

Excited state non-adiabatic dynamics of the smallest polyene, *trans* 1,3-butadiene. I. Time-resolved photoelectron-photoion coincidence spectroscopy

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The ultrafast excited state dynamics of the smallest polyene, *trans*-1,3-butadiene, were studied by femtosecond time-resolved photoelectron-photoion coincidence (TRPEPICO) spectroscopy. The evolution of the excited state wavepacket, created by pumping the bright ${}^{1}B_{\mu}$ ($\pi\pi^{*}$) electronic state at its origin of 216 nm, is projected via one- and two-photon ionization at 267 nm onto several ionization continua. The results are interpreted in terms of Koopmans' correlations and Franck-Condon factors for the excited and cationic states involved. The known predissociative character of the cation excited states is utilized to assign photoelectron bands to specific continua using TRPEPICO spectroscopy. This permits us to report the direct observation of the famously elusive $S_1(2^1A_g)$ dark electronic state during the internal conversion of trans 1,3-butadiene. Our phenomenological analysis permits the spectroscopic determination of several important time constants. We report the overall decay lifetimes of the $1^{1}B_{u}$ and $2^{1}A_{g}$ states and observe the re-appearance of the hot ground state molecule. We argue that the apparent dephasing time of the $S_2(1^1B_u)$ state, which leads to the extreme breadth of the absorption spectrum, is principally due to large amplitude torsional motion on the ${}^{1}B_{u}$ surface in conjunction with strong non-adiabatic couplings via conical intersections, whereupon nuclear wavepacket revivals to the initial Franck-Condon region become effectively impossible. In Paper II [W. J. Glover et al., J. Chem. Phys. 148, 164303 (2018)], ab initio multiple spawning is used for on-the-fly computations of the excited state non-adiabatic wavepacket dynamics and their associated TRPEPICO observables, allowing for direct comparisons of experiment with theory. Published by AIP Publishing. https://doi.org/10.1063/1.5016452

I. INTRODUCTION

The canonical π - π^* transition in the linear polyenes is very widely studied because it leads to the process of cis-trans isomerisation. The electronic spectroscopy of linear polyenes began with the pioneering work of Hudson and Kohler¹ and is well understood.^{2–5} Polyenes typically have a bright state of ¹B character, prepared by the π - π^* HOMO to LUMO transition. The singly excited 1¹B state is typically very short lived and internally converts to the lower lying dark 2¹A state which has multireference character. This conversion of electronic to vibrational energy through conical intersections is the origin of the large amplitude vibrational motions which lead to cis-trans isomerisation.⁶ Ethylene, H₂C=CH₂, is the smallest molecule exhibiting cis-trans isomerisation upon π - π^* excitation. Its internal conversion dynamics involve H atom transfer, isomerization, and a twisted-pyramidalized (Tw-Py)

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conical intersection,^{7,8} a feature which also appears in the linear polyenes. Ethylene's ultrafast C=C dynamics represent a local chemical moiety, which we termed a dynamophore,⁹ wherein localized dynamics can occur in all unsaturated hydrocarbons. The excited state nuclear dynamics of linear polyenes can be characterized as a competition between (i) the Tw-Py dynamics at a single C=C double bond (localized dynamics) and (ii) the bond-alternation dynamics, preserving π -system delocalization which maintains planarity (delocalized dynamics). The latter process is related to the appearance of fluorescence in longer-chain polyenes and their reduced rates of internal conversion to the ground electronic state. The smallest linear polyene, trans-1,3-butadiene (BD), bridging the gap between ethylene and the longer polyenes, exhibits dynamical aspects of each. In Paper I and Paper II,¹⁰ we present detailed time-resolved photoelectron-photoion coincidence (TRPEPICO) spectroscopy and ab initio multiple spawning (AIMS) studies of the π - π ^{*} excited state dynamics of BD.

As discussed in Paper II,¹⁰ the electronic structure of BD has long presented computational challenges, with the relative ordering of its two lowest excited states—1¹B_u vs. 2¹A_g being a source of controversy. The most accurate ab initio computations predict a vertical excitation energy of 6.2 eV to the $1^{1}B_{\mu}$ state, characterized as the HOMO \rightarrow LUMO transition, and 6.4 eV to the dark, doubly excited 2^1A_g state.^{11–13} However, the 2¹A_g potential energy surface displays steep gradients along the bond-alternation and torsional coordinates, such that the putative minimum on this surface lies below that of the 1¹B_u state.^{14,15} This suggests the presence of conical intersections near the 1¹B_u Franck-Condon (FC) region in BD, consistent with the observed lack of fluorescence. This is in contrast to the longer polyenes wherein the dark doubly excited 2¹A electronic state lies below the bright ¹B state in the Franck-Condon region.

In Fig. 1, we present the previously recorded high resolution UV absorption spectrum of BD.¹⁶ The extreme breadth of the absorption band is immediately apparent, suggesting ultrafast dephasing. At the $1^{1}B_{\mu}$ origin, the peak at 216 nm (5.74 eV, dashed vertical line) has (from a fit to a sum of Lorentzians) a half-width at half-maximum (HWHM) of 377 cm⁻¹. This corresponds to a phenomenological Lorentzian dephasing time of about 14 fs, consistent with the lack of fluorescence. The dotted curve is a reflection of the red side spectral line shape through the 216 nm vertical, giving a sense of the apparent width of the absorption band. The extreme width of this origin band has been a focus of many prior theoretical studies.¹⁷ More recently, it was shown that the inclusion of out-of-plane modes is essential^{18,19} in order to model the observed width of the absorption spectrum. In the experiments described below, we pumped BD at its 1¹B_u origin with a fs UV pulse centred at 216 nm.



FIG. 1. The UV absorption spectrum of *trans*-1,3-butadiene in the region of its π - π * transition to the bright S₂ 1¹B_u state, modified from Ref. 16. The apparent origin is at 216 nm. Although a vibrational progression is seen, there is an extreme broadening of the UV transition due to ultrafast excited state dynamics. A fit to a sum of Lorentzians yields a width of 377 cm⁻¹ and a phenomenological lifetime of about 14 fs. The excited state dynamics generating this apparent broadening is a central subject in this paper, Paper I, and the following companion theory paper, Paper II.¹⁰

The excited state dynamics of BD following excitation to the 1^1B_u state has equally been a subject of much discussion. As summarized by Levine and Martinez²⁰ and the references therein, competing views struggled over many years as to whether BD was more ethylene-like (ionic/charge transfer, localized dynamics) or more polyene-like (covalent/radicaloid, delocalized dynamics). Using a balanced treatment of the $1^{1}B_{u}$ and $2^{1}A_{g}$ states, Levine and Martinez unified these competing views and showed that both mechanisms are active in BD. They found two conical intersection pathways from the $1^{1}B_{u}$ Franck-Condon region: one that involves the commonly accepted "covalent" bond-alternation coordinate, leading to the $2^{1}A_{g}$ state; the other, an "ionic" ethylene-like Tw-Py conical intersection which leads to the ground state.²⁰ The ultrafast decay of the bright state presumably involves both paths, but a quantitative determination of the branching would require still higher levels of electronic structure theory. The first direct measures of the $1^{1}B_{u}$ excited state used time-resolved mass spectrometry, pumping at 200 nm



FIG. 2. A depiction of the electronic states, π electron orbital occupancies, energetics, and Koopmans' correlations involved in the pump-probe photoelectron spectroscopy of excited state dynamics in trans-1,3-butadiene, C₄H₆. The $S_0(1^1A_g)$ ground state HOMO is a single configuration. Upon UV excitation, a π electron is promoted to the LUMO, forming the single configuration $S_2(1^1B_u)$ excited state. Due to ultrafast excited state non-adiabatic dynamics, the initial S_2 state rapidly internally converts to the lower lying $S_1(2 \ ^1A_g)$ state. The latter is comprised of three dominant configurations, two of which are doubly excited. The Koopmans' allowed photoionization correlations are as indicated: $S_2(1^1B_u) \rightarrow D_0(^2B_g) + e^-$ and $S_1(2^1A_g) \rightarrow D_1(^2A_u) + e^-$. Dynamics in the bright $S_2(1^1B_u)$ state are probed by single photon ionization, a (1 + 1') process producing the photoelectron band ε_1 . Dynamics in the dark $S_1(2 \ ^1A_g)$ state are probed by two photon ionization, a (1 + 2') process producing the photoelectron band ε_2 . Near the origin of the cation $D_1({}^2A_{\mu})$ state, a unimolecular fragmentation channel producing $C_3H_3^+ + CH_3$ is shown. As discussed in Appendix C, this means that ionizing transitions to the D₁ excited state will very likely be detected as a C₃H₃⁺ daughter ion.

TABLE I. Single photon orbital ionization channels and associated energies for BD.35

Neutral state	Orbital configuration	Energy (eV)
$S_0(1 \ ^1A_g)$	$(3a_g)^2 (3b_u)^2 (4a_g)^2 (4b_u)^2 (5b_u)^2 (5a_g)^2 (6a_g)^2 (6b_u)^2 (7a_g)^2 (1a_u)^2 (1b_g)^2$	0.00
Cation state	Ionization channel	
$\overline{D_0(^2B_g)}$	1bg ⁻¹	9.07
$D_1(^2A_u)$	$1a_u^{-1}$	11.39
$D_2(^2A_g)$	$7a_g^{-1}$	~12
$D_3(^2B_u)$	$6b_u^{-1}$	13.16
$D_4(^2A_g)$	$6a_g^{-1}$	~13.5
$D_5(^2A_g)$	$5a_g^{-1}$	15.17
$D_6(^2B_u)$	$5b_u^{-1}$	~15.7

and probing via non-resonant multiphoton ionization, estimated a 35 fs lifetime for the 1^1B_u state²¹ and a subsequent multi-component sub-100 fs decay process.²² A time-resolved multi-dimensional (time-, energy-, angle-resolved) coincidence imaging spectroscopy study of BD excited at 200 nm revealed further details.²³ Here we apply the time-resolved photoelectron spectroscopy (TRPES) method, a powerful probe of ultrafast excited state non-adiabatic dynamics in polyatomic molecules.^{24–31} Although not related to 1^1B_u dynamics, two-photon excitation of BD—which directly prepares the dark 2^1A_g state—was previously studied using TRPES.^{32,33}

In Fig. 2, we present the energy level scheme and π orbital occupations for the TRPEPICO experiments reported here. The singly excited S₂ 1¹B_u state was pumped by a fs pulse at 216 nm (5.75 eV) to its vibronic origin. It undergoes ultrafast non-adiabatic processes which include the doubly excited S₁ 2¹A_g state, itself subsequently returning on ultrafast time scales to the S₀ 1¹A_g ground state with high internal energy. The highly transient S₁ 2¹A_g state has never been directly detected during internal conversion. As described below, we probed these processes via time-resolved photoionization using a fs 267 nm pulse.

