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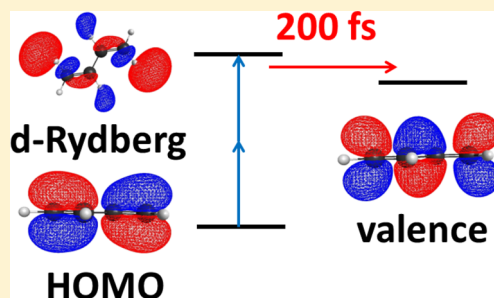
Oliver Schalk,^{†,‡} Andrey E. Boguslavskiy,[‡] and Albert Stolow^{*,‡}

[†]Stockholm University, AlbaNova University Center, Roslagstullsbacken 21, SE-106 91 Stockholm, Sweden

[‡]National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada

ABSTRACT: Two-photon absorption in systems with parity permits access to states that cannot be prepared by one-photon absorption. Here we present the first time-resolved photoelectron spectroscopy study using this technique, applied to 1,3-butadiene, in which we investigated the dynamics of its dark valence, Rydberg, and superexcited states. The dark valence state dynamics are accessed via the Rydberg manifold, excited by two photons of 400 nm. We find that the ‘dark’ 2^1A_g state populated in this manner has a much longer lifetime than when accessed via the 1^1B_u ‘bright’ valence state when populated by one photon of 200 nm. In addition, we compared the dynamics of the $3s\pi$ - and $3d\pi$ -Rydberg states. These Rydberg states relax to the valence manifold on a subpicosecond time scale, with the $3s\pi$ -Rydberg state decay rate being larger due to a stronger valence–Rydberg mixing. Finally, we investigated superexcited valence states that fragment or autoionize within 200 fs, likely without involving Rydberg states.

SECTION: Spectroscopy, Photochemistry, and Excited States



In systems with parity, nonresonant two-photon absorption is the easiest way to study the dynamics of states that are inaccessible by one photon absorption (so-called dark states). In combination with transient absorption, this technique was used to excite all-trans retinal¹ and carotenoid systems^{2,3} to decipher the role of their dark states in the relaxation dynamics upon one photon absorption. Ion mass spectrometry was used to study the Rydberg state dynamics upon two photon excitation in oxygen.⁴ Moreover, two-photon excitation is able to generate molecules in superexcited valence states and has been used to study ionization, fragmentation, and energy transfer processes.^{5–7} Since two photon excitation requires relatively high pump intensities, multiphoton excitation is practically unavoidable, especially when higher lying states have large absorption cross sections. However, when using time-resolved photoelectron spectroscopy (TRPES),⁸ such experiments become clearer if the excited states of interest are close enough to the ionization potential (IP) that three photon absorption from the excitation pulse leads to ionization of the ground state. In that case, the resulting ‘pump alone’ signal can be easily subtracted as a time independent background.

In the present manuscript, we exploit the TRPES technique to study: (i) ‘dark’ valence states, comparing their dynamics upon two-photon excitation via the Rydberg manifold with their dynamics upon one-photon excitation to the bright state, at the same internal energy; (ii) higher lying Rydberg states, deducing their coupling to the valence manifold; and (iii) superexcited states, following the dynamical pathways until the molecule dissociates or autoionizes. As it plays the role of a benchmark molecule for ab initio quantum chemistry and

nonadiabatic dynamics in excited states, we studied buta-1,3-diene, the simplest conjugated polyene.

The absorption spectrum of butadiene is known up to its vertical ionization potential (IP_v) at 9.29 eV (133 nm).⁹ At the ground state minimum energy geometry, the lowest lying excited state is the 1^1B_u state with origin at 216 nm (5.92 eV)^{10–12} and a short vibronic progression. The spectrum flattens at energies exceeding 6.32 eV (196 nm), indicating absorption to short-lived higher valence states. It is superimposed by a few sharp lines that are identified as *p*-Rydberg and, above 7.8 eV (159 nm), as *f*-Rydberg states. The optically ‘dark’ states are absent from the absorption spectrum, the most famous being the 2^1A_g -valence state, which has doubly excited character and is thought to lie slightly below the 1^1B_u state in the Franck–Condon region.^{13–15} We note that one photon excitation of the *s*- and *d*-Rydberg states is symmetry forbidden. Various methods were used to identify the origin of the lowest lying *s*-Rydberg state (1^1B_g) at 6.21 eV (199 nm)^{10,16,17} and detailed [2 + 1] resonance enhanced multiphoton ionization (REMPI) studies of the $3d\pi$ -Rydberg manifold revealed an extended vibrational progression, which spans several thousand wavenumbers. The state with the highest two-photon absorption cross section is the 3^1B_g state and has its origin at 7.61 eV (162.9 nm),^{18–20} due to excitation to the $3d_{x^2-y^2}$ orbital.¹¹ The 2^1B_g and the 3^1A_g states appear at 7.28 and 7.48 eV, respectively. They represent excitations to the $3d_{xy}$ and $3d_{xz}$ orbitals and have mixed valence–Rydberg charac-

