Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information - Resolving Competing Conical Intersection Pathways: Time-Resolved X-ray Absorption Spectroscopy of trans-1,3-Butadiene

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Ottawa, Ontario, K1N 6N5, Canada

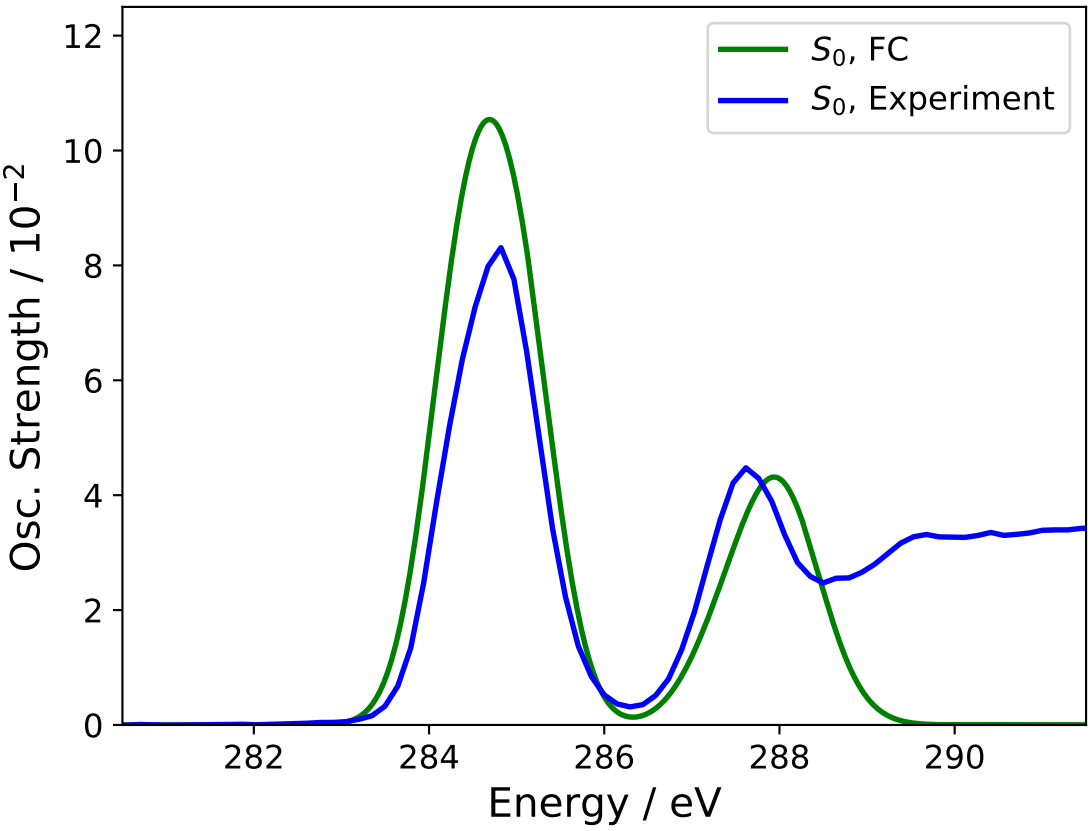


FIG. S1: Calculated XAS at CVS-DFT/MRCI/aug-cc-pVDZ level of theory for S_0 state at the FC compared to the experimental EELS spectrum[1]. The calculated spectrum is convoluted with a FWHM = 1.0 eV and shifted by 3.5 eV to higher energy to facilitate comparison to experimental spectrum.

TABLE S1: Transoid NTOs of the ground-state and excited-state XAS.

