

A Photoelectron Imaging and Quantum  
Chemistry Study of Phenolate,  
Difluorophenolate and Dimethoxyphenolate  
Anions

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# Supplementary Information

## Structural Comparisons

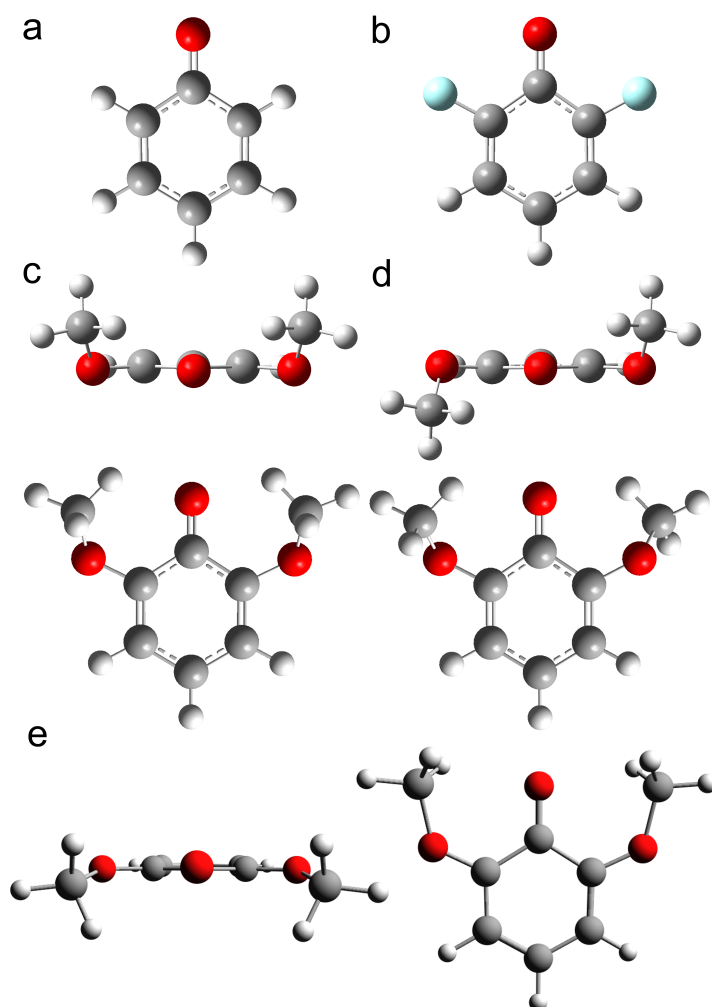


Figure S1: DFT B3LYP/6-311++G(3df,3pd) optimised geometries of PhO<sup>-</sup> (a); 2,6-DPhO<sup>-</sup> (b); the *syn* (c) and *anti* (d) rotamers of 2,6-DMPHO<sup>-</sup> which have two hydrogen bonding interactions between the phenolate oxygen and the hydrogen atoms on the methyl groups; and the 2,6-DMPHO<sup>·</sup> radical (e).

## Coordinates of Optimised Structures

**Table S1: Cartesian Coordinates of the Anionic and Neutral Radical Forms of Deprotonated Phenol Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	0.28569800	1.20358300	-0.00007200	0.28177290	1.30307312	-0.00006768
C	-1.09210300	1.19144600	0.00008600	-1.07277837	1.24170893	0.00001506
C	-1.81524500	0.00000000	0.00020900	-1.75289551	0.00002616	0.00007976
C	-1.09210300	-1.19144600	0.00016500	-1.07282542	-1.24168236	0.00006791
C	0.28569800	-1.20358300	0.00000700	0.28172351	-1.30309786	-0.00001226
C	1.06921200	0.00000000	-0.00012300	1.07594321	-0.00002741	-0.00008769
H	0.82897500	2.14151500	-0.00016600	0.78448720	2.24762505	-0.00011395
H	-1.62617600	2.13726600	0.00011700	-1.63886240	2.14970057	0.00003173
H	-2.89724100	0.00000000	0.00033300	-2.82289551	0.00004647	0.00014006
H	-1.62617600	-2.13726600	0.00025700	-1.63894386	-2.14965257	0.00012326
H	0.82897500	-2.14151500	-0.00002500	0.78440205	-2.24766881	-0.00001885
O	2.33058700	0.00000000	-0.00026800	2.33434320	-0.00005129	-0.00016335

