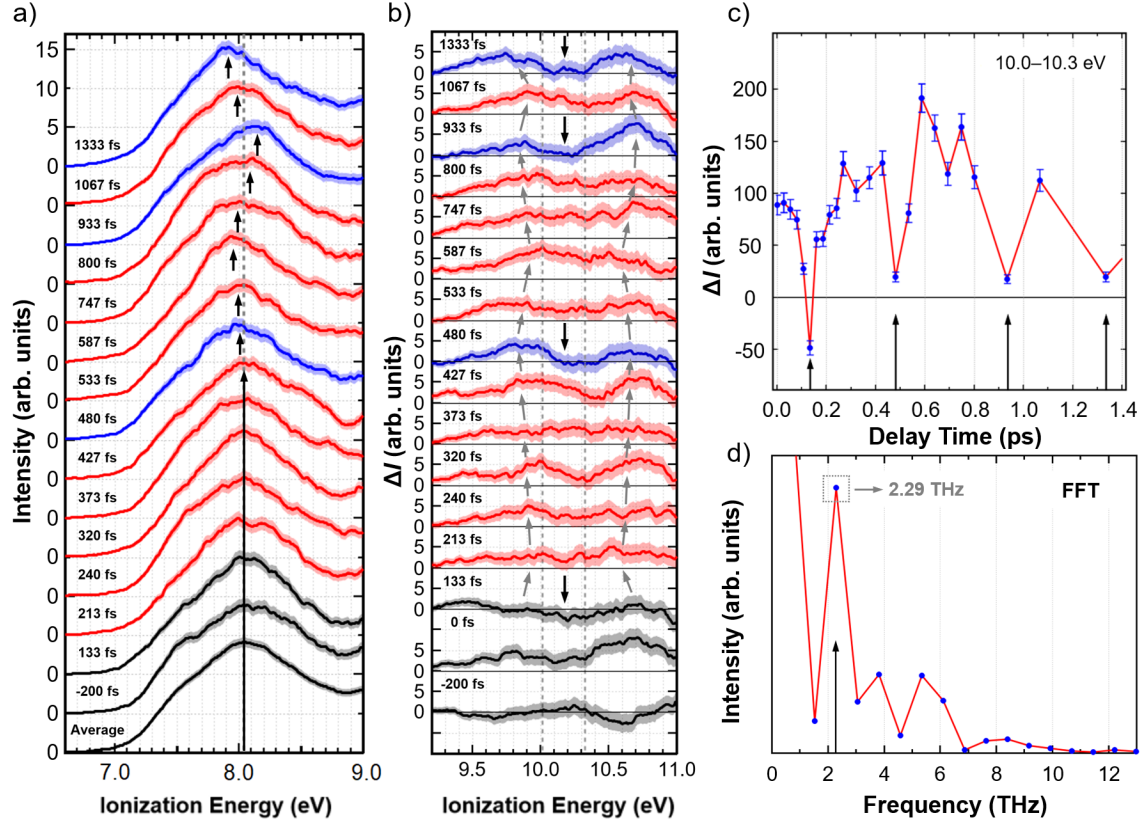


Figure 4. (a) Temporal evolution of the photoelectron spectrum of α PH in the 7.0–9.0 eV region, sourced from Fig. 2c. Adjacent data are offset by 5 units on the y-axis for better visualization. The black arrows indicate shifts in the HOMO peak of α PH. Shaded areas represent the errors estimated by Poisson statistics. (b) Temporal evolution of ΔI spectra between 9.2 and 11.0 eV, sourced from Fig. 2d. The gray dashed lines represent HOMO-1 and HOMO-2. The black and gray arrows indicate the decreasing spectral intensity trend and characteristic peak shifts, respectively. Shaded areas represent the errors estimated by Poisson statistics. (c) Time dependence of photoelectron yield of α PH integrated between 10.0 and 10.3 eV. The arrows mark the delay times corresponding to

signal intensity reductions. Error bars represent the counting uncertainty based on Poisson statistics. (d) Frequency spectrum obtained from the FFT of the spectral signal oscillations.