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ter.^{10,11,21,22} Their two photon absorption spectra were not reported in detail, but unassigned peaks in the REMPI spectra show that at least one of the lower lying Rydberg states has a significant two-photon absorption cross section.¹⁸

The ultrafast dynamics of the lowest lying *s*-Rydberg state has been previously reported for unsaturated hydrocarbons such as ethylene, methylated ethylenes and cyclohexene.^{23–26} This state is known to strongly couple with the valence manifold,^{27,28} which results in short lifetimes (<100 fs) unless it is the lowest lying excited state, in which case it lives much longer (ps–ns).²³ Strong Rydberg–valence coupling has also been reported for *p*-Rydberg states which interact with the bright 1B_u -valence state.^{29,30} In cis-butadienes (as, e.g., cyclopentadiene), on the contrary, this mixing was found to be small.^{29,30} Little is known about the nonadiabatic coupling of the 1B_g states of *trans*-butadiene with the valence states, which can have 1B_u and 1A_g symmetry only.

In contrast to the Rydberg states, dynamics following excitation to the bright 1B_u valence state has been studied both experimentally^{31–33} and theoretically.^{34–36} Upon light absorption, the molecule can evolve either on the 2^1B_u or the dark 2^1A_g state after passing a conical intersection close to the Franck–Condon region. The dynamics on each state involves a twist about the central C–C-single bond and a C=C-double bond twist plus pyramidalization at one of the two ethylene groups. This motion is experimentally evidenced by TRPES through a large spectral shift.^{33,37} The time scale of the reaction is sub 100 fs, although a small fraction might remain in the excited state for an extended period.³⁶ Upon direct two-photon excitation to Rydberg states that populate the dark 2^1A_g state, one might expect similar spectral dynamics as the motion toward the S_1 – S_0 intersection and localization at the same C=C-dynamophore^{25,37} should obtain whether the S_1 state is populated via the bright $1B_u$ state or the dark Rydberg states.

Typical two-photon TRPES spectra at an excitation wavelength of $\lambda_{pu} = 400$ nm (3.1 eV) are shown in Figure 1. Pulse energies were 24.5 μ J/pulse for the 400 nm pump pulse, while pulses with 1 μ J and $\lambda_{pr} = 267$ nm (4.65 eV) served as the probe (both focused at $f/100$). In the top panel of Figure 1, the two photon pump, one-photon probe ($[2,1']$)-region is shown. The sharp energy cutoff at 1.78 eV shows that electrons are created in a $[2 + 1']$ -process ($2E_{pu} + E_{pr} - IP_a = 1.78$ eV, where IP_a is the adiabatic IP of 9.07 eV⁹). Beyond this energy cutoff, the photoelectron count-rate is much lower but is rendered visible in the lower panel of Figure 1 where the different bands were normalized independently. A second cutoff is seen in this spectrum, which corresponds to one photon of 400 nm and 2 photons of 267 nm ($2E_{pr} + E_{pu} - IP_a = 3.33$ eV). The signal between these two cut-offs evolves in the negative time direction and results from excitation with two photons of 267 nm; this will be discussed below.

