

Ultrafast electronic relaxation pathways of the molecular photoswitch quadricyclane

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Abstract: The light-induced ultrafast switching between molecular isomers norbornadiene (NBD) and quadricyclane (QC) can reversibly store and release a significant amount of chemical energy. Prior work observed signatures of ultrafast molecular dynamics in both isomers upon ultraviolet (UV) excitation but could not follow the electronic relaxation all the way back to the ground state experimentally. We have studied the electronic relaxation of QC after exciting in the UV (201 nanometers) using time-resolved gas-phase extreme ultraviolet photoelectron spectroscopy combined with nonadiabatic molecular dynamics simulations. We identify two competing pathways by which electronically excited QC molecules relax to the electronic ground state. The fast pathway (< 100 femtoseconds) is distinguished by effective coupling to valence electronic states, while the

slow pathway involves initial motions across Rydberg states and takes several hundred femtoseconds. Both pathways facilitate interconversion between the two isomers, albeit on different timescales, and we predict that the branching ratio of NBD:QC products immediately after returning to the electronic ground state is approximately 3:2.

Molecular photo-switches are an exciting area with emerging applications in catalysis, photochromic materials, molecular machines, logic devices, and energy storage¹. The last example includes molecular solar thermal (MOST) energy storage solutions, whereby molecular isomers are exploited to absorb, store, and later release solar energy as heat^{2,3}. An important model system for such applications is the photoswitchable pair of isomers quadricyclane (QC), a highly strained multicyclic hydrocarbon, and its lower-energy isomer norbornadiene (NBD)^{4–9}, whose IUPAC names are (QC) tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane and (NBD) bicyclo[2.2.1]hepta-2,5-diene. The isomers, shown in Fig. 1, interconvert upon photoabsorption in the ultraviolet (UV)^{10–13}. More broadly, the photoisomerization of NBD → QC is an example of a [2+2] cycloaddition reaction, and the behavior of the molecule is reminiscent of the prototypical ethylene dimerization, with the bridging framework acting to hold the ethylene moieties together^{14,15}. We investigate the mechanism of the reverse interconversion, QC → NBD, which has both fundamental photochemical interest and practical importance since it represents the undesired UV-induced photoreversion process in QC/NBD-derived MOST systems.

Early time-resolved ion mass spectrometry experiments on gas-phase NBD noted signatures of ultrafast molecular dynamics upon UV excitation at 200 nm (6.20 eV) which were speculatively attributed to transitions from a superposition of Rydberg and valence states to the electronic ground state *via* a series of conical intersections on a sub-100 femtosecond time scale¹⁵. A subsequent study on QC excited at 208 nm (5.96 eV) employed time-resolved Rydberg fingerprint photoelectron spectroscopy. The latter work suggested that QC isomerizes to NBD on the 3s Rydberg state within 140 fs and that relaxation to the electronic ground state occurs within 400 fs¹⁶. Notably, that study could not observe the dynamics all the way to the ground state since the probe photons had insufficient energy to ionize ground-state molecules. Theoretical work has focused on the photorelaxation of NBD, examining the electronic structure^{4,9,17} and the dynamics^{18,19}. In both cases, the key role of interactions between the Rydberg manifold and valence states in NBD was highlighted.

In the present study, we use time-resolved photoelectron spectroscopy (TRPES) with extreme ultraviolet (XUV) probe pulses, capable of tracking the entire reaction path from the initial UV-excited states through to the electronic ground states of both isomers. TRPES with XUV pulses is a powerful method for mapping complex chemical dynamics^{20–24}. Our experimental data, supported by high-level simulations, provide a much fuller description of the deactivation mechanisms in QC, thus providing mechanistic insights that can be used to design more efficient MOST systems.

