SUPPORTING INFORMATION

Electronic structure of para-benzoquinone radical anion revisited

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I. ACTIVE ORBITALS

All CASSCF calculations were performed with (17,12) active space comprising the complete set of the valence π orbitals augmented by four lone-pair orbitals on oxygen atoms. Their symmetries and shapes are shown in Fig. 1.

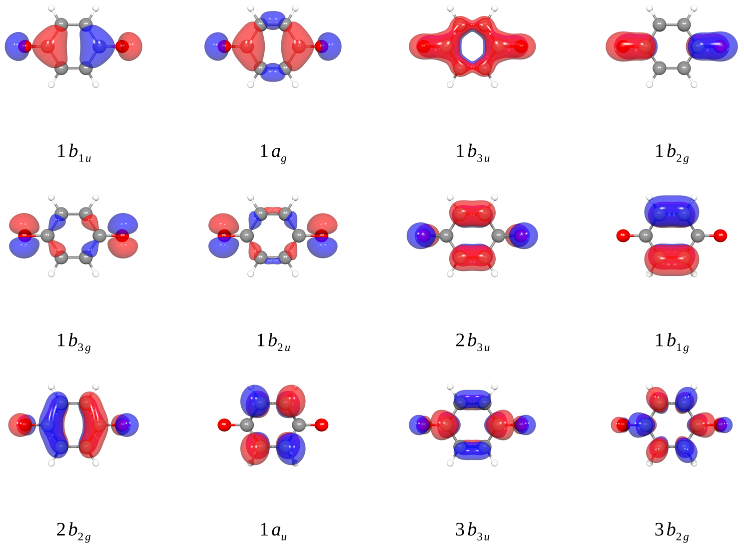

FIG. 1: Set of the active orbitals used for the CASSCF calculations.

II. PHENOLATE ANION PHOTOELECTRON SPECTRUM

In order to asses the accuracy of the computed pBQ$^{\bullet-}$ absorption spectra we used the same approach to simulate the phenolate anion photodetachment spectrum, measured experimentally with good resolution [1]. Our MRMP2/d-aug-cc-pVTZ estimate of adiabatic detachment energy (2.13 eV) is in good agreement with experimental value of 2.253 eV [1]. The $S_0 \rightarrow D_0$ Franck-Condon intensities computed in double-harmonic parallel normal mode approximation and experimental photoelectron spectrum are shown in Fig. 2.

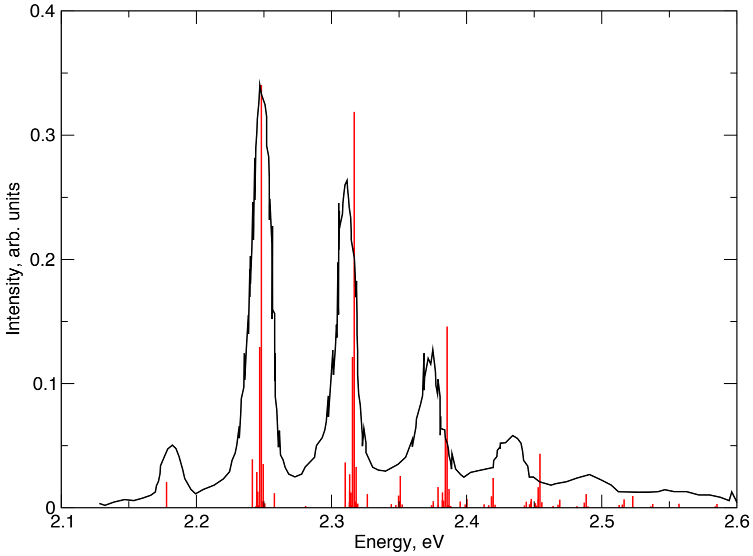

FIG. 2: Experimental photodetachment spectrum of the phenolate anion (black solid line) at T ≈ 300 K and the Franck-Condon intensities of the $S_0 \rightarrow D_0$ transition (red lines). Theoretical results are shifted by 0.12 eV to higher energies in order to match the position of the 0-0 transition in the experimental spectrum.

Our calculation reproduces the vibrational structure of the experimental photodetachment spectrum although the theoretical spectrum is shifted by 0.12 eV to low energies.

III. EFFECT OF DUSCHINSKY ROTATIONS ON THE $^2B_{2g} \rightarrow ^2A$ FRANCK-CONDON FACTORS

In order to test the validity of parallel normal mode approximation we performed the calculations of the $^2B_{2g} \rightarrow {}^2A$ Franck-Condon factors with and without Duschinsky rotation. Twisted D_2 equilibrium geometry was used in both cases. We note the differences in magnitudes of some Franck-Condon factors although the overall shape of excitation band is preserved (Figs. 3A and B).

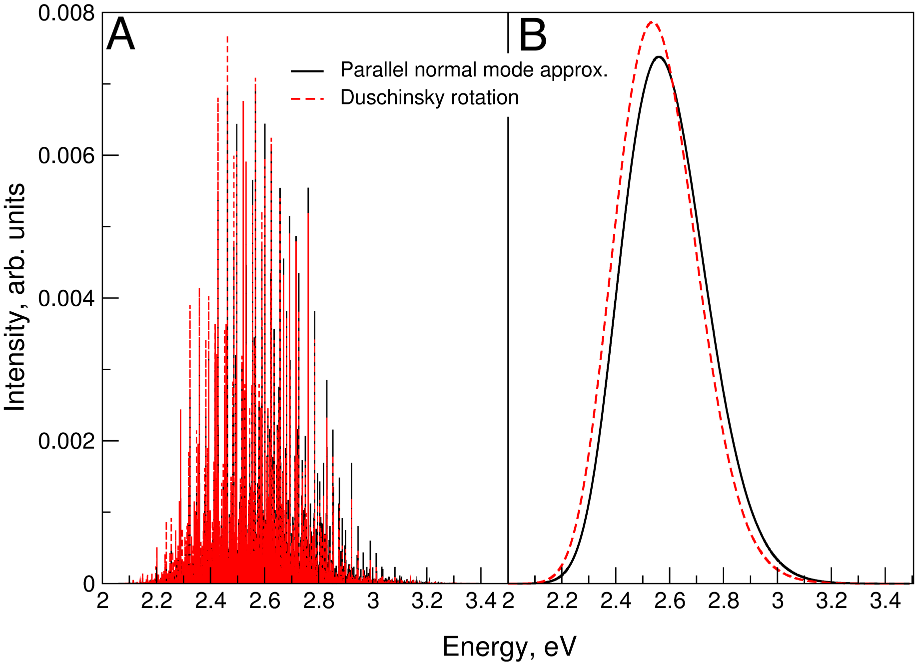

FIG. 3: The Franck-Condon intensities of the ${}^2B_{2g} \rightarrow {}^2A$ vibronic transitions computed in the parallel normal mode approximation (black solid line) and with Duschinsky rotation (red dashed line) at T = 298 K (A). Gaussian-dressed spectral profiles obtained from the Franck-Condon intensities (B).