We move on to the HOMO-energy shift highlighted in Figs. 2c and 2d. Figure 4a displays the enlarged view of the time-resolved photoelectron spectrum of the HOMO band of α PH, extracted from 6.5 to 9.0 eV in Fig. 2c. Before 480 fs, no substantial changes were observed in the spectrum. Thereafter, the spectrum sequentially shifted from 8.0 to 7.9 eV, then moved to 8.2 eV, and subsequently returned to 7.9 eV. Based on the calculated HOMO energy in Fig. 2b, the eventual leftward shift of the HOMO energy indicates that at longer delay times than 1 ps, some α PH molecules have already completed ring opening and are isomerized to DOT structures, because tZt-Z-DOT and tZt-E-DOT have lower HOMO ionization energies than ax- and eq- α PH. Simultaneously, the decrease in photoelectron yield above an ionization energy of 11 eV shown in Fig. 2d also suggests the isomerization of α PH at longer timescales. The dynamical processes beyond 480 fs will be discussed in detail later in Section 4.3 by incorporating the MO energy evolutions along the IRCs obtained from quantum chemical calculations.

Figure 4b presents the time-resolved ΔI spectra in the energy range of 9.2–11.0 eV, revealing that temporal modulation emerges at 133fs, followed by spectral splitting at 480, 933, and 1333 fs. To quantify this spectral modulation, the temporal evolution of ΔI

within the energy range of HOMO-1 and HOMO-2 (10.0–10.3 eV) is plotted in Fig. 4c. To extract the modulation frequency, the data were linearly interpolated onto an evenly spaced time domain for a fast Fourier transform (FFT) analysis in Fig. 4d, which reveals a dominant frequency component centered at $2.29 (76.4 \text{ cm}^{-1}) \pm 0.36 \text{ TH}$, corresponding to an oscillation period of $436 \pm 68 \text{ fs}$. In CHD, photoexcitation to Rydberg states is followed by ultrafast relaxation to the ground state, after which ballistic ring-opening occurs at approximately 400 fs.^{30, 32, 38} The present results show that the ring-opening of αPH also occurs in the ground state; however, the periodic spectral modulation suggests that the reaction pathway of αPH differs from that of CHD.

We propose that the observed coherent vibrations are initiated by displacement excitation and that the resulting shifts in the MO energies are associated with structural distortions induced by these vibrations. Upon excitation by ultrashort optical pulses, the FC region does not necessarily coincide with the minimum of the excited-state potential energy surface. The ensuing structural displacement toward a more stable configuration in the excited state, followed by ultrafast relaxation to the ground state, activates multiple coherent vibrational modes. This sequence generates a vibrational wavepacket in highly excited vibrational levels of the electronic ground state,⁵⁰ which periodically modulates the molecular structure of αPH and leads to shifts in MO energies.