The dominant feature of Figure 1 (top panel) is the exponential decay seen at the energy cutoff, which can be fitted by a 60 ± 15 fs time constant. Due to its sharp spectral structure, its energetic position (6.21 eV) and the required $g \rightarrow g$ -transition, which is favored by two photon absorption, we assign this band to the $3s\pi$ -Rydberg state (1^1B_g symmetry). The time constant agrees with the values found for other polyenes (see above) and is governed by the large quantum defect δ which was calculated to 0.76 for the *s*-Rydberg series in butadiene,³⁸ representing significant Rydberg–valence mixing. As usual, the quantum defect decreases for Rydberg series with higher orbital angular momentum and was calculated to be δ_{pz}

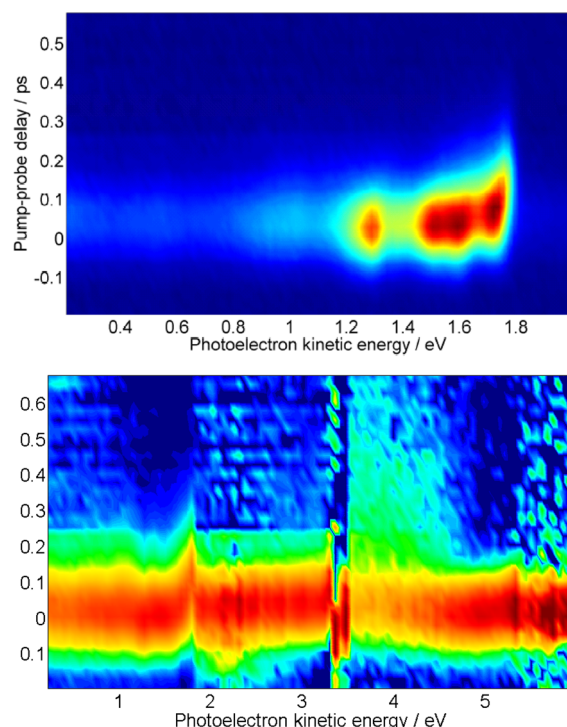


Figure 1. Top panel: Low energy region of the photoelectron spectrum of butadiene excited with two photons of 400 nm and probed with 267 nm. Lower panel: Full time-resolved photoelectron spectrum with the energy slices each independently normalized to constant intensity.

$= 0.52$ and $\delta_{dz} = 0.18$.³⁸ Upon decoupling from the valence manifold, one would also expect the Rydberg dynamics to slow down.

We checked this hypothesis in a separate experiment by exciting butadiene with 320 nm (3.88 eV) and probing with 400 nm (see Figure 2). In the negative direction (400 nm excitation), we once again find the $3s\pi$ -Rydberg state dynamics (here 70 fs, energy cutoff 1.05 eV), but we additionally observe dynamics following two photon excitation at 320 nm (cutoff

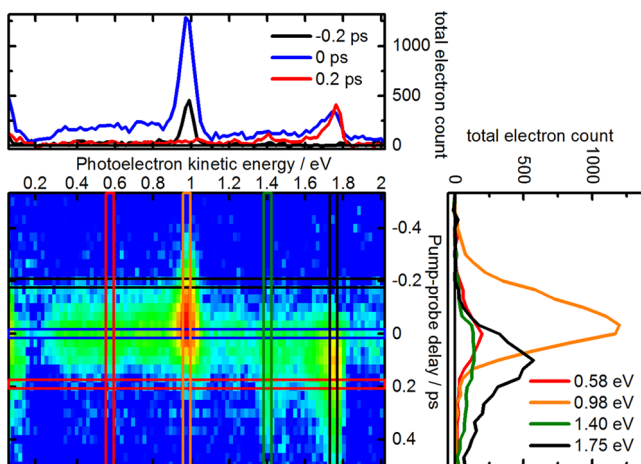


Figure 2. Time-resolved photoelectron spectrum of butadiene excited with two photons of 320 nm and probed at 400 nm. Signal in negative direction means that the 400 nm pulse precedes the 320 nm pulse; dynamics upon excitation with two photons of 400 nm are thus probed.

1.78 eV), which we identify as $3d\pi$ -Rydberg state dynamics, having a time constant of 200 ± 40 fs. In order to cover the spectral region of the $3d\pi$ -Rydberg states, we performed a series of experiments where we tuned our pump pulse between 305 and 344 nm (8.13 and 7.21 eV total energy in two photon absorption; see Figure 3) using 431 nm as a probe. Selected

