Supplementary Material for "THE THRESHOLD PHOTOELECTRON SPECTROSCOPY OF THE *cis-* AND *trans-* 1-CHLORO 2-FLUORO-ETHENE ISOMERS. AN EXPERIMENTAL AND QUANTUM CHEMICAL STUDY."

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FIG. S1: Schematic representation of the twelve vibrational normal modes of cis-1,2-C_2H_2FCl as calculated in the present work for (a) the $\tilde{X}\,^2A''$state, (b) the ν_1 and ν_2 modes in the $\tilde{A}\,^2A'$, and (c) the ν_1, ν_2, ν_{10} and ν_{11} in the $\tilde{B}\,^2A''$ states.

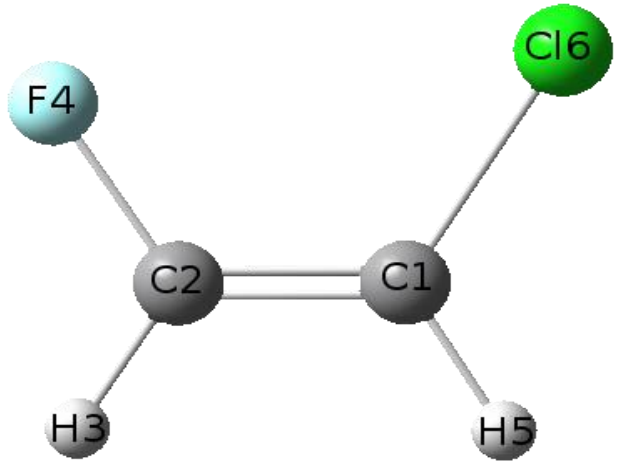
FIG. S2: Schematic representation of the twelve vibrational normal modes of trans-1,2-C_2H_2FCl as calculated in the present work for (a) the $\tilde{X}\,^2A''$state, (b) the ν_5, ν_6, ν_{10} and ν_{11} in the $\tilde{A}\,^2A'$, and (c) the ν_1, ν_2, ν_5 and ν_6 in the $\tilde{B}\,^2A''$ states.

FIG. S3: TPES and Δ-plot of cis-1,2-C_2H_2FCl in the 13.7-18.7 eV energy range on an expanded scale. Vertical lines highlight critical energies.

FIG. S4: TPES and Δ-plot of trans-1,2-C_2H_2FCl in the 14.0-18.6 eV energy range on an expanded scale. Vertical lines highlight critical energies.

TABLE S1: Optimized geometries of the neutral and the ionic ground states and the first two cationic excited state of Cis- and Trans-1,2-C_2H_2FCl in the C_S symmetry point group at different calculation levels. Internuclear distances in Å and angles in degrees.

Cis-1,2-C_2H_2FCl					
Neutral Ground State - $\tilde{X}$ ^{1}A'					
Level	C1-C2	C2-H3	C1-H5	C2-F4	C1-Cl6
CCSD(FC)	1.3401	1.0918	1.0903	1.3521	1.7389
M06-2X	1.3263	1.0878	1.0855	1.3366	1.7261
	H3-C2-C1	H5-C1-C2	F4-C2-C1	Cl6-C1-C2	
CCSD(FC)	123.61	121.06	122.46	122.94	
M06-2X	123.65	120.55	122.72	123.45	
Cation Ground State - $\tilde{X}$ ^{2}A″					
Level	C1-C2	C2-H3	C1-H5	C2-F4	C1-Cl6
CCSD(FC)	1.4154	1.0975	1.0961	1.2899	1.6567
M06-2X	1.4055	1.0937	1.0924	1.2775	1.6452
	H3-C2-C1	H5-C1-C2	F4-C2-C1	Cl6-C1-C2	
CCSD(FC)	123.44	119.63	120.19	121.54	
M06-2X	123.65	120.15	119.79	121.04	
Cation First Excited State - $\tilde{A}$ ^{2}A'					
Level	C1-C2	C2-H3	C1-H5	C2-F4	C1-Cl6
CCSD(FC)	1.3392	1.0939	1.0935	1.3338	1.7946
M06-2X	1.3282	1.0907	1.095	1.3179	1.7645
	H3-C2-C1	H5-C1-C2	F4-C2-C1	Cl6-C1-C2	
CCSD(FC)	123.32	131.45	120.03	116.87	
M06-2X	123.29	130.64	120.01	117.28	
Cation Second Excited State - $\tilde{B}$ ^{2}A"					
Level	C1-C2	C2-H3	C1-H5	C2-F4	C1-Cl6
TD-DFT	1.357	1.0958	1.0865	1.2889	1.9891
	H3-C2-Cl	H5-C1-C2	F4-C2-C1	Cl6-C1-C2	
TD-DFT	123	131.44	120.43	116.52	



