

Electronic Supplementary Information for:

Mixed transitions in the UV photodissociation of propargyl chloride revealed by slice imaging and multireference ab initio calculations

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Potential energy surfaces of **S**₀, **S**₁, **S**₂, **S**₃, **S**₄, and **S**₅ along the **q**₁₄ normal mode

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Energy, ZPE, Cartesian coordinates and vibrational frequencies of the ¹A' minimum

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Energy, ZPE, Cartesian coordinates and vibrational frequencies of the ³A minimum

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Energy, Cartesian coordinates and vibrational frequencies of the ³A" minimum of Fig. 6

Figure S1:

Potential energies of the ground state S_0 and the five first singlet excited states calculated at the SA6-CASSCF(10/9)/cc-pVTZ level along the q_{14} normal mode

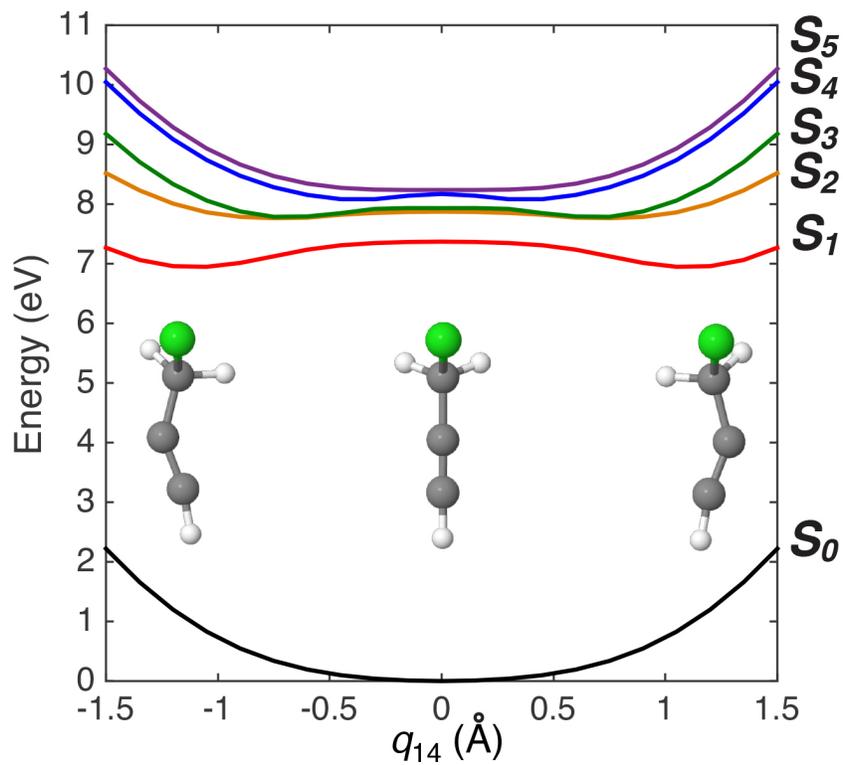


Table S1:**Ground state of C₃H₃Cl (¹A') optimized at the CCSD(T)/aug(Cl)-cc-pVTZ level**

ENERGY = -575.56728562 Ha

ZPE = 0.04716543 Ha

CARTESIAN COORDINATES

C	0.4367844380	0.0000000000	-2.3874194829
C	-0.1520975865	0.0000000000	-1.3297318213
C	-0.8768894695	0.0000000000	-0.0646301285
H	0.9580751769	0.0000000000	-3.3142810597
H	-1.4973763398	-0.8882609783	0.0313868647
H	-1.4973763398	0.8882609783	0.0313868647
Cl	0.2484590578	0.0000000000	1.3460919985

HARMONIC VIBRATIONAL FREQUENCIES

Mode	Wavenumber
v ₁₅	170.84
v ₁₄	301.29
v ₁₃	450.97
v ₁₂	629.72
v ₁₁	651.08
v ₁₀	732.85
v ₉	925.37
v ₈	967.08
v ₇	1204.77
v ₆	1295.56
v ₅	1482.75
v ₄	2177.33
v ₃	3097.40
v ₂	3151.86
v ₁	3464.36

Table S2:**Triplet state of C₃H₃Cl (³A) optimized at the CCSD(T)/aug(Cl)-cc-pVTZ level**

ENERGY = -575.41942349 Ha

ZPE = 0.04520042 Ha

CARTESIAN COORDINATES

C	-2.3684697260	-0.2858934013	-0.2622056316
C	-1.2545559590	-0.0353974356	0.4424412724
C	-0.0675225017	0.7232010646	0.0168929165
H	-3.2879363268	-0.8114955612	-0.0467411998
H	0.1635803920	1.5502375651	0.6854440770
H	-0.2489357151	1.1127077726	-0.9940194932
Cl	1.4084768366	-0.3067020041	-0.0662769413

HARMONIC VIBRATIONAL FREQUENCIES

Mode	Wavenumber
v ₁₅	121.77
v ₁₄	303.47
v ₁₃	367.11
v ₁₂	633.14
v ₁₁	744.94
v ₁₀	848.76
v ₉	909.52
v ₈	1081.01
v ₇	1163.71
v ₆	1267.70
v ₅	1436.15
v ₄	1627.73
v ₃	2992.13
v ₂	3125.09
v ₁	3218.48

Table S3:**Triplet minimum depicted in Figure 6 of the accompanying paper**

Structure optimized at the SA3-CASSCF(12/10)/6-311+G* level by averaging 3 states of $^3A''$ symmetry. Geometry optimization performed on the second state ($2^3A''$)

CARTESIAN COORDINATES

C	-2.5726863851	-0.2750602787	0.0000000000
C	-1.4071124980	0.3681859360	0.0000000000
C	-0.1554475076	0.9403644055	0.0000000000
H	-2.7229817860	-1.3405000015	0.0000000000
H	0.1194439651	1.4533595487	0.9041760805
H	0.1194439651	1.4533595487	-0.9041760805
CL	1.4835392466	-0.5937261587	0.0000000000

HARMONIC VIBRATIONAL FREQUENCIES

Mode	Wavenumber
v ₁₅	107.75
v ₁₄	201.58
v ₁₃	337.68
v ₁₂	690.16
v ₁₁	704.98
v ₁₀	904.38
v ₉	906.28
v ₈	1092.05
v ₇	1143.11
v ₆	1436.41
v ₅	1604.73
v ₄	3318.14
v ₃	3345.11
v ₂	3404.60
v ₁	3591.04

Single-point energies calculated at the SA12-CASSCF(10/11)/aug(Cl)-cc-pVTZ level

$E(X^1A')$ = -574.88799992 Ha

$E(1^1A')$ = -574.75772884 Ha

$E(2^1A')$ = -574.70259682 Ha

$E(1^1A'')$ = -574.76948111 Ha

$E(2^1A'')$ = -574.73499153 Ha

$E(3^1A'')$ = -574.67084574 Ha

$E(1^3A')$ = -574.80520730 Ha

$E(2^3A')$ = -574.76441731 Ha

$E(3^3A')$ = -574.72693181 Ha

$E(1^3A'')$ = -574.77697624 Ha

$E(2^3A'')$ = -574.75962547 Ha (energy depicted by an asterisk in Fig. 6)

$E(3^3A'')$ = -574.67301351 Ha