**Table S2: Cartesian Coordinates of the Anionic and Neutral Radical Forms of Deprotonated 2,6-difluorophenol Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.17899400	0.04224200	-0.00002900	-1.21981600	0.03902800	0.00002400
C	-1.19844400	-1.33523500	0.00001400	-1.22395300	-1.32920500	0.00002100
C	0.00000000	-2.05377700	-0.00001700	0.00000000	-2.01084000	0.00009900
C	1.19844400	-1.33523500	0.00001300	1.22395300	-1.32920500	0.00001900
C	1.17899400	0.04224200	-0.00003100	1.21981600	0.03902800	0.00002200
C	0.00000000	0.86690900	-0.00017900	0.00000000	0.83564200	0.00030500
H	-2.15716600	-1.84004700	0.00007400	-2.16350700	-1.86210800	-0.00006100
H	0.00000000	-3.13494000	0.00001900	0.00000000	-3.09153600	0.00005500
H	2.15716600	-1.84004700	0.00007100	2.16350700	-1.86210800	-0.00006400
O	0.00000000	2.12447900	0.00006600	0.00000000	2.07258400	-0.00009700
F	-2.38327500	0.69201800	0.00003900	-2.36426900	0.70935500	-0.00011500
F	2.38327500	0.69201800	0.00003600	2.36426900	0.70935500	-0.00011800

**Table S3: Cartesian Coordinates of the Anionic and Neutral Radical Forms of Deprotonated 2,6–dimethoxyphenol With No Hydrogen Bonding Interactions Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	1.20621200	0.03202100	-0.00002600	1.24523900	0.02180600	0.00001200
C	1.20353500	-1.35623000	-0.00005700	1.22476600	-1.36032000	-0.00002600
C	0.00000100	-2.06591300	-0.00006100	0.00000000	-2.03291800	-0.00005300
C	-1.20353400	-1.35623100	-0.00003600	-1.22476600	-1.36032000	-0.00004700
C	-1.20621300	0.03201900	-0.00000700	-1.24523900	0.02180600	-0.00001100
C	0.00000000	0.83110700	0.00000000	0.00000000	0.80314900	0.00002600
H	2.13528300	-1.90663500	-0.00008200	2.14087800	-1.93056000	-0.00003700
H	0.00000100	-3.14804300	-0.00008200	0.00000000	-3.11443100	-0.00008300
H	-2.13528000	-1.90663900	-0.00004000	-2.14087800	-1.93056000	-0.00007200
O	-0.00000200	2.08996200	0.00001800	0.00000000	2.03808200	0.00005000
O	2.36908700	0.78668200	-0.00003000	2.34941500	0.77671300	0.00003600
O	-2.36908600	0.78668100	0.00001800	-2.34941500	0.77671300	-0.00000500
C	3.58988300	0.10910300	0.00011400	3.61894000	0.14147800	0.00005500
H	4.36912700	0.87204100	0.00018700	4.35163800	0.94254100	0.00011300
H	3.71574300	-0.52479900	0.88843300	3.75068000	-0.47467500	0.89207200
H	3.71594600	-0.52482400	-0.88815900	3.75074200	-0.47460200	-0.89200500
C	-3.58988400	0.10910300	0.00001600	-3.61894000	0.14147800	-0.00003800
H	-4.36912500	0.87204200	0.00004000	-4.35163800	0.94254100	-0.00002500
H	-3.71585400	-0.52479200	-0.88829300	-3.75070000	-0.47461400	-0.89209500
H	-3.71583600	-0.52483100	0.88829900	-3.75072200	-0.47466300	0.89198100