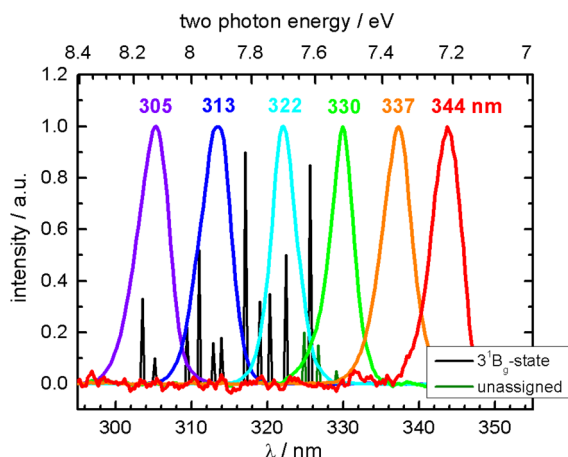


Figure 3. Spectra of the pump pulses used for excitation of the $3d\pi$ -Rydberg states of butadiene. In black, the main peaks of the two photon absorption spectrum of the transition to the 3^1B_g state are sketched as a reference. Peaks that could not be assigned to this state are in green. For the full 2 + 1 REMPI spectrum, see refs 18 and 20. Below 330 nm, the spectrum is unknown.

TRPES-spectra can be found in Figure 4a–d and the associated time constants and energy cut-offs are summarized in Table 1. The pump pulses at 330 and 337 nm (Figures 4c and d) do not reach the origin of the $3B_g$ state at 325.5 nm. However, they likely cover at least parts of the two photon spectrum¹⁸ associated with the lower lying $3d\pi$ -Rydberg state. This explains the weak signal at longer wavelengths and the complete absence of any dynamics in the 344 nm data. The 322 and 320 nm experiments show the clearest signature of the Rydberg states, while excitation at 314 and 305 nm leads to a progressively weaker signal. The fitted time constants of 200 fs are slower than those of the $3s\pi$ -Rydberg state but, nevertheless, fast for a state with relatively weak (as per the small quantum defects) coupling to the valence manifold. Consecutive relaxation on the valence manifold occurs in (500 ± 200) fs (low count rate). This time constant is in agreement with the time constant of 600 fs found upon two-photon excitation at $\lambda_{\text{pu}} = 400$ nm and energies exceeding 4.3 eV (see lower panel of Figure 1, [2,2']-region). This can be attributed to the dynamics following internal conversion between the $3s\pi$ -Rydberg and the lowest lying valence state ($2A_g$), indicating only small differences in valence dynamics following excitation to various Rydberg states. The relatively long time constant compared to direct excitation of the valence $1B_u$ state can be explained in terms of the relevant potential energy surfaces: The main difference between the dynamics upon $3s\pi$ versus 1^1B_u excitation is that the 1^1B_u state exhibits a strong gradient toward the S_1 – S_0 conical intersection. Moreover, the symmetry of the coupling mode for internal conversion to the 2^1A_g state is b_g in the case of excitation to the Rydberg state but b_u in the case of the valence state. Initial motion along a b_g coordinate seems to inhibit rapid access to the S_1 – S_0 intersection region. The S_1 state is reached from a different configuration via motions of different