Results

We initiate the photochemical reaction in gas-phase QC by a UV excitation pump pulse at 200.6 nm (6.18 eV), followed by a XUV ionization probe pulse at 18.97 eV (65.35 nm) from a seeded free-electron laser (FEL). The time-resolved photoelectron spectra obtained as the difference between the spectra acquired with and without the pump pulse (see Methods and Supplementary Information, SI, Section 1.4 for details) are shown as a two-dimensional false-color map in Fig. 2 (A). One-dimensional spectra obtained by averaging over selected time-delay ranges are displayed in Figs. 2 (B-C) (additional spectra are shown in Extended Data Fig. 2). Several prominent features are apparent. A narrow and long-lived feature at \sim 2.3 eV binding energy (BE), visible as a faint horizontal line in panel 2(A) and as a clear peak in panel 2(B), is assigned to two of the three 3p Rydberg states of QC in accordance with the literature¹⁶. The 3s Rydberg state can be seen at BE \sim 2.9 eV in panel 2(B) but has a weaker signature than in earlier studies¹⁶, suggesting less excitation to the 3s state at 200.6 nm compared to 208 nm. Panel 2(A) also shows a spectrally broad and short-lived vertical feature in the BE range of \sim 1.5-7 eV, which merges into a long-lived horizontal band at \sim 7-8 eV BE, both of which were not observed in the earlier work that did not have sufficient photon energy to ionize this BE region. These observations suggest the existence of a rapid (<100 fs) deexcitation pathway leading to the formation of vibrationally hot photoproducts, while the longer timescale of the Rydberg associated features indicate the existence of a second, slower decay mechanism, which corresponds to the pathway identified in earlier work¹⁶. Finally, there is a pronounced negative signal in the difference spectrum in the BE range 8-9 eV assigned to depletion of the QC ground state, followed by a partial recovery.

Delay-dependent photoelectron yields in selected spectral regions are shown in panels 2(D) and 2(E). They display a nearly Gaussian shape at low BE with a temporal width that is mostly given by the instrument response function (see Methods), while clear exponential ‘tails’ are visible in the range of the Rydberg excitations and in the high-BE yields. Least-square fits of the delay-dependent yields are provided in Supplementary Figs. 9, 10, and 11.

The nature of the previously unreported broad, short-lived feature with BEs in the range \sim 1.5-7 eV is investigated further using high-level electronic structure calculations and nonadiabatic dynamics simulations. Figure 3 shows calculated potential energy curves for the ground (S_0) and first five singlet excited (S_1 - S_5) electronic states identified as being active in the dynamics probed by the present experiment, plotted along a linear interpolation in internal coordinates (LIIC) from the equilibrium geometry of QC(S_0) to the S_1/S_0 minimum energy conical intersection (MECI) and then continued along a second LIIC from this MECI to the NBD(S_0) equilibrium geometry. The dominant electronic characters and adiabatic energies at the equilibrium geometries and the MECI are given in Table 1. In the Franck-Condon (FC) region of QC, the S_1 adiabatic state has 3s Rydberg character, S_3 and S_4 are 3p Rydberg states, and S_2 and S_5 are a pair of mixed $3p_x$ /valence (V) states. As the QC molecule approaches the MECI geometry, the S_1 state acquires valence character, which persists into the FC region of NBD. A complete discussion of the vertical electronic spectra of both isomers, complementing the work by Palmer et al.^{17,25}, is reserved for a separate publication²⁶.

Discussion

The potential energy curves in Fig. 3 suggest the possible mechanisms that underpin the features observed in the TRPES data, with the two pathways indicated schematically by black arrows. From the QC ground state, the bandwidth of the pump pulse (0.6 nm) allows excitation to a manifold of closely spaced states with 3p Rydberg character (see Extended Data Fig. 7). Population in the $3p_{y/z}$ Rydberg states (S_3 and S_4 in the FC region) then evolves via a (comparatively) *slow Rydberg* pathway on the rather flat Rydberg manifold at excitation energies ~ 6 eV; we anticipate that this would correspond to the pathway observed previously¹⁶. Due to the similar topographies of the Rydberg and ground-state ion (D_0) adiabatic potential energy surfaces, the BEs for the *slow Rydberg* pathway can be expected to be relatively constant – as observed experimentally. Conversely, in the *fast valence* pathway, the population in the strongly mixed Rydberg-valence $3p_x/V$ state (S_2 in the FC region) is subject to efficient nonadiabatic coupling to S_1 , funneling down toward a conical intersection with the S_0 state. In the proposed model, the BEs for the *fast valence* pathway would increase rapidly, consistent with the short-lived structure observed for experimental BEs in the range $\sim 1.5\text{-}7$ eV.