As discussed in Appendix B, Koopmans' ionization correlations for BD are completely analogous to those in the four C=C linear polyene 2,4,6,8-decate traene (DT).³⁴ Specifically, as shown in Fig. 2, the $S_2 1^1 B_u$ state correlates with the $D_0 {}^2 B_g$ cation ground state, whereas the $S_1 2^1 A_g$ correlates with the $D_1 {}^2A_u$ cation first excited state. As in the previous study of decatetraene,³⁴ the S_2 1¹ B_u state is probed via single photon (1 + 1') photoionization, whereas the S₁ 2¹A_g state is probed via two-photon (1 + 2') photoionization. The single photon ionization valence shell photoelectron spectrum of BD was previously studied in detail.³⁵ Shown in Table I are the orbital configurations, single photon Koopmans' ionization channels, and cation state energies for BD. At our total (1 + 2') photon energy of 15.0 eV, the D_0-D_4 cation states are vertically accessible from the BD ground state. Due to geometric distortions in excited states, the D₅ state may become adiabatically accessible via (1 + 2') ionization.

Importantly, the $D_1 {}^2A_u$ cation state is unstable with respect to unimolecular decay, with an energetic threshold shown by the red dashed line in Fig. 2. It undergoes

spontaneous methyl elimination to yield the $C_3H_3^+$ daughter ion.³⁶ As discussed in Appendix C, the internal energy dependence of fragmentation pathways of BD cations was previously studied in detail^{36–39} using single photon ionization Photoelectron-Photoion Coincidence (PEPICO) spectroscopy, yielding appearance energies (AEs) and breakdown curves for the ion fragments involved. The observed fragmentation channels and AEs are given in Table II.

Comparing Tables I and II, it is seen that photoionization to the (vibrationally excited) $D_1^2 A_u$ cation state will be correlated with the appearance of the $C_3H_3^+$ daughter ion. This indicates, as discussed in detail below, that TRPEPICO measurements will be helpful in clarifying the time-resolved photoelectron spectra of BD excited state dynamics.

In Fig. 3, we present a cartoon which conceptually illustrates the expected initial vibrational motions, C—C twist and C—C stretch, on the UV pumped $S_2 \ 1^1B_u$ state. Shown on the right are molecular models of the planar S_0 ground state and the twisted (upper) and pyramidalized (lower) geometries associated with the excited states. Time- and energy-resolved photoionization (TRPES) to the Koopmans' correlated D_0 cation ground state should thus be sensitive to the excited state vibrational motions on the $S_2 \ 1^1B_u$ potential, via the time evolution of the D_0 photoelectron spectrum.

This paper is organized as follows. We first present a detailed description of the pulsed molecular beam TRPEPICO experiment, based on a large bore permanent magnet bottle dual time-of-flight (TOF) design, and the fs laser systems

TABLE II. Observed fragmentation channels and appearance energies for single photon ionization of BD.^{35,38,39} The channels are labeled as to their temporal Group (*vide infra*, Fig. 7).

Parent ion	Fragmentation channel	Appearance energy (eV)	Group
	\rightarrow C ₄ H ₅ ⁺ (53 amu) + H	11.72	(b)
	\rightarrow C ₄ H ₄ ⁺ (52 amu) + H ₂	13.11	(b)
	$\rightarrow C_4 H_3^+ (51 \text{ amu}) + H_2 + H$	15.2	(c)
C ₄ H ₆ ⁺ (54 amu)	\rightarrow C ₃ H ₃ ⁺ (39 amu) + CH ₃	11.50	(b)
	\rightarrow C ₂ H ₄ ⁺ (28 amu) + C ₂ H ₂	12.44	(b)
	\rightarrow C ₂ H ₃ ⁺ (27 amu) + C ₂ H ₂ + H	15.1	(c)
	$\rightarrow C_2 H_2^+$ (26 amu) + $C_2 H_2$ + H_2	15.1	(c)



FIG. 3. A cartoon of the excited state motions expected to be involved in the excited state dynamics of planar *trans*-1,3-butadiene, excited to its bright $S_2(1^1B_u)$ state. This $\pi - \pi^*$ transition reduces the bond order in the excited state, leading to a stretching and large amplitude twisting about the C–C bonds. Twisting in the excited state also leads to conversion of the originally *sp*² hybridized C atoms to *sp*³, leading to a pyramidalization of the C–H bonds. These two motions (twisting and pyramidalization) are shown by the ball-and-stick figures in the excited states. Upon twisting, the system encounters a conical intersection with the dark $S_1(2^{-1}A_g)$ state, leading to an ultrafast non-adiabatic transition.

employed. In Sec. III, we describe our data analysis methods and their limitations, particularly when large amplitude motions are involved. We then present our experimental timeresolved mass spectrometry, TRPES, and TRPEPICO results for BD excited at 216 nm. These are discussed and compared in detail, and our phenomenological conclusions are presented. We report the first direct observation of the elusive dark S₁ 2^{1} A_g state of BD. We also consider, using a simple model, the excited state motions responsible for the extreme width of the BD UV absorption spectrum. In the following theory Paper II,¹⁰ we present detailed AIMS simulations of both the excited state non-adiabatic dynamics and, importantly, the experimental TRPES and TRPEPICO spectra. These reveal details of the ultrafast dynamical processes occurring in the excited state dynamics of the smallest linear polyene, 1,3-butadiene.

II. EXPERIMENTAL

We describe our femtosecond time-resolved PEPICO magnetic bottle spectrometer experiments. Femtosecond laser pulses were obtained from a fs Ti:sapphire regenerative

amplifier (Coherent, Legend, 800 nm). Part of the output (~700 μ J) was used for harmonic generation to produce 267 nm laser pulses. A second part (~700 μ J) was used to pump a travelling wave optical parametric amplifier system (TOPAS) (Light Conversion) system. The idler from the TOPAS was doubled in a β -barium borate (BBO) crystal and sum-frequency mixed with 800 nm (~460 μ J) pulses in a second BBO crystal. The resulting sum frequencies were then doubled in a third BBO crystal to generate 216 nm. The fs UV pulses were individually recompressed using vacuum ultraviolet (VUV) grade CaF₂ prism pairs, combined collinearly on a dichroic mirror, and then gently focused using an f/250 spherical reflective Al mirror to intersect a seeded molecular beam in the interaction region of a novel magnetic bottle PEPICO spectrometer, shown in Fig. 4 and described below. Typical pulse energies were ~ 25 nJ for the 216 nm pump and $\sim 1.5 \mu$ J for the 267 nm probe. Time delays between pump and probe pulses were scanned using a computer-controlled stepper motor. The temporal cross correlation (CC) between the 216 nm ($hv_1 = 5.74 \text{ eV}$) and 267 nm $(hv_2 = 4.64 \text{ eV})$ fs pulses was 155 ± 10 fs, determined in situ using (1 + 1') photoionization of nitric oxide (NO). This also served to determine the photoelectron kinetic energy calibration. The cross correlation for a (1 + 2') photoionization process was 130 ± 10 fs. Approximately 1% trans 1,3-butadiene (BD, Matheson, 99.9%) seeded in 1 bar helium was expanded continuously through a 100 μ m pinhole. The 216 nm fs pump pulse excited the molecules from their ground state into the optically bright S_2 ¹ B_u state, whereupon the delayed fs 267 nm probe pulse produced photoelectrons via one-photon or twophoton probe ionization. The accepted ionization potential (IP) of *trans* 1,3-butadiene is $9.072 \pm 0.007 \text{ eV}$.⁴⁰ For (1 + 1') photoionization, the total photon energy (hv_1+hv_2) was 10.37 eV, an excess energy of 1.30 eV above the IP. For (1 + 2') photoionization, the total photon energy (hv_1+2hv_2) was 15.0 eV, an excess energy of 5.93 eV above the IP. Photoelectron spectra arising from the pump and probe laser pulses at negative time delays (i.e., probe preceding the pump) were subtracted in order to correct for background photoelectrons generated from single color multiphoton ionization. Pump-probe time delays were scanned 155 times and co-added so as to minimize any small effects due to temporal and/or spatial laser drift.

