

Supplementary Information: Deconvolution of the X-ray Absorption Spectrum of *trans*-1,3-Butadiene with Resonant Auger Spectroscopy

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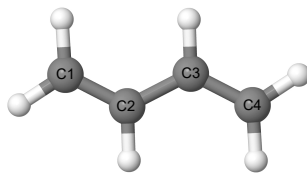


Figure S1 Structure of *trans*-butadiene with numbering of carbon atoms. Carbon atoms 1 and 4 are labeled as “edge”, carbons 2 and 3 are labeled as “central”.

Table S1 Optimised geometry in Cartesian coordinates of *trans*-butadiene at the MP2/aug-cc-pVTZ level (no symmetry applied).

	x	y	z
C	-1.523073	-0.494314	-0.093437
C	-0.721914	0.557579	0.123550
C	0.721913	0.557579	-0.123551
C	1.523074	-0.494314	0.093436
H	-1.133243	-1.413535	-0.511288
H	2.579623	-0.447045	-0.128570
H	1.133246	-1.413536	0.511288
H	1.158198	1.480994	-0.489070
H	-2.579620	-0.447049	0.128579
H	-1.158197	1.480992	0.489076

Table S2 Seven lowest energy vertical binding energies in eV of butadiene calculated at the CVS-EOM-IP-CCSD/cc-pVTZ and cc-pCVTZ level compared to experimental values¹ and theoretical values at the ADC(3)/aug-ANO level² with the ADC(3) spectroscopic factors given in parentheses.

State	Experiment ¹	EOM-IP-CCSD/cc-pVTZ + cc-pCVTZ	ADC(3)/aug-ANO ²
\tilde{X}^2B_g	9.29	9.127	8.988 (0.833)
\tilde{A}^2A_u	11.48	11.808	11.402 (0.613) 13.064 (0.290)
\tilde{B}^2A_g	12.2	12.482	12.481(0.890)
\tilde{C}^2B_u	13.49	13.750	13.688 (0.858)
\tilde{D}^2A_g	13.90	13.807	13.972 (0.885)
\tilde{E}^2A_g	15.3	15.792	15.709 (0.769)
\tilde{F}^2B_u	15.8	15.986	16.065 (0.616) 15.739 (0.198)

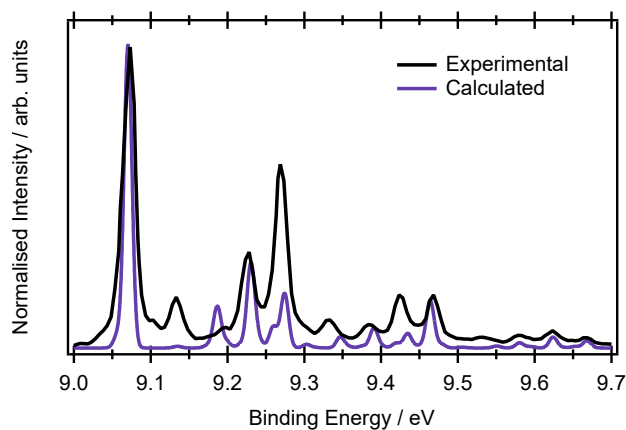


Figure S2 Vibrationally resolved spectrum of the first ionised state \tilde{X}^2B_g of butadiene compared to the spectrum calculated at the MOM/B3LYP/cc-pVTZ + cc-pCVTZ level. The assignments are provided in the Table S3. The experimental data are taken from Ref 1.

Table S3 Relative intensities and excitation energies (with respect to the adiabatic energy), and assignments of the photoelectron lines associated with the valence ionised \tilde{X}^2B_g ionic state of butadiene. Only values for relative intensities higher than 0.0055 are given. Relative intensities are calculated as $I \approx I^{calc} = \langle \xi' | \xi'' \rangle^2 e^{-E''/kT}$, $T = 300$ K. hb stands for hot band.

Valence-ionised state		
Energy / eV	Rel. Intensity	Assignment
0.0000	0.4120	0-0
0.0023	0.1807	ν_1 hb
0.1162	0.0559	ν_6
0.1185	0.0245	$\nu_1 + \nu_6$ hb
0.1285	0.0086	$2\nu_4$
0.1598	0.0945	ν_{12}
0.1607	0.0208	ν_{13}
0.1621	0.0415	$\nu_1 + \nu_{12}$ hb
0.1914	0.0108	$\nu_1 + \nu_{17}$ hb
0.2037	0.0750	ν_{18}
0.2060	0.0329	$\nu_1 + \nu_{18}$ hb
0.2760	0.0128	$\nu_6 + \nu_{12}$
0.3196	0.0132	$2\nu_{12}$
0.3199	0.0102	$\nu_6 + \nu_{18}$
0.3635	0.0172	$\nu_{12} + \nu_{18}$
0.3928	0.0314	ν_{20}
0.3940	0.0274	ν_{22}
0.3950	0.0138	$\nu_1 + \nu_{20}$ hb
0.3962	0.0120	$\nu_1 + \nu_{22}$ hb
0.4074	0.0055	$2\nu_{18}$
0.5526	0.0072	$\nu_{12} + \nu_{20}$
0.5538	0.0063	$\nu_{12} + \nu_{22}$

Table S4 Bond lengths in Å of optimised core-excited (XAS), core-ionised (XPS) and valence-ionised states of butadiene calculated at various levels of theory. *Ref 3.

	C1-C2 / Å	C2-C3 Å	C3-C4 Å
		MOM/B3LYP/cc-pCVTZ	
ground electronic state	1.334	1.453	1.334
XAS edge C	1.355	1.382	1.361
XAS central C	1.361	1.393	1.361
XPS edge C	1.298	1.425	1.328
XPS central C	1.307	1.399	1.307
valence-ionised state	1.382	1.404	1.382
		MP2/aug-cc-pVTZ	
ground electronic state	1.341	1.452	1.341
		MP2/cc-pVTZ and cc-pCVTZ	
ground electronic state	1.337	1.450	1.337
		experiment*	
ground electronic state	1.338	1.454	1.338

Table S5 Vibrational frequencies in cm^{-1} for optimised core-excited (XAS), core-ionised (XPS) and valence-ionised states of butadiene.

