Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The quest to uncover the nature of benzonitrile anion. Supplemental Information.

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1. COMPUTATIONAL DETAILS

All calculations were carried out using a modified version of the *Q-Chem* program package[1,2]. We used the standard aug-cc-pVTZ basis set was augmented by an additional sets of diffuse s and p functions on heavy atoms and s function on H, with the following exponents of the first additional basis functions: α(N,s) = 0.0288, α(N,p) = 0.0245, α(C,s) = 0.02201, α(C,p) = 0.017840, α(H,s) = 0.01263; the exponents of the subsequent sets of the additional functions were obtained according to $\alpha_{i+1} = 05 \cdot \alpha_i$. The basis set printout is given below. For frequencies calculations, we used aug-cc-pVDZ.

2. NORMAL MODES

TABLE S1: Frequencies(cm^{-1}) for the neutral and valence anion computed with RI-CCSD and RI-EOM-EA-CCSD using the aug-cc-pVDZ basis set

Mode	Neutral	Anion
0	145.95	110.11
1	160.86	165.23
2	377.10	209.18
3	398.67	433.07
4	458.94	440.53
5	544.92	478.20
6	550.26	518.61
7	626.34	549.59
8	649.87	583.59
9	756.86	621.66
10	762.82	687.67

Mode	Neutral	Anion
11	855.10	731.77
12	922.33	741.78
13	956.62	864.83
14	966.47	899.66
15	1007.98	973.11
16	1046.41	983.34
17	1098.78	1052.40
18	1169.55	1109.17
29	1193.67	1175.36
20	1217.71	1232.88
21	1298.16	1259.66

Mode	Neutral	Anion
22	1332.71	1347.77
23	1463.68	1378.79
24	1513.42	1454.09
25	1638.76	1497.91
26	1663.48	1649.02
27	2311.96	2161.34
28	3199.53	3142.57
39	3209.82	3145.13
30	3217.54	3176.54
31	3226.14	3177.02
32	3231.12	3196.85

3. ABSOLUTE CROSS SECTIONS

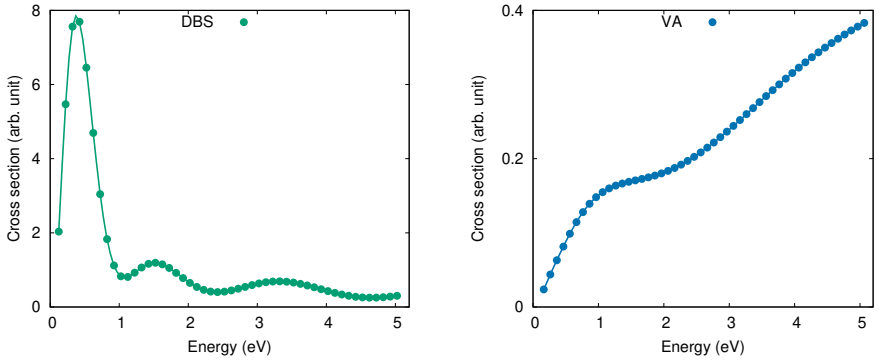

FIG. S1: Absolute cross sections for detachment from the dipole bound (left) and valence (right) states of $C_6H_5CN^-$.

[1] Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A.T.B.; Wormit, M.; Kussmann, J.; Lange, A.W.; Behn, A.; Deng, J.; Feng, X., et al. Advances in molecular quantum chemistry contained in the Q-Chem 4 program package *Mol. Phys.* **2015**, *113*, 184–215.

[2] Krylov, A. I.; Gill, P. M. W. Q-Chem: An engine for innovation *WIREs: Comput. Mol. Sci.* **2013**, *3*, 317–326.