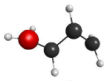
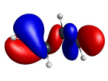
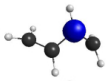
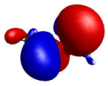
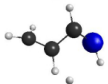
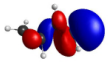
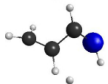
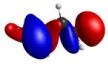
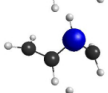
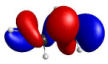
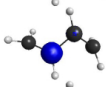
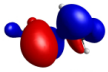
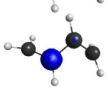
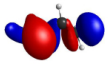
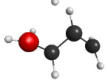
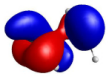
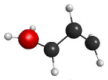
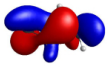
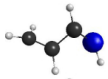
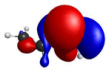
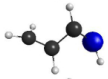
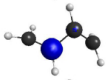
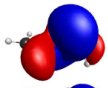
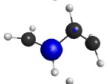
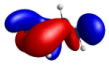
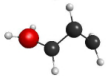
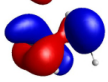
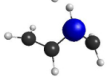
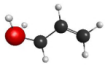
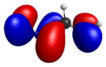
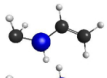
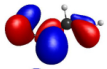
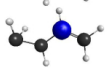
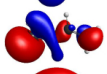
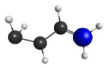
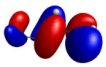
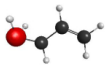
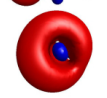
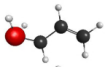
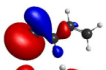
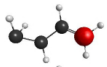
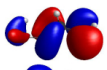
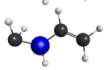
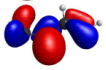
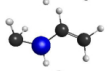
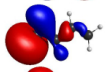
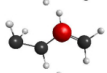
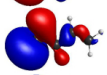
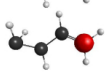
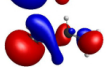
Peak/eV	State	Weight	Hole	Particle	Peak/eV	State	Weight	Hole	Particle
rad. 1									
A (282.4)	$1s_{C_1}\pi^*$	0.45			D (284.0)	$1s_{C_3}\pi^*$	0.58		
B (283.0)	$1s_{C_4}\pi^*$	0.26				$1s_{C_4}\pi^*$	0.46		
C (283.5)	$1s_{C_3}\pi^*$	0.36				$1s_{C_2}\pi^*$	0.40		
	$1s_{C_2}\pi^*$	0.20				$1s_{C_1}\pi^*$	0.26		
rad. 1									
A′ (282.0)	$1s_{C_1}\pi^*$	0.36			D′ (285.7)	$1s_{C_4}\pi^*$	0.48		
B′ (283.4)	$1s_{C_4}\pi^*$	0.22				$1s_{C_2}\pi^*$	0.43		
C′ (283.7)	$1s_{C_2}\pi^*$	0.42				$1s_{C_1}\pi^*$	0.39		
	$1s_{C_3}\pi^*$	0.39							

TABLE S2: Tw-Py NTOs of the ground-state and excited-state XAS.

Peak/eV	State	Weight	Hole	Particle	Peak/eV	State	Weight	Hole	Particle
				pol.					
A (283.0)	$1s_{C_1}\pi^*$	0.86			C (284.5)	$1s_{C_2}\pi^*$	0.88		
						$1s_{C_3}\pi^*$	0.83		
B (284.9)	$1s_{C_4}\pi^*$	0.72			D (287.0)	$1s_{C_1}$Ryd	0.81		
				rad.					
A′ (282.0)	$1s_{C_1}\pi^*$	0.48			C′ (283.5)	$1s_{C_4}\pi^*$	0.36		
B′ (283.0)	$1s_{C_2}\pi^*$	0.44			D′ (284.0)	$1s_{C_2}\pi^*$	0.37		
						$1s_{C_3}\pi^*$	0.27		
						$1s_{C_4}\pi^*$	0.25		