**Table S4: Cartesian Coordinates of the Anionic and Neutral Radical Forms of Deprotonated 2,6-dimethoxyphenol With One Hydrogen Bonding Interaction Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	1.24067200	0.39289300	-0.18312000	1.26828400	0.48401400	-0.00004700
C	0.97245100	1.75085500	-0.07883700	0.91739300	1.82907800	-0.00005300
C	-0.33158400	2.21461400	0.05416500	-0.41516900	2.20500700	-0.00002700
C	-1.37631300	1.28097500	0.09594000	-1.45690000	1.26316000	-0.00000500
C	-1.11631100	-0.07662900	-0.00467300	-1.15496200	-0.07958300	-0.00005300
C	0.21714000	-0.61870000	-0.17904300	0.23782700	-0.55546100	-0.00020600
H	1.80972400	2.43894100	-0.11325200	1.70647800	2.56717800	-0.00004400
H	-0.54110300	3.27364900	0.13007200	-0.66497900	3.25728700	-0.00001000
H	-2.39217100	1.63704100	0.20604300	-2.48002400	1.60536000	0.00004600
O	0.44604000	-1.85675000	-0.31468600	0.50180000	-1.77027200	-0.00049200
O	2.56859000	0.02857900	-0.38450200	2.58145200	0.22591500	-0.00004800
O	-2.10862500	-1.04221800	0.01762900	-2.05211700	-1.07545300	0.00000300
C	3.08961000	-0.89851400	0.55488400	3.14530800	-1.09403100	0.00040900
H	4.10886300	-1.12533300	0.23615300	4.21912800	-0.92624500	0.00058400
H	3.12324900	-0.45370500	1.55905600	2.84566500	-1.64912000	0.88503900
H	2.48611900	-1.80626300	0.57445200	2.84604700	-1.64959800	-0.88404400
C	-3.43471300	-0.61849600	0.13449400	-3.43367200	-0.75005700	0.00026800
H	-4.05058400	-1.51819300	0.12429000	-3.96234000	-1.69833200	0.00050000
H	-3.61830400	-0.07453000	1.07104900	-3.70366900	-0.18029600	0.89216600
H	-3.73953300	0.02951400	-0.69825100	-3.70404400	-0.18051900	-0.89166100

**Table S5: Cartesian Coordinates of the Anionic and Neutral Radical Forms of the *syn* Conformer of Deprotonated 2,6-dimethoxyphenol Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.20389100	0.33547700	-0.14292900	-1.24462900	0.38637400	-0.02362000
C	-1.19782300	1.70555700	0.06490400	-1.21714400	1.76804500	0.01937600
C	0.00001200	2.41378500	0.16031200	0.00000400	2.44407500	0.03560500
C	1.19783500	1.70554000	0.06488200	1.21715000	1.76804100	0.01936100
C	1.20388200	0.33545900	-0.14294500	1.24463000	0.38637000	-0.02363700
C	-0.00001200	-0.44221200	-0.30768300	-0.00000100	-0.38736100	-0.09280300
H	-2.15363700	2.21183300	0.13953200	-2.15495500	2.30395200	0.04347000
H	0.00002100	3.48499700	0.31499500	0.00000600	3.52493700	0.07356200
H	2.15365800	2.21180300	0.13949600	2.15496400	2.30394400	0.04344400
O	-0.00002800	-1.68493600	-0.58385400	-0.00000400	-1.62888600	-0.23696400
O	-2.44561800	-0.26682500	-0.31129400	-2.46103300	-0.17912500	-0.05641800
O	2.44560400	-0.26685300	-0.31132100	2.46103100	-0.17913500	-0.05644700
C	-2.70149300	-1.37791800	0.53338500	-2.70278400	-1.57726600	0.15016600
H	-3.68333600	-1.76298800	0.25226600	-3.78079800	-1.65084200	0.26947600
H	-1.93936200	-2.14595200	0.40081300	-2.37186500	-2.16475300	-0.70091800
H	-2.73260300	-1.06431500	1.58576200	-2.20127100	-1.93527700	1.04651000
C	2.70152000	-1.37790400	0.53340200	2.70278100	-1.57726700	0.15019700
H	3.68335500	-1.76298100	0.25226200	3.78079600	-1.65084100	0.26950300
H	2.73267300	-1.06424900	1.58576200	2.20127500	-1.93524000	1.04656000
H	1.93939000	-2.14595000	0.40090100	2.37185500	-2.16478900	-0.70086000

**Table S6: Cartesian Coordinates of the Anionic and Neutral Radical Forms of the *anti* Conformer of Deprotonated 2,6-dimethoxyphenol Optimised Using B3LYP/6-311++G(3df,3pd)**