Basis set

```
aug-cc-pVTZ+6s6p(3s) for C6H5CN

$basis
H     0
S   3   1.00
     33.8700000              0.0060680
      5.0950000              0.0453080
      1.1590000              0.2028220
S   1   1.00
      0.3258000              1.0000000
S   1   1.00
      0.1027000              1.0000000
S   1   1.00
      0.0252600              1.0000000
S   1   1.00
      0.0126300              1.0000000
S   1   1.00
      0.0063150              1.0000000
S   1   1.00
      0.0031570              1.0000000
P   1   1.00
      1.4070000              1.0000000
P   1   1.00
      0.3880000              1.0000000
P   1   1.00
      0.1020000              1.0000000
D   1   1.00
      1.0570000              1.0000000
D   1   1.00
      0.2470000              1.0000000
****
C     0
S   8   1.00
   8236.0000000              0.0005310
   1235.0000000              0.0041080
    280.8000000              0.0210870
     79.2700000              0.0818530
     25.5900000              0.2348170
      8.9970000              0.4344010
      3.3190000              0.3461290
      0.3643000             -0.0089830
S   8   1.00
   8236.0000000             -0.0001130
   1235.0000000             -0.0008780
    280.8000000             -0.0045400
```

```
     79.2700000            -0.0181330
     25.5900000            -0.0557600
      8.9970000            -0.1268950
      3.3190000            -0.1703520
      0.3643000             0.5986840
S   1   1.00
      0.9059000             1.0000000
S   1   1.00
      0.1285000             1.0000000
S   1   1.00
      0.0440200             1.0000000
S   1   1.00
      0.0220100             1.0000000
S   1   1.00
      0.0110000             1.0000000
S   1   1.00
      0.0055000             1.0000000
S   1   1.00
      0.0022500             1.0000000
S   1   1.00
      0.0011250             1.0000000
S   1   1.00
      0.0005625             1.0000000
P   3   1.00
     18.7100000             0.0140310
      4.1330000             0.0868660
      1.2000000             0.2902160
P   1   1.00
      0.3827000             1.0000000
P   1   1.00
      0.1209000             1.0000000
P   1   1.00
      0.0356900             1.0000000
P   1   1.00
      0.0178400             1.0000000
P   1   1.00
      0.0089200             1.0000000
P   1   1.00
      0.0044600             1.0000000
D   1   1.00
      1.0970000             1.0000000
D   1   1.00
      0.3180000             1.0000000
D   1   1.00
      0.1000000             1.0000000
F   1   1.00
      0.7610000             1.0000000
```

```
F   1   1.00
      0.2680000             1.0000000
****
N     0
S   8   1.00
  11420.0000000             0.0005230
   1712.0000000             0.0040450
    389.3000000             0.0207750
    110.0000000             0.0807270
     35.5700000             0.2330740
     12.5400000             0.4335010
      4.6440000             0.3474720
      0.5118000            -0.0085080
S   8   1.00
  11420.0000000            -0.0001150
   1712.0000000            -0.0008950
    389.3000000            -0.0046240
    110.0000000            -0.0185280
     35.5700000            -0.0573390
     12.5400000            -0.1320760
      4.6440000            -0.1725100
      0.5118000             0.5999440
S   1   1.00
      1.2930000             1.0000000
S   1   1.00
      0.1787000             1.0000000
S   1   1.00
      0.0576000             1.0000000
S   1   1.00
      0.0288000             1.0000000
S   1   1.00
      0.0144000             1.0000000
S   1   1.00
      0.0072000             1.0000000
S   1   1.00
      0.0036000             1.0000000
S   1   1.00
      0.0018000             1.0000000
S   1   1.00
      0.0009000             1.0000000
P   3   1.00
     26.6300000             0.0146700
      5.9480000             0.0917640
      1.7420000             0.2986830
P   1   1.00
      0.5550000             1.0000000
P   1   1.00
```

```
      0.1725000             1.0000000
P   1   1.00
      0.0491000             1.0000000
P   1   1.00
      0.0245500             1.0000000
P   1   1.00
      0.0122700             1.0000000
P   1   1.00
      0.0061350             1.0000000
D   1   1.00
      1.6540000             1.0000000
D   1   1.00
      0.4690000             1.0000000
D   1   1.00
      0.1510000             1.0000000
F   1   1.00
      1.0930000             1.0000000
F   1   1.00
      0.3640000             1.0000000
****
$end



aug-cc-pVTZ+4s4p(4s) for C6H5CN + H2O
$basis
H     0
S   3   1.00
     33.8700000             0.0060680
      5.0950000             0.0453080
      1.1590000             0.2028220
S   1   1.00
      0.3258000             1.0000000
S   1   1.00
      0.1027000             1.0000000
S   1   1.00
      0.0252600             1.0000000
S   1   1.00
      0.0126300             1.0000000
S   1   1.00
      0.0063150             1.0000000
S   1   1.00
      0.0031570             1.0000000
S   1   1.00
      0.0015785             1.0000000
P   1   1.00
      1.4070000             1.0000000
P   1   1.00
```

```
      0.3880000              1.0000000
P   1   1.00
      0.1020000              1.0000000
D   1   1.00
      1.0570000              1.0000000
D   1   1.00
      0.2470000              1.0000000
****
C     0
S   8   1.00
   8236.0000000              0.0005310