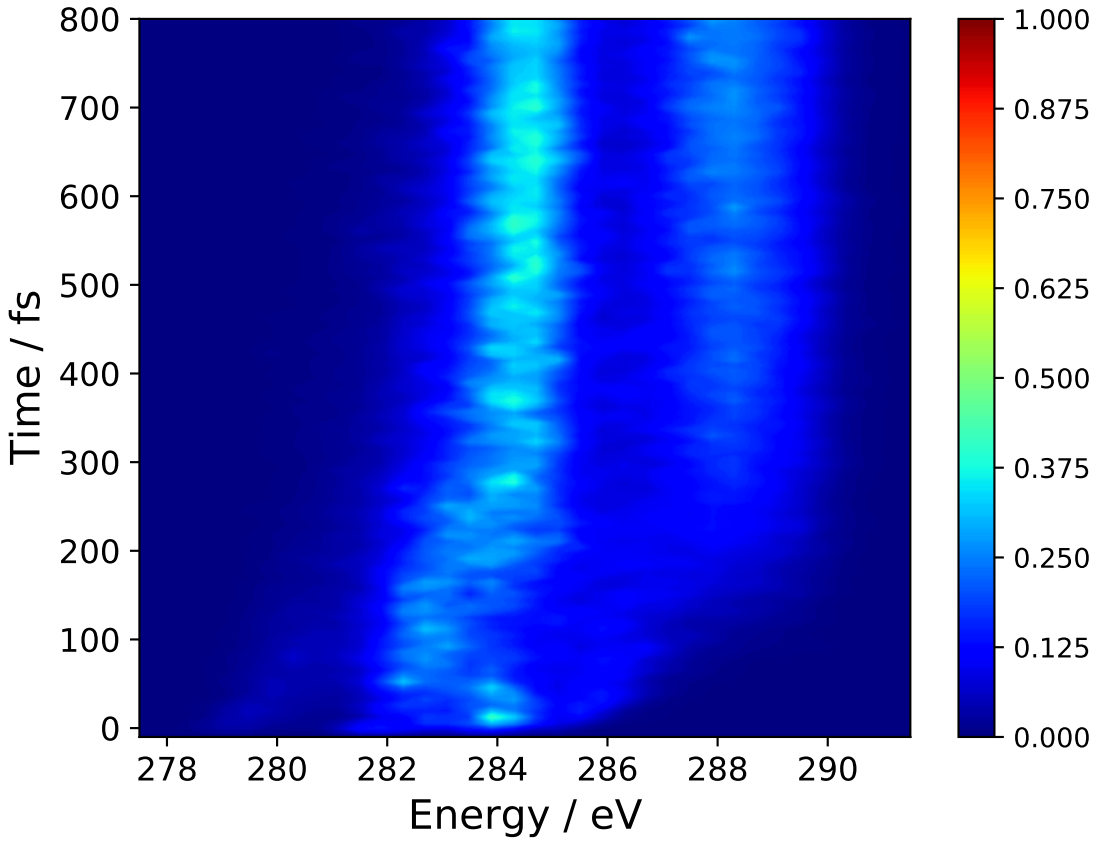


FIG. S2: Simulated parallel polarization TRXAS spectrum employing the results of AIMS dynamics simulations and CVS-DFT/MRCI X-ray absorption cross-sections. An isotropic axis distribution was assumed.