We confirm these hypothesized mechanisms using nonadiabatic mixed-quantum-classical trajectory simulations (see Methods). The simulations divulge that the photodynamics of excited QC is strongly dependent on the initial excited state. Figure 4 shows the results separated into two sets. Dynamics initiated on the S_2 ($3p_x/V$) state is labelled *fast valence*, shown in the top row, while dynamics initiated on the S_3 and S_4 ($3p_y$ and $3p_z$) is labelled *slow Rydberg* and is shown in the bottom row. The panels in Fig. 4 (A) show false-color maps of the nuclear dynamics along the coordinate associated with the making and breaking of the 1-2 and 3-4 carbon-carbon bonds during the interconversion between QC and NBD (see Methods). The left and right panels show the trajectories on the excited states and ground state, respectively. Figure 4 (B) shows the time-dependent electronic-state populations and the fraction of population best defined as NBD-like, while the false-color maps in Fig. 4(C) finally show the contributions to the simulated time-resolved photoelectron spectrum to aid comparison with the experimental data in Fig. 2 (A).

We first examine the simulation results for the *fast valence* mechanism shown in the top row of Fig. 4, corresponding to trajectories initiated on the S_2 ($3p_x/V$) state. One-photon excitation to the $3p_x/V$ state from the S_0 state is symmetry forbidden at the exact equilibrium geometry, but the transition gains strength from the Herzberg-Teller effect (45% excitation fraction, see Methods). The excited states nuclear dynamics, Fig. 4 (A) left panel, breaks the carbon-carbon bonds along r_{12} and r_{34} , allowing the molecule to deform towards NBD-like geometries ($r_{cc} > 2.0$ Å). The wave packet then returns towards QC-like geometries (smaller r_{cc}) and crosses to the S_0 ground state via a conical intersection, appearing in the right panel. It immediately partitions into QC- and NBD-like geometries. The recurrences in the upper panel reflect the persistence of the ‘butterfly’-like vibrational motion of the NBD products when they first reach the S_0 state (with wavenumber $\tilde{\nu} \sim 428$ cm⁻¹)²⁷. The corresponding motion in QC has higher wavenumber ($\tilde{\nu} \sim 721$ cm⁻¹)²⁸ but can also be discerned in the lower panel.

This picture is confirmed in the upper panel of Fig. 4 (B), which shows almost immediate population transfer from S_2 to S_1 via internal conversion (see also the zoomed-in Extended Data Fig. 6), followed by another rapid internal conversion to S_0 , with only a small fraction (< 10%) of the population remaining in the Rydberg manifold after 1 ps. The time-dependent fraction of molecules with NBD-like geometries (i.e., with $r_{cc} > 2.0 \text{ \AA}$) in the same graph shows a rapid early increase and then decline (mirroring the S_1 state population), finally converging to a branching ratio of ~3:2 for NBD-like to QC-like geometries in the S_0 state. This ratio is set by the decay dynamics rather than energetics, as the timescales are far too short for thermalization on the ground state.

The theoretically predicted TRPES signal in Fig. 4 (C) shows a curved band of intensity evolving from the BEs of the Rydberg state (~2.1 eV) down to that of the S_0 state (~7 eV) in good accord with the “hockey-stick” shaped feature in the experimental data (Fig. 2 (A)). In part, this broad feature reflects the very fast motion of the wavepacket down the $3p_x/V$ surface, with a corresponding rapid increase in the binding energy with respect to D_0 . In addition, there is a smaller contribution from the D_1 ionization channel when the wavepacket approaches the MECI. Figure 4 (A) (upper left panel) shows that the bond breaks and reforms in under 100 fs, faster than the IRF of the experiment, making these features appear almost simultaneously at $t=0$. A more detailed analysis of the components of the photoelectron signal is provided in the SI.