vibration	ground state	valence ionised	XPS – edge C	XPS – cent C	XAS – edge C	XAS – cent C
ν_1 C-C torsion	171	190	84	164	x	219
ν_2 CCC deform	295	298	311	336	x	296
ν_3 CCC deform	517	519	569	570	749	547
ν_4 CCH ₂ twist	538	434	538	549	143	446
ν_5 CH ₂ twist	784	518	845	804	757	598
ν_6 CH ₂ rock	898	937	958	969	852	955
ν_7 CH ₂ wagging	941	1062	1078	1084	429	514
ν_8 CH ₂ wagging	941	1055	1086	1079	540	545
ν_9 CH op bend	1001	921	984	992	819	883
ν_{10} CH ₂ rock	1004	1011	1136	1079	1133	1031
ν_{11} CH op bend	1054	1019	1036	1053	853	955
ν_{12} C-C stretch	1229	1289	1258	1336	1307	1302
ν_{13} CH ip bend	1317	1296	1336	1394	1338	1318
ν_{14} CH ip bend	1323	1273	1419	1410	1243	1293
ν_{15} CH ₂ scissor	1417	1373	1466	1464	1366	1411
ν_{16} CH ₂ scissor	1476	1503	1578	1523	1498	1550
ν_{17} C=C stretch	1652	1525	1803	1726	1609	1600
ν_{18} C=C stretch	1703	1643	1699	1804	1746	1708
ν_{19} CH stretch	3123	3168	3197	3383	2973	3132
ν_{20} CH ₂ s-stretch	3133	3142	2962	3156	3138	3386
ν_{21} CH ₂ s-stretch	3135	3144	3157	3156	3459	3420
ν_{22} CH stretch	3136	3178	3683	3387	3072	3142
ν_{23} CH ₂ a-stretch	3219	3249	3069	3261	3623	3532
ν_{24} CH ₂ a-stretch	3220	3249	3255	3261	3506	3531

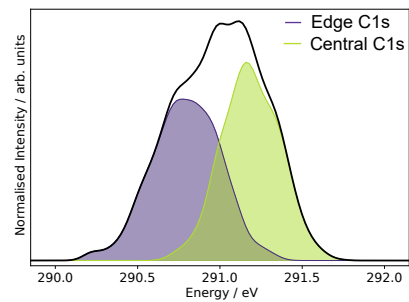


Figure S3 X-ray core-ionised spectra calculated within NEA at CVS-EOM-EE-CCSD/cc-pVTZ + cc-pCVZ level for an ensemble of 400 geometries with each line being Gaussian broadened by phenomenological 0.05 eV. The intensities were estimated as the squares of the respective Dyson orbitals.

Table S6 Relative intensities and excitation energies (with respect to the adiabatic energy), and assignments of the photoelectron lines associated with the core-ionised states of butadiene. Only values for relative intensities higher than 0.01 are given. Relative intensities are calculated as $I_{\circ} I^{calc} = \langle \xi' | \xi'' \rangle^2 e^{-E''/kT}$, $T = 300$ K.

XPS edge C		
Energy / eV	Rel. Intensity	Assignment
-0.0109	0.1143	ν_1 hb
0.0000	0.2951	0-0
0.0098	0.0204	$3\nu_1$ hb
0.0207	0.0175	$2\nu_1$
0.0276	0.0358	$\nu_1 + \nu_2$ hb
0.0385	0.0924	ν_2
0.0705	0.0252	ν_3
0.0771	0.0170	$2\nu_1$
0.1079	0.0209	$\nu_1 + \nu_6$ hb
0.1188	0.0541	ν_6
0.1300	0.0169	$\nu_1 + \nu_{10}$ hb
0.1409	0.0437	ν_{10}
0.1574	0.0169	$\nu_1 + \nu_6$
0.1759	0.0250	ν_{14}
0.1794	0.0137	$\nu_2 + \nu_{10}$
0.1848	0.0114	$\nu_1 + \nu_{16}$ hb
0.1957	0.0293	ν_{16}
0.4457	0.0132	$\nu_1 + \nu_{22}$ hb
0.4566	0.0340	ν_{22}
0.4952	0.0107	$\nu_2 + \nu_{22}$
XPS central C		
Energy / eV	Rel. Intensity	Assignment
-0.0009	0.1337	ν_1 hb
0.0000	0.3042	0-0
0.0698	0.0349	$\nu_1 + \nu_3$ hb
0.0707	0.0794	ν_3
0.1193	0.0741	$\nu_1 + \nu_6$ hb
0.1202	0.1685	ν_6
0.1414	0.0146	$2\nu_3$
0.1647	0.0176	$\nu_1 + \nu_{12}$ hb
0.1656	0.0401	ν_{12}
0.1728	0.0201	ν_{13}
0.1900	0.0193	$\nu_1 + \nu_3 + \nu_6$ hb
0.1909	0.0440	$\nu_3 + \nu_6$
0.2236	0.0102	ν_{18}
0.2363	0.0104	$\nu_3 + \nu_{12}$
0.2394	0.0234	$\nu_1 + 2\nu_6$ hb
0.2403	0.0533	$2\nu_6$
0.2858	0.0222	$\nu_6 + \nu_{12}$
0.2930	0.0112	$\nu_1 + \nu_{13}$
0.3110	0.0139	$\nu_3 + 2\nu_6$
0.3605	0.0125	$3\nu_6$
0.4185	0.0107	$\nu_1 + \nu_{19}$
0.4194	0.0243	ν_{19}
0.5396	0.0135	$\nu_6 + \nu_{19}$