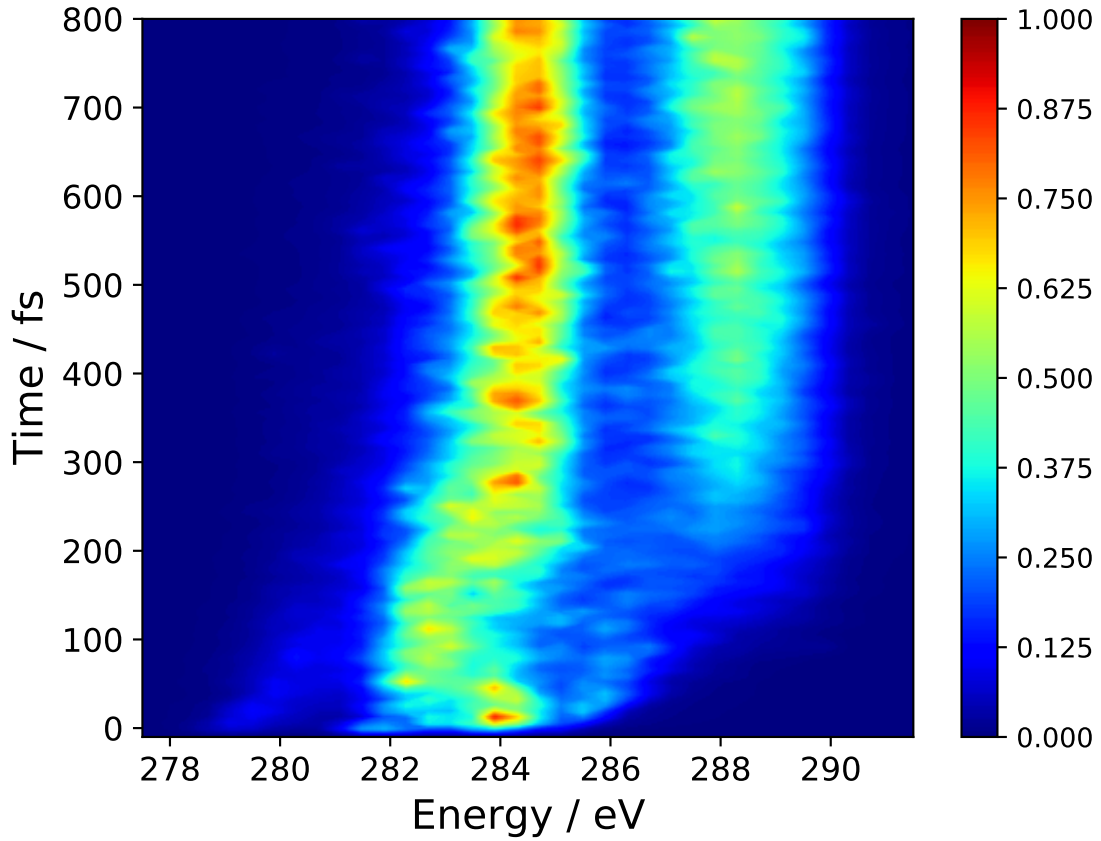


FIG. S3: Simulated perpendicular polarization TRXAS spectrum employing the results of AIMS dynamics simulations and CVS-DFT/MRCI X-ray absorption cross-sections. An isotropic axis distribution was assumed.

TABLE S3: MR-CIS optimized geometry of the terminal Tw-Py MECI.

C	1.841822	0.081208	0.057792
C	0.689252	-0.634435	-0.026686
C	-0.601894	0.013296	-0.099864
C	-1.816004	-0.716548	0.021817
H	2.804940	-0.398401	0.083936
H	1.828613	1.158278	0.096778
H	0.686535	-1.710894	-0.041153
H	-0.526661	1.104012	-0.129623
H	-2.674612	-0.198314	-0.418121
H	-1.816589	-0.006067	0.962993

TABLE S4: MR-CIS optimized geometry of the medial Tw-Py (mTw-Py) MECI.

C	1.363654	-1.476754	1.033232
C	0.534891	-0.949371	0.036100
C	-0.670059	-0.158282	0.076533
C	-1.952813	-0.537649	-0.176377
H	2.387907	-1.747905	0.815252
H	1.012393	-1.807281	2.008700
H	0.204967	-2.070707	0.266985
H	-0.474465	0.895795	0.220505
H	-2.217817	-1.566880	-0.361516
H	-2.737362	0.195240	-0.243732

TABLE S5: MR-CIS optimized geometry of the Transoid MECI.

C	-1.6964209992	0.0784200000	-0.3501989999
C	1.6837099992	-0.1305659999	-0.2390789999
C	-0.4545049998	-0.4328799998	0.2369249999
C	0.5936899998	0.4793759998	0.5337419997
H	-1.6246319993	0.7433189997	-1.2007419994
H	2.0114239991	-1.1354329995	0.0052020000
H	-2.5595129988	0.2052749999	0.2976069999
H	1.9171149992	0.2301169999	-1.2359359995
H	-0.2929549998	-1.4913829993	0.4101809998
H	0.3987159998	1.5435609993	0.4642279998

TABLE S6: Amplitude-weighted average polarized nuclear structure.

C	-1.74157096	0.29181917	0.03320491
C	-0.59423943	-0.41124976	0.05067867
C	0.65180151	0.27447095	0.12570390
C	1.75790994	-0.27729612	-0.03407427
H	-1.90570291	0.05433743	-0.93474674
H	-2.40665996	0.11383504	0.51013051
H	-0.42502721	-1.47340208	-0.13745125
H	0.52785253	1.31803074	0.23989687
H	2.58588754	0.22764448	0.04246069
H	1.78407045	-1.29318991	-0.21697182

TABLE S7: Amplitude-weighted average radicaloid nuclear structure.