Next, we consider the *slow Rydberg* pathway with trajectories initiated on the $S_{3/4}$ ($3p_{y/z}$) states shown in the bottom row of Fig. 4. Already in the left panel of Fig. 4 (A), it is apparent that the excited-state dynamics persist for significantly longer than in the *fast valence* mechanism, and that the dynamics are more centered at QC-like molecular geometries ($r_{cc} < 2.0 \text{ \AA}$), with only a small fraction of the trajectories exploring NBD-like geometries in the 3p excited states, discernable as a faint signal at $r_{cc} > 2.0 \text{ \AA}$. Examining the populations in Fig. 4 (B), we see a comparatively slow but steady deactivation of the Rydberg manifold states (S_2 and higher) with a matching increase in S_0 population. The decay proceeds via the same $3p_x/V$ state as the *fast valence* mechanism, evidenced by the build-up of population in the S_1 intermediate state, which acts as a funnel towards the S_0 state via the conical intersection. It appears that this conical intersection has a strong influence on the NBD:QC branching ratio in the S_0 state, since the fraction of NBD (Fig. 4 B, bottom row) approaches the same value as the *fast valence* pathway.

The simulated TRPES signal in Fig. 4 (C) shows a long-lived feature with BE ~2.1 eV, corresponding to the 3p Rydberg states (with potentials along the LIIC of interest that closely track that of the D_0 ionic state), in good accord with the experimental data, which show the corresponding feature attributable to ionization from these Rydberg states at BE ~2.3 eV, Fig. 2 (A). At long times, the TRPES signal seen in the *slow Rydberg* and *fast valence* dynamics are essentially identical. Both pathways involve similar ultimate decays to the S_0 state, yielding similar branching ratios of hot QC and NBD products. Note that the vertical ionization potentials of QC and NBD are similar, differing by ~0.3 eV (see Methods). Thus, the TRPES signals of hot ground state QC and NBD

species overlap, and the experimentally observed bleach recovery in Fig. 2 (E) includes components from both isomers.

Notwithstanding the very good agreement between experiment and theory, some discrepancies are evident. The simulations return longer Rydberg state lifetimes than observed experimentally, which could reflect shortcomings in the electronic structure theory, e.g., regarding the strength and location of the couplings with the $3p_x/V$ state, additional decay paths not accounted for by the active space used, or the accuracy of the predicted ionization cross sections.

In summary, TRPES studies using XUV photons from a seeded FEL have provided new and detailed insights into the relaxation pathways of electronically excited QC molecules formed by photoexcitation at 200.6 nm, from Rydberg states through to vibrationally excited hot ground-state QC and NBD molecules. We present first observations of the dominant relaxation pathway in QC, involving strong Rydberg-valence coupling, alongside the previously observed Rydberg-state-mediated isomerization¹⁶. The present combined experimental and theoretical study shows that all three 3p Rydberg states of QC are excited by the 200.6 nm pump pulse. The lowest-energy ($3p_x$) state is strongly coupled to a valence state, giving rise to the *fast valence* pathway characterized by ultrafast electronic decay and nuclear motion. The other two support initial nuclear dynamics in the Rydberg manifold, prior to comparatively slower decay to the ground state (identified here as the *slow Rydberg* pathway). The simulations suggest that ~40% of the vibrationally excited ground state products sampled at pump-probe delays of ~1 ps correspond to QC-like structures, irrespective of the decay pathway followed, and that this early-time partitioning is determined by the molecular dynamics rather than thermodynamics.

The insights provided by the present study point to key features which affect the photodynamics: the partial absorption cross sections, the strength of the nonadiabatic couplings to the valence excited state, and the relative stabilities and geometries of the regions of maximal intra-state coupling, i.e., the conical intersection between the S_1 and S_0 states. For potential applications, these properties could be manipulated using substituent groups, spatial confinement, and/or by choice of excitation wavelength^{5,8,19,29}. For instance, the detailed nature of valence/Rydberg mixing in the valence state controls its energy and accessibility, which could be used to affect the system's function as a molecular photoswitch. The manner in which the wavepacket approaches the S_1/S_0 conical intersection region is also important, and this could be manipulated either in the preparation of the wavepacket or by altering the position and shape of the conical intersection.