Our molecular beam ultrahigh vacuum PEPICO spectrometer (P < 5×10^{-10} mbar) was built around a large bore 20pole permanent magnet "magnetic bottle" design. As seen in Fig. 4, there are two collinear time-of-flight (TOF) spectrometers: a 30 cm TOF for photoelectrons [electron time-of-flight (e-TOF) for electron energy resolution] and a 50 cm TOF for photoions (i-TOF Wiley-McLaren design, for ion mass resolution), allowing for simple PEPICO and ion-electron covariance measurements. The large bore (0.75 cm ID) magnetic bottle design was based on magnetic field simulations using the Los Alamos Accelerator Code Group's finite element package "Poisson Superfish."⁴¹ The twenty individual rectangular bar magnets (gray rectangles) were Ni-coated Nd-Fe-B (Sumitomo NEOMAX 38 VH) with dimensions $5 \times 5 \times 30$ mm and magnetization direction along the radial 5 mm dimension. In our design, these twenty radially magnetized bar magnets were mounted vertically and distributed evenly around a 1 cm



FIG. 4. A depiction of the Photoelectron-Photoion Coincidence (PEPICO) apparatus used in these experiments. A molecular beam introduced cold BD molecules to the interaction region of a dual time-of-flight (TOF) magnetic bottle PEPICO spectrometer. Photoelectrons are collected along the e-TOF, yielding the energy-resolved photoelectron spectrum, whereas coincident ions are collected along the i-TOF, yielding the mass spectrum. The PEPICO spectrum is recorded as a function of the femtosecond pump-probe time delay Δt . For a detailed description of the permanent magnet large bore bottle, see the text.

bore cylindrical cone soft iron (Fe) core (inner cone, lined dark blue) which strongly focused the magnetic field to 0.2 T at the top of the magnet unit. A solenoidal coaxial field (10 G) was applied along the 30 cm e-TOF tube, completing the "bottle" and thereby guiding the electrons toward their detector. An outer steel core (large outer cylinder, lined light blue) served to further increase the divergence of magnetic field lines at the laser-molecule interaction point, located 4.5 mm above the magnet unit. The interaction point was chosen to be just beyond the field maximum, on the "downhill" slope of the magnetic field gradient. This is the so-called "magnetic mirror" mode which serves to collect a very large solid angle (in this design, 80%) of emitted electrons (green trajectory) at the expense of slightly poorer energy resolution. The magnetic field line distribution was experimentally measured using a SENIS (Baar, Switzerland) magnetic field Hall transducer. As can be seen in Fig. 5, the measured magnetic field closely matches that of the simulation. At the laser interaction point, the field strength is 0.175 T and the field gradient has a *l/e* length of 10 mm. Importantly, our design has a relatively large and uniform collection volume (~2 mm diameter) for photoelectrons and a large 0.75 cm ID open bore for collection of photoions in the opposite direction. A 1 mm wall thickness Mu-metal cylinder (Magnetic Shield Corp., 1000x field reduction) shielded the e-TOF from stray external magnetic fields. The photoelectrons pass through two homemade 98% open area gold wire (20 μ m ϕ , 2 × 2 mm grid)

meshes (dotted light blue lines) before entering the e-TOF. A 92% open area gold-coated Cu mesh (Buckbee-Mears) is in



FIG. 5. Measurement of the axial (black squares) and radial (arrows) variation of the magnetic field (B) for the magnetic bottle shown in Fig. 4. The maximum field strength is 0.2 T. A full simulation of the B field is shown, for the axial direction, as a solid line. The agreement is good. The dashed horizontal line, indicating the laser axis from where the photoelectrons originate, is located 4.5 mm above the magnet face. This is downhill from the field maximum, meaning that the bottle spectrometer is operated in the magnetic mirror mode which enhances collection efficiency. At the interaction point, the field strength is 0.175 T and the field gradient has a 1/e length of 10 mm. For details, see the text.

front of the 40 mm OD triple-stack MCP detector (Burle): the measured overall photoelectron detection efficiency was 40% for kinetic energies up to 5 eV. The measured kinetic energy resolution, determined via (1 + 1') photoionization of NO, was $\Delta E/E = 0.16$ at 1 eV.

Referring again to Fig. 4, once all photoelectrons have passed both 98% transmission grids (~185 ns after ionization) and are drifting along the e-TOF, a +0.5 kV pulse is applied to the middle grid (the upper grid, the entrance to the e-TOF, remained grounded, thereby shielding the drifting photoelectrons from the ion extraction voltage pulse), pushing the photoions (red trajectory) toward the magnet bore and the i-TOF. A cylindrical semiconductor tube (purple) provides, in a meshless and uniform manner, the second electric field gradient required for the Wiley-McLaren space-focusing condition. The drift tube was typically floated at +2 kV. Beneath this, a half-cylindrical deflection plate (steel blue, voltage V) removes the transverse molecular beam velocity component of the photoions and an Einzel lens (not shown) further down the 50 cm i-TOF focuses ion trajectories (red) onto a second 40 mm OD triple-stack MCP detector (Burle). The measured overall photoion collection efficiency was 37%. The TOF mass resolution was measured to be $\Delta M = 1$ amu at 100 amu.

III. DATA ANALYSIS

Often, in the analysis of TRPES data $S(\varepsilon_k, t)$, a 2D global least-squares method (e.g., Levenberg-Marquardt) is employed to fit all photoelectron kinetic energies ε_k and time delays *t* simultaneously. Thus, the $S(\varepsilon_k, t)$ surface is globally fitted to

$$S(\varepsilon_k, t) = g(t) \otimes \sum_i D_i(\varepsilon_k) e^{-t/\tau_i},$$
(1)

where the $D_i(\varepsilon_k)$ are the time independent decay associated spectra (DAS), the energy-resolved amplitudes of fit components having time constants τ_i . The convolution with g(t), the Gaussian cross-correlation function, accounts for the instrumental response. A given $D_i(\varepsilon_k)$ is related to the energy-resolved photoionization cross section $\sigma_i(\varepsilon_k)$ of the *i*th state.

Importantly, there is a critical assumption underlying such 2D global fitting. It is that the $D_i(\varepsilon_k)$ are themselves timeindependent in *form* and only their contribution (amplitude) varies with time. Physically, this demands that the Franck-Condon spectrum associated with the dynamical behavior of a given state remains "frozen" during the kinetics. In other words, the excited state molecular structure is nearly frozen (i.e., small amplitude motions) during the dynamics of state *i* but appears as a different, nearly frozen, structure for the dynamics of state j. As detailed previously, 2D global fitting gives meaningful results if the molecules do not undergo rapid large amplitude motions in the excited state.^{42,43} Large amplitude deformations of the molecular frame will, typically, cause the instantaneous vertical IP to vary during such dynamics, as Franck-Condon factors will typically force transitions to increasingly higher-lying vibrational states of the cation as a function of time. Since, in BD, the excited neutral and cation ground state potentials are anti-parallel along these

large amplitude coordinates (e.g., torsion), the Franck-Condon envelope of a given channel will "sweep" toward lower ε_k as a function of time and, therefore, 2D global fitting may not yield physically meaningful results. There are, however, ways to mimic this effect within a 2D global fitting framework. The "time zero" is normally fixed to be the centroid of the Gaussian cross-correlation function g(t). We previously employed a phenomenological method to account for rapid large amplitude motions by allowing the "time zero" of the fitting routine to be a free variable.⁹ The variation of the "time zero" fit parameter as a function of ε_k can be used as a phenomenological measure of large amplitude motion in the excited state. This is discussed in more detail in Sec. IV D.

In the present case of BD, as discussed in detail in Sec. IV, we did observe a significant and rapid sweep of ε_k toward lower energy within a given photoelectron band (specifically, that associated with the initial S₂ state). For BD, 2D global fitting fails in a specific region of the TRPES spectrum. In the following companion paper (Paper II),¹⁰ we present full *ab initio* simulations of the non-adiabatic dynamics in the excited states and the calculation of time-resolved observables (i.e., TRPES, TRPEPICO) from these dynamics in order to directly compare experiment with theory. Nevertheless, we employ here the floating "time zero" method discussed above in order to characterize phenomenological aspects of large amplitude motions in the excited states of BD: these are discussed in Sec. IV.

IV. RESULTS AND DISCUSSION

A. Time-resolved mass spectrometry

In Fig. 6, we present time-resolved mass spectra (TRMS) for pump-probe photoionization of excited state dynamics in BD. The $C_4H_6^+$ parent ion mass is 54 amu. The small mass peak at m/e = 55 is due to the 1% natural abundance of ¹³C. It can be seen that there are hydrogen loss channels (m/e = 50-53), methyl (m/e = 39), and further hydrogen loss



FIG. 6. Time-resolved mass spectra for BD pumped at 216 nm and probed at 267 nm. The parent ion, $C_4H_6^+$ (m/e = 54), is seen to rise promptly and decay very rapidly. Various fragmentation channels are seen in the mass spectrum. In the $C_4H_n^+$ region, H atom loss channels are seen. In the $C_3H_n^+$ region, a dominant methyl loss channel, producing $C_4H_3^+$ (m/e = 39), is seen and is delayed with respect to the parent ion. Various fragments seen in the $C_2H_n^+$ region, such as $C_2H_3^+$ (m/e = 27), are also delayed with respect to the parent ion. For details, see the text.

(m/e = 36-38) channels, and a group associated with the loss of two carbon atoms (m/e = 26-28). Two fragments, $C_3H_3^+$ (m/e = 39) and $C_2H_3^+$ (m/e = 27), are highlighted for reasons discussed below. It can be seen that, relative to the parent ion signal (m/e = 54), the other mass channels are delayed and have varying time dependencies. We have observed that these time-dependences fall into three distinct groups, shown in Fig. 7. The first group, (a), containing the $C_4H_6^+$ (m/e = 54) parent ion alone, is shown as the blue trace. All other signals are delayed with respect to this. The second group, (b), exemplified by $C_3H_3^+$ (m/e = 39, black trace), also contains the following fragment ions: $C_4H_5^+$ (m/e = 53), $C_4H_4^+$ (m/e = 52), and $C_2H_4^+$ (m/e = 28). The third group, (c), exemplified by $C_2H_3^+$ (m/e = 27, purple trace), also contains the fragment ions $C_4H_3^+$ (m/e = 51) and $C_2H_2^+$ (m/e = 26). It can be seen that all fragment ion channels show a non-zero signal (offset) persisting out to long time delays (exceeding the time range of the experiment): the ratio of this offset to the transient peak is significantly larger for group (c).

The time dependence of each group is non-trivial and requires fitting with both rising and decaying exponential components in order to adequately represent these data. Due to the intuitive expectation that the excited state dynamics follow a sequential $S_2({}^1B_u) \rightarrow S_1(2 {}^1A_g) \rightarrow S_0(1 {}^1A_g)$ mechanism and that the groups (a)–(c) in Fig. 7 appear sequentially, we employed a sequential kinetic model for a global fit to the data. Due to the time-dependences seen in groups (a)–(c) and the significant long-time offset observed in group (c), it is tempting to associate group (a) with the decay of the initially prepared $S_2({}^1B_u)$ state, group (b) with the formation and subsequent decay of the $S_1(2 {}^1A_g)$ state, and group (c) offset with the final appearance of the "hot" $S_0(1 {}^1A_g)$ ground state "product."



