Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Vibronic Spectra of the *p*-Benzoquinone Radical Anion and Cation: A Matrix Isolation and Computational Study.

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Full quotation of Reference 43 (Gaussian program)

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B3LYP/6-311+G(2d,p) cartesian coordinates of PBQ

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.438709
2	6	0.000000	1.267043	0.667870
3	6	0.000000	1.267043	-0.667870
4	6	0.000000	0.000000	-1.438709
5	6	0.000000	-1.267043	-0.667870
6	6	0.000000	-1.267043	0.667870
7	1	0.000000	2.177069	1.256376
8	1	0.000000	2.177069	-1.256376
9	1	0.000000	-2.177069	-1.256376
10	1	0.000000	-2.177069	1.256376
11	8	0.000000	0.000000	2.656604
12	8	0.000000	0.000000	-2.656604

Low freq. -8.4805 -1.7853 -0.0011 -0.0010 -0.0008 8.8918

B3LYP/6-311+G(2d,p) cartesian coordinates of $PBQ^{\bullet-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.465572
2	6	0.000000	1.219844	0.683154
3	6	0.000000	1.219844	-0.683154
4	6	0.000000	0.000000	-1.465572
5	6	0.000000	-1.219844	-0.683154
6	6	0.000000	-1.219844	0.683154
7	1	0.000000	2.149490	1.246991
8	1	0.000000	2.149490	-1.246991
9	1	0.000000	-2.149490	-1.246991
10	1	0.000000	-2.149490	1.246991
11	8	0.000000	0.000000	2.726726
12	8	0.000000	0.000000	-2.726726

Low freq. -2.6665 0.0006 0.0006 0.0007 8.3816 17.8805

B3LYP/6-311+G(2d,p) cartesian coordinates of $PBQ^{\bullet+}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.444523
2	6	0.000000	1.288339	0.658885
3	6	0.000000	1.288339	-0.658885
4	6	0.000000	0.000000	-1.444523
5	6	0.000000	-1.288339	-0.658885
6	6	0.000000	-1.288339	0.658885
7	1	0.000000	2.187567	1.264322
8	1	0.000000	2.187567	-1.264322
9	1	0.000000	-2.187567	-1.264322
10	1	0.000000	-2.187567	1.264322
11	8	0.000000	0.000000	2.642429
12	8	0.000000	0.000000	-2.642429

Low freq. -10.9031 -4.9197 -0.0006 -0.0005 0.0003 9.1984

results of TD-DFT calculations on $PBQ^{\bullet-}$ with B3LYP/6-311+G(2d,p)

```
Excitation energies and oscillator strengths (SOMO = 29A):
leading configurations in blue, observed excited states in red

 Excited State   1:   ?Spin  -B1G    2.2280 eV  556.48 nm  f=0.0000
     27B -> 39B       -0.11193
     28B -> 29B        0.99887

 Excited State   2:   ?Spin  -AU     2.2476 eV  551.63 nm  f=0.0000
     27B -> 29B        1.00016
     28B -> 39B       -0.11287

 Excited State   3:   ?Spin  -B2U    3.0150 eV  411.22 nm  f=0.0459
     29A -> 30A        0.97326
     25B -> 39B       -0.10643

 Excited State   4:   ?Spin  -B1U    3.0393 eV  407.94 nm  f=0.0654
     26A -> 30A       -0.19714
     29A -> 35A        0.50035
     29A -> 38A        0.21502
     26B -> 29B        0.88932

 Excited State   5:   ?Spin  -B2G    3.2031 eV  387.07 nm  f=0.0000
     29A -> 31A        0.99911

 Excited State   6:   ?Spin  -B3G    3.2742 eV  378.68 nm  f=0.0000
     20A -> 30A        0.11079
     25A -> 30A       -0.20351
     26A -> 53A       -0.10759
     25B -> 29B        0.99315
     26B -> 32B        0.14141

 Excited State   7:   ?Spin  -AU     3.4264 eV  361.85 nm  f=0.0000
     29A -> 32A        1.00045

 Excited State   8:   ?Spin  -B3U    3.8870 eV  318.97 nm  f=0.0004
     29A -> 33A        0.99873

 Excited State   9:   ?Spin  -B1U    4.1731 eV  297.11 nm  f=0.1409
     26A -> 30A        0.59994
     29A -> 35A        0.71760
     21B -> 29B        0.10484
     25B -> 32B       -0.31325
     26B -> 29B       -0.23579

... followed be forbidden or very weak transition to 6 more states
above 250 nm.
```

results of TD-DFT calculations on $PBQ^{\bullet+}$ with B3LYP/6-311+G(2d,p)

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Excited State   1:   ?Spin  -B1U    0.4638 eV 2673.48 nm  f=0.0159
     26A -> 29A       -0.41254
     25B -> 29B       -0.27819
     27B -> 28B        0.96808

... followed by 12 forbidden transitions above 260 nm amd a very
strong (and strongly mixed) one at 247 nm (f=0.1651)
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