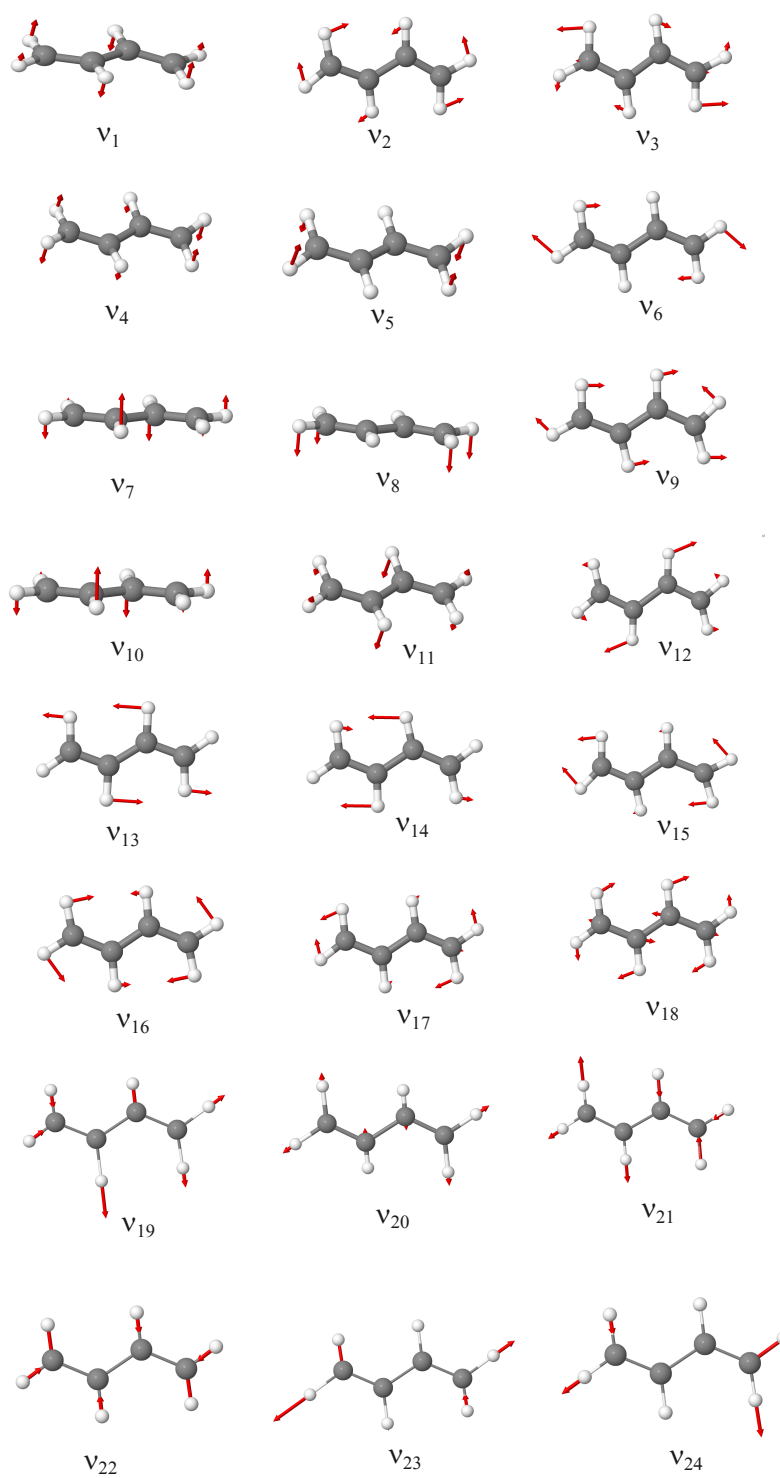


Figure S4 Sketch of vibrational modes 1-24 of butadiene.

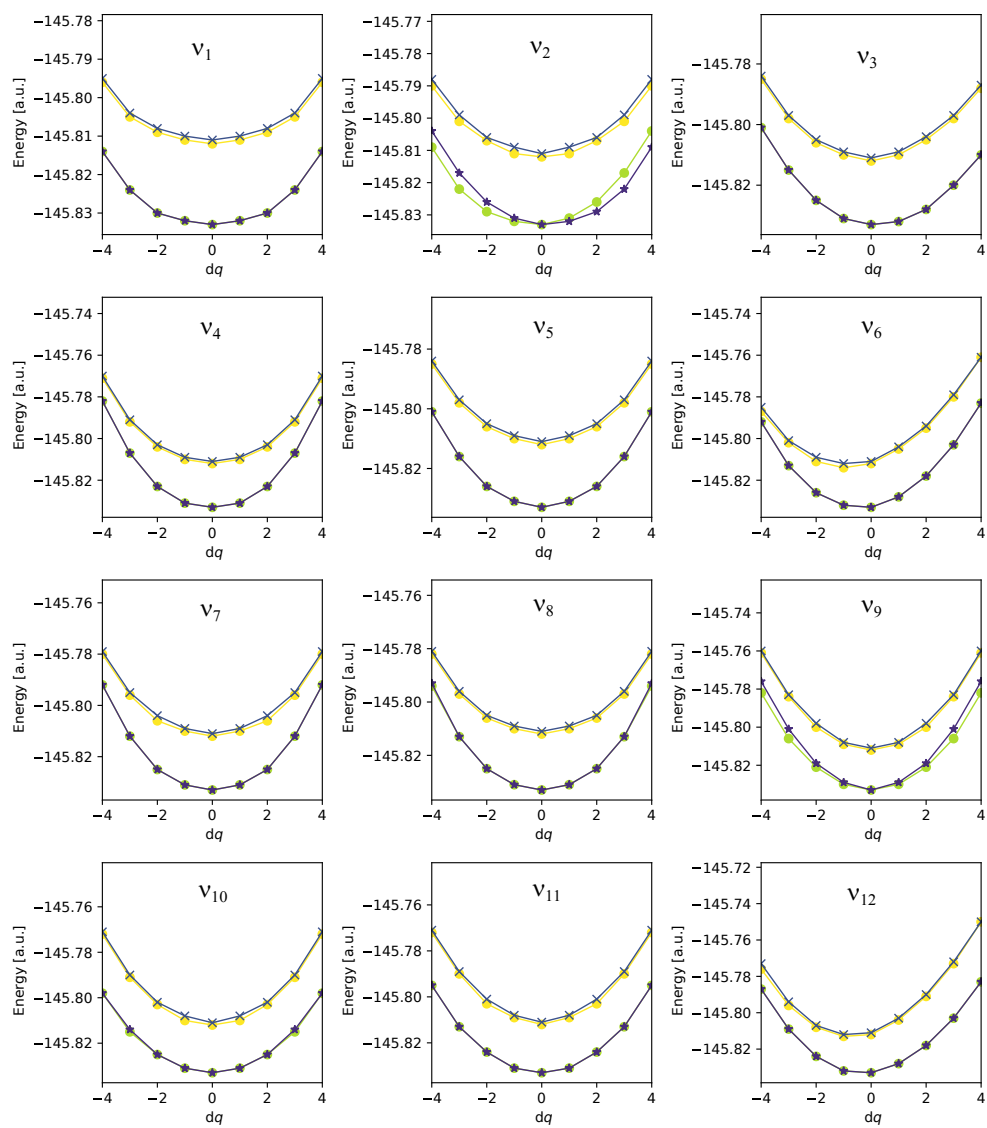


Figure S5 Energy profiles calculated at the SRC1-r1/cc-pVTZ and cc-CVTZ level for the four lowest core-excited states of butadiene along vibrational modes 1-12.