IV. EQUILIBRIUM GEOMETRIES OF THE BRIGHT STATES OF PBQ$^{\bullet-}$

TABLE I: Key geometrical parameters of pBQ$^{\bullet-}$ in its ground ($^2B_{2g}$) and bright excited states (^2A_u and $^2B_{3u}$). Both D_{2h} and D_2 structures are presented for the ^2A_u state.

	$^2B_{2g}$	^2A_u (D_{2h})	^2A (D_2)	$^2B_{3u}$
r(C=O)	1.272	1.256	1.25	1.336
r(C=C)	1.379	1.412	1.408	1.422
r(C-C)	1.445	1.461	1.469	1.416
r(C-H)	1.086	1.083	1.084	1.084
$\angle(C - C_O - C)$	115.5	120.8	118.6	117.7
$\angle(C = C - H)$	121.2	123.8	122.2	121.2

V. NUMERICAL SOLUTION OF THE VIBRATIONAL PROBLEM IN DOUBLE WELL POTENTIAL

One dimensional vibrational problem for the double well potential was solved numerically following procedure developed by Taseli et al. [2] for the case of symmetric potentials represented by polynomials in the interval $[-\alpha, \alpha]$:

$$V(x) = \sum_{k=0}^{L} a_{2k} x^{2k} \tag{1}$$

Resulting Hamiltonian has the following form (in atomic units and mass-weighted coordinates)

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + V(x) \tag{2}$$

Trigonometric basis was used to expand odd and even solutions of the eigenvalue problem (Eq. 2):

$$\phi^e_m(x) = \alpha^{-1/2} cos((m-1/2)\frac{\pi}{\alpha}x) \tag{3}$$
$$\phi^o_m(x) = \alpha^{-1/2} sin(m\frac{\pi}{\alpha}x) \tag{4}$$

Kinetic energy matrix is, then, diagonal:

$$T^e_{mn} = \frac{1}{2}(m-1/2)^2\frac{\pi^2}{\alpha^2}\delta_{mn} \tag{5}$$
$$T^o_{mn} = \frac{1}{2}m^2\frac{\pi^2}{\alpha^2}\delta_{mn} \tag{6}$$

Potential energy matrix can be expressed in terms of x^{2k} operators matrix elements:

$$\langle x^{2k}\rangle^e_{mn} = (\alpha/\pi)^{2k}(R^{(k)}_{m+n-1} + R^{(k)}_{m-n}) \tag{7}$$
$$\langle x^{2k}\rangle^o_{mn} = (\alpha/\pi)^{2k}(R^{(k)}_{m-n} - R^{(k)}_{m+n}) \tag{8}$$

where $R_s^{(k)} = \frac{1}{\pi}\int_0^\pi t^{2k} cos[st]dt$. It was shown [2] that $R_s^{(k)}$ can be efficiently evaluated using the following recurrence relation:

$$s^2 R_s^{(k)} = (2k)(-1)^s \pi^{2k-2} - (2k)(2k-1)R_s^{(k-1)} \tag{9}$$

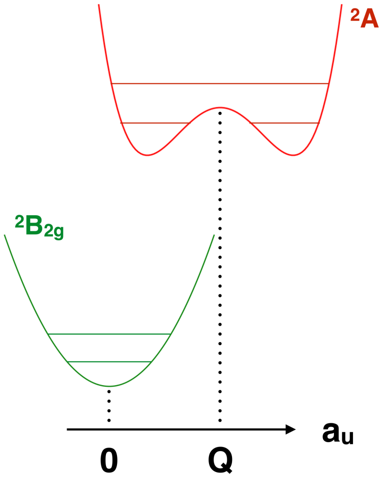

FIG. 4: Schematic reprsentation of potentials along the a_u normal mode in $^2B_{2g}$ and ^2A states. The D_{2h} stationary point on the ^2A potential energy surface is assumed to be shifted by Q whith respect to the $^2B_{2g}$ minimum

The resulting vibrational wave functions obtained for the double-well potential (see Fig. 4) were used for the calculations of the overlap integrals. Harmonic approximation was assumed for the $^2B_{2g}$ potential energy surface. The overlap integrals $I_{f\leftarrow i}$ can be represented in the following form:

$$I_{f\leftarrow i} = \sum_m c_m^f \int_{-\infty}^{+\infty} \phi_m^{e,o}(t)\psi_i(t)dt, \tag{10}$$

where c_m^f are expansion coefficients of the final vibrational function (^2A state) in trigonometric basis, and $\psi_i(t)$ is the initial state vibrational wave function, $\psi_i(t) = \frac{1}{\sqrt{2^i i!}}(\omega/\pi)^{1/4} e^{-\frac{\omega t^2}{2}} H_i(\sqrt{\omega}t)$ (H_i is i-th Hermite polynomial, i - vibrational quantum number, ω - vibrational frequency). Eq. 10 is valid provided α is large enough so that the contributions to the integrals coming from $|t| > \alpha$ are negligible. Analytic expressions for the elementary overlap integrals are shown below.