FIG. 7. Normalized time-dependence of the mass spectra shown in Fig. 6. These are arranged into three groups according to their time-dependence. Group (a) contains only the parent ion $C_4H_6^+$ (m/e = 54). It rises with the laser cross correlation and decays very rapidly, with no offset at long time delays. Group (b) contains four fragment ions, of which $C_4H_3^+$ (m/e = 39) is a prominent member, and has a clearly delayed rise with respect to Group (a). The group (b) channels also decay rapidly and have a long time delay offset. Finally, the group (c) channels contain three fragment ions, of which $C_2H_3^+$ (m/e = 27) is an example, and are even further delayed and have an even larger long time delay offset. This type of behavior is suggestive of a sequential kinetic mechanism: (a) \rightarrow (b) \rightarrow (c). The offsets seen in groups (b) and (c) at long time delays are due to dissociative photoionization (into several channels) of the "hot" ground state neutral subsequent to its internal conversion.

As will be discussed in a Sec. IV C (see Fig. 10 and associated discussion), the reason why both group (b) and group (c) ions have a long time offset is because the "hot" ground state neutral formed by internal conversion can undergo dissociative photoionization into both of these fragment ion groups. The time evolution of the initial parent ion into group (b) and then to group (c) fragment ions shown in Fig. 7 is suggestive of a sequential mechanism. The results of a fit to a sequential model $S_2(^1B_u) \rightarrow S_1(2^1A_g) \rightarrow S_0(^1A_g)$ yielded estimated lifetimes. The fit determined that group (a) can be uniquely assigned to the decay of $S_2(^1B_u)$, whereas groups (b) and (c) each have contributions from both $S_1(2 \ ^1A_g)$ and $S_0(1 \ ^1A_g)$. The decay time of the initial $S_2(^1B_u)$ state was found to be 28 \pm 10 fs, the lifetime of the intermediate S₁(2 ¹A_g) dark state was found to be 31 ± 10 fs, and the long lifetime (apparent offset) of the "hot" ground state was represented by a time constant of 10 ps. As detailed in Appendix A, we believe that it is difficult to develop an unambiguous mechanism for the excited state wavepacket dynamics in BD based on ion yields alone. As discussed in Sec. IV C, TRMS alone cannot distinguish two pathways: (i) ionization to a cation excited state followed by spontaneous fragmentation, from (ii) ionization to the cation ground state followed by photofragmentation of the ion. An example of the latter would be a (2 + 1') channel where two-photon ionization of the neutral ground state by the pump laser is subsequently fragmented by the probe laser. These two pathways can produce the same fragment ion, and a TRPES or TRPEPICO measurement is required to disentangle them. In our experiments, the pump laser fluence was reduced to the extent that two-photon ionization of the neutral ground state was negligibly small. More generally, we previously showed that in some cases TRMS can be very misleading²⁹ and may only be properly re-interpreted once the more differential TRPES measurements are known. Therefore, although there is clear evidence for a sequential mechanism, the fitted values of the TRMS time constants cannot be considered as quantitative and we do not report them as being the lifetimes of the states involved. In Secs. IV B and IV C, we investigate the use of more differential probes, specifically TRPES and TRPEPICO.

B. Time-resolved photoelectron spectroscopy

In Fig. 8, we present TRPES spectra for BD (under the same conditions as for TRMS). In Fig. 8(a), we show the full photoelectron kinetic energy spectrum out to 10 ps delay, using a time axis which is linear up to 1 ps and then logarithmic from 1-10 ps. In the following, we will use the adiabatic state labels S_2 , S_1 , and S_0 for notational convenience. The energetic thresholds for various processes are indicated by dashed lines. The energy limit for (1 + 1') processes is 1.30 eV (red line) above the D_0 origin (adiabatic IP). The energy limit for (1 + 2') processes is 5.93 eV (red line) above the D_0 origin. The (1 + 2') transition which leaves the ion in its electronically excited D_1 state has an energy limit of 3.61 eV (green line). For later reference, the dissociative ionization channel forming the $C_3H_3^+$ fragment has an energy threshold of 2.4 eV (grey line) with respect to the (1 + 2') energy limit.

The TRPES of Fig. 8 reveals the key features of excited state dynamics in BD. Figure 8(b) shows the same data as in



FIG. 8. Time-resolved Photoelectron Spectroscopy (TRPES) of BD pumped at 216 nm and probed at 267 nm. The time axis is linear in the -0.5-1.0 ps range and logarithmic in the 1-10 ps range. (a) The red dashed vertical line (1.30 eV) indicates the energetic limit for (1 + 1') photoionization. In this region, only the ion ground state $D_0(^2B_g) + e^-$ channel is open. The red dashed vertical line at 5.93 eV indicates the energetic limit for (1 + 2') photoionization to the $D_0(^2B_g)$ state. The energetic limit for forming the ion $D_1(^2A_u)$ electronically excited state, via a (1 + 2') process, is shown as the green dashed vertical line (3.61 eV). At 2.40 eV above the IP [the $D_0({}^2B_g)$ origin], a unimolecular fragmentation channel producing $C_3H_3^+ + CH_3$ becomes open, as shown in Fig. 2. This fragmentation channel is only accessible for a (1 + 2') process. The black dashed vertical line indicates the threshold for this channel, shifted by 2.40 eV relative to the (1 + 2') energy limit at 5.93 eV. (b) The data from (a) are replotted with a logarithmic intensity scale, revealing all contributions to the TRPES signals. (c) A 2D global fit to a sequential kinetic model $S_2 \rightarrow S_1 \rightarrow S_0$ describes the data very well. The expected Koopmans' correlations $S_2(1^1B_u) \rightarrow D_0(^2B_g)$ and $S_1(2^1A_g) \rightarrow D_1(^2A_u)$ are clearly reflected in these data, supporting the assignments. For details, see the text.

Fig. 8(a) but now with a logarithmic photoelectron intensity scale, revealing all large and small amplitude photoionization channels in one plot. We first discuss the energy region below the 1.30 eV (1 + 1') limit. We recall that the D₁ electronic origin is 2.32 eV above the IP. Therefore, in this region, only the D₀ ground state is energetically accessible. As illustrated by the orbital occupancy drawings in Fig. 1, the bright S₂(1¹B_u)

state is a single configuration which corresponds to a canonical $\pi\pi^*$ HOMO \rightarrow LUMO excitation. By contrast, the dark $S_1(2^{1}A_g)$ state contains multireference character (Fig. 2), with three approximately equal contributions from HOMO \rightarrow LUMO+1 (left configuration), HOMO-1 \rightarrow LUMO (middle configuration), and a $(\pi^*)^2$ double (right configuration) excitation. The electronic configurations of the cation are also shown in Fig. 2 (see also Table I) where it can be seen that the expected Koopmans' correlations are $S_2(1^1B_u) \rightarrow D_0(^2B_g) + e^-$ and $S_1(2^{1}A_g) \rightarrow D_1(^2A_u) + e^-$. We therefore assign this prompt (i.e., rising at $\Delta t = 0$) photoelectron band, which has an energy cut-off exactly where expected for $(1 + 1') S_2 \rightarrow D_0$ ionization, to the excited state dynamics of the initially prepared $S_2(1^1B_u)$ state.

In the energy region between 1.30 and 3.61 eV, there appears a delayed rise photoelectron band which has an energy cutoff exactly where expected for $(1 + 2') S_1 \rightarrow D_1$ ionization. We therefore assign this photoelectron band to the excited state dynamics of the dark $S_1(2 \ ^1A_g)$ state which appears following internal conversion of the initially prepared $S_2(1^1B_u)$ state. This assignment is further supported by arguments present in the following paragraph. It can be seen that the 3.6 eV photoelectron band also decays rapidly, as would be expected for an intermediate configuration in a sequential kinetic process.

As discussed in Appendix B, there are parallels in the ionization dynamics of the two double-bonded BD with the previously studied four double-bonded polyene *all trans* 2,4,6,8decatetraene (DT).³⁴ This strongly supports our assignment that the (1 + 1') band corresponds to the $S_2(1 \ {}^1B_u) \rightarrow D_0 + e^$ channel and the (1 + 2') bands corresponds to the $S_1(2 \ {}^1A_g)$ $\rightarrow D_1 + e^-$ channel. Therefore, based on the above, we claim to have directly detected and determined the lifetime of the famously elusive dark $S_1(2 \ {}^1A_g)$ during the internal conversion of BD.

In Fig. 8(c), we present the results of 2D global fitting (as described in Sec. III) to the experimental data of Fig. 8(a). It can be seen that, using a sequential kinetic model $S_2 \rightarrow S_1 \rightarrow S_0$, 2D global fitting reasonably describes the data. The quality of the fit is good and the essential dynamic features—the rapid decay of S_2 , the growth and then rapid decay of S_1 and, finally, the appearance of the "hot" S_0 ground state—are captured by this analysis. The 2D fit yields a (98% confidence interval) lifetime of 23 ± 4 fs for the bright $S_2(1 \ {}^1B_u)$ state and 42 ± 4 fs for the dark $S_1(2 \ {}^1A_g)$ state. We note that these values are in statistical agreement with the corresponding fits to the ion yields discussed above.

In Fig. 9, we present an expanded view of Figs. 8(a) and 8(c), focussing on the low energy region corresponding to (1 + 1') photoionization of S₂. In the upper left panel, we show the experimental data, whereas in the lower left panel we show the 2D global fit. Even in this expanded view, the quality of the fit seems good. However, on the right side of Fig. 9, we plot the residuals of the 2D fit (experiment minus fit). The red indicates a positive value, and the blue indicates a negative value. It can be seen that the fit errors are not statistically distributed in this (1 + 1') region. We note that the 2D global fit residuals in all other regions (not shown) are of very high quality and show no statistical bias. Therefore, there is a clear systematic



FIG. 9. Details of 2D global fitting to the data from Fig. 8(a), emphasizing the short time dynamics (0–200 fs) probed by the $S_2(1^1B_u) \rightarrow D_0(^2B_g)$ transition (0–1.3 eV). Linear time and intensity scales are used. The fit residuals, shown right, indicate a systematic error where red indicates positive (blue negative) residuals. Importantly, the fit residuals throughout the rest of the 2D fit regions show no systematic deviations. As discussed in the text, the observed deviation is due to large amplitude motion in the initial $S_2(1^1B_u)$ state which is not captured by 2D global fitting models.

error in the 2D global fit in the lowest energy (1 + 1') range. Specifically, at longer time delays, the fit does not capture the rising signal. As discussed above, this is due, to the fit constraint that the decay associated spectra are time independent. The systematic error seen in Fig. 9 (right) indicates that this fails to some degree and that there is a tilt of the S₂ photoelectron spectrum toward lower kinetic energy with time. This is a clear indication that there is rapid large amplitude motion in the Franck-Condon region of the bright S₂(1 ¹B_u) state. This tilt of the S₂ photoelectron spectrum, the large amplitude motion associated with it, and the relation of these to the apparent breadth of the UV absorption spectrum are discussed in Sec. IV D.