4.3 Intrinsic Reaction Coordinates and BOMD Trajectory Analyses

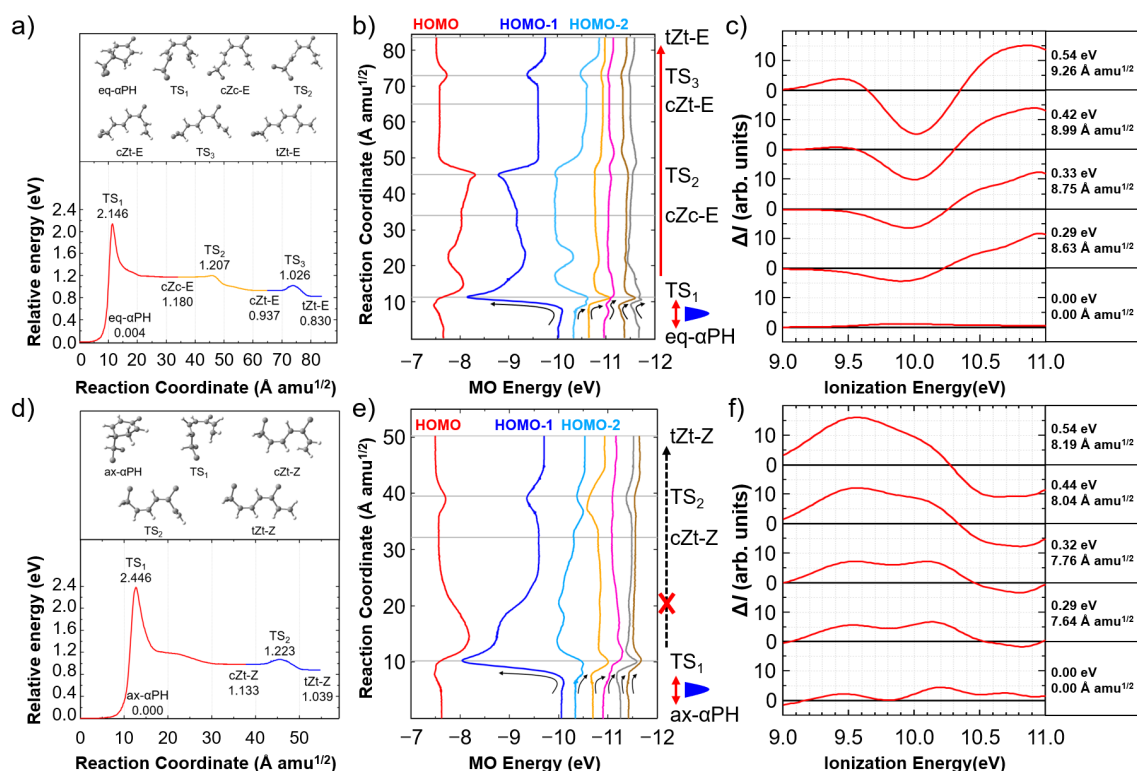


Figure 5. (a, d) Evolution of relative energies and molecular structures along the IRCs from eq- α PH to tZt-E-DOT and ax- α PH to tZt-Z-DOT, respectively. The relative energies are indicated in the figure. (b, e) Evolution of HOMO to HOMO-6 energies (indicated by different colors from left to right) along the IRCs from eq- α PH to tZt-E-DOT and ax- α PH to tZt-Z-DOT, respectively, calculated using DFT at the ω B97X-D/cc-pVDZ level. The vertical double-headed arrows on the right illustrate that most of the vibrational wavepacket (the blue cone) is confined to this region by the TS₁ energy barrier and exhibits oscillatory motion. Since the TS₁ energy of eq- α PH is relatively lower, ring opening proceeds exclusively via the equatorial conformation (solid red arrow), while the axial pathway is energetically unfavorable and thus prohibited (dashed black arrow). (c, f) Simulated ΔI spectra between 9.0 and 11.0 eV at relative energies of 0.00, 0.29, 0.33,

0.42, and 0.54 eV for eq- α PH and 0.00, 0.29, 0.32, 0.44, and 0.54 eV for ax- α PH. The corresponding reaction coordinates are 0.00, 8.63, 8.75, 8.99, and 9.26 Å amu^{1/2} for eq- α PH and 0.00, 7.64, 7.76, 8.04, and 8.19 Å amu^{1/2} for ax- α PH.

For further investigation, we calculated the ring-opening pathways along the IRCs for both eq- and ax- α PH. Figures 5a and 5d illustrate the potential energy profiles from eq- and ax- α PH to their respective photolysis-induced isomers, tZt-E-DOT and tZt-Z-DOT. TS₁, the first transition state along the IRCs, represents the highest energy barrier for isomerization and thus determines whether the ring-opening reaction can proceed. In contrast to the ballistic thermal ring-opening observed in CHD,^{30, 32, 38} the photoelectron spectrogram of α PH exhibits periodic modulation, indicating a stepwise ring-opening process. This difference in ring-opening dynamics can be attributed to the differing TS₁ energy barriers of the two molecules: the barriers for eq- and ax- α PH are 2.15 and 2.45 eV, respectively, whereas that of CHD is significantly lower at 1.90 eV.³⁸ The higher TS₁ barrier in α PH confines most of the vibrational wavepacket within the potential well, thereby suppressing ballistic passage over the barrier and allowing only a small fraction of the wavepacket to overcome it. Due to the strong coupling between molecular geometry and electronic structure, the instantaneous nuclear configurations sampled by the vibrational wavepacket along the IRCs are manifested in the time-resolved photoelectron spectra. Figures 5b and 5e show the evolution of the MO energies from HOMO to HOMO-6 (indicated by different colors from left to right) along the IRCs from

eq- α PH to tZt-E-DOT and ax- α PH to tZt-Z-DOT, respectively, calculated using DFT at the ω B97X-D/cc-pVDZ level. Since the high-energy barrier along the IRC confines majority of the vibrational wavepacket, we first focus on the evolution of the MO energies in the region preceding TS₁. The arrows in Figs. 5b and 5e indicate that, within the coordinate range of 0.0–11.3 Å amu^{1/2} for eq- α PH and 0.0–10.2 Å amu^{1/2} for ax- α PH, the ionization energies of HOMO and HOMO–1 are predicted to decrease, while those of other MOs increase. Therefore, the periodic spectral splitting observed between 9.2 and 11.0 eV is attributed to MO energy shifts along the IRCs, driven by intramolecular vibrations with a frequency of 2.29 THz (76.4 cm^{–1}).