Trans-1,2-C_2H_2FCl					
Neutral Ground State - $\tilde{X}$ ^{1}A'					
Level	C1-C2	C2-H3	C1-H6	C2-F4	C1-Cl5
CCSD(FC)	1.3396	1.0914	1.0911	1.3596	1.7450
M06-2X	1.3259	1.0879	1.0869	1.3432	1.7316
	H3-C2-C1	H6-C1-C2	F4-C2-C1	Cl5-C1-C2	
CCSD(FC)	126.32	123.46	119.96	120.58	
M06-2X	126.07	123.17	120.05	120.87	
Cation Ground State - $\tilde{X}$ ^{2}A″					
Level	C1-C2	C2-H3	C1-H6	C2-F4	C1-Cl5
CCSD(FC)	1.4122	1.0980	1.0973	1.2914	1.6602
M06-2X	1.4026	1.0948	1.0939	1.2787	1.6480
	H3-C2-C1	H6-C1-C2	F4-C2-C1	Cl5-C1-C2	
CCSD(FC)	125.09	121.50	118.30	119.33	
M06-2X	125.19	121.63	118.10	119.18	
Cation First Excited State - $\tilde{A}$ ^{2}A'					
Level	C1-C2	C2-H3	C1-H6	C2-F4	C1-Cl5
CCSD(FC)	1.3435	1.0942	1.1003	1.3234	1.7799
M06-2X	1.3342	1.0914	1.1051	1.3063	1.7347
	H3-C2-C1	H6-C1-C2	F4-C2-C1	Cl5-C1-C2	
CCSD(FC)	126.57	130.01	118.21	120.63	

M06-2X	126.13	127.14	118.41	123.71	
Cation Second Excited State - $\tilde{B}$ ²A"					
Level	C1-C2	C2-H3	C1-H6	C2-F4	C1-Cl5
TD-DFT	1.3539	1.0936	1.0873	1.2946	1.9943
	H3-C2-Cl	H6-C1-C2	F4-C2-C1	Cl5-C1-C2	
TD-DFT	125.98	133.58	118.04	116.30	

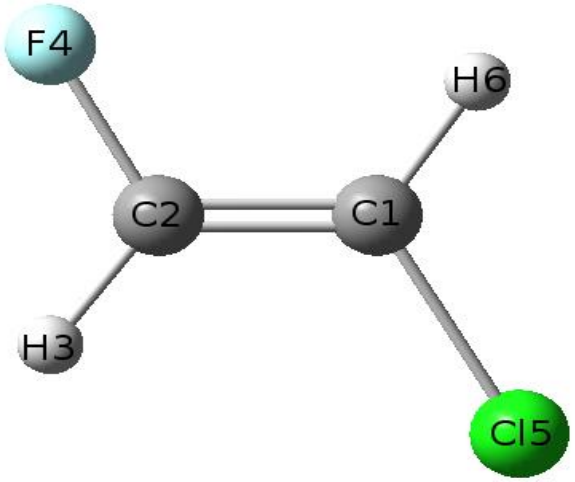


TABLE S2: Vertical ionization energies (IE_{vert}(eV)) calculated at the CCSD, M06-2X, CAS(5,8)/state average, CAS(9,8)/state average and the TDDTF levels with respect to the neutral ground state $\tilde{X}\,^1A'$ (ionic $\tilde{X}\,^2A''$ground state) of cis- and trans-1,2-C_2H_2FCl. MO descriptions include one-electron ionization as well as ionization and excitation (I&E) configurations. The adiabatic ionization energies IE_{ad}(eV) were determined at the CCSD(FC) and M06-2X levels for the ground and first excited states.

Cis-1,2-C_2H_2FCl		
Level	IE_{ad}(eV)	MO Description
CCSD(FC)	9.69	$(2a'')^2\ (9a')^2$ **$(3a'')^1$**
	11.66	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
M06-2X	9.75	$(2a'')^2\ (9a')^2$ **$(3a'')^1$**
	11.90	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
Level	IE_{vert}(eV)	MO Description
CCSD(FC)	10.01	$(2a'')^2\ (9a')^2$ **$(3a'')^1$**
	11.74	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
M06-2X	10.09	$(2a'')^2\ (9a')^2$ **$(3a'')^1$**
	11.96	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
CAS(5,8)/	10.85 (0,0)	$(2a'')^2\ (9a')^2$ **$(3a")^1$**
Stateaverage	12.36 (1.51)	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
	13.83 (2.98)	**$(2a'')^1$** $(9a')^2\ (3a'')^2$
	16.92 (6.07)	$(2a'')^2\ (9a')^2$ **$(4a'')^1$** (I&E)
	17.10 (6.25)	$(2a'')^2$ **$(9a')^1\ (3a'')^1\ (4a'')^1$** (I&E)
	17.40 (6.55)	$(2a'')^2\ (9a')^2$ **$(10a')^1$** (I&E)
	17.81 (6.96)	$(2a'')^2$ **$(9a')^1\ (3a'')^1\ (10a')^1$** (I&E)
	18.60 (7.75)	$(2a'')^2$ **$(9a')^1\ (3a'')^1\ (10a')^1$** (I&E)
CAS(9,8)/	9.84 (0.0)	$(7a')^2\ (8a')^2\ (2a'')^2\ (9a')^2$ **$(3a")^1$**