$$\int_{-\infty}^{+\infty} \phi_m^p(t)\psi_i(t)dt = \begin{cases} \frac{2\sqrt{2}}{\sqrt{\alpha 2^{2n}(2n)!}}(\frac{1}{\pi\omega})^{1/4} cos([m-1/2]\frac{\pi Q}{\alpha}) I_{2n}(\sqrt{2},[m-1/2]\frac{\pi}{\alpha\sqrt{\omega}}), p=e, i=2n \\ \frac{2\sqrt{2}}{\sqrt{\alpha 2^{2n+1}(2n+1)!}}(\frac{1}{\pi\omega})^{1/4} sin([m-1/2]\frac{\pi Q}{\alpha}) I_{2n+1}(\sqrt{2},[m-1/2]\frac{\pi}{\alpha\sqrt{\omega}}), p=e, i=2n+1 \\ (-1)\frac{2\sqrt{2}}{\sqrt{\alpha 2^{2n}(2n)!}}(\frac{1}{\pi\omega})^{1/4} sin(\frac{m\pi Q}{\alpha}) I_{2n}(\sqrt{2},\frac{m\pi}{\alpha\sqrt{\omega}}), p=o, i=2n \\ \frac{2\sqrt{2}}{\sqrt{\alpha 2^{2n+1}(2n+1)!}}(\frac{1}{\pi\omega})^{1/4} cos(\frac{m\pi Q}{\alpha}) I_{2n+1}(\sqrt{2},\frac{m\pi}{\alpha\sqrt{\omega}}), p=o, i=2n+1, \end{cases} \quad (11)$$

where Q is the shift along the a_u mode (Fig. 4). $I_k(a,b)$ have the following form:

$$I_{2n}(a,b) = \frac{1}{2}\pi^{1/2}(1-a^2)^n e^{-\frac{1}{2}b^2} H_{2n}(\frac{ab}{\sqrt{2(a^2-1)}}) \quad (12)$$

$$I_{2n+1}(a,b) = (-1)^n \frac{1}{2}\pi^{1/2}(a^2-1)^{n+1/2} e^{-\frac{1}{2}b^2} H_{2n+1}(\frac{ab}{\sqrt{2(a^2-1)}}) \quad (13)$$

where H_i is i-th Hermite polynomial.

The MRMP2 potential energy surface scan along the a_u mode was fitted with a sextic polynomial (see Fig. 5). Maximum residual for the fit was 0.000108 a.u.

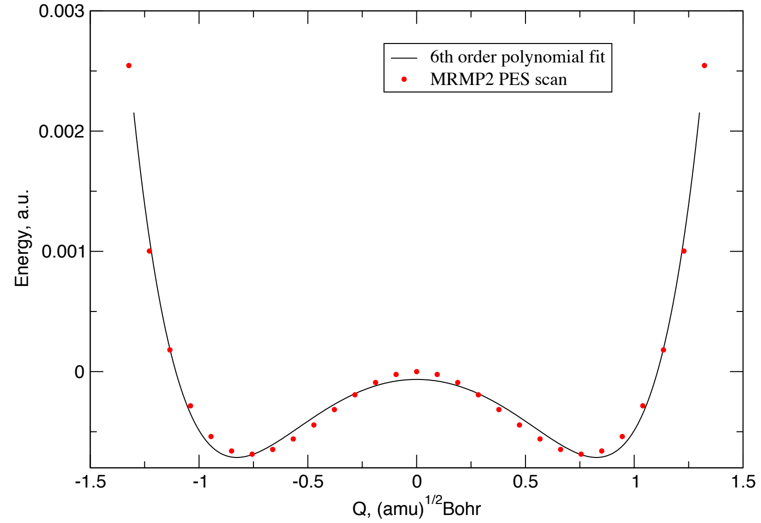

FIG. 5: ${}^2A$ potential energy surface cross section calculated using MRMP2/d-aug-cc-pVTZ, along the a_u normal mode (red dots) and its polynomial least-squares fit (black line)

The coefficients of the fitting polynomial are listed in Table II.

TABLE II: Coefficients of the polynomial representation of potential energy profile along a_u mode

Coefficient	Value
c_6	0.000854777363208
c_4	0.000219462439958
c_2	-0.00149838273611
c_0	-6.50218050084e-05

TABLE III: Vibrational energy levels in the ($^2A_u/^2A$) excited electronic state. The energies are given relative to the saddle point on the potential energy suface of the ^2A state.

Level #	Energy, a.u.
1	-2.46e-5
2	0.74e-3
3	2.37e-3
4	4.38e-3
5	6.75e-3
6	9.42e-3

The eigenvalue problem was solved with trigonometric basis set of 500 basis functions for the odd and even subsets separately, assuming $\alpha = 7$. Note, Q is equal to zero as non-zero displacements between geometries of the same symmetry can occur only along totally symmetric normal modes. The energies of several low-lying vibrational levels with respect to the top of the barrier are listed in Table III.

Resulting Franck-Condon (FC) factors are presented in Table IV. The FC factors for 0 - n transitions decrease rapidly as a function of n. For the purposes of the qualitative analysis (see the main text) we used computed FC factors of a_u mode for 0-0 and 0-2 transitions to scale FC factors obtained in double-harmonic parallel normal mode approximation with a_u mode excluded.

TABLE IV: FC factors of a_u mode. The number of quanta in a_u mode in the initial and final states are listed in the first column and the first row, respectively.

	0	1	2	3	4	5
0	0.886	0	0.112	0	0.00262	0
1	0	0.914	0	0.0813	0	0.00463

VI. PHOTOELECTRON SPECTRUM OF PBQ$^{\bullet-}$

Photodetachment from pBQ$^{\bullet-}$ is a complicated process owing to the presence of the dense manifold of overlapping resonances which contribute to the total photodetachment cross-section in the energy interval of 2.5 - 3.1 eV. Here, we consider direct photodetachment process neglecting resonant contributions.

$^1A_g \leftarrow {}^2B_{2g}$ direct photodetachment spectrum is shown in Fig. 6. Observed vibronic structure can be rationalized based on the shape of the SOMO of the $^2B_{2g}$ state and geometrical changes induced by electron detachment from the orbital. SOMO has significant contributions from the antibonding C=O orbitals and, thus, electron detachment from the SOMO should lead to the contraction of the C=O double bonds. Indeed, the length of the C=O bond is decreased by 0.04 $\AA$ in the ground state of the neutral pBQ. Less pronounced differences are seen for the single and double C-C bonds of the ring which are elongated and contracted by 0.03 $\AA$, respectively. Moderate detachment-induced geometry changes are consistent with the relaxation energy of 0.2 eV. They manifest themselves in the photoelectron spectrum as the ring deformation and C—O stretching vibrational progressions with the frequencies 478 and 1845 cm^{-1} (Fig. 6).