From a broader photochemical perspective, one might conjecture that the bipartite dynamics found here will be a common feature whenever a manifold of Rydberg states intersects valence states in the FC region^{30–32}. The excitation energies to Rydberg states typically fall within ~3 eV of the associated ionization limit, E^{IP} , and, in most small to medium sized molecules, will overlap with those of one or more excited valence states. Rydberg excitations will manifest as a longer-lived trapping component, whereas excitations to valence states (or, as here, to a mixed Rydberg-valence state) will lead to more rapid relaxation that gives rise to broad features in the photoelectron spectrum. Broadband excitation can excite both types of states, leading to both

types of mechanism. Bifurcation of wavepackets has been reported previously, e.g., in the photoisomerization of stilbene³³ and in photoexcited inverse dithienylethene derivatives³⁴ but, in most such cases studied hitherto, the bifurcation arises as a result of sampling a ‘transition-state’-like region of a common excited state (e.g., a $\pi\pi^*$ state), the potential energy surface for which supports multiple minima.

The current results demonstrate the utility of TRPES with XUV probes for characterizing complex photochemical mechanisms. Comparison to previous experiments¹⁶ indicates that a systematic examination of the effect of excitation wavelength would be useful. Ideally, this should be coupled to complementary experimental work more sensitive to molecular geometry. For instance, ultrafast electron diffraction and ultrafast X-ray scattering experiments³⁵⁻³⁸ might offer further insights into the dominant conical intersection and, at longer times, reveal fragmentation products from the hot ground state molecules. We anticipate that future experiments should provide even deeper understanding of the intriguing ultrafast ring reconfigurations in this photoswitch molecule.

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Author contributions

P.M.W. and D.R. conceived the experiment with further input from M.Ce. and A.Ru. The experiment at the FERMI free-electron laser facility was conducted by M. Bon., C.C., M.B.D., A.D., M.D.F., O.P., and K.C.P. with remote participation of K.D.B., M.N.R.A., S.B., R.B., M.Ce., B.E., R.Fe., R.J.G.F., C.S.H., D.M.P.H., R.A.I., L.M., H.G.M., S.B.M., J.P.F.N., A.O., S.P., A. Ro., A. Ru., R.J.S., A.S.V., P.M.W, and D.R. R.Fe. and R.J.S. provided the magnetic bottle spectrometer. M. Bon., C.C., M.D.F., O.P. and A.S. prepared and operated the beamline and the low-density matter (LDM) instrument. A.D. and M.B.D. prepared the optical laser setup and P.R. operated the free-electron laser. M.B. synthesized and characterized the sample with input from J.B. J.C.C. and A.K. performed the ab initio simulations, with contributions from B.F.E.C. and R.L. Experimental data were analysed by K.D.B. and D.R. K.D.B, J.C.C., M.N.R.A., D.M.P.H., P.M.W., A.K., and D.R. interpreted the results with input from all the authors, and K.D.B., J.C.C., A.K., and D.R., wrote the initial manuscript with further input from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

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Tables:

Table 1: Vertical excitation energies (eV) for each of the five excited singlet states, labelled S_1 - S_5 , with the dominant electronic character provided in parenthesis, as well as the $S_0 \rightarrow D_0$ ionization potential at the respective equilibrium geometries of QC and NBD and at the S_1/S_0 MECI geometry, calculated using RMS-CASPT2(2,6)/6-31G*+D. Note that the numbering of the states is directly related to the electronic structure model used. The geometries are shown in Extended Data Fig. 3. The value of the average carbon-carbon distance coordinate r_{cc} for the three geometries is $r_{cc}^{QC} = 1.51 \text{ \AA}$, $r_{cc}^{MECI} = 1.98 \text{ \AA}$, and $r_{cc}^{NBD} = 2.47 \text{ \AA}$. At the ground state geometry, in the two mixed states S_2 and S_5 , the $3p_x$ component is dominant in S_2 and vice versa in S_5 .

State	QC / eV (character)	MECI / eV (character)	NBD / eV (character)
S_1	5.29 (3s)	0.00 (V)	5.25 (V)
S_2	5.82 (3p _x /V)	2.74 (3s)	5.61 (3s)
S_3	5.88 (3p _y)	3.31 (3p _x)	6.11 (3p _y)
S_4	6.05 (3p _z)	3.47 (3p _y)	6.28 (3p _x)
S_5	7.53 (3p _x /V)	3.53 (3p _z)	6.34 (3p _z)
IP ($S_0 \rightarrow D_0$)	7.67	5.26	8.02

Figure captions:

Figure 1: Schematic of the QC \rightleftharpoons NBD interconversion. The isomerization reaction breaks (or forms) the 1-2 and 3-4 carbon-carbon bonds in QC, with the energy of the QC ground state located $\sim 1 \text{ eV}$ above the ground state of NBD. The interconversion can be driven by light absorption, allowing the system to act as a molecular photoswitch.