Stateaverage	11.49 (1.65)	$(7a')^2\ (8a')^2\ (2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
	12.85 (3.01)	$(7a')^2\ (8a')^2\ \mathbf{(2a'')^1}\ (9a')^2\ (3a'')^2$
	15.05 (5.21)	$(7a')^2\ \mathbf{(8a')^1}\ (2a'')^2\ (9a')^2\ (3a'')^2$
	16.10 (6.26)	$(7a')^2\ (8a')^2\ (2a'')^2\ (9a')^2\ \mathbf{(4a'')^1}$ (I&E)
	16.49 (6.65)	$(7a')^2\ (8a')^2\ (2a'')^2\ \mathbf{(9a')^1\ (3a'')^1\ (4a'')^1}$ (I&E)
	16.92 (7.08)	$\mathbf{(7a')^1}\ (8a')^2\ (2a'')^2\ (9a')^2\ (3a'')^2$
	17.33 (7.49)	$(7a')^2\ (8a')^2\ (2a'')^2(9a'')^2\ \mathbf{(10a')^1}$ (I&E)
TDDFT	10.09 (0.0)	$(6a')^2\ (7a')^2\ (8a')^2\ (2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$
	11.76 (1.67)	$(6a')^2\ (7a')^2\ (8a')^2\ (2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
	13.21 (3.12)	$(6a')^2\ (7a')^2\ (8a')^2\ \mathbf{(2a'')^1}\ (9a')^2\ (3a'')^2$
	13.97 (3.88)	$(6a')^2\ (7a')^2\ \mathbf{(8a')^1}\ (2a'')^2\ (9a')^2\ (3a'')^2$
	14.97 (4.88)	$(6a')^2\ \mathbf{(7a')^1}\ (8a')^2\ (2a'')^2\ (9a')^2\ (3a'')^2$
	16.30 (6.21)	$(6a')^2\ (7a')^2\ (8a')^2\ (2a'')^2\ (9a')^2\ \mathbf{(4a'')^1}$ (I&E)
	16.42 (6.33)	$\mathbf{(6a')^1}\ (7a')^1\ (8a')^2\ (2a'')^2\ (9a')^2\ (3a'')^2$
	16.91 (6.82)	$(6a')^2\ (7a')^2\ (8a')^2\ (2a'')^2(9a'')^2\ \mathbf{(10a')^1}$ (I&E)

Trans-1,2-C_2H_2FCl		
Level	IE_{ad}(eV)	MO Description
CCSD(FC)	9.67	$(2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$
	11.82	$(2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
M06-2X	9.73	$(2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$
	12.04	$(2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
Level	IE_{vert}(eV)	MO Description
CCSD(FC)	10.00	$(2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$
	11.89	$(2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
M06-2X	10.08	$(2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$
	12.11	$(2a'')^2\ \mathbf{(9a')^1}\ (3a'')^2$
CAS(5,8)/	10.97 (0.0)	$(2a'')^2\ (9a')^2\ \mathbf{(3a'')^1}$

Stateaverage	12.55 (1.58)	$(2a'')^2$ **$(9a')^1$** $(3a'')^2$
	14.09 (3.12)	**$(2a'')^1$** $(9a')^2$ $(3a'')^2$
	16.77 (5.80)	$(2a'')^2$ $(9a')^2$ **$(4a'')^1$** (I&E)
	17.16 (6.19)	$(2a'')^2$ **$(9a')^1$ $(3a'')^1$ $(4a'')^1$** (I&E)
	17.41 (6.44)	$(2a'')^2$ $(9a')^2$ **$(10a')^1$** (I&E)
	18.00 (7.03)	$(2a'')^2$ **$(9a')^1$ $(3a'')^1$ $(10a')^1$** (I&E)
	18.81 (7.84)	$(2a'')^2$ **$(9a')^1$ $(3a'')^1$ $(10a')^1$** (I&E)
CAS(9,8)/	10.31 (0.0)	$(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ **$(3a'')^1$**
Stateaverage	12.12 (1.81)	$(7a')^2$ $(8a')^2$ $(2a'')^2$ **$(9a')^1$** $(3a'')^2$
	13.40 (3.09)	$(7a')^2$ $(8a')^2$ **$(2a'')^1$** $(9a')^2$ $(3a'')^2$
	15.48 (5.17)	$(7a')^2$ **$(8a')^1$** $(2a'')^2$ $(9a')^2$ $(3a'')^2$
	16.34 (6.03)	$(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ **$(4a'')^1$** (I&E)
	16.79 (6.48)	$(7a')^2$ $(8a')^2$ $(2a'')^2$ **$(9a')^1$ $(3a'')^1$ $(4a'')^1$** (I&E)
	17.46 (7.15)	$(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ **$(10a')^1$** (I&E)
	17.89 (7.58)	$(7a')^2$ $(8a')^2$ $(2a'')^2$**$(9a'')^1(3a'')^1$ $(10a')^1$** (I&E)
TDDFT	10.08 (0.0)	$(6a')^2$ $(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ **$(3a'')^1$**
	11.90 (1.82)	$(6a')^2$ $(7a')^2$ $(8a')^2$ $(2a'')^2$ **$(9a')^1$** $(3a'')^2$
	13.31 (3.23)	$(6a')^2$ $(7a')^2$ $(8a')^2$ **$(2a'')^1$** $(9a')^2$ $(3a'')^2$
	14.20 (4.12)	$(6a')^2$ $(7a')^2$ **$(8a')^1$** $(2a'')^2$ $(9a')^2$ $(3a'')^2$
	14.73 (4.65)	$(6a')^2$ **$(7a')^1$** $(8a')^2$ $(2a'')^2$ $(9a')^2$ $(3a'')^2$
	16.16 (6.08)	$(6a')^2$ $(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ **$(4a'')^1$** (I&E)
	16.43 (6.35)	**$(6a')^1$** $(7a')^2$ $(8a')^2$ $(2a'')^2$ $(9a')^2$ $(3a'')^2$
	16.76 (6.68)	$(6a')^2$ $(7a')^2$ $(8a')^2$ $(2a'')^2(9a')^2$ **$(10a')^1$** (I&E)