atom	anion coordinates /Å			neutral coordinates /Å		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.18133500	0.29580700	0.23089100	-1.24461800	0.38637700	-0.02365800
C	-1.17589800	1.68122100	0.22776100	-1.21712200	1.76803700	0.01947100
C	0.00010900	2.39621300	-0.00004100	0.00004500	2.44405300	0.03571300
C	1.17603700	1.68106100	-0.22776300	1.21718000	1.76801000	0.01937100
C	1.18129100	0.29564700	-0.23095800	1.24463800	0.38633800	-0.02374700
C	-0.00012300	-0.49868200	-0.00022400	0.00000200	-0.38736100	-0.09306600
H	-2.11360800	2.19302700	0.41309400	-2.15491600	2.30396700	0.04366500
H	0.00018700	3.47852600	-0.00000500	0.00004900	3.52491200	0.07378000
H	2.11383700	2.19274600	-0.41297200	2.15500300	2.30389600	0.04348700
O	-0.00021700	-1.77160300	-0.00005300	-0.00001700	-1.62883300	-0.23764500
O	-2.38839700	-0.33073800	0.52267300	-2.46101400	-0.17914200	-0.05646900
O	2.38834300	-0.33098700	-0.52264400	2.46100200	-0.17922400	-0.05671100
C	-2.85859500	-1.23034600	-0.46982700	-2.70278900	-1.57719400	0.15049600
H	-3.77628100	-1.67366600	-0.07887600	-3.78078200	-1.65071500	0.27004600
H	-3.09289200	-0.69265100	-1.39860000	-2.37206200	-2.16491600	-0.70050200
H	-2.11776000	-2.00452200	-0.66963900	-2.20113000	-1.93503400	1.04683500
C	2.85871800	-1.23031000	0.47004400	2.70272400	-1.57723100	0.15073000
H	3.77636000	-1.67371300	0.07907800	3.78071000	-1.65075600	0.27032200
H	3.09315400	-0.69233300	1.39862000	2.20102500	-1.93472000	1.04718600
H	2.11794500	-2.00445400	0.67019300	2.37197500	-2.16521900	-0.70007400

**Table S7: Harmonic Vibrational Frequencies for the Phenolate Anion and Neutral Radical, Calculated using the B3LYP/6-311G++(3df,3pd) method. The Mode Numbering ( $\nu$ ) Employed in this Work is the One Used in the Gaussian 09 Software Package**

$\nu$	$\omega_e/\text{cm}^{-1}$ (anion)	$\omega_e/\text{cm}^{-1}$ (neutral radical)
1	192.55	188.79
2	437.27	384.48
3	454.84	453.80
4	511.39	485.51
5	541.34	535.93
6	624.65	602.48
7	696.03	651.92
8	727.63	810.40
9	813.89	815.11
10	837.98	817.88
11	871.85	948.06
12	951.01	981.80
13	965.26	1010.98
14	986.46	1011.60
15	1039.07	1021.39
16	1082.38	1101.44
17	1159.20	1164.56
18	1175.31	1171.82
19	1260.57	1292.15
20	1350.80	1341.39
21	1421.43	1442.97
22	1495.08	1459.89
23	1568.58	1514.83
24	1576.38	1569.03
25	1648.47	1610.05
26	3124.45	3194.38
27	3128.37	3201.96
28	3167.74	3215.50
29	3168.61	3223.59
30	3185.10	3226.82



**Table S8: Harmonic Vibrational Frequencies for the 2,6-Difluorophenolate Anion and Neutral Radical, Calculated using the B3LYP/6-311G++(3df,3pd) method. The Mode Numbering ( $\nu$ ) Employed in this Work is the One Used in the Gaussian 09 Software Package**

$\nu$	$\omega_e/\text{cm}^{-1}$ (anion)	$\omega_e/\text{cm}^{-1}$ (neutral radical)
1	126.06	122.31
2	264.97	234.63
3	289.50	310.39
4	309.52	316.89
5	315.12	317.85
6	469.46	474.05
7	507.86	498.64
8	540.77	506.80
9	550.29	544.80
10	589.54	588.07
11	681.00	700.98
12	692.16	761.93
13	733.07	799.99
14	854.97	866.24
15	863.55	905.30
16	870.12	962.18
17	968.28	1020.45
18	1070.84	1059.64
19	1144.63	1157.21
20	1202.92	1272.24
21	1231.70	1304.07
22	1305.76	1320.01
23	1367.79	1381.82
24	1503.13	1470.79
25	1546.77	1513.00
26	1563.75	1547.75
27	1617.24	1614.50
28	3149.58	3193.73
29	3155.54	3206.86
30	3182.83	3213.46