Figure 2: Experimentally measured time-resolved photoelectron spectra of UV-excited QC. (A) Photoelectron spectra as a function of binding energy (with respect to the first ionization potential, D_0) and pump-probe time delay between UV and XUV pulses, plotted as the electron yield *difference* between spectra taken with and without the UV-excitation pulse (see Extended Data Fig. 1). The respective electron yield at each delay is normalized to the FEL pulse energy before subtraction, and the difference signal is normalized to the integrated electron yield without UV-excitation, both summed over all shots at the respective delay. Negative delays correspond to the FEL pulse preceding the UV excitation pulse. (B), (C) Photoelectron BE spectra in the excited-state region (B) and at large BEs that sample the electronic ground state (C) at specific time delays. (D), (E) Lineouts of the delay-dependent electron yield in the denoted BE regions, normalized to have the same peak amplitudes. The data and error bands in (B), (C) and error bars in (D), (E) represent the mean value of

approximately 40,000 single-shot digitizer traces and the 68% confidence interval obtained from a bootstrapping analysis (see Methods).

Figure 3: Potential energy curves for QC and NBD along the Linear Interpolation in Internal Coordinates (LIICs). Potential energy curves for the ground S_0 and excited states S_1 - S_5 , as well as the cation ground state D_0 and first excited state D_1 (dashed lines), calculated along the LIICs, first from QC to the S_1/S_0 MECI and then from the MECI to NBD, using RMS-CASPT2(2,6)/6-31G*+D (see Methods and Section 2.1 of the SI). The two proposed reaction pathways are indicated schematically by black arrows, with the *slow Rydberg* pathway supporting vibrational motions on the Rydberg states before relaxing via the S_1 state, while the *fast valence* pathway descends on S_1 , bypassing the MECI on the initial descent, before crossing onto the S_0 ground state to form both products. The molecular geometry at the MECI has a distinct rhombic distortion (see Extended Data Fig. 3). E_{storage} indicates the energy stored in QC relative to NBD (~ 1 eV). See also corresponding vertical excitation energies listed in Table 1 and a plot including higher excited states and the approximate state characters in Extended Data Figure 4.

Figure 4: Simulated dynamics of UV-excited QC. The simulations are separated into the *fast valence* mechanism (top row, corresponding to trajectories starting on the S_2 state) and the *slow Rydberg* mechanism (bottom row, trajectories originating on the $S_{3/4}$ Rydberg states). A zoomed-in depiction of the first 200 fs is shown in Extended Data Fig. 6. (A) False-color maps for average carbon-carbon distance $r_{CC} = (r_{12} + r_{34})/2$ versus time (see Methods). The left and right panels show the dynamics for the excited states and the S_0 state, respectively. (B) Populations on the electronic states as a function of time, where $S_{n \geq 2}$ shows the cumulative population on the excited states other than S_1 . These plots also show the fraction of molecules with NBD-like geometry (defined as $r_{CC} > 2.0$ Å). (C) Simulated TRPES data, convoluted with a Gaussian function of FWHM 0.1 eV and 94 fs. Signals with BE > 3 eV (below the horizontal dashed line) have been multiplied by a factor 3 prior to display.

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Methods

Experiment: The experiment was performed at the FERMI free-electron laser facility³⁹ at the Low Density Matter (LDM) beamline^{40,41}. XUV probe pulses with a photon energy of 18.97 eV were generated at 50 Hz as the fourth harmonic of the seed laser wavelength at 261.4 nm. The UV pump pulses with a central wavelength of 200.6 nm and a bandwidth of 0.6 nm (6.18 ± 0.02 eV) were generated as the fourth harmonic of a Ti:Sapphire laser with a sequence of three -barium borate (BBO) crystals. For the data presented here, the pump-probe delay was scanned between –500 and 1000 fs with a step size of 25 and 50 fs near and far from the pump-probe overlap, respectively. At each delay point, 3000 shots were acquired. For every second shot, the UV pulse was blocked by inhibiting the trigger of the Ti:Sapphire amplifier. Shots without UV excitation pulses present were used to subtract static features in the signal and for additional normalization (see section 1.4 of the SI). The pump-probe instrument response function (IRF) was obtained by monitoring the UV-induced ionization of helium atoms following resonant $1s \rightarrow 4p$ excitation at 23.72 eV (5th harmonic of the seed laser), which yielded an IRF of 186 ± 28 fs (FWHM), as shown in Supplementary Fig. 3 and Supplementary Table 1.