TABLE S3: Energy positions (eV) of the features observed in the TPES between the $\tilde{X}\,^2A''$ and $\tilde{A}\,^2A'$ PES bands of cis-1,2-$C_2H_2FCl^+$ and in the corresponding photon energy range of the vacuum UV PAS of cis-1,2-C_2H_2FCl [1].

$\tilde{X}$ - $\tilde{A}$ Photon Energy Region		
PAS [2]	TPES (This work)	Assignment [2]
10.622	10.642	
10.685	-	
10.710	10.706	5p
10.731	10.734	(0,0)
10.757	10.750	
10.790	10.794	
-	10.804	
10.849	10.844	(0,0)+0.120
10.874	10.870	
-	10.888	
10.958	10.976	(0,0)+0.242
11.008	11.004	5d
11.037	11.022	
11.075	11.086	(0,0)+0.352
11.104	11.112	6s
11.130	11.134	
11.176	11.176	
11.218	11.218	6p (0,0)+0.484
-	11.232	
11.280	11.270	
11.306	11.308	
11.335	11.332	(0,0)+0.598
11.356	~11.36	7s/6d
11.402	11.410	
11.440	11.434	
11.503	-	
11.515	11.516	
11.532	~11.54	8s/8p
11.624	~11.63	8d
11.658	11.66	
11.700	~11.70	

[a] Uncertainty: ±0.01 eV [2]. [b] Uncertainty : ±0.003 eV (see section 2).

TABLE S4: Energy positions (eV) of the features observed in the TPES between the $\tilde{X}\,^2A''$ and $\tilde{A}\,^2A'$ states of trans-1,2-$C_2H_2FCl^+$ and in the corresponding photon energy range of the vacuum UV PAS of 1,1-C_2H_2FCl [1].

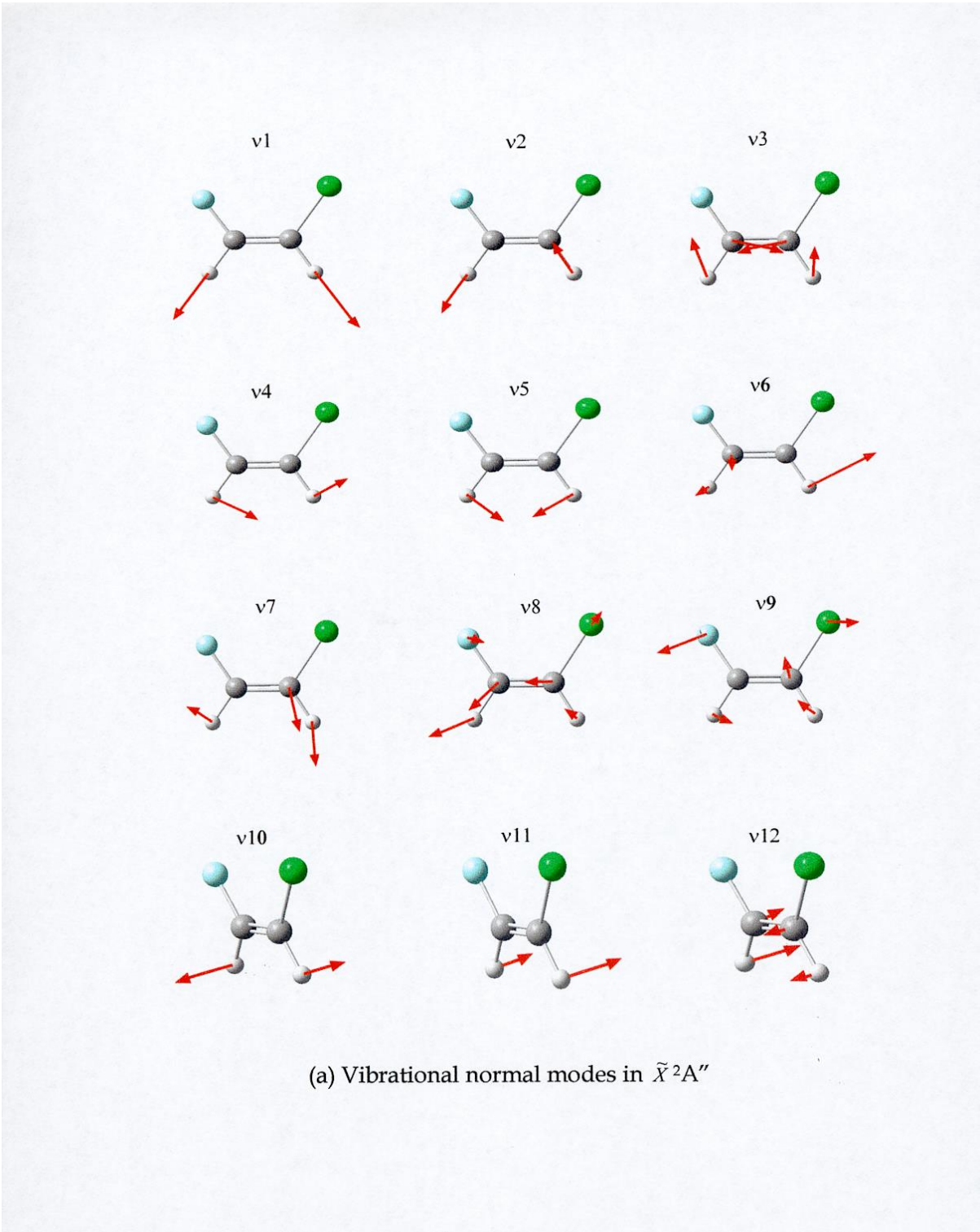
$\tilde{X}$ - $\tilde{A}$ Photon Energy Region		
PAS[a] [2]	TPES [b] (This work)	Assignment[c] [2]
10.422	10.438	$3\nu_3$[c]
10.503	10.502	
10.527	10.532	4d
10.560	10.564	
-	10.592	
10.617	10.620	$4\nu_3$[c]
10.662	10.654	5s
-	10.684	
10.706	10.716	
10.747	10.776	5pσ
10.804/10.868	10.830	5pπ
10.921	10.902	
-	10.952	
11.040	11.050	
11.075	11.088	
11.116	11.139	
-	11.144	
-	11.168	
11.181	11.182	
11.229	11.224	6s
11.258	11.270	6pσ
	11.300	
11.327	11.316	
-	11.340	
11.363/11.387	11.378	
11.420	11.406/11.436	6pπ
11.465	11.472	
11.493/11.513	11.502	
-	11.540	
11.574	11.564	
11.607	11.600	7pπ
11.622	11.618	

