Supporting Information: Velocity Map Imaging Spectroscopy of C_2H^- and C_2D^-: a benchmark study of vibronic coupling interactions

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1 C_2H^- Spectral Assignments

Spectral assignments for all peaks resolved in the photoelectron spectra of C_2H^- from this work are presented in Table S1. Peaks are labelled with respect to the photoelectron spectrum of C_2H^- at 300 nm in Figure S1. The experimental binding energy of each transition is given, alongside the anisotropy parameter sign $(+/-)$, the corresponding vibronic symmetry, and the calculated energy from Ref. S1. Assignments are given as $\tilde{X}(v_1, v_2, v_3)\tilde{A}(v_1, v_2, v_3)$ where any superscripts represent hot-band transitions.

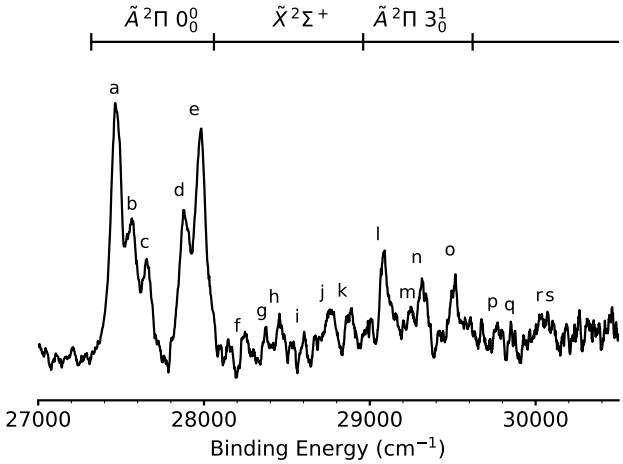

Figure S1: Photoelectron spectrum of C_2H^- at 300 nm, showing the alphabetic labelling of peaks used in this work.

2 C_2D^- Spectral Assignments

Spectral assignments for all peaks resolved in C_2D^- from this work are presented in Table S2. Peaks are labelled with respect to the photoelectron spectrum of C_2D^- at 355 nm in Figure S2. The experimental binding energy of each transition is given, alongside the anisotropy parameter sign $(+/-)$, the corresponding vibronic symmetry, and the calculated energy from Ref. S1.

Table S1: Peak positions (cm^{-1}), and assignments for the C_2H^- photoelectron spectra from this work. The sign of the anisotropy parameter is shown for each transition, along with it's vibronic symmetry, and the calculated position from Ref.[S1].

Peak	eBE (cm^{-1})	v (cm^{-1})	β	Symmetry	v_{calc} [a]	Assignment
	23 591	-231	+	Σ^+		$\tilde{X}(0,2^2,0)$
	23 685	-137	+	Σ^+		$\tilde{X}(0,1^1,0)$
	23 823	0	+	Σ^+	0	$\tilde{X}(0,0,0)$
	24 184	361	−	Π	371	$\tilde{X}(0,1,0)$
	24 630	807	+	Σ^+	794	$\tilde{X}(0,2,0)$
	25 663	1840	+	Σ^+	1838	$\tilde{X}(0,0,1)$
	25 916	2093	−	Π	2096	$\tilde{X}(0,1,1)$
	25 993	2170	−	Π	2166	$\tilde{X}(0,5,0)$
	26 362	2539	+	Σ^+	2536	$\tilde{X}(0,2,1)$
	26 757	2934	−	Π	2933	$\tilde{X}(0,3,1)$
	26 929	3106	−	Π	3104	$\tilde{X}(0,7,0)$
	27 175	3352	+	Σ^+	3371	$\tilde{X}(0,4,1)$
a	27 430	3607	−	Π	3604	$\tilde{X}(0,1,2)\tilde{X}(1,1,0)\tilde{A}(0,0,0)$
b	27 515	3692	−	Π	3690	$\tilde{X}(1,1,0)\tilde{X}(0,1,2)\tilde{A}(0,0,0)$
c	27 612	3788	−	Π	3790	$\tilde{X}(0,5,1)\tilde{A}(0,0,0)$
d	27 851	4028	−	Π	4011	$\tilde{X}(0,9,0)\tilde{X}(0,5,1)\tilde{A}(0,0,0)$
e	27 941	4118	−	Π	4093	$\tilde{X}(0,9,0)\tilde{A}(0,0,0)$
f	28 200	4377	+	Σ^+	4375	$\tilde{X}(0,6,1)$
g	28 349	4526	+	Σ^+	4524	$\tilde{X}(0,10,0)$
h	28 423	4600	−	Π	4593	$\tilde{X}(0,3,2)\tilde{A}(0,0,0)$
i	28 562	4739	−	Π	4702	$\tilde{X}(0,7,1)\tilde{A}(0,1,0)$
j	28 714	4891	−	Π	4879	$\tilde{X}(0,7,1)$
k	28 834	5011	−	Π	5004	$\tilde{X}(0,11,0)$
l	29 049	5226	−	Π	5222	$\tilde{X}(0,1,3)\tilde{A}(0,0,1)$
m	29 227	5404	+	Σ^+	5406	$\tilde{X}(0,12,0)\tilde{A}(0,1,0)$
n	29 283	5460	−	Π	5445	$\tilde{X}(0,5,2)\tilde{A}(0,0,1)$
o	29 465	5642	−	Π	5630	$\tilde{X}(0,9,1)\tilde{A}(0,0,1)$
p	29 740	5917	−	Π	5914	$\tilde{X}(0,13,0)$
q	29 844	6021	+	Σ^+	6054	$\tilde{X}(0,6,2)\tilde{X}(0,2,3)$
r	30 021	6198	−	Π	6200	$\tilde{X}(0,3,3)\tilde{A}(0,2,0)$
s	30 086	6263	−	Π	6266	$\tilde{X}(1,7,0)$