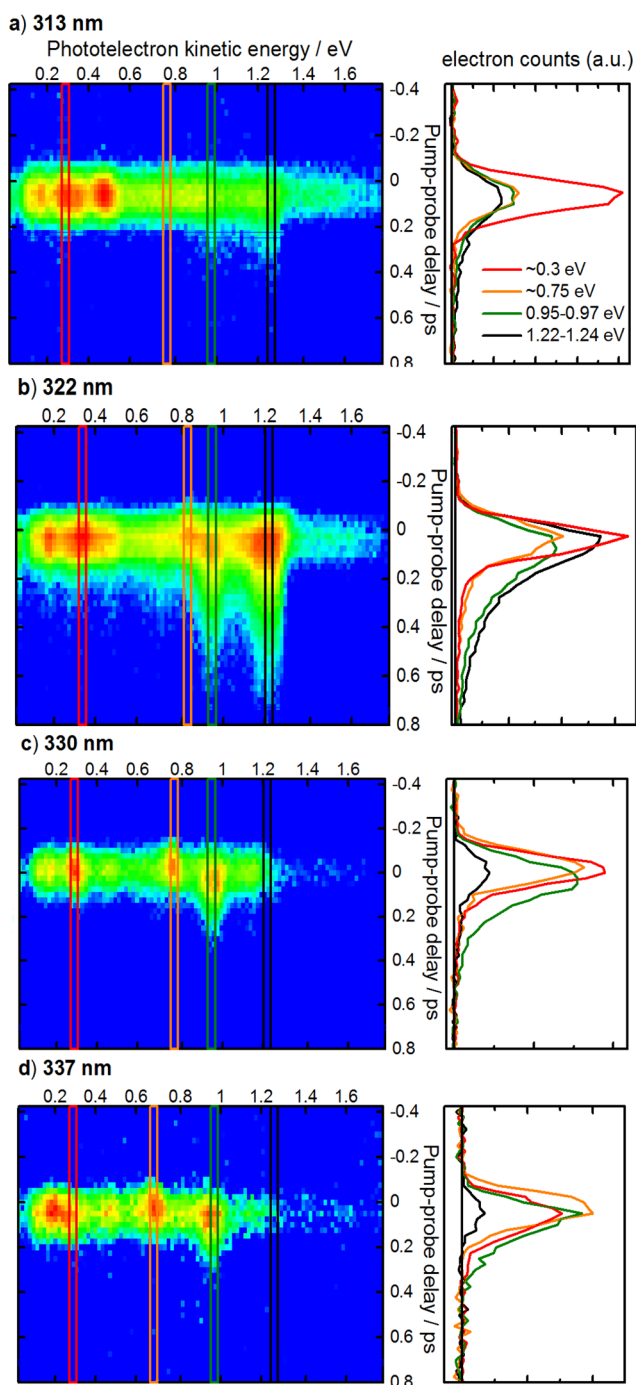


Figure 4. Time-resolved photoelectron spectra of butadiene pumped with two photons of (a) 313 nm (b) 322 nm (c) 330 nm and (d) 337 nm. The wavelength of the probe pulse was 431 nm. Time traces of the A and the B bands at 1.23 and 0.96 V as well as two slices at lower kinetic energies are shown on the right side of each spectrum.

symmetry and, therefore, different initial wavepacket momentum. We emphasize that the ‘lifetime of a state’ is not a characteristic of a state, even at constant excitation energy, but rather depends critically on how that state is prepared.

We return to Figure 2 and discuss the main features of the TRPES-signal upon d -Rydberg state excitation: (i) the independence of the electron kinetic energies of the main peaks from the excitation wavelength and (ii) the origin of the two peaks. As seen in the [2 + 1'] REMPI-spectrum of butadiene (adopted in Figure 3 from refs 18–20), the vibronic

Table 1. Two Photon Pump Energy, Energy Cut-off for a $[2,1']$ Experiment ($2 \cdot E_{\text{pu}} + E_{\text{pr}} - \text{IP}_{\text{a}}$) and Time Constants for the Rydberg States Excited by Two-Photon Absorption^a

	305 nm	313 nm	322 nm	330 nm	337 nm	344 nm
pump energy/eV	8.13	7.90	7.70	7.54	7.36	7.21
cutoff/eV ^b	1.94	1.71	1.51	1.35	1.17	1.02
band B 0.9–1.05 eV	- ^c	220 fs	190 fs	170 fs	250 fs	-
band A 1.1–1.3 eV	? ^d	250 fs	230 fs	-	-	-

^aSee Figure 4 for a plot of the data and assignment of the bands. ^bAdiabatic ionization threshold of $\text{IP}_{\text{a}} = 9.07$ eV used for calculation of the cutoff.

^cBand not observed. ^dBand too weak to determine time constant.

levels of the $3d\pi$ -Rydberg state cover the two-photon region between 330 and 305 nm and might even stretch a little further. They are mainly assigned to the $3B_g$ state (black in Figure 3), but some peaks originate from a lower lying state (green). When a Rydberg state is ionized, the diagonality of the Franck–Condon factors means that the internal vibrational energy is preserved upon ionization and, therefore, the excitation wavelength does not influence the position of the TRPES peaks. Hence, we only expect one (fairly sharp) photoelectron band per Rydberg state. Since excitation occurs from the Franck–Condon region and no energetic shifts are observed in the photoelectron spectra, ionization takes place along the vertical ionization potential IP_{v} . The total kinetic energy of the photoelectron is, therefore, expected at $E_{3B_g} + E_{\text{pr}} - \text{IP}_{\text{v}} = 7.61$ eV + 2.88 eV – 9.29 eV = 1.20 eV in agreement with the higher lying band (A) in Figure 3a,b centered at 1.23 eV. The second band (B) lies around 0.27 eV below band A, which would signify a Rydberg state originating at 7.34 eV. This is close to the $2B_g$ -Rydberg state ($3d_{xy}\pi$) and is in agreement with the fact that this band can also be observed at 337 nm excitation. The coupling of these Rydberg states with the valence manifold appears identical within the uncertainty of our measurements.

