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

Supplementary Information

Real-time observation of the Woodward-Hoffmann rule for 1,3-cyclohexadiene by femtosecond soft X-ray transient absorption

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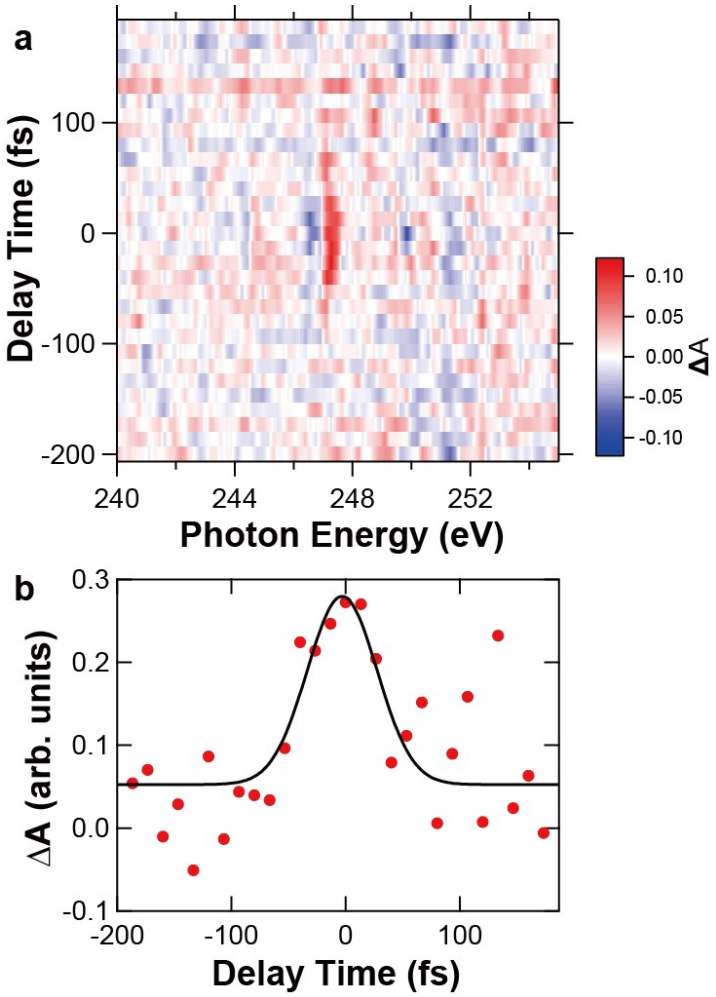


Fig. S1. Cross-correlation measurement between the pump and probe pulses by the AC Stark shift of Ar atoms. (a) Spectrogram of the AC Stark shift of the $2p_{3/2} \rightarrow 3d$ absorption line. (b) Temporal evolution of the absorbance change at 247.3 eV. The solid line is the fitting result to the Gaussian function.

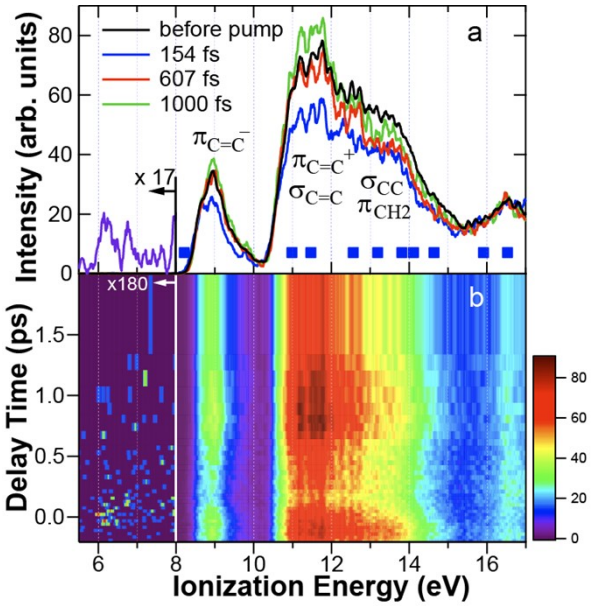


Fig. S2. Time-resolved photoelectron spectra of CHD. a) Photoelectron spectrum before pump (black) and the spectra at 154 fs (blue), 607 fs (red), and 1000 fs (green). The solid squares indicate the theoretical ionization energies of 1,3-cyclohexadiene. The spectrum of the excited states integrated between −140 and 250 fs is shown by the purple line below 8 eV. b) Photoelectron spectrogram between −0.2 and 2 ps. (Replot of Fig. 4 in ref 18 with permission from the Royal Society of Chemistry.)

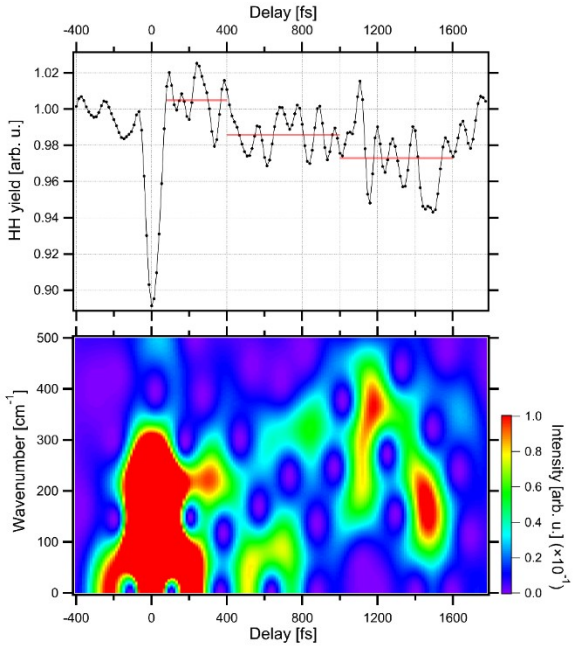


Fig. S3. (a) Experimentally observed yield of the 19th harmonic [identical to Fig. 4b]. The horizontal red lines show the average values of the data points (black dots) within the range of the length of each red line. (b) Short-time Fourier spectra of the transient harmonic yield [black dots in (a)]. (Replot of Fig. 5 in ref 21 with permission from the Optical Society of America)

Table S1. Cartesian coordinates (in Å) of the key structures, **CHD, TS1**, ***cZc*-HT**, ***cZt*-HT**, and ***tZt*-HT**, in the disrotatory reaction pathway. **TS1** is the disrotatory transition state which connects two equilibrium structures **CHD** and ***cZc*-HT** by the intrinsic reaction coordinate (IRC). The IRC was computed at B3LYP-D3/cc-pVDZ level of theory.