Quadricyclane (QC) was synthesized by adding recrystallized Michler's ketone (0.35 wt%) (98%, Sigma-Aldrich) to norbornadiene (NBD) (97%, Alfa Aesar) and irradiating the mixture for 48 hours (Thorlabs, M365LP1; 365 nm). The product was distilled, and the irradiation and distillation process repeated. The final product was checked by ¹H NMR (400 MHz) and resulted in 99% photoconversion of norbornadiene to quadricyclane, without significant contamination from other products (see Section 1.3 of the SI for further details). The molecules were delivered into an ultrahigh vacuum chamber as a supersonic molecular beam using a pulsed Even-Lavie valve without further heating and with helium at a backing pressure of 6 bar as a carrier gas.

Photoelectron spectra were measured with a magnetic bottle electron spectrometer described previously²³. For the data shown here, an effective retardation voltage of 9.7 V was used to increase the resolution in the BE region of interest containing the excited states as well as the lowest-BE peak of ground-state QC. The conversion from time of flight to kinetic energy was calibrated by measuring the helium 1s photoline at 28.46 eV (6th harmonic of the seed laser) and 33.20 eV (7th harmonic) photon energy. Weaker photoelectron signals corresponding to ionization with the third harmonic of the FEL tuned to the 4th, 5th, 6th, and 7th harmonic were also included in the calibration. For the conversion to binding energies, the photoelectron kinetic energy was subtracted from the central FEL photon energy. By comparing the XUV photoelectron spectrum of QC measured here with a high-resolution spectrum reported in the literature [16] (see Supplementary Fig. 4), we estimate the kinetic energy resolution to be 0.03 (i.e., $\sim \pm 0.3$ -0.5 eV) in the kinetic energy range shown in Fig. 2.

The statistical uncertainty of the experimental signal was estimated using a standard bootstrapping analysis. The $\sim 40,000$ single-shot digitizer traces that were analyzed to obtain Fig. 2 were randomly resampled with replacement 150 times. The conversion from time-of-flight to electron kinetic energy (incl. Jacobian correction) was performed on each bootstrap dataset

separately. The mean and standard deviation of these 150 datasets define the values and the corresponding error bars shown in Figs 2 (B)-(E). They were checked for convergence by repeating the bootstrapping analysis a second time and comparing the results of both procedures.

Calculations: Electronic structure calculations for the neutral species were performed using RMS-CASPT2⁴² based on SA(9)-CASSCF(2,6) with the 6-31G(d) basis augmented by additional diffuse functions (8s8p contracted to 1s1p) centered on the bridging CH₂ fragment. The active space contained two valence, one 3s Rydberg, and three 3p Rydberg orbitals (shown in Extended Data Fig. 5). No 3d orbitals were included in this study, as their presence was not seen in the experimental data. The lowest six (S₀–S₅) states were deemed sufficient to describe the dynamics observed, though state-averaging over the first nine roots returned by the calculations was required for convergence. All nine states were active in the simulations, however, only a very small fraction of population ever appeared on the states S₆ and above during the dynamics. We note that this approach fails to capture well the second valence excited state of NBD⁴ but, as discussed in the SI, this omission is judged to have little impact on the dynamics initiated by photoexciting QC. Electronic structure calculations for the molecular ion were performed with the same method and basis, although with one electron removed, i.e., RMS-CASPT2/SA(6)-CASSCF(1,6), using the neutral orbitals as an initial guess. This accounts for all ionizations from the active electron, including the D₀ and D₁ ionic states of interest (further details in SI). The absence of Rydberg states in the ion wavefunction leads to lower relative energies in the ion than the neutral, leading to a bias towards lower E^{IP} values (see SI). All calculations included an imaginary shift of 0.5 E_{h} to remove intruder states and were performed in a development branch of OpenMolcas⁴³ implementing gradients for RMS-CASPT2⁴⁴