C	1.37910228	-0.53731288	0.97351603
C	0.40371732	-0.43791040	-0.14218166
C	-0.16702140	0.75629531	-0.50559170
C	-1.56735250	0.27035629	-0.42560908
H	2.29933349	-0.49777234	0.81387909
H	1.21559161	-0.49793588	1.82447301
H	0.20243305	-1.29936522	-0.70451660
H	0.10246264	1.68714073	-0.17654197
H	-1.93632648	-0.43172744	-1.06541448
H	-2.09593225	0.49126615	0.38434477

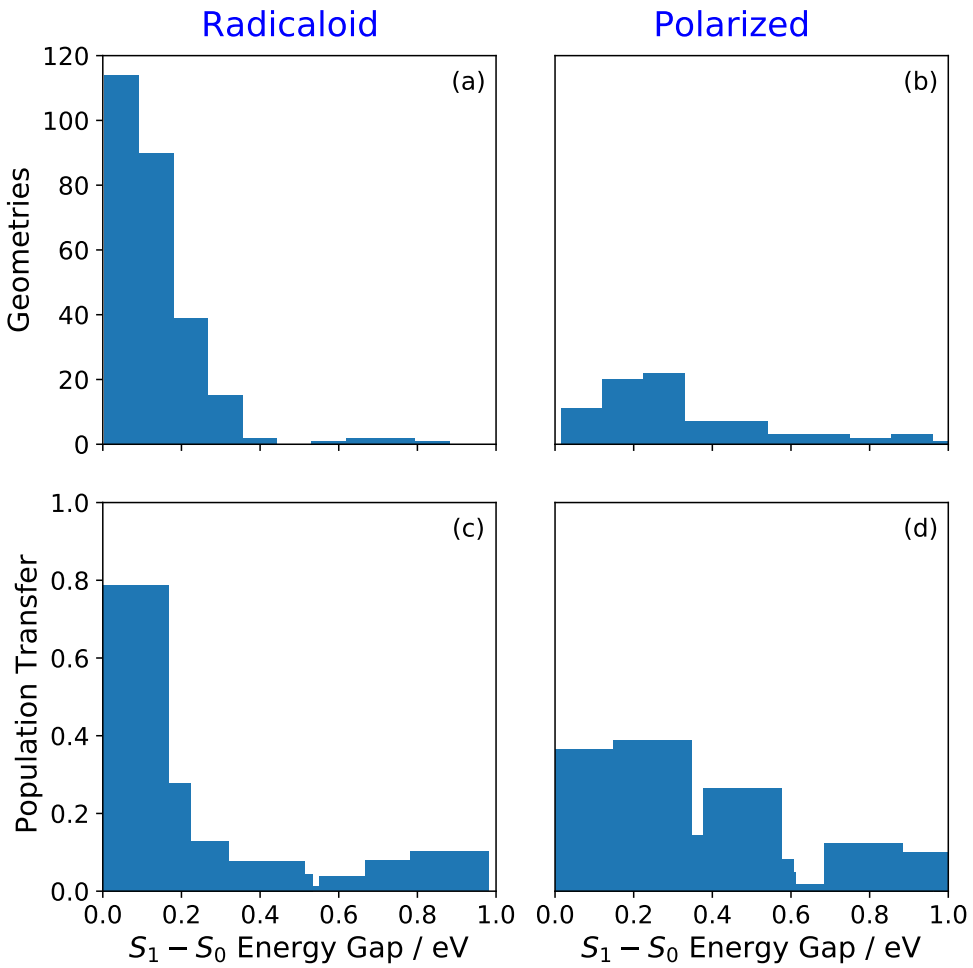


FIG. S4: (a) and (b) Distribution of the S_1/S_0 energy gaps for the radicaloid and polarized geometries, respectively. Population transfer as a function of the S_1/S_0 energy gap for the radicaloid (c) and polarized (d) geometries.

[1] R. McLaren, S. A. C. Clark, I. Ishii, and A. P. Hitchcock, Phys. Rev. A **36**, 1683 (1987).