CHD: $E(S_0)$ = -233.438398888499 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	1.204414024748	0.194063030519	-0.795001942760
C	0.066301788867	-0.328763702087	0.051865495176
C	0.068947775583	-0.132010412223	1.383878870708
C	1.191323142311	0.554997807423	2.035690776124
C	2.354470252371	0.738998442708	1.382856986293
C	2.531273675124	0.201871271723	-0.019310412057
H	1.308569851191	-0.391655858665	-1.722267313817
H	0.953460302793	1.228668116528	-1.110039101804
H	-0.784935404725	-0.807039799239	-0.440925333082
H	-0.773834193372	-0.460419621452	1.998358738512
H	1.071093441695	0.894084751561	3.068294957220
H	3.204095652649	1.217332291473	1.878358104099
H	2.923233917141	-0.834253806763	0.054601915469
H	3.291417802334	0.778256285704	-0.570419604690

TS1: $E(S_0)$ = -233.368601278395 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	0.927757194600	-0.099364818000	-0.970519529800
C	0.029270343800	-0.426602281500	0.054406645200
C	0.018876083900	0.142146363200	1.332672570700
C	1.178977451400	0.572558363900	2.008159076800
C	2.469171991300	0.478539781500	1.475137902900
C	2.794800405900	0.593040763700	0.116572417000
H	1.064241350700	-0.816861989300	-1.788784555300
H	0.986266794300	0.934913645400	-1.289583791400
H	-0.617914894800	-1.303334034900	-0.083180855400
H	-0.856458476900	-0.046057528600	1.963729036700
H	1.086075432600	0.674689342500	3.094806362400
H	3.247497207600	0.130714976100	2.167720241400
H	3.752227487700	0.179896938200	-0.223481688000
H	2.506258921700	1.498470041800	-0.404859311200

***cZc*-HT**: $E(S_0)$ = -233.400585023787 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	0.362278862371	0.096914728746	-1.168635160686
C	-0.033107722869	-0.547553875444	-0.060576651405
C	0.166706356812	-0.132711004174	1.337232119046
C	1.184551469480	0.528094555306	1.934877221781
C	2.496324923488	0.956728544818	1.423645500536

C	3.269091170593	0.326765847827	0.526190778094
H	0.108426274414	-0.286013003452	-2.159983436968
H	0.946475591300	1.018526609715	-1.118780615233
H	-0.644900067635	-1.450912046919	-0.180391748181
H	-0.669513559167	-0.402292485852	1.994311973052
H	1.023755667993	0.785566672205	2.989165076655
H	2.896590048999	1.857558999472	1.906322675398
H	4.254160360033	0.718797305563	0.261919469859
H	2.943198304187	-0.591592763310	0.032692897674

***cZt*-HT**: $E(S_0)$ = -233.410095333999 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	2.477124477498	0.674883932373	0.094210445496
C	1.156775078440	0.469976231119	0.250980288570
C	0.542322606246	-0.849275490226	0.263176088215
C	-0.781723093864	-1.137702200760	0.307690324208
C	-1.917846939575	-0.212313494068	0.260443945372
C	-2.021280023892	0.903860199001	-0.481120651630
H	2.905027759116	1.679420121731	0.116784833198
H	3.168346666805	-0.158457040127	-0.067265908303
H	0.497108754011	1.329540092999	0.403048781007
H	1.240130271927	-1.694758441755	0.279095289138
H	-1.054213381300	-2.193779304844	0.418926879588
H	-2.783632993599	-0.510548971308	0.865999300379
H	-2.922887459309	1.520135092141	-0.446107587542
H	-1.227266643958	1.217440699201	-1.163266778363

***tZt*-HT**: $E(S_0)$ = -233.415894962494 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	2.818129172513	0.235210402410	-0.112360114537
C	1.476664305263	0.337304198848	-0.141370942227
C	0.580742936644	-0.674825970119	0.393993470094
C	-0.776549968574	-0.642241712907	0.400454179176
C	-1.627934467629	0.411792462586	-0.126680725643
C	-2.972421444489	0.374375910265	-0.084513321185
H	3.459562717613	1.016635054467	-0.524876326215
H	3.312387133590	-0.637017509881	0.326908754431
H	1.029171458557	1.229113075058	-0.591552704716
H	1.069182070811	-1.550843416386	0.835656884538
H	-1.302253540961	-1.493891158858	0.846979772377
H	-1.142495483751	1.281119969595	-0.581458251988
H	-3.579503595135	1.185752428573	-0.491192102401
H	-3.503787391897	-0.473094784068	0.359909802773

TS1: $E(S_0)$ = -233.368601278395 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	0.927757194600	-0.099364818000	-0.970519529800
C	0.029270343800	-0.426602281500	0.054406645200
C	0.018876083900	0.142146363200	1.332672570700
C	1.178977451400	0.572558363900	2.008159076800
C	2.469171991300	0.478539781500	1.475137902900
C	2.794800405900	0.593040763700	0.116572417000
H	1.064241350700	-0.816861989300	-1.788784555300
H	0.986266794300	0.934913645400	-1.289583791400
H	-0.617914894800	-1.303334034900	-0.083180855400
H	-0.856458476900	-0.046057528600	1.963729036700
H	1.086075432600	0.674689342500	3.094806362400
H	3.247497207600	0.130714976100	2.167720241400
H	3.752227487700	0.179896938200	-0.223481688000
H	2.506258921700	1.498470041800	-0.404859311200

Table S2. Cartesian coordinates (in Å) of the key structures, **CHD, TS2**, ***cEc*-HT**, ***cEt*-HT**, and ***tEt*-HT**, in the conrotatory reaction pathway. **TS2** is the conrotatory transition state which connects two equilibrium structures **CHD** and ***cEc*-HT** by the intrinsic reaction coordinate (IRC). The IRC was computed at B3LYP-D3/cc-pVDZ level of theory. [a]This geometry came from the end point of the conrotatory IRC, and this structure is identical to **CHD** structure in the disrotatory IRC listed in Table S1.