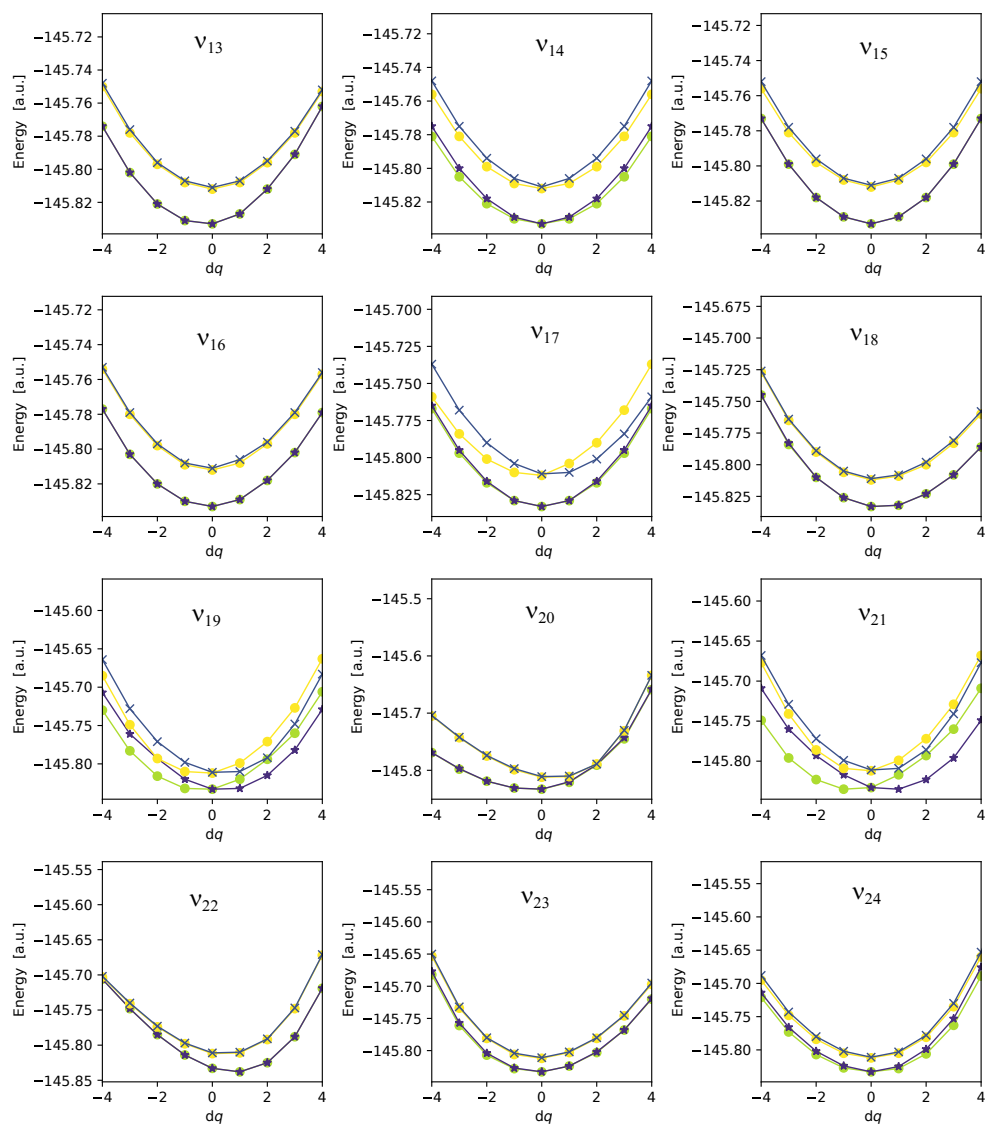


Figure S6 Energy profiles calculated at the SRC1-r1/cc-pVTZ and cc-CVTZ level for the four lowest core-excited states of butadiene along vibrational modes 13-24.

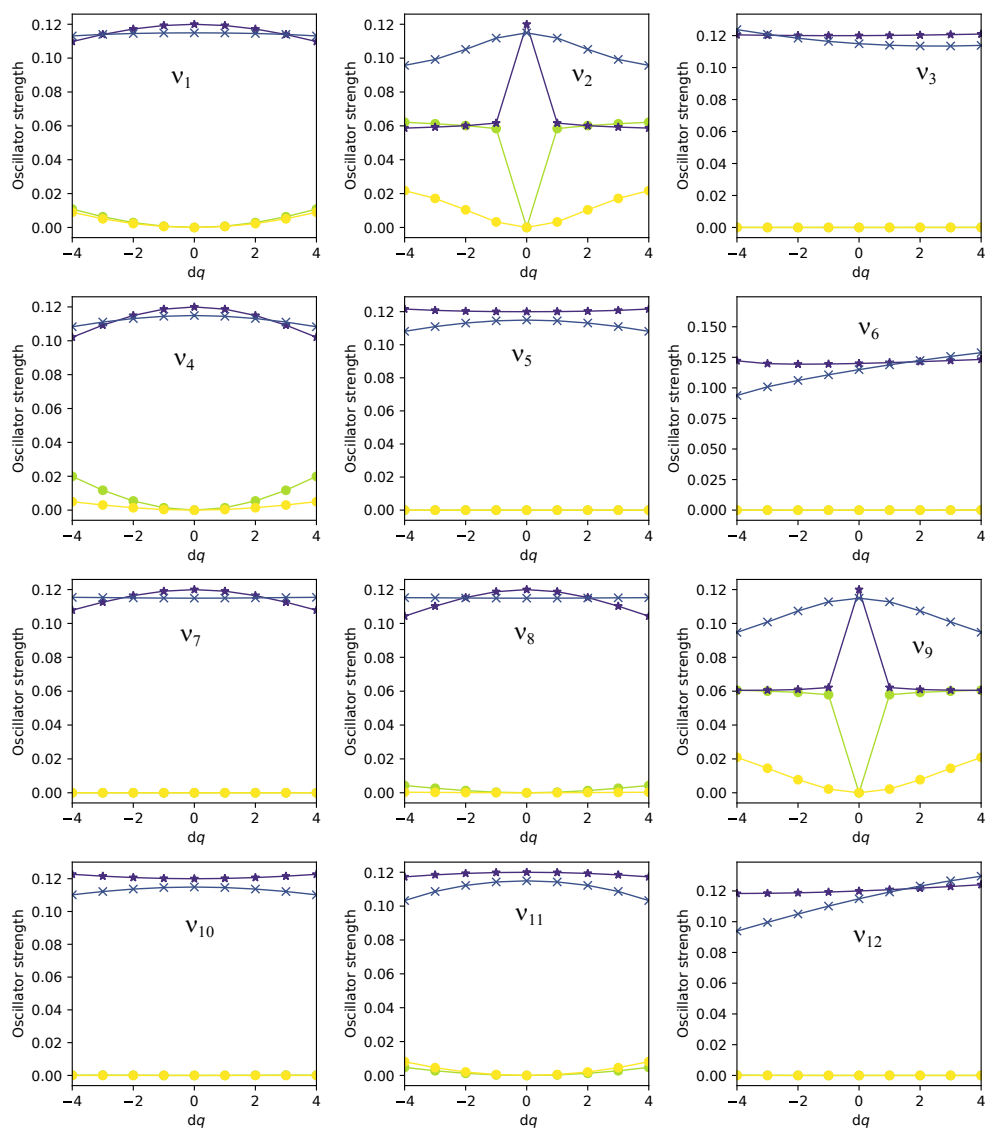


Figure S7 Oscillator strengths along vibrational coordinates 1-12 calculated at the SRC1-r1/cc-pVTZ and cc-CVTZ level.