-	11.650	
11.684	11.678	
11.697	11.700	
11.736	11.730	
11.769	11.756	
-	11.782	
11.809	11.808	
-	11.822	

[a] Uncertainty: ±0.01 eV [2].

[b] Uncertainty : ±0.003 eV (see section 2).

[c] For the assignments, see also Table 6 in the present work.



(a) Vibrational normal modes in $\tilde{X}\,^2A''$

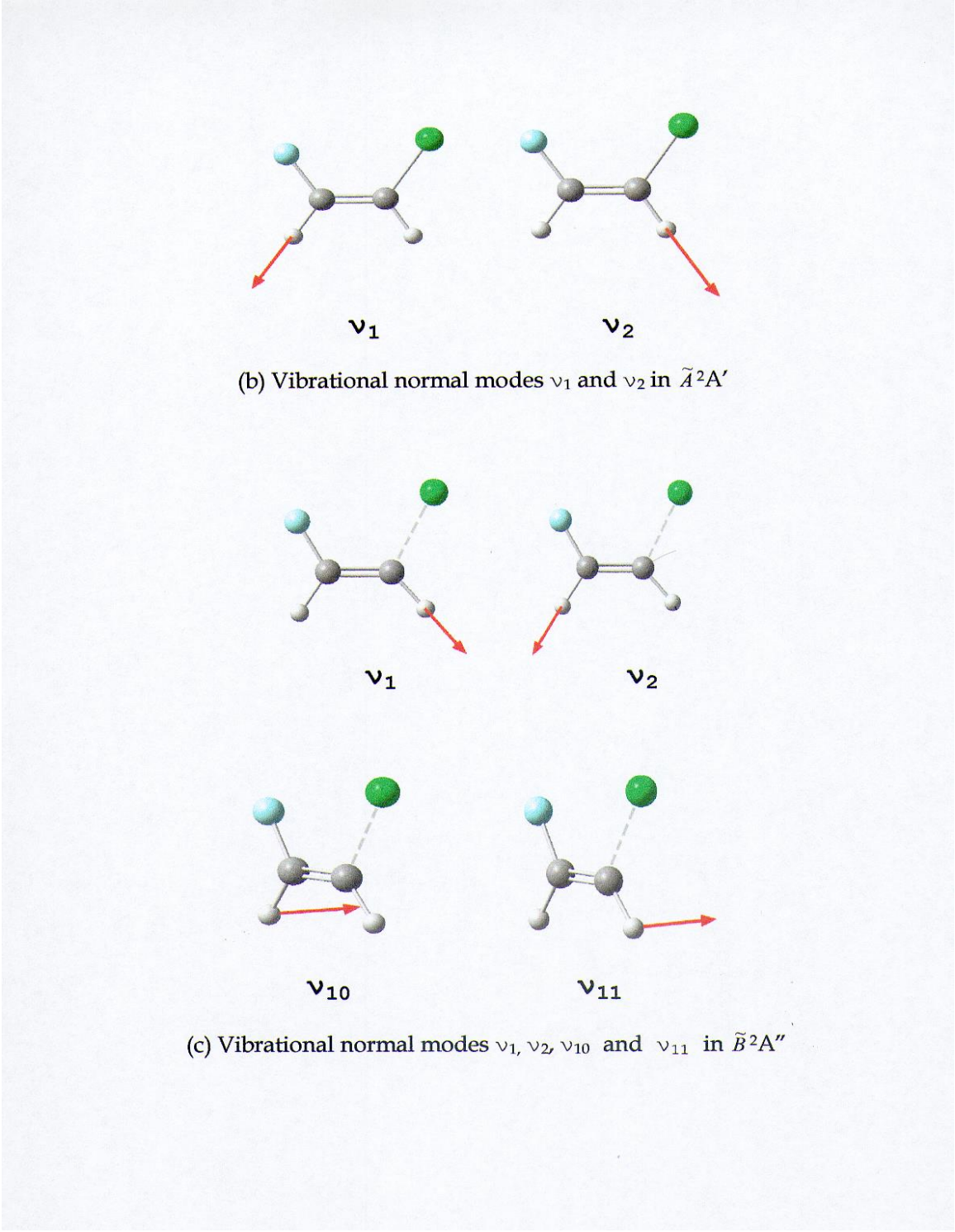