CHD[a]: $E(S_0)$ = -233.438398194973 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	0.261582208255	0.722570680709	-1.177508889835
C	-0.044289810589	1.426505026367	0.125092736558
C	-0.098445417215	0.727625047253	1.274711578166
C	0.098561088662	-0.727636814610	1.274722640416
C	0.044431702498	-1.426510987740	0.125108194683
C	-0.261522907746	-0.722593620780	-1.177472796535
H	-0.153371468794	1.277879321471	-2.033791338752
H	1.363012189048	0.717837990616	-1.317166556300
H	-0.153901365517	2.514718532942	0.126700325801
H	-0.267635456876	1.234571658028	2.228693907453
H	0.267966755408	-1.234554280620	2.228694182766
H	0.153984818871	-2.514705424486	0.126671763660
H	-1.362971320065	-0.717831614525	-1.316983445955
H	0.153324437487	-1.277953134127	-2.033764182555

TS2: $E(S_0)$ = -233.315028022028 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	0.725004425500	1.072256195300	-1.017455631200
C	0.014355905200	1.526951794300	0.120236010900
C	-0.321075740200	0.653620412100	1.137339253500
C	0.321075749600	-0.653620425100	1.137339302800
C	-0.014355928600	-1.526951786800	0.120236043600
C	-0.725004322900	-1.072256081600	-1.017455717500
H	0.767084376900	1.713644270700	-1.902766699900
H	1.460812722800	0.274629205000	-0.961437505900
H	-0.543547996100	2.466219249200	0.031820097900
H	-1.294333667100	0.788887110000	1.625071498700
H	1.294333720400	-0.788887172300	1.625071478600
H	0.543547865400	-2.466219332600	0.031820119200
H	-1.460812635100	-0.274629080600	-0.961437563900
H	-0.767084475900	-1.713644357600	-1.902766686700

***cEc*-HT**: $E(S_0)$ = -233.407463518297 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	1.352112888585	2.312445303562	-0.294194832370
C	0.164747032164	1.931507130936	0.207922584055
C	-0.367784609555	0.567593205834	0.233591188057

C	0.367754170603	-0.567592759622	0.233599995669
C	-0.164758151773	-1.931499801966	0.207789272769
C	-1.352061803843	-2.312433430950	-0.294466017271
H	1.677472831004	3.354090692781	-0.246576441741
H	2.027630686731	1.600580887976	-0.777085298607
H	-0.492884901479	2.702097961452	0.627794878982
H	-1.458611810135	0.480296010320	0.294427308125
H	1.458572824972	-0.480281125287	0.294617215555
H	0.492845176147	-2.702098098783	0.627671486830
H	-2.027531151523	-1.600577709989	-0.777430963633
H	-1.677356467916	-3.354115007147	-0.247073473287

***cEt*-HT**: $E(S_0)$ = -233.413038669106 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	1.438726002599	2.299528490643	-0.128450192038
C	0.159615884279	1.903144394611	-0.006621391804
C	-0.311982144523	0.550475892074	0.293926697377
C	0.381312560272	-0.598753926982	0.118279644236
C	-0.132393028310	-1.914112474254	0.454197590299
C	0.547058139769	-3.062296167014	0.278953184640
H	1.686402814876	3.334694291952	-0.373051096735
H	2.275200283810	1.611366703223	0.022602699122
H	-0.627504410772	2.657509010787	-0.122415797551
H	-1.335326236772	0.477055407084	0.681499458212
H	1.387845580459	-0.560637734350	-0.315020085312
H	-1.143065113986	-1.949548662492	0.879273780339
H	1.557821430594	-3.065574647141	-0.140469354482
H	0.116282655448	-4.028339730247	0.550004100685

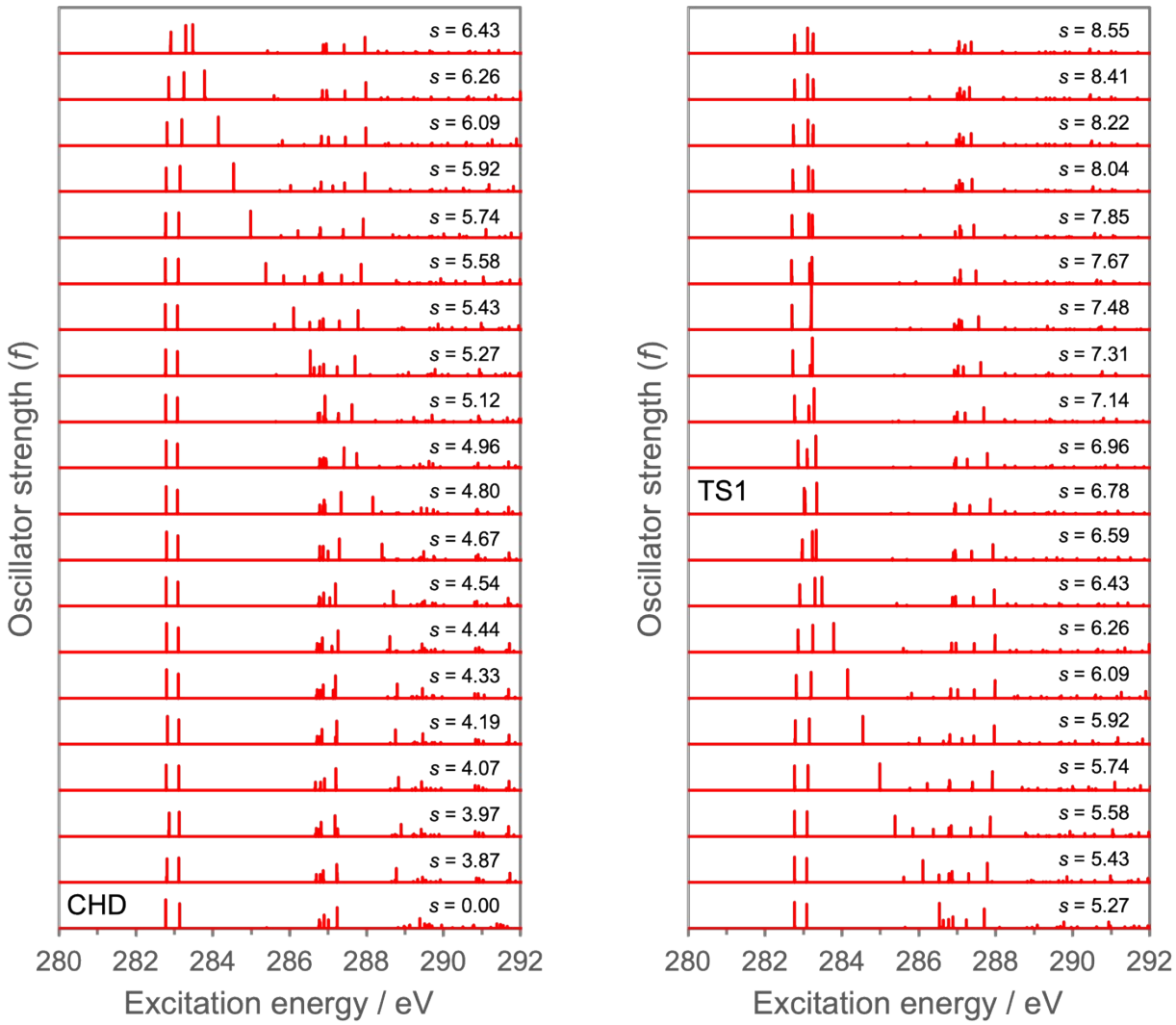
***tEt*-HT**: $E(S_0)$ = -233.418652857267 hartree, $\langle S^2 \rangle$ = 0.000000000000