   1235.0000000              0.0041080
    280.8000000              0.0210870
     79.2700000              0.0818530
     25.5900000              0.2348170
      8.9970000              0.4344010
      3.3190000              0.3461290
      0.3643000             -0.0089830
S   8   1.00
   8236.0000000             -0.0001130
   1235.0000000             -0.0008780
    280.8000000             -0.0045400
     79.2700000             -0.0181330
     25.5900000             -0.0557600
      8.9970000             -0.1268950
      3.3190000             -0.1703520
      0.3643000              0.5986840
S   1   1.00
      0.9059000              1.0000000
S   1   1.00
      0.1285000              1.0000000
S   1   1.00
      0.0440200              1.0000000
S   1   1.00
      0.0220100              1.0000000
S   1   1.00
      0.0110000              1.0000000
S   1   1.00
      0.0055000              1.0000000
S   1   1.00
      0.0027500              1.0000000
P   3   1.00
     18.7100000              0.0140310
      4.1330000              0.0868660
      1.2000000              0.2902160
P   1   1.00
      0.3827000              1.0000000
```

```
P   1   1.00
      0.1209000             1.0000000
P   1   1.00
      0.0356900             1.0000000
P   1   1.00
      0.0178400             1.0000000
P   1   1.00
      0.0089200             1.0000000
P   1   1.00
      0.0044600             1.0000000
P   1   1.00
      0.0022300             1.0000000
D   1   1.00
      1.0970000             1.0000000
D   1   1.00
      0.3180000             1.0000000
D   1   1.00
      0.1000000             1.0000000
F   1   1.00
      0.7610000             1.0000000
F   1   1.00
      0.2680000             1.0000000
****
N     0
S   8   1.00
  11420.0000000             0.0005230
   1712.0000000             0.0040450
    389.3000000             0.0207750
    110.0000000             0.0807270
     35.5700000             0.2330740
     12.5400000             0.4335010
      4.6440000             0.3474720
      0.5118000            -0.0085080
S   8   1.00
  11420.0000000            -0.0001150
   1712.0000000            -0.0008950
    389.3000000            -0.0046240
    110.0000000            -0.0185280
     35.5700000            -0.0573390
     12.5400000            -0.1320760
      4.6440000            -0.1725100
      0.5118000             0.5999440
S   1   1.00
      1.2930000             1.0000000
S   1   1.00
      0.1787000             1.0000000
S   1   1.00
```

```
      0.0576000             1.0000000
S   1   1.00
      0.0288000             1.0000000
S   1   1.00
      0.0144000             1.0000000
S   1   1.00
      0.0072000             1.0000000
S   1   1.00
      0.0036000             1.0000000
P   3   1.00
     26.6300000             0.0146700
      5.9480000             0.0917640
      1.7420000             0.2986830
P   1   1.00
      0.5550000             1.0000000
P   1   1.00
      0.1725000             1.0000000
P   1   1.00
      0.0491000             1.0000000
P   1   1.00
      0.0245500             1.0000000
P   1   1.00
      0.0122700             1.0000000
P   1   1.00
      0.0061350             1.0000000
P   1   1.00
      0.0030675             1.0000000
D   1   1.00
      1.6540000             1.0000000
D   1   1.00
      0.4690000             1.0000000
D   1   1.00
      0.1510000             1.0000000
F   1   1.00
      1.0930000             1.0000000
F   1   1.00
      0.3640000             1.0000000
****
O     0
S   8   1.00
  15330.0000000             0.0005080
   2299.0000000             0.0039290
    522.4000000             0.0202430
    147.3000000             0.0791810
     47.5500000             0.2306870
     16.7600000             0.4331180
      6.2070000             0.3502600
```

```
      0.6882000             -0.0081540
S   8   1.00
  15330.0000000             -0.0001150
   2299.0000000             -0.0008950
    522.4000000             -0.0046360
    147.3000000             -0.0187240
     47.5500000             -0.0584630
     16.7600000             -0.1364630
      6.2070000             -0.1757400
      0.6882000              0.6034180
S   1   1.00
      1.7520000              1.0000000
S   1   1.00
      0.2384000              1.0000000
S   1   1.00
      0.0737600              1.0000000
S   1   1.00
      0.0368800              1.0000000
S   1   1.00
      0.0184400              1.0000000
S   1   1.00
      0.0092200              1.0000000
S   1   1.00
      0.0046100              1.0000000
P   3   1.00
     34.4600000              0.0159280
      7.7490000              0.0997400
      2.2800000              0.3104920
P   1   1.00
      0.7156000              1.0000000
P   1   1.00
      0.2140000              1.0000000
P   1   1.00
      0.0597400              1.0000000
P   1   1.00
      0.0298700              1.0000000
P   1   1.00
      0.0149350              1.0000000
P   1   1.00
      0.0074675              1.0000000
P   1   1.00
      0.0037338              1.0000000
D   1   1.00
      2.3140000              1.0000000
D   1   1.00
      0.6450000              1.0000000
D   1   1.00
```

```
      0.2140000              1.0000000
F   1   1.00
      1.4280000              1.0000000
F   1   1.00
      0.5000000              1.0000000
****
$end
```