In the region between ~ 1.8 and 3.3 eV, the TRPES-spectrum shown in the lower panel of Figure 1 has an exponential decay in negative pump–probe direction, indicating dynamics which were initiated by the 267 nm pulse. Since one photon is nonresonant and two photons exceed the ionization potential of butadiene, these dynamics must originate from a two-photon excited molecular state lying above the ionization threshold. These so-called superexcited states can have relatively long (ps) lifetimes^{6,39} whereupon they autoionize or alternatively fragment into neutral species, often after internal conversion, e.g., between a doubly excited valence state and a vibrationally excited Rydberg states,⁵ followed by intramolecular vibrational redistribution.^{6,40}

The absence of structure as well as these subpicosecond time scale of the dynamics upon 267 nm excitation suggests that crossing from a superexcited valence to a superexcited Rydberg state is unlikely. The broad photoelectron band, ranging from the $[2 + 1']$ cutoff at 3.4 to 0.7 eV, shows a strongly energy dependent lifetime: from 20 fs at 3.4 eV to nearly 200 fs at 0.7 eV. This behavior is a likely sign of very large amplitude motions, similar to the dynamics found in lower lying valence states.³³ Upon large amplitude motion, the overlap between the superexcited state and the cation state to which it could autoionize might change rapidly upon distortion. Whether the molecule dissociates or autoionizes after 200 fs cannot be inferred from photoelectron spectroscopy alone.

In conclusion, we used two-photon absorption to excite and follow the dynamics of selected ‘dark’ excited states of butadiene, including the 2^1A_g valence state, the $3s\pi$ - and two $3d\pi$ -Rydberg states and superexcited states slightly above the

ionization potential. The dark valence state dynamics initiated by two-photon absorption to the Rydberg states are slower than those dynamics to the bright 1^1B_u state even though the valence manifold is reached within 60 ± 15 fs upon excitation to the $3s\pi$ -Rydberg state. It is emphasized that the ‘lifetime of a state’ depends on how it is populated, even if the total internal energy of the molecule is constant. The Rydberg state dynamics of butadiene is on a subpicosecond time scale, suggesting a strong Rydberg-valence mixing for the $3d_{xz}\pi$ and the $3d_{x^2-y^2}\pi$ states. The $3s\pi$ -Rydberg state decays as fast as expected from analogous results obtained in several other polyenes.^{24–26} The dynamics following excitation to superexcited valence states is different from what was previously observed in other hydrocarbons such as phenol and naphthalene.^{6,39,40} In butadiene, internal conversion to the Rydberg manifold could not be detected, possibly because of the rapid large amplitude distortion of the molecular frame, evidenced by the time-zero shift of the time-resolved phototransmission spectrum. These are due to Franck–Condon effects, in direct analogy with the valence state dynamics observed in the butadiene 1^2B_u state.^{33,37}

As a final note, we would like to mention that we did not observe any clear signs that we directly accessed the ‘dark’ 2^1A_g state. Possible reasons are a bad Franck–Condon overlap, the wrong spectral region, or a low two-photon oscillator strength. The same is true for the 3^1A_g ($3d_{xz}\pi$) state.

EXPERIMENTAL METHODS

The experimental setup including TRPES-design and the laser system used for this study was described previously.⁴¹ Butadiene (Matheson) with a nominal purity of >99% was diluted in helium (1:99 mixture) and expanded into vacuum using an Even–Lavie valve with a conical nozzle of 200 μm diameter at a repetition rate of 1 kHz. Laser wavelengths were generated by parametric amplification (TOPAS, Light Conversion) and subsequent mixing and doubling schemes. Spectra of the pulses between 305 and 344 nm are shown in Figure 3, superimposed on the two photon absorption spectrum of butadiene.^{19,20} The polarization of the pump beam was set to magic angle with respect to the probe beam. The cross correlation varied between $\tau_{\text{cc}} = 120$ and 150 fs depending on the pump and the probe wavelengths, as measured by the nonresonant ionization of NO. The measured pump–probe signal was corrected by dynamically subtracting background signals due to pump and probe pulses alone. The recorded data were analyzed separately for different regions of the spectra and fitted—when necessary—with a bidirectional decay function convoluted with the independently determined cross correlation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: albert.stolow@nrc-cnrc.gc.ca.

Notes

The authors declare no competing financial interest.

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