Atom	x	y	z
C	-0.327211843317	3.054940267588	0.445989274926
C	-0.124063921762	1.863023598482	-0.144598473114
C	-0.115042959967	0.591857340609	0.555406717372
C	0.089885664033	-0.606188973372	-0.042446483162
C	0.099104964815	-1.877307245124	0.657646118595
C	0.302275222984	-3.069277177655	0.067146827861
H	-0.324153410834	3.984414582151	-0.126971212759
H	-0.502929544945	3.132203254976	1.523371586183
H	0.048744431637	1.824537980862	-1.227142747392
H	-0.286831461705	0.622118878172	1.638816957173
H	0.262041071435	-0.636389513665	-1.125848716692
H	-0.073170405552	-1.838675607770	1.740262744515
H	0.477255607177	-3.146732349332	-1.010329720149
H	0.299489739982	-3.998660201568	0.640254041765

Table S3. Cartesian coordinates (in Å) of **CHD cation** in the cationic ground state. This geometry was optimized at B3LYP-D3/cc-pVDZ level of theory.

CHD cation: $E(D_0)$ = -233.146342193951 hartree, $\langle S^2 \rangle$ = 0.750025495088

Atom	x	y	z
C	0.079449382100	0.764067259800	-1.216813910200
C	-0.024506760400	1.416245446000	0.105659638600
C	-0.033443653500	0.707768520500	1.300652978400
C	0.033443653500	-0.707768520500	1.300652978400
C	0.024506760400	-1.416245446000	0.105659638600
C	-0.079449382100	-0.764067259800	-1.216813910200
H	-0.617778734100	1.251543194400	-1.922404662700
H	1.075498204900	1.055830482800	-1.620292351400
H	-0.052528339300	2.510223784000	0.135701051500
H	-0.078068162200	1.245604195100	2.250304255900
H	0.078068162200	-1.245604195200	2.250304255900
H	0.052528339400	-2.510223784000	0.135701051400
H	-1.075498204900	-1.055830482800	-1.620292351400
H	0.617778734000	-1.251543194400	-1.922404662800


Oscillator strength (f)
s = 6.43
s = 6.26
s = 6.09
s = 5.92
s = 5.74
s = 5.58
s = 5.43
s = 5.27
s = 5.12
s = 4.96
s = 4.80
s = 4.67
s = 4.54
s = 4.44
s = 4.33
s = 4.19
s = 4.07
s = 3.97
s = 3.87
CHD
s = 0.00
280 282 284 286 288 290 292
Excitation energy / eV
Oscillator strength (f)
s = 8.55
s = 8.41
s = 8.22
s = 8.04
s = 7.85
s = 7.67
s = 7.48
s = 7.31
s = 7.14
s = 6.96
TS1
s = 6.78
s = 6.59
s = 6.43
s = 6.26
s = 6.09
s = 5.92
s = 5.74
s = 5.58
s = 5.43
s = 5.27
280 282 284 286 288 290 292
Excitation energy / eV