C. Time-resolved PEPICO spectroscopy

In Fig. 10, we present TRPEPICO spectra for BD (under the same conditions as for TRPES). In Fig. 10(a), we present the total (uncorrelated) electron kinetic energy spectrum out to 10 ps delay, using a linear time axis for 0-1 ps and logarithmic time axis for 1-10 ps, and a linear photoelectron intensity scale. These are the same data presented in Fig. 8(a) and correspond to all photoelectrons irrespective of which photoion they are coincident with. For Figs. 10(b)-10(d), the time axis is linear, emphasizing the short time scale dynamics. In Fig. 10(b), we show the TRPEPICO spectrum for electrons coincident with the $C_4H_6^+$ parent ion [group (a) of Fig. 7]; in Fig. 10(c), the spectrum coincident with the $C_3H_3^+$ fragment ion [in group (b) of Fig. 7]; and in Fig. 10(d), for the $C_2H_3^+$ fragment ion [in group (c) of Fig. 7]. Shown are the kinetic energy limits for (1 + 1') ionization to D₀ at 1.3 eV (red dash) and for (1 + 2') ionization to D_1 at 3.6 eV (green dash). The dissociative ionization channel forming the $C_3H_3^+$ fragment³⁸ has an (1 + 2') energy threshold of 3.5 eV (gray dash): in other words, (1 + 2') photoelectrons with kinetic energy less than 3.5 eV will lead to parent ion fragmentation, forming $C_3H_3^+$, but with a rate that depends on internal energy.

In Fig. 10(b), we show the TRPEPICO spectrum for photoelectrons coincident with the $C_4H_6^+$ parent ion. The dominant band has a sharp cutoff at 1.3 eV (red dash). As discussed above, this is assigned to the $S_2(1 \ {}^1B_u) \rightarrow D_0$ channel and

therefore probes the excited state dynamics of the initially prepared ${}^{1}B_{u}$ state. Since C₄H₆⁺ is stable at internal energies below 1.3 eV, this channel is detected as the parent ion. It can be seen that this channel rises promptly at $\Delta t = 0$ and rapidly decays with a lifetime matching that obtained from the data of Fig. 8. Also observed in Fig. 10(b) is a much weaker photoelectron band with an energy cutoff at the $(1 + 2') D_1$ threshold of 3.6 eV. Due to the sharp cutoff at 3.6 eV, we assign this channel to (1 + 2') ionization of the dark $S_1(2^{-1}A_{\sigma})$ state. Supporting this assignment, it can be seen that this channel is delayed in time relative to the $S_2(1 \ ^1B_u)$ channel. The rise time of the small band near 3.6 eV matches that expected from the sequential kinetic model fit to the data of Fig. 8. It can be seen in Fig. 10(b) that the grey dashed line, which indicates the lowest energy threshold for parent ion fragmentation (forming $C_3H_3^+$) is just below the D_1 origin. This means that BD ions formed at the D_1 origin will not fragment and must therefore arrive at the i-TOF detector (see Fig. 4) as the parent ion. Concomitantly, parent ions with more internal energy (i.e., electrons slower than $\sim 3.1 \text{ eV}$) should fragment and therefore cannot be detected as the parent ion. As detailed in Appendix C, this "transition region" between parent ion and fragment ion detection is shown as a purple dashed line in Fig. 10. It can be seen that the coincident parent ion signal in Fig. 9(b) "fades" in quite reasonable agreement with this estimate. These arguments further support our assignment of the 3.6 eV photoelectron band as being due to the $S_1(2^1A_g) \rightarrow D_1$ channel.

In Fig. 10(c), we show the TRPEPICO spectrum for photoelectrons coincident with the $C_3H_3^+$ fragment ion. There are two regions of interest, one below 1.3 eV (red dash) and the other below 3.6 eV (green dash). We discuss the higher energy region first. This photoelectron band is delayed with respect to the S₂ band seen in Fig. 10(b) and has a rise time matching the S₁ photoelectron band of Fig. 10(b). It also has a rise time and decay matching, quantitatively, that of the S₁ band of Fig. 8. Interestingly, this band has an energy onset *not* at the 3.6 eV (green dash) limit expected for the S₁(2⁻¹A_g) \rightarrow D₁ channel but, rather, at lower energy, approximately at the "transition region" energy (purple dash) discussed in the paragraph above. Ions associated with photoelectrons above the purple line will be detected as the C₄H₆⁺ parent ion [Fig. 10(b)]. However,



FIG. 10. Time-resolved Photoelectron-Photoion Coincidence Spectroscopy (TRPEPICO) of BD pumped at 216 nm and probed at 267 nm. In (a), the time axis is linear in the -0.5-1.0 ps range and logarithmic in the 1-10 ps range, whereas in (b)-(d) a linear time axis is used in the -0.5-0.6 ps range. A linear intensity scale is used throughout. The red dashed line (1.3 eV) indicates the energetic limit for $(1 + 1') S_2(1^1B_u) \rightarrow D_0(^2B_g)$ photoionization. The green dashed line (3.6 eV) indicates the energetic limit for $(1 + 2') S_1(2^{-1}A_g) \rightarrow D_1(^2A_u)$ photoionization. The black dashed line (3.5 eV) indicates the threshold of the unimolecular decay channel $C_4H_6^+ \rightarrow C_3H_3^+ + CH_3$ (for which the decay rate is internal energy dependent). The purple dashed line (3.15 eV) indicates the $C_4H_6^+$ cation internal energy at which the parent cannot survive the ~200 ns transit time in the Wiley-McLaren extraction region (see Fig. 4). Electron kinetic energies below this value mean that the parent ion fragments in the extraction region and must be detected as $C_3H_3^+$. (a) Total electron TRPEPICO correlated with all ion masses. This is the same data as presented in Fig. 8(a). (b) TRPEPICO correlated with the $C_4H_6^+$ parent ion, revealing the dominant (1 + 1') $S_2(1^1B_u) \rightarrow D_0(^2B_g)$ transition. A small time delayed parent ion signal is seen near 3.6 eV, corresponding to the $S_1(2^{-1}A_g) \rightarrow D_1(^2A_u)$ transition. Parent C4H6⁺ ions with internal energies corresponding to photoelectrons between the green and purple lines survive the transit of the extraction region and are detected as the parent ion mass. (c) TRPEPICO correlated with the $C_3H_3^+$ fragment ion, revealing the dominant time-delayed $(1 + 2') S_1(2^{-1}A_g)$ $\rightarrow D_1 (^2A_u)$ transition. As discussed in Appendix C, this fragment appears only for photoelectron energies less the purple dashed line, corresponding to internal energies at which the parent ion cannot survive the extraction region transit time. In the 0-1.3 eV region, the $C_3H_3^+$ fragment ion is seen but with a photoelectron spectrum corresponding to the $S_2(1^1B_u) \rightarrow D_0(^2B_g)$ transition. This is due to post-ionization photodissociation of the $C_4H_6^+$ parent. A significant contribution is also seen at long time delays and low electron energies. This is due to dissociative photoionization of the "hot" S₀ neutral molecule formed by internal conversion. (d) TRPEPICO correlated with the C₂H₃⁺ fragment ion. As indicated in Table II, this high energy fragment requires a total energy of around 15 eV. Therefore, this channel is due to two-photon post-ionization photodissociation of the $C_4H_6^+$ parent and $C_3H_3^+$ fragment ions, echoing the dynamics seen in both panels (b) and (c). The dissociative photoionization contribution from "hot" S₀ appears more prominently and over a broader energy range in this channel. In panels (b)–(d), a dashed black line in the low energy region indicates the centroid of the $S_2(1^1B_u) \rightarrow D_0(^2B_g)$ photoelectron band. It is clearly negatively sloped toward lower energies, indicating a "sweep" of the Franck-Condon spectrum due to large amplitude motion during the dynamics. For further details, see the text.

ions associated with photoelectrons having kinetic energies below the purple line will likely fragment rapidly enough to be detected as the $C_3H_3^+$ fragment, as detailed in Appendix C. This supports the assignment of this photoelectron band as being due to the $S_1(2 \ ^1A_g) \rightarrow D_1$ channel. Finally, we note that the $C_3H_3^+$ fragment belongs to group (b) in Fig. 7. As discussed in the TRMS section, the group (b) ions exhibit the behavior of a transient intermediate in a sequential kinetic scheme. This confirms our direct detection of the transient $S_1(2 \ ^1A_g)$ state of BD.

We now discuss the lower energy photoelectron band in Fig. 10(c) which has a cutoff at the (1 + 1') limit of 1.3 eV. As discussed above, these (1 + 1') ionizing transitions do not produce a fragment ion. Therefore, this band in Fig. 10(c) must be due to post-ionization photodissociation. The S_2 photoelectron band of Fig. 10(b) produces a parent ion. However, after the photoelectron has departed (on subcycle time scales), the parent ion may persist in the probe laser field long enough to absorb a second probe photon, undergoing a resonant electronic transition $D_0(^2B_g) \rightarrow D_3(^2B_u)$, thus acquiring an additional 4.6 eV of internal energy. Following ultrafast internal conversion, the vibrationally "hot" cation dissociates producing a fragment, in this case $C_3H_3^+$. However, since the photoelectron had already departed, this fragment ion has as its coincident partner a photoelectron associated with the $S_2(1 \ ^1B_u) \rightarrow D_0$ channel, thus explaining the lower energy photoelectron band of Fig. 10(c). It is important to note that only PEPICO spectroscopy can readily distinguish post-ionization photodissociation from direct dissociative ionization. Time-resolved mass spectra, as shown in Figs. 6 and 7, inadvertently convolve these differing dynamical processes, confounding a clear view of the excited state dynamics.