[a] from calculations of Ref. S1

Table S2: Peak positions (cm^{-1}) and assignments for the C_2D^- photoelectron spectra from this work. The sign of the anisotropy parameter is shown for each transition, along with it's vibronic symmerty, and calculated position from Ref.[S1].

Peak	eBE (cm^{-1})	v (cm^{-1})	β	Symmetry	v_{calc} [a]	Assignment
	23 751	-197	+	$\Sigma+$		$\tilde{X}(0,2^2,0)$
	23829	-120	+	Σ^+		$\tilde{X}(0,2^1,0)$
	23 949	0	+	Σ^+	0	$\tilde{X}(0,0,0)$
	24 227	278	−	Π	287	$\tilde{X}(0,1,0)$
	24 577	629	+	Σ^+	615	$\tilde{X}(0,2,0)$
	24 906	957	−	Π	953	$\tilde{X}(0,3,0)$
	25 506	1557	+			
	25 688	1740	+	Σ^+	1744	$\tilde{X}(0,0,1)$
	25 901	1952	−	Π	1962	$\tilde{X}(0,1,1)$
	26 245	2297	+	Σ^+	2302	$\tilde{X}(0,2,1)$
	26 556	2607	−	Π	2612	$\tilde{X}(0,3,1)$
	26 747	2798	−	Π	2796	$\tilde{X}(1,1,0)$
a	27 253	3304	−	Π	3309	$\tilde{X}(0,5,1)$
b	27 369	3420	−	Π	3426	$\tilde{X}(1,3,0)$
c	27 450	3501	−	Π	3511	$\tilde{X}(0,1,2)$
d	27 552	3603	−			
e	27 793	3844	−	Π	3838	$\tilde{A}(0,0,0)$
f	27 906	3957	+	Σ^+	3967	$\tilde{X}(0,2,2)$

[a] from calculations of Ref. S1

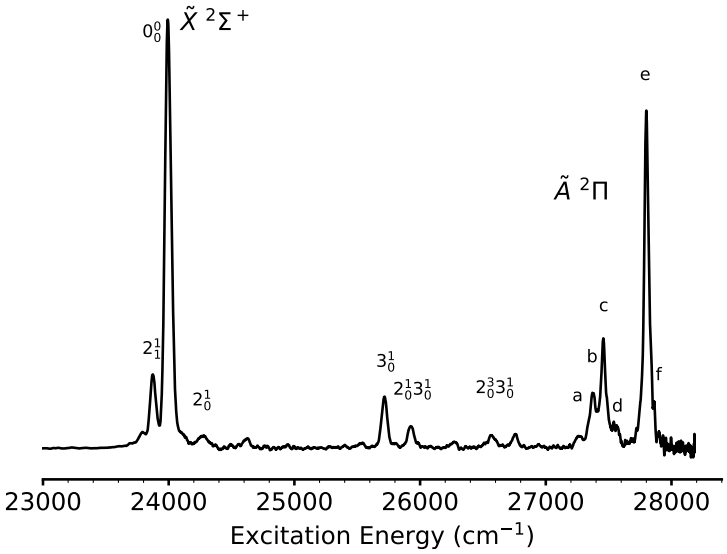

Figure S2: Photoelectron spectrum of C_2D^- at 266 nm, showing the alphabetic labelling of peaks used in this work.

References

(S1) Tarroni, R.; Carter, S. Theoretical calculation of vibronic levels of C_2H and C_2D to 10,000 cm^{-1}. *The Journal of Chemical Physics* **2003**, *119*, 12878–12889.