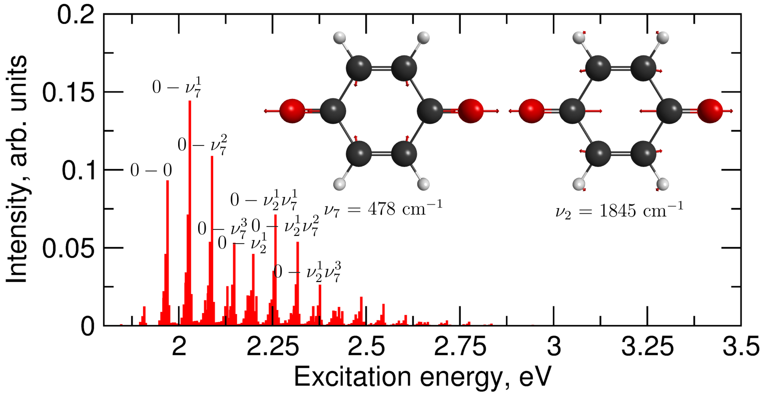

FIG. 6: Stick photoelectron spectrum of pBQ$^{\bullet-}$ at T = 298 K. Normal modes excited upon photodetachment are shown with their frequencies. Herzberg's numbering convention is used.

VII. EXCITATION ENERGIES OF PBQ$^{\bullet-}$ AT THE EQUILIBRIUM GEOMETRIES OF EXCITED STATES

TABLE V: Vertical excitation energies (eV) of pBQ$^{\bullet-}$ at the equilibrium geometries of excited states (listed in the first row) and at the equilibrium geometry of the neutral pBQ. Energies were calculated with respect to the ground state of pBQ$^{\bullet-}$

$^2B_{2g}$	^1A_g	^2A_u	^2A (D_2)	$^2B_{3u}$	$^2B_{2u}$	$^2B_{3g}$	$^2B_2$ (C_{2v})
$^2B_{2g}$ 0.00	$^2B_{2g}$ 0.00	$^2B_{2g}$ 0.00	$^2B_2$ 0.00	$^2B_{2g}$ 0.00	$^2B_{2g}$ 0.00	$^2B_{2g}$ 0.00	$^2A_2$ 0.00
$^2B_{2u}$ 2.14	^2A_u 2.31	$^2B_{2u}$ 2.19	^2A 1.87	$^2B_{2u}$ 1.75	$^2B_{2u}$ 1.83	$^2B_{2u}$ 1.91	$^2A_1$ 1.84
$^2B_{3g}$ 2.23	$^2B_{2u}$ 2.43	^2A_u 2.22	$^2B_2$ 2.30	$^2B_{3g}$ 1.92	$^2B_{3g}$ 1.99	$^2B_{3g}$ 2.03	$^2B_1$ 2.00
^2A_u 2.55	$^2B_{3g}$ 2.45	$^2B_{3g}$ 2.33	$^2B_1$ 2.39	$^2B_{3u}$ 2.43	$^2B_{3u}$ 2.56	$^2B_{3u}$ 2.65	$^2B_2$ 2.49
$^2B_{3u}$ 2.93	$^2B_{3u}$ 3.18	$^2B_{3u}$ 2.95	$^2B_1$ 3.05	$^2B_{1g}$ 2.64	^2A_u 2.71	^2A_u 2.73	$^2A_2$ 2.60
$^2B_{1g}$ 3.07	$^2B_{1g}$ 3.49	$^2B_{1g}$ 3.08	$^2B_3$ 3.08	^2A_u 2.68	$^2B_{1g}$ 2.77	$^2B_{1g}$ 2.85	$^2B_2$ 2.77
$^2B_{3u}$ 4.25	$^2B_{3u}$ 3.90	$^2B_{3u}$ 4.02	$^2B_1$ 3.91	^2A_g 4.32	$^2B_{3u}$ 4.42	$^2B_{3u}$ 4.42	$^2B_2$ 4.33
^2A_g 4.63	^2A_g 4.70	^2A_g 4.34	^2A 4.14	$^2B_{3u}$ 4.34	^2A_g 4.44	^2A_g 4.54	$^2A_1$ 4.34
$^2B_{1u}$ 4.73	$^2B_{1u}$ 4.77	$^2B_{1u}$ 4.50	$^2B_3$ 4.26	$^2B_{1u}$ 4.46	$^2B_{1g}$ 4.57	$^2B_{2g}$ 4.65	$^2A_2$ 4.47
$^2B_{2g}$ 5.27	$^2B_{2g}$ 5.72	$^2B_{1g}$ 5.19	$^2B_3$ 4.96	$^2B_{1g}$ 4.92	$^2B_{2g}$ 5.10	$^2B_{1g}$ 4.86	$^2B_2$ 4.80

TABLE VI: Vertical excitation energies (eV) of pBQ$^{\bullet-}$ at the equilibrium geometries of excited states (listed in the first row) and at equilibrium geometry of the neutral pBQ. Energies were calculated with respect to the ground state of the neutral pBQ