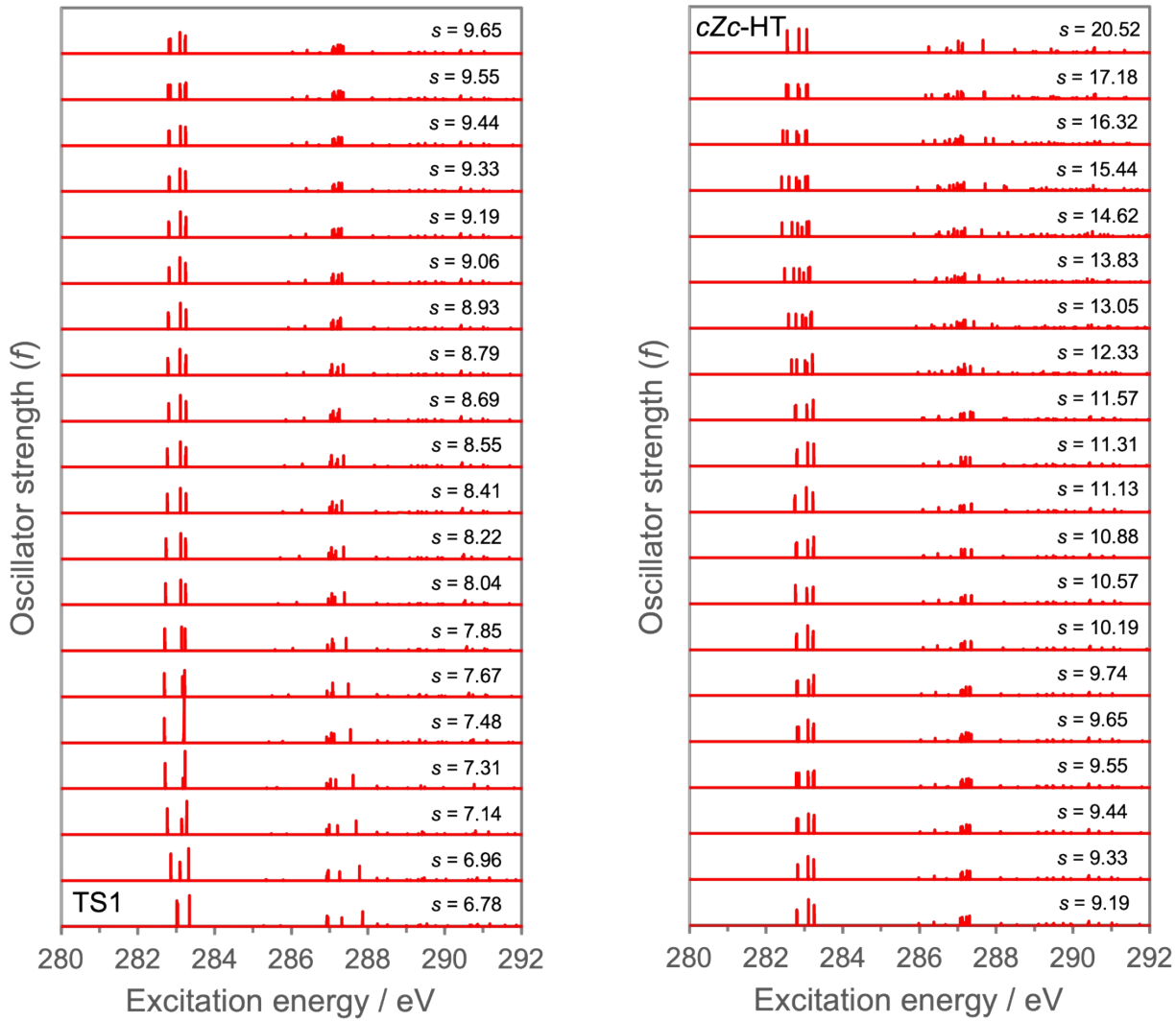
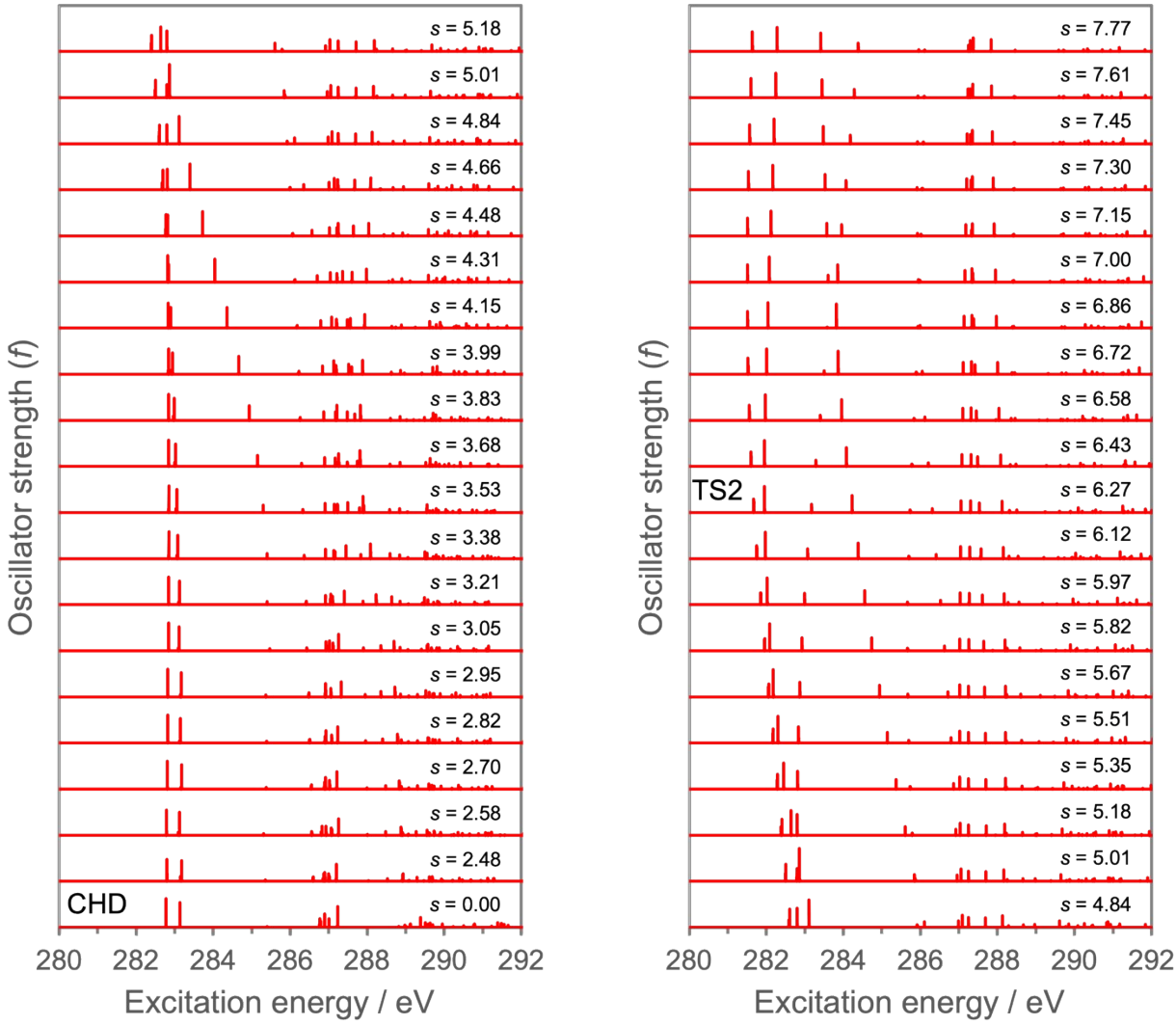
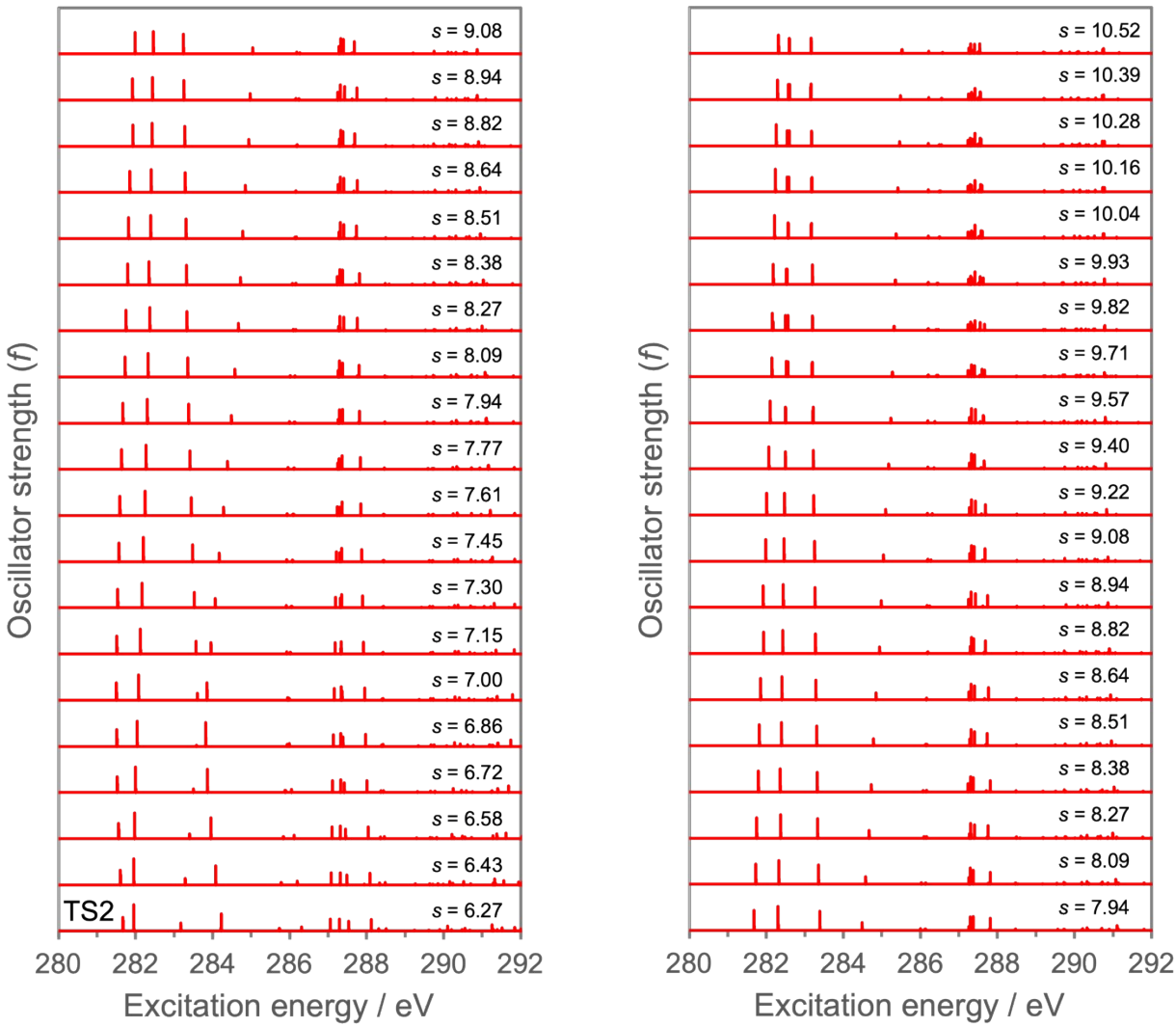