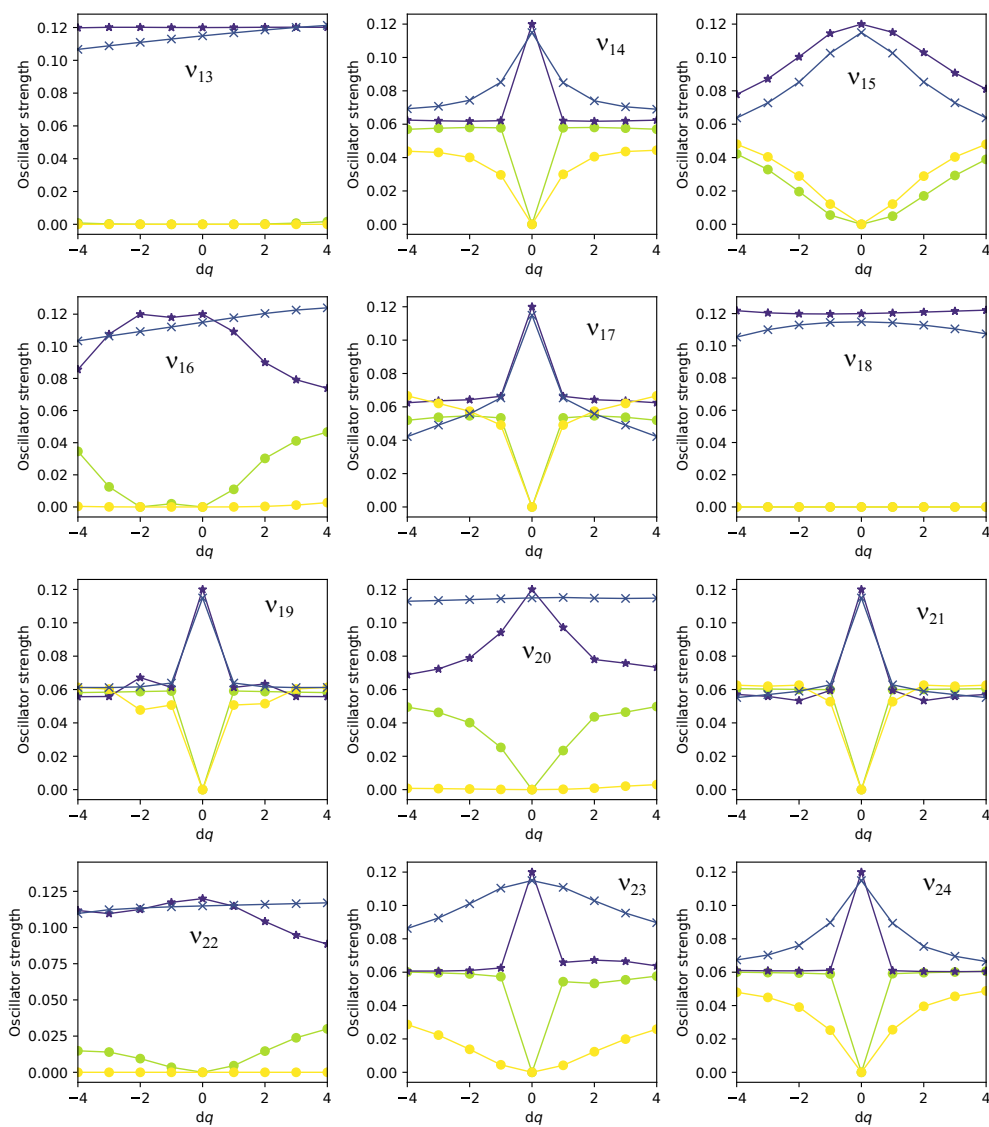


Figure S8 Oscillator strengths along vibrational coordinates 13-24 calculated at the SRC1-r1/cc-pVTZ and cc-CVTZ level.

Table S7 Relative intensities and excitation energies (with respect to the adiabatic energy), and assignments of the X-ray absorption spectral lines associated with the core-excited states of butadiene. Only values for relative intensities higher than 0.01 are given. Relative intensities are calculated as $I_{\circ}^{calc} = \langle \xi' | \xi'' \rangle^2 e^{-E''/kT}$, $T = 300$ K.

XAS edge C		
Energy / eV	Rel. Intensity	Assignment
-0.0188	0.0408	ν_1 hb
0.0000	0.1352	0-0
0.0178	0.0190	ν_1
0.0482	0.0154	$\nu_1 + \nu_2$ hb
0.0670	0.0511	$2\nu_2$
0.1056	0.0108	ν_{10}
0.1057	0.0095	ν_5
0.1064	0.0091	$2\nu_7$
0.1340	0.0108	$2\nu_2$
0.1541	0.0166	ν_{12}
0.1621	0.0163	ν_{11}
0.1659	0.0146	ν_{14}
0.4101	0.0058	$\nu_1 + \nu_{21}$ hb
0.4289	0.0194	ν_{21}
0.4959	0.0073	$\nu_2 + \nu_{21}$
XAS central C		
Energy / eV	Rel. Intensity	Assignment
0.0000	0.3928	0-0
0.0678	0.0073	ν_2
0.1106	0.0017	$2\nu_3$
0.1184	0.0309	ν_5
0.1274	0.0169	$2\nu_6$
0.1352	0.0137	$2\nu_7$
0.1614	0.0270	ν_{11}
0.1922	0.0190	ν_{15}
0.2117	0.1217	ν_{17}
0.3301	0.0096	$\nu_5 + \nu_{17}$
0.4234	0.0190	$2\nu_{17}$
0.4240	0.1019	ν_{20}
0.6357	0.0316	$\nu_{17} + \nu_{20}$

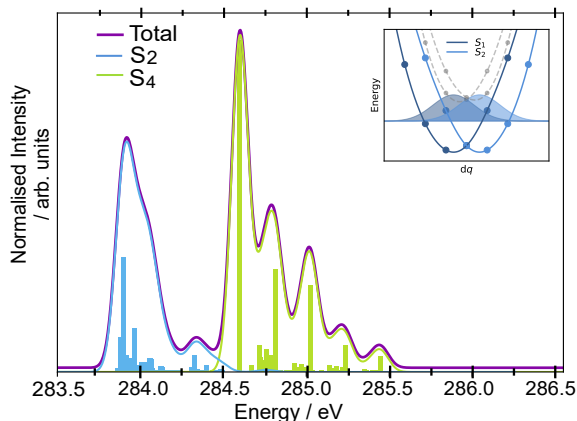


Figure S9 Theoretical core X-ray absorption vibronic spectrum calculated at the MOM/B3LYP/cc-pVTZ + cc-pCVTZ level with a double harmonic approximation. The peaks were broadened by a phenomenological 0.05 eV. The 0-0 transition for the S_2 state was shifted to 283.9 eV, and the 0-0 transition for the S_4 state was shifted to 285.6 eV to match the experimental spectrum. Inset is a schematic of the lowest vibrational energy level of S_1 and S_2 in the harmonic approximation (S_1 is equal to S_2) for mode ν_{21} to show the harmonic approximation (yielding diabatic states).