## Difference photoelectron spectra

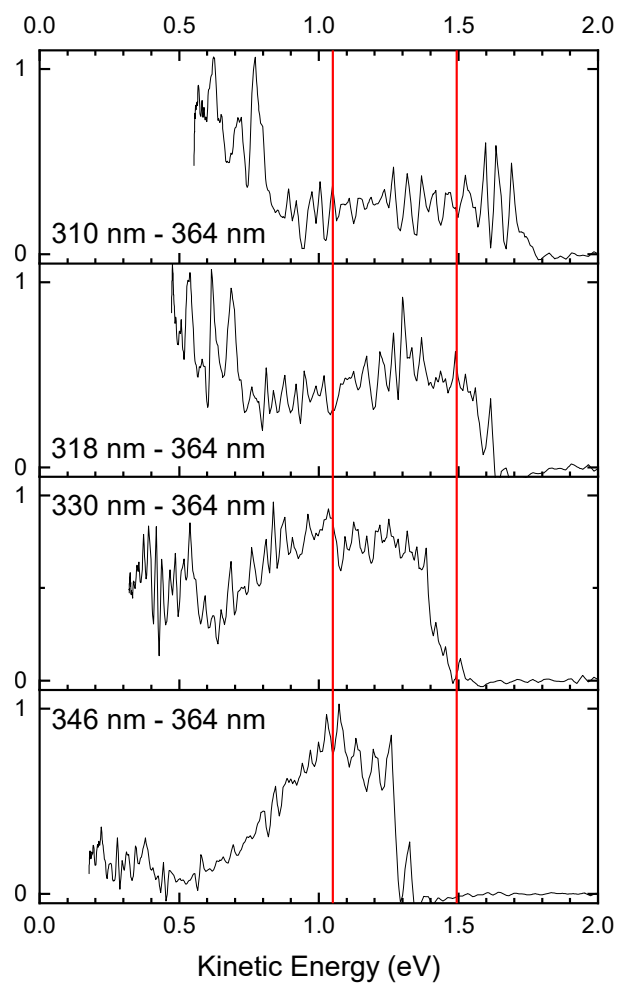


Figure S2: Difference photoelectron spectra of  $\text{PhO}^-$  created by subtracting the 364 nm spectral profile from the photoelectron spectra at the specified wavelengths. As such, these spectra highlight direct detachment to the  $D_1$  threshold and indirect detachment processes. The red lines mark the assigned eKEs of the resonant features referred to in the paper.

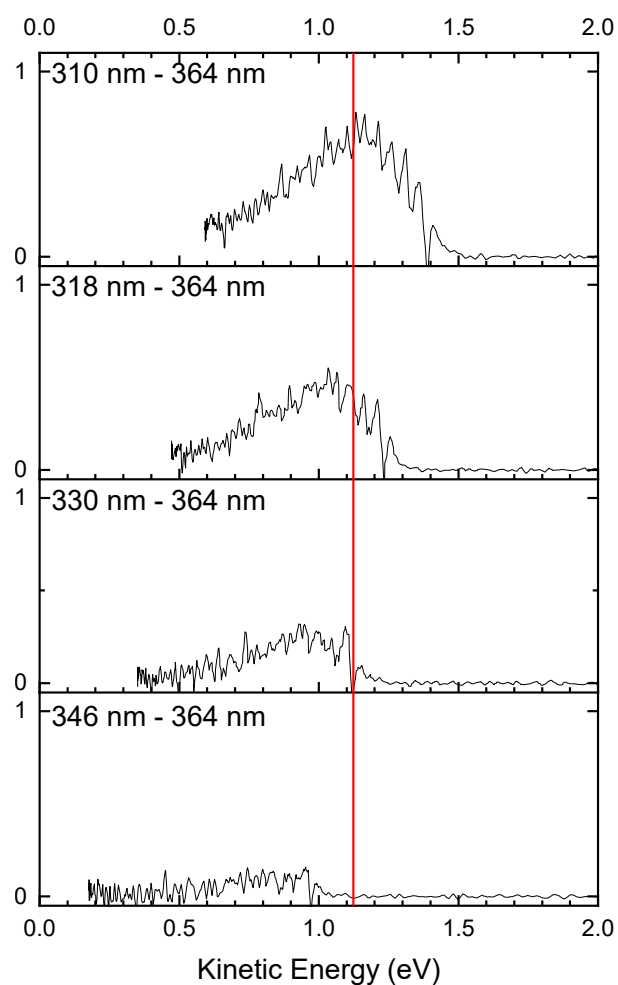


Figure S3: Difference photoelectron spectra of DFPhO<sup>-</sup> created by subtracting the 364 nm spectral profile from the photoelectron spectra at the specified wavelengths. As such, these spectra highlight direct detachment to the D<sub>1</sub> threshold and indirect detachment processes. The red line marks the assigned eKEs of the resonant features referred to in the paper.