Fig. S4. Computed absorption spectra along the disrotatory pathway. The value *s* stands for the reaction coordinate [Å amu$^{1/2}$] where $s = 0$ corresponds to CHD (see **Figs. 5a** and **6a**).


Oscillator strength (f)
s = 5.18
s = 5.01
s = 4.84
s = 4.66
s = 4.48
s = 4.31
s = 4.15
s = 3.99
s = 3.83
s = 3.68
s = 3.53
s = 3.38
s = 3.21
s = 3.05
s = 2.95
s = 2.82
s = 2.70
s = 2.58
s = 2.48
CHD
s = 0.00
280 282 284 286 288 290 292
Excitation energy / eV
Oscillator strength (f)
s = 7.77
s = 7.61
s = 7.45
s = 7.30
s = 7.15
s = 7.00
s = 6.86
s = 6.72
s = 6.58
s = 6.43
TS2
s = 6.27
s = 6.12
s = 5.97
s = 5.82
s = 5.67
s = 5.51
s = 5.35
s = 5.18
s = 5.01
s = 4.84
280 282 284 286 288 290 292
Excitation energy / eV


Oscillator strength (f)
s = 9.08
s = 8.94
s = 8.82
s = 8.64
s = 8.51
s = 8.38
s = 8.27
s = 8.09
s = 7.94
s = 7.77
s = 7.61
s = 7.45
s = 7.30
s = 7.15
s = 7.00
s = 6.86
s = 6.72
s = 6.58
s = 6.43
TS2
s = 6.27
280 282 284 286 288 290 292
Excitation energy / eV
Oscillator strength (f)
s = 10.52
s = 10.39
s = 10.28
s = 10.16
s = 10.04
s = 9.93
s = 9.82
s = 9.71
s = 9.57
s = 9.40
s = 9.22
s = 9.08
s = 8.94
s = 8.82
s = 8.64
s = 8.51
s = 8.38
s = 8.27
s = 8.09
s = 7.94
280 282 284 286 288 290 292
Excitation energy / eV

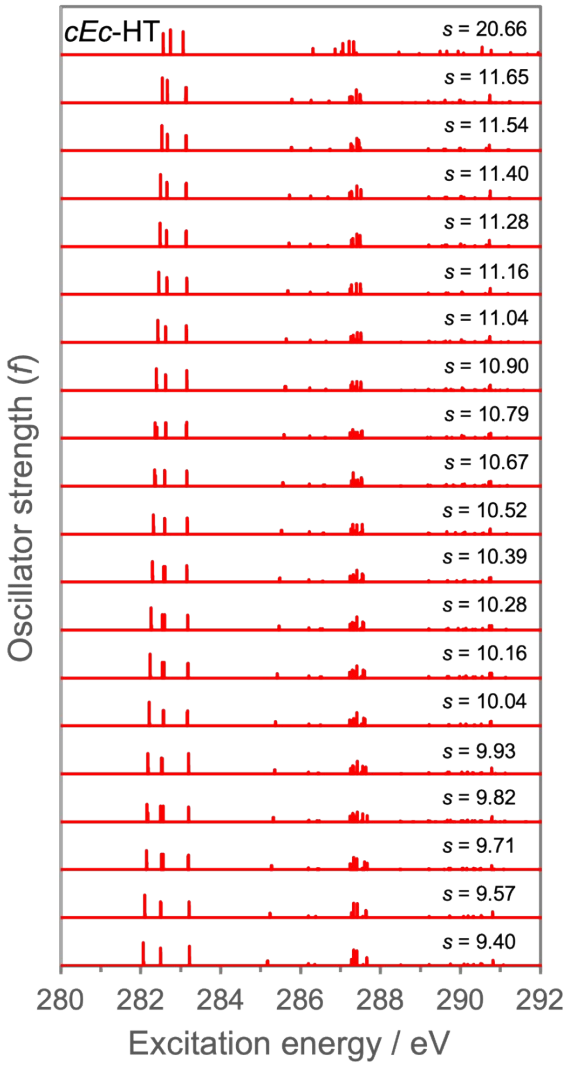


Fig. S5. Computed absorption spectra along the conrotatory pathway. The value *s* stands for the reaction coordinate [Å amu$^{1/2}$] where $s = 0$ corresponds to CHD (see **Figs. 5b** and **6b**).

Table S4. List of excited states with the oscillator strength *f* greater than 0.1 in the region of the peak X (core excitation energy ω_i = 280−285 eV) of the five key structures of the neutral state, **CHD, cZc-HT**, **cEc-HT**, **TS1**, and **TS2**, computed at TD-BHHLYP/cc-pCVDZ level of theory.