To verify the consistency between the theoretically predicted MO energy shifts and the uniquely experimental observed spectral signal splitting, we simulated the ΔI spectra along the IRCs. Details of the simulation procedure are provided in Section S3 of SI. Briefly, the spectrum without photoexcitation was first reproduced by modeling MOs located between 10 and 12 eV using seven independent Gaussian functions centered at the computed MO energies. The amplitudes and widths of the peak were determined by fitting to the experimental ground-state spectrum of α PH shown in Fig. 2a. To simulate the spectra following photoexcitation, the peak widths were fixed to the fitted values, and the computed MO energies along the IRCs were served as the peak positions. The ΔI spectra were then obtained by subtracting the pre-pump spectrum from those recorded post-pump. Figures 5c and 5f show the simulated ΔI spectra for eq- and ax- α PH,

respectively, before reaching the transition state TS_1 , with both at the same relative energy. The spectral evolution of eq- α PH reproduces the peak splitting observed in Figs. 2d and 4b, whereas ax- α PH exhibits only a peak shift. Considering the lower TS_1 barrier height of eq- α PH compared to that of ax- α PH, the peak splitting and the subsequent ring-opening dynamics are primarily attributed to the eq- α PH pathway.

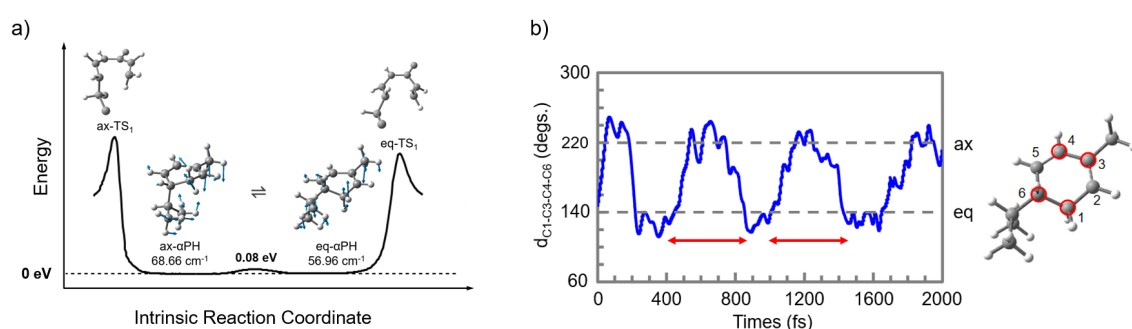


Figure 6. (a) Out-of-plane wagging vibrational modes facilitate interconversion between eq- and ax- α PH. Blue arrows indicate the direction of atomic motion, with their lengths proportional to the displacement amplitude. (b) Time evolution of the dihedral angle obtained from the BOMD trajectory. Red bidirectional arrows ($\leftrightarrow$) indicate the isomerization period of α PH.

To investigate the structural evolution of α PH in the electronic ground state, we performed BOMD trajectory calculation. As described in Section 3, the calculation assumed that the entire photon energy is initially deposited into this lowest-frequency normal mode of eq- α PH (56.96 cm^{-1}), owing to both its relatively low TS_1 barrier and the nature of the vibrational motion that promotes isomerization. Under this assumption, we

observed periodic interconversion between the eq- and ax- α PH conformers. Although these conformers are separated by an energy barrier of 80 meV, which was calculated using the SC-AFIR/DS-AFIR method described in Section 3, the vibrational energy imparted by photoexcitation is on the order of several eV, enabling the wavepacket to repeatedly traverse the barrier. Figure 6a summarizes the results, schematically illustrating how the vibrational wavepacket is confined within a double-well potential corresponding to ax- and eq- α PH along with the associated molecular structures. The oscillatory motion of the wavepacket is closely correlated with low-frequency intramolecular vibrational modes in the range of several tens of cm^{-1} . The blue arrows in the molecular structures in Fig. 6a represent the lowest-frequency vibrational modes, characterized by out-of-plane wagging motions that bend the molecular framework. Unlike higher-frequency modes, which are typically associated with localized motions such as rotation of the isopropyl group in α PH, these lower-frequency modes are more effective in driving global molecular structural transformations.