$^2B_{2g}$	^1A_g	^2A_u	^2A (D_2)	$^2B_{3u}$	$^2B_{2u}$	$^2B_{3g}$	$^2B_2$ (C_{2v})
$^2B_{2g}$ -2.17	$^2B_{2g}$ -1.75	$^2B_{2g}$ -1.98	$^2B_2$ -1.93	$^2B_{2g}$ -2.52	$^2B_{2g}$ -2.45	$^2B_{2g}$ -2.43	$^2A_2$ -2.54
$^2B_{2u}$ -0.03	^2A_u 0.56	$^2B_{2u}$ 0.21	^2A -0.05	$^2B_{2u}$ -0.77	$^2B_{2u}$ -0.62	$^2B_{2u}$ -0.53	$^2A_1$ -0.70
$^2B_{3g}$ 0.06	$^2B_{2u}$ 0.68	^2A_u 0.24	$^2B_2$ 0.37	$^2B_{3g}$ -0.60	$^2B_{3g}$ -0.46	$^2B_{3g}$ -0.41	$^2B_1$ -0.54
^2A_u 0.38	$^2B_{3g}$ 0.70	$^2B_{3g}$ 0.35	$^2B_1$ 0.46	$^2B_{3u}$ -0.09	$^2B_{3u}$ 0.11	$^2B_{3u}$ 0.21	$^2B_2$ -0.05
$^2B_{3u}$ 0.76	$^2B_{3u}$ 1.43	$^2B_{3u}$ 0.98	$^2B_1$ 1.13	$^2B_{1g}$ 0.12	^2A_u 0.27	^2A_u 0.30	$^2A_2$ 0.06
$^2B_{1g}$ 0.89	$^2B_{1g}$ 1.73	$^2B_{1g}$ 1.11	$^2B_3$ 1.15	^2A_u 0.16	$^2B_{1g}$ 0.32	$^2B_{1g}$ 0.41	$^2B_2$ 0.23
$^2B_{3u}$ 2.07	$^2B_{3u}$ 2.14	$^2B_{3u}$ 2.05	$^2B_1$ 1.98	^2A_g 1.80	$^2B_{3u}$ 1.97	$^2B_{3u}$ 1.98	$^2B_2$ 1.79
^2A_g 2.46	^2A_g 2.95	^2A_g 2.37	^2A 2.22	$^2B_{3u}$ 1.82	^2A_g 1.99	^2A_g 2.10	$^2A_1$ 1.80
$^2B_{1u}$ 2.56	$^2B_{1u}$ 3.01	$^2B_{1u}$ 2.53	$^2B_3$ 2.33	$^2B_{1u}$ 1.94	$^2B_{1g}$ 2.13	$^2B_{2g}$ 2.22	$^2A_2$ 1.93
$^2B_{2g}$ 3.09	$^2B_{2g}$ 3.96	$^2B_{1g}$ 3.21	$^2B_3$ 3.04	$^2B_{1g}$ 2.40	$^2B_{2g}$ 2.65	$^2B_{1g}$ 2.43	$^2B_2$ 2.26

VIII. EQUILIBRIUM GEOMETRIES OF THE NEUTRAL AND ANIONIC PBQ IN LOW-LYING EXCITED STATES

MRMP2/d-aug-cc-pVTZ. Coordinates are given in Å.

pBQ$^{\bullet-}$ $^2B_{2g}$ *state*

C	6.0	-1.4607214803	0.0000000000	0.0000000000
C	6.0	1.4607214803	0.0000000000	0.0000000000
O	8.0	-2.7331514884	0.0000000000	0.0000000000
O	8.0	2.7331514884	0.0000000000	0.0000000000
C	6.0	-0.6896293788	-1.2219863021	0.0000000000
C	6.0	0.6896293788	-1.2219863021	0.0000000000
C	6.0	-0.6896293788	1.2219863021	0.0000000000
C	6.0	0.6896293788	1.2219863021	0.0000000000
H	1.0	-1.2514284403	-2.1512250120	0.0000000000
H	1.0	1.2514284403	-2.1512250120	0.0000000000
H	1.0	-1.2514284403	2.1512250120	0.0000000000
H	1.0	1.2514284403	2.1512250120	0.0000000000

pBQ$^{\bullet-}$ $^2B_{2u}$ *state*

C	6.0	-1.4404601270	0.0000000000	0.0000000000
C	6.0	1.4404601270	0.0000000000	0.0000000000
O	8.0	-2.7602899198	0.0000000000	0.0000000000
O	8.0	2.7602899198	0.0000000000	0.0000000000
C	6.0	-0.7023655413	-1.2063671298	0.0000000000
C	6.0	0.7023655413	-1.2063671298	0.0000000000
C	6.0	-0.7023655413	1.2063671298	0.0000000000
C	6.0	0.7023655413	1.2063671298	0.0000000000
H	1.0	-1.2465710195	-2.1447836622	0.0000000000
H	1.0	1.2465710195	-2.1447836622	0.0000000000
H	1.0	-1.2465710195	2.1447836622	0.0000000000
H	1.0	1.2465710195	2.1447836622	0.0000000000

pBQ$^{\bullet-}$ $^2B_{3g}$ *state*

C	6.0	-1.4630351316	0.0000000000	0.0000000000
C	6.0	1.4630351316	0.0000000000	0.0000000000
O	8.0	-2.7759084554	0.0000000000	0.0000000000
O	8.0	2.7759084554	0.0000000000	0.0000000000
C	6.0	-0.6954229899	-1.2002093352	0.0000000000
C	6.0	0.6954229899	-1.2002093352	0.0000000000
C	6.0	-0.6954229899	1.2002093352	0.0000000000
C	6.0	0.6954229899	1.2002093352	0.0000000000
H	1.0	-1.2348597793	-2.1376836674	0.0000000000
H	1.0	1.2348597793	-2.1376836674	0.0000000000
H	1.0	-1.2348597793	2.1376836674	0.0000000000
H	1.0	1.2348597793	2.1376836674	0.0000000000

$pBQ^{\bullet-}\ {}^2A_u$ *state*

C	6.0	-1.4270928128	0.0000000000	0.0000000000
C	6.0	1.4270928128	0.0000000000	0.0000000000
O	8.0	-2.6834408483	0.0000000000	0.0000000000
O	8.0	2.6834408483	0.0000000000	0.0000000000
C	6.0	-0.7059651593	-1.2706164894	0.0000000000
C	6.0	0.7059651593	-1.2706164894	0.0000000000
C	6.0	-0.7059651593	1.2706164894	0.0000000000
C	6.0	0.7059651593	1.2706164894	0.0000000000
H	1.0	-1.3082241291	-2.1708336649	0.0000000000
H	1.0	1.3082241291	-2.1708336649	0.0000000000
H	1.0	-1.3082241291	2.1708336649	0.0000000000
H	1.0	1.3082241291	2.1708336649	0.0000000000