Finally, we note that in Fig. 10(c) there is a weak coincident photoelectron signal at low kinetic energies which persists out to long time delays. This channel is therefore a contributor to the long-lived photoelectron signals seen in the logarithmic plot of Fig. 10(a). Since this featureless photoelectron band does not match those of either the $S_2 \rightarrow D_0$ or $S_1 \rightarrow D_1$ transitions, or post-ionization photodissociation of cations formed in these channels, they must have another origin. We propose that this long-lived signal is due to photoionization of the "hot" S_0 ground state formed, as expected, via internal conversion from the dark $S_1(2^{-1}A_g)$ state.

In Fig. 10(d), we show the TRPEPICO spectrum for photoelectrons coincident with the $C_2H_3^+$ fragment ion. As shown in Table I, this high energy fragment has an appearance energy (AE) at the 15 eV energy limit for (1 + 2') ionization and belongs to group (c) of Fig. 7. There are three regions of interest: a short-lived band below 1.3 eV, a transient band below the "transition region" cutoff (purple dash) near 3.1 eV, and a long-lived diffuse band at low kinetic energies. The first two are assigned to post-ionization photodissociation of the ions produced by the $S_2 \rightarrow D_0$ and $S_1 \rightarrow D_1$ photoionization channels discussed for Figs. 10(b) and 10(c). The latter (long-lived) channel is considerably stronger in Fig. 10(d). It matches the temporal [far exceeding the $S_1(2 \ A_g)$ lifetime], fragmentation [highest energy fragmentation channel (c)], and photoelectron spectral behavior (broad, featureless) expected for (1 + 2') photoionization of the "hot" S₀ ground state.

In Figs. 10(b)–10(d), we also show a dashed black line indicating the centroid of the low energy (S₂) band as a function of photoelectron kinetic energy. It can be seen that these bands slope toward lower kinetic energy, relative to the horizontal $\Delta t = 0$ line, at longer time delays. This indicates large amplitude motion on the S₂(¹B_u) potential surface. Significantly, this motion occurs while retaining zeroth order S₂(¹B_u) electronic character—in other words, before reaching a ¹B_u–¹A_g conical intersection. This important point will be discussed in more detail below.

In Fig. 10(c), we show photoelectrons coincident with the $C_3H_3^+$ fragment ion [group (b) of Fig. 7]. The region of interest below 1.3 eV is assigned to post-ionization photo dissociation of the ions produced by the (1 + 1') S₂ \rightarrow D₀ transition, as discussed above. Interestingly, by comparing the tilted dashed black centroid line with the horizontal $\Delta t = 0$ line, we can see that these post-ionization photodissociation ions are delayed with respect to the analogous tilted line for the parent ion signal shown in Fig. 10(b). This means that the parent ion photodissociation channel producing $C_3H_3^+$ requires some vibrational evolution on the cation D₀ potential before the fragment signal is maximized. This preferentially selects out of the photoelectrons coincident with the parent ion [Fig. 10(b)], those that are somewhat delayed, as these more favourably produce the $C_3H_3^+$ fragment. This delay is perhaps unsurprising, as time-resolved photodissociation of neutral molecules has been previously used in a pumpprobe scheme, but with neutral photofragment detection as a probe.44

The region of interest between 1.3 and 3.1 eV is assigned to the $(1 + 2') S_1 \rightarrow D_1$ transition, as discussed for Fig. 10(c). The dotted black (nearly horizontal) line marks the centre of this S_1 band and it is clearly delayed with respect to that of the S_0 band (dashed black). This, combined with its rapid decay, strongly supports the sequential kinetic scheme. Interestingly, the slope of the (nearly) horizontal dotted black line (S_1) is different from the slope of the dashed black line (S_2). This indicates that vibrational energy spreads much more rapidly in S_1 than in S_2 . This is unsurprising, given that the greatly increased excess vibrational energy in S_1 should lead to faster intramolecular vibrational energy redistribution (IVR) within that state.

In Fig. 10(d), we show photoelectrons coincident with the $C_2H_3^+$ fragment ion [group (c) of Fig. 7]. This high energy fragment has an AE of 15 eV (Table I) and requires extensive internal energy in the BD cation. There are two post-ionization photodissociation processes appearing in the $C_2H_3^+$ channel, as discussed above. Again, there is a delay between the D_0 post-ionization photodissociation channel and the data in Fig. 10(c). There is photoelectron intensity, spread over a broad energy range, at longer time delays for the $C_2H_3^+$ channel. This further supports the assignment that the photoelectron signals at long time delays (Figs. 7 and 9), and the group (c) fragment ions (Fig. 7) probe the vibrationally hot ground state neutral following the sequential internal conversion pathway $S_2 \rightarrow S_1 \rightarrow S_0$.

D. Franck-Condon region dynamics and apparent width of the UV absorption spectrum

As discussed above, due to the slope of the Franck-Condon spectrum in the (1 + 1') region, 2D global fitting of the TRPES and TRPEPICO spectra may not yield accurate results: the decay associated spectrum (DAS) for the S₂ \rightarrow D₀ transition does not retain a time independent form $D_i(\varepsilon_k)$. Ab initio excited non-adiabatic state dynamics and simulated "on-the-fly" TRPES spectra will be presented and discussed in detail in the following Paper II,¹⁰ allowing a direct "zero-adjustable-parameter" comparison of experiment with theory. In the following, however, we independently extract some information directly from the experimental data alone regarding the dynamical evolution of the excited state wavepacket on the S₂ potential surface.

In Fig. 11, we present a more detailed analysis of the slope of the Franck-Condon spectrum and its relation to large amplitude motion within a given zeroth order electronic state (e.g., $S_2 1^1 B_u$). In Fig. 11(a), we show the dashed lines at 1.3 (red), 3.6 (green), and 5.9 (red) eV associated with the various energetic limits discussed above. In Fig. 11(a), we replot the photoelectron data of Fig. 10(a) but now normalize each kinetic energy slice to unit intensity. This helps to reveal the temporal behavior of each of the various channels, independent of their amplitude. In order to focus on the short time dynamics, in Fig. 11(b), we replot this using a narrower time range of 50–150 fs. For each kinetic energy slice, we fit the photoelectron band to a Gaussian function of time and determined the centroid. The locus of all centroid points is shown as the white line in Fig. 11(b). This line shows the motion of the effective "time zero" point (effectively, the sweep of the Franck-Condon spectrum) as a function of time delay. In Fig. 11(c), we plot separately the locus of Gaussian centroids, showing their behavior as a function of time and photoelectron kinetic energy. In a ballistic picture of localized Gaussian wavepacket motion, the rate of change of photoelectron kinetic energy with time delay, $d\varepsilon_k/dt$, within a given photoelectron band, should relate to the rate of change of the molecular geometry as viewed by the cation potential surface. The energy region above ~5.5 eV corresponds to very small signals and is dominated by Poisson noise: we do not consider this region further here. We have divided the plot into two regions, labeled I and II, corresponding to the regions between the known energy limits (dashed lines) for the various channels. In region I, the average slope $d\varepsilon_k/dt = -40$ meV/fs. This region rises promptly with the pump laser pulse and, as discussed above, corresponds to the $S_2 \rightarrow D_0$ transition. Therefore, we suggest that this slope corresponds to the rapid motion of the initially prepared wavepacket out of the vertical Franck-Condon region. Due to the geometry change between S_0 and S_2 , we believe that the steepest gradient at the Franck-Condon point of the $S_2(^1B_u)$ potential will be along the bond-alternation coordinate. However, the largest amplitude motion will be along the torsional coordinate and it is due to displacements along this mode that (higher frequency C=C stretch) vibrational revivals in the nuclear autocorrelation function are strongly attenuated, leading to significant broadening of the absorption spectrum. Some of these vibrational motions are depicted in Fig. 3. We note that



FIG. 11. (a) The photoelectron spectrum of Fig. 10(a) is split into two regions separated by a black vertical dashed line. The energy-resolved photoelectron spectrum is divided into thin bins (slices) of width 0.1 eV. Within each bin, the photoelectron intensity is normalized, allowing for comparison of the timedependent behavior within each region. (b) The data from (a) are plotted over a small time range (-0.05-0.2 ps), revealing the fastest excited state dynamics. Within each bin, the centroid of the normalized photoelectron band is given by the white solid line. It can be seen that these clearly vary with energy. (c) The centroid of the photoelectron bands is plotted (blue squares) as a function of energy and time delay. In region I, a linear fit (red dashed line) yields a slope of -40 meV/fs. In region II, the behavior is more complex and cannot be fit with a single slope. Rather, three different slopes (-400 meV/fs, -100 meV/fs, -40 meV/fs) are used to indicate the trends (green dashed lines). The light gray solid lines indicate the expectations (hyperbolic functions) of a simple model of wavepacket motion on an inverted harmonic surface. As shown in Fig. 10, region I corresponds to $(1 + 1') S_2(1^1B_u) \rightarrow D_0(^2B_g)$ and region II below 4 eV corresponds to (1+2') S₁ $(2^{1}A_{g}) \rightarrow D_{1}({}^{2}A_{u})$ photoionization. These data indicate that large amplitude motion leads to a "sweep" of the Franck-Condon spectrum. For details, see the text.

the instantaneous vertical IP (i.e., the instantaneous ε_k) reflects the instantaneous difference potential between the neutral and cation states involved and, therefore, the geometry dependence of both neutral and cationic potentials determines $d\varepsilon_k/dt$. In BD, this difference potential increases monotonically via displacements along the torsional mode, whereas motion along the bond alternation coordinate will result in a smaller modulation of the IP. Thus, the slope $d\varepsilon_k/dt$ is mostly sensitive to nuclear dynamics involving large amplitude torsional motion. In the following, we assume displacements along the torsional coordinate are chiefly responsible for the slope in region **I**. In the high energy side of region II below ~5.5 eV, we have reproduced the $d\varepsilon_k/dt = -40$ meV/fs sloped line obtained from the linear fit to region I. Although much noisier, this slope is also roughly consistent with the data in the region above 5.5 eV which corresponds to a (1 + 2') S₂ \rightarrow D₀ ionization process, as discussed above (see Fig. 8). This region therefore reveals the same S₂(¹B_u) large amplitude vibrational dynamics via a (1 + 2') process that region I reveals via a (1 + 1') process and is not discussed further here.