The potential energy curves in Fig. 3 are calculated along linear interpolation in internal coordinates (LIIC) that connects the ground state equilibrium geometry of QC to the S₁/S₀ MECI, and then along a LIIC from this MECI geometry to the ground state equilibrium geometry of NBD. The C₄-ring geometry at the MECI is rhombic [4,18] and does not lie directly between the equilibrium geometries of the two isomers, as shown in Extended Data Fig. 3. Since this is an essentially barrierless process, there is no obvious conceptual advantage in considering a minimum energy pathway over the LIICs.

Nonadiabatic trajectories were run using the surface-hopping method with a locally modified version of SHARC 2.1⁴⁵. Couplings were calculated using the local-diabatic approach. Limited numerical issues with the stability of the gradients were mitigated by a variable time step for the integration (see SI Section 2.2 for details). The surface-hopping simulations were performed using an electronic time-step 1/25 times smaller than the nuclear time step, and used the energy-based decoherence correction with the standard C=0.1 E_{h} .

The initial conditions were selected from a Wigner-sampled ground state QC geometry using the delta-pulse method⁴⁶ inside a 5.75 ± 0.07 eV window, chosen to overlap well with the calculated partial absorptions to the 3p Rydberg states of QC (Extended Data Fig. 7). Trajectories were categorized into those excited into S₂ (121 trajectories, 45%) and those excited into S₃ and S₄ (146

trajectories, 55%). Strictly, one-photon excitation S_0S_2 is forbidden at the equilibrium geometry and the excitation is therefore attributable to the Herzberg-Teller effect with the transition gaining strength from the mixing of valence character into the S_2 state. Inspection showed that within the envelope of the Wigner sampling, the character of the states remained separated, with the S_2 state corresponding to the $3p_x/V$ configuration, whereas the S_3 and S_4 states each involved a mixture of excitations to the $3p_y$ and $3p_z$ orbitals. This separation is confirmed by the distinctly different, excitation character dependent, dynamics displayed by the respective sets of trajectories. A very small sample (5 trajectories) was excited to the S_1 (3s) state at this energy. These are not considered further in the current analysis.

For the analysis, the trajectories were sorted according to initial state, allowing resolution of the dynamics into state specific components. A small portion (7% of the total) of trajectories undergo a retro-Diels-Alder reaction from NBD-like geometries after passing through the MECI geometry, yielding C_5H_6 and C_2H_2 fragments, but these were excluded from the analysis as the selected active space cannot describe the fragmentation pathway accurately. Molecular geometries were differentiated by the average carbon-carbon distance $r_{CC} = (r_{12} + r_{34})/2$ (atom numbers shown in Fig. 1), with QC-like geometries defined to have $r_{CC} < 2.0 \text{ \AA}$ and NBD-like geometries to have $2.0 \text{ \AA} < r_{CC} < 3.5 \text{ \AA}$.

Photoionization cross sections and energies were calculated by selecting a random time point in each 5-fs period within each trajectory. The squared Dyson norm⁴⁷ was calculated between the active state in the surface hopping and all ionic states, and used as an approximation to the photoionization cross-section. The method yields qualitatively lower cross-sections for valence states than for Rydberg states when compared to experiment so, for display purposes, the intensities in Fig. 4 (C) with $BE > 3 \text{ eV}$ have been multiplied by a factor of 3 (see further discussion in SI Section 2.3). The ionization potential difference between QC and NBD is roughly 0.3 eV with eV and eV (first value from present vertical calculations in Table 1 and second value from experiment [16], respectively).

Data availability

Data generated or analysed during this study are included in this Article (and its Supplementary Information). Source data are provided with this paper.

Code availability

The analysis codes used to generate the data presented in this study are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

Methods-only references

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Table of content summary:

Light-induced ultrafast switching between the molecular isomers norbornadiene and quadricyclane can reversibly store and release a significant amount of chemical energy. Two competing pathways have now been identified by which electronically excited quadricyclane molecules relax to the electronic ground state, facilitating interconversion between the two isomers on different timescales.