The time evolution of the dihedral angle defined by the four carbon atoms (C1–C3–C4–C6), as shown in Fig. 6b, clearly demonstrates this oscillatory behavior. The interconversion occurs approximately every 450 fs, corresponding to a vibrational frequency of 74.13 cm^{-1} , which is in excellent agreement with the experimentally observed period of 436 fs. Similar dynamics were observed in the BOMD trajectory calculation initiated from ax- α PH; however, no conformational transitions were detected

when the calculations were started from higher-frequency vibrational modes for either conformer. These results strongly suggest that the periodic spectral splitting observed at 10.2 eV (Figs. 2d and 4b) originates primarily from lower-frequency intramolecular vibrations excited by displacement excitation.

These dynamics manifest in the lower-lying MOs, specifically between HOMO-1 and HOMO-6, which sensitively reflect structural modulations induced by vibrational motions. Then, what information does the HOMO itself provide? The IRC calculations depicted in Fig. 5b and 5e address this question. Within the IRC region from eq-/ax- α PH to TS₁, HOMO-1 exhibits significant energy variations along the IRC, whereas HOMO-2 to HOMO-6 display smaller energy shifts but denser distributions. In contrast, the HOMO is energetically isolated and shows energy shifts that are less pronounced than those of the other orbitals. This minimal shift explains why synchronous oscillations, such as those observed in lower-lying Mos, are initially absent in the HOMO region.

However, as illustrated in Fig. 4a, a clear temporal evolution of the HOMO emerges around 480 fs, closely following the theoretically predicted energy variation tendency along the isomerization pathway from α PH to ZE-/ZZ-DOT. This observation suggests that, under periodic structural distortions triggered by impulsively excited intramolecular vibrational modes, the wavepacket intermittently traverses the TS₁ energy barrier. Consequently, a portion of α PH molecules begins to isomerize toward DOT structures,

thereby initiating the stepwise ring-opening process at intervals of approximately 436 fs (see also Section S4 in SI). Although the HOMO itself is relatively insensitive to structural changes, its subtle yet discernible energy evolution serves as a clear indicator of ring-opening reaction progress.

To summarize, upon photoexcitation to the Rydberg states, α PH undergoes ultrafast relaxation to the ground state, releasing energy that activates coherent vibrational modes. In response, oscillatory motion of the wavepacket is induced on the vibrationally excited levels within the TS₁-defined potential well, as evidenced by the periodic signal splitting in Fig. 4b. Throughout this oscillatory process, most α PH molecules remain confined within the potential well, undergoing periodic eq-ax interconversion. However, a small fraction of the wavepacket acquires sufficient energy to overcome the TS₁ barrier each time it is reflected from the potential wall of eq- α PH. The ring-opening reaction predominantly originates from the eq- α PH conformer, owing to its lower barrier height compared to that of ax- α PH. Through repeated interactions with the potential well, the number of α PH molecules, that complete the ring-opening reaction, gradually increases over time, leading to the evolution of α PH into the DOT isomer. This process gives rise to the pronounced HOMO energy variation that becomes observable in Fig. 4a.