In region **II**, we do not see a simple behavior for the slopes $d\varepsilon_k/dt$ as a function of time. We can roughly divide region II into three ranges: one from 1.3 to 2.8 eV, the next from 2.8 to 3.8 eV, and the last from 3.8 to 5.0 eV. In the higher energy range, which appears simultaneously with region I, we replot the -40 meV/fs line from region I. Although much noisier, the same slope line roughly captures the trend. In the middle range, slightly delayed with respect to region B, we again treat the behavior as quasi-linear and find a slope of $d\varepsilon_k/dt$ = -100 meV/fs. In the lowest energy range, which appears at longer time delays, we find a quasi-linear slope of $d\varepsilon_k/dt$ = -400 meV/fs. The latter two slopes represent a much greater $d\varepsilon_k/dt$ than seen in region I. This means that the photoelectron band in region II is broadening energetically much more rapidly with time delay than that in region I. We remind that region II below 4 eV corresponds to the (1 + 2') photoionization process $S_1 \rightarrow D_1$. In our sequential kinetic model, the photoelectrons at 3.6 eV kinetic energy correspond to ionization of the $S_1(^1A_g)$ wavepacket prepared by internal conversion from the $S_2(^1B_u)$ state. We suggest that the increased slope $d\varepsilon_k/dt$ in the energy range from 3.6 eV to 2.8 eV is due to the greatly increased rate of internal vibrational energy flow following internal conversion to the $S_1({}^1A_g)$ state. This should lead to a significantly increased rate of IVR. In fact, as the wavepacket evolves further (i.e., longer time delays) on the $S_1({}^1A_g)$ potential, it is seen that the rate $d\varepsilon_k/dt$ increases further to -400 meV/fs, approximately 10x the rate seen in region I. This suggests that the rate of IVR on $S_1({}^1A_g)$ increases with time over this period. This is consistent with what is expected for vibrational dynamics following rapid internal conversion and is discussed in greater detail in the following companion theory paper, Paper II.¹⁰

The sweep in the Franck-Condon spectrum can be directly correlated with motion along an effective large amplitude coordinate, tentatively assigned to an out-of-plane torsional mode. We argue that it is precisely this motion (upon excitation to S_2 $1^{1}B_{u}$) which leads to irreversible decay of the nuclear autocorrelation function: it is this motion which is responsible for the phenomenological breadth of the UV absorption band of BD. Without relying on theory (Paper II^{10}), we now develop an internally consistent argument-based on our data alone-that the width of the UV absorption spectrum is due to large amplitude motion. In the following, we show that the increase in the instantaneous vertical IP due to large amplitude wavepacket motion in the S_2 1¹ B_u state can be observed via the timedependent shift of the Franck-Condon (FC) spectrum in the TRPES. This result can be combined with a very simple model in order to extract the motion of the initial wavepacket from the FC region, thereby offering a mechanistic explanation of



FIG. 12. A cartoon summarizing the excited state dynamics of BD, as probed by the (1 + 1') and (1 + 2') TRPEPICO measurements in our experiments. Due to large amplitude motion (torsion) on the S₂ potential, the initially prepared wavepacket rapidly moves away from the Franck-Condon region, producing the -40 meV/fs sloped S₂ \rightarrow D₀ photoelectron band seen in region I of Fig. 11(c). This motion is the origin of the extreme width of the BD absorption spectrum. At larger displacements (later times), the conical intersection with S₁ is reached and the Koopmans' correlations and energetic considerations favour (1 + 2') photoionization to the D₁ state, region II of Fig. 11(c). At these ion internal energies, the unimolecular decay channel producing C₃H₃⁺ is open. Due to the rapidly increasing internal energy, the photoelectron spectrum in region II shows a large and increasing slope with time delay. For details, see the text.

the observed extreme width of the lowest UV absorption band of BD.

As illustrated in Fig. 12, we consider an oversimplified but nevertheless instructive model of frozen Gaussian wavepacket dynamics in the FC region of the $S_2 \ 1^1 B_u$. We assume that the curvatures along the relevant large amplitude (torsional) coordinate of the D₀ cationic ground and S₀ neutral ground state potential energy surfaces are each harmonic and quite similar. This is a reasonable assumption, given the lack of a torsional vibrational progression seen in this mode in the He(I) photoelectron spectrum. In such a situation, the nuclear autocorrelation function for the decay of the initial $S_2 \ 1^1 B_u$ wavepacket from the FC region would appear very similar, whether correlated with respect to the neutral S_0 vibrationless ground state (related to the absorption spectrum) or the cation D_0 vibrationless ground state. Thus, the slope of the instantaneous vertical IP observed in the TRPES can be used as a proxy for visualizing the differential displacements-along the large amplitude (torsional) mode—between the $S_2 \ 1^1 B_u$ and D_0 cation states. Since, in our model, the D_0 and S_0 states are parallel along this torsional coordinate, this measureby proxy-relates to the decay of the nuclear autocorrelation function with respect to the S₀ ground state. It is this latter quantity which is responsible for the width of the UV absorption spectrum.

As seen in Fig. 12, upon excitation to the S₂ 1¹B_u state, a frozen Gaussian wavepacket (black) evolves on an inverted harmonic surface. This inverted potential is merely a cartoon picture but one which represents an effective imaginary frequency responsible for removing wavepacket density from the initial Franck-Condon region. During this effective motion (horizontal axis), the vertical IP increases as a function of time [region I in Fig. 11(c)] until it exceeds the energy of a single probe photon. In this cartoon picture, the ballistic motion of the frozen Gaussian wavepacket maps the instantaneous vertical IP. The classical equations of motion for position x(t) and momentum p(t) on an inverted harmonic potential are given by the hyperbolic functions,

$$x(t) = x_0 \sinh(\omega_1 t) + p_0 \cosh(\omega_1 t), \qquad (2)$$

$$p(t) = x_0 \cosh(\omega_1 t) + p_0 \sinh(\omega_1 t), \qquad (3)$$

where ω_1 is the harmonic (negative) curvature of the inverted potential along the effective coordinate and x_0 and p_0 are the Gaussian initial position and momentum obtained from the S_0 ground state v = 0 Wigner distribution. In this simple picture, the vertical energy difference between the S_2 1¹ B_u and D_0 states monotonically follows the effective coordinate x(t), thus determining the instantaneous vertical IP as a function of time. Rather than attempting to extract meaningful parameters from such an oversimplified model, we simply wish to see if the variation of vertical IP with time delay matches the expectations (functional form) of a large amplitude motion. To proceed, we self-consistently fit both regions I and II to the data in Fig. 11(c) in order to obtain a phenomenological x(t). This fit is shown as the light grey curve overlapping the data in Fig. 11(c). It can be seen that the hyperbolic form is consistent with the variation in vertical IP seen in both regions. This supports the argument that the initial slopes of the photoelectron bands in regions I and II are due to a large amplitude effective motion. We assume that this motion contains a significant torsional component.

Importantly, via this cartoon, we can propose a mechanistic explanation of the much debated extreme width of the UV absorption spectrum of BD as seen in Fig. 1. We emphasize that the apparent width is not due to non-adiabatic dynamics in the FC region–i.e., the rapid development of $S_1 2^1 A_g$ character within the FC region. Rather, it is due large amplitude (mostly torsional) motion within the $S_2 1^1 B_u$ state which rapidly moves the initial wavepacket away from the FC region. As discussed in detail in the following companion paper, Paper II,¹⁰ large amplitude torsional motion does indeed lead to a conical intersection between S_2 and S_1 , but at a large torsional displacement (away from the FC region), thus generating an apparent irreversibility⁴⁵ in the nuclear autocorrelation function.

V. CONCLUSIONS

The smallest linear polyene, *trans*-1,3-butadiene, bridges the gap between ethylene and the longer polyenes, exhibiting dynamical aspects of each. Its dynamics following π - π * excitation to the bright S₂ 1¹B_u state have long been a controversial

subject. Using a balanced treatment of the non-adiabatically coupled S_2 1¹ B_u and S_1 2¹ A_g states, Levine and Martinez previously proposed²⁰ that both ethylene-like and polyenelike mechanisms are active in BD. In this paper (Paper I), we presented detailed time-resolved photoelectron-photoion coincidence (TRPEPICO) spectroscopy studies of the π - π * excited state dynamics of BD. Specifically, we excited BD with a fs pulse at 216 nm, corresponding to the apparent origin of its $\pi - \pi^*$ HOMO to LUMO transition. The evolving excited state wavepacket was subsequently photoionized with a delayed probe pulse at 267 nm using either a one photon (1 + 1') or a two-photon (1 + 2') process: the emitted photoelectrons were analyzed as to their kinetic energy spectrum as a function of time. Due to the specific electronic structure of the neutral and ionic states of BD, the complementary Koopmans' correlations are $S_2(1^1B_u) \rightarrow D_0(^2B_g) + e^-$ and $S_1(2^1A_g) \rightarrow D_1(^2A_u) + e^-$. This favoured the separation of the TRPES spectra associated with the bright and dark states. Furthermore, due to an open fragmentation channel lying near the $D_1(^2A_u)$ origin, the pump-probe preparation of vibrationally excited D1 unavoidably leads to post-ionization fragmentation forming $C_3H_3^+$. Using the TRPEPICO method, we correlated photoelectrons with either the parent ion or a fragment ion, allowing for disentangling of these ionization channels. Using 2D global fitting to a sequential kinetic model $S_2 \rightarrow S_1 \rightarrow S_0$, we could represent the data with a good quality (98% confidence) fit. The essential dynamic features-the rapid decay of S_2 , the growth and then rapid decay of S_1 , and, finally, the appearance of the "hot" S₀ ground state—were all seen in this analysis. This allowed us to report the first direct observation of the famously elusive $S_1(2 \ ^1A_g)$ state of BD during its ultrafast internal conversion. The 2D global fit yielded lifetimes of 23 fs for the bright $S_2(1 \ ^1B_u)$ state and 42 fs for the dark $S_1(2 \ ^1A_g)$ state.