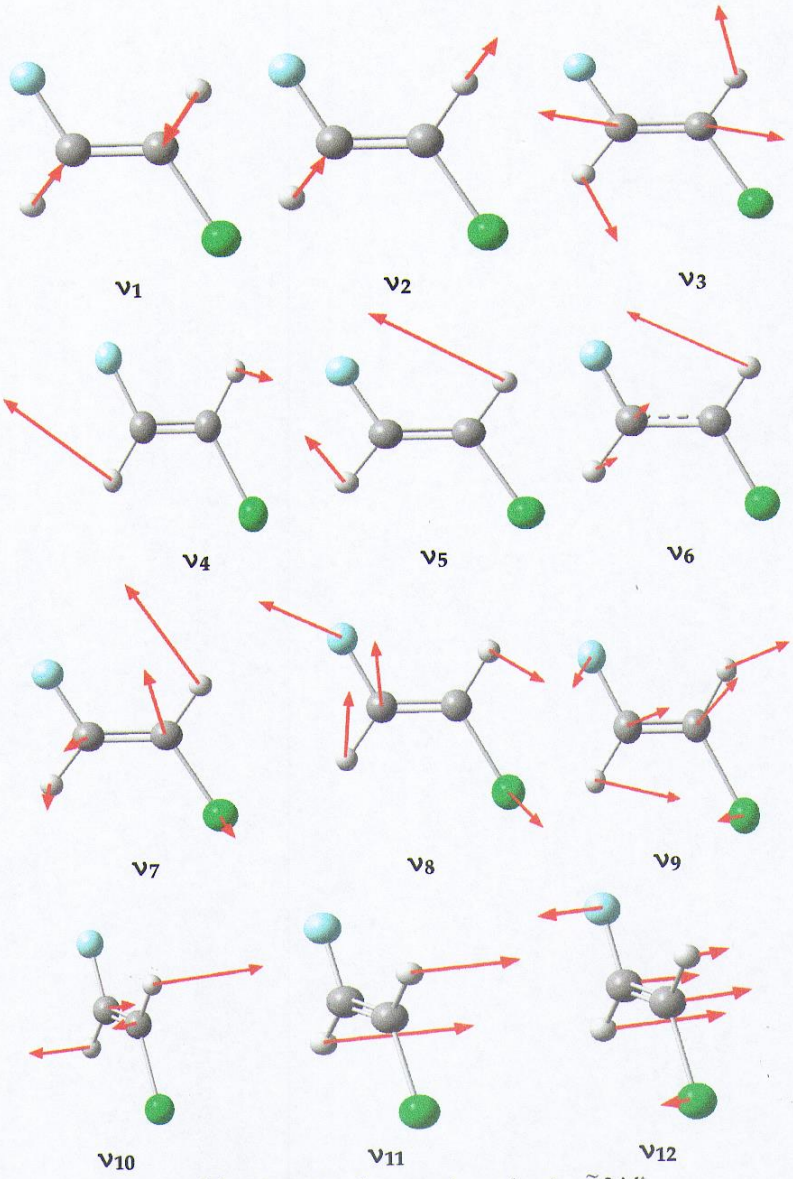


FIG. S1: Schematic representation of the twelve vibrational normal modes of cis-1,2-C_2H_2FCl as calculated in the present work for (a) the $\tilde{X}^2A''$ state, (b) the ν_1 and ν_2 modes in the $\tilde{A}^2A'$, and (c) the ν_1, ν_2, ν_{10} and ν_{11} in the $\tilde{B}^2A''$ states.