Relevant Cartesian geometries

C6H5CN (anion) [EOM-EA-CCSD/aug-cc-pVTZ]
Nuclear Repulsion Energy = 297.4254488750 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	0.0000000000	0.0000000000	2.2198396566
2	C	1.2148152484	0.0000000000	1.4847353494
3	C	1.2286801655	0.0000000000	0.1090561197
4	C	0.0000000000	0.0000000000	-0.6418412548
5	C	-1.2286801655	0.0000000000	0.1090561197
6	C	-1.2148152484	0.0000000000	1.4847353494
7	H	0.0000000000	0.0000000000	3.3013966583
8	H	2.1614221562	0.0000000000	2.0155280474
9	H	2.1721584196	0.0000000000	-0.4237371437
10	H	-2.1721584196	0.0000000000	-0.4237371437
11	H	-2.1614221562	0.0000000000	2.0155280474
12	C	0.0000000000	0.0000000000	-2.0456075662
13	N	0.0000000000	0.0000000000	-3.2200270210

C6H5CN (neutral) [CCSD/aug-cc-pVTZ]
Nuclear Repulsion Energy = 300.0912167081 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	0.0000000000	0.0000000000	2.1806397523
2	C	1.2072838898	0.0000000000	1.4863451086
3	C	1.2122184965	0.0000000000	0.0965882257
4	C	0.0000000000	0.0000000000	-0.5963508767
5	C	-1.2122184965	0.0000000000	0.0965882257
6	C	-1.2072838898	0.0000000000	1.4863451086
7	H	0.0000000000	0.0000000000	3.2620055195
8	H	2.1441224787	0.0000000000	2.0255164220
9	H	2.1428929996	0.0000000000	-0.4529820599
10	H	-2.1428929996	0.0000000000	-0.4529820599
11	H	-2.1441224787	0.0000000000	2.0255164220
12	C	0.0000000000	0.0000000000	-2.0378191747
13	N	0.0000000000	0.0000000000	-3.1939971402