A detailed analysis of the residuals of the global fits revealed a systematic error due to extensive large amplitude motion in the Franck-Condon region. 2D global fitting assumes a time-independent form of the decay associated spectra. In the case of large amplitude motion, this constraint may lead either to poor fits or, worse, to a misinterpretation of the dynamics. We presented a purely phenomenological analysis of this large amplitude motion which leads to a time dependence (slope) of the photoelectron spectrum associated with a given channel. In particular, by analyzing the slope of the photoelectron spectrum in the region of the $S_2(1^1B_u) \rightarrow D_0(^2B_g) + e^-$ transition (region I), we were able to determine that the initially prepared wavepacket rapidly leaves the Franck-Condon region due to large amplitude (predominantly torsional) motions but, importantly, while retaining zeroth order $S_2(1 \ ^1B_u)$ electronic character. This allowed us to propose a clear dynamical mechanism for the extreme breadth of the trans-1,3-butadiene UV absorption spectrum. We emphasize that the origin of this breadth is not due to strong non-adiabatic coupling to S₁ within the Franck-Condon region. Rather, it is large amplitude (torsional) motion on the zeroth order S_2 potential which rapidly moves the wavepacket from the Franck-Condon region. As will be detailed in the following paper, Paper II,¹⁰ the S_2 - S_1 conical intersection is indeed encountered but at larger values of the torsional angle (i.e., not in the Franck-Condon region).

This subsequent conical intersection along the large amplitude torsional coordinate leads to the apparent irreversibility of the wavepacket dynamics, thereby broadening the UV absorption spectrum.

The following paper, Paper II,¹⁰ presents detailed *ab initio* multiple spawning (AIMS) calculations of the same wavepacket dynamics in *trans*-1,3-butadiene. This method permits on-the-fly calculations of observables, in this case the TRPES and TRPEPICO spectra. These are compared with the experimental results of Paper I. This comparison also reveals the intramolecular motions and non-adiabatic crossings which underlie the TRPES and TRPEPCIO results. As suggested by the results presented here and by Paper II,¹⁰ we believe that the combination of TRPES (and its imaging and coincidence variants) with AIMS theory is particularly powerful at revealing details of the dynamics involved in the complex non-adiabatic processes of polyatomics molecules.

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APPENDIX A: TIME RESOLVED MASS SPECTROMETRY (TRMS)

It is important to note that the TRMS of Fig. 6 offers no direct spectroscopic identification of the neutral $S_2({}^1B_u)$, $S_1(2 {}^1A_g)$, or $S_0(1 {}^1A_g)$ states of BD. Rather, these TRMS channels comprise various processes in the molecular ionization continuum. As illustrated in Fig. 2, we expect that there will be both one-photon probe (1 + 1') and two-photon probe (1 + 2') processes, meaning that there could be several open channels for BD cation fragmentation, with differing timedependences.

The fragmentation data presented in Figs. 5 and 6 may originate from (i) neutral excited state dynamics prior to ionization or (ii) post-ionization photodissociation of a cationic state, or both. In the first process, direct ionization of electrons from lower lying molecular orbitals would lead, via Koopmans' correlations, to the formation of cation excited states which may subsequently spontaneously fragment. In the second process, direct ionization to the cation ground state followed (within the same probe pulse) by absorption of further probe photons would also lead to the formation of cation excited states which subsequently fragment. From TRMS measurements alone, it is very difficult to discern these two ion fragmentation processes.

The fragmentation channels shown in Table II are labeled (right column) in terms of which Fig. 7 group they belong to. It can be seen that the lower AE (11.4–13.1 eV) channels (53, 52, 39, 28 amu) all belong to group (b), whereas the higher

AE (~15 eV) channels (51, 27, 26 amu) belong to group (c). We remind that the total (1 + 1') photon energy is 10.37 eV and the total (1 + 2') photon energy is 15.0 eV, indicating that no fragment channels are open for (1 + 1') photoionization: these fragment channels must all arise from (1 + 2') processes. The dominant fragment is the low energy methyl loss channel forming C₃H₃⁺, corresponding almost exactly to the origin of the D₁ state. The other group (b) channels below 15 eV may correspond to ionizing transitions to the D₂–D₄ cation states. From energetic considerations alone, the group (c) channels may require significant geometric distortion in order to be adiabatically accessible via a (1 + 2') process. This may potentially involve the D₅ cation state.

The channel forming $C_3H_3^+$ was further analyzed, ^{37,38} and a two-well Rice-Ramsperger-Kassel-Marcus (RRKM) unimolecular decay mechanism was established.³⁸ Briefly, the BD parent ion formed by an ionizing transition to the D_1 (or higher) cation state undergoes rapid internal conversion (k_{IC} $> 10^{11} \text{ s}^{-1})^{46}$ to form a vibrationally "hot" D₀ ground state. Once in the cation ground state, it overcomes a 2.0 eV isomerization barrier to form the 3-methylcyclopropene cation which subsequently fragments via methyl loss, forming $C_3H_3^+$, at a dissociation threshold of 2.4 eV above the adiabatic IP, with a rate that depends steeply on the excess energy above threshold. This means that vibrationally hot C₄H₆⁺ cations with internal energies just above 2.4 eV may not dissociate rapidly enough within the extraction region of the Wiley-McLaren i-TOF to be detected as the $C_3H_3^+$ fragment: these would fragment during their μ s transit of the i-TOF drift tube and would therefore retain the TOF arrival of the $C_4H_6^+$ parent ion. However, due to the steep energy dependence of the dissociation rates,^{37,38} at slightly higher internal energies, these would fragment within the TOF extraction region and thus be detected as $C_{3}H_{3}^{+}$.

APPENDIX B: COMPARISON WITH ALL-TRANS-2,4,6,8-DECATETRATENE

The orbital configurations of the neutral and ionic states and corresponding Koopmans' correlations in BD are homomorphic with those of the longer linear polyene all-trans 2,4,6,8-decatetraene (DT), previously studied in detail.^{34,47} A key difference is that in DT there is much less large amplitude motion in the excited states: the adiabatic state labels S₂ and S₁ are arguably better defined. In DT, the single configuration bright $S_2(1^1B_u)$ correlates upon ionization to the D_0 ground state, whereas the multi-configurational dark S₁(2¹A_g) correlates upon (1 + 1') ionization to the D₁ electronically excited state. This favourable type of Koopmans' ionization correlation was termed "complementary."⁴⁷ In this prior TRPES study,³⁴ the S₂ photoelectron band decayed on a 380 fs time scale-the lifetime of the DT bright S2 state-and the S1 photoelectron band rose on the same (380 fs) time scale and subsequently decayed on a ~ 2 ps time scale. Both the S₂ and S₁ states were probed by (1 + 1') photoionization and the switching as a function of time between the energetically open S_2 \rightarrow D₀ and S₁ \rightarrow D₁ ionization channels represents the direct observation of non-adiabatic charge and vibrational energy flow during internal conversion. Of relevance to the present

study, when the excited state of DT was probed instead via (1 + 2') ionization [where the (1 + 1') energy was chosen to be above D₀ but below D₁], a low kinetic energy band due to (1 + 1') S₂ \rightarrow D₀ ionization was observed along with a time-delayed, higher kinetic energy band due to (1 + 2') S₁ \rightarrow D₁ ionization. In DT, the observed switching from (1 + 1') to (1+2') ionization as a function of time was directly related⁴⁷ to the non-adiabatic change in electronic configuration S_2 \rightarrow S₁. The dark S₁ state could not energetically access the D_1 continuum via a (1 + 1') process. Instead, it made an optical transition to superexcited states (quasi-bound high lying Rydberg states) lying above D_0 but which converge to the D₁ threshold. Upon absorption of a second probe photon, these superexcited states are directly photoionized into the D₁ continuum. In this case, the competition between vibrational autoionization of these superexcited states and second photon absorption favours the latter process. For the S₂ state, the (1 + 1') ionization into D_0 is direct and further photon absorption (i.e., above threshold ionization, ATI) cannot compete.

APPENDIX C: INTERNAL ENERGY DEPENDENT CATION FRAGMENTATION RATES

Following (1 + 2') photoionization of BD, as the cation internal energy increases (slower electrons), the C₃H₃⁺ fragment channel opens, but with a dissociation rate that depends on internal energy. For internal energies just above threshold, the rate will be slow enough that parent ions will enter the drift tube and therefore be detected at the parent ion TOF. At high internal energies, the parent ion will fragment rapidly within the extraction region of the i-TOF and cannot therefore be detected at the parent ion TOF. This explains why, in Fig. 10(b), no (1 + 2') photoelectrons are coincident with the $C_4H_6^+$ ion in the energy range below, say, 3 eV. The transition from the parent ion to fragment ion TOF is, of course, due to the internal energy dependence of the ion dissociation rate and will not give a very sharp transition energy, but rather a transition region. Nevertheless, we can roughly estimate this transition region energy as follows. As discussed in Sec. II, in the PEPICO detection mode, we applied a "wait time" of ~185 ns, letting the kinetic electrons escape the interaction region before applying a high voltage pulse to extract the ions. Using the known applied voltages and internal dimensions of the field regions of our PEPICO spectrometer, and a ~ 10 ns rise time for the high voltage pulse, we estimate that a $C_4H_6^+$ parent ion would enter the field-free TOF drift region in about 650 ns. As such, it would necessarily be detected as the parent ion. Converting to a rate, 650 ns would correspond to a dissociation rate of 1.5×10^6 s⁻¹. Referring to the previous experimentally determined BD ion fragmentation rates, we estimate that a fragmentation rate of 1.5 $\times 10^{6}$ s⁻¹ corresponds to a "single-photon equivalent" energy of about 11.85 eV.^{38,39} Converting to electron kinetic energy in Fig. 10, this corresponds to a (1 + 2') kinetic energy of about 3.15 eV. Roughly speaking, this means that parent ions with less internal energy (i.e., electrons faster than ~3.1 eV) should be detected as the parent ion. Concomitantly, parent ions with more internal energy (i.e., electrons slower than $\sim 3.1 \text{ eV}$) should fragment and therefore not be detected as the parent ion. This "transition region" energy is shown as a purple dashed line in Fig. 10. It can be seen that the coincident parent ion signal in Fig. 9(b) "fades" in quite reasonable agreement with this estimate.

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