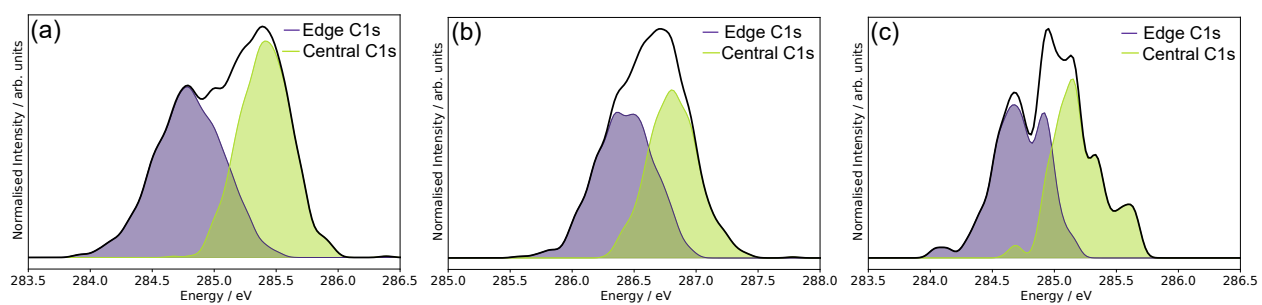


Figure S10 X-ray absorption spectra calculated within NEA at TDDFT/SRC1-r1/cc-pVTZ (a), CVS-EOM-EE-CCSD/cc-pVDZ + cc-pCDZ (b) levels for an ensemble of 400 geometries and CVS-EOM-EE-CCSD/cc-pVTZ + cc-pCVZ (c) level for an ensemble of 50 geometries.

1 Details on theoretical methods for XAS spectra modelling

The Auger spectra are complex because they involve both core-excited (or core-ionised) and valence ionised states. All of these states can contain vibrational structure which may be convoluted in the Auger signal. Theoretical methods are typically tailored specifically for either the core or the valence region, but in our case a common approach is beneficial and we opt for a compromise. To model the vibrationally resolved spectra, the Maximum Overlap Method (MOM) was used with the B3LYP functional and the cc-pVTZ basis sets on the hydrogen atoms and the cc-pCVTZ basis sets on the carbon atoms (hereafter referred to as cc-pVTZ + cc-pCVTZ). The B3LYP functional was selected because of its accurate performance in combination with Δ SCF methods.^{4,5} The MOM method is in principle a ground state method and allows both gradients and Hessians to be estimated analytically, and it provides results for vibrationally resolved core-excited, core-ionised and valence ionised spectra that are directly comparable. We are aware that the absolute errors provided by the MOM/B3LYP method for energies of core-excited or core-ionised states are on the order of several eVs, but the relative positions of peaks, gradients and Hessians are comparable to those obtained by more accurate methods.

Beyond harmonic approximation

To model the core-excited absorption spectra beyond the harmonic approximations, we adapted our own approach. The potential energy surfaces of the ground and first four core-excited states were calculated along the ground-state normal modes q_i , see Figures S5 and S6. The global potential energy surface of the j -th electronic state was assumed in the following form:

$$E^j(q_1, \dots, q_{24}) = E_0^j + \sum_{i=1}^{24} E_i^j(q_i) \quad (1)$$

where E_0^j is the electronic energy of the j -th state at the ground-state minimum geometry and $E_i^j(q_i)$ captures its dependence on the normal mode q_i . The total Hamiltonian of the j -th electronic states then appears as

$$\hat{H} = - \sum_{i=1}^{24} \frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial q_i^2} + E_0^j + \sum_{i=1}^{24} E_i^j(q_i) = E_0^j + \sum_{i=1}^{24} [\hat{T}_i + E_i^j(q_i)] = E_0^j + \sum_{i=1}^{24} \hat{H}_i^j(q_i) \quad (2)$$

and leads to a series of one-dimensional Schrödinger equations for each normal mode

$$\hat{H}_i^j(q_i) \chi_{i,n}^j(q_i) = \epsilon_{i,n}^j \chi_{i,n}^j(q_i) \quad (3)$$

These one-dimensional Schrödinger equations were solved with imaginary time (τ) propagation using the split operator method

$$\chi_{i,0}^j(\tau) = \exp\left(-\frac{\hat{H}_i^j \tau}{\hbar}\right) \chi_{\text{trial}} \quad (4)$$

The wave function was normalised at every step. To obtain higher eigenstates $\chi_{i,n>0}^j$, the lower eigenfunctions were projected out of the trial function. The overlaps between the initial and final vibrational states were integrated numerically. For all the calculations, we wrote our own Fortran and Python codes.

Table S8 Double ionisation potential (DIP) energies in eV for butadiene for the minimum energy optimised structure of butadiene at the EOM-DIP-CCSD/cc-pVTZ + cc-pCVTZ level. Molecular orbitals dominantly involved in the doubly ionised states are listed. The ground state valence shell electronic configuration of butadiene is given as $(3a_g)^2(3b_u)^2(4a_g)^2(4b_u)^2(5b_u)^2(5a_g)^2(6a_g)^2(6b_u)^2(7a_g)^2(1a_u)^2(1b_g)^2$.