$pBQ^{\bullet-}\ {}^2A$ *state*

C	6.0	-1.4365365158	0.0000000000	0.0000000000
C	6.0	1.4365365158	0.0000000000	0.0000000000
O	8.0	-2.6866039788	0.0000000000	0.0000000000
O	8.0	2.6866039788	0.0000000000	0.0000000000

C	6.0	-0.6867858251	-1.2538739222	0.1540165049
C	6.0	0.6867858251	-1.2538739222	-0.1540165049
C	6.0	-0.6867858251	1.2538739222	-0.1540165049
C	6.0	0.6867858251	1.2538739222	0.1540165049
H	1.0	-1.2757216894	-2.1643648836	0.1703096948
H	1.0	1.2757216894	-2.1643648836	-0.1703096948
H	1.0	-1.2757216894	2.1643648836	-0.1703096948
H	1.0	1.2757216894	2.1643648836	0.1703096948

$pBQ^{\bullet -}$ $^2B_{3u}$ state

C	6.0	-1.4437849545	0.0000000000	0.0000000000
C	6.0	1.4437849545	0.0000000000	0.0000000000
O	8.0	-2.7795319535	0.0000000000	0.0000000000
O	8.0	2.7795319535	0.0000000000	0.0000000000
C	6.0	-0.7108700450	-1.2114855684	0.0000000000
C	6.0	0.7108700450	-1.2114855684	0.0000000000
C	6.0	-0.7108700450	1.2114855684	0.0000000000
C	6.0	0.7108700450	1.2114855684	0.0000000000
H	1.0	-1.2728978307	-2.1385605358	0.0000000000
H	1.0	1.2728978307	-2.1385605358	0.0000000000
H	1.0	-1.2728978307	2.1385605358	0.0000000000
H	1.0	1.2728978307	2.1385605358	0.0000000000

$pBQ^{\bullet -}$ $^2B_2$ state

C	6.0	-1.4619187306	0.0000000000	0.0026716769
C	6.0	1.4619187306	0.0000000000	0.0026716769
O	8.0	-2.7791775074	0.0000000000	0.0007780515
O	8.0	2.7791775074	0.0000000000	0.0007780515
C	6.0	-0.7235747879	0.0000000000	1.2113469611
C	6.0	0.7235747879	0.0000000000	1.2113469611
C	6.0	-0.6961858381	0.0000000000	-1.2141057624
C	6.0	0.6961858381	0.0000000000	-1.2141057624

H	1.0	-1.2744026615	0.0000000000	2.1458130643
H	1.0	1.2744026615	0.0000000000	2.1458130643
H	1.0	-1.2516117439	0.0000000000	-2.1446539914
H	1.0	1.2516117439	0.0000000000	-2.1446539914

pBQ ^1A_g *state*

C	6.0	-1.4340538629	0.0000000000	0.0000000000
C	6.0	1.4340538629	0.0000000000	0.0000000000
O	8.0	-2.6674929619	0.0000000000	0.0000000000
O	8.0	2.6674929619	0.0000000000	0.0000000000
C	6.0	-0.6762877384	-1.2635547696	0.0000000000
C	6.0	0.6762877384	-1.2635547696	0.0000000000
C	6.0	-0.6762877384	1.2635547696	0.0000000000
C	6.0	0.6762877384	1.2635547696	0.0000000000
H	1.0	-1.2605122338	-2.1756256174	0.0000000000
H	1.0	1.2605122338	-2.1756256174	0.0000000000
H	1.0	-1.2605122338	2.1756256174	0.0000000000
H	1.0	1.2605122338	2.1756256174	0.0000000000

CASSCF/6-311++G(2d,p). Coordinates are given in Å.

pBQ$^{\bullet-}$ $^2B_{2g}$ *state*

C	6.0	-1.4604965203	0.0000000000	0.0000000000
C	6.0	1.4604965203	-0.0000000000	0.0000000000
O	8.0	-2.7039424342	0.0000000000	0.0000000000
O	8.0	2.7039424342	-0.0000000000	0.0000000000
C	6.0	-0.6833818110	-1.2156490357	0.0000000000
C	6.0	0.6833818110	-1.2156490357	-0.0000000000
C	6.0	-0.6833818110	1.2156490357	-0.0000000000
C	6.0	0.6833818110	1.2156490357	-0.0000000000
H	1.0	-1.2301934598	-2.1438385304	-0.0000000000
H	1.0	1.2301934598	-2.1438385304	0.0000000000

H	1.0	-1.2301934598	2.1438385304	0.0000000000
H	1.0	1.2301934598	2.1438385304	0.0000000000

$pBQ^{\bullet-}$ $^2B_{2u}$ *state*

C	6.0	-1.4370562520	0.0000000000	-0.0000000000
C	6.0	1.4370562520	0.0000000000	-0.0000000000
O	8.0	-2.7366089473	0.0000000000	-0.0000000000
O	8.0	2.7366089473	-0.0000000000	-0.0000000000
C	6.0	-0.6948309776	-1.2005330543	-0.0000000000
C	6.0	0.6948309776	-1.2005330543	0.0000000000
C	6.0	-0.6948309776	1.2005330543	0.0000000000
C	6.0	0.6948309776	1.2005330543	0.0000000000
H	1.0	-1.2273694044	-2.1374940743	-0.0000000000
H	1.0	1.2273694044	-2.1374940743	0.0000000000
H	1.0	-1.2273694044	2.1374940743	0.0000000000
H	1.0	1.2273694044	2.1374940743	0.0000000000

$pBQ^{\bullet-}$ $^2B_{3g}$ *state*

C	6.0	-1.4446397303	0.0000000000	0.0000000000
C	6.0	1.4446397303	0.0000000000	0.0000000000
O	8.0	-2.7428495375	0.0000000000	-0.0000000000
O	8.0	2.7428495375	0.0000000000	-0.0000000000
C	6.0	-0.6910111034	-1.1994386348	0.0000000000
C	6.0	0.6910111034	-1.1994386348	-0.0000000000
C	6.0	-0.6910111034	1.1994386348	-0.0000000000
C	6.0	0.6910111034	1.1994386348	-0.0000000000
H	1.0	-1.2215781907	-2.1358197815	0.0000000000
H	1.0	1.2215781907	-2.1358197815	-0.0000000000
H	1.0	-1.2215781907	2.1358197815	-0.0000000000
H	1.0	1.2215781907	2.1358197815	-0.0000000000

