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

Benjamin A. Laws,[*,†,‡] Zachariah D. Levey,[†] Andrei M. Sanov,[¶] John F. Stanton,[§] Timothy W. Schmidt,[†] and Stephen T. Gibson[‡]

†*School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia*

‡*Research School of Physics, The Australian National University, Canberra ACT 2601, Australia*

¶*Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721, United States*

§*Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States*

E-mail: b.laws@unsw.edu.au

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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 **??**. The experimental binding energy of each transition is given, alongside the anisotropy ($+/-$), the corresponding vibronic symmetry, the calculated energy from Ref. **?** . Assignments are given as $\tilde{X}(v_1, v_2, v_3)\tilde{A}(v_1, v_2, v_3)$ where superscripts represent hot-band transitions.

Additional mass spectra are presented in Fig. **??**, to highlight the role of the CH radical in the formation of phenalenyl. Fig. **??**(a) and (b) show the mass spectrum (on and off resonance) when neat Ar gas is passed through the high voltage discharge. from a 1% mixture of CH_4 in Ar gas passed through the HV discharge. The bottom plots, Fig. **??** (c) and (d) show the resulting mass spectrum when a 1% mixture of CH_4 in Ar gas is used instead. A clear increase in both the resonant and non-resonant signal is observed when CH_4 is included in the gas mixture, confirming that the CH radicals formed in the discharge are involved in the formation of phenalenyl.

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.[?] .

Peak	eBE (cm^{-1})	v (cm^{-1})	β	Symmetry	A_{SO} [a]	v_{calc} [b]	Assignment	
							$\tilde{X}$	$\tilde{A}$
	23 591	-231	+	Σ^+			2_2^2	–
	23 685	-137	+	Σ^+			2_1^1	–
	23 823	0	+	Σ^+	–	0	0_0^0	–
	24 184	361	−	Π	-0.35[c]	371	2_0^1	–
	24 630	807	+	Σ^+	–	794	2_0^2	–
	25 663	1840	+	Σ^+	–	1838	3_0^1	–
	25 916	2093	−	Π	-1.02[d]	2096	$2_0^1 3^1 0$	–
	25 993	2170	−	Π	-0.66	2166	2_0^5	–
	26 362	2539	+	Σ^+		2536	$2^2 0 3_0^1$	–
	26 757	2934	−	Π	-1.52[e]	2933	$2_0^3 3^1 0$	–
	26 929	3106	−	Π	-0.52	3104	2_0^7	–
	27 175	3352	+	Σ^+	–	3371	$2^4 3^1$	–
a	27 430	3607	−	Π	-7.22[f]	3604	$2_0^1 3_0^2 / 1_0^1 2_0^1$	0_0^0
b	27 515	3692	−	Π	-5.41[g]	3690	$1_0^1 2_0^1 / 2_0^1 3_0^2$	0_0^0
c	27 612	3788	−	Π	-2.51	3790	$2_0^5 3_0^1$	0_0^0
d	27 851	4028	−	Π	-2.22	4011	$2_0^9 / 2_0^5 3_0^1$	0_0^0
e	27 941	4118	−	Π	-3.28	4093	2_0^9	0_0^0
f	28 200	4377	+	Σ^+		4375	$2^6 0 3_0^1$	–
g	28 349	4526	+	Σ^+	–	4524	2_0^{10}	–
h	28 423	4600	−	Π		4593	$2^3 3^2$	0_0^0
i	28 562	4739	−	Π		4702	$2^7 3^1$	$2^1 0$
j	28 714	4891	−	Π		4879	$2^7 3^1$	–
k	28 834	5011	−	Π		5004	2^{11}	–
l	29 049	5226	−	Π		5222	$2_0^1 3_0^3$	3_0^1
m*	29 227	5404	+	Σ^+	–	5406	2^{12}	2_0^1
n	29 283	5460	−	Π		5445	$2_0^5 3_0^2$	3_0^1
o	29 465	5642	−	Π		5630	$2_0^9 3_0^1$	3_0^1
p	29 740	5917	−	Π		5914	2^{13}	–
q	29 844	6021	+	Σ^+		6054	$2^6 3^2 / 2^2 3^3$	–
r	30 021	6198	−	Π		6200	$2^3 3^3$	2^2
s	30 086	6263	−	Π		6266	$1^1 2^7$	–

* transition only partially resolved in photoelectron spectrum.

[a] from infra-red measurements of Refs. **?** and **?** , onless otherwise indicated.

[b] from calculations of Ref. **?**

[c] Ref. **?**

[d] Ref. **?**

[e] Ref. **?**

[f] Ref. **?**

[g] Ref. **?**