Singlet states		Triplet states	
Orbitals	Energy / eV	Orbitals	Energy / eV
$(1b_g 1b_g)^{-2}$	25.37	$(1a_u 1b_g)^{-2}$	26.88
$(7a_g 1b_g)^{-2}$	28.40	$(7a_g 1b_g)^{-2}$	28.26
$(6b_u 1b_g)^{-2}$	29.33	$(6b_u 1b_g)^{-2}$	29.18
$(6a_g 1b_g)^{-2}$	30.15	$(6a_g 1b_g)^{-2}$	29.88
$(1a_u 1b_g)^{-2}$	30.23	$(5b_u 1b_g)^{-2}$	31.21
$(5b_u 1b_g)^{-2}$	31.26	$(5a_g 1b_g)^{-2}$	31.39
$(5a_g 1b_g)^{-2}$	31.47	$(7a_g 1a_u)^{-2}$	31.92
$(7a_g 7a_g)^{-2}$	31.74	$(6b_u 7a_g)^{-2}$	31.99
$(1a_u 1a_u)^{-2}$	32.36	$(6a_g 7a_g)^{-2}$	33.06
$(7a_g 1a_g)^{-2}$	32.48	$6b_u 1a_u)^{-2}$	33.14
$(6a_g 7a_g)^{-2}$	33.36	$(6a_g 6b_u)^{-2}$	33.73
$(6b_u 1a_u)^{-2}$	33.76	$(4b_u 1b_g)^{-2}$	33.88
$(6a_g 6b_u)^{-2}$	33.80	$(6a_g 1a_u)^{-2}$	34.04
$(4b_u 1b_g)^{-2}$	33.89	$(5a_g 7a_g)^{-2}$	34.84
$(6b_u 7a_g)^{-2}$	34.10	$(5b_u 1a_u)^{-2}$	35.03
$(6b_u 6b_u)^{-2}$	34.43	$(5a_g 6b_u)^{-2}$	35.59
$(6a_g 1a_u)^{-2}$	34.95	$(5b_u 6a_g)^{-2}$	35.66
$(6a_g 6a_g)^{-2}$	35.04	$(5a_g 1a_g)^{-2}$	35.79
$(5b_u 1a_u)^{-2}$	35.29	$(5b_u 7a_g)^{-2}$	36.04
$(5a_g 6a_g)^{-2}$	36.49	$(5a_g 6a_g)^{-2}$	36.06
$(5a_g 1a_u)^{-2}$	36.74	$(4a_g 1b_g)^{-2}$	36.23
$(5b_u 7a_g)^{-2}$	36.78	$(5a_g 6a_g)^{-2}$	37.60
$(5a_g 7a_g)^{-2}$	36.95	$(4b_u 7a_g)^{-2}$	37.82
$(4a_g 1b_g)^{-2}$	37.16	$(4b_u 1a_u)^{-2}$	38.08
$(4b_u 7a_g)^{-2}$	37.46		

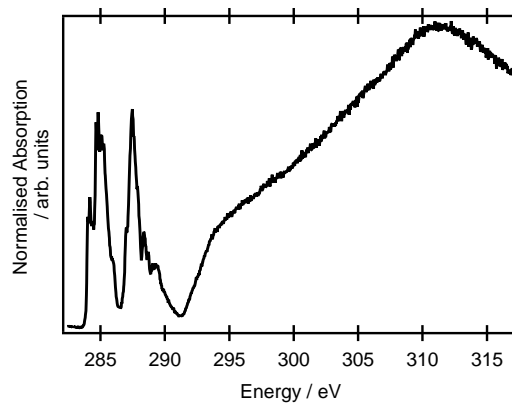


Figure S11 X-ray absorption spectrum (XAS) of butadiene over an extended energy range.

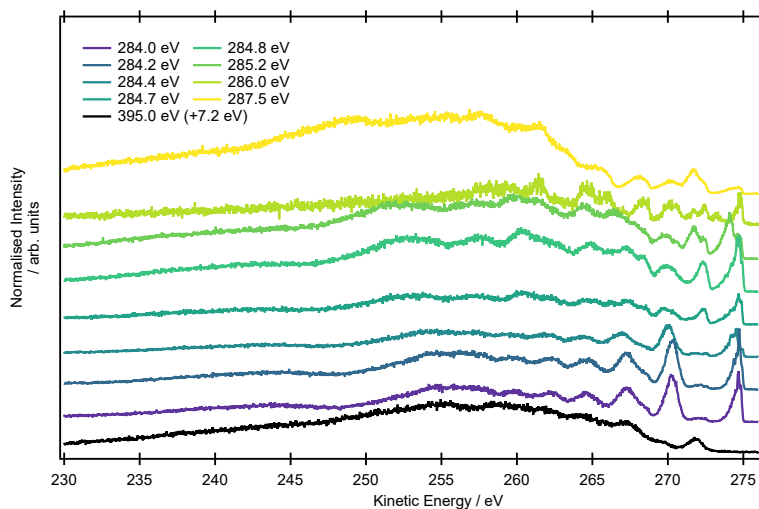


Figure S12 Comparison of the non-resonant Auger spectrum to the resonant Auger spectra at a series of incident photon energies. The spectra have been arbitrarily shifted to match the kinetic energies of the first spectral feature. The spectral intensities have been scaled relative to the intensities in the measured XAS spectrum.

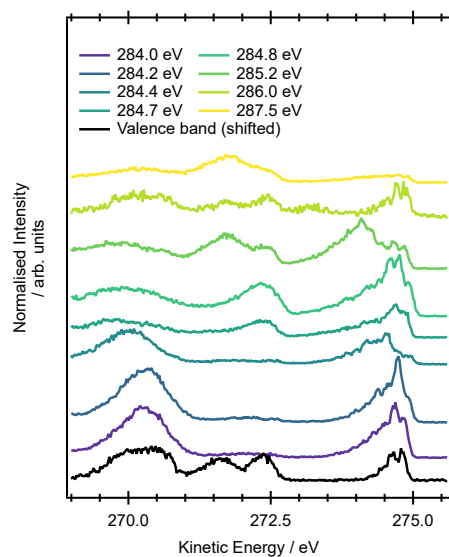


Figure S13 The high kinetic energy region of the resonant Auger spectra of butadiene compared to the valence band photoelectron spectrum that has been arbitrarily shifted. The spectral intensities have been scaled relative to the intensities in the measured XAS spectrum.

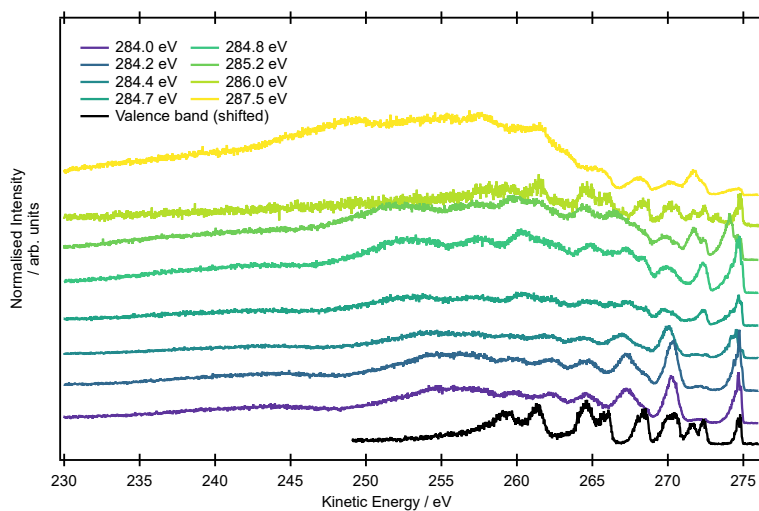


Figure S14 Resonant Auger spectra of butadiene compared to the valence band photoelectron spectrum that has been arbitrarily shifted. The spectral intensities have been scaled relative to the intensities in the measured XAS spectrum.