$pBQ^{\bullet-}$ ^2A_u *state*

C	6.0	-1.4325553646	0.0000000000	-0.0000000000
C	6.0	1.4325553646	0.0000000000	-0.0000000000
O	8.0	-2.6572050618	0.0000000000	-0.0000000000
O	8.0	2.6572050618	0.0000000000	-0.0000000000
C	6.0	-0.6942213400	-1.2670924206	0.0000000000
C	6.0	0.6942213400	-1.2670924206	-0.0000000000
C	6.0	-0.6942213400	1.2670924206	-0.0000000000
C	6.0	0.6942213400	1.2670924206	-0.0000000000
H	1.0	-1.2786305456	-2.1679103512	0.0000000000
H	1.0	1.2786305456	-2.1679103512	-0.0000000000
H	1.0	-1.2786305456	2.1679103512	-0.0000000000
H	1.0	1.2786305456	2.1679103512	-0.0000000000

$pBQ^{\bullet -}$ ^{2}A *state*

C	6.0	-1.4299384363	0.0000000000	0.0000000000
C	6.0	1.4299384363	-0.0000000000	-0.0000000000
O	8.0	-2.6495589090	0.0000000000	0.0000000000
O	8.0	2.6495589090	-0.0000000000	-0.0000000000
C	6.0	-0.6701604715	-1.2497629173	0.1654434967
C	6.0	0.6701604715	-1.2497629173	-0.1654434967
C	6.0	-0.6701604715	1.2497629173	-0.1654434967
C	6.0	0.6701604715	1.2497629173	0.1654434967
H	1.0	-1.2482113351	-2.1551676467	0.2040606168
H	1.0	1.2482113351	-2.1551676467	-0.2040606168
H	1.0	-1.2482113351	2.1551676467	-0.2040606168
H	1.0	1.2482113351	2.1551676467	0.2040606168

$pBQ^{\bullet -}$ $^{2}B_{3u}$ *state*

C	6.0	-1.4474465061	0.0000000000	-0.0000000000
C	6.0	1.4474465061	-0.0000000000	-0.0000000000
O	8.0	-2.7482730393	0.0000000000	-0.0000000000
O	8.0	2.7482730393	-0.0000000000	-0.0000000000

C	6.0	-0.7015157950	-1.2048314286	-0.0000000000
C	6.0	0.7015157950	-1.2048314286	0.0000000000
C	6.0	-0.7015157950	1.2048314286	0.0000000000
C	6.0	0.7015157950	1.2048314286	0.0000000000
H	1.0	-1.2408495432	-2.1363713078	0.0000000000
H	1.0	1.2408495432	-2.1363713078	-0.0000000000
H	1.0	-1.2408495432	2.1363713078	-0.0000000000
H	1.0	1.2408495432	2.1363713078	-0.0000000000

$pBQ^{\bullet -}$ $^{2}B_{2}$ *state*

C	6.0	-1.5162705672	0.0000000000	-0.0119083216
C	6.0	1.5162705672	0.0000000000	-0.0119083216
O	8.0	-2.7678663346	0.0000000000	-0.0149865067
O	8.0	2.7678663346	0.0000000000	-0.0149865067
C	6.0	-0.7535655563	0.0000000000	1.1955666392
C	6.0	0.7535655563	0.0000000000	1.1955666392
C	6.0	-0.6957794111	0.0000000000	-1.1789812821
C	6.0	0.6957794111	0.0000000000	-1.1789812821
H	1.0	-1.2687447509	0.0000000000	2.1376455654
H	1.0	1.2687447509	0.0000000000	2.1376455654
H	1.0	-1.2083474693	0.0000000000	-2.1254860943
H	1.0	1.2083474693	0.0000000000	-2.1254860943

pBQ $^{1}A_{g}$ *state*

C	6.0	-1.4369411508	0.0000000000	0.0000000000
C	6.0	1.4369411508	-0.0000000000	0.0000000000
O	8.0	-2.6437605871	0.0000000000	0.0000000000
O	8.0	2.6437605871	-0.0000000000	0.0000000000
C	6.0	-0.6700477857	-1.2655554356	0.0000000000
C	6.0	0.6700477857	-1.2655554356	0.0000000000
C	6.0	-0.6700477857	1.2655554356	0.0000000000
C	6.0	0.6700477857	1.2655554356	0.0000000000

H	1.0	-1.2443164796	-2.1729265557	-0.0000000000
H	1.0	1.2443164796	-2.1729265557	0.0000000000
H	1.0	-1.2443164796	2.1729265557	0.0000000000
H	1.0	1.2443164796	2.1729265557	0.0000000000

IX. GEOMETRIES OF THE MECP BETWEEN THE ELECTRONIC STATES OF PBQ$^{\bullet-}$

SA(2)-CASSCF(17/12)/d-aug-cc-pVTZ. Coordinates are given in Å.

${}^2A_u \times {}^2B_{2g}$

C	6.0	-1.4008589319	0.0000000000	0.0000000000
C	6.0	1.4008589319	0.0000000000	0.0000000000
O	8.0	-2.5996912738	0.0000000000	0.0000000000
O	8.0	2.5996912738	0.0000000000	0.0000000000
C	6.0	-0.5912708464	-1.2043702607	-0.3710035680
C	6.0	0.5912708464	-1.2043702607	0.3710035680
C	6.0	-0.5912708464	1.2043702607	0.3710035680
C	6.0	0.5912708464	1.2043702607	-0.3710035680
H	1.0	-1.1538933937	-2.1062939196	-0.5429130968
H	1.0	1.1538933937	-2.1062939196	0.5429130968
H	1.0	-1.1538933937	2.1062939196	0.5429130968
H	1.0	1.1538933937	2.1062939196	-0.5429130968