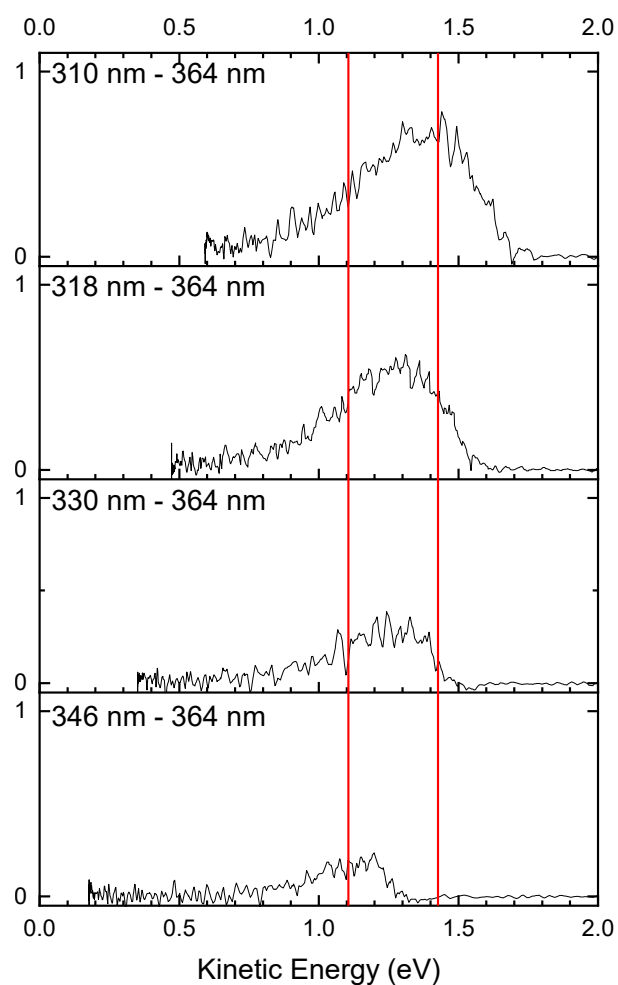


Figure S4: Difference photoelectron spectra of  $\text{DMPHO}^-$  created by subtracting the 364 nm spectral profile from the photoelectron spectra at the specified wavelengths. As such, these spectra highlight direct detachment to the  $D_1$  threshold and indirect detachment processes. The red lines mark the assigned eKEs of the resonant features referred to in the paper.

## Anion temperature

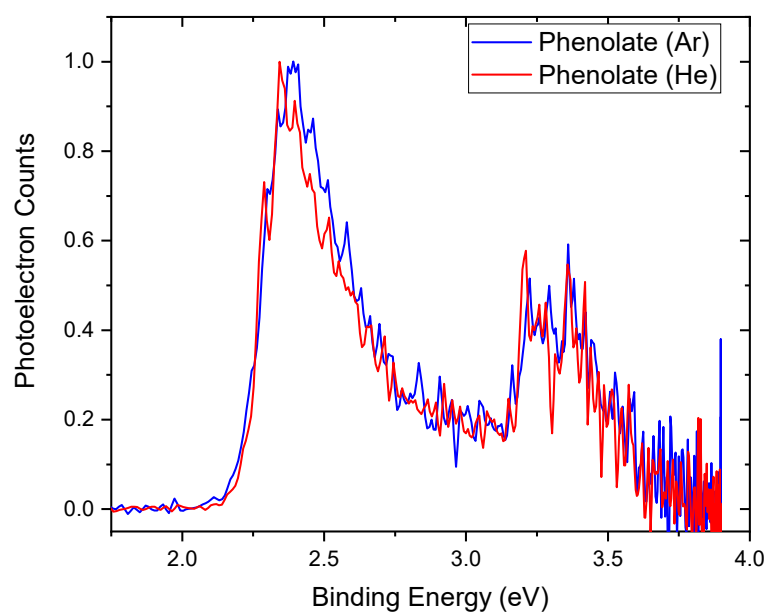


Figure S5: 318 nm phenolate photodetachment spectra using Ar (blue) and He (red) as the collision gas. The similarity of the spectra suggests that 300 K is a reasonable estimate of the temperature of the anions.