(a) Vibrational normal modes in $\tilde{X}\,^2A''$

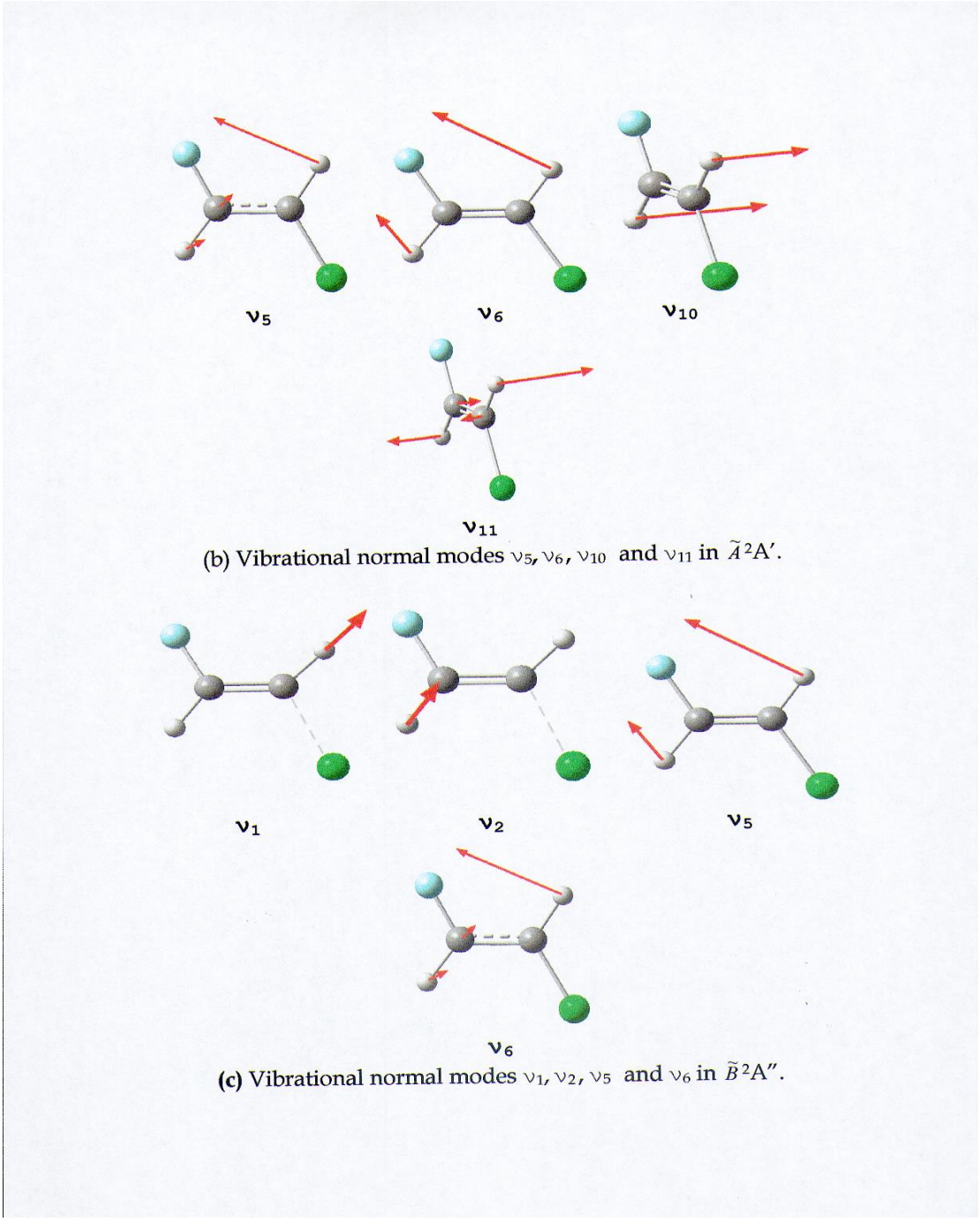


FIG. S2: Schematic representation of the twelve vibrational normal modes of trans-1,2-C_2H_2FCl as calculated in the present work for (a) the $\tilde{X}$ ^{2}A″state, (b) the ν_5, ν_6, ν_{10} and ν_{11} in the $\tilde{A}$ ^{2}A′, and (c) the ν_1, ν_2, ν_5 and ν_6 in the $\tilde{B}$ ^{2}A″ states.