4.4 Perspective on the ring-opening dynamics of the CHD moiety

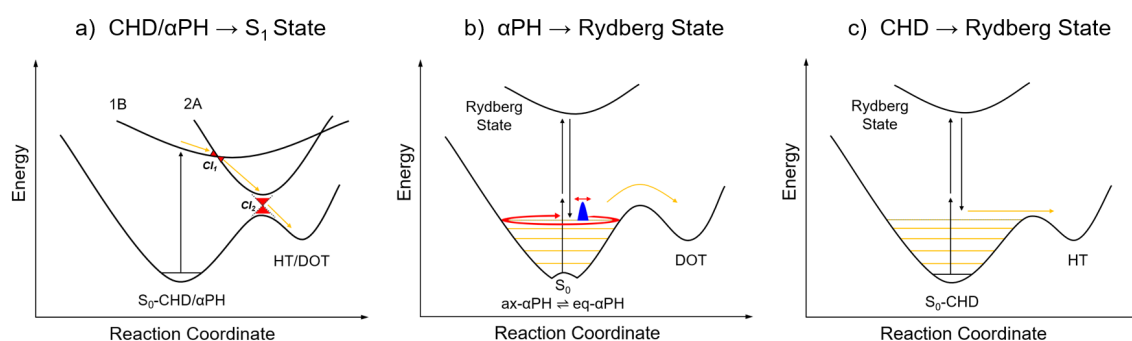


Figure 7. Schematic diagrams of the ring-opening pathways: (a) excitation to the S_1 state in CHD^{18, 33} and α PH; excitation to the Rydberg state in (b) α PH and (c) CHD. Orange arrows represent the dynamic evolution of molecules on the potential energy surfaces. The blue cone and red arrows in (b) highlight the confinement of the vibrational wavepacket within the potential well.

Based on these findings, we propose a general perspective on the ring-opening dynamics of the CHD moiety following excitation to Rydberg states. Previous studies have reported no substantial differences between the ring-opening mechanisms of the α PH and CHD upon excitation to the S_1 state,^{5, 14} which is attributed to their essentially barrierless reaction pathways. As shown in Fig. 7a, the potential energy surfaces from the FC region to the ring-opened products are connected through CIs, formed by the degeneracy of electronic states.^{18, 33, 46} In contrast, excitation to Rydberg states leads first to ultrafast relaxation to the ground state (Figs. 7b and 7c), after which the ring-opening dynamics are governed by the energy barrier between the cyclic molecule in the ground state and the corresponding photoproduct. In CHD, where this barrier is relatively low, the

molecule undergoes ballistic ring opening.^{30, 32, 38} In α PH, however, the higher barrier traps most portions of the vibrational wavepacket in highly excited vibrational levels of the ground state. This wavepacket exhibits oscillatory motion, accompanied by periodic interconversion between eq- and ax- α PH, primarily driven by out-of-plane wagging vibrational modes. The difference in ring-opening behavior between CHD and α PH arises from both mass effects and steric hindrance introduced by substitution on the ring. In α PH, the bulky isopropyl group and the adjacent methylene group likely cause steric interference, impeding the ring-opening pathway and raising the TS₁ energy. These structural effects may also influence the disrotatory bond cleavage pathway of the CHD moiety, as predicted by the WH rules.⁴⁷⁻⁴⁹

5. CONCLUSION

In this study, we employed TRPES with an EUV light source to directly probe the lower-lying MOs of α PH. Our measurement revealed periodic modulations in MO energies, reflecting coherent distortions of the molecular structure along the ring-opening pathway in the electronic ground state. These oscillations originate from the confinement of a vibrational wavepacket by an energy barrier, indicating that the ring-opening process of α PH proceeds in a non-ballistic manner. This behavior contrasts with the ballistic ring opening observed in CHD, which leads to limited formation of the DOT isomer. Quantum chemical calculations and BOMD trajectory calculations support this interpretation,

demonstrating that the elevated TS₁ energy barrier in α PH arises from both mass effects and steric hindrance introduced by the isopropyl substituent. These findings offer a unified perspective on the structural and dynamic factors that govern ring-opening reactivity in substituted CHD derivatives and may guide the rational design of photoresponsive molecular systems through strategic substitution on cyclic frameworks.

ASSOCIATED CONTENT

The Supporting Information is available free of charge.

Cross-correlation function, Cartesian coordinates of geometry-optimized conformers, MO energies, and the detailed theoretical calculations and simulations (PDF)

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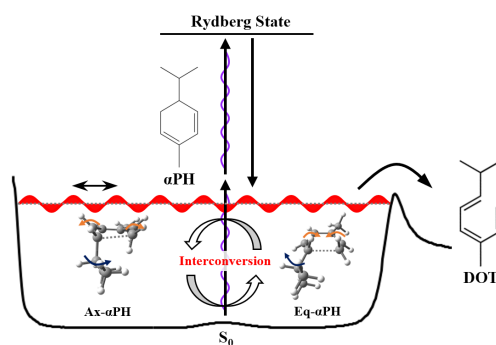
Notes

The authors declare no competing financial interests.

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TOC GRAPHIC



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