${}^2B_{3u} \times {}^2B_{2g}$

C	6.0	0.6629414704	1.2769434132	-0.5488602123
C	6.0	-0.6629414704	1.2769434132	-0.5488602123
C	6.0	0.6629414704	-1.2769434132	-0.5488602123
C	6.0	-0.6629414704	-1.2769434132	-0.5488602123
C	6.0	1.1622310826	0.0000000000	0.1220946431
C	6.0	-1.1622310826	0.0000000000	0.1220946431
O	8.0	2.1565115897	0.0000000000	0.8590417926
O	8.0	-2.1565115897	0.0000000000	0.8590417926

H	1.0	1.3103064200	2.0152423163	-1.0050440932
H	1.0	-1.3103064200	2.0152423163	-1.0050440932
H	1.0	1.3103064200	-2.0152423163	-1.0050440932
H	1.0	-1.3103064200	-2.0152423163	-1.0050440932

$^2B_{3u} \times ^2 B_{1g}$

C	6.0	-1.4773293474	0.0000000000	0.0000000000
C	6.0	1.4773293474	0.0000000000	0.0000000000
O	8.0	-2.7533724762	0.0000000000	0.0000000000
O	8.0	2.7533724762	0.0000000000	0.0000000000
C	6.0	-0.7121049986	-1.1979975223	0.0000000000
C	6.0	0.7121049986	-1.1979975223	0.0000000000
C	6.0	-0.7121049986	1.1979975223	0.0000000000
C	6.0	0.7121049986	1.1979975223	0.0000000000
H	1.0	-1.2404531018	-2.1340963308	0.0000000000
H	1.0	1.2404531018	-2.1340963308	0.0000000000
H	1.0	-1.2404531018	2.1340963308	0.0000000000
H	1.0	1.2404531018	2.1340963308	0.0000000000

$^2B_{3u} \times ^2 B_{2u}$

C	6.0	-1.5757623831	0.0000000000	0.0000000000
C	6.0	1.5757623831	0.0000000000	0.0000000000
O	8.0	-2.7886009893	0.0000000000	0.0000000000
O	8.0	2.7886009893	0.0000000000	0.0000000000
C	6.0	-0.7673281110	-1.2275246095	0.0000000000
C	6.0	0.7673281110	-1.2275246095	0.0000000000
C	6.0	-0.7673281110	1.2275246095	0.0000000000
C	6.0	0.7673281110	1.2275246095	0.0000000000
H	1.0	-1.2996446555	-2.1570314574	0.0000000000
H	1.0	1.2996446555	-2.1570314574	0.0000000000
H	1.0	-1.2996446555	2.1570314574	0.0000000000
H	1.0	1.2996446555	2.1570314574	0.0000000000

$^2B_{3u} \times {}^2B_{3g}$

C	6.0	-1.5274857643	0.0000000000	0.0000000000
C	6.0	1.5274857643	0.0000000000	0.0000000000
O	8.0	-2.7626739982	0.0000000000	0.0000000000
O	8.0	2.7626739982	0.0000000000	0.0000000000
C	6.0	-0.7628725853	-1.2222814027	0.0000000000
C	6.0	0.7628725853	-1.2222814027	0.0000000000
C	6.0	-0.7628725853	1.2222814027	0.0000000000
C	6.0	0.7628725853	1.2222814027	0.0000000000
H	1.0	-1.3017943318	-2.1519179297	0.0000000000
H	1.0	1.3017943318	-2.1519179297	0.0000000000
H	1.0	-1.3017943318	2.1519179297	0.0000000000
H	1.0	1.3017943318	2.1519179297	0.0000000000

$^2A_u \times {}^2B_{2u}$

C	6.0	0.0000000000	0.0000000000	1.4355387414
C	6.0	0.0000000000	0.0000000000	-1.4329757970
O	8.0	0.0000000000	0.0000000000	2.6589645224
O	8.0	0.0000000000	0.0000000000	-2.6590648308
C	6.0	1.2654402749	0.0000000000	0.6953495673
C	6.0	-1.2654402749	0.0000000000	0.6953495673
C	6.0	1.2657128484	0.0000000000	-0.6963063884
C	6.0	-1.2657128484	0.0000000000	-0.6963063884
H	1.0	2.1666510325	0.0000000000	1.2770502325
H	1.0	-2.1666510325	0.0000000000	1.2770502325
H	1.0	2.1653835038	0.0000000000	-1.2802895436
H	1.0	-2.1653835038	0.0000000000	-1.2802895436

$^2A_u \times {}^2B_{3g}$

C	6.0	-1.4391885264	0.0000000000	0.0000000000
C	6.0	1.4391885264	0.0000000000	0.0000000000
O	8.0	-2.7032160373	0.0000000000	0.0000000000

O	8.0	2.7032160373	0.0000000000	0.0000000000
C	6.0	-0.6947236205	-1.2279384785	0.0000000000
C	6.0	0.6947236205	-1.2279384785	0.0000000000
C	6.0	-0.6947236205	1.2279384785	0.0000000000
C	6.0	0.6947236205	1.2279384785	0.0000000000
H	1.0	-1.2480348481	-2.1480513372	0.0000000000
H	1.0	1.2480348481	-2.1480513372	0.0000000000
H	1.0	-1.2480348481	2.1480513372	0.0000000000
H	1.0	1.2480348481	2.1480513372	0.0000000000

$^2A_u \times ^2 B_{3u}$

C	6.0	-1.4493938181	0.0000000000	0.0000000000
C	6.0	1.4493938181	0.0000000000	0.0000000000
O	8.0	-2.7466213387	0.0000000000	0.0000000000
O	8.0	2.7466213387	0.0000000000	0.0000000000
C	6.0	-0.7032870058	-1.2053267045	0.0000000000
C	6.0	0.7032870058	-1.2053267045	0.0000000000
C	6.0	-0.7032870058	1.2053267045	0.0000000000
C	6.0	0.7032870058	1.2053267045	0.0000000000
H	1.0	-1.2417324348	-2.1358201638	0.0000000000
H	1.0	1.2417324348	-2.1358201638	0.0000000000
H	1.0	-1.2417324348	2.1358201638	0.0000000000
H	1.0	1.2417324348	2.1358201638	0.0000000000

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