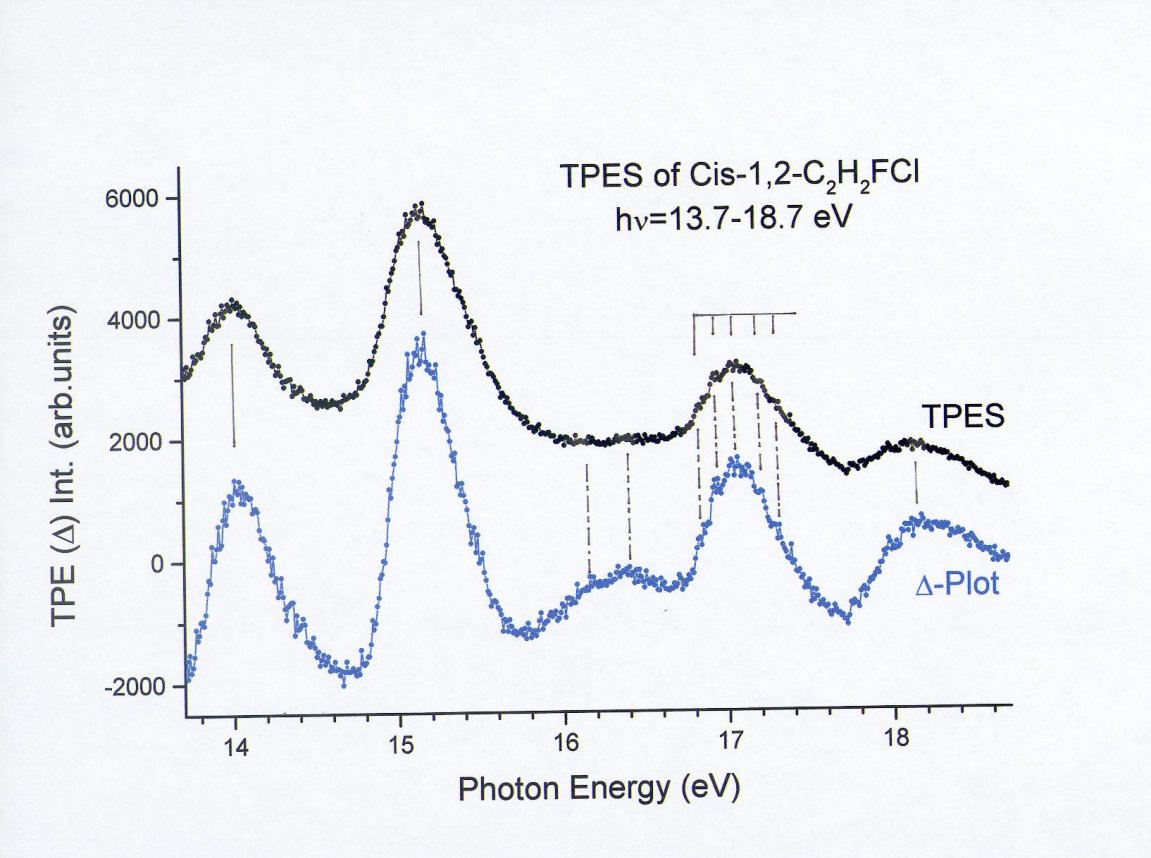


FIG. S3: TPES and Δ-plot of cis-1,2-C_2H_2FCl in the 13.7-18.7 eV energy range on an expanded scale. Vertical lines highlight critical energies.

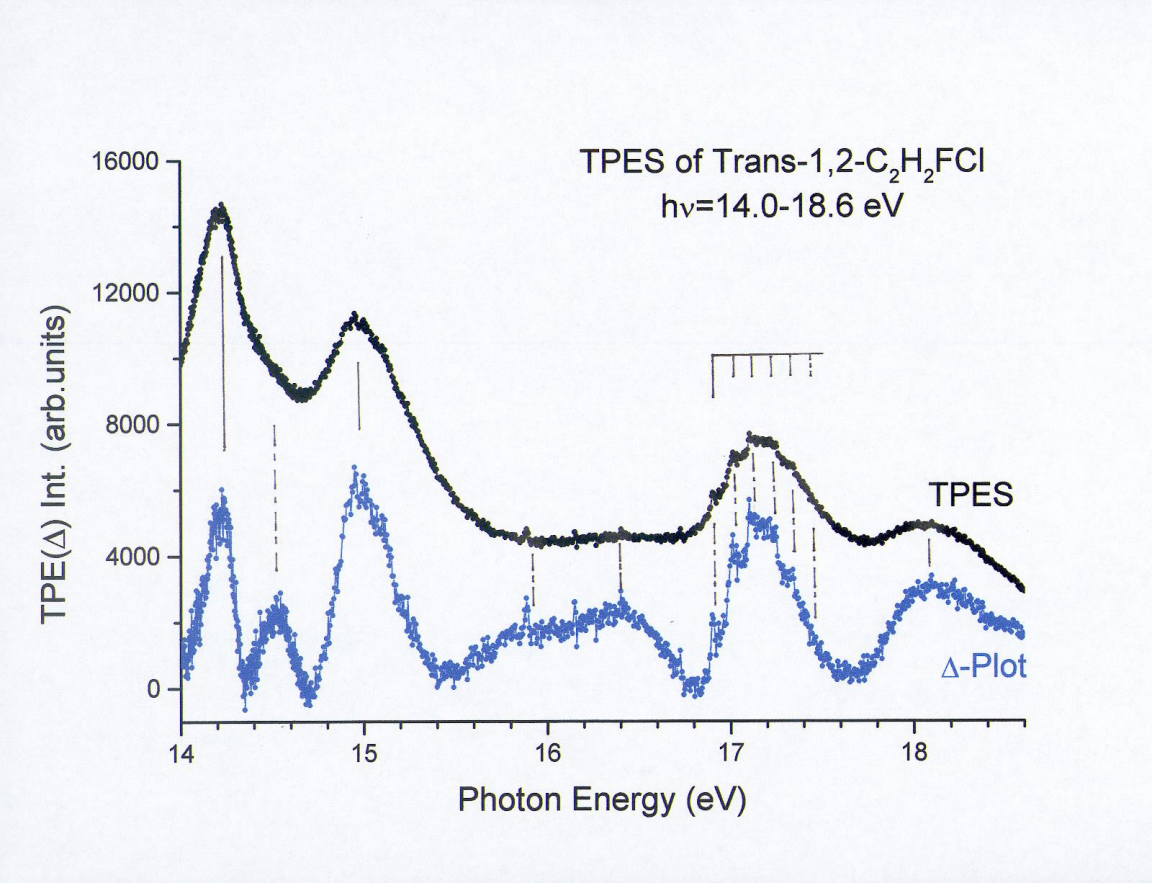


FIG. S4: TPES and Δ-plot of trans-1,2-C_2H_2FCl in the 14.0-18.6 eV energy range on an expanded scale. Vertical lines highlight critical energies.