Structure	State	ω_i / eV	*f*	Primary excitation	Coeff.
CHD	1634	282.7688	0.1255	$3a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.62428
	1636	283.1304	0.1071	$5a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.60812
TS1	1633	283.0102	0.1118	$1a \rightarrow 24a$ ($C_{1s} \rightarrow \pi^*$)	0.55988
	1635	283.0319	0.0478	$6a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.50121
	1636	283.0361	0.0997	$5a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.48712
	1638	283.3448	0.1351	$4a \rightarrow 24a$ ($C_{1s} \rightarrow \pi^*$)	0.49740
cZc-HT	1633	282.5548	0.0958	$5a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.54782
	1634	282.5562	0.0248	$6a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.54788
	1635	282.8526	0.1032	$4a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.49214
	1637	283.0629	0.0209	$3a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.51551
	1638	283.0636	0.1014	$2a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.42316
TS2	1633	281.6656	0.0589	$6a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.64077
	1634	281.6763	0.0446	$5a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.63936
	1635	281.9497	0.1138	$1a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.63686
	1636	281.9565	0.0125	$2a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.63704
	1637	283.1704	0.0244	$4a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.59745
	1638	283.1704	0.0350	$3a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.59648
	1639	284.2208	0.0136	$3a \rightarrow 24a$ ($C_{1s} \rightarrow \pi^*$)	0.46426
	1640	284.2210	0.0744	$4a \rightarrow 24a$ ($C_{1s} \rightarrow \pi^*$)	0.46508
cEc-HT	1633	282.5665	0.0308	$6a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.56751
	1634	282.5668	0.0881	$5a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.56745
	1635	282.7384	0.1046	$4a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.63838
	1637	283.0629	0.0228	$1a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.52848
	1638	283.0639	0.0963	$2a \rightarrow 23a$ ($C_{1s} \rightarrow \pi^*$)	0.53418

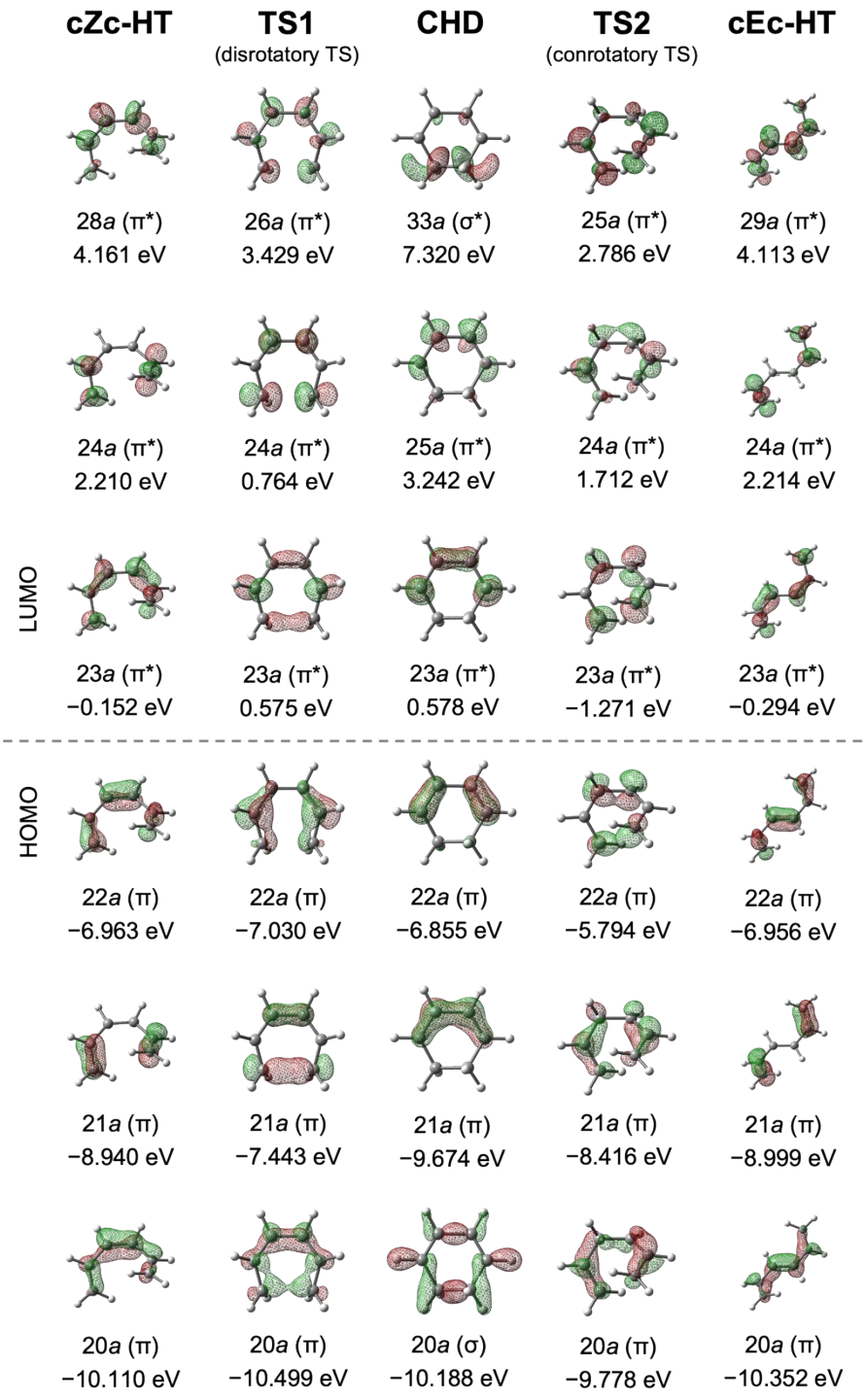


Fig. S6. Low-lying valence (occupied and virtual) molecular orbitals of the five key structures of the neutral state, **CHD, cZc-HT**, **cEc-HT**, **TS1**, and **TS2**, computed at BHHLYP/cc-pCVDZ level of theory. The character and orbital energy of each MO are also indicated.