C6H5CN (anion) [RI-EOM-EA-CCSD/aug-cc-pVDZ]
Nuclear Repulsion Energy = 294.24941846 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	0.0000000000	0.0000000000	2.2385619165
2	C	1.2270100469	0.0000000000	1.4955660302
3	C	1.2414555922	0.0000000000	0.1048278944
4	C	0.0000000000	0.0000000000	-0.6517153293
5	C	-1.2414555922	0.0000000000	0.1048278944
6	C	-1.2270100469	0.0000000000	1.4955660302
7	H	0.0000000000	0.0000000000	3.3333378557
8	H	2.1849792477	0.0000000000	2.0326591595
9	H	2.1961421075	0.0000000000	-0.4345093168
10	H	-2.1961421075	0.0000000000	-0.4345093168
11	H	-2.1849792477	0.0000000000	2.0326591595
12	C	0.0000000000	0.0000000000	-2.0709831529
13	N	0.0000000000	0.0000000000	-3.2613636061

C6H5CN (neutral) [RI-CCSD/aug-cc-pVDZ]
Nuclear Repulsion Energy = 296.89544041 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	0.0000000000	0.0000000000	2.1973518112
2	C	1.2198603297	0.0000000000	1.4955590882
3	C	1.2256042525	0.0000000000	0.0911948716
4	C	0.0000000000	0.0000000000	-0.6074800981
5	C	-1.2256042525	0.0000000000	0.0911948716
6	C	-1.2198603297	0.0000000000	1.4955590882
7	H	0.0000000000	0.0000000000	3.2914713787
8	H	2.1676784048	0.0000000000	2.0411918025
9	H	2.1671350168	0.0000000000	-0.4645081830
10	H	-2.1671350168	0.0000000000	-0.4645081830
11	H	-2.1676784048	0.0000000000	2.0411918025
12	C	0.0000000000	0.0000000000	-2.0630362867
13	N	0.0000000000	0.0000000000	-3.2352712420

C6H5CN + H2O (anion) [EOM-EA-CCSD/aug-cc-pVDZ]
Nuclear Repulsion Energy = 356.60342912 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	-1.0559591922	-1.2416910481	0.0000000000
2	C	-0.2962128176	-0.0021660398	0.0000000000
3	C	-1.0459008917	1.2434058339	0.0000000000
4	C	-2.4367045617	1.2324629599	0.0000000000

5	C	-3.1822450186	0.0092421753	0.0000000000
6	C	-2.4462223691	-1.2203476331	0.0000000000
7	H	-0.5186771746	-2.1970717339	0.0000000000
8	H	-0.5018692828	2.1950706178	0.0000000000
9	H	-2.9720373840	2.1909451057	0.0000000000
10	H	-4.2767950617	0.0135752338	0.0000000000
11	H	-2.9885843803	-2.1748283637	0.0000000000
12	C	1.1169746423	-0.0112036653	0.0000000000
13	N	2.3065654217	-0.0249614375	0.0000000000
14	O	5.2039805652	-0.0787786240	0.0000000000
15	H	5.3301318889	0.8760470161	0.0000000000
16	H	4.2276501721	-0.1569943179	0.0000000000

C6H5CN + H20 (neutral) [CCSD/aug-cc-pVDZ]
Nuclear Repulsion Energy = 357.0277249080 hartrees

Standard Nuclear Orientation (Angstroms)

I	Atom	X	Y	Z
1	C	-1.0860467968	-1.2296201743	0.0000000000
2	C	-0.3819739079	-0.0069710232	0.0000000000
3	C	-1.0708767787	1.2244245809	0.0000000000
4	C	-2.4750926197	1.2261974571	0.0000000000
5	C	-3.1828604323	0.0096059813	0.0000000000
6	C	-2.4898591578	-1.2153419764	0.0000000000
7	H	-0.5357320682	-2.1741751448	0.0000000000
8	H	-0.5114531691	2.1637519582	0.0000000000
9	H	-3.0175160887	2.1761282806	0.0000000000
10	H	-4.2767261424	0.0160758864	0.0000000000
11	H	-3.0424983076	-2.1592565052	0.0000000000
12	C	1.0724883600	-0.0234315776	0.0000000000
13	N	2.2425517096	-0.0481918041	0.0000000000
14	O	5.3364158461	-0.0671302711	0.0000000000
15	H	5.5137281879	0.8800305480	0.0000000000
16	H	4.3695459215	-0.1193901367	0.0000000000