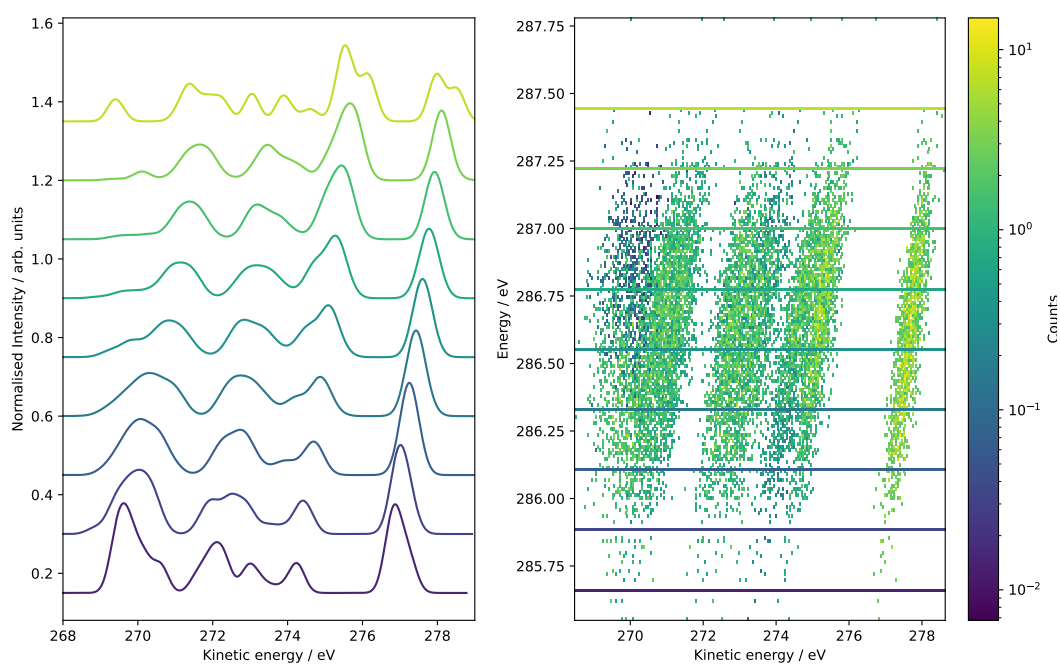


Figure S15 Resonant Auger spectra calculated across the pre-edge region of butadiene in 2D for an ensemble of 400 geometries at the EOM-CCSD/cc-pVDZ + cc-pCVDZ level. Spectra were Gaussian broadened by 0.2 eV.

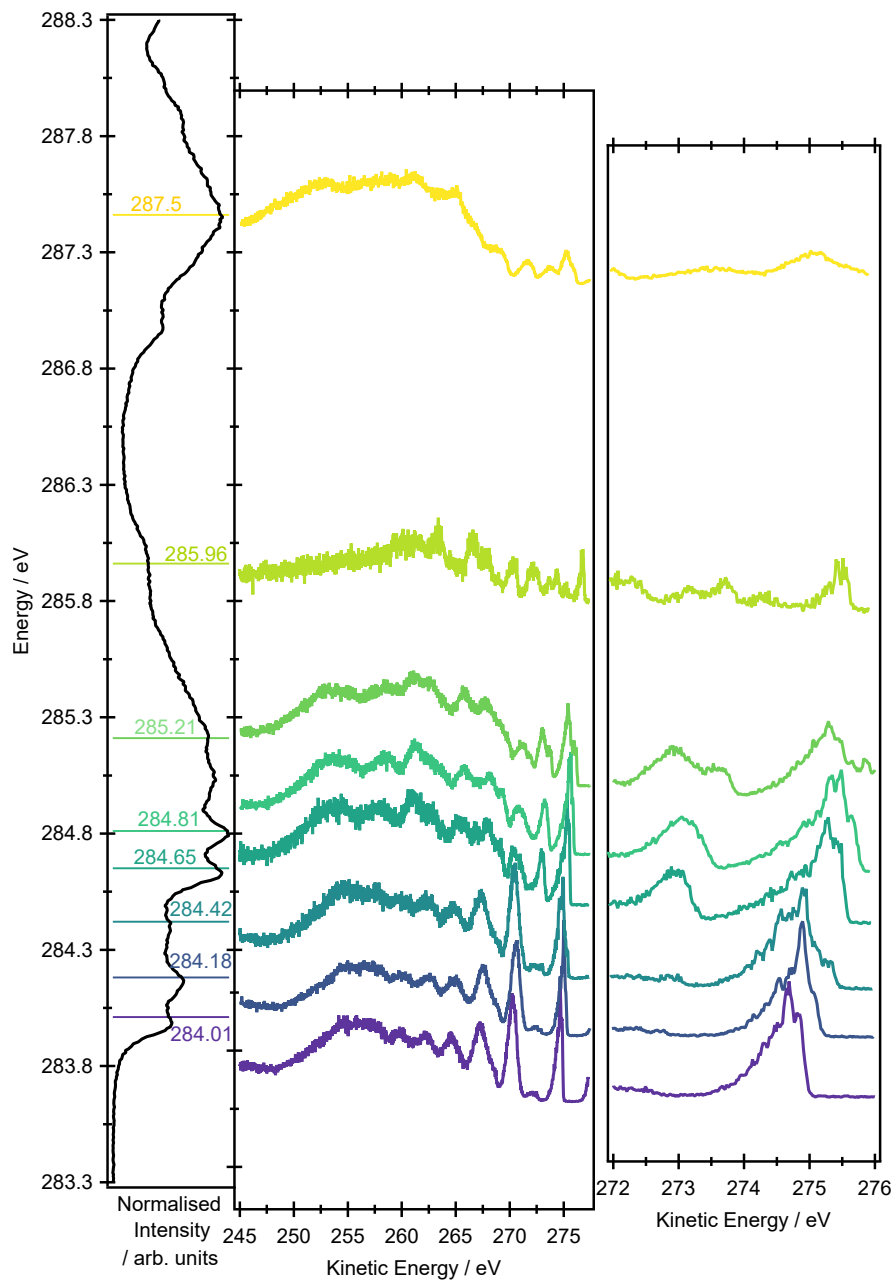


Figure S16 Resonant Auger measurements across the pre-edge region of butadiene recorded with an incident photon bandwidth of ~ 65 meV. The left-most panel is the absorption spectrum where the lines denote the excitation energies used for the Auger measurements. The right-most panel focuses on the band in the resonant Auger measurements which corresponds to the participator decay into the $\tilde{X} \ ^2B_g$ final state.

Notes and references

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