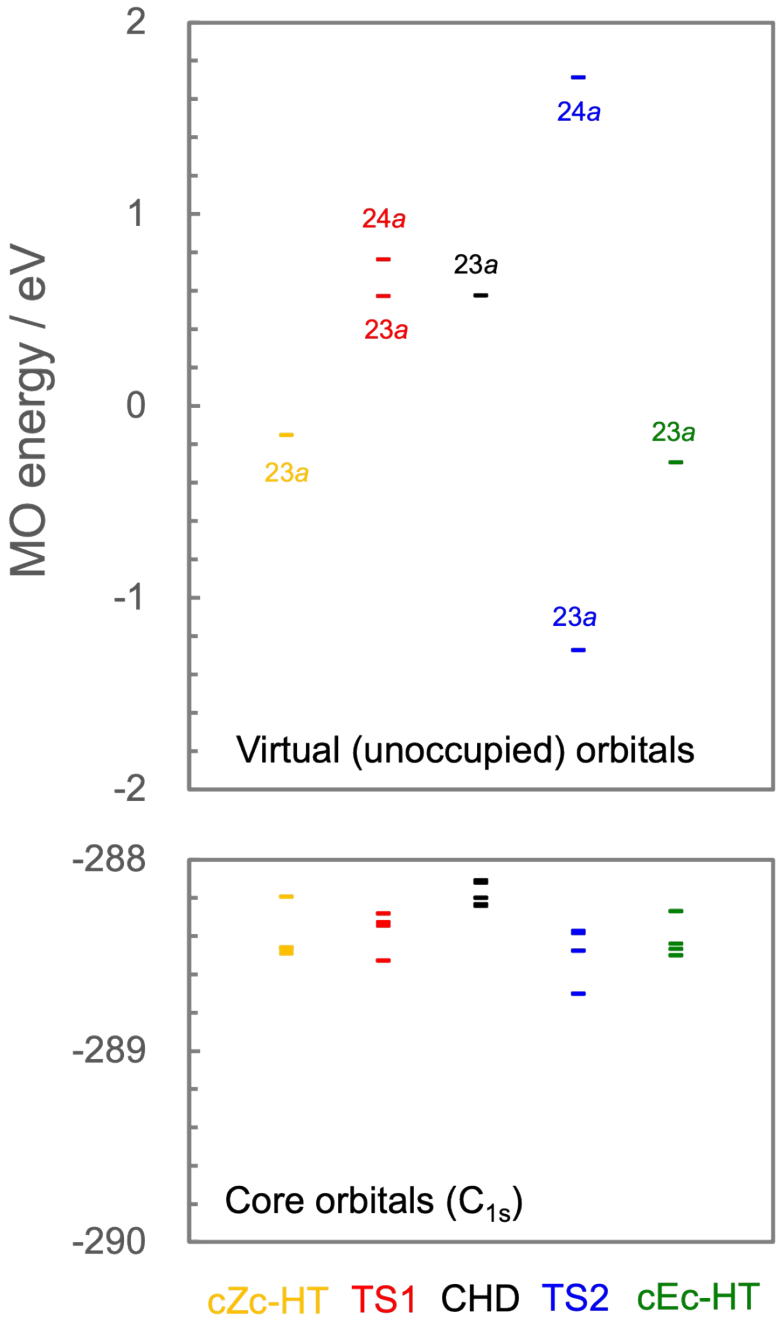


Fig. S7. Energies of the molecular orbitals which are related to the excitations listed in **Table S4**, computed at BHHLYP/cc-pCVDZ level of theory.

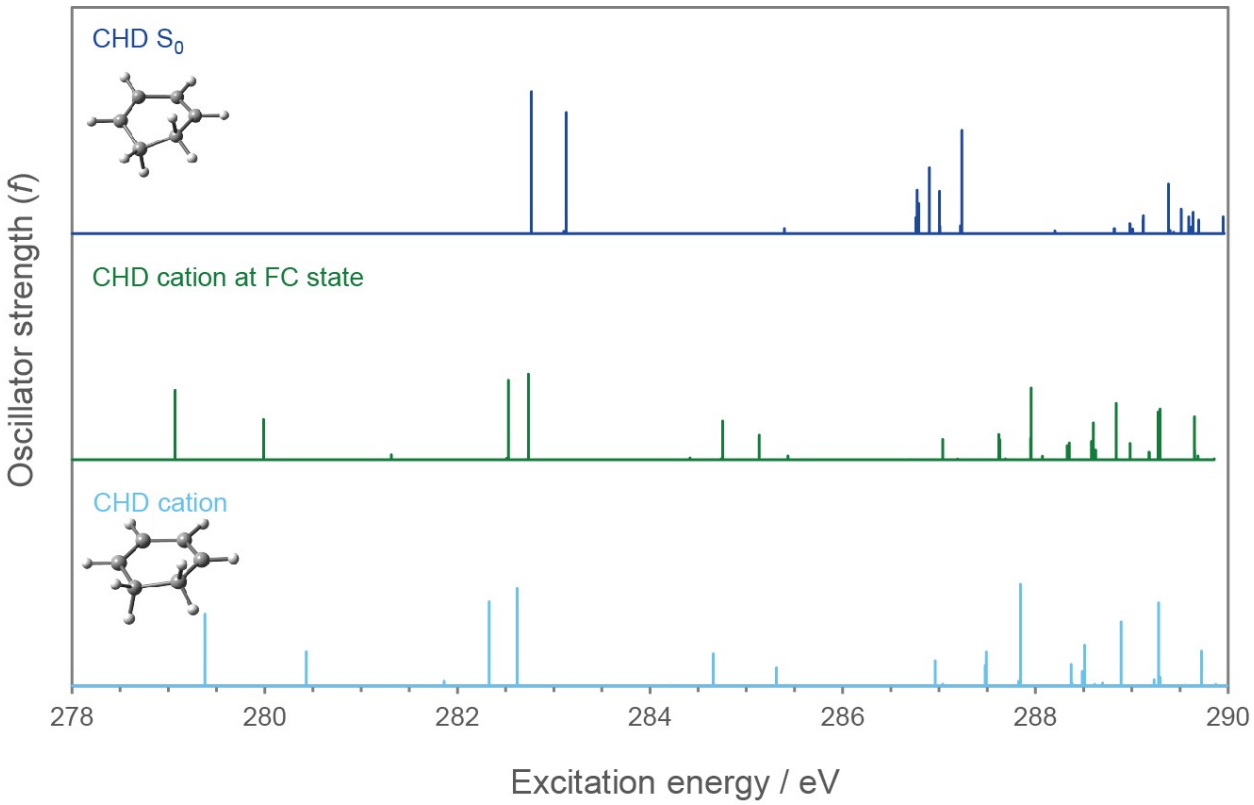


Fig. S8. Absorption spectra of **CHD** in the ground state, **CHD cation at FC state**, and the optimized (relaxed) **CHD cation**.